ARCADIS

Appendix C

Laboratory Standard Operating Procedures

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Methods 8290, 8290A, 1613B, 23, 0023A, and TO-9A

(SUPERSEDES: KNOX-ID-0004, Rev. 9)

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1. Scope and Application

1.1 This procedure is used for the determination of tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soils, solids, sediments, wipes, biological samples, fly ash, XAD resin, filters, still bottoms, waste oils, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This procedure is designed to meet analytical program requirements where US EPA Method 8290, 8290A, 1613B, 23, 0023A, or TO-9A is specified.

1.2 The seventeen 2,3,7,8-substituted and total Tetra-Hepta PCDDs/PCDFs listed in Table 1 can be determined by this procedure. Specifications are also provided for separate determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). In addition, total homologs (i.e., Total TCDD, Total TCDF, etc.) can be identified by this method.

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the PCDDs/PCDFs can be quantitated with no interferences present.

1.4 This procedure is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1 This procedure uses high resolution capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques.

2.2 Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 13 and Table 15. The samples are then extracted using matrix specific extraction procedures.

2.2.1 Water samples are extracted using separatory funnel techniques with methylene chloride as the extraction solvent.

2.2.2 Solid samples are extracted by Soxhlet extraction with the appropriate solvent.

2.2.3 Organic liquid waste samples are diluted in solvent.

2.3 After extraction, the sample is concentrated and solvent exchanged to hexane. The extract is then subjected to one or more optional cleanup steps to remove the sample of

interferences. The final extract is prepared by adding a known amount of the labeled recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) and concentrating to the final volume.

2.4 The acid-base cleanup of the sample is used before column chromatography for samples that contain large amounts of basic and acidic coextractable compounds. If such interferences are not removed before column chromatography, they can cause a shift in the predicted elution pattern. Conditions which can indicate the need for this procedure are as follows: Samples which are highly colored, samples which contain lipids or other oxidizable compounds or samples which contain known large amounts of polar organics.

2.5 Dual Column Cleanup: Silica gel is effective in removing chlorophenoxy herbicide residues, while alumina partitions PCBs, 2,4,5-trichlorophenol and hexachlorophene.

2.6 When the above cleanup techniques do not completely remove interferences, an activated carbon cleanup is used to remove interferences.

2.7 An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution ($\geq$10,000 resolution) mass spectrometer (HRMS). Two exact m/z's are monitored for each analyte.

2.8 The identification of the target 2,3,7,8 substituted isomers is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of the two most abundant ions in the molecular ion region. All other PCDD/PCDF congeners are identified by their retention times falling within retention time windows as established during routine calibration, and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation of identification is based on comparing the calculated ion ratios with the theoretical ion abundances. The identification of 2,3,7,8-TCDF is confirmed on an isomer specific (DB-225) GC column.

2.9 Quantitation of the 2,3,7,8-substituted PCDD/PCDF isomers, total PCDDs, and total PCDFs is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks, initial precision and recovery samples, and ongoing precision and recovery samples.

3. Definitions

3.1 Analyte: A PCDD or PCDF tested for by this method. The analytes are listed in Table 1.

3.2 Calibration Standard: A solution prepared from a secondary standard and/or stock solution and used to calibrate the response of the instrument with respect to analyte concentration.

3.3 Calibration Verification Standard (VER): The mid-point calibration standard (CS3) that is used to verify calibration. See Table 5 and Table 6.

3.4 Cleanup Standard: Solution containing $^{37}Cl_4$-2,3,7,8-TCDD that is added to the calibration solutions and to every 1613B and 8290A sample, blank, and quality control spike sample. It is added after extraction but prior to extract cleanup, and the analysis results are used to judge the efficiency of the cleanup procedures.

3.5 Column Performance Solution Mixture (CPSM): A mixture of TCDD or TCDF isomers (including the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer) known to elute close to the retention time of 2,3,7,8-TCDD or 2,3,7,8-TCDF on the analytical column being used. It is used to demonstrate acceptable resolution between the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer and all other TCDD or TCDF isomers on analytical column (percent valley ≤ 25).

3.6 Congener: Any member of a particular homologous series, for example, 1,2,3,7,8-pentachlorodibenzofuran.

3.7 CS1, CS2, CS3, CS4, CS5: See Calibration Standard and Table 5 and Table 6.

3.8 Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.9 Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal in the same retention time region as a target analyte but which does not meet the other qualitative identification criteria defined in the procedure.

3.10 GC: Gas chromatograph or gas chromatography

3.11 Homologous Series: A series of compounds in which each member differs from the next member by a constant amount. The members of the series are called homologs.

3.12 HRGC: High resolution GC

3.13 HRMS: High resolution MS

3.14 ICV: Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the initial calibration to verify the concentration of the Initial Calibration Standards.

3.15 Internal Standards: Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.16 Initial Precision and Recovery (IPR): See Initial Demonstration of Capability in Sections 9.1 and 13.2.

3.17 Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

3.18 Laboratory Blank: See Method Blank.

3.19 Laboratory Control Sample (LCS): A laboratory blank spiked with known quantities of analytes. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery..

3.20 Maximum Level (MaxL): The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. Also referred to as the upper method calibration limit (UMCL). It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.21 Method Blank: An aliquot of reagent water, sand, sodium sulfate, or other representative matrix, free of the targets of interest and interferences, that is extracted and analyzed along with the samples to monitor for laboratory contamination.

3.22 Minimum Level (MinL): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. Also referred to as the lower method calibration limit (LMCL). It is equivalent to the concentration of the lowest calibration standard assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.23 MS: Mass spectrometer or mass spectrometry.

3.24 Multiple Ion Detection (MID): A MS operational mode in which only selected ions are monitored rather than scanning the instrument to obtain a complete mass spectrum.

3.25 Ongoing precision and recovery standard (OPR): See Laboratory Control Sample.

3.26 PCDD: Polychlorinated dibenzo-p-dioxins.

3.27 PCDF: Polychlorinated dibenzofurans.

3.28 PFK: Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.29 FC-43 (PFTBA): Perfluorotributylamine

3.30 Recovery Standard: Solution containing $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD that is added to every sample, blank, and quality control spike sample extract just prior to analysis. The results are used to measure the recovery of the internal standards and the cleanup standard.

3.31 Percent Difference (%D): A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.32 Relative Response Factor (RRF): The ratio of the response of the mass spectrometer to a known amount of a compound relative to that of a known amount of a reference standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used to calculate the concentration of target analytes, internal standard recoveries, or detection limits in samples, blanks, and quality control samples.

3.33 Signal to Noise Ratio: The ratio of the mass spectrometer response of a GC peak to the background noise signal.

3.34 Split Ratio (S): The decimal expression of the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards.

3.35 Window Defining Mix: A solution which contains the first and last eluting isomers of each homologue group and is used to verify that the switching times between the MID descriptors have been appropriately set.

3.36 Additional definitions can be found in the Test America Knoxville QAM.

4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware can yield discrete artifacts or elevated baselines that can cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts must not use PVC gloves, powdered gloves, or gloves with levels of phthalates which cause interference.

4.2 The use of high purity reagents and solvents (pesticide grade) helps minimize interference problems. Where necessary, reagents are cleaned by extraction or solvent rinse.

4.3 Interferences coextracted from the samples can vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that can be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. While certain cleanup techniques are provided as part of this method, unique samples can require additional cleanup steps to achieve lower detection limits.

5. Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated must be removed and discarded, other gloves must be cleaned immediately.

5.2.1 Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile gloves are to be worn. For operations using solvents that may splash, SilverShield® gloves are recommended. SilverShield® gloves protect against breakthrough for most of the solvents used in this procedure.

5.3 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.4 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them or use thermal protection when working on them while they are above room temperature.

5.5 The mass spectrometer is under high vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source. Alternatively, the source can be removed from the vacuum manifold through a vacuum interlock.

5.6 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power. If the work involved requires measurement of voltage supplies, the instrument can be left on.

5.7 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene chloride	Carcinogen, Irritant	25 ppm-TWA, 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. Can be absorbed through skin.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure can cause lightheadedness, nausea, headache, and blurred vision. Vapors can cause irritation to the skin and eyes.
Methanol	Flammable, Poison, Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure can include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and can cause skin to become dry and cracked. Skin absorption can occur; symptoms can parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation can cause irritation of the upper respiratory tract. Symptoms of overexposure can include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness can be produced. Causes severe eye and skin irritation with redness and pain. Can be absorbed through the skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Can cause coughing, dizziness, dullness, and headache.
Cyclohexane	Flammable, Irritant	300 ppm TWA	Inhalation of vapors causes irritation to the respiratory tract. Symptoms can include coughing, shortness of breath. High concentrations have a narcotic effect.
Tetradecane	Irritant	None established	Inhalation of vapors can cause difficulty breathing, headache, intoxication and central nervous system damage.
Benzene	Flammable, Toxic, Carcinogen	PEL: 1 ppm TWA ; 5 ppm, 15 min. STEL	Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations can have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim can experience tightness in the chest, breathlessness, and loss of consciousness.
Nonane	Flammable	None established	Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous membranes and upper respiratory tract. Causes skin irritation.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.7.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA regulations include benzene and methylene chloride, 2,3,7,8-TCDD and all other 2,3,7,8- substituted PCDD or PCDF isomers.

NOTE: The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.8 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers must be kept closed unless transfers are being made.

5.9 All procedures that involve solvents such as acetone, toluene, methylene chloride, and hexane (e.g., glassware cleaning and the preparation of standards and reagents) must be conducted in a fume hood with the sash closed as far as the operations permit.

5.10 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.11 All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported immediately to a laboratory supervisor.

6. Equipment and Supplies

6.1 Sample Analysis Equipment.

6.1.1 Gas Chromatograph – Must have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and must meet all of the performance specification in Section 10.

6.1.1.1 GC column for PCDDs/PCDFs and for isomer specificity for 2,3,7,8-TCDD – 60m x 0.32mm ID x 0.25µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062, Restek No.10227 or 10227-125 IntegraGuard) or equivalent is required.

6.1.1.2 GC column for isomer specificity for 2,3,7,8-TCDF – 30m x 0.32mm ID x 0.25µm film thickness DB-225 or RTX-225 fused silica capillary column (J&W No. 123-2232 or Restek No.14024) or equivalent is required.

6.1.2 Mass Spectrometer – Electron impact ionization with the filament electron volts (eV) optimized for best instrument sensitivity, stability and signal to noise ratio. Must be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately 1 second and must meet all of the performance specifications in Section 10.

6.1.3 GC/MS Interface – The mass spectrometer (MS) must be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beam.

6.1.4 Data System – Capable of collecting, recording, and storing MS data.

7. Reagents and Standards

7.1 Standards and Calibration Solutions: Certified Reference Standards purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts), and Wellington Laboratories (Guelph, Ontario, Canada). If the chemical purity is 98% or greater, the weight can be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with PTFE-lined caps. Standards are used as received after being sonicated and transferred to 2.0 mL amber glass vials with PTFE lined caps.

7.1.1 Stability of Solutions: Standards have an expiration of ten (10) years from date of receipt unless otherwise specified by the manufacturer. Standard solutions used for quantitative purposes must be analyzed periodically, and must be assayed against reference standards before use.

7.2 Initial Calibration Standards:

7.2.1 1613B/8290/8290A: CS1-CS5. CIL Catalog No. EDF-9999. (See Table 5).

7.2.2 23/0023A/TO-9A: CS1-CS5. Wellington Catalog No. EPA-23 CS1-5. (See Table 6).

7.3 Initial Calibration Verification Standards:

7.3.1 1613B/8290/8290A: Wellington Catalog No. EPA-1613-CS3.

7.3.2 23/0023A/TO-9A: CS3. CIL Catalog No. EDF-4052-3.

7.4 Daily Calibration Verification Standards

7.4.1 1613B/8290/8290A: CS3. CIL Catalog No. EDF-9999-3. (See Table 7).

7.4.2 1613B/8290/8290A: CS3. CIL Catalog No. EDF-4141. (See Table 7).

NOTE: This standard can be used as both the Continuing Calibration Standard and the DB/Rtx-5 GC Window Defining Mix/Column Performance Check Solution.

7.4.3 23/0023A/TO-9A: CS3. Wellington Catalog No. EPA-23-CS3. (See Table 8).

7.5 Native Standards

7.5.1 Native Standard Stock Solution: CIL Catalog No. EDF-7999-10x, 400-4000 ng/mL in nonane, 1.2 mL.

7.5.2 Native Standard Working Stock Solution: Dilute 0.300 mL of the native standard stock solution to 3.0 mL in a volumetric flask with nonane for a final concentration of 40-400 ng/mL.

7.5.3 Native LCS Spiking Solution: Dilute 500 µL of the native standard working stock solution to 100 mL in a 125 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 0.2-2.0 ng/mL. 1.0 mL of this solution is added to each LCS, LCSD or MS/MSD sample. See Table 11 for a complete list of compounds and their concentrations.

7.6 1613B/8290/8290A Internal Standards

7.6.1 1613B/8290/8290A Internal Standard Stock Solution: CIL Catalog No. EDF-8999, 100 ng/mL ($^{13}C_{12}$-OCDD 200 ng/mL) in nonane, 500 µL.

7.6.2 1613B/8290/8290A Internal Standard Spiking Solution: Dilute 2000 µL of the internal standard stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank and QC sample. See Table 12 for a complete list of compounds and their concentrations.

7.7 2,3,7,8-TCDD/2,3,7,8-TCDF Internal Standards

7.7.1 $^{13}C_{12}$-2,3,7,8-TCDD Internal Standard Stock Solution: CIL Catalog No. ED-900, 50 µg/mL in nonane, 1.2 mL

7.7.2 $^{13}C_{12}$-2,3,7,8-TCDF Internal Standard Stock Solution: CIL Catalog No. EF-904, 50 µg/mL in nonane, 1.2 mL

7.7.3 $^{13}C_{12}$-TCDD/$^{13}C_{12}$-TCDF Internal Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solutions above to 5 mL in a volumetric flask with nonane to a final concentration of 1000 ng/mL.

7.7.4 $^{13}C_{12}$-TCDD/$^{13}C_{12}$-TCDF Internal Standard Spiking Solution: Dilute 200 µL of the internal standard secondary stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL. 1.0 mL of this solution is added to each sample, method blank and QC sample extract that is extracted for TCDD and/or TCDF analysis only. See Table 2 for a complete list of compounds and their concentrations.

7.8 23/0023A/TO-9A Internal Standards

7.8.1 23/0023A/TO-9A Internal Standard Stock Solution: Wellington Catalog No. EPA-23ISS, 1000 ng/mL ($^{13}C_{12}$-OCDD 2000 ng/mL) in nonane/toluene (80:20 v:v), 1.2 mL.

7.8.2 23/0023A/TO-9A Internal Standard Spiking Solution: Dilute 200 µL of the internal standard stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 15 for a complete list of compounds and their concentrations.

7.9 Recovery Standards

7.9.1 $^{13}C_{12}$-1,2,3,4-TCDD Recovery Standard Stock Solution: CIL Catalog No. ED-911, 50 µg/mL in nonane, 1.2 mL

7.9.2 $^{13}C_{12}$-1,2,3,7,8,9-HxCDD Recovery Standard Stock Solution: CIL Catalog No. ED-996, 50 µg/mL in nonane, 1.2 mL

7.9.3 Recovery Standard Secondary Stock Solution: Dilute 1.0 mL of the stock solutions above to 10 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.9.4 Recovery Standard Spiking Solution: Add 10 mL of nonane to a 12 mL amber vial with a Class A glass pipette. With a syringe, remove 200 µL of nonane from the vial and add 200 µL of the recovery standard secondary stock solution to a final concentration of 0.1 µg/mL. 20 µL of this solution is added to each sample, method blank and QC sample extract. See Table 2 for a complete list of compounds and their concentrations.

7.10 1613B and 8290A Cleanup Standards

7.10.1 Cleanup Standard Stock Solution: CIL Catalog No. ED-907, 50 µg/mL in nonane, 1.2 mL

7.10.2 Cleanup Standard Secondary Stock Solution: Dilute 0.100 mL of the 50 µg/mL cleanup standard stock solution to 1.0 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.10.3 Cleanup Standard Working Stock Solution: Dilute 0.120 mL of the 5.0 µg/mL cleanup standard secondary stock solution to 3.0 mL in a volumetric flask with nonane to a final concentration of 200 ng/mL.

7.10.4 Cleanup Standard Spiking Solution: Dilute 200 µL of the 200 ng/mL working stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with hexane to a final concentration of 0.20 ng/mL. 1.0 mL of this solution is added to each 1613B or 8290A sample, method blank and QC sample extract prior to cleanup. See Table 17 for a complete list of compounds and their concentrations.

7.11 23/0023A/TO-9A Surrogate Standards

7.11.1 23/0023A/TO-9A Surrogate Standard Stock Solution: Wellington Catalog No. EPA-23SSS, 1000 ng/mL in nonane/toluene (95:5 v:v), 1.2 mL.

7.11.2 23/0023A/TO-9A Surrogate Standard Spiking Solution: Dilute 500 µL of the surrogate standard stock solution to 25 mL in a graduated cylinder with nonane to a final concentration of 20 ng/mL. 100 µL of this solution is added to each sample train components before sampling. See Table 16 for a complete list of compounds and their concentrations.

7.12 PCDD/PCDF Window Defining and Isomer Specificity Standard

7.12.1 PCDD/PCDF Window Defining and Isomer Specificity Mixture: CIL Catalog No. EDF-4141. This standard contains the daily standard, window defining mix and the isomer specificity mix.

7.13 Perfluorokerosene (PFK) is used in neat form to tune and calibrate the mass spectrometer. Fluka (Catalog No. - 77275) has been found to be superior to other sources of PFK.

7.14 FC-43 (PFTBA) is used in neat form to tune and calibrate the mass spectrometer. (Scientific Instrument Services Catalog No. FC-43-35).

8. Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, "Sample Receipt and Log In", current revision. Sample container and preservation recommendations are listed in the table below.

Method:	**1613B**	**8290/8290A[1]**	**23**	**0023A[1]**	**TO-9A**
Holding Times	Samples – 1 year from collection to extraction Extracts – 1 year from extraction to analysis	Samples – 30 days from collection to extraction Extracts – 45 days from extraction to analysis Tissue Extracts –45 days from collection to analysis	Samples – 30 days from collection to extraction Extracts – 45 days from extraction to analysis	Samples – 30 days from collection to extraction Extracts – 45 days from extraction to analysis	Samples – 7 days from collection to extraction Extracts – 40 days from extraction to analysis
Containers	Amber Glass	Amber Glass	See KNOX-ID-0012	See KNOX-ID-0012	See KNOX-ID-0012

Method:	**1613B**	**8290/8290A[1]**	**23**	**0023A[1]**	**TO-9A**
Preservation:					
Aqueous Samples	≤6 °C in the dark If residual chlorine is present, add 80 mg/L sodium thiosulfate. If pH > 9, adjust to pH 7-9 with sulfuric acid	≤6 °C in the dark If residual chlorine is present, add 80 mg/L sodium thiosulfate.	N/A	N/A	N/A
Solid Samples	<-10 °C in the dark	≤6 °C in the dark	N/A	N/A	N/A
Tissue Samples	<-10 °C in the dark	<-20 °C in the dark[2]	N/A	N/A	N/A
Air Samples	N/A	≤6 °C in the dark	≤6 °C in the dark	≤6 °C in the dark	≤6 °C in the dark

Notes:

1 For method 8290, 8290A and 0023A the holding times listed are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed can be as high as a year for certain matrices. The results of samples analyzed after the holding time expiration date must be considered to be minimum concentrations and must be identified as such in the final report. Sample extracts, however, must always be analyzed within 45 days of extraction. (For the State of South Carolina and the New Jersey DEP, the holdings times are as listed in the table and are not considered recommendations.)

2 If the freezer used to store samples is not capable of reaching a temperature of <-20 °C when the temperature control is set to its maximum limit, a storage higher temperature is acceptable as long as it is <-10 °C.

9. Quality Control

9.1 The Initial Demonstration of Capability (IDOC) studies described in Section 13 must be completed with acceptable results before analysis of samples can begin.

9.2 The Method Detection Limit (MDL) study described in Section 13 must be completed with acceptable results before analysis of samples can begin.

9.3 A laboratory method blank must be run along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. The method blank is normally analyzed immediately after the calibration standards. The method blank must meet the following acceptance criteria:

9.3.1 The concentration of target analytes in the method blank must be less than the minimum level (ML) and “B” qualifiers are added to all associated samples with analytes detected in the method blank above the estimated detection limit (EDL).

9.3.2 If the concentration of target analytes in the method blank is greater than minimum level (ML) but less than 5% of the concentration in the associated samples, corrective action is required but the associated data can be reported. At a minimum, corrective action must include the addition of "B" qualifiers to all associated samples with analytes detected in the method blank above the ML and documentation in the case narrative.

9.3.3 If the method blank sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

9.3.4 If there is no target analyte greater than the minimum levels (ML) in the samples associated with an unacceptable method blank, the data can be reported with qualifiers. Such action must be done in consultation with the client.

9.3.5 The method blank internal standard recoveries must be within the established control limits. If internal standard recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination.

9.3.5.1 If internal standard recoveries are low in the method blank and there are analytes >ML in the associated samples re-extraction of the blank and affected samples is required if the method blank does not demonstrate that the analysis is free of contamination.

9.3.5.2 If the method blank internal standard recoveries are outside the QC limits and the decision is made to report the sample results, an NCM must be initiated and the reason for accepting the sample results clearly documented. Consultation with the client before acceptance must take place.

9.3.6 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.4 Instrument Blank

9.4.1 Instruments must be evaluated for contamination during each 12 hour analytical sequence. This is accomplished by analysis of a method blank if available. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.5 Laboratory Control Sample

An LCS is analyzed along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. The LCS consists of reagent water for aqueous samples, and a clean solid matrix (sodium sulfate) for solid samples. The LCS extract must be subject to the same clean up procedures as the associated sample extracts. LCS spike components, concentrations, and control limits are given in Table 11.

9.5.1 If any analyte in the LCS is outside the control limits, corrective action must occur. Corrective action includes:

9.5.1.1 If the LCS fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

9.5.1.2 If the batch is not re-extracted and reanalyzed, an NCM must be initiated and the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of an acceptable reason for not reanalyzing might be that the matrix spike and matrix spike duplicate recoveries are within control limits, the method blank and sample internal standard recoveries are within limits, and the data clearly demonstrates that the problem was confined to the LCS).

9.5.1.3 For method TO-9A calculate the precision (%D) from the LCS/LCSD. The precision must be within ± 30%.

9.5.2 Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.6 Internal Standards

Internal standards are spiked into all samples, blanks, and laboratory control samples to assess method performance on the sample matrix. The recovery of each labeled internal standard must be within the limits in Table 13 for methods 1613B, 8290 and 8290A or in Table 15 for methods 23, 0023A, and TO-9A.

9.6.1 If the recovery is outside these limits the following corrective action must be taken:

9.6.1.1 Check all calculations for error.

9.6.1.2 Ensure that instrument performance is acceptable.

9.6.1.3 Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

9.6.1.4 If the recovery of any internal standard is less than the lower control limit, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDLs) are less than the

minimum levels (MLs), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDLs) are greater than the minimum levels (MLs), re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample can be re-extracted or additional clean-ups can be employed. The decision to reanalyze or flag the data is made in consultation with the client.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Method 8290 only.

When method 8290 is performed a matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every 20 samples of a given matrix. **Note that a MS/MSD is not required for Method 8290A**. The MS/MSD is spiked with the same subset of analytes as the LCS (See Table 12). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

9.7.1 If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action is to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis can proceed. The reasons for accepting the batch must be documented in the report narrative.

9.7.2 If the recovery for any component is outside QC limits for both the MS/MSD and the LCS, the analysis is out of control and corrective action must be taken. Corrective action normally includes repreparation and reanalysis of the batch.

9.7.3 If a MS/MSD is not possible due to limited sample, then a LCSD must be analyzed. The LCSD is evaluated using the same acceptance criteria as the LCS. The RPD of the LCS and LCSD are compared to the acceptance limits in Table 12.

9.7.4 The MS/MSD must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds are diluted out.

9.8 Surrogate Standards – Methods 23, 0023A, TO-9A

Field surrogate standards are added to the collection media prior to sample collection when performing methods 23, 0023A, or TO-9A. The surrogate recoveries are calculated relative to the internal standards and are a measure of sampling efficiency. The recovery of the surrogate standards must be within the limits specified in Table 16. Poor recoveries of the surrogate standards can indicate breakthrough in the sampling train.

9.8.1 If the recovery is outside these limits the following corrective action must be taken:

9.8.1.1 Check all calculations for error.

9.8.1.2 Ensure that instrument performance is acceptable.

9.8.1.3 Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

9.8.1.4 Flag the results that are outside control limits and notify the Project Manager. The client must be notified and consulted for additional corrective action.

10. Calibration and Standardization

10.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the column performance check solution and a calibration solution (CS3). No samples are to be analyzed until acceptable calibration as described in sections 10.2 and 10.2.9.1 is demonstrated and documented. A 2uL injection volume is specified for all extracts, blanks, calibration solutions and performance check samples. A 1uL injection volume can be used; however, the laboratory must keep the injection volume the same throughout calibration and analysis.

10.2 Initial Calibration

10.2.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 5 for methods 1613B and 8290/8290A or in Table 6 for methods 23, 0023A, or TO-9A. Store calibration standards at room temperature in the dark. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.2.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). For method 1613B adjust the GC conditions to meet the relative retention times for the PCDDs/PCDFs listed in Table 3. The cycle time for MID descriptors must be $\leq$ 1 sec.

10.2.3 By using a PFK or FC-43 molecular leak, tune the instrument to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or 313.9838 (FC-43) or any other reference signal close to the m/z 303.9016 (from TCDF).

10.2.4 By using peak matching conditions and the aforementioned either PFK or FC-43 reference peak, verify that the exact mass of m/z 380.9760 (PFK) or m/z 363.9807 (FC-43) is within 5 ppm of the required value. Document that the resolving power at reduced accelerating voltage of m/z 380.9760 (PFK) or m/z 363.9807 (FC-43) is greater than 10,000 (10 percent valley).

10.2.5 Analyze 2µL of the Window Defining Mixture and set the switchpoints for the MID descriptors. The switchpoints must be set to encompass the retention time window of each congener group.

10.2.6 If the initial calibration is being performed on the DB-5 or RTX-5 column, analyze 2µL of the Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDD and the closest eluting non-2,3,7,8-TCDD isomer must be resolved with a % Valley of ≤ 25, where

$$\% \text{ Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8 - TCDD}} \times 100$$

If the initial calibration is being performed on the DB-225 or RTX-225 column, analyze 2µL of the TCDF Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDF and the closest eluting non-2,3,7,8-TCDF isomer must be resolved with a % Valley of ≤ 25, where

$$\% \text{ Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8 - TCDF}} \times 100$$

10.2.7 Analyze 2µL of each of the five calibration standards and calculate the RRF of each analyte vs. the appropriate internal standard listed in Table 3 for methods 1613B, 8290/8290A or in Table 4 for methods 23, 0023A, and TO-9A using the following equation;

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Cis = concentration of the appropriate internal standard
Cs = concentration of the compound of interest

10.2.7.1 Calculate the mean relative response factor (mean RRF) and the percent relative standard deviation (RSD) of the relative response factors for each compound of interest in the five calibration standard solutions using the following equations;

$$\overline{RRF}_{n=5} = \frac{1}{n} \times \sum_{i=1}^{n} RF_i$$

$$RSD_{n=5} = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)^2}{n-1}} \times \frac{100}{\overline{RRF}}$$

10.2.8 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met for each initial calibration standard before sample analyses are performed. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, follow the procedure in Test America Policy CA-T-P-002 Selection of Calibration Points, current revision (see reference section 16.10).

10.2.8.1 The percent relative standard deviation (RSD) for the mean relative response factors must be within the acceptance criteria listed in Table 5 for methods 1613B, 8290/8290A or in Table 6 for methods 23, 0023A, and TO-9A.

10.2.8.2 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standards must have signal-to-noise ratios (S/N) ≥ 10.

10.2.8.3 The ion abundance ratios must be within the specified control limits in Table 22.

10.2.8.4 For method 1613B the absolute retention time of $^{13}C_{12}$-1234-TCDD must exceed 25.0 minutes on the DB/Rtx-5 column and 15.0 minutes on the DB/Rtx-225 column.

10.2.8.5 Corrective action can include replacing the injector port liner, replacing the injector port septum, removal of a small portion of the front of the analytical column, replacing the autosampler syringes and rinse solvent, adjusting the instrument tuning, cleaning the ion volume or ion source, installing a new analytical column and replacing the calibration standard solutions.

10.2.9 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.3 after the completion of the initial calibration prior to sample analysis. Calculate the concentration of the ICV using the RRFs from the CS3 standard analyzed in section 10.2.7 and the formula in section 12.3.4. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula.

$$\%D = \frac{\left(C_{Exp} - C_{Calc}\right)}{C_{Exp}} \times 100$$

Where:
C_{Exp} = The expected concentration of the Standard.

C_{Calc} = The calculated concentration of the Standard.

10.2.9.1 The general criteria for percent difference acceptance limits is ±25% for all native compounds. The warning limits for percent difference is ±25% to ±35%.

10.2.9.2 All data associated with compounds with percent differences in the warning limits must be reviewed before acceptance.

10.2.9.3 All data associated with compounds with percent differences outside the warning limits must be documented as an NCM. Corrective action must be taken and can include the following:

- Reanalyze the ICV Standard
- Replace and reanalyze the ICV Standard
- Evaluate the instrument performance
- Evaluate the Initial Calibration Standards

10.3 Continuing Calibration

10.3.1 Continuing calibration is performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A calibration check is also required at the end of a 12 hour period when performing method 8290/8290A or 0023A.

10.3.2 Document the mass resolution performance as specified in sections 10.2.3 and 10.2.4. The mass resolution checks must be performed at the beginning and at the end of each 12-hour shift.

10.3.3 Analyze 2µL of the Window Defining Mixture and/or Column Performance Solution Mixture under the same instrument conditions used to perform the initial calibration. Determine and document acceptable column performance as described in section 10.2.5 and 10.2.6.

10.3.4 Analyze 2µL of the Daily Calibration Standard Solution (CS3). Calculate the concentrations and percent difference of the standard using the formulas in sections 12.3.4 and 10.2.9.

NOTE: The combined Continuing Calibration Standard/Window Defining Mix/Column Performance Solution specified in section 7.4.2 can be used in section 10.3.2, 10.3.4, and 10.3.6.

10.3.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met at the beginning of each 12 hour period that samples are analyzed. If acceptable beginning continuing calibration criteria is not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive beginning continuing calibration does not

meet acceptance criteria, additional corrective action must be performed. Acceptable performance must be demonstrated after two consecutive failing beginning continuing calibrations by the analysis of two consecutive acceptable beginning continuing calibrations or by analysis of a new initial calibration.

10.3.5.1 The measured concentration or percent difference for each compound must be within the acceptance criteria limits in Table 7 for methods 1613B, 8290/8290A or in Table 8 for methods 23, 0023A and TO-9A.

10.3.5.2 For method 1613B the relative retention times of PCDDs/PCDFs and labeled compounds in the standard must be within the limits in Table 3.

10.3.5.3 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standard must have signal-to-noise ratios (S/N) ≥ 10.

10.3.5.4 The ion abundance ratios must be within the specified control limits in Table 22.

10.3.5.5 Corrective action can include all of the items specified in section 10.2.8.5.

10.3.5.6 When performing method 8290/8290A or 0023A, if the continuing calibration fails at the beginning of a 12-hour shift, the instructions in section 10.3.5 must be followed. If the continuing calibration check performed at the end of a 12 hour period fails by no more than ±25 %D for unlabeled native analytes and ±35 %D for labeled standards, the closing standard must not be used as a beginning calibration standard for the next 12-hour shift and the requirements in section 10.3.5 must be met before analysis can continue. Use the mean RRF from the two daily continuing calibration runs to compute the analyte concentrations instead of the RRFs obtained from the initial calibration. If the continuing calibration check performed at the end of a 12 hour period fails by more than ±25 %D for unlabeled native analytes and ±35 %RPD for labeled standards initiate corrective action and reanalyze all sample extracts analyzed during the 12 hour period encompassing the failed end of shift calibration check.

It is realized that it might not always be possible to achieve all RF criteria. For example, the RF criteria for $^{13}C_{12}$-HpCDD and $^{13}C_{12}$-OCDD were not met, however the RF values for the corresponding unlabeled compounds were within the criteria established in this procedure. The data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. In these situations, the analyst must consult with the group manager and

the project manager to assess the impact on the data quality objectives on the affected samples. Corrective action must be taken and any decision to report sample data in this situation must be made in conjunction with the client. An NCM must be initiated if the data is to be reported.

10.3.6 Daily calibration must be performed every 12 hours of instrument operation. The 12 hour shift begins with the documentation of the mass resolution followed by the injection of the Window Defining Mixture or Column Performance Solution Mixture and the Daily Calibration Standard.

10.3.6.1 For methods 1613B, 23, TO-9A- The mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12 hour shifts, the mass resolution check from the end of the previous period can be used for the beginning of the next period.

10.3.6.2 For method 8290/8290A or 0023A - The Continuing Calibration Standard check and mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12-hour shifts, the Window Defining Mixture and/or Column Performance Solution Mixture must be analyzed at the beginning of each 12-hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

11. Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variations in the procedure, except those specified by project specific instructions, must be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager and QA Manager. If contractually required the client must be notified.

11.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3 Sample Extract Analysis

11.3.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data until OCDF has eluted from the column.

11.3.2 Record analysis information in the instrument logbook. The following information is required:

Date of analysis

Time of analysis
Instrument data system filename
Analyst
Lab sample identification

Additional information can be recorded in the logbook if necessary.

11.3.3 Generate ion chromatograms for the masses listed in Table 21 that encompass the expected retention windows of the PCDD and PCDF homologous series.

11.4 Refer to the TestAmerica Knoxville Quality Assurance Manual, current revision for the GC/MS instrument equipment maintenance table.

11.5 Refer to TestAmerica Knoxville SOP KNOX-IT-0001, current revision for requirements for computer hardware and software.

12. Data Analysis and Calculations

12.1 Refer to Figure 3 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2 Qualitative identification criteria for PCDDs and PCDFs. For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

12.2.1 The ion current response for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

12.2.2 The signal-to-noise ratio (S/N) for each GC peak at each exact m/z must be ≥ 2.5 for positive identification of a PCDD/PCDF compound.

12.2.3 The ratio of the integrated areas of the two exact m/z's specified in Table 21 must be within the limits specified in Table 22, or alternatively when performing method 1613B, within ±10 percent of the ratio in the midpoint (CS3) calibration or the calibration verification (VER), whichever is most recent.

12.2.4 Method 1613B only - The relative retention time of the peak for a 2,3,7,8-substituted PCDD or PCDF must be within the limits in Table 3.

12.2.5 Method 8290, 8290A and 0023A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within -1 to +3 seconds of the isotopically labeled standard.

12.2.6 Method 23 and TO-9A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within ±3 seconds of the isotopically labeled standard.

12.2.7 Method 8290, 8290A, 23, 0023A, and TO-9A only - For 2,3,7,8-substituted isomers, which do not have an isotopically labeled internal standard present in the sample extract, the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration.

12.2.8 The retention time of peaks representing non-2,3,7,8-substituted PCDDs/PCDFs must be within the retention time windows established in section 10.2.5.

12.2.9 No peaks detected in the polychlorinated diphenyl-ether (PCDPE) mass channel in the same retention time region (± 2 sec for method 8290, 8290A & 0023A) as a PCDF peak.

12.3 Quantitation for PCDDs and PCDFs.

12.3.1 Calculate the Internal Standard and Cleanup Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$\text{Ris} = \frac{\text{Ais} \times \text{Qrs}}{\text{Ars} \times \text{RRFis} \times \text{Qis}} \times 100\%$$

Where:

Ais = sum of the areas of the quantitation ions of the appropriate internal standard (cleanup standard is single ion)
Ars = sum of the areas of the quantitation ions of the recovery standard
Qrs = ng of recovery standard added to extract
Qis = ng of internal standard or cleanup standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

NOTE: In some situations, such as high-volume water sampling or air train samples, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$Qrs = \frac{Crs \times Vrs}{S}$$

Where:
Qrs = ng of recovery standard added to extract
Crs = concentration of recovery standard added to the split portion of the extract
Vrs = volume of recovery standard added to the split portion of the extract
S = split ratio of the extract (decimal fraction of the extract used)

12.3.2 The split ratio represents the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards.

The split ratio is calculated as the product of all split ratios generated between these steps:

$$S = Spis \times Spcs \times Spfc$$

Where:

Spis = the decimal fraction of extract used from split taken once the internal standard has been added and the extraction is performed.

Spcs = the decimal fraction of extract used from split taken once the cleanup standard (if used) has been added.

Spfc = the decimal fraction of extract used from split taken once the cleanup fractionation column has been run.

12.3.3 When properly applied, isotope dilution techniques produce results that are independent of recovery. The recovery of each internal standard must be within the limits specified in Table 13 for method 1613B, 8290 or 8290A or in Table 15 for method 23, 0023A, or TO-9A. If the recovery of any internal standard is not within the specified limits, calculate the S/N ratio of the internal standard. If the S/N is $\geq$ 10 and the method minimum levels are met, report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the minimum levels are not achieved, re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample can be re-extracted or additional clean-ups can be employed.

12.3.4 Calculate the concentration of the 2,3,7,8 isomers according to the following equation:

$$C_{2,3,7,8\,\text{isomers}} = \frac{\text{Ata} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{Ws}}$$

Where:
C = Concentration of 2,3,7,8 isomers
Ata = sum of the areas of the quantitation ions of the target analyte
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor from initial calibration.
Ws = amount of sample spiked and extracted (grams or liters)

12.3.5 The concentrations of non-2,3,7,8-isomers are calculated using the RRF for the corresponding 2,3,7,8-isomer. If more than one 2,3,7,8-isomer exist for a

particular level of chlorination, the average of the individual 2,3,7,8-isomer RRFs is used in the calculation.

$$C_{\text{non 2,3,7,8 isomer}} = \frac{\text{Ata} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{Ws}}$$

Where:
Ata = sum of the areas of the quantitation ions of the non-2,3,7,8 isomer
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor from initial calibration for the corresponding 2,3,7,8 isomer.
Ws = amount of sample spiked and extracted (grams or liters)

12.3.6 Calculate the total concentration of all isomers within each homologous series of PCDDs and PCDFs by summing the concentrations of the individual PCDD or PCDF 2,3,7,8 and non-2,3,7,8 isomers.

$$C_{\text{Total}} = \sum C_{\text{2,3,7,8 isomers}} + \sum C_{\text{non 2,3,7,8 isomers}}$$

12.3.7 If solid samples are to be reported on a dry weight basis, the laboratory LIMS system performs the following calculation:

$$\text{Concentration (Dry Weight)} = \frac{\text{C}}{\%\text{Solids} \div 100}$$

Where:
C = Concentration of the target analyte
%Solids = The sample percent solids determined by moisture analysis

12.3.8 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$\text{EDL} = \frac{\text{N} \times 2.5 \times \text{Qis}}{\text{His} \times \text{RRFs} \times \text{Ws} \times \text{Ssl}}$$

Where:
N = average peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute
His = peak height of quantitation ions for appropriate internal standard
Qis = ng of internal standard added to sample
RRFs = mean relative response factor of compound from initial calibration
W = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

NOTE: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.3.9 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.2, calculate an Estimated Maximum Possible Concentration (EMPC). Two different calculation formulas can be used depending upon specific client requirements.

12.3.9.1 When performing methods 8290, 8290A for EPA regulated analyses where the currently promulgated method is required by law (e.g. Trial Burns) and for all other analyses unless the client has specified otherwise, use the equation in section 12.3.4, except that Ata represents the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area is the one which gives the lower of the two possible results (i.e. the EMPC is lower than the result calculated from the uncorrected areas).

12.3.9.2 When the client has specifically requested, use the equation in section 12.3.4 without correcting the areas. This method gives an EMPC which is always higher than the method above and would be considered the worst case.

12.3.10 If peaks are present in the diphenyl ether mass channel at the same retention time as a PCDF peak, the peak cannot be identified as a PCDF. Calculate the concentration of the peak using the equation in section 12.3.4 but report the concentration as an Estimated Maximum Possible Concentration.

12.3.11 If the concentration in the final extract of any 2,3,7,8-substituted PCDD/PCDF isomer (except OCDD or OCDF) exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. For OCDD and OCDF, report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Dilutions of up to 1/10 can be performed on the extract. If the compounds that exceed the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample can be performed or the sample can be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client must occur before any re-extraction is performed.

12.3.12 Evaluate the ion chromatograms of the PFK or FC-43 lock mass and calibration mass for each MID group. The PFK or FC-43 mass intensity must be consistent throughout the retention time of the target compounds. Negative excursions or variations in the PFK or FC-43 mass intensity indicate the elution of interferences from the GC column that are causing suppression in the ion source of the mass spectrometer. This ion suppression can reduce the instrument

sensitivity and quantitative result of any peaks that elute at the same retention time. Either additional extract cleanup or dilutions can reduce ion suppression. The quantitative results must be carefully evaluated when there is evidence of ion suppression present in the PFK or FC-43 mass traces.

12.4 The DB-5 (RTX-5) column does not provide for isomer specificity of 2,3,7,8-TCDF using the operating condition required for this method. If a peak is determined to be present at the expected retention time of 2,3,7,8-TCDF and its calculated concentration is above the MinL, the sample extract must be analyzed on the DB-225 (RTX-225) column.

12.5 The Minimum Level (MinL) is defined as the level at which the instrument gives acceptable calibration assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviation from the extraction amounts or final volumes listed Table 2 changes the MinL. The MinL is calculated as shown in the following equation:

$$\text{MinL} = \frac{C\,\text{min} \times Vfe}{W\text{s}}$$

Where:

Cmin = the concentration the analyte in the lowest calibration standard
Ws = amount of sample spiked and extracted (grams or liters)
Vfe = the final volume of the extract, corrected for all splits and dilutions

$$\text{V}fe = \frac{Vdel \times DFpr}{Spr \times S}$$

Where:

Vdel = the volume of extract delivered to the analysis
DFpr = the dilution factor for dilutions performed to the final extract
Spr = the split ratio for any post-recovery standard splits
S = the split ratio for any post-internal standard and post-cleanup standard splits

12.6 The Maximum Level (MaxL) is defined as the concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The MaxL is calculated as shown in the following equation:

$$\text{M}axL = \frac{C\,\text{max} \times Vfe}{W\text{s}}$$

Where:

Cmax = the concentration the analyte in the highest calibration standard Vfe and Ws are defined in Section 12.5.

12.7 Flag all compound results in the sample that were detected in the method blank with a "B" qualifier.

12.8 Flag all compound results in the sample that are below the minimum level with a "J" qualifier.

12.9 Flag all compound results in the sample that are above the upper calibration limit with an "E" qualifier.

12.10 Flag all compound results in the sample that are "Estimated Maximum Possible Concentrations" with a "Q" qualifier.

12.11 Flag compound results in the sample that exhibit chromatographic evidence of co-eluting compounds with a "C" qualifier.

12.12 Flag compound results in the sample that are affected by ion suppression with a "S" qualifier.

12.13 Data Review

12.13.1 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.13.2 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.13.3 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.13.4 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.13.5 All items listed on the data review check list must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data. An example data review check list is shown in Figure 3.

13. Method Performance

13.1 Method Detection Limit (MDL): An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP CA-Q-S-006, current revision, based on 40

CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2 Initial Demonstration of Capability: Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in Test America Knoxville SOP KNOX-QA-0009, current revision. Demonstration for both aqueous and solid matrices is required.

13.2.1 For aqueous samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with labeled internal standards and native analytes according to the procedures in section 11. For non-aqueous samples, extract, concentrate, and analyze four aliquots of sodium sulfate spiked with labeled internal standards and native analytes according to the procedures in section 11. It is recommended that a method blank be prepared with the IDOC samples. Extracts must be stored in the dark at room temperature in amber or clear glass vials prior to analysis.

13.2.2 Using the results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation (S) of the concentration in ng/mL for each compound.

13.2.3 For each compound, compare S and X with the corresponding limits for initial precision and recovery in Table 9 for method 1613B and Table 10 for methods 8290, 8290A 23, 0023A, and TO-9A. If S and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples can begin. If, however, any individual S exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009, current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

14. Pollution Prevention

14.1 All attempts will be made to minimize, as far as practical, the use of solvents and standard materials.

15. Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the

policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 See the current revision of SOP KNOX-HS-0002 for specific waste handling guidelines.

15.3 The following waste streams are produced when this method is carried out.

15.3.1 Waste solvents must be placed in the flammable waste stream, contained in a steel satellite accumulation container or flammable solvent container.

15.3.2 Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous must be placed in the incinerable laboratory waste stream, contained in a HDPE satellite accumulation container.

16. References

16.1 TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

16.2 EPA Method 1613: Tetra- Through Octa- Chlorinated Dioxins and Furans by Isotope Dilutions HRGC/HRMS, Revision B, October 1994.

16.3 SW-846 Method 8290, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 0, September 1994.

16.4 SW-846 Method 8290A, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 1, February 2007.

16.5 SW-846 Method 0023A, Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofuran Emissions from Stationary Sources, Revision 1, December 1996.

16.6 USEPA Method 23 – Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors. 40 CFR Part 60 Appendix A.

16.7 Method TO-9A: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition EPA/625/R-96/010b.

16.8 TestAmerica Knoxville SOP KNOX-ID-0012, "Method 0023A and Method 0010 Sampling Train Pre-Sampling Preparation and Sample Extraction Procedure (Includes TO-9A Sampling Components)", current revision.

16.9 TestAmerica Knoxville SOP KNOX-OP-0001, "Extraction of Polychlorinated Dioxins/Furans for Analysis by HRGC/HRMS Based on Methods 8290, 8290A and 1613B", current revision.

16.10 TestAmerica Policy, CA-T-P-002, Selection of Calibration Points, current revision.

17. Miscellaneous

17.1 Deviations from Reference Methods.

17.1.1 Spiking levels have been reduced to minimize the amount of dioxin contaminated waste generated by this procedure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.2 The absolute retention time requirements in Method 1613 section 15.4.1.1 is not required in this procedure. The routine maintenance required of GC columns when analyzing samples from hazardous waste sites makes this requirement virtually impossible to meet in a commercial laboratory environment. This requirement provides no additional quality assurance purpose beyond those already provided by the use of labeled internal standards and required relative retention time limits.

17.1.3 This procedure provides for additional calculation and reporting of sample specific detection limits and estimated maximum possible concentrations not required by Method 1613. These reporting conventions are similar to those required by EPA SW-846 Method 8290 and expected by data users familiar with EPA Office of Solid Waste program requirements.

17.1.4 Methods 8290/8290A do not require dilution and reanalysis of samples for which OCDD exceeds the calibration range. Although this allowance is not made by method 1613B, this procedure does not require dilution for OCDD on samples analyzed by that method.

17.1.5 The calibration standards specified in method 23 are used for method 0023A and TO-9A.

17.1.6 Extracts are stored at room temperature rather than at <10 °C as specified in method 1613B. Methods 8290 and 8290A allow for the storage of extracts at room temperature in the dark. All of the reference methods require that standards be stored at room temperature. Recovery studies performed by Cambridge Isotopes Laboratories (CIL) indicate freezing or refrigeration of standards causes problems with precipitation and irreversible adsorption to the inside surface of the vial. CIL recommends the storage of standards and extracts at room temperature as long as they are protected from exposure to UV and evaporative losses.

17.1.7 This procedure allows for the use of perfluorotributylamine (FC43) for mass calibration and resolution instead of the method recommended reference compound, Perfluorokerosene (PFK). FC43 is used on the newest HRMS instrument in the laboratory based on the manufacturer's recommendation. The

use of another mass reference substance is noted in both reference methods 1613B and 8290A. FC43 provides for less noise and less ion source contamination than the method recommended PFK.

17.1.8 The percent valley column resolution criteria is ≤ 25% for this SOP. Among the reference methods both ≤ 25% and < 25% are represented.

17.2 List of tables and figures referenced in the body of the SOP.

17.2.1 Table 1 – Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography /High Resolution Mass Spectrometry (HRGC/HRMS)

17.2.2 Table 2 – Methods – All, Minimum Levels by Matrix

17.2.3 Table 3 – Methods – 1613B and 8290/8290A, Retention Time References, Quantitation References, and Relative Retention Times

17.2.4 Table 4 – Methods – 23, 0023A, and TO-9A, Retention Time References and Quantitation References

17.2.5 Table 5 – Methods – 1613B and 8290/8290A, Initial Calibration Standard Concentrations and Acceptance Criteria

17.2.6 Table 6 – Methods – 23, 0023A, and TO-9A, Initial Calibration Standard Concentrations and Acceptance Criteria

17.2.7 Table 7 – Methods – 1613B and 8290/8290A, Daily Verification Standard (VER) Concentrations and Acceptance Criteria

17.2.8 Table 8 – Methods – 23, 0023A, and TO-9A, Daily Verification Standard (VER) Concentrations and Acceptance Criteria

17.2.9 Table 9 – Method – 1613B, Initial Demonstration of Capability (IDOC) Acceptance Criteria

17.2.10 Table 10 – Methods – 8290/8290A, 23, 0023A, and TO-9A, Initial Demonstration of Capability (IDOC) Acceptance Criteria

17.2.11 Table 11 – Laboratory Control Sample (LCS) Spiking Solution Component Concentrations and Acceptance Limits

17.2.12 Table 12 – Method – 8290/8290A. Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits

17.2.13 Table 13 - Methods – 1613B and 8290/8290A, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.14 Table 14 – Method – 1613B, Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.15 Table 15 – Methods – 23, 0023A, and TO-9A, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.16 Table 16 – Methods – 23, 0023A, and TO-9A, Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.17 Table 17 – Methods – All, Recovery Standard Spiking Solution Component Concentrations

17.2.18 Table 18 – Rtx-5/DB-5 Column Window Defining Standard Mixture Components. – Rtx-5 (DB-5) Column Performance Standard Mixture Components

17.2.19 Table 19 – Rtx-5/DB-5 Column Performance Standard Mixture Components

17.2.20 Table 20 – Rtx-225/DB-225 Column Performance Standard Mixture Components

17.2.21 Table 21 – DB-225 (Rtx-225) Column Performance Standard Mixture Components

17.2.22 Table 21 – Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

17.2.23 Table 22 – Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

17.2.24 Figure 1 – Recommended GC Operating Conditions

17.2.25 Figure 2 – Recommended MID Descriptors

17.2.26 Figure 3 – Example Data Review Checklist

17.2.27 Figure 4 – Analysis of PCDDs and PCDFs by HRGC/HRMS Flowchart

Table 1

Polychlorinated Dibenzo-p-dioxins/Dibenzofurans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)

PCDDs/PCDFs [1] Isomer/Congener	CAS Registry	Labeled Analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD $^{37}Cl_4$-2,3,7,8-TCDD	76523-40-5 85508-50-5
Total TCDD	41903-57-5		
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total TCDF	55722-27-5		
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total PeCDD	36088-22-9		
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total PeCDF	30402-15-4		
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total HxCDD	34465-46-8		
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
Total HxCDF	55684-94-1		
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total HpCDD	37871-00-4		
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total HpCDF	38998-75-3		
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	none	

Notes:

1. Polychlorinated dioxins and furans

TCDD	= Tetrachlorodibenzo-p-dioxin	TCDF	= Tetrachlorodibenzofuran
PeCDD	= Pentachlorodibenzo-p-dioxin	PeCDF	= Pentachlorodibenzofuran
HxCDD	= Hexachlorodibenzo-p-dioxin	HxCDF	= Hexachlorodibenzofuran
HpCDD	= Heptachlorodibenzo-p-dioxin	HpCDF	= Heptachlorodibenzofuran
OCDD	= Octachlorodibenzo-p-dioxin	OCDF	= Octachlorodibenzofuran

Table 2

Methods – All
Minimum Levels by Matrix

Analyte	Extract (ng/mL) [1]	Water (pg/L) [2]	Solids (pg/g) [3]	Biological Tissue (pg/g) [3]	Waste (pg/g) [4]	Air/Wipe (pg) [5]
2,3,7,8-TCDD	0.5	10	1	1	10	10
2,3,7,8-TCDF	0.5	10	1	1	10	10
1,2,3,7,8-PeCDD	2.5	50	5	5	50	50
1,2,3,7,8-PeCDF	2.5	50	5	5	50	50
2,3,4,7,8-PeCDF	2.5	50	5	5	50	50
1,2,3,4,7,8-HxCDD	2.5	50	5	5	50	50
1,2,3,6,7,8-HxCDD	2.5	50	5	5	50	50
1,2,3,7,8,9-HxCDD	2.5	50	5	5	50	50
1,2,3,4,7,8-HxCDF	2.5	50	5	5	50	50
1,2,3,6,7,8-HxCDF	2.5	50	5	5	50	50
2,3,4,6,7,8-HxCDF	2.5	50	5	5	50	50
1,2,3,7,8,9-HxCDF	2.5	50	5	5	50	50
1,2,3,4,6,7,8-HpCDD	2.5	50	5	5	50	50
1,2,3,4,6,7,8-HpCDF	2.5	50	5	5	50	50
1,2,3,4,7,8,9-HpCDF	2.5	50	5	5	50	50
OCDD	5.0	100	10	10	100	100
OCDF	5.0	100	10	10	100	100

Notes:

1 Concentration in the extract assuming a 20 µL volume.
2 Based on a sample volume of 1.0 L.
3 Based on a sample weight of 10.0 g.
4 Based on a sample weight of 1.0 g.
5 Based on extraction of the entire sample.

Table 3

Methods – 1613B and 8290/8290A
Retention Time References, Quantitation References and Relative Retention Times

Analyte	Retention Time and Quantitation Reference	Relative Retention Time
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard		
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999-1.002
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999-1.003
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999-1.002
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999-1.002
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999-1.002
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976-1.043
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989-1.052
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923-1.103
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.567
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.425
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011-1.526
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard		
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999-1.001
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998-1.004
1,2,3,7,8,9-HxCDD	--[1]	1.000-1.019
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999-1.001
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997-1.005
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999-1.001
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999-1.001
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999-1.001
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999-1.001
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999-1.001
OCDD	$^{13}C_{12}$-OCDD	0.999-1.001
OCDF	$^{13}C_{12}$-OCDD	0.999-1.008
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981-1.003
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944-0.970
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949-0.975
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959-1.021
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.047
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086-1.110
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043-1.085
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057-1.151
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032-1.311

Notes:

1 The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD. 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

Table 4

Methods – 23, 0023A and TO-9A
Retention Time References and Quantitation References

Analyte	Retention Time and Quantitation Reference
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard	
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard	
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDD	$^{13}C_{12}$-OCDD
OCDF	$^{13}C_{12}$-OCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

Table 5

Methods – 1613B and 8290/8290A
Initial Calibration Standard Concentrations and Acceptance Criteria

	CS1	CS2	CS3	CS4	CS5	1613B	8290	8290A
Analyte	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**%RSD**	**%RSD**	**%RSD**
Native PCDD's and PCDF's								
2,3,7,8-TCDD	0.5	2.0	10	40	200	±20	±20	±20
2,3,7,8-TCDF	0.5	2.0	10	40	200	±20	±20	±20
1,2,3,7,8-PeCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,7,8-PeCDF	2.5	10	50	200	1000	±20	±20	±20
2,3,4,7,8-PeCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000	±35	±20	±20
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20	±20
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000	±20	±20	±20
OCDD	5.0	20	100	400	2000	±20	±20	±20
OCDF	5.0	20	100	400	2000	±35	±20	±20
Labeled Internal Standards								
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-OCDD	200	200	200	200	200	±35	±30	±20
Labeled Cleanup Standard								
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2.0	10	40	200	±35	-	-
Labeled Recovery Standard								
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-	-

Table 6

Methods – 23, 0023A and TO-9A
Initial Calibration Standard Concentrations and Acceptance Criteria

	CS1	CS2	CS3	CS4	CS5	23 / TO-9A	0023A
Analyte	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**%RSD**	**%RSD**
Native PCDDs and PCDFs							
2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±20
2,3,7,8-TCDF	0.5	1.0	5	50	100	±25	±20
1,2,3,7,8-PeCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8-PeCDF	2.5	5	25	250	500	±25	±20
2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
2,3,4,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±20
OCDD	5.0	10	50	500	1000	±25	±20
OCDF	5.0	10	50	500	1000	±30	±20
Labeled Internal Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-OCDD	200	200	200	200	200	±30	±30
Surrogate Standards							
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±30
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±30
Labeled Recovery Standard							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-

Table 7

Methods – 1613B and 8290/8290A
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

Analyte	VER (ng/mL)	1613B All Isomers (ng/mL)	1613B Tetra only (ng/mL)		8290/8290A Shift Open %D	8290/8290A Shift Close[1] %D
Native PCDDs and PCDFs						
2,3,7,8-TCDD	10	7.8-12.9	8.2-12.3		±20	±25
2,3,7,8-TCDF	10	8.4-12.0	8.6-11.6		±20	±25
1,2,3,7,8-PeCDD	50	39-65	-		±20	±25
1,2,3,7,8-PeCDF	50	41-60	-		±20	±25
2,3,4,7,8-PeCDF	50	41-61	-		±20	±25
1,2,3,4,7,8-HxCDD	50	39-64	-		±20	±25
1,2,3,6,7,8-HxCDD	50	39-64	-		±20	±25
1,2,3,7,8,9-HxCDD	50	41-61	-		±20	±25
1,2,3,4,7,8-HxCDF	50	45-56	-		±20	±25
1,2,3,6,7,8-HxCDF	50	44-57	-		±20	±25
2,3,4,6,7,8-HxCDF	50	44-57	-		±20	±25
1,2,3,7,8,9-HxCDF	50	45-56	-		±20	±25
1,2,3,4,6,7,8-HpCDD	50	43-58	-		±20	±25
1,2,3,4,6,7,8-HpCDF	50	45-55	-		±20	±25
1,2,3,4,7,8,9-HpCDF	50	43-58	-		±20	±25
OCDD	100	79-126	-		±20	±25
OCDF	100	63-159	-		±20	±25
Labeled Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	100	82-121	85-117		±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	71-140	76-131		±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62-160	-		±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76-130	-		±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77-130	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	85-117	-		±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85-118	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76-131	-		±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70-143	-		±30	±35
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	73-137	-		±30	±35
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	74-135	-		±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72-138	-		±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78-129	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77-129	-		±30	±35
$^{13}C_{12}$-OCDD	200	96-415	-		±30	±35
Labeled Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9-12.7	8.3-12.1		-	-
Labeled Recovery Standard						
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-		-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-		-	-

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

Table 8

Methods – 23, 0023A and TO-9A
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

			0023A	
	VER	23 and TO-9A	Shift Open	Shift Close[1]
Analyte	(ng/mL)	%D	%D	%D
Native PCDDs and PCDFs				
2,3,7,8-TCDD	5	±25	±20	±25
2,3,7,8-TCDF	5	±25	±20	±25
1,2,3,7,8-PeCDD	25	±25	±20	±25
1,2,3,7,8-PeCDF	25	±25	±20	±25
2,3,4,7,8-PeCDF	25	±25	±20	±25
1,2,3,4,7,8-HxCDD	25	±25	±20	±25
1,2,3,6,7,8-HxCDD	25	±25	±20	±25
1,2,3,7,8,9-HxCDD	25	±25	±20	±25
1,2,3,4,7,8-HxCDF	25	±25	±20	±25
1,2,3,6,7,8-HxCDF	25	±25	±20	±25
2,3,4,6,7,8-HxCDF	25	±25	±20	±25
1,2,3,7,8,9-HxCDF	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDD	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDF	25	±25	±20	±25
1,2,3,4,7,8,9-HpCDF	25	±25	±20	±25
OCDD	50	±25	±20	±25
OCDF	50	±30	±20	±25
Labeled Internal Standards				
$^{13}C_{12}$-2,3,7,8-TCDD	100	±25	±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	±25	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	±30	±30	±35
$^{13}C_{12}$-OCDD	200	±30	±30	±35
Surrogate Standards				
$^{37}Cl_4$-2,3,7,8-TCDD	5	±25	±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	±25	±30	±35
Labeled Recovery Standard				
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-	

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

Table 9

Method – 1613B
Initial Demonstration of Capability (IDOC) Acceptance Criteria

	Test	1613B			1613B Tetra Only	
Analyte	Conc. (ng/mL) [1]	s^2 (ng/mL) [1]	X^3 (ng/ml) [1]		s^2 (ng/mL) [1]	X^3 (ng/ml) [1]
Native PCDDs and PCDFs						
2,3,7,8-TCDD	10	2.8	8.3-12.9		2.7	8.7-12.4
2,3,7,8-TCDF	10	2.0	8.7-13.7		2.0	9.1-13.1
1,2,3,7,8-PeCDD	50	7.5	38-66		-	-
1,2,3,7,8-PeCDF	50	7.5	43-62		-	-
2,3,4,7,8-PeCDF	50	8.6	36-75		-	-
1,2,3,4,7,8-HxCDD	50	9.4	39-76		-	-
1,2,3,6,7,8-HxCDD	50	7.7	42-62		-	-
1,2,3,7,8,9-HxCDD	50	11.1	37-71		-	-
1,2,3,4,7,8-HxCDF	50	8.7	41-59		-	-
1,2,3,6,7,8-HxCDF	50	6.7	46-60		-	-
2,3,4,6,7,8-HxCDF	50	7.4	37-74		-	-
1,2,3,7,8,9-HxCDF	50	6.4	42-61		-	-
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65		-	-
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56		-	-
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63		-	-
OCDD	100	19	89-127		-	-
OCDF	100	27	74-146		-	-
Labeled Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	50	18.5	14-67		17.5	16-57.5
$^{13}C_{12}$-2,3,7,8-TCDF	50	17.5	15.5-56.5		17	17.5-49.5
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	19.5	13.5-92		-	-
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	17.0	13.5-78		-	-
$^{13}C_{12}$-2,3,4,7,8-PeCDF	50	19.0	8-139.5		-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	50	20.5	14.5-73.5		-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	50	19.0	17-61		-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	50	21.5	13.5-76		-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	50	17.5	15-61		-	-
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	50	18.5	14.5-68		-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	50	20.0	12-78.5		-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	50	17.5	17-64.5		-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	50	20.5	16-55		-	-
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	50	20.0	14-70.5		-	-
$^{13}C_{12}$-OCDD	100	47.5	20.5-138		-	-
Labeled Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4		3.4	4.5-13.4

Notes:

1 All specifications are given as concentration in the final extract, assuming a 20-µL volume.

2 s = standard deviation of the concentration

3 X = average concentration. The acceptance range for average recovery can be normalized (shifted to center on 100% recovery) to compensate for the bias in the collaborative study used to develop the acceptance criteria.

Table 10

Methods – 8290/8290A, 23, 0023A and TO-9A
Initial Demonstration of Capability (IDOC) Acceptance Criteria

Analyte	Test Conc (ng/mL)[1]	s[2] (%Rec)	X[3] (%Rec)
Native PCDDs and PCDFs			
2,3,7,8-TCDD	10	15[4]	70-130[4]
2,3,7,8-TCDF	10	15[4]	70-130[4]
1,2,3,7,8-PeCDD	50	15[4]	70-130[4]
1,2,3,7,8-PeCDF	50	15[4]	70-130[4]
2,3,4,7,8-PeCDF	50	15[4]	70-130[4]
1,2,3,4,7,8-HxCDD	50	15[4]	70-130[4]
1,2,3,6,7,8-HxCDD	50	15[4]	70-130[4]
1,2,3,7,8,9-HxCDD	50	15[4]	70-130[4]
1,2,3,4,7,8-HxCDF	50	15[4]	70-130[4]
1,2,3,6,7,8-HxCDF	50	15[4]	70-130[4]
2,3,4,6,7,8-HxCDF	50	15[4]	70-130[4]
1,2,3,7,8,9-HxCDF	50	15[4]	70-130[4]
1,2,3,4,6,7,8-HpCDD	50	15[4]	70-130[4]
1,2,3,4,6,7,8-HpCDF	50	15[4]	70-130[4]
1,2,3,4,7,8,9-HpCDF	50	15[4]	70-130[4]
OCDD	100	15[4]	70-130[4]
OCDF	100	15[4]	70-130[4]

Notes:
1 All specifications are given as concentration in the final extract, assuming a 20 µL volume.
2 s = standard deviation of the percent recovery
3 X = average percent recovery
4 Inhouse generated historical control limits can be used in place of the specified limit.

Table 11

Laboratory Control Sample (LCS) Spiking Solution Component Concentrations and Acceptance Limits

Analyte	LCS Solution Conc. (ng/mL)[1]	Final Extract Conc (ng/mL)[2]	1613B LCS Conc (ng/mL)[2]	8290/8290A, 23, 0023A, TO-9A Recovery (%Rec)
2,3,7,8-TCDD	0.2	10	6.7-15.8	70-130[4]
2,3,7,8-TCDF	0.2	10	7.5-15.8	70-130[4]
1,2,3,7,8-PeCDD	1.0	50	35-71	70-130[4]
1,2,3,7,8-PeCDF	1.0	50	40-67	70-130[4]
2,3,4,7,8-PeCDF	1.0	50	34-80	70-130[4]
1,2,3,4,7,8-HxCDD	1.0	50	35-82	70-130[4]
1,2,3,6,7,8-HxCDD	1.0	50	38-67	70-130[4]
1,2,3,7,8,9-HxCDD	1.0	50	32-81	70-130[4]
1,2,3,4,7,8-HxCDF	1.0	50	36-67	70-130[4]
1,2,3,6,7,8-HxCDF	1.0	50	42-65	70-130[4]
2,3,4,6,7,8-HxCDF	1.0	50	35-78	70-130[4]
1,2,3,7,8,9-HxCDF	1.0	50	39-65	70-130[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	35-70	70-130[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	41-61	70-130[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	39-69	70-130[4]
OCDD	2.0	100	78-144	70-130[4]
OCDF	2.0	100	63-170	70-130[4]
Tetras Only				
2,3,7,8-TCDD	0.2	10	7.3-14.6	70-130[4]
2,3,7,8-TCDF	0.2	10	8.0-14.7	70-130[4]

Notes:

1 1.0 mL of this solution is added to the LCS before extraction (see section 7.11.2).

2 The final extract concentration is based on an extract volume of 20 µL.

3 Spike concentrations are based on a 1.0 L extraction for water, 10.0g extraction for solids, and entire sample extraction for air/wipe samples.

4 Inhouse generated historical control limits can be used in place of the specified limit.

Table 12

Method – 8290/8290A
Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits[1]

Analyte	LCS Solution Conc. (ng/mL)[2]	Final Extract Conc (ng/mL)[3]	8290 Recovery (%Rec)	8290 Precision (RPD)
2,3,7,8-TCDD	0.2	10	70-130[4]	±15[4]
2,3,7,8-TCDF	0.2	10	70-130[4]	±15[4]
1,2,3,7,8-PeCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
2,3,4,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
2,3,4,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	70-130[4]	±15[4]
OCDD	2.0	100	70-130[4]	±15[4]
OCDF	2.0	100	70-130[4]	±15[4]

Notes:
1 If insufficient sample exists for MS/MSD analysis, these limits apply to LCS/LCSD samples.
2 1.0 mL of this solution is added to the LCS before extraction (see section 1.1).
3 The final extract concentration is based on an extract volume of 20 µL.
4 Inhouse generated historical control limits can be used in place of the specified limit.

Table 13

Methods – 1613B and 8290/8290A
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B LCS Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	8290 Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	10.0-87.5	12.5-82.0	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	11.0-76.0	12.0-84.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	10.5-113.5	12.5-90.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	10.5-96.0	12.0-92.5	40-135
$^{13}C_{12}$-2,3,4,7,8-PeCDF	1.0	50	6.5-164.0	10.5-89.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	1.0	50	10.5-96.5	16.0-70.5	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	12.5-81.5	14.0-65.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1.0	50	9.5-101.0	13.0-76.0	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	10.5-79.5	13.0-61.5	40-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	1.0	50	11.0-88.0	14.0-68.0	40-135
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	1.0	50	8.5-102.5	14.5-73.5	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	13.0-83.0	11.5-70.0	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	10.5-79.0	14.0-71.5	40-135
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	1.0	50	10.0-93.0	13.0-69.0	40-135
$^{13}C_{12}$-OCDD	2.0	100	13.0-198.5	17.0-157	40-135
Tetras Only					
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	12.5-70.5	15.5-68.5	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	13.0-63.0	14.5-70.0	40-135

Notes:
1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS prior to extraction (see section 1.1).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 14

Method – 1613B
Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B LCS Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	1613B LCS Tetra Only Conc (ng/mL)[2]	1613B Sample Tetra Only Conc (ng/mL)[2]
$^{37}Cl_4$-2,3,7,8-TCDD	0.2	10	3.1-19.1	3.5-19.7	3.7-15.8	4.2-16.4

Notes:
1 1.0 mL of the Cleanup Standard Spiking Solution is added to each sample, method blank and LCS prior to cleanup (see section 7.11.6).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 15

Methods – 23, 0023A and TO-9A
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-OCDD	2.0	100	25-130	40-135	40-120

Notes:

1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS prior to extraction (see section 7.11.4).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 16

Methods – 23, 0023A, and TO-9A
Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{37}Cl_4$-2,3,7,8-TCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-2,3,4,7,8-PeCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	20	100	70-130	70-130	40-120

Notes:

1 100 µL of the Surrogate Standard Spiking Solution is added to each sample train prior to sampling (see section 1.1).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 17

Methods – All
Recovery Standard Spiking Solution Component Concentrations

Labeled Analyte	Solution Conc (µg/mL)[1]	Test Conc. (ng/mL)[2]
$^{13}C_{12}$-1,2,3,4-TCDD	0.1	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.1	100

Notes:
1 20 µL of the Recovery Standard Spiking Solution is added to each sample, method blank and LCS prior to analysis (see section 1.1).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 18

Rtx-5/DB-5 Column Window Defining Standard Mixture Components

Congener	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,6,8-/1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-/1,2,4,6,8,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

Table 19

Rtx-5 (DB-5) Column Performance Standard Mixture Components

Isomer
1,2,3,7/1,2,3,8-TCDD
1,2,3,9-TCDD
2,3,7,8-TCDD

Table 20

DB-225 (Rtx-225) Column Performance Standard Mixture Components

Isomer
2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

Table 21

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
1	292.9825 (313.9834)	LOCK	$C_7F_{11}(C_6NF_{12}^+)$	PFK (FC43)
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	342.9792 (363.9802)	QC	$C_8F_{13}(C_7NF_{14}^+)$	PFK (FC43)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
2	330.9792 (313.9834)	LOCK	$C_7F_{13}(C_6NF_{12}^+)$	PFK (FC43)
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	380.9760 (375.9802)	QC	$C_8F_{15}(C_8NF_{14}^+)$	PFK (FC43)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	380.9760 (375.9802)	LOCK	$C_8F_{15}(C_8NF_{14}^+)$	PFK (FC43)
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	404.9760 (413.9770)	QC	$C_{10}F_{15}(C_8NF_{16}^+)$	PFK (FC43)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE

Table 21 (Continued)

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
4	404.9760 (413.9770)	LOCK	$C_{10}F_{15}(C_8NF_{16}^+)$	PFK (FC43)
	407.7818	M+2	$C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$	HpCDF
	409.7788	M+4	$C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0$	HpCDF
	417.8250	M	$^{13}C_{12}H\ ^{35}Cl_7\ 0$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$	HpCDF (S)
	423.7767	M+2	$C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$	HpCDD
	425.7737	M+4	$C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$	HpCDD (S)
	442.9728 (463.9738)	QC	$C_{10}F_{17}(C_9NF_{18}^+)$	PFK (FC43)
	479.7165	M+4	$C_{12}H\ ^{35}Cl_7\ ^{37}Cl_2\ 0$	NCDPE
5	430.9728 (425.9770)	LOCK	$C_9F_{17}(C_9NF_{16}^+)$	PFK (FC43)
	441.7428	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0$	OCDF
	443.7399	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0$	OCDF
	457.7377	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$	OCDD
	459.7348	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$	OCDD
	469.7780	M+2	$^{13}C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$	OCDD (S)
	480.9696 (501.9706)	QC	$C_{10}F_{19}(C_9NF_{20}^+)$	PFK (FC43)
	513.6775	M+4	$C_{12}\ ^{35}Cl_8\ ^{37}Cl_2\ 0$	DCDPE

Notes:

1 Nuclidic masses used:

H = 1.007825	C = 12.00000	^{13}C = 13.003355	F = 18.9984
O = 15.994915	^{35}Cl = 34.968853	^{37}Cl = 36.965903	

Table 22

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

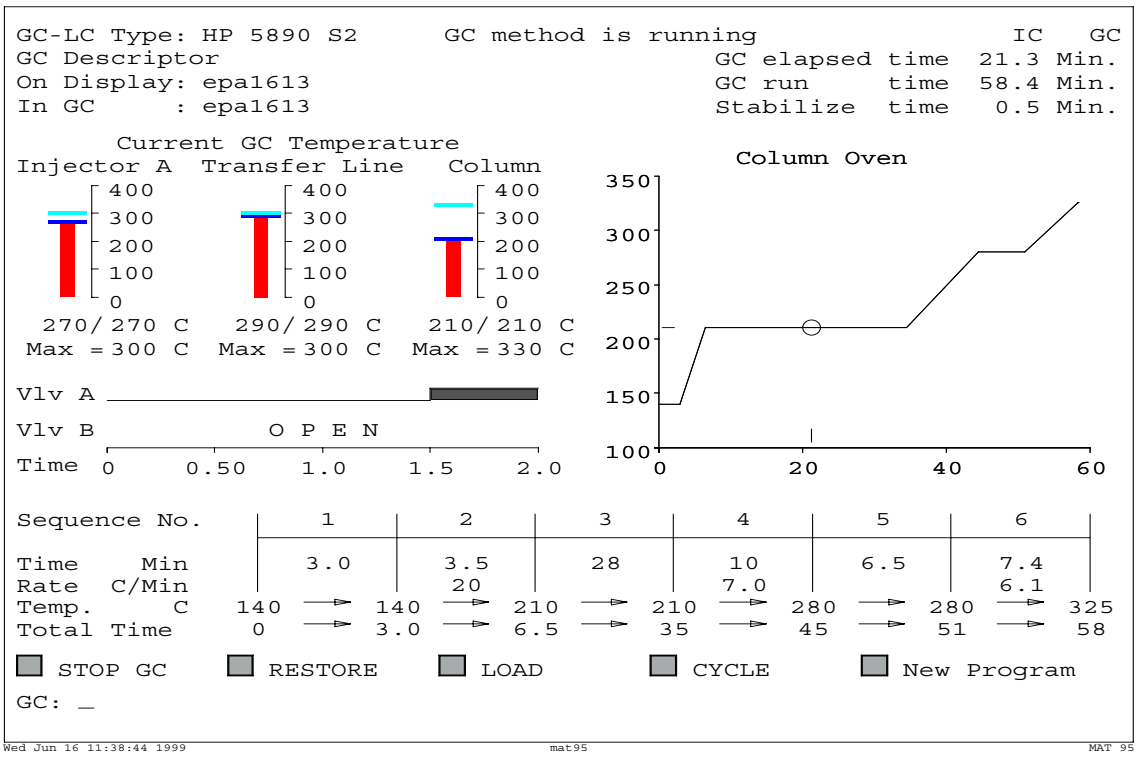
Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6 [1]	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.04/1.05 [3]	0.88	1.20
7 [2]	M/M+2	0.44	0.37	0.51
8	M+2/M+4	0.89	0.76	1.02

Notes:

1 Used for ^{13}C-HxCDF (IS).
2 Used for ^{13}C-HpCDF (IS).
3 Method 1613B Theoretical Ratio

Figure 1

Rtx-5 Recommended GC Operating Conditions



DB-225 Recommended GC Operating Conditions

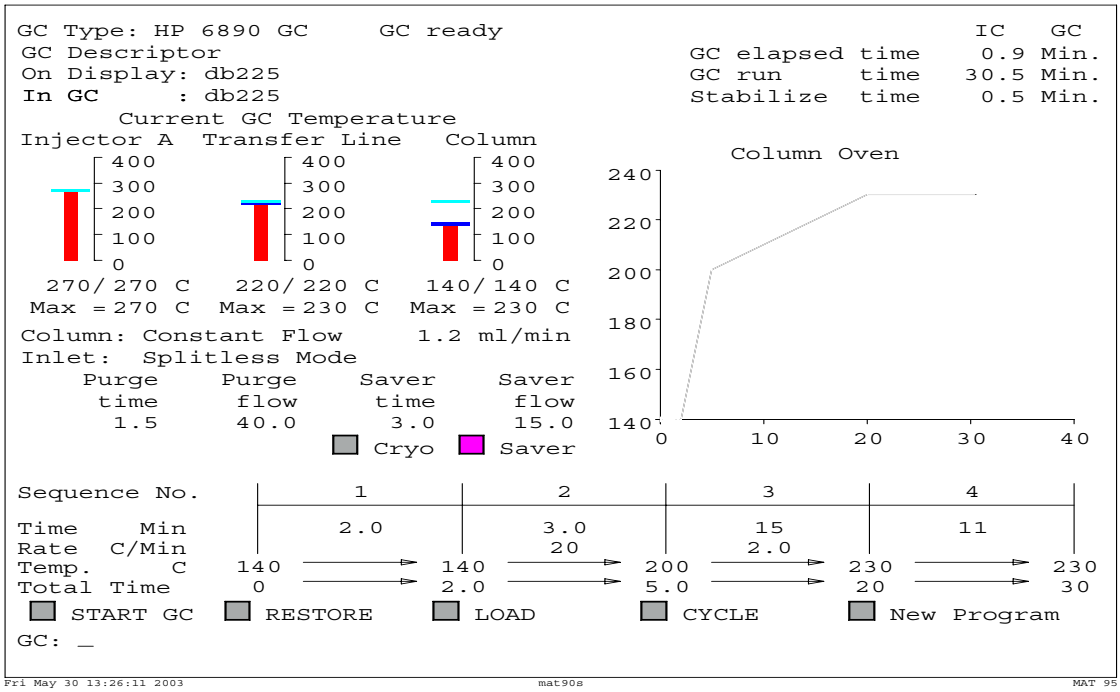
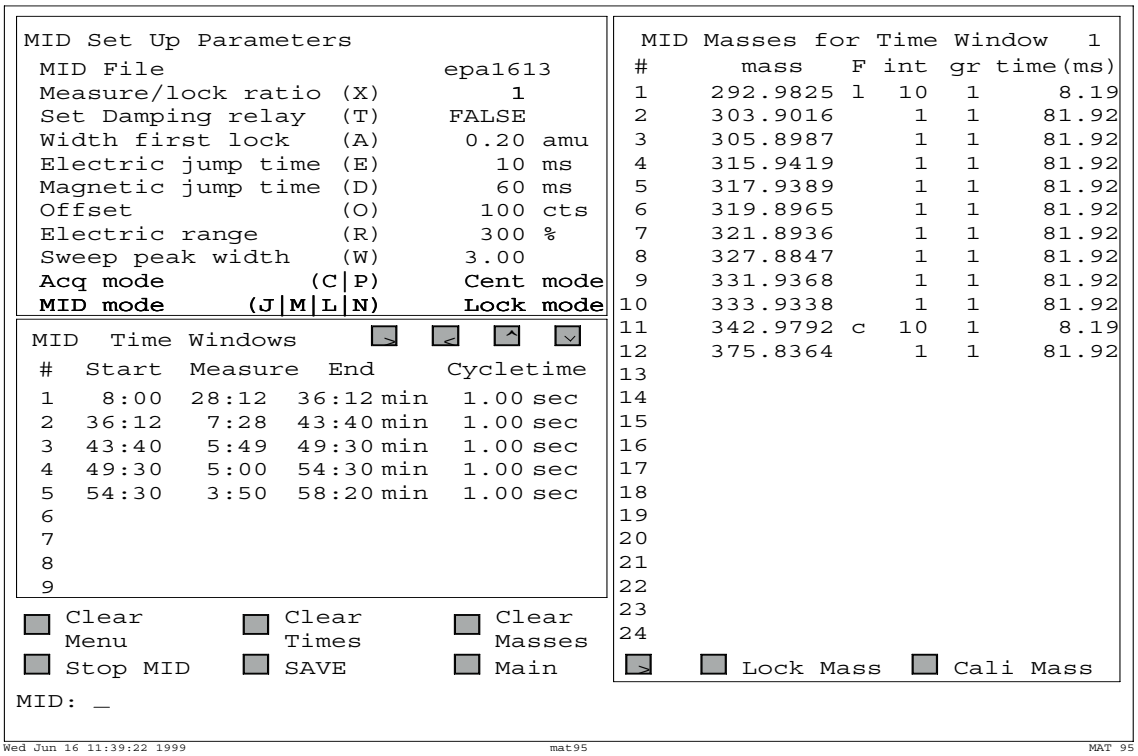


Figure 2

Rtx-5 Recommended MID Descriptors



MID Set Up Parameters

MID File		epa1613
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.20 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	**(C|P)**	**Cent mode**
MID mode	**(J|M|L|N)**	**Lock mode**

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	28:12	36:12 min	1.00 sec
2	36:12	7:28	43:40 min	1.00 sec
3	43:40	5:49	49:30 min	1.00 sec
4	49:30	5:00	54:30 min	1.00 sec
5	54:30	3:50	58:20 min	1.00 sec
6				
7				
8				
9				

Clear Menu | Clear Times | Clear Masses
Stop MID | SAVE | Main

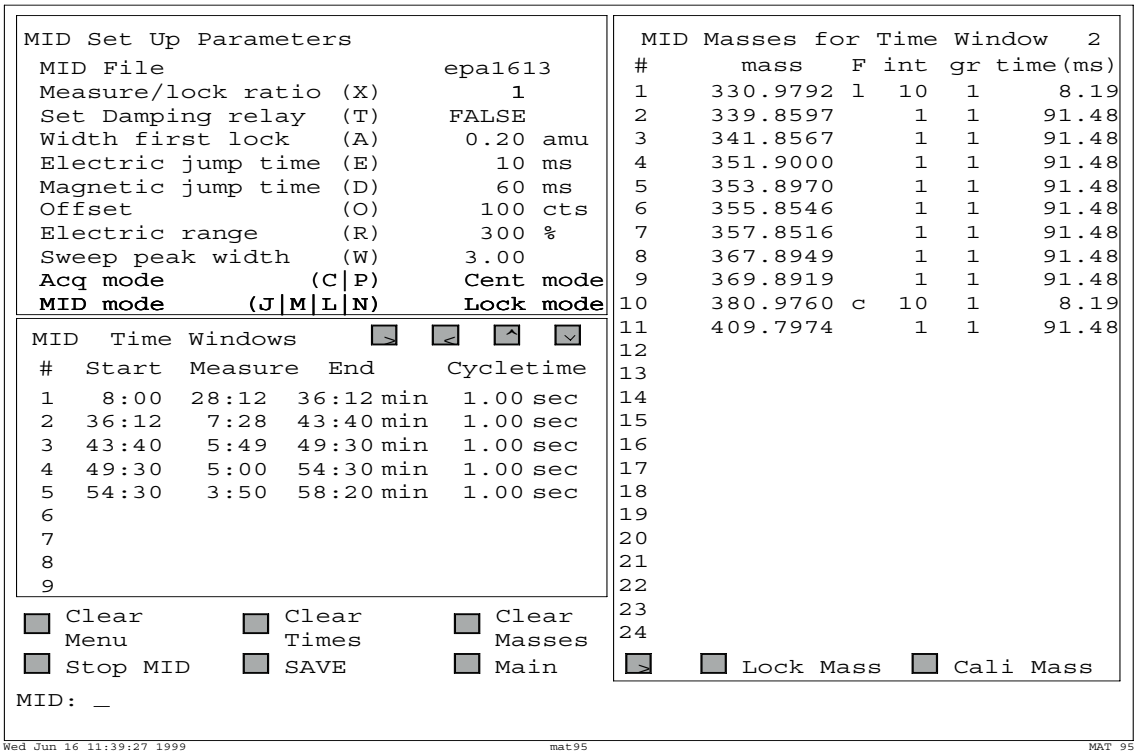
MID Masses for Time Window 1

#	mass	F	int	gr	time(ms)
1	292.9825	l	10	1	8.19
2	303.9016		1	1	81.92
3	305.8987		1	1	81.92
4	315.9419		1	1	81.92
5	317.9389		1	1	81.92
6	319.8965		1	1	81.92
7	321.8936		1	1	81.92
8	327.8847		1	1	81.92
9	331.9368		1	1	81.92
10	333.9338		1	1	81.92
11	342.9792	c	10	1	8.19
12	375.8364		1	1	81.92
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Lock Mass | Cali Mass

MID: _

Wed Jun 16 11:39:22 1999 mat95 MAT 95



MID Set Up Parameters

MID File		epa1613
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.20 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	**(C|P)**	**Cent mode**
MID mode	**(J|M|L|N)**	**Lock mode**

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	28:12	36:12 min	1.00 sec
2	36:12	7:28	43:40 min	1.00 sec
3	43:40	5:49	49:30 min	1.00 sec
4	49:30	5:00	54:30 min	1.00 sec
5	54:30	3:50	58:20 min	1.00 sec
6				
7				
8				
9				

Clear Menu | Clear Times | Clear Masses
Stop MID | SAVE | Main

MID Masses for Time Window 2

#	mass	F	int	gr	time(ms)
1	330.9792	l	10	1	8.19
2	339.8597		1	1	91.48
3	341.8567		1	1	91.48
4	351.9000		1	1	91.48
5	353.8970		1	1	91.48
6	355.8546		1	1	91.48
7	357.8516		1	1	91.48
8	367.8949		1	1	91.48
9	369.8919		1	1	91.48
10	380.9760	c	10	1	8.19
11	409.7974		1	1	91.48
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Lock Mass | Cali Mass

MID: _

Wed Jun 16 11:39:27 1999 mat95 MAT 95

Figure 2 (Continued)

Rtx-5 Recommended MID Descriptors

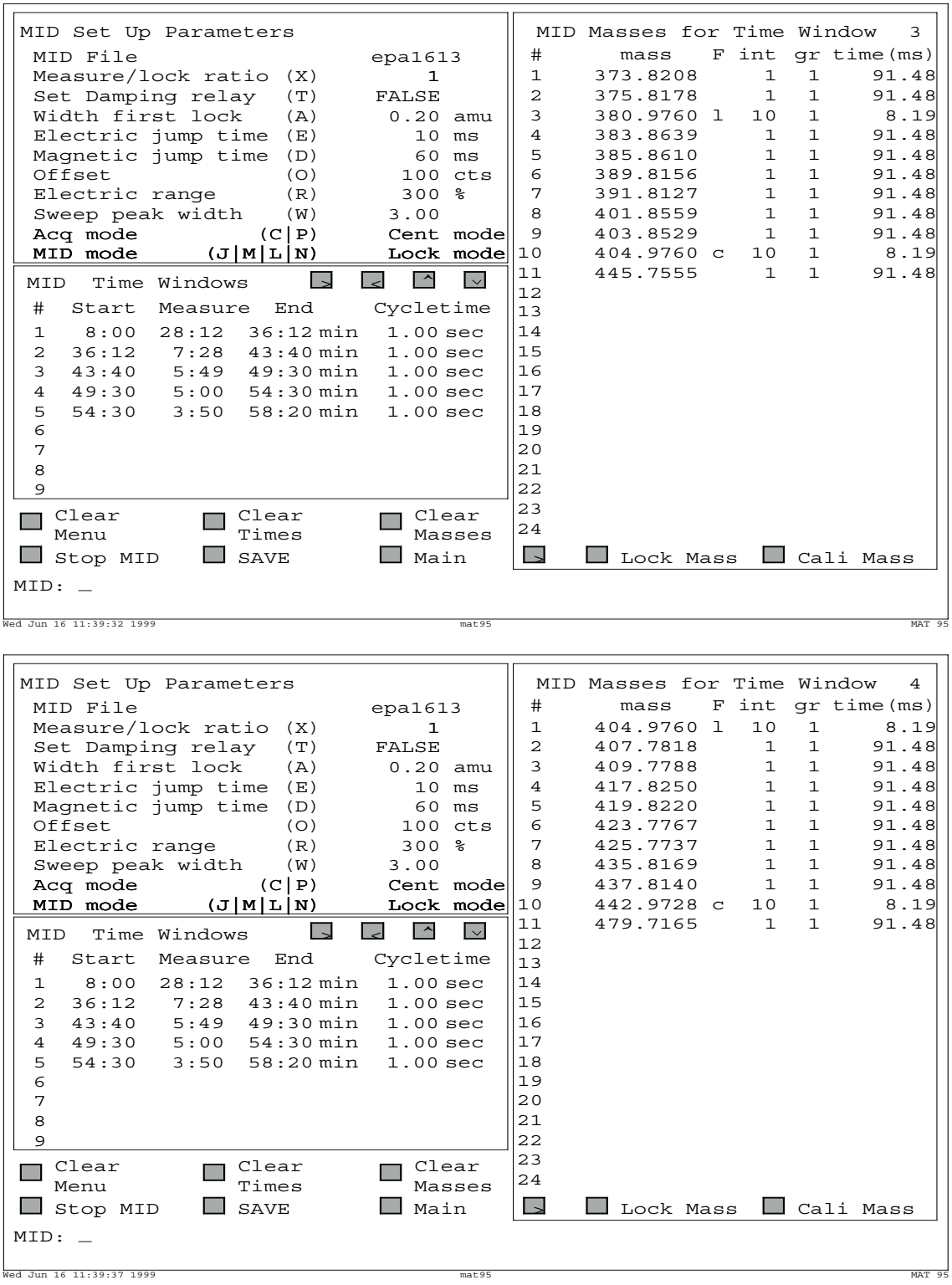
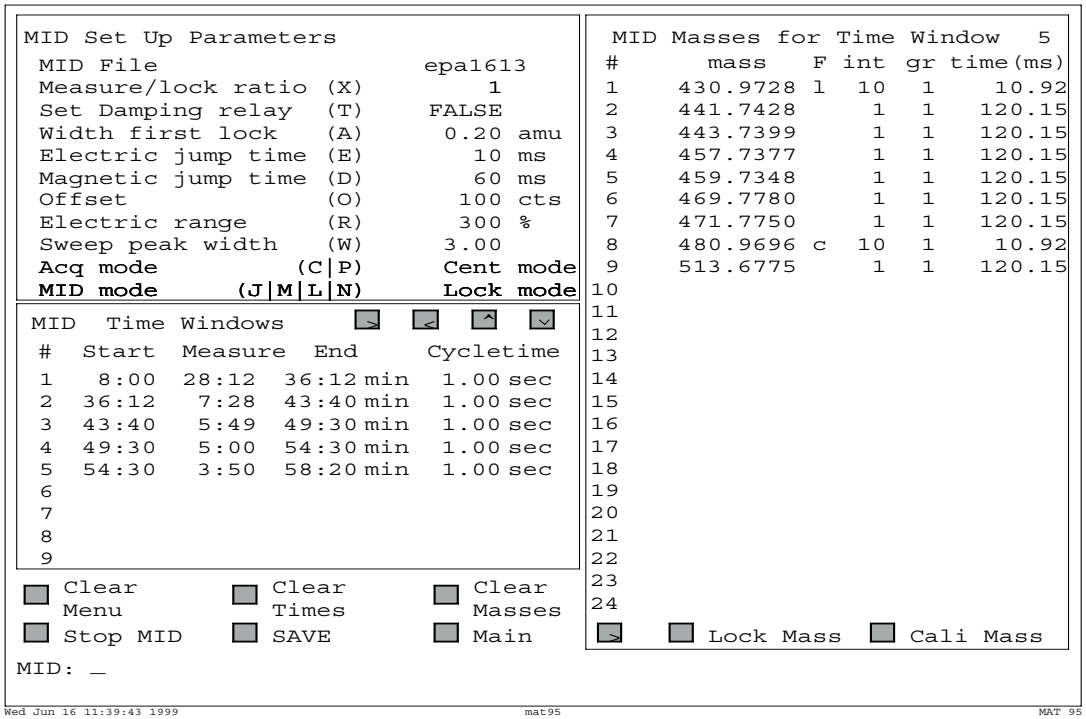


Figure 2 (Continued)

Rtx-5 Recommended MID Descriptors



DB-225 Recommended MID Descriptor

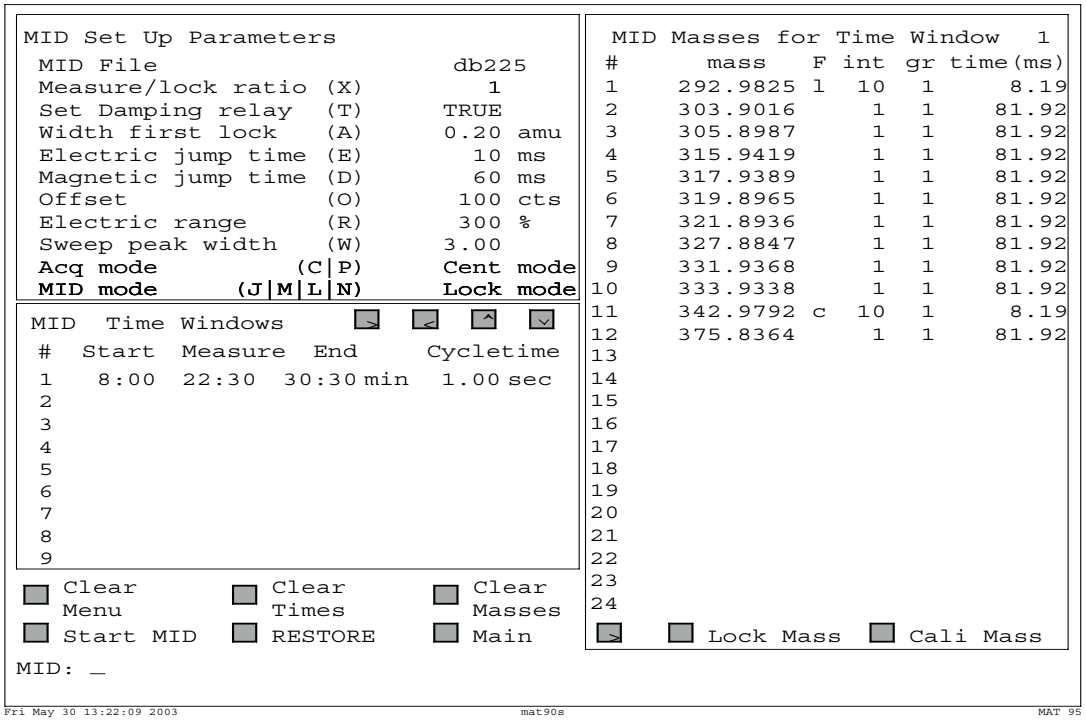


Figure 3

Example Sample Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Initial Calibration Data Review / Narrative Checklist
Method: 8290/8290A - KNOX-ID-0004-R9

Mass Res. ✓ Date/Time:		Inst:		Win Filename:		Col Perf Filename:	

CS1 Filename	CS2 Filename	CS3 Filename	CS4 Filename	CS5 Filename

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented before beginning the initial calibration?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 or FC43 m/z 313.9838 and m/z 363.9807?					
3. Was the measured exact mass of m/z 380.9760 (PFK) or 363.9807 (FC43) within 5 ppm at reduced accelerating voltage?					
4. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
5. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
6. Were the five calibration standard solutions, at the concentrations specified in Table 5 of the SOP, analyzed?					
7. Was date/time of analysis verified between analysis header and logbook as correct?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 5), quantitation ions (Table 22), and formula (Section 10.2.6)?					
9. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3?					
10. Are %RSD ≤20% for all unlabeled native analytes?					
11. **8290**, are %RSD ≤30% for all labeled internal standards?					
12. **8090A**, are %RSD ≤20% for all labeled internal standards?					
13. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
14. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP?					
15. Was the second source (Wellington) ICV standard analyzed, and the %D calculated and within the acceptance criteria of < ±35%?					
16. If manual integrations were performed, are they clearly identified, initialed and dated?					
17. Were before/after chromatograms reviewed to determine whether the software and manual integrations were appropriate?.					
18. Were manual integrations performed properly?.					
19. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
20. Does the ICAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard, ICV Summary Table, Calculation Summary, and chromatograms?					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

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Figure 3 (Continued)

Example Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Continuing Calibration Review / Narrative Checklist
Method: 8290/8290A - KNOX-ID-0004-R9

Start Mass Res. ✓:		**Ver Filename:**		**Inst:**	
End Mass Res. ✓:		**Win Filename:**		**ICAL Date:**	
		Col Perf Filename:			
		End Ver Filename:			

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented at both the beginning and end of the 12 hour shift?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 or FC43 m/z 313.9838 and m/z 363.9807?					
3. Was the measured exact mass of m/z 380.9760 (PFK) or 363.9807 (FC43) within 5 ppm at reduced accelerating voltage?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
6. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
7. Were continuing calibrations performed at the beginning and end of the 12-hour period, with successful mass resolution and GC resolution performance checks?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 3), quantitation ions (Table 22), and formula (Section 10.2.6)?					
9. Are the measured RRFs for each compound within the specified control limits in Table 7 for all PCDDs/PCDFs?					
10. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3?					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. Were before/after chromatograms reviewed to determine whether the software and manual integrations were appropriate?.					
15. Were manual integrations performed properly?.					
16. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
17. Does the CCAL folder contain **complete** data in the following order: Data review checklist, a **complete** runlog, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards?					

Analyst:	**Date:**	**2nd Level Reviewer :**	**Date:**
Comments:		**Comments:**	

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Figure 3 (Continued)

Example Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Data Review / Narrative Checklist LOT #_____
Method: 8290/8290A- KNOX-ID-0004-R9 Page 1 of 1 Batch#_____

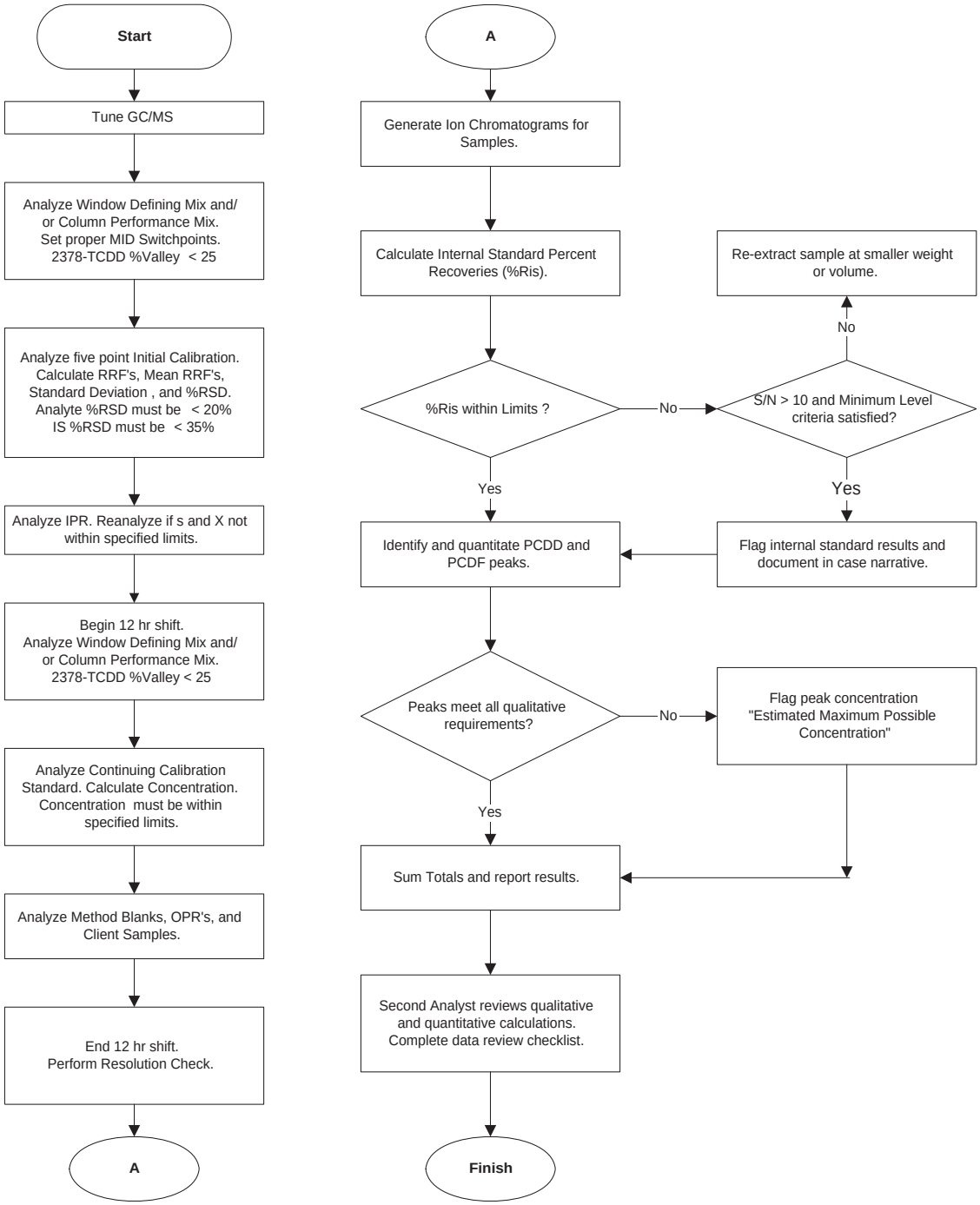
Review Items **A. Initial Calibration**	N/A	Yes	No	Why is data reportable?	2nd Level
1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.)					
B. Continuing Calibration	**N/A**	**Yes**	**No**		**2nd**
1. Has a Continuing Calibration Checklist been completed for each analytical batch?					
C. Client Sample AND QC Sample Results	**N/A**	**Yes**	**No**		**2nd**
1. Were all special project requirements met?					
2. Were the header information, prep factors, and dilution factors verified?					
3. Is logbook date/time of analysis correct?					
4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:*_____				HT expired upon receipt. * Client requested analysis after HT expired. Re-extraction done after HT expired.	
5. Are internal standards within QC limits specified in Table 13? *If no, list samples and reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____				* **[sup]** Ion suppression due to matrix. * **[low]** Low recovery. S/N >10 and EDL<ML. **[sam]** Not enough sample to re-extract. **[dil]** Dilution showed acceptable %R. **[mtx]** Obvious matrix interference. Further cleanup not possible. * **[unk]** At client's request, data was flagged as estimated and released without further investigation.	
6. Were reported PCDD/Fs which did not meet the criteria below, properly calculated and reported as EMPCs?: • RT of 2378 isomers within -1 to +3 seconds of associated labeled isomer. • RT of non-2378 isomers within established first/last windows. • Both native ions maximized within ±2 seconds. • Ion abundance ratios within the control limits specified in Table 22. • No corresponding peak at PCDPE mass.					
7. Were all 2378-TCDF hits ≥ ML confirmed by analysis on DB-225?					
8. Are positive results > ML within calibration range? *If no, list samples:*_____				OCDD/F or non-2378 exceeded calibration range Sample extracted at lowest possible volume	
9. Are all manual integrations performed properly and clearly identified and approved?					
10. Were before/after chromatograms reviewed to determine whether the software and manual integrations were appropriate?.					
11. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					
12. Was a narrative prepared and all deviations noted?					
D. Preparation/Matrix QC	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd**
1. LCS(OPR) done per prep batch and all analytes within the limits specified in QuantIMS reference data?				* Reanalysis not possible-insufficient sample. LCS %R high and affected analyte(s) were <ML in associated samples.	
2. Method blank done per prep batch, method/instrument blank analyzed with each sequence and analytes present in the method blank ≤ ML? *If no, list blank ID:* _____				Sample results are > 20x higher than blank. * There is no analyte > RL in the samples associated with method blank. * Reanalysis not possible-insufficient sample	
3. MS/MSD recoveries and RPDs within laboratory generated QC limits? *If no, list MS/MSD* _____				LCS acceptable, indicating sample matrix effects. LCS acceptable, high analyte concentration. LCS acceptable, lack of sample homogeneity.	
E. Other	**N/A**	**Yes**	**No**		**2nd**
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	**Date:**	**Analyst:**	**Date:**
Comments:		**Comments:**	

* Such action must be taken in consultation with client.

Figure 4

Analysis of PCDDs and PCDFs by HRGC/HRMS



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TESTAMERICA KNOXVILLE
SOP CHANGE FORM

SOP NUMBER: KNOX-OP-0001 Revision 1

SOP TITLE: Extraction of Polychlorinated Dioxins/Furans for Analysis by HRGC/HRMS Based on Methods 8290, 8290A, and 1613B

SOP SECTIONS AFFECTED BY CHANGE: 3.1, 7.13, 7.13.4, 9.2, and 11.11.2

REASON FOR ADDITION OR CHANGE: Method 8290A does not require the use of a Cleanup Standard. Therefore, only Method 1613 will be spiked with the Cleanup Standard.

CHANGE EFFECTIVE FROM: 4/22/11

CHANGE OR ADDITION (SPECIFY SECTION; USE ADDITIONAL SHEETS IF NECESSARY)

3.1 Cleanup Standard: Solution containing $^{37}Cl_4$-2,3,7,8-TCDD that is added to every 1613B ~~and 8290A~~ sample, blank and quality control spike sample after extraction but prior to extract cleanup. The analysis results are used to judge the efficiency of the cleanup procedures.

7.13 1613B ~~and 8290A~~ Cleanup Standards

7.13.4 Cleanup Standard Spiking Solution: Dilute 200 µL of the 200 ng/mL working stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with hexane to a final concentration of 0.20 ng/mL. 1.0 mL of this solution is added to each 1613B ~~or 8290A~~ sample, method blank and QC sample extract prior to cleanup. See Table 2 for a complete list of compounds and their concentrations.

9.2 Cleanup Standards: For methods 1613B ~~and 8290A~~, every sample, blank and QC sample extract is spiked with labeled cleanup standards after extraction but prior to extract cleanup. They are used to assess the efficiency of the cleanup procedures.

11.11.2 For 1613B ~~and 8290A~~ samples that are to be subjected to one or more cleanup steps, add 1.0 mL of the $^{37}Cl_4$-2,3,7,8-TCDD cleanup standard (section 7.13.4) to each sample, method blank and LCS/LCSD extract before any cleanup steps are performed.

SUBMITTED BY/DATE: MSP 4/22/11

Controlled Copy
Copy No. 4/14/11

APPROVED BY:

Technical Reviewer Signature	Date 4/22/11
Environmental Health & Safety Signature	Date 4-25-11
QA Signature	Date 04/25/11
Management Signature	Date 4/25/11

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Extraction of Polychlorinated Dioxins/Furans for Analysis by HRGC/HRMS Based on Methods 8290, 8290A and 1613B

(SUPERSEDES: KNOX-ID-0004, Rev. 9)

Prepared By: Michael S. Patty

Reviewed By: Robyn M. Wagner 4/12/11
Technical Specialist

Approved By: Christopher White Rogell 04/12/11
Quality Assurance Manager

Approved By: Barbara Daly 4-12-11
Environmental, Health and Safety Coordinator

Approved By: 4-12-11
Laboratory Director

1. Scope and Application

1.1 This procedure is used by TestAmerica Knoxville for the extraction of tetra- through octa-chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) from a variety of environmental matrices (including water, soil, solids, sediments, wipes, biological samples, fly ash, still bottoms and waste oils) for analysis by high resolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS). This procedure is designed to meet analytical program requirements where EPA Method 8290, 8290A or 1613B is specified.

1.2 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1 Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 2. The samples are then extracted using matrix specific extraction procedures.

2.2 Water samples are extracted using separatory funnel techniques with methylene chloride as the extraction solvent. Solid samples are extracted by Soxhlet extraction with the appropriate solvent and organic liquid waste samples are diluted in solvent.

2.3 After extraction, the sample is concentrated and solvent exchanged to hexane. The extract is then subjected to one or more optional cleanup steps to remove interferences. The final extract is prepared by adding a known amount of the labeled recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) and concentrating to the final volume.

2.4 The acid-base cleanup of the sample is used before column chromatography for samples that contain large amounts of basic and acidic coextractable compounds. If such interferences are not removed before column chromatography, they can cause a shift in the predicted elution pattern. Conditions which can indicate the need for this procedure are as follows: Samples which are highly colored, samples which contain lipids or other oxidizable compounds or samples which contain known large amounts of polar organics.

2.5 Dual Column Cleanup: Silica gel is effective in removing chlorophenoxy herbicide residues, while alumina partitions PCBs, 2,4,5-trichlorophenol and hexachlorophene.

2.6 When the above cleanup techniques do not completely remove interferences, an activated carbon cleanup is used to remove interferences.

3. Definitions

3.1 Cleanup Standard: Solution containing $^{37}Cl_4$-2,3,7,8-TCDD that is added to every 1613B and 8290A sample, blank and quality control spike sample after extraction but prior to

extract cleanup. The analysis results are used to judge the efficiency of the cleanup procedures.

3.2 Internal Standards: Solution containing isotopically labeled analogs of the target analytes that is added to every sample, blank and quality control spike sample before extraction. The analysis results are used to calculate the concentration of the target analytes or detection limits.

3.3 Recovery Standard: Solution containing $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD that is added to every sample, blank and quality control spike sample just prior to analysis. The analysis results are used to measure the recovery of the internal standards and the cleanup standard.

3.4 Additional definitions can be found in the Test America Knoxville Quality Assurance Manual (QAM).

4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware can yield discrete artifacts or elevated baselines that can cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts must not use PVC gloves, powdered gloves, or gloves with levels of phthalates which cause interference.

4.2 The use of high purity reagents and solvents (pesticide grade) helps minimize interference problems. Where necessary, reagents are cleaned by extraction or solvent rinse.

4.3 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface. For specific glassware cleaning procedures, see SOP KNOX-QA-0002, “Glassware Cleaning”, current revision.

4.4 Interferences coextracted from the samples can vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes and polychlorinated alkyldibenzofurans that can be found at concentrations several orders of magnitude higher than the analytes of interest. While certain cleanup techniques are provided as part of this method, unique samples can require additional cleanup steps to achieve lower detection limits.

5. Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents

are being handled. Disposable gloves that have become contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.3 Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile gloves are to be worn. For operations using solvents that may splash, SilverShield® gloves are recommended. SilverShield® gloves protect against breakthrough for most of the solvents used in this procedure.

5.4 Finely divided dry soils contaminated with PCDDs and PCDFs can be particularly hazardous because of the potential for inhalation and ingestion. Such samples are to be processed in a hood.

5.5 When using a scalpel, wear cut-resistant gloves and cut away from your hand.

5.6 Primary Materials Used: The following is a list of the materials used in this method which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid (1)	Corrosive, Oxidizer, Dehydradator	1 mg/m^3	This material will cause burns if it comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive, Poison	2 ppm, 5 mg/m^3	This material will cause burns if it comes into contact with the skin or eyes. Inhalation of sodium hydroxide dust will cause irritation of the nasal and respiratory system.
Hydrochloric Acid	Corrosive, Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure and death. Can cause redness, pain and severe skin burns. Vapors are irritating and can cause damage to the eyes. Contact can cause severe burns and permanent eye damage.
Methylene chloride	Carcinogen, Irritant	25 ppm-TWA, 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. Can be absorbed through skin.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure can cause lightheadedness, nausea, headache and blurred vision. Vapors can cause irritation to the skin and eyes.
Methanol	Flammable, Poison, Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure can include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and can cause skin to become dry and cracked. Skin absorption can occur; symptoms can parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA, 300 ppm-Ceiling	Inhalation can cause irritation of the upper respiratory tract. Symptoms of overexposure can include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e.g., pins and needles) or numbness can be produced. Causes severe eye and skin irritation with redness and pain. Can be absorbed through the skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Can cause coughing, dizziness, dullness and headache.
Cyclohexane	Flammable, Irritant	300 ppm TWA	Inhalation of vapors causes irritation to the respiratory tract. Symptoms can include coughing and shortness of breath. High concentrations have a narcotic effect.
Tetradecane	Irritant	None established	Inhalation of vapors can cause difficulty breathing, headache, intoxication and central nervous system damage.
Benzene	Flammable, Toxic, Carcinogen	PEL: 1 ppm TWA; 5 ppm, 15 min. STEL	Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations can have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim can experience tightness in the chest, breathlessness and loss of consciousness.
Nonane	Flammable	None established	Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous membranes and upper respiratory tract. Causes skin irritation.
Potassium Hydroxide	Corrosive, Poison	2 mg/m^3 ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on the severity of exposure. Symptoms can include coughing, sneezing and damage to the nasal or respiratory tract. High concentrations can cause lung damage. Corrosive! Contact with skin can cause irritation or severe burns and scarring with greater exposures.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.7 Chemicals that have been classified as carcinogens or potential carcinogens under OSHA regulations include benzene and methylene chloride, 2,3,7,8-TCDD and all other 2,3,7,8-substituted PCDD or PCDF isomers.

NOTE: The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.8 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste containers must be kept closed unless transfers are being made.

5.9 All procedures that involve solvents such as acetone, toluene, methylene chloride and hexane (e.g., glassware cleaning and the preparation of standards and reagents) must be conducted in a fume hood with the sash closed as far as the operations permit.

5.10 Safety glasses or a face shield must be used when employees are using solvents to rinse or clean glassware.

5.11 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch and shifts).

5.12 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.13 All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported immediately to a laboratory supervisor.

6. Equipment and Supplies

NOTE: All glassware used in extraction and cleanup procedures is precleaned as described in SOP KNOX-QA-0002, “Glassware Cleaning”, current revision.

6.1 Miscellaneous Laboratory Equipment

6.1.1 Laboratory fume hood of sufficient size to contain the equipment used for sample preparation

6.1.2 Oven, capable of maintaining a temperature of 105 ± 5°C and 125 to 135°C

6.1.3 Balance, >100 g capacity, accurate to ± 0.01 g

6.1.4 Syringes, various sizes

6.1.5 Borosilicate 5.75 inch and 9.0 inch disposable pipettes with rubber bulbs

6.1.6 Class A 1 mL pipettes

6.1.7 Graduated cylinders, 25 mL, 100 mL and 1000 mL volume

6.1.8 Vials, 40 mL volume, with PTFE lined caps

6.1.9 Glass wool, precleaned with methylene chloride

6.1.10 Bottle top solvent dispensers

6.1.11 PTFE boiling chips

6.1.12 PTFE squirt bottles, 500 mL

6.2 Tissue Homogenization Equipment

6.2.1 Laboratory blender with glass body and stainless steel blades

6.2.2 Industrial meat grinder, Intedge Industries, Model C2H or equivalent

6.2.3 Laboratory homogenizer, OMNI GLH-01, Model LR060902 or equivalent

6.2.4 Scalpels or knives

6.2.5 Cut-resistant gloves

6.3 Aqueous Sample Extraction

6.3.1 Multi-position separatory funnel rotator

6.3.2 2000 mL separatory funnels with PTFE stopcocks and PTFE stoppers

6.3.3 100 mm glass funnels with short stems

6.3.4 600 mL concentration tubes

6.3.5 Buchner funnels with filter flasks, rubber stopper and GF/D filters

6.3.6 Vacuum source

6.4 Soxhlet Extraction

6.4.1 Soxhlet extractors or Dean-Stark Soxhlet extractors

6.4.2 Heating mantles with temperature controls

6.4.3 500 mL boiling flasks, flat or round bottom

6.4.4 Glass condensers, compatible with the Dean-Stark extractors

6.4.5 High purity glass fiber Soxhlet thimbles

6.4.6 Boiling beads, 6 mm glass

6.4.7 Recirculating chillers

6.4.8 Stainless steel spatulas

6.4.9 Stainless steel tweezers

6.5 Dual Column (Silica Gel/Alumina) Cleanup

6.5.1 Disposable glass columns

6.5.1.1 20mm x 240mm custom glass column with support ring and tapered tip

6.5.1.2 16mm x 240mm custom glass column with support ring and tapered tip

6.5.2 Tornado II portable paint shaker or equivalent (for mixing reagents)

6.5.3 Aluminum support rack for custom columns

6.5.4 Amber-colored glass jars with a PTFE lined screw caps, 250mL and 500 mL

6.5.5 Solvent waste collection jars, 125mL

6.6 Activated Carbon Cleanup

6.6.1 31 cm glass columns (pre-cut), 8 mm ID

6.7 Concentration Equipment

6.7.1 Labconco Rapid-Vap concentrator

6.7.2 600 mL sample concentrator tubes, Labconco or equivalent

6.7.3 Heating mantles with temperature controls

6.7.4 Three-ball macro Snyder columns

6.7.5 Nitrogen evaporator, N-EVAP or equivalent

6.7.6 Mini vials, 1.1 mL capacity with tapered bottom, PTFE faced rubber septa and screw caps

7. Reagents and Standards

7.1 Solvents

7.1.1 Acetone, pesticide quality or equivalent

7.1.2 Benzene, pesticide quality or equivalent

7.1.3 Cyclohexane, pesticide quality or equivalent

7.1.4 Hexane, pesticide quality or equivalent

7.1.5 Iso-octane, pesticide quality or equivalent

7.1.6 Methanol, pesticide quality or equivalent

7.1.7 Methylene chloride, pesticide quality or equivalent

7.1.8 Nonane, pesticide quality or equivalent

7.1.9 Tetradecane, pesticide quality or equivalent

7.1.10 Toluene, pesticide quality or equivalent

7.2 Reagents

7.2.1 Reagent water must be produced by a Millipore DI system or equivalent, that is capable of producing water with ≥18 megohm-cm (MΩ-cm) resistivity. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2.2 Sodium sulfate, reagent grade, granular, anhydrous, J.T Baker 3375 or equivalent

7.2.2.1 Sodium sulfate is cleaned by putting approximately 600 g of sodium sulfate in large amber glass jars and completely covering with methylene chloride, stirring the mixture with a stirring rod and letting the sodium sulfate soak for 5 minutes. The methylene chloride is drained and this step is repeated. After the methylene chloride is drained, the sodium sulfate is transferred to a Buchner funnel fitted onto a vacuum flask and rinsed 2 times with methylene chloride while a vacuum is being applied. The sodium sulfate is then placed into shallow borosilicate glass dishes where it is allowed to dry. After the sodium sulfate is air dried, it is placed in an oven at 125 – 135°C for one hour to drive off any residual moisture. After drying in the oven, the sodium sulfate is

transferred into precleaned glass jars with PTFE lined screw caps and is placed in a desiccator until needed.

7.3 Fly Ash Sample Pretreatment

7.3.1 Hydrochloric acid (HCl), concentrated, Mallinckrodt AR Select or equivalent

7.3.2 1N HCl - Carefully add 83 mL of concentrated HCl to 917 mL of reagent water in a glass container

7.4 Tissue Sample Pretreatment

7.4.1 Dry ice, purchased from local vendor

7.5 Acid-Base Cleanup

7.5.1 Sulfuric acid, concentrated, ACS grade, specific gravity 1.84

7.5.2 Potassium hydroxide 20% (w/v) - Cautiously dissolve 200 g of potassium hydroxide pellets in reagent water and dilute to 1000 mL final volume. This solution is stored at room temperature in a HDPE bottle.

7.5.3 Sodium chloride, NaCl, analytical reagent, 5 percent (w/v) in reagent grade water

7.6 Silica Gel/Alumina Column Cleanup

7.6.1 Silica gel, F679-212, Fisher Chromatographic Silica Gel, 100-200 mesh or equivalent. Prepare by Soxhlet extraction with methylene chloride for at least 6 hours. Transfer to a shallow, borosilicate glass dish and air dry. After drying, cover with aluminum foil and activate in an oven at 125 - 130°C for a minimum of four (4) hours. Store in labeled glass jars in a desiccator until use.

7.6.2 3.3% Deactivated silica gel – To prepare add 6.6 mL of reagent water to 200 g of silica gel (section 7.6.1) in a 500 mL amber glass jar with a PTFE lined screw cap. Mix thoroughly by shaking until no lumps are visible and the silica gel is free flowing and no longer sticks to the side of the jar. The Tornado II portable paint shaker may be used to aid in mixing these reagents.

7.6.3 Acidic silica gel - To prepare, add 57 mL of concentrated sulfuric acid to 180 g silica gel (section 7.6.1) in a 500 mL amber glass jar with a PTFE lined screw cap. Mix thoroughly by shaking until no lumps are visible and the silica gel is free flowing and no longer sticks to the side of the jar. The Tornado II portable paint shaker may be used to aid in mixing these reagents.

7.6.4 Alumina, Neutral - Super I - Scientific Absorbents. Purchase and use only activated alumina. Store in an oven at 125 - 130°C when not in use.

7.6.4.1 Each new lot of alumina must be tested upon receipt and before use. Elute a solution containing all of the ^{13}C labeled internal standards and native analytes through a column packed with the new lot of alumina. Collect the 65% fraction and analyze by HRMS. The target analytes and internal standard recoveries must be greater than 85% in the final fraction. If the recovery is less than 85% for any compound or internal standard, the ratios and volumes of the elution solvents must be optimized and the test repeated until all compounds meet the recovery criteria.

7.6.5 95:5 Hexane:Methylene Chloride - Add 15 mL methylene chloride to 285 mL hexane. Store in an amber glass bottle at room temperature until use. Other amounts may be prepared based on the dual column set size.

7.6.6 35:65 Hexane:Methylene Chloride - Add 390 mL methylene chloride to 210 mL hexane. Store in an amber glass bottle at room temperature until use. Other amounts may be prepared based on the dual column set size.

7.7 Activated Carbon Cleanup

7.7.1 Silica gel, F679-212, Fisher Chromatographic Silica Gel, 100-200 mesh or equivalent. Prepare by Soxhlet extraction with methylene chloride for at least 6 hours. Transfer to a shallow, borosilicate glass dish and air dry. After drying, cover with aluminum foil and activate in an oven at 125 - 130°C for a minimum of four (4) hours. Store in labeled glass jars in a desiccator until use.

7.7.2 J.T Baker Carbon, Activated Powder, E345-07 or equivalent

7.7.3 Activated Carbon - Thoroughly mix 5% (by weight) activated J.T Baker carbon and 95% (by weight) Fisher Chromatographic silica gel (100-200 mesh). The Tornado II portable paint shaker may be used to aid in mixing these reagents. Activate in an oven at 125 - 130°C for 6 hours. Store in a desiccator in an amber colored bottle with a PTFE lined lid until use. Do not label the bottle until oven activation is completed to avoid heat damage to the label.

7.8 Standard Solutions

7.8.1 Certified reference standards are purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts). If the chemical purity is 98% or greater, the weight can be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with PTFE lined caps. Standards are used as received after being sonicated and transferred to 2.0 mL amber glass vials with PTFE lined caps.

7.8.2 Stability of Solutions: Standards have an expiration of ten (10) years from date of receipt unless otherwise specified by the manufacturer. Standard solutions used for quantitative purposes must be analyzed periodically and must be assayed against reference standards before use.

7.9 Native Standards

7.9.1 Native Standard Stock Solution: CIL Catalog No. EDF-7999-10x, 400-4000 ng/mL in nonane, 1.2 mL.

7.9.2 Native Standard Working Stock Solution: Dilute 0.300 mL of the native standard stock solution to 3.0 mL in a volumetric flask with nonane for a final concentration of 40-400 ng/mL.

7.9.3 Native LCS Spiking Solution: Dilute 500 µL of the native standard working stock solution to 100 mL in a 125 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 0.2-2.0 ng/mL. 1.0 mL of this solution is added to each LCS, LCSD or MS/MSD sample. See Table 1 for a complete list of compounds and their concentrations.

7.10 1613B/8290/8290A Internal Standards

7.10.1 1613B/8290/8290A Internal Standard Stock Solution: CIL Catalog No. EDF-8999, 100 ng/mL ($^{13}C_{12}$-OCDD 200 ng/mL) in nonane, 500 µL.

7.10.2 1613B/8290/8290A Internal Standard Spiking Solution: Dilute 2000 µL of the internal standard stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank and QC sample. See Table 2 for a complete list of compounds and their concentrations.

7.11 2,3,7,8-TCDD/2,3,7,8-TCDF Internal Standards

7.11.1 $^{13}C_{12}$-2,3,7,8-TCDD Internal Standard Stock Solution: CIL Catalog No. ED-900, 50 µg/mL in nonane, 1.2 mL

7.11.2 $^{13}C_{12}$-2,3,7,8-TCDF Internal Standard Stock Solution: CIL Catalog No. EF-904, 50 µg/mL in nonane, 1.2 mL

7.11.3 $^{13}C_{12}$-TCDD/$^{13}C_{12}$-TCDF Internal Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solutions in sections 7.11.1 and 7.11.2 to 5 mL in a volumetric flask with nonane to a final concentration of 1000 ng/mL.

7.11.4 $^{13}C_{12}$-TCDD/$^{13}C_{12}$-TCDF Internal Standard Spiking Solution: Dilute 200 µL of the internal standard secondary stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL. 1.0 mL of this solution is added to each sample, method blank and

QC sample extract that is extracted for TCDD and/or TCDF analysis only. See Table 2 for a complete list of compounds and their concentrations.

7.12 Recovery Standards

7.12.1 $^{13}C_{12}$-1,2,3,4-TCDD Recovery Standard Stock Solution: CIL Catalog No. ED-911, 50 µg/mL in nonane, 1.2 mL

7.12.2 $^{13}C_{12}$-1,2,3,7,8,9-HxCDD Recovery Standard Stock Solution: CIL Catalog No. ED-996, 50 µg/mL in nonane, 1.2 mL

7.12.3 Recovery Standard Secondary Stock Solution: Dilute 1.0 mL of the stock solutions in sections 7.12.1 and 7.12.2 to 10 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.12.4 Recovery Standard Spiking Solution: Add 10 mL of nonane to a 12 mL amber vial with a Class A glass pipette. With a syringe, remove 200 µL of nonane from the vial and add 200 µL of the recovery standard secondary stock solution to a final concentration of 0.1 µg/mL. 20 µL of this solution is added to each sample, method blank and QC sample extract. See Table 2 for a complete list of compounds and their concentrations.

7.13 1613B and 8290A Cleanup Standards

7.13.1 Cleanup Standard Stock Solution: CIL Catalog No. ED-907, 50 µg/mL in nonane, 1.2 mL

7.13.2 Cleanup Standard Secondary Stock Solution: Dilute 0.100 mL of the 50 µg/mL cleanup standard stock solution to 1.0 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.13.3 Cleanup Standard Working Stock Solution: Dilute 0.120 mL of the 5.0 µg/mL cleanup standard secondary stock solution to 3.0 mL in a volumetric flask with nonane to a final concentration of 200 ng/mL.

7.13.4 Cleanup Standard Spiking Solution: Dilute 200 µL of the 200 ng/mL working stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with hexane to a final concentration of 0.20 ng/mL. 1.0 mL of this solution is added to each 1613B or 8290A sample, method blank and QC sample extract prior to cleanup. See Table 2 for a complete list of compounds and their concentrations.

8. Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, “Sample Receipt and Log In”,

current revision. Sample container and preservation recommendations are listed in the table below.

Method:	**1613B**	**8290/8290A[1]**
Holding Times	Samples – 1 year from collection to extraction. Extracts – 1 year from extraction to analysis.	Samples – 30 days from collection to extraction. Extracts – 45 days from extraction to analysis. Tissue Extracts –45 days from collection to analysis.
Containers	Amber Glass	Amber Glass
Preservation:		
Aqueous Samples	≤6 °C in the dark. If residual chlorine is present, add 80 mg/L sodium thiosulfate. If pH > 9, adjust to pH 7-9 with sulfuric acid.	≤6 °C in the dark.
Solid Samples	<-10 °C in the dark.	≤6°C in the dark.
Tissue Samples	<-10 °C in the dark.	<-20 °C in the dark[2].

Notes:

1 For methods 8290 and 8290A, the holding times listed are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed can be as high as a year for certain matrices. The results of samples analyzed after the holding time expiration date must be considered to be minimum concentrations and must be identified as such in the final report. Sample extracts, however, must always be analyzed within 45 days of extraction. (For the State of South Carolina and the New Jersey DEP, the holdings times are as listed in the table and are not considered recommendations.)

2 If the freezer used to store samples is not capable of reaching a temperature of <-20 °C when the temperature control is set to its maximum limit, storage at a higher temperature is acceptable as long as it is <-10 °C.

9. Quality Control

9.1 Internal Standards: Every sample, blank and QC sample is spiked with labeled internal standards prior to extraction. Internal standards in samples, blanks and QC samples are used to calculate the concentration of the target analytes or detection limits.

9.2 Cleanup Standards: For methods 1613B and 8290A, every sample, blank and QC sample extract is spiked with labeled cleanup standards after extraction but prior to extract cleanup. They are used to assess the efficiency of the cleanup procedures.

9.3 Recovery Standards: Every sample, blank and QC sample extract is spiked with labeled recovery standards prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standards.

9.4 Method Blank: A laboratory method blank must be run along with each batch of 20 or fewer samples. The method blank is processed in the same manner and at the same time as

the associated samples. The method blank is used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false positive data. Refer to the table below for a cross-reference between the sample matrix and method blank matrix.

Matrix	Method Blank Matrix
Aqueous	Reagent water
Solid	Sodium sulfate
Tissue	Sodium sulfate
Wipe	Sterile gauze pad
Waste	Hexane

9.5 Laboratory Control Sample: A laboratory control sample (LCS) is prepared and analyzed with every batch of 20 or fewer samples. The LCS extract must be subject to the same cleanup procedures as the associated sample extracts. LCS spike components and concentrations are listed in Table 1. Refer to the table below for a cross-reference between the sample matrix and LCS matrix.

Matrix	LCS Matrix
Aqueous	Reagent water
Solid	Sodium sulfate
Tissue	Sodium sulfate and corn oil
Wipe	Sterile gauze pad
Waste	Hexane

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Method 8290 only.

When method 8290 is performed, a matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every 20 samples of a given matrix. **Note that an MS/MSD is not required for Method 8290A**. The MS/MSD is spiked with the same subset of analytes as the LCS (see Table 1). If an MS/MSD is not possible due to limited sample, then an LCSD must be analyzed.

10. Calibration and Standardization

10.1 Not applicable.

11. Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variations in the procedure, except those specified by project specific instructions, must be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager and QA Manager. If contractually required the client must be notified.

11.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3 Samples are extracted by the following procedures depending upon sample matrix. Water samples are prepared by separatory funnel liquid/liquid extraction. Solid samples, including soils, sediments, tissues and solid waste materials, are prepared by Soxhlet extraction. Non-aqueous liquid wastes and organic solvents are prepared by waste dilution techniques.

11.4 Aqueous Sample Extraction

11.4.1 Remove samples from the refrigerator and allow them to come to room temperature before measuring the volume or performing the extraction. Inspect the samples carefully for biphasic sample characteristics. If this condition exists, document the observation and contact the project manager for instructions before proceeding with the extraction.

11.4.2 For aqueous samples that potentially contain >1% visible solids (as determined visually by an experienced analyst), a percent solid determination must be performed using the following procedure.

11.4.2.1 Add 10 mL of the well shaken sample to a tared aluminum weighing dish. Weigh the dish to three significant figures. Dry the dish overnight in an oven at 105 °C. Reweigh the dish and calculate the percent solids using the following equation.

$$\%\,\text{Solids} = \frac{\text{weight of dish plus sample after drying} - \text{weight of dish}}{\text{weight of dish plus sample before drying} - \text{weight of dish}} \times 100$$

11.4.3 8290/8290A aqueous extraction: For samples with ≤ 1% visible solids (as determined visually by an experienced analyst), follow the normal extraction procedure (i.e., without filtration).

11.4.4 1613B aqueous extraction: For samples with ≤ 1% visible solids (as determined visually by an experienced analyst), samples must be filtered and extracted as solid and aqueous fractions. The extracts from each fraction are then combined into one extract. See section 11.4.11 for filtration procedures.

11.4.5 8290/8290A/1613B aqueous extraction: For samples with > 1% visible solids, consult the project manager for further instructions before proceeding with extraction using one of the options listed below:

11.4.5.1 Samples can be filtered, extracted separately as solid and aqueous fractions, and analyzed separately.

11.4.5.2 Samples can be filtered, extracted separately as solid and aqueous fractions, and the extracts combined for a single analysis.

11.4.5.3 The client may decide to resample if they determine that solids should not have been present.

11.4.6 Refer to Knoxville SOP KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware. Visually inspect all glassware prior to use for scratches or cracks. Retire, repair or replace any glassware found to be damaged.

11.4.7 Place separatory funnels (one for each sample, the method blank and the LCS) in the positions in the rotary extractor.

11.4.8 Place a 600 mL concentration tube directly beneath each separatory funnel in the tube holder.

11.4.9 Plug a glass funnel with glass wool and pour in sodium sulfate (about 1 to 2 inches from the top). Rinse the sodium sulfate with methylene chloride over a waste container to catch the solvent waste. When the funnel stops dripping, place the funnel on top of the concentrator tube.

11.4.10 If solids are not observed in the sample, mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the separatory funnel, taking care not to spill any sample. Using a Class A 1000 mL graduated cylinder, measure out 1000 mL of reagent water and add to the separatory funnels marked for the method blank, LCS and LCSD (if required).

11.4.11 Sample Filtration

11.4.11.1 Assemble a Buchner funnel with a rubber stopper on top of a precleaned vacuum filter flask. Wet a 15 cm diameter, 2.7 µm particle retention glass fiber filter with a few mL of reagent water and carefully fit the filter into the funnel.

11.4.11.2 Apply vacuum to the flask. Mark the level of the sample on the sample bottle in order to measure the volume later. Carefully add the sample to the Buchner funnel, swirling the sample remaining in the bottle to suspend any particles.

11.4.11.3 Rinse the sample bottle twice with approximately 10 mL portions of reagent water to transfer any remaining particles onto the filter. Rinse any particles off the sides of the Buchner funnel with small quantities of reagent water.

11.4.11.4 If the percent solids in a 1613B sample are ≤ 1%, extract the filtrate in a separatory funnel by proceeding to section 11.4.12. Extract the solids on the filter and the filter itself following the procedure in section 11.5. **Do not add internal standards to this portion of the sample; only add internal standards to the**

aqueous portion of the sample! The resulting extract is combined with the extract of the aqueous portion during the concentration step in section 11.9.19.

11.4.12 Using a Class A 1 mL volumetric pipette or syringe, add 1 mL of the appropriate 1.0 ng/mL internal standard spiking solution (see sections 7.10.2 and 7.11.4) to each sample, the method blank, LCS, LCSD (as required) and MS/MSD (as required). Record the amount of spike used and the spike solution number on the extraction benchsheet.

11.4.13 Using a Class A 1 mL volumetric pipette or syringe, add 1 mL of the native LCS spiking solution (see section 7.9.3) to the designated LCS, LCSD (as required) and MS/MSD (as required). Record the amount of spike used and the spike solution number on the extraction benchsheet.

11.4.14 Add 60 mL of methylene chloride to the sample bottle and shake. Then carefully pour the methylene chloride into the separatory funnel. Add 60 mL of methylene chloride to the method blank, LCS and LCSD (if required) as well.

11.4.15 Secure the separatory funnel with the rotator retaining straps and rotate for 2 minutes.

CAUTION: Care must be used while performing this operation. Vent the separatory funnel frequently.

11.4.16 Allow the water and the methylene chloride to separate. If it is not separated after 10 minutes, attempt to break up the emulsion layer by gently swirling the sample or tilting the separatory funnel on its side.

11.4.17 Drain the methylene chloride from the separatory funnel into the glass funnel that is filled with sodium sulfate, allowing the extract to drip into the concentrator tube. Be careful not to allow water to escape the separatory funnel or the sodium sulfate will harden and block the flow of the extract. If at least 10 minutes has elapsed and other ways of breaking up or reducing the size of the emulsion have failed, the following steps can be tried to reduce the impact of the emulsion on the sodium sulfate.

11.4.17.1 Place a large piece of precleaned glass wool in the funnel containing the sodium sulfate.

11.4.17.2 Spread the glass wool out, covering the entire surface of the sodium sulfate to a depth of ~5 to 10 mm. If the emulsion is hard to break up and persistent, a small, additional layer of sodium sulfate is added on top of the glass wool.

11.4.17.3 Drain the solvent and emulsion layer into the funnel being careful to drain no more than 60 mL of volume if a clear phase layer cannot be determined.

11.4.17.4 If this procedure is used, the funnel is rinsed with an extra 30 mL of methylene chloride after the emulsion layer is drained into the funnel to ensure all analytes are rinsed into the concentrator tube.

11.4.18 Repeat steps 11.4.14 through 11.4.17 two more times.

11.4.19 After the third methylene chloride portion has filtered through the sodium sulfate, rinse the funnel with approximately 40 mL of methylene chloride.

11.4.20 Remove the separatory funnel from the hood and pour the extracted water into the extracted water waste container.

11.4.21 Fill the empty sample bottle to the marked level with tap water. Pour the tap water into a Class A 1000 mL graduated cylinder. Record the volume of sample used on the extraction benchsheet.

11.4.22 Proceed to Macro Extract Concentration of Aqueous Extracts by Rapid-Vap in section 11.5.

11.5 Macro Extract Concentration of Aqueous Extracts by Rapid-Vap

11.5.1 Preheat the unit to the appropriate temperature for the solvent used in the extraction.

11.5.2 Set the operating parameters on the programmer. For example, if there is 300 mL of a methylene chloride extract, the following parameters are used and adjusted as needed:

Temperature:	30 °C
Vortex Speed:	30%, initially
Nitrogen:	7-9 psi
Timer Set:	30 minutes

11.5.3 Place 600 mL concentrator tubes containing the extract in the Rapid-Vap. Begin concentrating the extract, adjusting the vortex speed for the proper rate of concentration.

11.5.4 When the extract has been concentrated to less than 20 mL, add approximately 60 mL of hexane. Concentrate the extract to a final volume of approximately 2 mL (that is the volume contained in the reservoir tip of the Rapid-Vap). Shut off the nitrogen flow and turn off the Rapid-Vap or remove the 600 mL concentrator tube to prevent further concentration.

11.5.5 Transfer the extract to a 40 mL vial with a 9” disposable pipette, rinsing the sample tube 3 times with approximately 3 mL of hexane. Reduce the volume

in the 40 mL vial using the N-EVAP to approximately 2 mL and proceed to extract cleanup in section 11.11. If no cleanups are to be performed, continue with the following steps to dry the extract. The sample extracts sometimes contain small amounts of water due to condensation forming on the glassware during the concentration steps. Take care to ensure the water is removed.

11.5.6 Prepare a small funnel by placing a small plug of precleaned glass wool at the bottom of the funnel and adding a layer of sodium sulfate on top of the glass wool. Rinse the funnel with approximately 5 mL of hexane to pre-wet the sodium sulfate.

11.5.7 Pipette the extract from the Rapid-Vap concentrator tube and through the funnel containing the sodium sulfate into a 40 mL vial.

11.5.8 Rinse the concentrator tube 3 times with approximately 3 mL of hexane for each rinse. Rinse the sodium sulfate funnel with an additional 2 mL of hexane. Proceed to micro concentration in section 11.12.

11.6 Screening Process for Samples with High Concentration of Dioxins/Furans

11.6.1 Samples received are carefully reviewed before starting the extraction process. Any samples that are received from known dioxin/furan sites and samples that contain keywords such as PCP (pentachlorophenol) site, wood treaters, PCB sites and fire/burn sites can be subjected to the screening process.

11.6.2 Screening is done as a precaution to minimize the chance of having high level samples exposing the preparation and analytical areas to excessive amounts of dioxins/furans, thereby potentially contaminating areas and other samples contained in those areas. See Appendix III for LRMS Dioxin Screen Strategy.

11.6.3 Mix sample well, weigh out 2.5 g (± 0.1 g) and place in a 40 mL vial.

11.6.4 Add 10 mL of toluene and shake on a shaker table for 3 hours.

11.6.5 After the contents have settled, remove the toluene supernatant from the vial and place in a fresh, clean vial containing 100 µL of tetradecane as a keeper. Rinse the vial 3 times with 1 mL of toluene to insure complete transfer of the extract.

11.6.6 Solvent exchange the extract by placing it on the nitrogen concentration device. Concentrate the extract to near dryness. Add 4 mL of hexane and concentrate to near dryness again. Repeat again and then bring the extract to volume with 2 mL of hexane.

11.6.7 Run the extract through a silica gel/alumina column cleanup as detailed in section 11.11.4. After the silica gel/alumina column cleanup is completed, put

the extract back on the nitrogen concentration device and concentrate to approximately 0.5 mL.

11.6.8 Transfer the concentrated extract to a 2 mL clear, screw cap vial marked at 1.0 mL. Rinse the 40 mL vial several times with small amounts of hexane to complete the transfer. Adjust volume of the extract to 1.0 mL. Take extract to the GC/MS Semivolatiles group for analysis.

11.7 Pretreatment for Fly Ash Samples

11.7.1 If the sample matrix is fly ash and is to be analyzed by method 8290 or 8290A, pretreat the sample with HCl. Weigh 10 g (± 0.5 g) of the fly ash sample and transfer to a 250 mL glass jar. Record the sample weight on the extraction benchsheet. If a sample is designated for MS/MSD analysis, prepare two additional portions of the sample and label them as the MS and MSD.

11.7.2 Add 150 mL of 1N HCl to the sample. Seal the jar with a PTFE lined screw cap and shake for 3 hours at room temperature.

11.7.3 Rinse a 15 cm diameter, 2.7 μm particle retention glass fiber filter with reagent water. Carefully fit the glass fiber filter into a Buchner funnel and filter the sample through the funnel attached to a 1 L vacuum flask. Rinse the sample bottle twice with small amounts of reagent water, making sure that all particulate matter is transferred onto the glass fiber filter. Wash the fly ash cake with approximately 500 mL reagent water.

11.7.4 Transfer the filter and fly ash filter cake sample to a Dean-Stark Soxhlet. Proceed to section 11.9.

11.8 Sample Pretreatment for Tissues

11.8.1 If the sample matrix is tissue and has not been homogenized prior to receipt, the entire sample is homogenized prior to extraction using an industrial meat grinder, a laboratory blender, or a laboratory homogenizer. Select the equipment that is most appropriate for the size and type of tissue received.

11.9 Solid/Tissue/Wipe Sample Extraction

11.9.1 Prepare and label the required number of Soxhlet or Dean-Stark Soxhlet systems. Refer to Knoxville SOP KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware. Visually inspect all glassware prior to use for scratches or cracks. Retire, repair or replace any glassware found to be damaged.

NOTE: A Dean-Stark extractor is used to remove the water from all sample matrices except tissue and wipes. The Dean-Stark apparatus is installed between the Soxhlet body and the condenser when the components are

assembled. All method 1613B solid samples and extremely wet 8290/8290A solid samples (e.g., samples with standing water) are extracted using Dean-Stark Soxhlets.

11.9.2 For 8290 and 8290A soil samples, transfer a well-mixed 10 g (± 0.5 g) aliquot of the sample into a glass microfiber extraction thimble. Record the sample weight on the extraction benchsheet.

11.9.3 For method 1613B solids and for all sediment samples, adjust the amount weighed to achieve 10 to 10.5 g dry weight. Determine the amount of sediment sample to extract using the "Sediment Extraction Amounts" spreadsheet (refer to Appendix IV) on the local area network in the MSOffice\template\Knx OrgPrep directory. Transfer a well-mixed aliquot of the sample into a glass microfiber extraction thimble. Record the sample weight on the extraction benchsheet.

11.9.4 For tissue samples, weigh out 10 g (± 0.5 g) of homogenized tissue into a beaker or extraction thimble. Mix thoroughly with ~20 g of sodium sulfate. Record the sample weight on the extraction benchsheet.

NOTE: If gravimetric lipids are to be determined using the tissue extracts, refer to SOP KNOX-OP-0020, "Gravimetric Lipids Determination", current revision.

11.9.5 For wipes samples, place the wipe directly into the Soxhlet extractor. Rinse the sample container with ~30 mL of toluene and transfer the rinsate to the top of the Soxhlet extractor.

11.9.6 Refer to the Section 9.4 for a cross-reference between the sample matrix and method blank matrix and Section 9.5 for the LCS matrix.

11.9.7 Pour approximately 350 mL toluene into a 500 mL boiling flask. For tissue samples, use methylene chloride as the extraction solvent. Place the flask in the heating mantle.

11.9.8 Place the extraction thimble in the glass Soxhlet extractor.

11.9.9 Assemble the Soxhlet system and secure to the lab supports.

11.9.9.1 Place the method blank and QC samples in random positions within the available prep positions in the hood (i.e., do not use the same positions each time for the method blank and QC samples).

11.9.10 Spike each sample and QC samples with 1.0 mL of the appropriate internal standard spiking solution (see sections 7.10.2 and 7.11.4) and add a small amount of glass wool to the top of the thimble, if needed, to secure the sample material. Record the standard solution ID and volume spiked on the extraction benchsheet.

NOTE: Each time the samples are spiked, the spiking process should be witnessed by another analyst. Refer to Appendix II for the steps that must be taken.

11.9.11 Spike the LCS (and LCSD, MS/MSD, if required) with 1.0 mL of the native LCS spiking solution (see section 7.9.3) prior to adding the glass wool. Record the standard solution ID and volume spiked on the extraction benchsheet.

11.9.11.1 If a sample is designated for MS/MSD analysis, prepare two additional portions of the sample and label them as the MS and MSD.

11.9.11.2 The MS and MSD samples must be prepared at the same weight to avoid calculation errors in the RPD values.

11.9.12 Add approximately 10 boiling beads and several PTFE boiling chips to the boiling flask.

CAUTION: When extracting or concentrating a sample with hexane, toluene or any mixture containing these solvents, the analyst **must** add the boiling chips within 5 minutes of placing the flask on the heat source in order to prevent bumping of the solvent.

11.9.13 Adjust the temperature of the heating mantle to bring the solvent in the boiling flask to a rolling boil. There must be a steady drip from the condensers so that the solvent completely cycles at least 5 times an hour. Record the date and time that the Soxhlet extraction was started on the extraction benchsheet and initial and date.

11.9.14 Soxhlet extract the sample in the above manner for a minimum of 16 hours. At the end of the extraction period, turn off the heating mantles. Record the date and time that the Soxhlet extraction was completed on the extraction benchsheet and initial and date.

11.9.15 Remove the condensers. If a Dean Stark condenser is used, drain the water from the Dean Stark (the bottom layer of liquid). Then drain the remaining liquid into the Soxhlet. Empty the Soxhlet extractor chamber into the boiling flask and remove the Soxhlet extractor from the 500 mL boiling flask.

11.9.16 Add several (2-3) fresh boiling chips to the flask. Insert a three-ball macro Snyder column into the top of the 500 mL boiling flask.

CAUTION: When extracting or concentrating a sample with hexane, toluene or any mixture containing these solvents, the analyst **must** add the boiling chips within 5 minutes of placing the flask on the heat source in order to prevent bumping of the solvent.

11.9.17 Apply heat to the 500 mL flask in the heating mantle and reduce the extract volume to approximately 10-15 mL.

11.9.18 For tissue samples, transfer the concentrated methylene chloride extract to a 40 mL vial rinsing the 500 mL flask 3 times with approximately 3 mL of methylene chloride. Place the 40 mL vial into the nitrogen concentration device and reduce the volume to approximately 6 to 8 mL. Follow the instructions in SOP KNOX-OP-0022, current revision, for GPC cleanup.

11.9.19 For samples that were extracted using toluene, follow the steps listed below:

11.9.19.1 Transfer the extract into a 40 mL vial containing 100 µL of tetradecane, rinsing the 500 mL flask 3 times with approximately 3 mL of hexane. Add the rinsings to the 40 mL vial.

11.9.19.2 Place the 40 mL vial into the nitrogen concentration device and reduce the volume to near dryness. Add 4 mL of hexane and swirl the vial. Reduce the volume of hexane to near dryness again to complete the solvent exchange. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipette to the vial to aid in dissolving the residue. Adjust the final volume of the extract with hexane to 12 mL for acid-base cleanup or 2 mL for column cleanup. Proceed to sample cleanup in section 11.11.

11.10 Waste Dilution

11.10.1 Organic wastes, oil and solids that dissolve in solvent and non-aqueous sludge samples can be prepared by the waste dilution technique.

11.10.2 Tare a clean 40 mL vial on a laboratory balance. Add an appropriate amount of sample (e.g., 1.0 ± 0.1 g) to the vial. If a sample is designated for MS/MSD analysis, prepare two additional portions of the sample and label them as the MS and MSD samples. Prepare method blank, LCS and LCSD (if required) samples by adding 12 mL of hexane to a 40 mL vial.

11.10.3 Record the weights and volumes used on the extraction benchsheets and initial and date.

11.10.4 Add 1.0 mL of the appropriate internal standard spiking solution (see sections 7.10.2 and 7.11.4) to the samples, method blank and QC samples. Record the standard solution ID and volume spiked on the extraction benchsheet. Add hexane to bring the volume to 12 mL. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene to the vial to aid in dissolving the sample.

11.10.5 Add 1.0 mL of the native LCS spiking solution (see section 7.9.3) to the designated LCS, LCSD (as required) and MS/MSD (as required). Record the

amount of spike used and the spike solution number on the extraction benchsheet.

11.10.6 Proceed to sample extract cleanup in section 11.11.

11.11 Sample Extract Cleanup

11.11.1 Any or all sample cleanup techniques may be employed to remove sample interferences as necessary. The same cleanup techniques must also be performed on the associated quality control samples (method blank, LCS/LCSD). MS/MSD samples must undergo the same cleanup procedures as the associated parent sample.

11.11.2 For 1613B and 8290A samples that are to be subjected to one or more cleanup steps, add 1.0 mL of the $^{37}Cl_4$-2,3,7,8-TCDD cleanup standard (section 7.13.4) to each sample, method blank and LCS/LCSD extract before any cleanup steps are performed.

11.11.3 Acid-Base Cleanup

The acid-base cleanup is employed when sample extracts are colored and/or oily in appearance, or if specified by the client or project manager.

11.11.3.1 Bring the extract volume up to ~12 mL with hexane in a 40 mL vial.

NOTE: If the extracts are from fish tissue, omit sections 11.11.3.2 and 11.11.3.3.

11.11.3.2 Wash the extract by adding approximately 10 mL of 20% aqueous potassium hydroxide to the vial and gently shaking for 20 seconds. If an emulsion begins to form, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer (the bottom layer) with a glass pipette, taking care not to remove any of the solvent layer or remaining emulsion. Repeat the base washing until no color is visible in the base layer (perform a maximum of two base washings).

11.11.3.3 Add approximately 10 mL of 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. If an emulsion forms, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer (the bottom layer) with a glass pipette, taking care not to remove any of the solvent layer or remaining emulsion.

11.11.3.4 Slowly add approximately 15 mL of concentrated sulfuric acid to the vial. If an emulsion remains from the previous step, slowly add concentrated sulfuric acid (drop by drop) to the vial. **CAUTION: HEAT CAN BE GENERATED DURING THIS STEP**. Shake the vial for 30 seconds. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion settles out. Carefully remove the bottom layer (i.e., the aqueous, acid or base layer) with a glass pipette, taking care not to remove any of the solvent layer. Repeat the acid washing if the solvent layer is still darkly colored (perform a maximum of four acid washings). An option to employ if the acid layer is large or very dark and thick is to remove the hexane layer (the top layer) and any emulsion to a fresh 40 mL vial. Rinse the vial containing the acid 2 times with 2 mL of hexane and add these rinsings to the sample vial.

NOTE: Centrifuging is an option for extracts with emulsions that will not break up after 10 minutes.

11.11.3.5 Add approximately 10 mL 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer (the bottom layer) with a glass pipette, taking care not to remove any of the solvent layer. Dry the hexane extract by adding 1 to 2 grams of sodium sulfate and swirling the vial.

11.11.3.6 Reduce the extract volume to approximately 6 to 8 mL.

11.11.3.7 Proceed to section 11.11.4 for dual column (silica gel/alumina) cleanup.

11.11.4 Dual Column (Silica Gel/Alumina) Cleanup

Dual column cleanup is employed for most sample extracts. If treated drinking water samples are being analyzed, cleanup may not be necessary.

11.11.4.1 Prepare a 20 mm diameter column and a 16mm diameter column for each extract by rinsing, in order, with acetone and hexane. Place a large ball of precleaned glass wool in the bottom of each column before rinsing the columns.

11.11.4.2 Mark the level to which the column packings are to be added with a marking pen starting at the top of the glass wool plug and proceeding from bottom to top. The levels for each type column are as follows;

20 mm diameter silica gel column:
12 mm – 2g of 3.3% deactivated silica gel
16 mm – 4g of acidic silica gel
12 mm – 2g of 3.3% deactivated silica gel
10 mm – sodium sulfate

16 mm diameter alumina column:
40 mm – 6 g of neutral alumina
10 mm – sodium sulfate

11.11.4.3 Place the columns in the lab supports in the hood so that the 20 mm silica gel column is above the 16 mm alumina column. Offset the columns slightly so that the packings can be added and the columns rinsed.

11.11.4.4 Add the column packing materials in the order listed above (while tapping the column with a marking pen) to settle the contents and to prevent channeling. When the columns have been completely packed, remove the ink markings with a paper towel moistened with acetone or rinse the outside of the column with methylene chloride.

11.11.4.5 Place a 125 mL glass jar under the lower alumina column to catch the solvent wastes and eluents as they filter through the column.

11.11.4.6 Add 20 mL of hexane to each column to rinse the packing. Collect the hexane from the columns in the 125 mL glass jar; the columns must be aligned so that the waste from both columns drips directly into the 125 mL jar. When the level of solvent in the silica gel column approaches the top of the packing, move the upper column support so that the tips of the upper columns are inserted into the tops of the lower columns and the solvent drips into the lower columns.

11.11.4.7 Just as the level of hexane reaches the top of the packing in the silica gel column, transfer the sample extract into the top of the column. Rinse the extract vial 3 times with small amounts of hexane and add each of these rinses to the silica gel column.

11.11.4.8 Just as the solvent level reaches the top of the column packing, add 70 mL of hexane (via a solvent bottle top dispenser in 20 to 30 mL increments) into the top of the silica gel column and allow this to drip into and through the alumina column and into the collection jar. When the hexane has completely drained from the silica gel column, remove the column from the support rack and dispose of it in the appropriate waste container.

11.11.4.9 Just as the level of hexane reaches the top of the packing in the alumina column, replace the 125 mL glass jar containing the solvent waste with a 40 mL vial which has been labeled with the sample workorder number. Using a solvent dispenser, add 10 mL of 5% methylene chloride/hexane mixture. Dispose of the solvent waste in the 125 mL glass jar in the appropriate waste container.

11.11.4.10 Just as the level of the 5% mixture reaches the top of the packing in the alumina column, add 30 mL of 65% methylene chloride/hexane using a solvent dispenser and continue to catch the eluents in the 40 mL vial.

11.11.4.11 When the solvent has completely drained from the alumina column, cap the 40 mL vial containing the eluent and dispose of the alumina column in the appropriate waste container.

11.11.4.12 If no further cleanup is to be performed, proceed to final extract concentration detailed in section 11.12. Otherwise, reduce the volume of the extract to approximately 2 mL using the nitrogen concentration apparatus and proceed to the next cleanup.

11.11.5 Activated Carbon Cleanup

Carbon column cleanup is performed to remove diphenyl ether interferences and when site history indicates they are necessary for removal of other interferences. Carbon column cleanup is also performed when sample extracts cause the acid silica layer of the dual column cleanup to become colored along the entire length of the acid silica. Most solid samples meet these criteria.

11.11.5.1 Prepare a 31 cm pre-cut glass column (8mm ID) by rinsing, in order, with acetone and hexane, and then inserting a glass wool plug of about 1 cm in length approximately 10 cm into the column. Pack the column with 5.0 cm of the J.T Baker Carbon/Silica Gel mixture (section 7.7.3). Hold the packing by inserting an additional glass wool plug, again about 1 cm in length, in the other end.

11.11.5.2 Orient the carbon column in the carbon column rack so that the end with approximately 16 cm of space between the column packing and the end of the column is upright.

11.11.5.3 Pre-elute the column with 10 mL of cyclohexane/methylene chloride (50:50 v/v). Turn the column over and pre-elute in the opposite direction with another 5 mL of cyclohexane/methylene chloride (50:50 v:v).

11.11.5.4 When the solvent reaches the glass wool, add the sample extract. Rinse the sample vial 2 times with approximately 2 mL of 50:50

cyclohexane/methylene chloride. Add these rinses to the column. Elute the column with the following sequence of solvents:

11.11.5.4.1 6 mL of cyclohexane/methylene chloride (50:50 v/v).

11.11.5.4.2 5 mL of methylene chloride/methanol/benzene (75:20:5 v/v).

11.11.5.5 Allow the 75:20:5 methylene chloride/methanol/benzene to drain completely. Turn the column over and in the direction of reverse flow, elute the column with 30 mL toluene into a 40 mL vial.

11.11.5.6 Place vials containing the extract in the nitrogen concentration apparatus and reduce the solvent volume to approximately 0.3 mL. Proceed to section 11.12 for final concentration.

11.12 Final Concentration by Nitrogen Evaporation

11.12.1 When all sample cleanup steps have been completed, add 20 µL of the 0.1 µg/mL recovery standard spiking solution (section 7.12.4) using a 25 µL Hamilton syringe to an empty, clean 1.1 mL tapered mini-vial that has been labeled with the sample ID. (Assure that the vial and cap fit together properly before use.) Mark the level of the recovery standard on the mini-vial. Mark half the level, i.e., 10 µL, if the extracts are from treated drinking waters. Record the volume of recovery standard added and the standard ID on the extraction benchsheet.

11.12.2 Transfer the concentrated extract into the mini-vial. Rinse the 40 mL vial at least twice with a small amount of hexane and add the rinses to the mini-vial. Put the mini-vial on the N-EVAP nitrogen concentration apparatus and reduce the volume to the mark on the vial. Put the cap with PTFE-faced septa securely on the vial. Record the final extract volume on the extraction benchsheet.

11.12.3 All items listed on the data review checklist must be checked by both the analyst who performed the extraction and cleanup steps and the analyst who performed the second level review.

11.12.4 Transfer the extracts and paperwork to the HRMS group for analysis.

12. Data Analysis and Calculations

12.1 Not applicable.

13. Method Performance

13.1 Method Detection Limit (MDL): An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in SOP CA-Q-S-006, current revision, based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2 Initial Demonstration of Capability: Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in Test America Knoxville SOP KNOX-QA-0009, current revision.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009, current revision, for further requirements for performing and documenting initial and ongoing demonstrations of capability.

14. Pollution Prevention

14.1 All attempts will be made to minimize the use of solvents and standard materials.

15. Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 See the current revision of SOP KNOX-HS-0002 for specific waste handling guidelines.

15.3 The following waste streams are produced when this method is carried out.

15.3.1 Waste solvents must be placed in the flammable waste stream, contained in a steel satellite accumulation container or flammable solvent container.

15.3.2 Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous must be placed in the incinerable laboratory waste stream, contained in a HDPE satellite accumulation container.

15.3.3 Extracted solid/tissue samples, paper funnel filters, glass wool, etc., that has been contaminated with solvents shall be placed in the incinerable laboratory waste stream, contained in a steel or HDPE satellite accumulation container.

15.3.4 Contaminated sulfuric acid used during extract cleanup must be placed in the acidic laboratory waste stream, contained in a HDPE satellite accumulation container or 55 gallon HDPE drum.

15.3.5 Extracted aqueous samples contaminated with methylene chloride must be placed in the organic water waste stream, contained in a HDPE satellite accumulation container.

15.3.6 Silica gel, alumina, carbon and sodium sulfate that has been contaminated with various solvents and eluents, must be placed in the incinerable laboratory waste stream, contained in a HDPE satellite accumulation container.

16. References

16.1 TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

16.2 EPA Method 1613: Tetra- Through Octa- Chlorinated Dioxins and Furans by Isotope Dilutions HRGC/HRMS, Revision B, October 1994.

16.3 SW-846 Method 8290, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 0, September 1994.

16.4 SW-846 Method 8290A, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 1, February 2007.

16.5 TestAmerica Knoxville SOP KNOX-ID-0004, "Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Methods 8290, 8290A, 1613B, 23, 0023A and TO-9A", current revision.

16.6 TestAmerica Knoxville SOP KNOX-OP-0020, "Gravimetric Lipids Determination", current revision.

16.7 TestAmerica Knoxville SOP KNOX-OP-0022, "GPC Cleanup", current revision.

16.8 TestAmerica Knoxville SOP KNOX-QA-0002, "Glassware Cleaning", current revision.

17. Miscellaneous

17.1 Deviations from Reference Methods

17.1.1 Spiking levels have been reduced to minimize the amount of dioxin contaminated waste generated by this procedure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.2 Method 1613B employs a gravimetric determination of sample size rather than a volumetric determination. This procedure employs a volumetric determination of sample size to allow reporting of sample concentration in the standard units of pg/L (ppq). This modification has no impact on the performance criteria of this method.

17.1.3 The determination of solids content procedure used for aqueous samples is the same as the 1613B procedure used for solid samples rather than the 1613B procedure for aqueous samples. The aqueous sample procedure in 1613B is subject to error if the sample density is not exactly 1.0 g/mL.

17.1.4 The amount of hexane used in the solvent exchange step has been reduced from that specified in the reference methods. The reduction in solvent used is a pollution prevention measure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.5 Method 1613B specifies that the sample bottle is rinsed twice with 5 mL of reagent water after the sample is transferred to the separatory funnel. This procedure specifies that the sample bottle is rinsed three times with methylene chloride after the sample is transferred to the separatory funnel. This modification improves the removal of target compounds from the sample bottle.

17.1.6 Toluene volumes and cycle rates for Soxhlet extractors have been optimized for the specific size of glassware used and might not be the same as those specified in the referenced method. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.7 Soxhlet extracts are not filtered before concentration and solvent exchange. The use of glass wool in the extraction thimbles eliminates the transfer of particles to the extraction solvent. The column cleanup procedures remove any particulate that might not be removed by the glass wool. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.8 Particle size determination and reduction as specified in method 1613B is not performed on a routine basis. Silica and sand is not added to the Soxhlet extraction thimble as specified in method 1613B. These procedures are considered to be outside the scope of the laboratories routine extraction procedures and are only performed on a client specific or project specific basis. These procedures, if required, must be specified and documented in the appropriate QAPPs.

17.1.9 Benzene is used to aid in dissolving the samples and/or extracts in hexane. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.10 The acid-base cleanup procedure is carried out in a 40 mL vial instead of a separatory funnel. Disposable glassware is used to decrease the risk of cross contamination. The volumes of the washes used have been adjusted for use in the 40 mL vial. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.11 The silica gel/alumina column cleanup and carbon column cleanup procedures described in this SOP have been optimized and may vary significantly from the referenced methods. It has been demonstrated that the performance criteria specified in the methods is not affected by these modifications.

17.1.12 Extracts are stored at room temperature rather than at <10 °C as specified in method 1613B. Methods 8290 and 8290A allow for the storage of extracts at room temperature in the dark. All of the reference methods require that standards be stored at room temperature. Recovery studies performed by Cambridge Isotopes Laboratories (CIL) indicate freezing or refrigeration of standards causes problems with precipitation and irreversible adsorption to the inside surface of the vial. CIL recommends the storage of standards and extracts at room temperature as long as they are protected from exposure to UV and evaporative losses.

17.2 List of Tables, Figures and Appendices

17.2.1 Table 1 – Concentration of Native Stock and Spiking Solutions

17.2.2 Table 2 – Concentration of Labeled Stock and Spiking Solutions

17.2.3 Appendix I – Example Extraction Benchsheet

17.2.4 Appendix II – Guidelines for the Spike Witnessing Process

17.2.5 Appendix III –LRMS Dioxin Screen Strategy

17.2.6 Appendix IV – Example Determination of Sediment Sample Extraction Amounts Spreadsheet

Table 1 – Concentration of Native Stock and Spiking Solutions

Native Analyte	Standard Source	Catalog Number	Vendor Conc (ng/mL)	Working Stock Conc. (ng/mL)	LCS Spiking Solution Conc (ng/mL)
2,3,7,8-TCDD	CIL	EDF-7999-10x	400	40	0.2
2,3,7,8-TCDF	CIL	EDF-7999-10x	400	40	0.2
1,2,3,7,8-PeCDD	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,7,8-PeCDF	CIL	EDF-7999-10x	2000	200	1.0
2,3,4,7,8-PeCDF	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,4,7,8-HxCDD	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,6,7,8-HxCDD	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,7,8,9-HxCDD	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,4,7,8-HxCDF	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,6,7,8-HxCDF	CIL	EDF-7999-10x	2000	200	1.0
2,3,4,6,7,8-HxCDF	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,7,8,9-HxCDF	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,4,6,7,8-HpCDD	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,4,6,7,8-HpCDF	CIL	EDF-7999-10x	2000	200	1.0
1,2,3,4,7,8,9-HpCDF	CIL	EDF-7999-10x	2000	200	1.0
OCDD	CIL	EDF-7999-10x	4000	400	2.0
OCDF	CIL	EDF-7999-10x	4000	400	2.0

Table 2 – Concentration of Labeled Stock and Spiking Solutions

Labeled Analyte	Standard Source	Catalog Number	Vendor Conc (ng/mL)	Stock Conc (ng/mL)	Working Stock Conc. (ng/mL)	Spiking Solution Conc (ng/mL)
Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-2,3,7,8-TCDF	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,7,8-PeCDD	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,7,8-PeCDF	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-2,3,4,7,8-PeCDF	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	CIL	EDF-8999	100	N/A	N/A	1.0
$^{13}C_{12}$-OCDD	CIL	EDF-8999	100	N/A	N/A	2.0
Internal Standards - Tetras Only						
$^{13}C_{12}$-2,3,7,8-TCDD	CIL	ED-900	50000	1000	N/A	1.0
$^{13}C_{12}$-2,3,7,8-TCDF	CIL	EF-904	50000	1000	N/A	1.0
Recovery Standards						
$^{13}C_{12}$-1,2,3,4-TCDD	CIL	ED-911	50000	5000	N/A	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	CIL	ED-996	50000	5000	N/A	100
Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	CIL	ED-907	50000	5000	200	0.2

Appendix I – Example Extraction Benchsheet

1613B ☐ 8290 ☐ 8290A ☐

TestAmerica Knoxville Extraction Sheet
1613/8290/8290A Sediment/Soil by Soxhlet - KNOX-ID-0004

Batch Number: _____ Native Spike (0.20/1.0/2.0 ng/mL) ID: _____ Spiked by: _____ Witness: _____ Date: _____ Delivered: _____ Initials/Date/Time

Soxhlet Start Date/Time: _____ Internal Std (1.0/2.0 ng/mL) ID: _____ Spiked by: _____ Witness: _____ Date: _____

Soxhlet Stop Date/Time: _____ Cleanup Std (0.20 ng/mL) ID: _____ Spiked by: _____ Witness: _____ Date: _____ Received: _____ Initials/Date/Time

Soil ☐ Sediment ☐ Recovery Std (100 ng/mL) ID: _____ Spiked by: _____ Witness: _____ Date: _____

Lot Sample Number	Work Order Number	Suf	Add sample to Soxhlet thimble. Record weight (g).	Water layer decanted? (Y/N/NA)	Add IS to all samples & QC. Record volume (mL).	Add native spike to LCS, LCSD, MS, MSD. Record volume (mL).	Extract for a minimum of 16 hr in toluene.	Concentrate extracts on heating mantles.	Add 100 µL tetradecane to rinsed 40 mL vials. Concentrate extracts on N-EVAP.	Solvent exchange to hexane on N-EVAP. Bring to ~12 mL in hexane.	Add cleanup std to all 1613B and 8290A extracts. Record volume (mL).	Acid/Base wash extracts if needed.	Concentrate extracts on N-EVAP to 2-4 mL in hexane.	Perform silica gel/alumina column cleanup.	Concentrate to ~2 mL on N-EVAP for carbon cleanup.	Perform carbon cleanup.	Concentrate to <1 mL.	Add recovery std to mini-vial. Record volume added (µL). Transfer extract to vial.	Conc to delivery volume in nonane. Record delivery vol (µL).

Extr Toluene Lot #: _____ 5% NaCl ID: _____ Deact Silica ID: _____ 95/5 Hex/$MeCl_2$ ID: _____ 75/20/5 $MeCl_2$/MeOH/Benz ID: _____

Tetradecane Lot #: _____ H_2SO_4 Lot #: _____ Acid Silica ID: _____ 65/35 $MeCl_2$/Hex ID: _____ Carbon Col Toluene Lot #: _____

Conc Hexane Lot #: _____ A/B Na_2SO_4 Lot #: _____ SG/A Col Na_2SO_4 Lot #: _____ Carbon Lot #: _____

20% KOH ID: _____ Alumina Lot #: _____ SG/A Col Hex Lot #: _____ 50/50 $MeCl_2$/Cyclo ID: _____

Comments: _____

Appendix II – Guidelines for the Spike Witnessing Process

- Make sure there are no distractions, for example, phone calls, checking samples on water bath, people coming in to ask questions.
- The person spiking must tell the person who is witnessing what is being spiked and how much. Make sure the paperwork shows the spike amounts and spike IDs.
- The person witnessing should make sure they know and understand what is to be spiked and how much. Check the paperwork to verify.
- Check the syringe for air bubbles and also check the spike volume.
- It is a good idea to also check for cracks in the glassware.
- If client service requires spiking to occur when another analyst is not available, a witness is not required. In this case, the analyst will serve as his/her own witness and must carefully double check the spike solutions and spike amounts added to the client samples and associated quality control samples. The analyst enters his/her initials as both the analyst and witness.

Appendix III – LRMS Dioxin Screen Strategy

LRMS Dioxin Screen Strategy

Analyte	10g LCL ppt pg/g	10g UCL ppt pg/g	5X UCL 10 g 20 uL	**5X UCL @ 1 g pg/g**	Level 4 Samp Conc pg/g	Level 4 Screen Using 1 g 20uL pg/g	Level 4 Screen Using 1 g 500 uL vs 20uL (pg/g)	Level 4 Screen Using 1.25 g 500 uL vs 20uL (pg/g)	**Level 4 Screen Using 2.5 1000 uL vs 20uL (pg/g)**
2,3,7,8-TCDD	1	400	2000	**20000**	100	1000	25000	20000	**20000**
2,3,7,8-TCDF	1	400	2000	**20000**	100	1000	25000	20000	**20000**
1,2,3,7,8-PeCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,7,8-PeCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
2,3,4,7,8-PeCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,7,8-HxCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,6,7,8-HxCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,7,8,9-HxCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,7,8-HxCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,6,7,8-HxCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
2,3,4,6,7,8-HxCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,7,8,9-HxCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,6,7,8-HpCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,6,7,8-HpCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,7,8,9-HpCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
OCDD	10	4000	20000	**200000**	1000	10000	250000	200000	**200000**
OCDF	10	4000	20000	**200000**	1000	10000	250000	200000	**200000**

If levels in screen are greater than the level 4 standard, do not prep. Send for 8280 analysis.
If peaks are observed at 1/5 to 1 time(s) the areas of the level 4 standard, prep at 1 g, 1/10 bench dilution.***
If peaks are observed at 1/50 to 1/5 time(s) the areas of the level 4 standard, prep at 1 g.***
If no peaks are observed, prep 10 grams.

*** In these cases, the glassware used is treated as contaminated. Post- Clean with solvent before washing.

Appendix IV – Example Determination of Sediment Sample Extraction Amounts Spreadsheet

TestAmerica Knoxville
Determination of Sediment Sample Extraction Amounts

Prep Batch #: 1033072
OR Lot ID: Meth. Code:

	Lot #	Sample Number	Work Order ID	Percent Moisture	Percent Solids	Extraction Amount (g)
1	H1A280439	1	MDT431AK	51.50	N/A	**40 to 41**
2	H1A280448	1	MDT861AK	50.07	N/A	**40 to 41**
3	H1A280448	6	MDT911AK	54.08	N/A	**40 to 41**
4	H1A280448	7	MDVAC1AW	45.60	N/A	**36.8 to 37.7**
5	H1A280448	7S	MDVAC1DU	45.60	N/A	**36.8 to 37.7**
6	H1A280448	7D	MDVAC1DV	45.60	N/A	**36.8 to 37.7**
7	H1A280448	12	MDVDF1AC	54.65	N/A	**40 to 41**
8	H1A300404	1	MDWC91AK	53.07	N/A	**40 to 41**
9	H1A300404	2	MDWDA1AW	48.36	N/A	**38.7 to 39.7**
10	H1A300404	3	MDWDC1AW	45.28	N/A	**36.5 to 37.5**
11	H1A300404	5	MDWDE1AW	48.43	N/A	**38.8 to 39.8**
12	H1A300404	6	MDWDF1AW	43.85	N/A	**35.6 to 36.5**
13	H1A300404	7	MDWDG1AW	41.62	N/A	**34.3 to 35.1**
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						

LIQUID EXTRACTION PROCEDURES: CONTINUOUS LIQUID-LIQUID & SEPARATORY FUNNEL

(Methods: EPA 3520C, EPA 3510C, and EPA 600-series, EPA 8276, and SM6000-series extraction procedures)

Approvals (Signature/Date):

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November 5, 2010
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Facility Distribution No. 1 **Distributed To:** QA Navigator

1.0 Scope and Application

This SOP gives the procedures for extracting semivolatile organic compounds (SVOCs) in water samples. The laboratory currently employs two extraction procedures for water samples: continuous liquid-liquid extraction (CLLE) followed by extract concentration via Zymark TurboVap technique, and separatory funnel extraction followed by extract concentration via Kuderna-Danish (K-D) technique.

The CLLE procedure is the laboratory's default procedure. The separatory funnel procedure can be employed to meet compressed turn-around-times or upon client request.

The following classes of SVOCs can be extracted using the procedures outlined in this SOP:

Fraction	Analytical Method	SOP #
Organochlorine Pesticides & PCBs	EPA 608 EPA 8081A EPA 8081B EPA 8082 EPA 8082A SM6431B SM6630C	SOP SA-SG-045
Organophosphorous Pesticides	EPA 614 EPA8141A EPA 8141B	SOP SA-SG-050
Diesel Range & Oil Range Organics (DRO and ORO)	EPA 8015B EPA 8015C (DRO and ORO)	SOP SA-SG-070
Polychlorinated Biphenyls	EPA 680	SOP SA-SM-007
Base Neutrals / Acids & PAHs	EPA 625 EPA 8270C EPA 8270D EPA 8270C_LL EPA 8270D_LL EPA 8270C_LL_PAH EPA 8270D_LL_PAH SM6410B (BNAs) SM6420C (Phenols)	SOP SA-SM-033
Toxaphene Congeners (i.e., Parlars) and Technical Toxaphene	EPA 8276	SOP SA-SM-034

Note: Herbicides by EPA 515.1, EPA 615, and EPA 8151 and Pesticides and PCBs by EPA 508 are extracted by separatory funnel; however, these procedures are very specialized and are included in their own method-specific SOPs (Herbicides: SA-SG-065; Pesticides and PCBs: SA-SG-046).

This SOP includes the Work Instructions outlining the extract clean-up procedures employed by the laboratory. These clean-up procedures include Gel-Permeation

Chromatography (GPC), Florisil, copper (sulfur), and sulfuric acid as outlined in Attachment 8 through Attachment 11.

A complete target analyte lists, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

2.1 Continuous Liquid-Liquid Extraction Procedure

A known volume of sample is adjusted to a specific pH, if required by the analytical method, transferred to a continuous liquid-liquid extractor, and extracted using the solvent and conditions specified in Attachment 5. The extract is concentrated to an appropriate final volume using the Zymark TurboVap apparatus.

2.2 Zymark TurboVap Concentration Procedure

After the CLLE procedure is completed, the solvent is transferred to a glass Zymark concentration tube. The tube is placed in the Zymark TurboVap concentration device, which has been heated to a specified temperature. A stream of nitrogen is directed into the tube to evaporate the solvent and to concentrate the target compounds. When the volume of solvent reaches the specified volume, normally 1mL, the nitrogen stream is automatically stopped. An alarm sounds to alert the analyst, and the extract is removed from the device and transferred to a storage vial.

If a solvent exchange is required, the exchange solvent is added to the tube, the solvent is evaporated to the specified final volume, and the extract is transferred to a storage vial.

The extracts are stored at 4°C until the time of analysis.

2.3 Separatory Funnel Extraction Procedure

In separatory funnel extraction a known volume of sample is placed into a separatory funnel, adjusted to a specified pH if required by the analytical method, and extracted using the solvent and conditions specified in Attachment 6. The extract is concentrated to an appropriate final volume using the Kuderna Danish (KD) concentration procedure.

2.4 Kuderna-Danish Concentration Procedure

After the separatory funnel extraction procedure is completed, the extract is transferred to a glass Kuderna-Danish (K-D) concentration apparatus. The K-D is placed in a water bath that has been heated to 60-90°C. As the solvent evaporates, the target compounds are collected in the concentration tube. When the apparent volume of solvent reaches 1mL, the K-D is removed from the water bath and allowed to cool. The extract is removed from the device and transferred to a storage vial or container.

If a solvent exchange is required, the exchange solvent is added to the K-D, the solvent is evaporated to the specified final volume, and the extract is transferred to a storage vial or container.

The extracts are stored at 4°C until the time of analysis.

Note: The K-D cannot be used for extracts that must be evaporated to a final volume of 1mL or less. Nitrogen blow-down or a micro K-D must be used to evaporate an extract to 1mL or less.

2.5 Extract Clean-up Procedures

GPC, Florisil, copper, and acid clean-up procedures can be performed to remove interferences from extracts as outlined in the Attachment 8 through Attachment 11 of this SOP.

2.6 Method References

This SOP is based on the following methods: EPA 3510C (Separatory Funnel), EPA 3520C (CLLE), EPA 8276 (CLLE), and the extractions sections of EPA 608, EPA 614, EPA 625, EPA 680, and SM6431B, SM6630B, SM6410B, and SM6420C (all of which are performed by CLLE).

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

After cleaning the CLLE apparatus, inspect the glassware for the presence of water, especially in the small tubing of the extractor. Water can block the solvent return tube and prevent efficient extraction of the sample. A thorough acetone rinsing will help to eliminate or minimize this problem.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Acetone, hexane, methylene chloride, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. The clean-ups employed by the laboratory include Gel Permeation Chromatography (GPC), Florisil, sulfuric acid, and copper (sulfur) clean-ups as outlined in Attachment 8 through Attachment 11.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be processed first.

4.2.3 Samples with large amounts of sediments or particulate may clog the solvent return line of the CLLE. A layer of glass wool, placed in the bottom of the extractor, may be helpful when sediments or particulate are present.

4.2.4 Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction if separatory funnels are used. Emulsions will occur most readily if the sample is adjusted to a basic pH. The extract may be filtered or stirred to remove the emulsion. If the emulsion cannot be broken, the sample and extract should be transferred to a continuous liquid-liquid extractor.

4.2.5 During extract cleanup an emulsion may form in the acid/solvent interface. A small quantity of sodium sulfate or sodium chloride may be gently added to the emulsion. The salt will generally cause the emulsion to break up.

4.2.6 Extracts with particulates and precipitates will clog the Florisil Solid Phase Extraction (SPE) cartridges and the GPC. Filter the extract through a syringe with 0.45um filter as necessary.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of chemicals used in this procedure has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

Methylene chloride is a carcinogen and an irritant. It causes irritation to the respiratory tract and has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting, and headache. Methylene chloride may be absorbed through the skin and can cause irritation and pain to the skin and eyes.

Hexane and acetone are flammable solvents. They can cause irritation to the respiratory tract. Overexposure can cause fatigue, lightheadedness, headache, dizziness, and blurred vision.

Sodium hydroxide is a severe corrosive. Contact with the skin can cause irritation or severe burns and scarring. Contact with the eyes can cause irritation, burns, permanent vision impairment or even blindness.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

Compressed gasses have specific hazards. The employee must be familiar with the MSDS for each of the compressed gasses. The employee must also be familiar with the compressed gas section (Section 11) of the Environmental Health and Safety Manual.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

Note: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" button on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Acetone	Flammable	1000ppm TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500ppm TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25ppm TWA 125ppm STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive	2mg/m^3 Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1mg/m^3 TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Florisil	Irritant	10mg/m^3 TLV 5mg/m^3 PEL	May cause irritation if inhaled or adsorbed through the skin.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
Note: Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

6.1.1 CLLE-specific Equipment

Continuous Liquid-Liquid Extractor – with compatible condenser, extractor body, and receiving flask

Heating Mantle and Adjustable Support – The heating mantle must be connected to a rheostat to control the temperature.

Rheostat or Variable Transformer

6.1.2 Separatory Funnel-specific Equipment

Separatory funnels – 1L and 2L, Teflon or glass with Teflon stopcocks

Mechanical shaking device

6.1.3 Concentration-specific Equipment

Zymark TurboVap II concentration device or equivalent – The instrument must be vented into an operating fume hood.

Concentration tubes – 200mL with 1.0mL tip. Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use).*

Kuderna-Danish apparatus – consists of the K-D body, three-ball Snyder column, and a graduated concentration tube with springs or clips to hold the concentration tube to the K-D body. Verify the concentration tube in accordance with SA-AN-100: *Support Equipment (Verification and Use).*

Water bath – compatible with the K-D apparatuses, located under an operating fume hood

6.1.4 Support Equipment

Analytical Balance – Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*

Thermometers – Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*

6.1.5 Cleanup-specific Equipment

Florisil solid phase extraction (SPE) columns – Bakerbond 6mL Solid Phase Extraction cartridge packed with 1g Florisil. Other size SPE may be used; however, the volume of elution solvents and sample loading capacity must be adjusted to compensate for the amount of Florisil. Each lot of cartridges must be verified prior to use.

The lot of Florisil cartridges is acceptable if all the following criteria are met:
- the pesticides in the check mix are recovered at 80-110% percent
- the percent recovery of 2,4,6-trichlorophenol is less than 5%
- there are no peaks interfering with the target compounds are detected

Florisil Cartridge Manifold

GPC System – includes autoinjector, autosampler, UV detector, glass column, solvent pump, solvent reservoir, waste reservoir, and applicable software

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Transfer Pipettes – various sizes

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

pH paper – Narrow range.

Residual Chlorine Check Strips – starch iodide strips. Store in original, capped container and use within the manufacturer's expiration date.

Filter Paper, grade 414 – 18.5cm diameter

Glass Funnels

Pyrex Glass Wool – rinsed with methylene chloride prior to use

2mL vials with Teflon lined crimp caps or 2mL screw cap vials with PFTE-faced septa: compatible with the autosampler. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

12mL glass vials with Teflon-lined or PFTE-lined caps. A storage vial may be calibrated by adding a known volume of liquid to the container and marking the volume on the side of the container.

11mm crimp-type capper and decapper

Detergent – FL-70 or equivalent, used for washing non-disposable labware.

6.2.1 CLLE-specific Lab Supplies

Receiving Flask – 250mL with Teflon stoppers

Boiling Stones

6.2.2 Cleanup-specific Lab Supplies

Vials – 40mL or smaller; equipped with Teflon-lined caps

Filters – 0.45um syringe filters

Bio-Beads – packing material for GPC column (200–400 mesh)

Glass Sample Tubes – threaded, with a septa in cap

Zymark Tubes – sized to fit the GPC System

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

1L amber glass container– purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

Unless listed elsewhere in this SOP, the expiration dates given below apply.

7.1.1 The expiration date for unopened standards and reagents is the manufacturer's expiration date.

7.1.2 The expiration date for opened stock reagents is the manufacturer's expiration date or 5 years from the date opened, whichever is sooner.

7.1.3 The expiration date for opened stock standards is the manufacturer's expiration date or 6 months from the date opened, whichever is sooner.

7.1.4 The expiration date for prepared reagents is 6 months from the date prepared or the expiration date of the parent reagent, whichever is sooner.

7.1.5 The expiration date for prepared standards is 3 months from the date prepared or the expiration date of the parent standard, whichever is sooner.

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.*

Acetone, hexane, methylene chloride, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Purchased Reagents

7.2.1.1 Laboratory Reagent Water – ASTM Type II

7.2.1.2 Methylene Chloride– pesticide quality or equivalent
LIMS Reagent Name: EX_MECL2_00001
Storage: Flammables Cabinet

7.2.1.3 Acetone– pesticide quality or equivalent
LIMS Reagent Name: EX_Acetone_00001
Storage: Flammables Cabinet

7.2.1.4 Hexane – residue grade or better
LIMS Reagent Name: EX_Hexane_00001
Storage: Flammables Cabinet

7.2.1.5 Sodium Hydroxide (NaOH) – pellets, reagent grade
LIMS Reagent Name: EX_NaOH_00001
Storage: cool, dry cabinet

7.2.1.6 Sulfuric Acid (H_2SO_4) – concentrated reagent grade
LIMS Reagent Name: EX_H2SO4_00001
Storage: cabinet under a hood

7.2.1.7 Sodium Sulfate – anhydrous, granular
LIMS Reagent Name: EX_Na2SO4_00001
Storage: cool, dry place

7.2.2 Prepared Reagents

7.2.2.1 Sodium Hydroxide Solution (10N) – Dissolve 400g of NaOH pellets into approximately 500mL of reagent water contained in a 2L beaker on a magnetic stirrer. Add the NaOH in small portions, with constant stirring, to minimize the time it takes to dissolve the pellets. A good deal of heat will be generated as the NaOH dissolves. After all 400g have been added and the flask is cooled, carefully dilute to 1000mL with reagent water. Mix the solution thoroughly and transfer to a storage container. Do not store sodium hydroxide solution in volumetric glassware or in containers with ground glass joints.
LIMS Reagent Name: EX-10NNaOH_00001
Storage: dry, cool cabinet or under a hood

7.2.2.2 Sulfuric Acid Solution (1:1 v/v) – Slowly and carefully add 500mL of concentrated H_2SO_4 to 500mL of reagent water contained in a 2L beaker on a magnetic stirrer. Add the acid in small portions with constant stirring to reduce the heat evolved when the acid and water are combined. Cool and transfer the solution to a labeled storage container.
LIMS Reagent Name: EX_10N_H2SO4_00001

Storage: dry, cool cabinet or under a hood

7.2.2.3 Sodium Sulfate, Baked – anhydrous, granular, purified by heating for 4 hours at 400°C in a shallow tray. Store in glass containers.
LIMS Reagent Name: EX_Baked NaSO4_00001
Storage: cool, dry place

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

All of the standards used from this SOP must be stored at a temperature of 4°C (less than 6°C and not frozen). Unless otherwise noted, all purchased standards have an expiration date of 6 months from date of opening, and all prepared standard have an expiration date of 3 months from date of preparation.

Note: This standards list is comprised of the routine standards used by the laboratory. Information on project-specific, non-routine standards is found in the Reagent Module in LIMS.

7.3.1 Purchased Standards

7.3.1.1 Organochlorine Pesticide Surrogate Stock, 200ug/mL – Purchased from Supelco (catalog # 505935)
LIMS Reagent Name: SGPESTSURR_00001

7.3.1.2 Triphenylphosphate (Organophosphorous Surrogate Stock), 1000 ug/mL – Purchased from Restek (catalog # 32281)
LIMS Reagent Name: SG_TPP_00001

7.3.1.3 Pesticide A\B Mix, varied concentrations – Purchased from Ultra (Custom#5454)
LIMS Reagent Name: SG_ABICV_00001

7.3.1.4 Aroclor 1016/1260 Spike Mix, 1000ug/mL – Purchased from Restek (catalog # 32039)
LIMS Reagent Name: SG_AR1660_00001

7.3.1.5 O-terphenyl Standard, 10000ug/L – Purchased from NSI (catalog # C-1341H-TP)
LIMS Reagent Name: SG_OTP_00001

7.3.1.6 #2 Diesel Fuel, 100mg/mL – Purchased from Accustandard (catalog # FU-009-D-200X)
LIMS Reagent Name: SG_DIESEL_00001

7.3.1.7 680 Surrogate Mix, 50ug/mL Decachlorobiphenyl-13C12 – Purchased from Wellington (catalog # MBP-209)
LIMS Reagent Name: DB(680)SURR

7.3.1.8 680 Concentration Calibration Standard, varied concentrations – Purchased from Ultra Scientific (catalog # CB-681)

LIMS Reagent Name: LAB(CH) MeOH

7.3.1.9 BNA Surrogate Standard, 10000ug/mL – Purchased from Supelco (catalog # custom quote)
LIMS Reagent Name: 8270cuSuRR

7.3.1.10 Benzidine Mix, 2000ug/mL – Purchased from NSI (catalog # C-402-22)I
LIMS Reagent Name: BENZIDINES

7.3.1.11 BNA Full Spike Mix – Purchased from NSI (catalog # Q-4717)
LIMS Reagent Name: BNAFULLSPIKE

7.3.1.12 LL_BNA Spike Mix – Purchased from NSI (catalog number is Q-5118)
LIMS Reagent Name: LLBNASPK

7.3.1.13 AP9 Spike Mix – Purchased from NSI (catalog number is Q-5131)
LIMS Reagent Name: EXAP9SPK

7.3.1.14 AR_MIX_SPK, client specific PCB spike – Supplied from Solutia to be used with every batch of 8082 that include samples from the Solutia-Anniston Residential site. The standard has varied concentrations of Aroclors and has no reported expiration date.

7.3.2 Prepared Standards

7.3.2.1 Working Pesticide / PCB / OP Pesticide Surrogate Mix – prepared by adding 1.25mL Pesticide Surrogate Stock (200ug/mL) and 2.0mL of Triphenylphosphate (1000 ug/mL) diluted to a final volume of 500mL in methanol.
LIMS Reagent Name: PESTwkSURR_xxxxx

7.3.2.2 Working Pesticide Spike Mix – prepared by adding 1mL Pesticide Mix A and 1mL Pesticide Mix B diluted to a final volume of 100mL in hexane.
LIMS Reagent Name: 608wkSPIKE_xxxxx

7.3.2.3 Working PCB Spike Mix – prepared by adding 1mL of Aroclor 1016/1260 Spike Mix diluted to a final volume of 100mL in methanol.
LIMS Reagent Name: 1660wkSPIKE_xxxxx

7.3.2.4 Working OP Pesticide Spike Mix – prepared by adding 0.250mL of OP Pesticide MS mix diluted to a final volume of 50 mL in acetone.
LIMS Reagent Name: tallWKspike_xxxxx

7.3.2.5 Working DRO Surrogate Mix – prepared by adding 2.5mL of O-terphenyl standard (2000 ug/L) diluted to a final volume of 250mL in acetone.
LIMS Reagent Name: DROwkSURR_xxxxx

7.3.2.6 Working DRO Spike Mix – prepared by adding 1.0mL of #2 Diesel Fuel (100 mg/mL) diluted to a final volume of 100mL in acetone.
LIMS Reagent Name: DIESELWK_xxxxx

7.3.2.7 Working 680 Surrogate Mix – prepared by adding 2.5mL of Decachlorobiphenyl-13C12 (50ug/mL) catalog number MBP-209 from Wellington diluted to a final volume of 50mL in

acetone.
LIMS Reagent Name: 680wkSURR_xxxxx

7.3.2.8 Working 680 Spike Mix – prepared by adding 1.0 mL of Concentration Calibration Standard mix (varied concentrations) diluted to a final volume of 25 mL in acetone.
LIMS Reagent Name: 680wkSPIKE_xxxxx

7.3.2.9 Working BNA Surrogate Mix – prepared by adding 5.0mL of Organic Acid Surrogates (10000 ug/mL) and 10.0mL of Base/Neutral Surrogates (5000 ug/mL) diluted to a final concentration of 500mL in acetone.
LIMS Reagent Name: BNAwkSURR_xxxxx

7.3.2.10 Working LLBNA / LLPAH Surrogate Mix – prepared by adding 0.5mL of Organic Acid Surrogates (10000 ug/mL), 1.0mL of Base/Neutral Surrogates (5000 ug/mL), and 0.5mL of O-Terphenyl standard (2000 ug/L) diluted to a final concentration of 500mL in acetone.
LIMS Reagent Name: LLBNAwkSUR_xxxxx

7.3.2.11 Working Benzidine Spike Mix – prepared by adding 5.0mL of Benzidine Mix (2000 ug/mL) diluted to a final volume 100mL in acetone.
LIMS Reagent Name: BENZIDINwk_xxxxx

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

With the exception of DRO samples, aqueous samples are routinely collected in 1L amber glass containers without preservative. Samples for DRO are routinely collected in 1L amber glass containers with HCl preservative sufficient to achieve pH<2.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation and/or analysis. Samples must be prepared within 7 days of collection and analyzed within 40 days of extraction.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives and/or de-chlorination agents.

8.1.1 Preservation Checks

8.1.1.1 pH Verification

For each sample,
- Place a piece of pH paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the pH paper.
- If the pH is outside the range of 5–9 (or, for DRO/ORO, pH is >2), initiate a Nonconformance Memo. Adjust the sample pH to between pH 5-9 (or, for DRO/ORO, to <2) using either 10N sodium hydroxide or 1:1 sulfuric acid.

Note: Sulfuric acid will cause the pH of the sample to decrease; sodium hydroxide will

cause the pH of the sample to increase.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the pH paper into the sample container. The pH paper dye may bleed into the sample and affect sample results.

8.1.1.2 Residual Chlorine Check

For each sample
- Place a piece of starch-iodide paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the paper.
- If the paper turns blue or black, residual chlorine is present. Initiate a Nonconformance Memo.

Note: To avoid cross-contamination, use a separate medicine cup and residual chlorine strip per sample. Do not dip the strip into the sample container.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

9.1.1 EPA 600-Series Methods

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period. The default QC items required for each extraction batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS) performed per 10 % of samples or 1 per batch – whichever is greater, and a matrix spike duplicate (MSD).

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, 1 matrix spike, and a matrix spike duplicate.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), another matrix spike (from sample 11-20), and a matrix spike duplicate.

The routine container supplied for this method is a 1L container. 1L is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 500mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample to perform the MS/MSD, the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated to denote this situation. Insufficient sample volume is defined as receiving less than a total of 2L.

Note: If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.1.2 EPA 3510C, EPA 3520C, EPA 8276, and the SM 6000-Series Methods

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period. The default QC items required for each extraction batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD).

The routine container supplied for this method is a 1L container. 1L is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 500mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample to perform the MS/MSD, the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated to denote this situation. Insufficient sample volume is defined as receiving less than a total of 2L.

Note: If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

Refer to the applicable analytical SOP (Section 1.0) for information on instrument QC.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* and the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

Remove the samples from the refrigerator and allow them to come to room temperature.

Inspect the samples. Determine if the samples have multiple layers such as sediment or an oil layer. Consult with the Department Manager or Technical Manager if the sample matrix is unusual or difficult to categorize.

Mark the level of the sample on the outside of the container. This marking will be used to determine the original sample volume actually used in the extraction process. After the sample has been added to the extractor body, fill the empty container with water to the mark. Pour the water into a graduated cylinder, and determine the volume. Record the volume to the nearest 5mL.

Note: If samples are received in duplicate, use the sample bottle that contains the most volume. Extracting less than 1L of sample will result in elevated reporting limits. Selecting the sample bottle with the most volume will ensure the lowest possible RL is used.

Note: If a reduced volume of sample must be extracted in order to provide sufficient sample volume to meet state or other program QC requirements, the sample is thoroughly mixed and an aliquot is measured with a graduated cylinder and poured into the extractor body.

Add surrogate spiking solution directly to the each sample in the sample container, prior to pouring into separatory funnel or CLLE apparatus. The surrogate solutions are designed such that 1.0mL of the solution will be added to each sample container to achieve the required concentration. Be sure to use the correct solutions for the analytical procedure of concern. The addition of the surrogates ***must*** be witnessed by another analyst to ensure that the proper volume of the spiking solution is added to each sample.

Note: If the volume of sample extracted must be reduced to provide sufficient sample to meet state or other program requirements, the volume of surrogate spiking solution must be reduced proportionately (i.e., if 500mL is extracted instead of 1L, then only 0.50mL of surrogate is added to the sample).

10.2 CLLE Procedures

All glassware preparation steps must be performed under or near a fume hood to minimize the evaporation of methylene chloride into the lab.

10.2.1 Prepare the continuous liquid-liquid extraction apparatus by rinsing the extractor body, receiving flask, and condenser with acetone. Pay particular attention to the solvent return line for the presence of water drops or solids.

10.2.2 Set the extractor body on the holder in front of the fume hood. Add methylene chloride (50-100mL) to the extractor body in order to fill the drain tube and ensure that a continuous flow of solvent from the extractor body to the receiving flask is maintained.

Note: Inspect the solvent layer when the sample is added. Large quantities of sediment may plug the tube such that extraction will not occur.

10.2.3 In a fume hood, add 70mL of methylene chloride (or 200mL for EPA 8276) to the receiving flask, and add a few boiling stones to the flask. Add the same volume to each flask in the batch. Leave the receiving flask with the methylene chloride under the hood until ready to attach it to the extractor or cover tightly with aluminum foil.

10.2.4 Securely attach the receiving flask to the extractor body, and secure the heating mantle

around the flask.

10.2.5 As soon as possible after the methylene chloride is added to the extractor, gently pour the entire sample into the extractor body, trying not to let the sample leak into the sidearm. If the sample leaks into the sidearm, the sidearm can be drained back into the sample container and the sample can then be poured back into the extractor body.

The extractor body will be approximately one-half to two-thirds full, and the methylene chloride in the solvent return should be about 3/4 of the way to the receiving flask.

Note: If a sub-sample must be extracted (e.g., half volume is used to perform MS/MSD) measure the sample volume in a graduated cylinder prior to pouring into the extractor body.

10.2.6 Add 50mL of methylene chloride to the sample container (or the graduated cylinder, if used). Swirl the solvent around the inside of the container to thoroughly rinse the sample bottle (or graduated cylinder), and add this rinse to the extractor body.

10.2.7 Adjust the pH of the samples to the range specified in Attachment 5. The pH is adjusted by adding small aliquots of 10N sulfuric acid or 10N sodium hydroxide directly to the 1L sample bottle or sample extraction body. Stir the sample with a Pasteur pipette. To ensure cross-contamination does not occur, use a new pipette for each sample. Check the pH after each acid/base addition with pH paper as stated in Section 8.1.1.1.

Note: Sulfuric acid will cause the pH of the sample to decrease; sodium hydroxide will cause the pH of the sample to increase.

10.2.8 Slowly add reagent water to the extractor body until the level of the liquid causes the methylene chloride to just flow over to the receiving flask.

10.2.9 Place the condenser securely on the extractor body. Make sure that water is flowing through the condenser and turn the heating mantle on. Observe the extraction for the first hour or so to ensure that the solvent is being boiled, condensed, and returned to the receiving flask. Extract the samples for the time listed in Attachment 5. The batch start time and stop time must be recorded in the AD batch in LIMS. If a single pH extraction is performed, skip to Section 10.2.13; if a two-pH extraction must be performed, continue to Section 10.2.10.

10.2.10 If a dual pH extraction is required, turn the heating mantle "off" to stop the extraction at the appropriate time, and allow the extraction vessel to cool (at least 30 minutes). Remove the receiving flask from the extractor body and cover with a Teflon stopper. Store extract sealed in the liquid room. Place a new receiving flask on the extractor body.

10.2.11 Move the extractor body under a hood and adjust the pH of the sample (as indicated in Attachment 5) by adding small aliquots of 10N sulfuric acid or 10N sodium hydroxide. Stir the sample with a disposable Pasteur pipette, and check the pH after each addition in accordance with Section 8.1.1.1. Do not dip the pH paper into the sample. Use a pipette to remove a small aliquot of the sample and touch the liquid to the pH paper.

Note: Sulfuric acid will cause the pH of the sample to decrease; sodium hydroxide will cause the pH of the sample to increase.

10.2.12 Turn the heating mantle on and extract the sample at the second pH for the time listed in Attachment 5.

10.2.13 After the samples have extracted for the required time, turn the heating mantle "off", and allow the extraction vessel to cool to room temperature. It is important to allow the receiving flask to cool before it is removed from the extractor.

10.2.14 Remove the receiving flask from the extractor body to look for signs of water, and cover it with a Teflon stopper. The extract is stored sealed until the concentration step is performed.

Note: If water is present in the receiving flask the sample must be filtered. Store the extract under a hood until the filtration step is performed. If filtration is necessary, working under a hood, place a piece of filter paper into a glass funnel and add a small amount of purified sodium sulfate. Filter the extract through the glass funnel, and collect the extract directly into a labeled Zymark tube.

10.2.15 Working under a hood, place a piece of filter paper into a glass funnel and add a small amount of baked sodium sulfate. Filter the extract through the glass funnel and collect the extract directly into a labeled Zymark tube. Repeat the extraction two more times with fresh 50mL aliquots of methylene chloride, combining each extract into the same vessel.

Note: The "acid" and "base" extracts are collected in separate Zymark tubes. The volume of solvent used to extract the sample (300mL total) will not fit into a single tube. The two fractions are routinely concentrated and combined prior to analysis. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts are required. (Always refer to the worksheet notes for guidance.)

10.2.16 The extract is now ready for concentration. The sample may be kept tightly covered with aluminum foil until the concentration step if it is to be performed the same day. Otherwise, transfer samples to the refrigerator until the concentration step occurs. If, due to space limitations in the refrigerator, the samples must be stored on the counter or on carts, they must be shielded from light with a black-out blanket.

Note: If performing GC/MS analysis, the acid/neutral and base extracts are combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts are required. (Always refer to the worksheet notes for guidance.)

10.2.17 Rinse the ground-glass joint of the condenser with acetone and wrap in aluminum foil before placing the condenser in the rack. Collect the acetone rinsate in a separate container for disposal.

10.2.19 After the receiving flask has been removed from the extractor body, the methylene chloride remaining in the extractor body must be properly disposed. The extractor must be handled with minimum agitation to minimize the amount of solvent allowed to

evaporate into the lab and stored in the chlorinated solvent waste container. Place the receiving flask side-arm over the chlorinated waste container. Add tap water to the extractor body to displace the methylene chloride into the waste container.

The liquid remaining in the extractor body must be poured carefully down the sink and flushed continuously with water.

10.2.20 Clean the glassware in accordance with the procedures in Attachment 7.

10.3 Separatory Funnel Procedures

10.3.1 Prepare the separatory funnels and receiving flasks or beakers by rinsing with acetone. Use a separatory funnel that will hold approximately 2 times the volume of sample being extracted.

10.3.2 Gently pour the entire sample into the separatory funnel.

Note: If a sub-sample must be extracted (e.g., half volume is used to perform MS/MSD) measure the sample volume in a graduated cylinder prior to pouring into the extractor body.

10.3.3 Add 50mL of methylene chloride to the sample container. Swirl the solvent around the inside of the container to thoroughly rinse the sample bottle (or graduated cylinder) and add this rinse to the separatory funnel.

10.3.4 Adjust the pH of the samples to the range specified in Attachment 5. The pH is adjusted by adding small aliquots of 10N sulfuric acid or 10N sodium hydroxide directly to the separatory funnel. Shake the separatory funnel to mix the sample with the acid or base. Check the pH after each acid/base addition with pH paper as stated in Section 8.1.1.1. Do not dip the pH paper into the sample. Use a pipette to remove a small aliquot of the sample and touch the liquid to the pH paper.

Note: Sulfuric acid will cause the pH of the sample to decrease; sodium hydroxide will cause the pH of the sample to increase.

10.3.5 Shake each separatory funnel for three minutes with periodic venting (under a hood) to release any excess pressure. If a mechanical shaker is used, extract the sample for five minutes. The extraction must be performed under or near a hood to minimize the solvent vapors released into the laboratory. Allow approximately ten minutes for complete separation between the lower organic and upper water phase.

Note: The separatory funnel must be vented under a hood to remove the methylene chloride fumes from the lab.

10.3.6 Working under a hood, place a piece of filter paper into a glass funnel and add a small amount of purified sodium sulfate. Filter the extract through the glass funnel and collect the extract directly into a labeled collection tube. Repeat the extraction two more times with fresh 50mL aliquots of methylene chloride, combining each extract into the same vessel. If a single pH extraction is performed, skip to Section 10.3.11; if a two-pH extraction must be performed, continue to Section 10.3.7.

10.3.7 If a dual pH extraction is required, adjust the pH of the sample by adding small aliquots of 10N sulfuric acid or 10N sodium hydroxide. Gently swirl the flask to mix the acid or base and the sample. Check the pH after each addition. Do not dip the pH paper into the sample but use a pipette to remove a small aliquot of the sample and touch the liquid to the pH paper.

Note: Sulfuric acid will cause the pH of the sample to decrease; sodium hydroxide will cause the pH of the sample to increase.

10.3.8 Add 50mL of methylene chloride to each separatory funnel.

10.3.9 Shake each separatory funnel for three minutes with periodic venting to release any excess pressure. The extraction must be performed under or near a hood to minimize the solvent vapors released into the laboratory. Allow ten minutes for complete separation between the lower organic and upper water phase.

Note: The separatory funnel must be vented under a hood to remove the methylene chloride fumes from the lab.

10.3.10 Working under a hood, place a piece of filter paper into a glass funnel and add a small amount of purified sodium sulfate. Filter the extract through the glass funnel and collect the extract directly into a labeled collection tube. Repeat the extraction two more times with fresh 50mL aliquots of methylene chloride, combining each extract into the same vessel.

Note: The "acid" and "base" extracts are collected in separate Zymark tubes. The volume of solvent used to extract the sample (300mL total) will not fit into a single tube. The two fractions are routinely concentrated and combined prior to analysis. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts are required. (Always refer to the worksheet notes for guidance.)

10.3.11 The extract is now ready for concentration. The sample may be kept under a hood, tightly covered with aluminum foil until the concentration step if it is to be performed the same day. Otherwise, transfer samples to the refrigerator until the concentration step occurs. If, due to space limitations in the refrigerator, the samples must be stored on the counter or on carts, they must be shielded from light with a black-out blanket.

Note: Perform the extract filtration and drying steps in batches to minimize the loss of solvent into the lab. Cover the remaining containers tightly with aluminum foil and leave under or near a hood.

10.3.12 Pour the liquid remaining in the separatory funnel carefully down the sink and flush continuously with cold tap water. Wash the separatory funnels in accordance with the applicable glassware cleaning posting for this procedure.

10.3 QC Sample Preparation

10.4.1 Method Blank – Add 1L of reagent water to the extraction vessel. Prepare as a sample following the steps outlined in Section 10.2 or Section 10.3.

10.4.2 Laboratory Control Sample – Add 1L of reagent water to the extraction vessel. Spike with 1.0mL of the appropriate matrix spiking solution. Be sure to use the correct solutions for the analysis of concern. The addition of the spike mixes ***must*** be witnessed by another analyst to ensure that the proper volume of the spiking solution is added to each sample. Prepare as a sample following the steps outlined in Section 10.2 or Section 10.3.

10.4.3 Matrix Spike(s) – Spike sample container with 1.0mL of the appropriate matrix spiking solution. Be sure to use the correct solutions for the analysis of concern. The addition of the matrix spike mixes ***must*** be witnessed by another analyst to ensure that the proper volume of the spiking solution is added to each sample. Prepare as a sample following the steps outlined in Section 10.2 or Section 10.3.

10.5 Zymark Concentration Procedures

Note: If the volume of sample extracted has been reduced to provide sufficient sample to meet state or other program QC requirements, the final volume of the extract must be reduced proportionately.

10.5.1 Pre-rinse each Zymark concentration tube with acetone and methylene chloride.

10.5.2 Turn on TurboVap evaporation unit. Set the water bath temperature to 50°C. Set the gas pressure to zero initially for each cell in the TurboVap unit.

10.5.3 Pre-rinse each concentration cap on the TurboVap evaporation unit with methylene chloride.

10.5.4 If the sample extracts have been collected in any container other than a Zymark tube, transfer the extract to a Zymark tube. Working under a hood, pour 150-200mL of the extract (depending on the size of the tube) into a labeled Zymark concentration tube, and place the tube into a cell of the evaporation unit. Repeat for all samples in the analytical batch. The remaining extract must be tightly covered with a piece of aluminum foil to minimize evaporation of the solvent.

10.5.5 Carefully close the cover of the Zymark TurboVap unit completely. Make sure that each tube is seated properly and that the individual covers are positioned directly over each tube. Note: When the elongated tubes are used, care must be taken to position the tubes to avoid breaking the tube covers and to completely close the instrument cover.

10.5.6 Concentrate extracts at a constant temperature of 50°C with a pressure range from 4 to 15psi. Zymark tubes with smaller sample volumes are processed with higher pressures (15psi); while, Zymark tubes with larger volumes (those approaching the red "fill" line) are processed with lower pressures (4-5psi).

10.5.7 As extracts are concentrated, periodically add more sample until the entire sample has been transferred to the Zymark concentration tube.

10.5.8 Concentrate the extract until the cell alarm sounds. This indicates the sample is at approximately a 1mL volume.

10.5.9 If the solvent must be exchanged, add 20mL of the exchange solvent to the Zymark concentration tube. Continue concentration until the cell alarm sounds. This indicates the sample is at approximately a 1mL volume.

10.5.10 Remove Zymark concentration tubes from evaporation unit as transfer to storage vials as outlined in Section 10.7.

10.6 Kuderna-Danish Concentration Procedures

Note: If the volume of sample extracted has been reduced to provide sufficient sample to meet state or other program QC requirements, the final volume of the extract must be reduced proportionately.

10.6.1 Turn on the water bath and set to the temperature to 60-90°C. Record the temperature of the waterbath with each batch of samples.

10.6.2 Pre-rinse each K-D apparatus with acetone and methylene chloride. Pay particular attention to the concentration tube and the ground glass joints of the K-D. Add a few boiling beads to the concentration tube and assemble the K-D apparatus, ensuring that the concentration tube is secured to the body.

10.6.3 Remove the three-ball Snyder column from the apparatus. Working under a hood, pour the extract into the labeled K-D apparatus. Replace the Snyder column. Repeat above step for all samples in analytical batch.

Note: After the extract has been transferred to the K-D, the condenser is attached and the apparatus can be stored in the lab; that is, the K-D does not need to stay under the hood. The condenser will prevent methylene chloride and other solvents from evaporating outside of the hood.

10.6.4 Add a few milliliters of solvent to the top of the Snyder column. Place the K-D into the water bath. The K-D should be placed as vertically as possible. As the solvent begins to boil, the column will start to "chatter". At the proper rate of evaporation, the column will actively "chatter" but the spaces around the balls will not flood with solvent.

10.6.5 Watch the K-Ds closely as the solvent level gets low. When the apparent volume of the solvent reaches 1-2mL, the K-D is removed from the heat and the apparatus is allowed to cool. As the K-D cools, solvent that has collected in the column will gradually flow down to the concentration tube. Add a few milliliters of solvent to the top of the column to rinse.

10.6.6 If the solvent must be exchanged, add 25mL of the exchange solvent and set the water bath to the temperature optimized for that solvent and the target compounds. Return the K-D to the water bath and concentrate the extract as outlined above.

10.6.7 Add a second 25mL aliquot of the exchange solvent to the K-D and concentrate the extract until the apparent volume of the extract is 1-2mL. Remove the K-D from the heat and allow the apparatus to cool. As the K-D cools, solvent that has collected in the column will gradually flow down to the concentration tube. Add a few milliliters of solvent to the top of the column to rinse.

Note: The K-D cannot be used for extracts that must be evaporated to a final volume of 1mL or less. Nitrogen blow-down or a micro K-D must be used to evaporate an extract to 1mL or less.

10.7 Extract Transfer Procedures

10.7.1 Adjust the extract volume to the required final volume by adding small aliquots of the required solvent. If the final volume is to be greater than 1mL, add an appropriate volume of solvent to the tube using a volumetric pipette or calibrated solvent dispensing device. For example, if the final volume is to be 10mL, adjust the volume in the tube to 1mL and then add 9mL of solvent to give a final volume of 10mL.

Note: If the extract cannot be evaporated to 1mL, the extract must be transferred to a volumetric flask or to a calibrated storage vial. Use several small aliquots of solvent to transfer the entire extract to the vial.

10.7.2 Transfer the final extract to a Teflon-lined crimp top or 12-mL scintillation vial. Mark the volume of the extract on the side of the container to allow the analyst to judge whether the sample extract has evaporated during storage and handling. Store concentrated extracts at 4°C until time of analysis.

10.8 Analysis

Refer to the applicable analytical SOP (Section 1.0) for information on sample analysis.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data reduction and review tasks include the following items:

- Employ spike witness procedures to ensure proper spiking solutions and volume are used.
- Ensure all LIMS batch Data Type fields are completed so that proper traceability is maintained.
- Check to ensure that each sample extract is properly identified and that the extracts are transferred to the analytical groups with proper documentation.
- Mark the final volume of the extract on the outside of the storage container as a check on extract evaporation.
- QC items must be treated in the same manner as samples.
- Ensure samples are evaporated at the appropriate rate. Unacceptable surrogate or spike recoveries may be attributed to evaporating the samples too quickly or to improper solvent exchange.
- Document any unusual circumstances and procedural violations using the LIM Nonconformance Module. This can include: samples problematic matrices such as color, odor, or emulsions; initial or final amount changes; deviations to the SOP, etc.

Batch data must be reviewed and evaluated in accordance with SOP SA-QA-02: *Data Generation and Review*.

Additional details on data reduction procedures are given in the associated analytical SOPs.

11.1.1 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify TALS Worksheet Notes and/or use the Historical Data Tracker feature to determine if historical data is available for review.

11.2 Calculations

Details on sample calculations are given in the associated analytical SOPs listed in Section 1.

12.0 Method Performance

12.1 Reporting Limit Verification (RLV)

At a minimum, RLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

For analytes and methods certified by DOD ELAP, RLVs must also be performed quarterly thereafter. For all other analytes and methods, RLVs must also be performed annually thereafter. Exceptions may be made for project-specific non-routine analytes.

12.2 Method Detection Limit (MDL) Study

The MDL is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDLs associated with this procedure are given in the Method Limit Group (MLG) in TALS.

At a minimum, MDL Studies must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

Note: MDL Studies are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.3 Method Detection Limit Verification (MDLV)

At a minimum, MDLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

For analytes and methods certified by DOD ELAP, MDLVs must also be performed quarterly thereafter. For all other analytes and methods, MDLVs must also be performed annually thereafter.

Note: MDLVs are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.4 QC Limit Generation, Control Charting, and Trend Analysis

12.4.1 EPA 600-Series and SM6000-Series Methods

The control limits for the batch QC items (LCS and MS/MSD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.4.2 EPA 3510C and EPA 3520C

The control limits for the batch QC items (LCS, MS/MSD, SD) for this procedure are not specified by the reference method; therefore, the laboratory defaults to in-house and/or laboratory-derived limits for the evaluation of batch QC items.

Control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.5 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Methylene chloride extracts – Dispose according to characterization on sample disposal sheets. If non-hazardous, transfer extract to chlorinated waste container. If hazardous, transfer to hazardous waste department for storage.

- Methylene chloride waste – Transfer to chlorinated waste container.

- Hexane extracts – If non-hazardous, transfer to flammable waste containers and dispose of as flammable waste. If hazardous, transfer to the waste disposal department for disposal as hazardous waste.

- Flammable waste (hexane or acetone from extracts, rinsings, and standards) – Transfer to a satellite container designated for flammable waste and transfer to waste disposal department when the container is full.

- Aqueous acidic waste from samples – Collect into the disposal area and neutralize

before release to the sewer system.

15.0 References / Cross-References

- SOP SA-AN-041: *Reagent and Standard Materials Procedures*
- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs)*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- *Test Methods for Evaluating Solid Waste*, Third Edition (Updates III and IV), SW-846; EPA Office of Solid Waste and Emergency Response: Washington, DC.
    - Chapter 4: *Organic Analytes*; Revision 3, December 1996
    - Chapter 4: *Organic Analytes*; Revision 4, February 2007
    - EPA 3500C: *Organic Extraction and Sample Preparation*; Revision 3, February 2007
    - EPA 3510C: *Separatory Funnel Liquid-Liquid Extraction*; Revision 3, December 1996
    - EPA 3520C: *Continuous Liquid-Liquid Extraction*; Revision 3, December 1996
    - EPA 3600C: *Cleanup*; Revision 3, December 1996
    - EPA 3620B: *Florisil Cleanup*; Revision 2, December 1996
    - EPA 3620C: *Florisil Cleanup*; Revision 3, February 2007
    - EPA 3640A: *Gel-Permeation Cleanup*; Revision 1, September 1994
    - EPA 3660B: *Sulfur Cleanup*; Revision 2, December 1996
    - EPA 3665A: *Sulfuric Acid/Permanganate Cleanup*; Revision 1, December 1996
- Code of Federal Regulations, Title 40 (Protection of Environment), Chapter 1 (Environmental Protection Agency), Subchapter D (Water Programs), Part 136 (Guidelines Establishing Test Procedures for the Analysis of Pollutants), Appendix A (Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater)
    - EPA 608: *Organochlorine Pesticides and PCBs*
    - EPA 614: *The Determination of Organophosphorous Pesticides in Municipal and Industrial Wastewater*
    - EPA 625: *Base/Neutrals and Acids*
- *Standard Methods for the Examination of Water and Wastewater, Online Edition;* American Public Health Association: Washington, DC.
    - SM6020: Quality Assurance/Quality Control
    - SM6410B: *Extractable Base Neutrals and Acids; Liquid-Liquid Extraction Gas Chromatographic/Mass Spectrometric Method*; 2000
    - SM6420B: *Phenols; Liquid-Liquid Extraction Gas Chromatographic/Mass Spectrometric Method*; 2000
    - SM6431B: *Polychlorinated Biphenyls (PCBs); Liquid-Liquid Extraction Gas Chromatographic Method*; 2000
    - SM6630C: *Organochlorine Pesticides; Liquid-Liquid Extraction Gas Chromatographic Method II*; 2000

16.0 Method Modifications and Clarifications

16.1 Incorporation of Other Matrices

This procedure may be modified to analyze other matrices (e.g., TCLP/SPLP leachate samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project.

The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and soil QC limits to evaluate TCLP/SPLP leachate samples. Water DOCs can be used to satisfy analyst demonstrations of capability for TCLP/SPLP matrices.

16.1.1 Collection and Handling Procedures

Once the TCLP/SPLP extraction procedure has been performed, the TCLP/SPLP leachate must be transferred to a 1L amber bottle. The TCLP/SPLP leachate must be preserved in accordance with the associated method and stored at 4°C (less than 6°C abut not frozen) until the time of extraction. The leachate must be extracted within 7 days of completion of the TCLP/SPLP leaching procedure.

Note: The sample leachate chosen as the MS/MSD must be spiked prior to adjusting the pH.

16.1.2 Preparation and Analytical Procedures

TCLP/SPLP matrices are prepared in the same manner as routine water samples as outlined in this SOP. Refer to Attachment 6 for the extraction conditions. The following volumes are utilized for TCLP samples for SVOCs:

TCLP PARAMETER	Volume of Sample Extracted (mL)	Final Volume (mL)
BNA by GC/MS (EPA 8270C & EPA 8270D)	200	1.0
Pesticides by GC (EPA 8081B)	20	10

TCLP/SPLP matrices are analyzed in the same manner as routine samples as outlined in the associated analytical SOPs (Section 1.0).

16.2 Other Considerations

16.2.1 The analyte lists in Section 1.1 of EPA 608, Section 1.1 of EPA 614, Tables 1, 2, and 3 of EPA 625, have been expanded to include all analytes currently performed by the laboratory.

16.2.2 The volume of solvent added to the receiving flask for CLLE has been modified from the guidance in EPA 3520C and EPA 625. EPA 3520C specifies 300-500mL of methylene chloride to be added to the receiving flask, and EPA 625 specifies that 200-500mL be added to the flask. The laboratory adds 70-100mL to the receiving flask. This volume

provides sufficient solvent volume to efficiently extract the sample since the CLLE is a closed system, minimizes solvent exposure to the analyst, and allows the extract to be concentrated faster. Laboratory control standard (LCS) and performance testing (PT) data using the reduced solvent volumes meet or exceed the minimum accuracy and precision criteria specified in the reference method. The Methods Update Rule specifically allows this type of method modification to be made.

16.2.3 The volume of solvent added to the separatory funnel has been modified from the guidance in EPA 3510C. EPA 3510C specifies 60mL of methylene chloride to be added to the separatory funnel. The laboratory adds 50mL to the separatory funnel. This volume provides sufficient solvent volume to efficiently extract the sample, minimizes solvent exposure to the analyst, and allows the extract to be concentrated faster. Laboratory control standard (LCS) and performance testing (PT) data using the reduced solvent volumes meet or exceed the minimum accuracy and precision criteria specified in the reference method.

16.2.4 EPA 614 requires the use of 15% Methylene Chloride/ Hexane as the extraction solvent. The laboratory currently performs EPA 614 via continuous liquid-liquid extraction (CLLE). This preparation technique is not conducive to the 15% $MeCl_2$/Hexane mixture; therefore, the laboratory prepares all QC samples, MDLs, DOCs, PTs, and field samples using CLLE with methylene chloride. The Methods Update Rule specifically allows this type of method modification to be made.

16.2.5 A specific temperature set-point for the K-D water bath has not been established at this time, but rather a temperature range of 60-90°C is used. There should be little impact on the analyte recoveries provided the temperature is hot enough the boil the solvent.

16.2.6 The laboratory's default required batch QC items differ from those outlined in the reference methods. For example, there is no method-defined batch precision requirement listed in EPA Method 608; however, the EPA does require precision for all samples analyzed under the Clean Water Act. In order to satisfy this and other client-specific and/or regulatory program requirements and expectations, matrix spike duplicates and laboratory control sample duplicates have been incorporated.

16.2.7 Dependent on capacity, and with the approval of Technical Management, the laboratory may employ the option to reduce CLLE times from those specified in Attachment 5. The batch QC and an additional RLV performed within the batch will be used to verify sensitivity and recovery. An NCM must be initiated to denote this situation.

16.2.8 Chapter 4 of SW-846 specifies to send sample collection bottles containing dechlorination agent for those samples from a chlorinated water source. Since the laboratory often is not made aware of the source of the water, dechlorination agent is not routinely provided. Samples are checked for residual chlorine prior to extraction, and an NCM must be initiated for any samples that test positive.

16.2.9 Modifications have been made to the extraction solvents and solvent volumes used for the SM6000-series procedures to make them consistent with those used by the laboratory for EPA 3520C. The Methods Update Rule specifically allows this type of method modification to be made.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Extraction Conditions – CLLE
Attachment 6: Extraction Conditions – Separatory Funnel
Attachment 7: Glassware Cleaning Procedures
Attachment 8: Sulfur Cleanup
Attachment 9: Sulfuric Acid Cleanup
Attachment 10: Florisil Cleanup
Attachment 11: Gel-Permeation Cleanup
Attachment 12: Standard Preparation
Attachment 13: Zymark Sensor Diagnostic Test and Maintenance Log
Attachment 14: Zymark-specific Maintenance Instructions

Attachment 1:
SOP Summary

Sample Preparation Summary

Continuous Liquid-Liquid Extraction Procedure
In continuous liquid-liquid extraction a known volume of sample is adjusted to a specific pH, if required by the analytical method, transferred to a continuous liquid-liquid extractor, and extracted using the solvent and conditions specified in Attachment 5. The extract is concentrated to an appropriate final volume using either the Zymark TurboVap concentration procedure or the Kuderna Danish (KD) concentration procedure.

Separatory Funnel Extraction Procedure
In separatory funnel extraction a known volume of sample is placed into a separatory funnel, adjusted to a specified pH if required, and extracted using the solvent and conditions specified in Attachment 6. The extract is concentrated to an appropriate final volume using either the Zymark TurboVap concentration procedure or the Kuderna Danish (KD) concentration procedure.

Zymark Concentration Procedure
After the extraction procedure is completed, the solvent is transferred to a glass Zymark concentration tube. The tube is placed in the Zymark concentration device, which has been heated to a specified temperature. A stream of nitrogen is directed into the tube to evaporate the solvent and to concentrate the target compounds. When the volume of solvent reaches the specified volume, normally 1mL, the nitrogen is automatically stopped. An alarm sounds to alert the analyst, and the extract is removed from the device and transferred to a storage vial or container.

If a solvent exchange is required, the exchange solvent is added to the tube, the solvent is evaporated to the specified final volume, and the extract is transferred to a storage vial or container. The concentrated extracts are stored at 4°C until the time of analysis.

Kuderna-Danish Procedure
After the extraction procedure is completed, the extract is transferred to a glass Kuderna-Danish (K-D) concentration apparatus. The K-D is placed in a water bath that has been heated to 60-90°C. As the solvent evaporates, the target compounds are collected in the concentration tube. When the apparent volume of solvent reaches 1mL, the K-D is removed from the water bath and allowed to cool. The extract is removed from the device and transferred to a storage vial or container.

Note: A specific temperature set-point for the water bath has not been established at this time, but rather a temperature range of 60-90°C is used. There should be little impact on the analyte recoveries provided the temperature is hot enough the boil the solvent.

If a solvent exchange is required, the exchange solvent is added to the K-D, the solvent is evaporated to the specified final volume, and the extract is transferred to a storage vial or container. The vials are stored at 4°C until the time of analysis.

Sample Analysis Summary
Analyze samples in accordance with the following SOPs:

Fraction	Analytical Method	SOP #
Organochlorine Pesticides & PCBs	EPA 608 EPA 8081A EPA 8081B EPA 8082 EPA 8082A SM6431B SM6630C	SOP SA-SG-045
Organophosphorous Pesticides	EPA 614 EPA8141A EPA 8141B	SOP SA-SG-050
Diesel Range & Oil Range Organics (DRO and ORO)	EPA 8015B EPA 8015C (DRO and ORO)	SOP SA-SG-070
Polychlorinated Biphenyls	EPA 680	SOP SA-SM-007
Base Neutrals / Acids & PAHs	EPA 625 EPA 8270C EPA 8270D EPA 8270C_LL EPA 8270D_LL EPA 8270C_LL_PAH EPA 8270D_LL_PAH SM6410B (BNAs) SM6420C (Phenols)	SOP SA-SM-033
Toxaphene Congeners (i.e., Parlars) and Technical Toxaphene	EPA 8276	SOP SA-SM-034

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Matrix	Routine Sample Container	Routine Sample Size	Minimum Sample Size	Chemical Preservation	Thermal Preservation	Dechlorination Agent	Holding Time [1]
Water (CLLE)	1L amber glass	1L	500mL	None	4°C[2]	None	7 days
Water (Separatory Funnel)	1L amber glass	1L	500mL	None	4°C[2]	None	7 days

[1] Time from collection to initiation of extraction.
[2] Samples must be maintained at 0-6 °C, with no frozen samples.

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Batch Definition	Up to 20 field samples prepared together within a 24-hour time period	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Laboratory Control Sample (LCS)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Laboratory Control Sample Duplicate (LCSD)	One per batch, if insufficient sample is provided for the MS/MSD	Refer to analytical SOP	Refer to analytical SOP
Matrix Spike (MS)	EPA 600-Series: One per 10% of samples EPA 3510C and EPA 3520C: One per batch	Refer to analytical SOP	Refer to analytical SOP
Matrix Spike Duplicate (MSD)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per method/analyte combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06 (Note: Unsupervised work must not begin until successful IDOC has been obtained.)
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per method/analyte combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06

QC Item	Frequency	Criteria	Corrective Action
Reporting Limit Verification (RLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Method Detection Limit Study (MDL)	Upon method/instrument set-up, per analyte/method/matrix combination	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
MDL Verification (MDLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling

Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log

A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance

Zymark Maintenance

It is recommended to change the water in the water bath weekly. Add 1-2 drops of Clear Bath to prevent bacteria and algae growth. Methylene chloride that dissolves in the water bath will damage the sensors.

The Zymark sensor diagnostic test must be performed weekly. If the sensors do not meet criteria the sensor may need replacing. Refer to the manufacturer's manual for replacement procedures if necessary.

The thermometer for the Zymark must be calibrated in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*.

K-D Apparatus Maintenance

The K-D apparatuses must be inspected periodically for leaks and cracks. Leaks will allow the infiltration of water into the extract and compromise the entire extraction procedure. Glassware with leaks, cracks, and broken joints must be repaired or replaced.

Inspect the Snyder columns frequently. The balls in the condenser will sometimes stick, causing pressure from the evaporating solvent to build up and spew the extract out of the top of the column. Wetting the column with a small volume of solvent will help to keep the balls from sticking.

The thermometer for the water bath must be calibrated in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*.

Troubleshooting

Troubleshooting should be documented as outlined above. If possible, troubleshooting is best performed in a step-wise manner to systematically isolate instrument components. Refer to the instrument manufacturer's guides for specific information and strategies. Enlist assistance from technical and/or department management as needed.

Contingency Plan

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
Extraction Conditions - CLLE

Methods	Extraction Conditions	Extraction Time (Hours)	Extraction Solvent	Final Solvent	Final Volume (mL)
SEMIVOLATILE GC EXTRACTIONS					
608, 8081, 8082	Single pH at neutral pH (5-9)	18-24	$MeCl_2$	Hexane	10
614, 8141	Single pH at neutral pH (5-9)	18-24	$MeCl_2$	Hexane	10
8015-EXT (DRO, ORO)	Single pH as received or at pH<2	18-24	$MeCl_2$	$MeCl_2$	1.0
SM6431B	Single pH at neutral pH (5-9)	18	$MeCl_2$	Hexane	10
SM6630C	Single pH at neutral pH (5-9)	18	$MeCl_2$	Hexane	10
SEMIVOLATILE GC/MS EXTRACTIONS					
8270-TCL, 8270-LLPAH, 8270-K001	Single pH <2	18-24	$MeCl_2$	$MeCl_2$	1.0
8270-AP9, 8270-TCLP	Dual pH: pH<2 followed by pH>12	18-24 / 18-24	$MeCl_2$	$MeCl_2$	1.0
EPA 625	Dual pH: pH<2 followed by pH>12	24 / 24	$MeCl_2$	$MeCl_2$	1.0
EPA 625-CPSF APP, BNPP	Dual pH: pH>12 followed by pH<2. Extracts are kept separate.	24 / 24	$MeCl_2$	$MeCl_2$	1.0 Acid 1.0 Base
EPA 680	Single pH at neutral pH (5-9)	18-24	$MeCl_2$	Hexane	1.0
SM6410B	Dual pH: pH>11 followed by pH<2. Extracts are kept separate.	24 / 24	MeCl2	MeCl2	1.0
SM6420C	Dual pH: pH>11 followed by pH<2. Extracts are kept separate.	24 / 24	MeCl2	MeCl2	1.0
8276[1]	Single pH at neutral pH (5-9)	18-24	MeCl2	Hexane	5.0

[1]The EPA 8276 preparation procedures mirror those used for EPA 8081A, with the exception that 200mL of extraction solvent is used.

Attachment 6:
Extraction Conditions – Separatory Funnel

Methods	Extraction Conditions	Extraction Solvent	Final Solvent	Final Volume (mL)
TCLP (EPA 8081A & EPA 8081B)	Single pH at neutral pH (5-9)	$MeCl_2$	Hexane	10
TCLP (EPA 8270C & EPA 8270D)	Dual pH: pH<2 followed by pH>12	$MeCl_2$	$MeCl_2$	1.0

Attachment 7:

CLLE BODY BREAKDOWN AND GLASSWARE CLEANING PROCEDURES

PPE: **Lab coat**
Eye protection
Kevlar gloves

This procedure assumes that the round-bottom flasks containing the extracts have been removed and that the CLLE bodies are at room temperature.

1. Turn on the fan and start working at the CLLE position furthest from the fan, from the window to the center of the room.

2. Remove the condenser and place on the rack. Be careful not to tip the CLLE body forward and cause methylene chloride to leak on to the table top. Gently remove the CCLE body from the rack and carry the CLLE bodies one at a time to the hood.

3. Empty the methylene chloride layer into the satellite waste container designated for chlorinated waste.

4. Turn on the water and pour the water layer from the CLLE into the sink. Rinse the CLLE body with water and discard down the sink. Repeatedly rinse the CLLE body with water until all of the solids are rinsed down the sink.

> Note: Be careful not to pour methylene chloride down the sink-it will dissolve the drain pipes.

5. Fill one side of the sink with hot water and add about ¼ cup of FL-70 detergent per gallon of water.

6. Note the condition of the CLLE body. If heavily contaminated, do not place into the soak water. Keep this glassware separate and contact the supervisor or department manager to determine the best course of action to clean the glassware.

> It is important to segregate heavily contaminated glassware from use until verified clean by the analysis of a method blank. Discard glassware if the condition of the glassware cannot be verified or if the glassware is obviously not salvageable.

7. Place CLLE bodies into soak water and allow to soak for a minimum of 10-15 minutes.

8. Scrub the inside of the CLLE bodies with a soft brush.

9. Rinse a minimum of three times with hot tap water. It is important to remove all of the soap film at this point.

10. With cold water running, rinse the entire CLLE body with acetone, paying particular attention to the smaller glass tubing. It is important to remove as much water as possible from the CLLE body at this point. Discard the acetone down the sink.

10. Place the CLLE body on the rack inverted to help drain the water and acetone and to dry the CLLE body.

ZYMARK TUBE AND CLLE ROUNDBOTTOM FLASK CLEANING PROCEDURES

PPE: **Lab coat**
Eye protection
Kevlar gloves or equivalent

1. Note the condition of the Zymark tube or receiving flask. If heavily contaminated, do not place into the sink. Keep this glassware separate and contact the supervisor or Department Manager to determine the best course of action to clean the glassware.

It is important to segregate heavily contaminated glassware from use until verified clean by the analysis of a method blank. Discard if the condition of the glassware cannot be verified or if the glassware is obviously not salvageable.

2. Rinse each tube or flask thoroughly with water and discard down the sink drain.

3. Fill dishpan with hot water and add about ¼ cup of FL-70 detergent per gallon of water.

4. For Zymark tubes, use a small brush to clean the tip of the tube and a larger brush to clean the walls of the tube.

For receiving flasks, use a brush that will allow you to scrub the inside walls of the flask.

5. Rinse each tube and flask thoroughly a minimum of three times with hot tap water until no traces of soap are present in the tube. It is important to remove all traces of soap at this point.

6. Rinse each tube and flask thoroughly with acetone and place on covered counter or rack to dry.

Discard acetone rinses down the sink drain with the cold tap water running.

7. Rinse each tube with a small aliquot of methylene chloride and place on covered counter or rack until ready for use.

Discard methylene chloride in the satellite waste container designated for chlorinated waste.

Attachment 8:
Sulfur (Copper) Cleanup

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THE LEADER IN ENVIRONMENTAL TESTING

Work Instruction
FEX096:01.28.09:0
Page 1 of 1

Sulfur Cleanup Procedures

Method: 3660B

Summary of Procedure
This procedure is based on EPA Method 3660B and is used in conjunction with the following SOPs:

Method	SOP #
EPA 3510C / EPA 3520C	SA-EX-030
EPA 3550C	SA-EX-040
EPA 508	SA-SG-046
EPA 608 / EPA 8081B / EPA 8082A	SA-SG-045

The sulfur cleanup uses copper granules to eliminate elemental sulfur from PCB or pesticide extracts. Copper is added to the extract, and the vial is shaken. If sulfur is present, a black precipitate (copper sulfide) will form. The extract is treated with copper until no further precipitate is formed.

The method blank and LCS must be subjected to the same cleanup steps as the samples.

Perform all cleanup steps under a fume hood or in a well-ventilated area.

Reagents
Copper granules – the surface of the copper should be "shiny".

Cleanup Instructions
1. Ensure the sample extract has been exchanged into the applicable final solvent (e.g., MTBE for EPA 508, Hexane for EPA 608/8081B/8082A) prior to performing the sulfur cleanup procedure.

2. Add approximately 0.1g of "shiny" copper to the vial, and vortex for approximately two minutes.

   Note: If the extract is for EPA 614 or EPA 8141B in addition to one of the analytical methods listed above, transfer an aliquot of the extract to another vial for the copper cleanup.

3. If sulfur is present, a black precipitate will form. Allow the extract to sit for 2-3 minutes for any additional precipitate to form and settle out.

   If the precipitate does not settle out, additional copper treatments and/or filtration may be required. Contact the Technical Manager for instructions on how to proceed.

4. The sample is now ready for analysis as outlined in Section 10 of the associated analytical SOP.

Attachment 9:
Sulfuric Acid Cleanup

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Work Instruction
FEX097:01.28.09:0
Page 1 of 2

Sulfuric Acid Cleanup Procedures

Method: 3665A

Summary of Procedure
This procedure is based on EPA Method 3665A and is used in conjunction with the following SOPs:

Method	SOP #
EPA 3510C / EPA 3520C	SA-EX-030
EPA 3550C	SA-EX-040
EPA 680	SA-SM-007
EPA 608 (PCBs only) / EPA 8082A	SA-SG-045

The acid cleanup procedure is used for PCBs only. Sulfuric acid is added to the extract, and the vial is shaken. The layers are allowed to separate, and the sample layer is removed. Large organic-soluble compounds that are present in the sample will extract into the acid and are discarded.

Note: This procedure will destroy pesticide compounds. Sulfuric acid cleanups must only be used for PCB samples and cannot be used for samples requesting pesticides by EPA 8081B, EPA 8141B, or EPA 608.

The method blank and LCS must be subjected to the same cleanup steps.

Perform all cleanup steps under a fume hood or in a well-ventilated area.

Reagents
Sulfuric acid (H_2SO_4) – reagent grade, concentrated

Cleanup Instructions
1. Ensure the sample extract has been exchanged into hexane prior to performing the sulfuric acid cleanup.
2. Transfer an aliquot of the extract to a vial for the cleanup. The recommended aliquot volume is 5.0mL.
3. Add approximately 2mL of concentrated sulfuric acid and cap the vial. Mark the vial to denote the total volume on the vial. Also mark the vial to denote the separation of the acid (bottom) layer and the extract (top) layer.
4. Ensure the vial cap is secure, and gently shake the vial. Open the vial, and allow any pressure that has built up to dissipate. Repeat these steps until no pressure is noted when the cap is opened, and then shake the vial for one additional minute. A vortex mixer can also be used.
5. Allow the extract (top) layer and the acid (bottom) layer to separate. This separation may take a few minutes or several hours depending on the nature of the sample extract. Use the marks on the side of the vial to judge if the volume of extract (top) layer is the same as when it was originally added to the vial.

6. Remove the extract (top) layer from the vial using a disposable Pasteur pipette, and transfer the extract to a clean vial. If greater than 80% of the extract is recovered, no additional preparation is necessary.

7. If an emulsion has formed (i.e., there are bubbles or a cloudy area in between the top and bottom layers), add sodium sulfate crystals to the vial and gently stir the top layer with a glass rod. The sodium sulfate should help to break the emulsion so the top layer can be adequately recovered.

8. If the extract has color, perform an additional cleanup by adding 5mL more of concentrated acid and repeating Steps 3-6.

   Note: Use good judgment when determining how many acid cleanups to use. If it takes more than three cleanups to clean the extract, it is recommended to start over with a smaller aliquot of sample or to dilute the extract before proceeding with additional cleanups. A diluted extract can be concentrated back to the equivalent volume after the cleanup steps. Contact the Technical Manager for assistance with this task.

9. The sample is now ready for analysis as outlined in Section 10 of the associated analytical SOP.

Attachment 10:
Florisil Cleanup

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Work Instruction
FEX098:01.28.09.0
Page 1 of 3

Florisil Cleanup Procedures

Method: 3620C

Summary of Procedure
This procedure is based on EPA Method 3620C and is used in conjunction with the following SOPs:

Method	SOP #
EPA 3510C / EPA 3520C	SA-EX-030
EPA 3550C	SA-EX-040
EPA 608 / EPA 8081B / EPA 8082A	SA-SG-045

The Florisil cleanup uses a solid phase extraction (SPE) cartridge to remove polar interferences in PCB and/or pesticide extracts. After the sample extraction procedure is completed, a measured portion of the pesticide/PCB extract (usually 1mL) is transferred to a 1g Florisil cartridge. The target and non-target compounds are separated by elution with successive solvents at ambient (atmospheric) pressure. The solvent that elutes the target compounds is collected and concentrated to an appropriate final volume, routinely the same volume as the extract applied to the cartridge.

The method blank and LCS must be subjected to the same cleanup steps as the samples.

Perform all transfer and cleanup steps under a fume hood or in a well-ventilated area.

Reagents
Hexane – residue grade or better
Acetone – pesticide quality or equivalent
Methylene chloride – pesticide quality or equivalent
Sodium sulfate – granular, purified at 450-500°C

90:10 Hexane/Acetone Solution – Mix 90mL of hexane with 10mL acetone in a clean glass container. Larger volumes can be prepared at the discretion of the analyst.

60:40 Hexane/Acetone Solution – Mix 60mL of hexane with 40mL acetone in a clean glass container. Larger volumes can be prepared at the discretion of the analyst.

Standards
Florisil Pesticide Check Mix – Prepare a standard in hexane containing the compounds listed in the following table. This standard is equivalent to the ISMA mid-level standard cited in CLP 3/90, Rev 3.1. Alternatively, an EPA 8081 midlevel calibration standard can be used.

Compound	Concentration (µg/mL)
Alpha-BHC	0.020
Heptachlor	0.020
Gamma-BHC	0.020
Endosulfan I	0.020
Dieldrin	0.040
Endrin	0.040

Compound	Concentration (µg/mL)
4,4'-DDD	0.040
4,4'-DDT	0.040
Methoxychlor	0.20
TCMX	0.020
DCB	0.020

Cleanup Instructions

1. Ensure sample extract has been exchanged into hexane prior to performing the cleanup.

2. Prepare the manifold and label each Florisil cartridge with the corresponding sample ID.

3. Condition the cartridges as follows:

   - Place the SPE cartridges on the manifold.
   - Rinse each cartridge with 5mL 60:40 hexane/acetone with the valves open. Follow with 5mL methylene chloride. Discard these rinses.
   - Add 5mL 60:40 hexane/acetone to each cartridge.
   - Slowly open the valves to allow hexane/acetone to pass through the sorbent beds to the lower frits, allowing a few drops per cartridge to pass through the manifold to remove all air bubbles.
   - Close the valves when there is at least 1mm of solvent above the solvent bed. Do not allow the cartridges to become dry. If a cartridge becomes dry, repeat the conditioning.

   Caution: Do not allow the SPE cartridge to go dry from this point forward. If the cartridge goes dry, start over with a new SPE cartridge and a new aliquot of extract.

4. Place the receiving flask beneath the corresponding cartridge.

5. Transfer 1.0mL of the sample extract onto the corresponding labeled Florisil column. Open the valve and allow the extract to pass through the cartridge through the sorbent bed at approximately 2mL/minute. When the level of the extract is a few millimeters above the top of the sorbent layer, wash down the sides of the cartridge with 1.0mL of acetone and allow this wash to pass into the sorbent. Close the valve when the solvent layer reaches the top of the column. The solvent that has passed through the cartridges to this point can be discarded.

6. Add 9.0mL of 90:10 hexane/acetone solution to each cartridge. Open the valve and allow the solvent to pass through the cartridge. Collect the eluent. As the solvent level gets to the top of the cartridge's sorbent bed, add two additional 1mL aliquots of hexane to the cartridge and collect these two eluates. The final volume should be 11mL.

7. Adjust the extract volume to the original volume (routinely 1.0mL) using the nitrogen evaporator or hot water bath as outlined in Section 10 of the associated preparation SOP.

8. The sample is now ready for analysis as outlined in Section 10 of the associated analytical SOP.

Quality Control
Each lot of Florisil cartridges must be checked and approved prior to use as follows:

Combine 0.50mL of the 2,4,6-Trichlorophenol solution, 0.50mL of hexane, and 1.0mL of the Florisil Pesticide Check Mix in a clean, glass container. Concentrate to a final volume of 0.50mL and analyze according to SOP SA-SG-045.

Combine 0.50mL of the 2,4,6-Trichlorophenol solution, 0.50mL of hexane, and 1.0mL of the Florisil Pesticide Check Mix in a clean, glass container. Concentrate to a final volume of 0.50mL and perform the cartridge cleanup on this solution as described in Steps 1 through 8. Analyze according to SOP SA-SG-045.

The Florisil cartridge lot is acceptable if all pesticides in the check mix are recovered at 80-110% percent, if the percent recovery of 2,4,6-trichlorophenol is less than 5%, and if no peaks interfering with the target compounds are detected.

Attachment 11:
Gel-Permeation Cleanup

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Gel-Permeation Cleanup Procedures

Method: 3640A

Summary of Procedure
This procedure is based on EPA Method 3640A and is used in conjunction with the following SOPs:

Method	SOP #
EPA 3510C / EPA 3520C	SA-EX-030
EPA 3550C	SA-EX-040
EPA 625 / EPA 8270D	SA-SM-033
EPA 8270D (LL)	SA-SM-008
EPA 608 / EPA 8081B / EPA 8082A	SA-SG-045

Gel-Permeation Cleanup (GPC) is a size-exclusion cleanup based on the molecular size of the analytes rather than molecular weight. Molecules are too large to ever enter the GPC bead pores or so small they freely pass through bead pores are considered beyond resolution and are not collected. The remaining molecules (those with sizes between the two limits) are collected based on the elution times of the calibration compounds. GPC is best for samples with large biological molecules such as plant or animal tissues. GPC will not separate the target analytes from petroleum hydrocarbons.

The method blank, LCS, and MS/MSD must be subjected to the same cleanup steps as the samples as a check on recovery of the target compounds.

Perform all transfer and cleanup steps under a fume hood or in a well-ventilated area.

Note: For each 10mL of extract that is loaded onto the GPC instrument, 5mL is lost and routed to the waste reservoir. The remaining 5mL of extract is passed through the GPC instrument and collected in the Zymark tube in a final volume of approximately 150mL of methylene chloride. This is concentrated to a final volume equal to one-half the final volume normally required for that analysis.

> For example: for pesticide analyses by EPA 8081, 10mL of extract is loaded onto the GPC instrument and 5mL of extract is routed to the waste reservoir. The remaining 5mL of extract is passed through the GPC instrument and collected in a final volume of 150mL methylene chloride. This 150-mL extract is evaporated to a final volume of approximately one milliliter, exchanged into hexane, and adjusted to a final volume of 5mL. The 5mL final volume compensates for the 5mL of sample lost in the GPC instrument and is equivalent to the standard initial sample and final extract volumes for this procedure (i.e., 1000mL initial sample volume to 10mL final extract volume).

Reagents
Hexane – residue grade or better

Acetone – pesticide quality or equivalent

Methylene chloride – pesticide quality or equivalent

Sodium sulfate – granular, purified at 450-500°C

90:10 Hexane/Acetone Solution – Mix 90mL of hexane with 10mL acetone in a clean glass container. Larger volumes can be prepared at the discretion of the analyst.

60:40 Hexane/Acetone Solution - Mix 60mL of hexane with 40mL acetone in a clean glass container. Larger volumes can be prepared at the discretion of the analyst.

Standards
2,4,6-trichlorophenol standard – prepare at a concentration of 0.10µg/mL in acetone.

GPC Calibration Mix – prepare a standard in methylene chloride containing the compounds listed in the following table.

Compound	Concentration (mg/mL)
Sulfur	0.080
Perylene	0.020
Methoxychlor	0.20
Corn Oil	25
Bis (2-ethylhexl) phthalate	1.0

GPC PCB Check Mix – prepare a standard in methylene chloride containing PCB-1016/PCB-1260 at 1ug/mL.

GPC Pesticide Spike Mix – prepare a standard in methylene chloride containing the compounds listed in the following table.

Compound	Concentration (µg/mL)
Gamma-BHC (Lindane)	10
Aldrin	10
Heptachlor	10
Endrin	20
4,4'-DDT	20
Dieldrin	20

Cleanup Instructions
1. Ensure sample extract has been exchanged into methylene chloride prior to performing the cleanup.

2. Be certain the GPC has been calibrated appropriately within the last seven days.

3. Filter each 10mL sample to be cleaned using a glass syringe fitted with a 0.45um filter. Transfer each filtered sample into a threaded glass tube. Cover each tube with a screw cap which has been fitted with a septum.

4. Load all filtered samples into the sample tray.

5. Place the corresponding number of appropriately sized Zymark tubes into the collect tray.

6. Using the appropriate calibration and method, set up the proper sequence to run the

loaded samples with the software program. Check more than once to be certain the sequence, method, and calibration all match each of the loaded samples.

7. Fill the solvent reservoir with methylene chloride to a level such that it will NOT go dry during the cleanup process.

8. Check tube(s) leading to the waste reservoir to be certain all waste is correctly collected. Also be certain enough space remains in the waste reservoir to collect the anticipated volume of waste from the cleanup process.

9. Start the run sequence using the software program.

10. As the autosampler begins operating, visually check that the solvent pump is operating normally and that there are no leaks in any of the tubing.

11. If the sequence is to run after business hours/overnight, visually check the system before leaving for the day – especially the level of solvent in the solvent reservoir.

12. Concentrate the extract as detailed in Section 10 of the associated preparation SOP.

13. Sample is now ready for analysis as outlined in Section 10 of the associated analytical SOP.

Quality Control

GPC Calibration
The GPC column must be calibrated prior to use, and every seven days thereafter, in order to set the proper collection time for the method. To calibrate the GPC instrument, load 10mL of the GPC Calibration Mix into a designated position on the collect tray. The flow rate should be 5mL/minute (+/- 0.5mL/min), the column pressure between 6 and 10 psi, and the spiking solution fraction is run for 60 minutes. Verify the flow rate using a 10- to 25-mL Class A volumetric flask.

The following criteria must be met for the calibration to pass:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and Methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.
- Columns should be tested with the semivolatiles matrix spiking solution and the GPC time should continue until either after perylene has eluted or until at least 85% of the analytes have recovered, whichever time is longer.
- The retention time shift for the analytes must be <5% when compared to the retention time of the last calibration.

Calibration of Semivolatiles – Initiate column eluate collection just before the elution of bis(2-ethylhexyl)phthalate and after the elution of corn oil. Stop collection just after the elution of perylene but before sulfur elutes.

Calibration of Organochlorine Pesticides/PCBs – Determine the elution times for phthalate, methoxychlor, perylene, and sulfur. A time should be chosen that removes >85% of the phthalate, but collects >95% of the methoxychlor. Stop collection just after the elution of perylene but before sulfur elutes.

Reinject the GPC calibration solution after the appropriate collection and dump times have been set. The retention times for bis(2-ethylhexyl)phthalate and perylene must not vary by more than +/- 5% between calibrations.

GPC Quality Control Samples

Analyze a GPC blank using 5mL of methylene chloride. Concentrate the methylene chloride that passes through the system and analyze using the using the same detectors that will be used to analyze the samples. If the blank exceeds half the reporting limit for the analytes of interest, pump additional methylene chloride through the system for 1-2 hours and analyze a new blank.

When PCB samples are to be cleaned using the GPC, load 10mL of the PCB Check Mix as a sample (after calibration has passed) in order to check that the GC can visually see the AR1660 analytes.

When CLP criteria are required for pesticide samples needing GPC cleanup, load 10mL of the GPC Pest Spike as a sample (after calibration has passed). The recovery from this sample (as reported by GC according to SOP SA-SG-045) must be between 80 and 110%.

Attachment 13:
Zymark Sensor Diagnostic Test and Maintenance Log

ZYMARK SENSOR DIAGNOSTIC TEST AND MAINTENANCE LOG

Turbo Vap #: _____
Date:_____
Initials:_____
Thermometer #:_____

Maintenance Schedule
Weekly: Perform sensor diagnostic test
Empty, clean, and refill water bath, recommended
*See page 1 of logbook for directions

SENSOR #	1	2	3	4	5	6
INITIAL VALUE						
FINAL VALUE						
% VALUE						
Turbo-Vap Temperature Display Reading (°C)						
Thermometer Temperature Reading (°C)						

If any of the values do not meet the criteria, perform the Bubble Dislodging Procedure and repeat the diagnostic. If the test still fails, the sensor may need replacing. Record any additional maintenance, including sensor replacement, in the space provided below.
Bubble Dislodging Procedure: insert a clean Zymark tube and using a pumping motion, raise and lower the tube approximately an inch several times.

Criteria:		
Final Value (with empty tube) / Initial Value (without tube)	=<67%	90 < Initial Value < 410

Maintenance Performed:
Date & Initials:

FEX035.05.08.06.3

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Attachment 14:
Zymark-specific Maintenance Instructions

Zymark Sensor Diagnostic Test

- Lift the concentrator's cover, remove any tubes, and turn the power on.
- Press the SELECT DISPLAYED CONDITION button within 4 seconds.
  The CONDITION and VALUE displays show the current software version, for example:
  [V] [1.0]
  After 3 seconds the displays reflect the pushwheel settings.
  - ⇒ Press the CELL ONE button and keep it depressed for the next step.
    The CONDITION and VALUE displays show the maximum bath temperature rating for cell one's sensor. This tests the Sample Temperature Rating.
    [50] [°C]
  - ⇒ Release the CELL ONE button, the CONDITION and VALUE displays show

COND.	VALUE
[1.2] ↑	[10] ↑
Cell #	Sensor Output Value

    The first digit displayed is the sensor location. The remaining digits are the sensor output value. In the above example, the sensor location is 1 and the sensor output value is 210.
  - ⇒ Record initial sensor output value.
  - ⇒ Place a clean, empty Zymark tube into the cell.
  - ⇒ Record the final sensor output value.
- Repeat the above process (marked with an arrow) for cells 2-6.
- When all sensors are tested, press ENDPOINT SELECT to exit the diagnostic.
- Repeat the entire process for all Turbo-Vaps

Cleaning and Refilling the Water Bath

- Turn the unit off and unplug the power cord.
- Remove all glassware.
- Remove the top plate.
- Carefully lift the rack out of the bath.
- Siphon off the water in the bath.
  - ⇒ Close siphon bulb vent.
  - ⇒ Place siphon's suction tube in the water bath.
  - ⇒ Place drain tubing in sink.
  - ⇒ Squeeze siphon bulb to start.
- Wipe and rinse the bath walls.
- Clean the rack by rinsing with water.
- Replace the rack in the water bath.
- Replace the top plate.
- Place a concentrator tube in *five* positions.
- Pour approximately 1L of distilled water through the empty position.
- Add 15 drops of *Clear Bath*.
- Add more distilled water until the level is AS HIGH AS the initial solvent level in the sample tube without causing an overflow when all six tubes are in position.
- Plug in the power cord and turn the power on.
- Allow 20-30 minutes for the bath to reach temperature, the air to come out of solution, and for most bubbles to dissipate.
- Perform the Bubble Dislodging Procedure.

18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial and grammatical changes and/or clarifications made. Boilerplate text added.
- Incorporated procedures and QC requirements from SM6000-series methods.
- Incorporated procedures and QC requirements from EPA 8276 method.
- Added requirement to spike sample bottle with surrogate and spike mixes prior to any sample manipulation steps (i.e., pouring sample into CLLE or separatory funnel apparatus). Section 10.1 and Section 10.4.3 (Corporate Internal Audit Finding, May 2010)
- Added requirement to rinse original sample container with extraction solvent to ensure quantitative transfer. (Previously SOP was worded as if this was required only if sample contained residual chlorine.) Section 10.2.6 and Section 10.3.3. (Corporate Internal Audit Finding, May 2010)
- Added reference to TALS Historical Data Tracker feature. Section 11.1.1
- Clarified requirements and frequency for RLVs, MDL Studies, and MDLVs to be consistent with SOP SA-QA-07 and to include the quarterly frequency as defined by DOD. Section 12.1 - 12.3 and Attachment 3
- Added note that unsupervised work must not begin until acceptable IDOC is obtained. Attachment 3
- Added requirement that if an LCS and LCSD are performed, both QC items must be evaluated and reported. Section 9.1.1 and Section 9.1.2
- Added note that if, due to space limitations in the refrigerator, the samples must be stored on the counter or on carts, they must be shielded from light with a black-out blanket. Section 10.2.16 and Section 10.3.11

SOIL EXTRACTION PROCEDURES (MICROWAVE AND SONICATION)

(Methods: EPA 3546, 3550B, and 3550C)

Approvals (Signature/Date):

Andrea Teal — March 12, 2010	Benjamin Gulizia — March 10, 2010
Andrea Teal — Date	Benjamin Gulizia — Date
Quality Assurance Manager	Laboratory Director/Lead Technical Director
Ernest B. Walton — March 22, 2010	Charlton A. Riegner — March 11, 2010
Ernest Walton — Date	Charlton Riegner — Date
Technical Director / EH&S Coordinator	Operations Manager

Facility Distribution No. 1 Distributed To: QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the extracting semivolatile organic compounds (SVOCs) in soil and tissue samples. Ultrasonic (sonication) extraction or microwave extraction is used followed by extract concentration via Zymark TurboVap technique.

The following classes of SVOCs can be extracted using the procedures outlined in this SOP:

Analyte Class	Analytical Method	Analytical SOP
PCB Homologues	EPA 680	SA-SM-007
Diesel Range Organics	EPA 8015B EPA 8015C	SA-SG-070
Oil Range Organics	EPA 8015B EPA 8015C	SA-SG-070
Product Identification	EPA 8015B EPA 8015C	SA-SG-070
Chlorinated Pesticides	EPA 8081A EPA 8081B	SA-SG-045
PCBs as Aroclors	EPA 8082 EPA 8082A	SA-SG-045
Organophosphorous Pesticides	EPA 8141A EPA 8141B	SA-SG-050
BNAs	EPA 8270C EPA 8270D	SA-SM-033

This SOP includes the Work Instructions outlining the extract clean-up procedures employed by the laboratory. These clean-up procedures include Gel-Permeation Chromatography (GPC), Florisil, copper (sulfur), and sulfuric acid as outlined in Attachment 8 through Attachment 11.

This SOP includes the procedures for determining the percent lipid content of tissue samples, as outlined in Attachment 5.

Note: Soil results are routinely reported on a dry weight basis. The procedure for determining the moisture content of soil samples is given in SOP SA-GE-190: *Solid/Residue Determinations.*

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

2.1 Sonication Extraction Procedure

A known weight of a sample is combined with anhydrous, purified sodium sulfate to form a free flowing, sandy mixture. A solvent is added to the dried sample, and the sample is extracted using an ultrasonic disrupter (i.e., sonicator) for three minutes. The solvent is decanted, and the extraction is repeated two more times. The extract is filtered, solvent exchanged if required by the analytical procedure, and concentrated to an appropriate final volume. Attachment 6 defines the extraction conditions for the applicable analytical procedures.

2.2 Microwave Extraction Procedure

A known weight of a sample is transferred to a Teflon extraction vessel. The sample is spiked with surrogate compounds and an analyte-specific solvent is added to the vessel. The vessel is placed on the instrument and the sample extracted at an elevated temperature and pressure. The vessel is cooled to room temperature, the extract is passed through sodium sulfate to remove the water from the sample, and the extract is collected in a concentration tube. The solvent is evaporated and the extract is concentrated to a nominal final volume of 1.0mL. If required by the analytical procedure, the extract may be exchanged to another solvent and concentrated to an appropriate final volume. Attachment 6 defines the extraction conditions for the applicable analytical procedures.

2.2 Zymark TurboVap Concentration Procedure

After the sonication procedure is completed, the solvent is transferred to a glass Zymark concentration tube. The tube is placed in the Zymark TurboVap concentration device, which has been heated to a specified temperature. A stream of nitrogen is directed into the tube to evaporate the solvent and to concentrate the target compounds. When the volume of solvent reaches the specified volume, normally 1mL, the nitrogen stream is automatically stopped. An alarm sounds to alert the analyst, and the extract is removed from the device and transferred to a storage vial.

If a solvent exchange is required, the exchange solvent is added to the tube, the solvent is evaporated to the specified final volume, and the extract is transferred to a storage vial.

The concentrated extracts must be stored in the refrigerator at 0-6°C until the time of analysis.

2.4 Extract Clean-up Procedures

GPC, Florisil, copper, and acid clean-up procedures can be performed to remove interferences from extracts as outlined in the Attachment 8 through Attachment 11 of this SOP.

2.5 Percent Lipids Procedures

Percent lipids analysis is routinely requested for tissue samples prepared via sonication procedures. The percent lipids procedure is summarized in Attachment 5 and involves weighing the extract before and after drying overnight. The ratio of the two weights is equivalent to the percent lipids content of the sample.

2.6 Method References

This SOP is based on the following methods: EPA Method 3550B and EPA Method 3550C (for sonication) and EPA Method 3546 (for microwave). Biological tissue-specific guidance is taken from EPA Region IV Method 0B 10.90 *"Extraction and Analysis of Organics in Biological Tissue."*

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Acetone, hexane, methylene chloride, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences.

4.2.2 Biological tissues contain high levels of lipids that are not routinely encountered in environmental samples. Gel permeation chromatography (GPC) is routinely used to reduce the lipid concentration of the extract in accordance with Attachment 11.

4.2.3 Samples for PCB analysis-only are often acid cleaned in accordance with Attachment 9.

4.2.3.1 In addition to GPC and acid clean-ups, Florisil and copper clean-ups can be performed to remove interferences from extracts as outlined in the applicable attachments to this SOP.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is processed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be processed first.

4.2.3 During extract cleanup, an emulsion may form in the acid/solvent interface. A small quantity of sodium sulfate or sodium chloride may be gently added to the emulsion. The salt will generally cause the emulsion to break up.

4.2.4 Extracts with particulates and precipitates will clog the Florisil Solid Phase Extraction (SPE) cartridges and the GPC. Filtration of the extract through a syringe with 0.45um filter may be necessary.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of the chemicals used in this procedure has not been precisely defined. Each chemical must be treated as a potential health hazard, and exposure to these chemicals must be minimized.

Methylene chloride is a carcinogen and an irritant. It causes irritation to the respiratory tract and has a strong narcotic effect with symptoms of mental confusion, light-

headedness, fatigue, nausea, vomiting, and headache. Methylene chloride may be absorbed through the skin and can cause irritation and pain to the skin and eyes.

Hexane and acetone are flammable solvents. They can cause irritation to the respiratory tract. Overexposure can cause fatigue, lightheadedness, headache, dizziness, and blurred vision.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

Compressed gasses have specific hazards. The employee must be familiar with the MSDS for each of the compressed gasses. The employee must also be familiar with the compressed gas section (Section 11) of the Environmental Health and Safety Manual.

The sonication procedure produces piercing, high frequency noise. It is imperative that the sonication instruments be housed in the "sonabox" enclosures under the fume hoods to minimize the effect of the noise.

The microwave procedure produces high temperatures (~100C) and high pressures (~200psi) during the extraction process. The analyst must be familiar with the manufacturer's instructions for properly loading and unloading samples from the device and for the safe use and handling of the extraction vessels.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Acetone	Flammable	1000ppm TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500ppm TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25ppm TWA 125ppm STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1mg/m^3 TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Florisil	Irritant	10mg/m^3 TLV 5mg/m^3 PEL	May cause irritation if inhaled or adsorbed through the skin.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
Note: Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

6.1.1 Sonication-specific Equipment

Ultrasonic Disrupter (sonicator) – Tekmar Model or equivalent with ¾-inch horn-type titanium-tipped sonication probe. The sonicator must be capable of operating in the pulse mode at full power. The sonicator must have a minimum power wattage of 300 watts.

Sonabox – the sonicator must be placed in the sonabox to reduce noise. The sonabox must be placed under a fume hood.

6.1.2 Microwave Extraction Equipment

Microwave extractor – CEM MARS Model 907501, includes carrousel

Microwave extraction vessels – Teflon

6.1.2 Concentration-specific Equipment

Zymark TurboVap II concentration device or equivalent – The instrument must be vented into an operating fume hood.

Concentration tubes – 200mL (for liquids) or 225mL elongated tubes (for soils) with 1.0mL tip. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

6.1.5 Support Equipment

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Stainless Steel Blender or Meat Grinder – heavy-duty type capable of blending tissues.

6.1.6 Cleanup-specific Equipment and Supplies

Florisil solid phase extraction (SPE) columns – Bakerbond 6mL Solid Phase Extraction cartridge packed with 1g Florisil. Other size SPE may be used; however, the volume of elution solvents and sample loading capacity must be adjusted to compensate for the amount of Florisil. Each lot of cartridges must be verified prior to use.

The lot of Florisil cartridges is acceptable if all the following criteria are met:
- the pesticides in the check mix are recovered at 80-110% percent
- the percent recovery of 2,4,6-trichlorophenol is less than 5%
- there are no peaks interfering with the target compounds are detected

Florisil Cartridge Manifold

GPC System – includes autoinjector, autosampler, UV detector, glass column, solvent pump, solvent reservoir, waste reservoir, and applicable software

6.2 Other Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).* Includes Tilt-Pours calibrated for 70mL and 100mL, used to measure and deliver solvents.

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Disposable Transfer Pipettes – various sizes

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Detergent – FL-70 or equivalent, used for washing non-disposable labware

Pre-Cleaned 500mL Extraction Bottles

Filter Funnel - Large glass funnels with 18.5cm filter paper

Stainless Steel Spatulas

Dry ice

2mL vials with Teflon lined crimp caps or 2mL screw cap vials with PFTE-faced septa: compatible with the autosampler. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

12mL glass vials with Teflon-lined or PFTE-lined caps. A storage vial may be calibrated by adding a known volume of liquid to the container and marking the volume on the side of the container. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

11mm crimp-type capper and decapper

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

16oz glass soil jars – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.*

Acetone, hexane, and methylene chloride must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Blank Matrix – Ottawa Sand, purified by heating at 400°C for four hours in a shallow tray. Used for the preparation of soil QC samples.
Storage: sealed glass jar at room temperature
Expiration:
Unopened: Manufacturer's expiration date
Opened: 1 year from purification date

7.2.2 Sodium sulfate, granular, anhydrous – purified by heating at 400°C for four hours in a shallow tray. Used as a drying agent.
Storage: sealed glass jar at room temperature
Expiration:
Unopened: Manufacturer's expiration date
Opened: 1 year from purification date

7.2.3 Methylene chloride – pesticide grade or better. Used for EPA 8015B, EPA 8015C, and all tissue extractions. Used as extraction solvent.
Storage: Flammables cabinet
Expiration:
Unopened: Manufacturer's expiration date
Opened: Manufacturer's expiration date

7.2.4 Acetone – pesticide grade or better. Used for glassware rinsing and as solvent for some spiking mixes.
Storage: Flammables cabinet
Expiration:
Unopened: Manufacturer's expiration date
Opened: Manufacturer's expiration date

7.2.5 1:1 acetone/methylene chloride – Purchased in pre-mixed in 215L cycletainers. Used for EPA 8270C and EPA 8270D, and the low-level and PAH-only variations of these methods.
Storage: room temperature in cycletainer
Expiration:
Unopened: Manufacturer's expiration date
Opened: Manufacturer's expiration date

7.2.6 Hexane – residue grade or better. Used for EPA 680 (PCB Homologue analysis)
Storage: Flammables cabinet
Expiration:
Unopened: Manufacturer's expiration date
Opened: Manufacturer's expiration date

7.2.7 1:1 Acetone/Hexane – Purchase pre-mixed in 215L cycletainers. Used for EPA 8081, EPA 8141, and EPA 8082
Storage: room temperature in cycletainer
Expiration:
Unopened: Manufacturer's expiration date
Opened: Manufacturer's expiration date

7.2.8 Sulfuric Acid (H_2SO_4) – concentrated reagent grade. Used for clean-up procedures.
Storage: acids cabinet
Expiration: Manufacturer expiration date
Unopened: Manufacturer's expiration date
Opened: Manufacturer's expiration date

7.2.9 Sulfuric Acid Solution (1:1 v/v) – Used for clean-up procedures. Slowly and carefully add 500mL of concentrated H_2SO_4 to 500mL of reagent water contained in a 2L beaker on a magnetic stirrer. Add the acid in small portions with constant stirring to reduce the heat evolved when the acid and water are combined. Cool and transfer the solution to a labeled storage container.
Storage: acids cabinet
Expiration: 6 months from preparation date

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

All of the standards used from this SOP must be stored at a temperature of 4°C (less than 6°C and not frozen). Unless otherwise noted, all purchased standards have an expiration date of 6 months from date of opening, and all prepared standard have an expiration date of 3 months from date of preparation.

Note: This standards list is comprised of the routine standards used by the laboratory. Information on project-specific, non-routine standards is found in the Reagent Module in LIMS.

7.3.1 Purchased Standards

7.3.1.1 Organochlorine Pesticide Surrogate Stock, 200ug/mL – Purchased from Supelco (catalog # 505935)

7.3.1.2 Triphenylphosphate (Organophosphorous Surrogate Stock), 1000 ug/mL – Purchased from Restek (catalog # 32281)

7.3.1.3 Pesticide Mix A, varied concentrations – Purchased from NSI (catalog # Q-2108)

7.3.1.4 Pesticide Mix B, varied concentrations – Purchased from NSI (catalog # Q-2109)

7.3.1.5 Aroclor 1016/1260 Spike Mix, 1000ug/mL – Purchased from Restek (catalog # 32039)

7.3.1.6 OP Pesticide MS Mix, 1000ug/mL Atrizine, Diazinon, Ethyl Parathion, Methyl Parathion, Ronnel and Thionazin – Purchased from NSI (catalog # Q-2031)

7.3.1.7 O-terphenyl Standard, 2000ug/L – Purchased from Restek (catalog # 31066)

7.3.1.8 #2 Diesel Fuel, 100mg/mL – Purchased from Accustandard (catalog # FU-009-D-200X)

7.3.1.9 680 Surrogate Mix, 50ug/mL Decachlorobiphenyl-13C12 – Purchased from Wellington (catalog # MBP-209)

7.3.1.10 680 Concentration Calibration Standard, varied concentrations – Purchased from Ultra Scientific (catalog # CB-681)

7.3.1.11 BNA Organic Acid Surrogate Standard, 10000ug/mL – Purchased from NSI (catalog # C-131-33)

7.3.1.12 Base/Neutral Surrogate Standard, 5000ug/mL – Purchased from NSI (catalog # C-376-46)

7.3.1.13 O-Terphenyl Standard, 2000ug/L – Purchased from Restek (catalog # 31066)

7.3.1.14 Benzidine Mix, 2000ug/mL – Purchased from NSI (catalog # C-402-22)l

7.3.1.15 BNA Full Spike Mix – Purchased from NSI (catalog # Q-4717)

7.3.1.16 LL_BNA Spike Mix – Purchased from NSI (catalog number is Q-5118)

7.3.1.17 AP9 Spike Mix – Purchased from NSI (catalog number is Q-5131)

7.3.1.18 AR_MIX_SPK, client specific PCB spike – Supplied from Solutia to be used with every batch of 8082 that include samples from the Solutia-Anniston Residential site. The standard has varied concentrations of Aroclors and has no reported expiration date.

7.3.2 Prepared Standards

7.3.2.1 Working Pesticide Surrogate Mix (PESTwkSURR_xxxxx) – prepared by adding 1.25mL Pesticide Surrogate Stock (200ug/mL) and 2.0mL of Triphenylphosphate (1000 ug/mL) diluted to a final volume of 500mL in methanol.

7.3.2.2 Working Pesticide Spike Mix (608wkSPIKE_xxxxx) – prepared by adding 1mL Pesticide Mix A and 1mL Pesticide Mix B diluted to a final volume of 100mL in hexane.

7.3.2.3 Working PCB Spike Mix (1660wkSPIKE_xxxxx) – prepared by adding 1mL of Aroclor 1016/1260 Spike Mix diluted to a final volume of 100mL in methanol.

7.3.2.4 Working OP Pesticide Spike Mix (tallWKspike_xxxxx) – prepared by adding 0.250mL of OP Pesticide MS mix diluted to a final volume of 50 mL in acetone.

7.3.2.5 DROwkSURR_xxxxx is 2.5mL of O-terphenyl standard (2000 ug/L) diluted to a final volume of 250mL in acetone.

7.3.2.6 DIESELWK_xxxxx is 1.0mL of #2 Diesel Fuel (100 mg/mL) diluted to a final volume of 100mL in acetone.

7.3.2.7 680wkSURR_xxxxx is 2.5mL of Decachlorobiphenyl-13C12 (50ug/mL) catalog number MBP-209 from Wellington diluted to a final volume of 50mL in acetone.

7.3.2.8 680wkSPIKE_xxxxx is 1.0 mL of Concentration Calibration Standard mix (varied concentrations) diluted to a final volume of 25 mL in acetone.

7.3.2.9 BNAwkSURR_xxxxx is 5.0mL of Organic Acid Surrogates (10000 ug/mL) and 10.0mL of Base/Neutral Surrogates (5000 ug/mL) diluted to a final concentration of 500mL in acetone.

7.3.2.10 LLBNAwkSUR_xxxxx is 0.5mL of Organic Acid Surrogates (10000 ug/mL), 1.0mL of Base/Neutral Surrogates (5000 ug/mL), and 0.5mL of O-Terphenyl standard (2000 ug/L) diluted to a final concentration of 500mL in acetone.

7.3.2.11 BENZIDINwk_xxxxx is 5.0mL of Benzidine Mix (2000 ug/mL) diluted to a final volume 100mL in acetone.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Soil Samples

Soil samples are routinely collected in 16oz glass soil containers.

Soil samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis.

Refer to the associated analytical SOPs for information on analysis holding times.

8.2 Tissue Samples

Tissue samples are routinely collected in unpreserved glass containers, with the size dependent upon the type of tissue being collected, or wrapped in aluminum foil. Plastic jars or plastic baggies can be used.

Upon receipt, tissue samples must be placed in the freezer at -10° to -20°C, if preparation cannot be completed that day, and must be kept frozen until the time of preparation. A holding time of six months from the date of collection for frozen fish fillets is recommended by Alabama Department of Environmental Management (ADEM) and will be used for all biological tissues.

Once the tissue sample has been thawed, it must be stored at 4°C (less than 6°C but not frozen), and preparation must take place within 14 days.

Refer to the associated analytical SOPs for information on analysis holding times.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 of each analytical SOP provide requirements for evaluating QC data.

9.1 Batch QC

An extraction batch consists of up to 20 environmental samples and the associated QC items. The minimum QC items required for each extraction batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD) or a sample duplicate. If there is insufficient sample to perform the MS/MSD or sample duplicate, this situation must be noted in the Batch Information section of the extraction log.

The routine container supplied for this method is a 16oz (400g) container. Generally 30g of sample is used for extraction. Reduced sample initial amounts may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction weight to be used for the matrix spike samples is 15g. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample submitted to perform the required matrix spike(s) and/or sample duplicates, the LCS must be prepared in duplicate (LCS/LCSD). Insufficient sample is defined as receiving less than a total of 60g. If insufficient sample is provided to perform the MS/MSD or MS/SD, An NCM must be initiated on all samples within the batch to denote this situation

Batch QC must meet the criteria given in Attachment 3 of the associated analytical SOP.

9.2 Instrument QC

The instrument QC for the analytical procedures associated with this extraction procedure are given in the analytical SOPs listed in Section 1.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* and the QC Summary Table in Attachment 3 of the associated analytical SOPs. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation Procedures

10.1.1 Remove the samples from the refrigerator and allow them to come to room temperature.

10.1.2 Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Compositing, Homogenization, and Segregation of Samples.*

10.1.3 Tissue samples must be homogenized prior to preparation since organic compounds are generally not evenly distributed throughout biological tissue. The entire sample should be ground into a homogenous consistency. To do this, chop the sample into one inch or smaller chunks and place in the blender or meat grinder. Note: Slightly frozen tissue is easier to work with at this point. Add dry ice to the blender or meat grinder. Blend or grind on appropriate power level until the tissue is thoroughly ground and homogenized. Inspect the tissue for the presence of "chunks" of tissue. Remove the well-homogenized tissue and blend the remaining "chunks" until homogenized. Mix the tissue thoroughly and separate into 10g portions for the required analyses. If the extraction is not to take place soon after homogenization, the homogenized tissue or the individual 10g portions can be frozen. Note, however, that the holding begins with the date of the original thawing process.

10.1.4 Weigh the appropriate amount of homogenized sample into a labeled 500mL extraction bottle or labeled microwave extraction vessel. Refer to Attachment 6 for sample weights for each of the analytical methods.

Note: A larger amount of tissue may be extracted if lower reporting limits (RLs) are required for the project. Refer to project notes or project-specific quality assurance plans (QAPP) for required RLs.

10.1.5 Add the appropriate surrogate spiking solution to each sample. (Refer to Attachment 7.)

Note: Be sure to use the correct spiking solution for the analytical method of concern.

The addition of the surrogate spiking solutions must be witnessed by another analyst to ensure the correct spiking solution and the proper volume of spiking solution is added to each sample.

Note: If the final volume of the extract must be reduced to achieve the required reporting limits, the amount of surrogate and matrix spiking solutions must be reduced proportionately.

10.1.6 For the sonication procedure, add approximately 60g of granular, purified sodium sulfate to each sample and stir with a glass rod or stainless steel spatula to form a sandy, free-flowing mixture. The sodium sulfate combines with the water in the sample to "dry" the sample (i.e., remove the water). Additional sodium sulfate may be required if the sample is very wet.

Immediately add 70mL of the appropriate extraction solvent as outlined in Attachment 6. Additional solvent may be needed to cover the sample approximately one inch above the

solids. Stir the sample to break up any lumps that may have formed. Proceed to Section 10.3.

10.1.7 For the microwave procedure, **immediately** add 25mL of the appropriate extraction solvent as outlined in Attachment 7 and cap the vessel. Proceed to Section 10.4.

10.2 QC Sample Preparation

QC samples must be processed in the same manner as field samples.

10.2.1 To prepare the method blank, weigh an amount of Ottawa sand equivalent to that used for samples into a labeled 500mL extraction bottles or a microwave extraction vessel. Process the method blank in the same manner as the associated field samples, beginning with Section 10.1.5.

Note: If a "control tissue" has been obtained for biological tissue QC, use the control tissue for the method blank and LCS, treating them in the same manner as the sample tissues.

10.2.2 To prepare the laboratory control sample (LCS), weigh an amount of Ottawa sand equivalent to that used for samples into a labeled 500mL extraction bottles or a microwave extraction vessel(s). Add the appropriate spiking solution to the LCS. Process the laboratory control sample in the same manner as the associated field samples, beginning with Section 10.1.5.

The addition of the LCS spiking solutions must be witnessed by another analyst to ensure the correct spiking solution and the proper volume of spiking solution is added to each sample.

Note: Some agencies and client quality assurance plans have specific extraction and/or spiking requirements. Verify project plans and worksheet notes prior to beginning the extraction to ensure state and/or project-specific requirements are followed.

10.2.3 To prepare the matrix spike (MS) and matrix spike duplicate (MSD), weigh two additional portions of a sample in the batch into labeled 500mL extraction bottles or microwave extraction vessels. Add the appropriate spiking solution to the MS/MSD. Process the MS/MSD in the same manner as the associated field samples, beginning with Section 10.1.5.

The addition of the MS/MSD spiking solutions must be witnessed by another analyst to ensure the correct spiking solution and the proper volume of spiking solution is added to each sample.

Note: The MS/MSD or MS/SD may be specified by the client or may be chosen from the samples in the batch.

Note: Some agencies and client quality assurance plans have specific extraction and/or spiking requirements. Verify project plans and worksheet notes prior to beginning the extraction to ensure state and/or project-specific requirements are followed.

10.2.4 To prepare the sample duplicate (SD), weigh one additional portion of a sample in the batch into a labeled 500mL extraction bottle or a microwave extraction vessel. Process the SD in the same manner as the associated field samples, beginning with Section 10.1.5.

10.3 Sonication Extraction Procedures

10.3.1 Place each extraction bottle under the hood near the sonicator.

10.3.2 Check the "tune" of the sonicator using the procedure outlined in Attachment 4.

10.3.3 Place the tip of the sonicator horn in the center of the beaker about ½ inch below the surface of the solvent but above the solid portion. More solvent may be added to bring the level to approximately one inch above the solid layer.

10.3.4 Sonicate each sample for three minutes with the output control knob set at 10, mode switch set to pulse, and percent duty cycle set at 50%. If the sonication is properly performed, the solids and solvent will vigorously mix each time the sonicator pulses.

10.3.5 Decant the extract through the filter funnel. Collect the extract in a beaker or directly into a labeled, "elongated" Zymark tube. Note: If the sample is very wet and requires a large amount of sodium sulfate and a larger volume of solvent, the extracts are collected in separate Zymark tubes and combined prior to analysis.

10.3.6 Repeat Sections 10.3.3 through 10.3.6 two more times with fresh 70mL portions of extraction solvent, collecting all extracts in the same Zymark tube.

10.3.7 After the third sonication, pour the solids portion of the sample into the filter funnel. Rinse the extraction vessel and solids in the filter funnel with several small aliquots of the extraction solvent, collecting all of the extraction solvent in the Zymark tube.

10.3.8 Cover the Zymark tube with aluminum foil, and leave it under the hood until ready to perform the concentration step as outlined in Section 10.5.

Note: Clean the sonicator horn between samples by rinsing with methylene chloride.

Note: The extraction steps from weighing to sonication should be carried out quickly to minimize the loss of SVOC through evaporation.

10.4 Microwave Extraction Procedures

10.4.1 Make sure that the caps are fastened properly on each extraction vessel.

10.4.2 Place the vessels on the carrousel in the appropriate slot.

10.4.3 Enter the parameters for the extraction on the keyboard. The default parameters are as follows:

Parameter	Program
Time	10 minutes to reach 110°C; then hold10 minutes
Temperature	110°C
Pressure	50-150psi
Watts	<24 Samples: 800 watts >24 samples: 1600 watts

10.4.4 Allow the extracts to reach room temperature. Concentrate as described in Section 10.5.

10.5 Concentration Procedures

10.4.1 Pre-rinse each Zymark concentration tube with acetone and methylene chloride.

10.4.2 Turn on TurboVap evaporation unit. Set the water bath temperature to 50°C. Set the gas pressure to zero initially for each cell in the TurboVap unit.

10.4.3 Pre-rinse each concentration cap on the TurboVap evaporation unit with methylene chloride.

10.4.4 If the sample extracts have been collected in any container other than a Zymark tube, transfer the extract to a Zymark tube.

Sonication Extracts:
Working under a hood, pour 150-200mL of the extract (depending on the size of the tube) into a labeled Zymark concentration tube, and place the tube into a cell on the evaporation unit. Repeat for remaining samples in the batch. The remaining extract must be tightly covered with a piece of aluminum foil to minimize evaporation of the solvent.

Microwave Extracts:
- Add a piece of folded filter paper to a clean glass funnel.
- Add approximately 30g of purified sodium sulfate to the funnel.
- Place the funnel over a Zymark tube.
- Working under a hood, rinse the filtering funnel and labeled Zymark tube with methylene chloride. Discard the solvent in the waste container.
- Working with one sample at a time and continuing to work under a hood, pour the extract from the extraction vessel into the funnel. It is important that the extract contact the sodium sulfate to remove the water from the extract.
- Rinse the microwave vessel with 20mL of extraction solvent and pour through the funnel and collect in the Zymark tube. Repeat with three additional 20mL aliquots of solvent.
- Rinse the funnel with three 20mL aliquots of solvent and allow the solvent to drain and collect in the tube.
- Place the tube into a cell on the evaporation unit. Repeat for remaining samples in the batch.

10.4.5 Carefully close the cover of the Zymark TurboVap unit completely. Make sure that each tube is seated properly and that the individual covers are positioned directly over each tube. Note: When the elongated tubes are used, care must be taken to position the tubes to avoid breaking the tube covers and to completely close the instrument cover.

10.4.6 Concentrate extracts at a constant temperature of 50°C with a pressure range from 4 to 15psi. Zymark tubes with smaller sample volumes are processed with higher pressures (15psi); while, Zymark tubes with larger volumes (those approaching the red "fill" line) are processed with lower pressures (4-5psi).

10.4.7 As extracts are concentrated, periodically add more sample until the entire sample has been transferred to the Zymark concentration tube.

10.4.8 Concentrate the extract until the cell alarm sounds. This indicates the sample is at a 1mL volume. (Note: For many soil extracts, the alarm will beep prior to this point, so extra care must be taken to observe samples between this point and when 1mL is actually achieved.)

10.4.9 If the solvent must be exchanged, add 20mL of the exchange solvent to the Zymark concentration tube. Continue concentration until the cell alarm sounds. This indicates the sample is at a 1mL volume.

10.4.10 Remove Zymark concentration tubes from evaporation unit and transfer to storage vials as outlined in the following Section.

10.5 Extract Transfer Procedures

10.5.1 Adjust the extract volume to the required final volume by adding small aliquots of the required solvent. If the final volume is to be greater than 1mL, add an appropriate volume of solvent to the tube using a volumetric pipette or calibrated solvent dispensing device. For example, if the final volume is to be 10mL, adjust the volume in the tube to 1mL and then add 9mL of solvent to give a final volume of 10mL.

Note: If the extract cannot be evaporated to 1mL, the extract must be transferred to a volumetric flask or to a calibrated storage vial. Use several small aliquots of solvent to transfer the entire extract to the vial.

10.5.2 Transfer the final extract to a Teflon-lined crimp top or 12-mL scintillation vial. Mark the volume of the extract on the side of the container to allow the analyst to judge whether the sample extract has evaporated during storage and handling. Store concentrated extracts at 4°C until time of analysis.

10.6 Analysis

Details on sample analysis are given in the associated analytical SOPs listed in Section 1.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data reduction and review tasks include the following items:

- Employ spike witness procedures to ensure proper spiking solutions and volume are used.
- Ensure all LIMS batch Data Type fields are completed so that proper traceability is maintained.
- Check to ensure that each sample extract is properly identified and that the extracts are transferred to the analytical groups with proper documentation.
- Mark the final volume of the extract on the outside of the storage container as a check on extract evaporation.
- QC items must be treated in the same manner as samples.
- Ensure samples are evaporated at the appropriate rate. Unacceptable surrogate or spike recoveries may be attributed to evaporating the samples too quickly or to improper solvent exchange.
- Document any unusual circumstances and procedural violations using the LIMS Nonconformance Module. This can include: samples problematic matrices such as color, odor, or emulsions; initial or final amount changes; deviations to the SOP, insufficient sample provided to perform batch QC (such as MS/MSD), etc.

Batch data must be reviewed and evaluated in accordance with SOP SA-QA-02: *Data Generation and Review*.

Additional details on data reduction procedures are given in the associated analytical SOPs.

11.1.1 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.2 Calculations

Details on sample calculations are given in the associated analytical SOPs listed in Section 1.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDLs associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and annually thereafter, and verified annually in accordance with SOP SA-QA-07: *Determination of Detection Limits (MDLs and IDLs).*

Note: Tissue matrices are non-routine, and the laboratory is not currently NELAC certified for this matrix. Additionally, Ottawa sand (as opposed to a "true" tissue matrix) is used for tissue QC samples unless the laboratory is specifically requested by the client to procure a "true" tissue matrix. As such, the soil MDL is converted to tissue units and used to satisfy the MDL requirement for this matrix.

12.2 Reporting Limit Verification

Reporting limits must be verified annually in accordance with SA-QA-07: *Determination and Verification of Reporting and Detection Limits.*

12.3 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP QA06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

Note: Tissue matrices are non-routine, and the laboratory is not currently NELAC certified for this matrix. Additionally, Ottawa sand (as opposed to a "true" tissue matrix) will be used for tissue QC samples unless the laboratory is specifically requested by the client to procure a "true" tissue matrix. As such, the soil DOC is used to satisfy the DOC requirement for this matrix.

12.4 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Methylene chloride extracts – Dispose according to characterization on sample disposal sheets. If non-hazardous, transfer extract to chlorinated waste container. If hazardous, transfer to hazardous waste department for storage.

- Methylene chloride waste – Transfer to chlorinated waste container.

- Hexane extracts – If non-hazardous, transfer to flammable waste containers and dispose of as flammable waste. If hazardous, transfer to the waste disposal department for disposal as hazardous waste.

- Flammable waste (hexane or acetone from extracts, rinsings, and standards) – Transfer to a satellite container designated for flammable waste and transfer to waste disposal department when the container is full.

- Aqueous acidic waste from samples – Collect into the disposal area and neutralize before release to the sewer system.

15.0 References / Cross-References

- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-AN-41: *Reagent and Standard Materials Procedures*

- SOP SA-GE-190: *Solid/Residue Determinations*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- *Test Methods for Evaluating Solid Waste*, Third Edition (Updates III and IV), SW-846; EPA Office of Solid Waste and Emergency Response: Washington, DC.
    - Chapter 4: *Organic Analytes*; Revision 3, December 1996
    - Chapter 4: *Organic Analytes*; Revision 4, February 2007
    - EPA 3500C: *Organic Extraction and Sample Preparation*; Revision 3, February 2007
    - EPA 3550B: *Ultrasonic Extraction*; Revision 2, December 1996
    - EPA 3550C: *Ultrasonic Extraction*; Revision 3, February 2007
    - EPA 3600C: *Cleanup*; Revision 3, December 1996
    - EPA 3620B: *Florisil Cleanup*; Revision 2, December 1996
    - EPA 3620C: *Florisil Cleanup*; Revision 3, February 2007
    - EPA 3640A: *Gel-Permeation Cleanup*; Revision 1, September 1994
    - EPA 3645: *Microwave Extraction*; Revision 0, February 2007
    - EPA 3660B: *Sulfur Cleanup*; Revision 2, December 1996
    - EPA 3665A: *Sulfuric Acid/Permanganate Cleanup*; Revision 1, December 1996
- Tekmar sonicator instruction manual.
- *"Extraction and Analysis of Organics in Biological Tissues"*, Method 0B 10/90, USEPA Environmental Services Division, Region IV, Analytical Support Branch, Athens, GA.

16.0 Method Modifications

16.1 This procedure may be modified to analyze other matrices (e.g., wipe samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project. The instructions for the preparation of wipe samples are given in the Wipe-specific Work Instruction (FQA086).

16.2 Tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.), and soil QC limits to evaluate tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. Ottawa sand is used as the blank matrix for tissue samples unless a "true" tissue matrix is required by the project.

16.3 The initial amount and final volumes used for organochlorine pesticide, PCBs as Aroclors, and organophosphorous pesticide extractions have been changed from 30g and 10mL to 15g and 5mL. This change is not a significant method modification as the ratio of initial amount to final volume is consistent.

16.4 The volumes used for the extraction solvents have been modified from the reference method from three 100mL portions to three 70mL portions. All MDL studies, DOCs, and PTs have been performed in this manner and have met acceptance criteria which indicate this modification has little impact on the data.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Determination of Percent Lipids
Attachment 6: Extraction Solvents and Volumes
Attachment 7: Sample and QC Sample Spiking Solutions
Attachment 8: Sulfur Cleanup
Attachment 9: Sulfuric Acid Cleanup
Attachment 10: Florisil Cleanup
Attachment 11: Gel-Permeation Cleanup
Attachment 12: Standard Preparation
Attachment 13: Zymark Sensor Diagnostic Test and Maintenance Log
Attachment 14: Zymark Instructions for the Sensor Diagnostic Test and Cleaning and Refilling the Water Bath

Attachment 1:
SOP Summary

Sample Preparation Summary

Sonication Extraction Procedure

A known weight of a sample is combined with anhydrous, purified sodium sulfate to form a free flowing, sandy mixture. A solvent is added to the dried sample, and the sample is extracted using an ultrasonic disrupter (i.e., sonicator) for three minutes. The solvent is decanted, and the extraction is repeated two more times. The extract is filtered and concentrated to an appropriate final volume. Attachment 6 defines the extraction conditions for the applicable analytical procedures.

Note: The routine initial weights are given in Attachment 6 for each procedure. If the sample contains high levels of contaminants (target or non-target), a smaller aliquot of the sample may be weighed and extracted according to this procedure. The minimum weight of sample is 1g.

Microwave Extraction Procedure

A known weight of a sample is transferred to a Teflon extraction vessel. The sample is spiked with surrogate compounds and an analyte-specific solvent is added to the vessel. The vessel is placed on the instrument and the sample extracted at an elevated temperature and pressure. The vessel is cooled to room temperature, the extract is passed through sodium sulfate to remove the water from the sample, and the extract is collected in a concentration tube. The solvent is evaporated and the extract is concentrated to a nominal final volume of 1.0mL. If required by the analytical procedure, the extract may be exchanged to another solvent and concentrated to an appropriate final volume. Attachment 6 defines the extraction conditions for the applicable analytical procedures.

Zymark TurboVap Concentration Procedure

After the extraction procedure is completed, the solvent is transferred to a glass Zymark concentration tube. The tube is placed in the Zymark TurboVap concentration device, which has been heated to a specified temperature. A stream of nitrogen is directed into the tube to evaporate the solvent and to concentrate the target compounds. When the volume of solvent reaches the specified volume, normally 1mL, the nitrogen is automatically stopped. An alarm sounds to alert the analyst, and the extract is removed from the device and transferred to a storage vial or container.

If a solvent exchange is required, the exchange solvent is added to the tube, the solvent is evaporated to the specified final volume, and the extract is transferred to a storage vial or container. The concentrated extracts are stored at 4°C until the time of analysis.

Sample Analysis Summary
Samples are analyzed in accordance with the appropriate method-specific SOP.

Analyte Class	Analytical Method	Analytical SOP
PCB Homologues	EPA 680	SA-SM-007
Diesel Range Organics	EPA 8015B EPA 8015C	SA-SG-070
Oil Range Organics	EPA 8015B EPA 8015C	SA-SG-070
Product Identification	EPA 8015B EPA 8015C	SA-SG-070
Chlorinated Pesticides	EPA 8081A EPA 8081B	SA-SG-045
PCBs as Aroclors	EPA 8082 EPA 8082A	SA-SG-045
Organophosphorous Pesticides	EPA 8141A EPA 8141B	SA-SG-050
BNAs	EPA 8270C EPA 8270D	SA-SM-033

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Listed below are the holding times and preservation requirements:

Matrix	Sample Container	Routine Sample Size	Preservation	Holding Time
Soil	16oz glass soil jar	15g-30g (See Attachment 6)	Less than 6°C with no frozen samples	14 days
Tissue	glass jar or aluminum foil	10g	-10 to -20°C	6 months frozen 14 days once defrosted

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Batch Definition	Up to 20 field samples extracted together within 24-hour time period	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Laboratory Control Sample (LCS)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Laboratory Control Sample Duplicate (LCSD)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Matrix Spike (MS)	One set per batch	Refer to analytical SOP	Refer to analytical SOP
Matrix Spike Duplicate (MSD)	One set per batch	Refer to analytical SOP	Refer to analytical SOP
Sample Duplicate (SD)	One set per batch (Can be performed in lieu of MSD)	Refer to analytical SOP	Refer to analytical SOP
Initial Demonstration of Capability (IDOC)	Initially, per analyst/matrix/method/analyte combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06 (Unsupervised work cannot begin until acceptable IDOC is achieved.)
Continuing Demonstration of Capability (CDOC)	Annually, per analyst/matrix/method/analyte combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Method Detection Limit (MDL)	Upon method/instrument set-up, and then annually thereafter (Includes MDLV)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

QC Item	Frequency	Criteria	Corrective Action
Reporting Limit Verification (RLV)	Upon method/instrument set-up, and then annually thereafter (for non-routine methods, matrices, or analytes)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:
- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

Chipped or broken glassware must be removed from service.

Sonicator Weekly Maintenance
- Turn the instrument off. Disconnect both horns from the back of the instruments.
- Place both horns on a clean padded surface.
- Remove the 1" tip from the horn. Inspect the tip for any pitting and any irregularities. The tip is to be replaced with a new tip if any pitting or irregularities are found. Clean the tip and its threads with a paper towel and methylene chloride.
- Check to ensure that the connection with the horn is tight and free of any foreign matter.
- Carefully reinsert the 1" tip into the horn and tighten the tip. Care must be taken to ensure that the tip is as tight as possible, re-inspect the tip for any irregularities after tightening.
- Perform the above procedure on the second horn.
- After maintenance is complete, re-connect the bottom horn and re-tune the instrument. If the horn will not re-tune, see the department manager.
- Any horn that cannot be re-tuned will be replaced. If the instrument will not tune, a service technician will be called. The instrument will not be used until all tuning criteria are met.

Sonicator Tuning
A tune check must be performed on the sonic dismembrator each day it is used. This tune is to ensure that the sonic dismembrator is operating within the manufacturer's specifications and that the instrument is delivering the minimum wattage output specified by the procedure. Full maintenance is performed as needed by the Department Manager or Supervisor.

- All checks and adjustments to the sonicator must be documented in the maintenance log.
- Unplug the top horn connection on the rear panel of the instrument.
- Check to ensure that the bottom horn connection is as tight as possible.
- Turn the pulser switch off.
- Turn the output to 10.
- Check to ensure that the horn being tuned is free of obstruction.
- Carefully push the tune switch in. At the same time, adjust the tuning knob so that the output meter reads as low as possible. The output meter must read below 20%. If the instrument will not tune to below 20%, a shift supervisor must be informed immediately.

Note: The tuning switch must not be held in for longer than 10 seconds. Holding the switch in for more than 10 seconds may cause the horn being tuned to overheat.

Microwave Maintenance

Other than wiping down the inside of the microwave unit on an as needed basis, with a paper towel moistened with reagent water, there are no maintenance procedures performed by the laboratory. This type of equipment is covered under a service contact, and the service technician is contacted if the equipment malfunctions. Unacceptable recoveries for laboratory control samples (LCS) could indicate a service call is warranted.

Zymark Maintenance

It is recommended to change the water in the water bath weekly. Add 1-2 drops of Clear Bath to prevent bacteria and algae growth. Methylene chloride that dissolves in the water bath will damage the sensors.

The Zymark sensor diagnostic test must be performed weekly. If the sensors do not meet criteria the sensor may need replacing. Refer to the manufacturer's manual for replacement procedures if necessary.

The thermometer for the Zymark must be calibrated in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*.

Contingency Plan

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique, or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:

TestAmerica
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Determination of Percent Lipids

Summary of Procedure
Percent lipids is determined by weighing a sample prior to and after drying. The ratio of the weights is equivalent to the percent lipids content of the sample. The percent lipids are determined on the tissue sample extract prior to GPC extract cleanup. The final volume of the extract must be adjusted to 10mL prior to the determination of the percent lipids.

Standards
Cod liver oil - commercially available.
Storage: room temperature;
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

Percent Lipids QC Check Standard – add 10g of cod liver oil to a 100mL volumetric flask and dilute to volume with methylene chloride. Each 1.0mL aliquot of this solution contains 100mg of lipid.
Expiration: 12 months from preparation date

Procedure
Clean an aluminum weigh boat. Note: From this point onward the boat must be handled with tongs and protected from particulates. Record the weight of the clean aluminum weigh boat. Transfer 1.0mL of the extract (final volume 10mL) into the aluminum weigh boat. Place the boat in a hood and allow the solvent to evaporate overnight. Reweigh the boat.

Calculate the percent lipids as follows:

$$\%\ Lipids = \frac{(Wr - Wb)}{SV \otimes \frac{Wsample}{FV}} \otimes 100$$

Where:
W_r = weight of residue and aluminum weigh boat (g)
W_b = tare weight of the aluminum weigh boat (g)
W_{sample} = weight of sample extracted (g)
SV = volume of sample added to the aluminum weigh boat
FV = final volume of the extract (mL)

Note: If percent lipids are to be determined on the samples, a method blank and laboratory control standard (LCS) must be prepared and analyzed. The LCS is prepared by adding 1.0mL of the percent Lipids QC Check Standard to 10g of Ottawa sand. The method blank is prepared by adding 1mL of solvent (MeCl2 or Hexane depending on project) to 10g of Ottawa sand. These are extracted in the same manner as the samples. Assuming a sample weight of 10g, the percent lipids in the QC Check sample is 1.0%. The QC check sample must recover with 0.80 to 1.20%.

Attachment 6:
Extraction Volumes and Solvents

Soil Samples					
Method	**Analyte Class**	**Extraction Amount (g)**	**Extraction Solvent**	**Final Solvent**	**Final Volume (mL)**
EPA 8081A EPA 8081B	Chlorinated Pesticides	15	1:1 Acetone / Hexane	Hexane	5.0
EPA 8082 EPA 8082A	PCBs				
EPA 8141A EPA 8141B	Organophosphorous Pesticides				
EPA 8270C EPA 8270D	BNAs	30	1:1 Acetone / $MeCl_2$	$MeCl_2$	1.0
EPA 680	PCB Homologues	30	Hexane	Hexane	1.0
EPA 8015B EPA 8015C	DRO, ORO, & Product Identification	30	$MeCl_2$	$MeCl_2$	1.0

Tissue Samples					
Method	**Analyte Class**	**Extraction Amount (g)**	**Extraction Solvent**	**Final Solvent**	**Final Volume (mL)**
EPA 8081A EPA 8081B	Chlorinated Pesticides	10	$MeCl_2$	Hexane	10
EPA 8082 EPA 8082A	PCBs				
EPA 8141A EPA 8141B	Organophosphorous Pesticides				
EPA 8270C EPA 8270D	BNAs	10	$MeCl_2$	$MeCl_2$	1.0
EPA 680	PCB Homologues	10	$MeCl_2$	Hexane	1.0
EPA 8015B EPA 8015C	DRO, ORO, & Product Identification	10	$MeCl_2$	$MeCl_2$	1.0

Attachment 7:
Sample and QC Sample Spiking Solutions

Method	Analyte Class	Surrogate Standard	LCS/MS/MSD Standard
EPA 8081A EPA 8081B	Chlorinated Pesticides	PESTwkSURR_xxxxx	608wkSPIKE_xxxxx 1660wkSPIKE_xxxxx tallwkSPIK_xxxxx
EPA 8082 EPA 8082A	PCBs		
EPA 8141A EPA 8141B	Organophosphorous Pesticides		
EPA 8270C EPA 8270D	BNAs _LLPAH	BNAwkSURR_xxxxx LLBNAwkSURR_xxxxx	BNAFULLSPK_xxxxx BENZIDINEwk_xxxxx LLBNASPIKE_xxxxx
EPA 680	PCB Homologues	680wkSURR_xxxxx	680wkSPIKE_xxxxx
EPA 8015B EPA 8015C	DRO, ORO, & Product Identification	DROwkSURR_xxxxx	DIESELwk_xxxxx OROwkspike_xxxxx

Attachment 8:
Sulfur (Copper) Cleanup

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Sulfur Cleanup Procedures

Method: 3660B

Summary of Procedure
This procedure is based on EPA Method 3660B and is used in conjunction with the following SOPs:

Method	SOP #
EPA 3510C / EPA 3520C	SA-EX-030
EPA 3550C	SA-EX-040
EPA 508	SA-SG-046
EPA 608 / EPA 8081B / EPA 8082A	SA-SG-045

The sulfur cleanup uses copper granules to eliminate elemental sulfur from PCB or pesticide extracts. Copper is added to the extract, and the vial is shaken. If sulfur is present, a black precipitate (copper sulfide) will form. The extract is treated with copper until no further precipitate is formed.

The method blank and LCS must be subjected to the same cleanup steps as the samples.

Perform all cleanup steps under a fume hood or in a well-ventilated area.

Reagents
Copper granules – the surface of the copper should be "shiny"

Cleanup Instructions
1. Ensure the sample extract has been exchanged into the applicable final solvent (e.g., MTBE for EPA 508, Hexane for EPA 608/8081B/8082A) prior to performing the sulfur cleanup procedure.

2. Add approximately 0.1g of "shiny" copper to the vial, and vortex for approximately two minutes.

   Note: If the extract is for EPA 614 or EPA 8141B in addition to one of the analytical methods listed above, transfer an aliquot of the extract to another vial for the copper cleanup.

3. If sulfur is present, a black precipitate will form. Allow the extract to sit for 2-3 minutes for any additional precipitate to form and settle out.

   If the precipitate does not settle out, additional copper treatments and/or filtration may be required. Contact the Technical Manager for instructions on how to proceed.

4. The sample is now ready for analysis as outlined in Section 10 of the associated analytical SOP.

Attachment 9:
Sulfuric Acid Cleanup

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Work Instruction
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Sulfuric Acid Cleanup Procedures

Method: 3665A

Summary of Procedure
This procedure is based on EPA Method 3665A and is used in conjunction with the following SOPs:

Method	SOP #
EPA 3510C / EPA 3520C	SA-EX-030
EPA 3550C	SA-EX-040
EPA 680	SA-SM-007
EPA 608 (PCBs only) / EPA 8082A	SA-SG-045

The acid cleanup procedure is used for PCBs only. Sulfuric acid is added to the extract, and the vial is shaken. The layers are allowed to separate, and the sample layer is removed. Large organic-soluble compounds that are present in the sample will extract into the acid and are discarded.

Note: This procedure will destroy pesticide compounds. Sulfuric acid cleanups must only be used for PCB samples and cannot be used for samples requesting pesticides by EPA 8081B, EPA 8141B, or EPA 808.

The method blank and LCS must be subjected to the same cleanup steps.

Perform all cleanup steps under a fume hood or in a well-ventilated area.

Reagents
Sulfuric acid (H_2SO_4) – reagent grade, concentrated

Cleanup Instructions
1. Ensure the sample extract has been exchanged into hexane prior to performing the sulfuric acid cleanup.
2. Transfer an aliquot of the extract to a vial for the cleanup. The recommended aliquot volume is 5.0mL.
3. Add approximately 2mL of concentrated sulfuric acid and cap the vial. Mark the vial to denote the total volume on the vial. Also mark the vial to denote the separation of the acid (bottom) layer and the extract (top) layer.
4. Ensure the vial cap is secure, and gently shake the vial. Open the vial, and allow any pressure that has built up to dissipate. Repeat these steps until no pressure is noted when the cap is opened, and then shake the vial for one additional minute. A vortex mixer can also be used.
5. Allow the extract (top) layer and the acid (bottom) layer to separate. This separation may take a few minutes or several hours depending on the nature of the sample extract. Use the marks on the side of the vial to judge if the volume of extract (top) layer is the same as when it was originally added to the vial.

6. Remove the extract (top) layer from the vial using a disposable Pasteur pipette, and transfer the extract to a clean vial. If greater than 80% of the extract is recovered, no additional preparation is necessary.

7. If an emulsion has formed (i.e., there are bubbles or a cloudy area in between the top and bottom layers), add sodium sulfate crystals to the vial and gently stir the top layer with a glass rod. The sodium sulfate should help to break the emulsion so the top layer can be adequately recovered.

8. If the extract has color, perform an additional cleanup by adding 5mL more of concentrated acid and repeating Steps 3-6.

   Note: Use good judgment when determining how many acid cleanups to use. If it takes more than three cleanups to clean the extract, it is recommended to start over with a smaller aliquot of sample or to dilute the extract before proceeding with additional cleanups. A diluted extract can be concentrated back to the equivalent volume after the cleanup steps. Contact the Technical Manager for assistance with this task.

9. The sample is now ready for analysis as outlined in Section 10 of the associated analytical SOP.

Attachment 10:
Florisil Cleanup

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Work Instruction
FEX098:01.28.09.0
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Florisil Cleanup Procedures

Method: 3620C

Summary of Procedure
This procedure is based on EPA Method 3620C and is used in conjunction with the following SOPs:

Method	SOP #
EPA 3510C / EPA 3520C	SA-EX-030
EPA 3550C	SA-EX-040
EPA 608 / EPA 8081B / EPA 8082A	SA-SG-045

The Florisil cleanup uses a solid phase extraction (SPE) cartridge to remove polar interferences in PCB and/or pesticide extracts. After the sample extraction procedure is completed, a measured portion of the pesticide/PCB extract (usually 1mL) is transferred to a 1g Florisil cartridge. The target and non-target compounds are separated by elution with successive solvents at ambient (atmospheric) pressure. The solvent that elutes the target compounds is collected and concentrated to an appropriate final volume, routinely the same volume as the extract applied to the cartridge.

The method blank and LCS must be subjected to the same cleanup steps as the samples.

Perform all transfer and cleanup steps under a fume hood or in a well-ventilated area.

Reagents
Hexane – residue grade or better
Acetone – pesticide quality or equivalent
Methylene chloride – pesticide quality or equivalent
Sodium sulfate – granular, purified at 450-500°C

90:10 Hexane/Acetone Solution – Mix 90mL of hexane with 10mL acetone in a clean glass container. Larger volumes can be prepared at the discretion of the analyst.

60:40 Hexane/Acetone Solution – Mix 60mL of hexane with 40mL acetone in a clean glass container. Larger volumes can be prepared at the discretion of the analyst.

Standards
Florisil Pesticide Check Mix – Prepare a standard in hexane containing the compounds listed in the following table. This standard is equivalent to the ISMA mid-level standard cited in CLP 3/90, Rev 3.1. Alternatively, an EPA 8081 midlevel calibration standard can be used

Compound	Concentration (µg/mL)
Alpha-BHC	0.020
Heptachlor	0.020
Gamma-BHC	0.020
Endosulfan I	0.020
Dieldrin	0.040
Endrin	0.040

Compound	Concentration (µg/mL)
4,4'-DDD	0.040
4,4'-DDT	0.040
Methoxychlor	0.20
TCMX	0.020
DCB	0.020

Cleanup Instructions

1. Ensure sample extract has been exchanged into hexane prior to performing the cleanup.

2. Prepare the manifold and label each Florisil cartridge with the corresponding sample ID.

3. Condition the cartridges as follows:

   - Place the SPE cartridges on the manifold.
   - Rinse each cartridge with 5mL 60:40 hexane/acetone with the valves open. Follow with 5mL methylene chloride. Discard these rinses.
   - Add 5mL 60:40 hexane/acetone to each cartridge.
   - Slowly open the valves to allow hexane/acetone to pass through the sorbent beds to the lower frits, allowing a few drops per cartridge to pass through the manifold to remove all air bubbles.
   - Close the valves when there is at least 1mm of solvent above the solvent bed. Do not allow the cartridges to become dry. If a cartridge becomes dry, repeat the conditioning.

   Caution: Do not allow the SPE cartridge to go dry from this point forward. If the cartridge goes dry, start over with a new SPE cartridge and a new aliquot of extract.

4. Place the receiving flask beneath the corresponding cartridge.

5. Transfer 1.0mL of the sample extract onto the corresponding labeled Florisil column. Open the valve and allow the extract to pass through the cartridge through the sorbent bed at approximately 2mL/minute. When the level of the extract is a few millimeters above the top of the sorbent layer, wash down the sides of the cartridge with 1.0mL of acetone and allow this wash to pass into the sorbent. Close the valve when the solvent layer reaches the top of the column. The solvent that has passed through the cartridges to this point can be discarded.

6. Add 9.0mL of 90:10 hexane/acetone solution to each cartridge. Open the valve and allow the solvent to pass through the cartridge. Collect the eluent. As the solvent level gets to the top of the cartridge's sorbent bed, add two additional 1mL aliquots of hexane to the cartridge and collect these two eluates. The final volume should be 11mL.

7. Adjust the extract volume to the original volume (routinely 1.0mL) using the nitrogen evaporator or hot water bath as outlined in Section 10 of the associated preparation SOP.

8. The sample is now ready for analysis as outlined in Section 10 of the associated analytical SOP.

Quality Control
Each lot of Florisil cartridges must be checked and approved prior to use as follows:

Combine 0.50mL of the 2,4,6-Trichlorophenol solution, 0.50mL of hexane, and 1.0mL of the Florisil Pesticide Check Mix in a clean, glass container. Concentrate to a final volume of 0.50mL and analyze according to SOP SA-SG-045.

Combine 0.50mL of the 2,4,6-Trichlorophenol solution, 0.50mL of hexane, and 1.0mL of the Florisil Pesticide Check Mix in a clean, glass container. Concentrate to a final volume of 0.50mL and perform the cartridge cleanup on this solution as described in Steps 1 through 8. Analyze according to SOP SA-SG-045.

The Florisil cartridge lot is acceptable if all pesticides in the check mix are recovered at 80-110% percent, if the percent recovery of 2,4,6-trichlorophenol is less than 5%, and if no peaks interfering with the target compounds are detected.

Attachment 11:
Gel-Permeation Cleanup (GPC)

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Work Instruction
FEX099.01.28.09.0
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Gel-Permeation Cleanup Procedures

Method: 3640A

Summary of Procedure
This procedure is based on EPA Method 3640A and is used in conjunction with the following SOPs:

Method	SOP #
EPA 3510C / EPA 3520C	SA-EX-030
EPA 3550C	SA-EX-040
EPA 625 / EPA 8270D	SA-SM-033
EPA 8270D (LL)	SA-SM-008
EPA 608 / EPA 8081B / EPA 8082A	SA-SG-045

Gel-Permeation Cleanup (GPC) is a size-exclusion cleanup based on the molecular size of the analytes rather than molecular weight. Molecules are too large to ever enter the GPC bead pores or so small they freely pass through bead pores are considered beyond resolution and are not collected. The remaining molecules (those with sizes between the two limits) are collected based on the elution times of the calibration compounds. GPC is best for samples with large biological molecules such as plant or animal tissues. GPC will not separate the target analytes from petroleum hydrocarbons.

The method blank, LCS, and MS/MSD must be subjected to the same cleanup steps as the samples as a check on recovery of the target compounds.

Perform all transfer and cleanup steps under a fume hood or in a well-ventilated area.

Note: For each 10mL of extract that is loaded onto the GPC instrument, 5mL is lost and routed to the waste reservoir. The remaining 5mL of extract is passed through the GPC instrument and collected in the Zymark tube in a final volume of approximately 150mL of methylene chloride. This is concentrated to a final volume equal to one-half the final volume normally required for that analysis.

> For example: for pesticide analyses by EPA 8081, 10mL of extract is loaded onto the GPC instrument and 5mL of extract is routed to the waste reservoir. The remaining 5mL of extract is passed through the GPC instrument and collected in a final volume of 150mL methylene chloride. This 150-mL extract is evaporated to a final volume of approximately one milliliter, exchanged into hexane, and adjusted to a final volume of 5mL. The 5mL final volume compensates for the 5mL of sample lost in the GPC instrument and is equivalent to the standard initial sample and final extract volumes for this procedure (i.e., 1000mL initial sample volume to 10mL final extract volume).

Reagents
Hexane – residue grade or better

Acetone – pesticide quality or equivalent

Methylene chloride – pesticide quality or equivalent

Sodium sulfate – granular, purified at 450-500°C

90:10 Hexane/Acetone Solution – Mix 90mL of hexane with 10mL acetone in a clean glass container. Larger volumes can be prepared at the discretion of the analyst.

60:40 Hexane/Acetone Solution – Mix 60mL of hexane with 40mL acetone in a clean glass container. Larger volumes can be prepared at the discretion of the analyst.

Standards
2,4,6-trichlorophenol standard – prepare at a concentration of 0.10µg/mL in acetone.

GPC Calibration Mix – prepare a standard in methylene chloride containing the compounds listed in the following table.

Compound	Concentration (mg/mL)
Sulfur	0.080
Perylene	0.020
Methoxychlor	0.20
Corn Oil	25
Bis (2-ethylhexl) phthalate	1.0

GPC PCB Check Mix – prepare a standard in methylene chloride containing PCB-1016/PCB-1260 at 1ug/mL.

GPC Pesticide Spike Mix – prepare a standard in methylene chloride containing the compounds listed in the following table.

Compound	Concentration (µg/mL)
Gamma-BHC (Lindane)	10
Aldrin	10
Heptachlor	10
Endrin	20
4,4'-DDT	20
Dieldrin	20

Cleanup Instructions
1. Ensure sample extract has been exchanged into methylene chloride prior to performing the cleanup.

2. Be certain the GPC has been calibrated appropriately within the last seven days.

3. Filter each 10mL sample to be cleaned using a glass syringe fitted with a 0.45um filter. Transfer each filtered sample into a threaded glass tube. Cover each tube with a screw cap which has been fitted with a septum.

4. Load all filtered samples into the sample tray.

5. Place the corresponding number of appropriately sized Zymark tubes into the collect tray

6. Using the appropriate calibration and method, set up the proper sequence to run the

loaded samples with the software program. Check more than once to be certain the sequence, method, and calibration all match each of the loaded samples.

7. Fill the solvent reservoir with methylene chloride to a level such that it will NOT go dry during the cleanup process.

8. Check tube(s) leading to the waste reservoir to be certain all waste is correctly collected. Also be certain enough space remains in the waste reservoir to collect the anticipated volume of waste from the cleanup process.

9. Start the run sequence using the software program.

10. As the autosampler begins operating, visually check that the solvent pump is operating normally and that there are no leaks in any of the tubing.

11. If the sequence is to run after business hours/overnight, visually check the system before leaving for the day – especially the level of solvent in the solvent reservoir.

12. Concentrate the extract as detailed in Section 10 of the associated preparation SOP.

13. Sample is now ready for analysis as outlined in Section 10 of the associated analytical SOP.

Quality Control

GPC Calibration
The GPC column must be calibrated prior to use, and every seven days thereafter, in order to set the proper collection time for the method. To calibrate the GPC instrument, load 10mL of the GPC Calibration Mix into a designated position on the collect tray. The flow rate should be 5mL/minute (+/- 0.5mL/min), the column pressure between 6 and 10 psi, and the spiking solution fraction is run for 60 minutes. Verify the flow rate using a 10- to 25-mL Class A volumetric flask.

The following criteria must be met for the calibration to pass:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and Methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.
- Columns should be tested with the semivolatiles matrix spiking solution and the GPC time should continue until either after perylene has eluted or until at least 85% of the analytes have recovered, whichever time is longer.
- The retention time shift for the analytes must be <5% when compared to the retention time of the last calibration.

Calibration of Semivolatiles – Initiate column eluate collection just before the elution of bis(2-ethylhexyl)phthalate and after the elution of corn oil. Stop collection just after the elution of perylene but before sulfur elutes.

Calibration of Organochlorine Pesticides/PCBs – Determine the elution times for phthalate, methoxychlor, perylene, and sulfur. A time should be chosen that removes >85% of the phthalate, but collects >95% of the methoxychlor. Stop collection just after the elution of perylene but before sulfur elutes.

Reinject the GPC calibration solution after the appropriate collection and dump times have been set. The retention times for bis(2-ethylhexyl)phthalate and perylene must not vary by more than +/- 5% between calibrations.

GPC Quality Control Samples

Analyze a GPC blank using 5mL of methylene chloride. Concentrate the methylene chloride that passes through the system and analyze using the using the same detectors that will be used to analyze the samples. If the blank exceeds half the reporting limit for the analytes of interest, pump additional methylene chloride through the system for 1-2 hours and analyze a new blank.

When PCB samples are to be cleaned using the GPC, load 10mL of the PCB Check Mix as a sample (after calibration has passed) in order to check that the GC can visually see the AR1660 analytes.

When CLP criteria are required for pesticide samples needing GPC cleanup, load 10mL of the GPC Pest Spike as a sample (after calibration has passed). The recovery from this sample (as reported by GC according to SOP SA-SG-045) must be between 80 and 110%.

Attachment 13:
Zymark Sensor Diagnostic Test and Maintenance Log

ZYMARK SENSOR DIAGNOSTIC TEST AND MAINTENANCE LOG

Turbo Vap #: _____
Date: _____
Initials: _____
Thermometer #: _____

Maintenance Schedule
Weekly: Perform sensor diagnostic test
Empty, clean, and refill water bath, recommended
*See page 1 of logbook for directions.

SENSOR #	1	2	3	4	5	6
INITIAL VALUE						
FINAL VALUE						
% VALUE						
Turbo-Vap Temperature Display Reading (°C)						
Thermometer Temperature Reading (°C)						

If any of the values do not meet the criteria, perform the Bubble Dislodging Procedure and repeat the diagnostic. If the test still fails, the sensor may need replacing. Record any additional maintenance, including sensor replacement, in the space provided below.

Bubble Dislodging Procedure: Insert a clean Zymark tube and using a pumping motion, raise and lower the tube approximately an inch several times.

Criteria:	
Final Value (with empty tube) / Initial Value (without tube) =<67%	90 < Initial Value < 410

Maintenance Performed:
Date & Initials:

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Attachment 14:
Zymark-specific Maintenance Instructions

Zymark Sensor Diagnostic Test

- Lift the concentrator's cover, remove any tubes, and turn the power on.
- Press the SELECT DISPLAYED CONDITION button within 4 seconds.
  The CONDITION and VALUE displays show the current software version, for example:
  [ ][1.0]
  After 3 seconds the displays reflect the pushwheel settings.
  - ⇒ Press the CELL ONE button and keep it depressed for the next step.
    The CONDITION and VALUE displays show the maximum bath temperature rating for cell one's sensor. This tests the Sample Temperature Rating.
    [50][°C]
  - ⇒ Release the CELL ONE button, the CONDITION and VALUE displays show

    COND. VALUE
    [1.2] [10]
    ↑ ↑
    Cell # Sensor Output Value

    The first digit displayed is the sensor location. The remaining digits are the sensor output value. In the above example, the sensor location is 1 and the sensor output value is 210.
  - ⇒ Record initial sensor output value.
  - ⇒ Place a clean, empty Zymark tube into the cell.
  - ⇒ Record the final sensor output value.
- Repeat the above process (marked with an arrow) for cells 2-6.
- When all sensors are tested, press ENDPOINT SELECT to exit the diagnostic.
- Repeat the entire process for all Turbo-Vaps.

Cleaning and Refilling the Water Bath

- Turn the unit off and unplug the power cord.
- Remove all glassware.
- Remove the top plate.
- Carefully lift the rack out of the bath.
- Siphon off the water in the bath.
  - ⇒ Close siphon bulb vent.
  - ⇒ Place siphon's suction tube in the water bath.
  - ⇒ Place drain tubing in sink.
  - ⇒ Squeeze siphon bulb to start.
- Wipe and rinse the bath walls.
- Clean the rack by rinsing with water.
- Replace the rack in the water bath.
- Replace the top plate.
- Place a concentrator tube in *five* positions.
- Pour approximately 1L of distilled water through the empty position.
- Add 15 drops of *Clear Bath*.
- Add more distilled water until the level is AS HIGH AS the initial solvent level in the sample tube without causing an overflow when all six tubes are in position.
- Plug in the power cord and turn the power on.
- Allow 20-30 minutes for the bath to reach temperature, the air to come out of solution, and for most bubbles to dissipate.
- Perform the Bubble Dislodging Procedure.

FEX082:05.08.06:0

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18.0 Revision History

Summary of Changes from Previous Revision:

- Review and revision of this SOP was precipitated by the addition of the microwave extraction procedure to the laboratory's capabilities. This SOP was re-written to incorporate this procedure. All applicable sections (including SOP title) have been revised to accommodate.
- Added requirement to Safety section to ensure sonication is performed in sonabox within fume hood. Section 5.0
- Added reference to the preparation of wipe samples (also performed via sonication) and the Wipe-specific Work Instruction (FQA086). Section 16.1
- Added note regarding Zymark alarm sounding prior to achieving 1mL final volume. Section 10.4.8
- Referenced SOP titles and document control numbers have been revised to reflect current versions.
- Corrected final volume for pesticide and PCB fractions from 10mL to 5mL. Attachment 6

CYANIDE: TOTAL, AMENABLE, AND WEAK ACID DISSOCIABLE

(Methods: Various)

Approvals (Signature/Date):

Andrea Teal February 2, 2010
Andrea Teal Date
Quality Assurance Manager

Benjamin Gulizia February 2, 2010
Benjamin Gulizia Date
Laboratory Director/Lead Technical Director

Ernest B. Walton February 12, 2010
Ernest Walton Date
EH&S Coordinator / Technical Manager

Jerry Lanier March 4, 2010
Jerry Lanier Date
Department Manager

Facility Distribution No. 1 Distributed To: QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of total cyanide, amenable cyanide, and weak acid dissociable (WAD) cyanide via MIDI distillation or Micro distillation followed by colorimetric analysis using the Lachat Autoanalyzer. The routine matrices associated with this procedure are water and soils.

The reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

When total cyanide is requested, the sample is refluxed with a strong acid. The cyanide (as HCN) is released and distilled into an absorber-scrubber containing NaOH solution. The cyanide ion in the absorbing solution is then determined colorimetrically at a wavelength of 570nm. The cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at pH <8 without hydrolyzing to the cyanate ion. After the reaction is complete, a colored complex is formed upon the addition of pyridine-barbituric acid reagent.

When amenable cyanide is requested, the sample is treated with residual chlorine (calcium hypochlorite) for one hour. After one hour, the excess chlorine is destroyed and the sample is distilled and analyzed for cyanide. The cyanide amenable to chlorination is the difference between the total cyanide and the cyanide measured in the sample after treatment with chlorine. If cyanide amenable to chlorination is requested for a soil sample, the sample is extracted with a sodium hydroxide solution. A portion of the leachate is distilled and reported as the extractable cyanide, and a portion of the leachate is treated with chlorine and distilled. The leaching procedure is required because the direct chlorination of the sample may solubilize metal cyanides that will not be recovered by the direct distillation of the soil.

When weak acid dissociable cyanide is requested, the analysis is performed in the same manner as total cyanide except the sample is refluxed with a weak acid (i.e., acetic acid) and buffered with zinc acetate.

This SOP is based on the following methods:

Method Number	Method Type		Analyte
	Preparation	Analytical	
EPA 335.1	X	X	Amenable Cyanide
EPA 335.4	X	X	Total Cyanide
EPA 9012A	X	X	Total Cyanide Amenable Cyanide
EPA 9012B	X	X	Total Cyanide Amenable Cyanide
EPA 9013 (followed by EPA 9012A or EPA 9012B)	X (Soils Only)		Total Cyanide Amenable Cyanide
SM4500-CN^- G (followed by SM4500-CN^- C and SM4500-CN^- E)	X		Amenable Cyanide
SM4500-CN^- I (followed by SM4500-CN^- C and SM4500-CN^- E)	X		Weak Acid Dissociable Cyanide
SM4500-CN^- C (followed by SM4500-CN^- E)	X (Distillation)		Total Cyanide Amenable Cyanide Weak Acid Dissociable
SM4500-CN^- E		X	Total Cyanide Amenable Cyanide Weak Acid Dissociable

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require dilution prior to analysis to reduce or eliminate the interferences.

4.2.2 Carbonates dissolved in the distillate will be released as carbon dioxide in the colorimetric reaction. The carbon dioxide gas will cause air spikes and peak shifts. If carbonates are present in the distillate, add a small portion of hydrated lime (calcium hydroxide) to the distillate and shake the distillate to mix. Filter an aliquot of the treated sample for analysis.

4.2.3 Chlorine and sulfide may be present in samples. Chlorine will cause a negative interference. Sulfide will cause a positive interference with the colorimetric determination of cyanide. The samples must be screened for chlorine and sulfide upon arrival in the lab. Refer to Section 8 for information on the screening procedure.

4.2.4 Nitrates and nitrites can cause a positive interference when the concentration exceeds 10mg/L and certain organic materials are present in the sample. The addition of 2g of reagent grade sulfamic acid to the sample at the time of distillation will eliminate the formation of cyanide from nitrates, nitrites, and organic materials. If nitrates and nitrites are suspected to be present, samples should be screened for their presence upon arrival in the lab. Refer to Section 8 for information on the screening procedure.

4.2.5 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile (or equivalent) gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

Hydrochloric acid is extremely hazardous as an oxidizer, a corrosive, a poison, and is reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Potassium cyanide and sodium cyanide will give off hydrogen cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

Pyridine is flammable and will cause severe irritation to the respiratory tract. It can cause dizziness, headaches, nausea, and shortness of breath. Vapors can cause irritation of the eyes. Contact with the eyes can cause severe irritation, possible corneal burns and eye damage.

Sodium hydroxide is a severe corrosive. Contact with the skin can cause irritation or severe burns and scarring. Contact with the eyes can cause irritation, burns, permanent vision impairment or even blindness.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Acetic Acid[2]	Corrosive Poison Flammable	10ppm TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Cadmium Carbonate	Poison Irritant	0.002mg (Cd)/m^3 TWA	Symptoms of inhalation include respiratory tract irritation, nausea and dyspnea. Ingestion causes salivation, choking, vomiting, stomach pains and diarrhea.
Hydrochloric Acid[2]	Corrosive Poison	5ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Potassium Cyanide, Sodium Cyanide	Poison Corrosive	5mg/m^3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Potassium Permanganate	Oxidizer	5mg/m^3 for Mn Cmpds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Pyridine	Flammable Irritant	5ppm TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Sodium Arsenite	Poison Reproductive Hazard Carcinogen	0.010 mg(As) / m^3 TWA	Symptoms of inhalation include respiratory tract irritation. Causes skin irritation, and may be fatal if absorbed through skin.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Sodium Hydroxide	Corrosive	2mg/m^3 Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid[2]	Corrosive Oxidizer Dehydrator Poison Carcinogen	1mg/m^3 TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
[2]Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Lachat Quickchem 8000

Analytical Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Magnetic stir plate

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Disposable Transfer Pipettes – various sizes

Autosampler cups or tubes

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

pH paper – narrow range and wide range; provides a quick and easy way to approximate the pH of a sample to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step.

Residual Chlorine Check Strips – starch iodide strips; provide a quick and easy way to verify if the sample was dechlorinated properly. Store in original, capped container and use within the manufacturer's expiration date.

DPD-Free Chlorine Reagent, Powder Pillows

Lead acetate paper – used to indicate the presence of sulfide

Nitrate/Nitrite test strips

Teflon stir bars

Detergent – used for washing non-disposable labware

Midi-distillation apparatus – purchased from Kimble-Chase

Micro-distillation apparatus – purchased from Hach

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

250mL plastic containers – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

Unless listed elsewhere in this SOP, the expiration dates given below apply.

7.1.1 The expiration date for unopened standards and reagents is the manufacturer's expiration date.

7.1.2 The expiration date for opened stock reagents is the manufacturer's expiration date or 5 years from the date opened, whichever is sooner.

7.1.3 The expiration date for opened stock standards is the manufacturer's expiration date or 3 months from the date opened, whichever is sooner.

7.1.4 The expiration date for prepared reagents is 6 months from the date prepared or the expiration date of the parent reagent, whichever is sooner.

7.1.5 The expiration date for prepared standards is 1 month from the date prepared or the expiration date of the parent standard, whichever is sooner.

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.* Unless stated otherwise in the SOP, all standards and reagents are stored at room temperature.

7.2.1 Preparatory Reagents

7.2.1.1 Blank Matrix – Ottawa Sand. Used for the preparation of soil QC samples.

7.2.1.2 Laboratory Reagent Water – ASTM Type I.

7.2.1.3 Hydrochloric acid and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1.4 Calcium Hypochlorite – reagent grade

7.2.1.5 Calcium Hypochlorite solution (0.35M), $Ca(OCl)_2$ – Combine 5g Calcium hypochlorite to 100mL reagent water and shake before using.

7.2.1.6 Sodium arsenite ($NaAsO_2$) - reagent grade, used to eliminate interferences from chlorine and to destroy the excess chlorine in the cyanide amenable to chlorination procedure.

7.2.1.7 Cadmium carbonate ($CdCO_3$) - reagent grade, used to eliminate interferences from sulfides

7.2.1.8 Sulfamic acid (H_2NSO_3H) - reagent grade, used to eliminate interferences from nitrates and nitrites

7.2.1.9 Sodium hydroxide (NaOH) - reagent grade

CAUTION: Heat will be evolved as the sodium hydroxide is dissolved in the water. Sodium hydroxide solutions are caustic and will cause skin burns and destroy unprotected clothing.

7.2.1.10 Sodium Hydroxide (NaOH) – 1.0N solution (purchased solution) for MicroDist

7.2.1.11 Dilution solution (0.25N sodium hydroxide) - Dissolve 10g of sodium hydroxide in 800mL of reagent water in a 1L volumetric flask. Dilute to volume with reagent water. Transfer the reagent to a 1L **PLASTIC** container.

7.2.1.12 Sodium hydroxide (50%) - Measure 100mL of reagent water into a 400mL beaker. Place the beaker on a magnetic stir plate and add a Teflon stir bar to the beaker. Weigh out 100g of sodium hydroxide into a plastic container. Add a small quantity of the sodium hydroxide from the container to the reagent water in the beaker on the magnetic stir plate. As the sodium hydroxide dissolves, add more of the sodium hydroxide from the beaker until all 100g have been added. Cool and transfer the reagent to a **PLASTIC** container.

7.2.1.13 Sulfuric acid (H_2SO_4) - reagent grade, concentrated

7.2.1.14 Sulfuric acid solution (1:1) - Measure 500mL of reagent water into a 2L beaker. Place the beaker on a magnetic stir plate and add a Teflon stir bar to the beaker. Carefully and slowly add 500mL of concentrated sulfuric acid to the reagent water in the beaker on the magnetic stir plate. Transfer the reagent to a 1L bottle. Do not store reagents in volumetric glassware.

CAUTION: Use extreme caution when preparing this solution. Heat will be evolved as the acid and water combine. This solution will cause skin burns and destroy unprotected clothing.

7.2.1.15 Magnesium chloride hexa-hydrate ($MgCl_2 \cdot 6H_2O$) - reagent grade

7.2.1.16 Magnesium chloride solution - While stirring, add 510g $MgCl_2 \cdot 6H_2O$ in 500mL of reagent water in a 1L volumetric flask. After the salt dissolves, dilute to volume with reagent water. Transfer the reagent to a 1L bottle. Do not store reagents in volumetric glassware.

7.2.1.17 Micro-Dist 7.11M sulfuric acid / 0.79 magnesium chloride solution – Note: This procedure should be performed under a hood as HCl fumes will be released.

Place a 500mL beaker on a top-loading balance and tare the beaker. Place 110.8g of deionized water and add 32.2g magnesium chloride hexa-hydrate. Completely dissolve the magnesium chloride. Slowly add 139g concentrated sulfuric acid in increments of 40g at a time, swirling and allowing to cool. **HCl fumes will be released.** Transfer the solution to a storage container and cover loosely until the solution cools to room temperature. When cool, tightly cap the container.

7.2.1.18 Acetic acid – reagent grade

7.2.1.19 Acetic acid 1:9 – Prepared using 10mL acetic acid and 90mL reagent water.

7.2.1.19 Sodium Acetate Trihydrate – reagent grade

7.2.1.20 Acetic Buffer Solution – Prepared with 410g sodium acetate trihydrate. Add glacial acetic acid until a pH 4-5 is obtained (~500mL). Dilute to 1L with reagent water.

7.2.1.21 Zinc Acetate – reagent grade

7.2.1.22 Zinc Acetate Buffer Solution – Prepared by adding 120g zinc acetate to approximately 500mL reagent water. Bring to 1L final volume with reagent water.

7.2.1.23 Methyl red color indicator stock – purchased from Ricca

7.2.1.24 Methyl red color indicator solution – Prepared by adding 10mL methyl red color indicator stock to 90mL of reagent water.

7.2.2 Analytical Reagents

7.2.2.1 Sodium hydroxide (NaOH) - reagent grade. Record the date opened on the container.

7.2.2.2 Sodium hydroxide solution, 0.25 N - (Diluent solution) Dissolve 10 g NaOH pellets in 800mL DI water. Cool to room temperature and dilute to 1000mL with DI water. Transfer to a labeled plastic container for storage.

7.2.2.3 Barbituric acid ($C_4H_4N_2O_5$) - reagent grade

7.2.2.4 Pyridine (C_5H_5N) - reagent grade

7.2.2.5 Hydrochloric acid (HCl) - concentrated, reagent grade

7.2.2.6 Pyridine-barbituric acid reagent - This solution must be prepared exactly as written and must be prepared under a hood.

Place a stir bar and 15.0g of barbituric acid into a 1000-mL volumetric flask. Wash the walls of the flask with approximately 100mL of reagent water, swirling the flask to wet all of the barbituric acid. Add via a 100-mL glass graduated cylinder, 75.0mL of pyridine. Place the volumetric flask on the stir plate and begin mixing. While mixing, add via a 25-mL graduated cylinder, 15.0mL of concentrated hydrochloric acid. Remove the magnetic stirring bar, bring to volume with reagent water. The solution should become clear when diluted to volume. Transfer this solution to an amber glass container for storage at 4C. For reference only: the pH of this solution should be 5.6 ± 0.2.

7.2.2.7 Potassium dihydrogen phosphate (KH_2PO_4) - reagent grade

7.2.2.9 Phosphate Buffer - To about 800mL DI contained in a 1000mL volumetric flask, add 97.0g KH_2PO_4. Add a magnetic stirring bar and mix vigorously until the salt has dissolved. Remove the magnetic stir bar. Dilute to 1000mL with DI water. Store the solution in a plastic container.

7.2.2.10 Chloramine-T ($1\text{-}CH_3C_6H_4\text{-}4\text{-}SO_2NClNa^*3H_2O$) - reagent grade

7.2.2.11 Chloramine-T reagent - Dissolve by swirling 2.0g Chloramine-T in about 250mL of reagent water contained in a 500mL volumetric flask. Bring to volume with DI water and mix until homogeneous. For reference only: the pH of this solution should be 8.9 ± 0.2. This reagent must be prepared daily.

7.2.2.12 Silver nitrate solution (AgNO3) - purchased at 0.141N

7.2.2.13 Rhodanine indicator - reagent grade

7.3 Standards

Standards must be prepared and documented in accordance with SOP *SA-AN-41: Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive. Unless stated otherwise in the SOP, all standards and reagents are stored at room temperature.

7.3.1 Cyanide Stock Standards

Two stock standards are prepared from different sources of cyanide. The potassium cyanide stock standard is used to prepare the calibration standards and the spiking solution for the LCS and MS/MSD. The sodium cyanide stock standard is used to prepare the initial and continuing verification standards.

Potassium Cyanide (KCN) - reagent grade

KCN Stock Standard, 1000mgCN/L - Transfer 2.503g of KCN and 2g of NaOH into a 1L volumetric flask. Add 400-500mL of reagent water and swirl the flask to dissolve the KCN and NaOH. Dilute to volume with reagent water and transfer the stock standard to a labeled plastic container.

Sodium Cyanide (NaCN) - reagent grade

NaCN Stock Standard, 1000 mgCN/L - Transfer 1.885g of NaCN and 2g of NaOH into a 1L volumetric flask. Add 400-500mL of reagent water and swirl the flask to dissolve the NaCN and NaOH. Dilute to volume with reagent water and transfer the stock standard to a labeled plastic container.

7.3.2 Standardization of the Cyanide Stock Standards

The 1000mg/L cyanide stock standards (KCN and NaCN) are standardized each time an intermediate (10mg/L) is prepared or the 1000mg/L standard goes out of date.

7.3.2.1 Add three 1.0mL aliquots of the 1000mg/L cyanide stock standard into each of three 250mL Erlenmeyer flasks. Add 99mL of the 0.25N dilution solution to each flask. Add 100mL of the 0.25N dilution solution to a fourth Erlenmeyer flask to serve as a blank.

Note: It is important that the pH is above 12 or the indicator will not give a clear endpoint.

7.3.2.2 Add 2-4 drops of rhodanine indicator and a Teflon stir bar to each beaker and place the flask on a magnetic stirrer.

7.3.2.3 Titrate each cyanide solution with 0.0141N silver nitrate. Titrate the solution drop-wise near the endpoint until one drop of the titrant changes the color from yellow to salmon-pink. Record all standardization information into the cyanide stock standard standardization log.

Calculate the concentration of the cyanide stock standard as follows:

$$CN\ (mg\ /\ L) = \frac{Na \otimes Va}{V_x} \otimes 52.04\ \frac{mg}{meq} \otimes \frac{1000\ mL}{1L}$$

Where:
Na = normality of the silver nitrate solution
Va = volume of the silver nitrate solution used in titration (mL)
V_x = volume of cyanide stock standard titrated (mL)

The concentration of the cyanide solution is the average of the three individual calculations:

$$CN_{\ avg} = \frac{CN_{\ 1} + CN_{\ 2} + CN_{\ 3}}{3}$$

7.3.3 Cyanide Intermediate Standards

The intermediate standards are prepared from the cyanide stock standards (after standardization) according to the following equation:

$$V_{stock} = \frac{C_{int} \otimes V_{int}}{C_{stock}}$$

Where:
V_{stock} = volume of stock standard required to prepare the intermediate standard (mL)
C_{stock} = concentration of the cyanide stock standard (mg/L) (use CN_{avg})
C_{int} = concentration of the intermediate standard to prepare (mg/L)
V_{int} = volume of intermediate standard to prepare (mL)

7.3.3.1 KCN Cyanide Intermediate Standard, 10mg/L - To a 1000mL volumetric flask, add V_{stock} mL stock cyanide solution and bring to volume with diluent solution.

7.3.3.2 NaCN Cyanide Intermediate Standard, 10mg/L - To a 1000mL volumetric flask, add V_{stock} mL stock cyanide solution and bring to volume with diluent solution.

7.3.4 Standardization of Cyanide Intermediate Standards

The standardization of the intermediate cyanide standards must occur once per week.

7.3.4.1 Add three 10.0mL aliquots of the 10mg/L Cyanide Intermediate standard into each of three 250mL Erlenmeyer flasks. Add 90mL of 0.25N NaOH into each flask. Add 100mL of the 0.25N dilution solution to a fourth Erlenmeyer flask to serve as a blank.

Note: It is important that the pH is above 12 or the indicator will not give a clear endpoint.

7.3.4.2 Add 2-4 drops of rhodanine indicator and a Teflon stir bar to each beaker and place the flask on a magnetic stirrer.

7.3.4.3 Titrate each cyanide solution with 0.0141N silver nitrate. Titrate the solution drop-wise near the endpoint until one drop of the titrant changes the color from yellow to salmon-pink.

Calculate the concentration of the cyanide stock standard using the calculation in 8.1.3.3.

7.5 Cyanide Calibration and Verification Standards

Use the 10mg/L KCN cyanide working standard to prepare calibration standards as shown below. Calculate the amount needed according to the standardized value of the intermediate stock. Bring all calibration standards to final volume with diluent solution.

Standard Concentration (mg/L)	Final Volume (mL)
0.5	1000
0.3	1000
0.1	1000
0.07	1000
0.04	1000
0.01	1000
0.030	1000
0.005	1000
Cal Blank	100

7.6 ICV/CCV

The ICV and the CCV are prepared from the NaCN Intermediate Cyanide Standard at a concentration of 200ug/L. Add 20mL of the 10mg/L NaCN Intermediate Standard to a 1000mL volumetric flask and dilute to a final volume of 250mL with 0.25N NaOH (diluent solution). Calculate the amount needed according to the standardized value of intermediate stock.

7.7 ICB/CCB

The 0.25N NaOH diluent solution is used as the ICB and CCB.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

Non-drinking water samples are routinely collected in 250mL plastic containers containing 0.5mL NaOH preservative. The preservative should be sufficient to achieve a sample pH of >12.

Drinking water samples are routinely collected in 250mL plastic containers containing 200uL sodium arsenite dechlorination agent. Once collected, 10 drops of 1:1 NaOH preservative is added to the container. The preservative should be sufficient to achieve a sample pH of >12. The dechlorination agent should be sufficient to remove residual chlorine from the sample.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but

not frozen) until the time of preparation (distillation) and analysis. Samples must be distilled and analyzed within 14 days of collection. Distillates must be stored at 4°C (less than 6°C but not frozen) until the time of analysis.

Note: SW-846 Methods 9012A and 9012B require samples to be prepared within 14 days of collection and do not specify an analysis holding time. The laboratory has adopted EPA Region IV guidance (as stated per SC DHEC) for cyanide distillates and requires analysis of the sample within 24 hours of distillation. Therefore, samples must be prepared within 14 days of collection and analyzed within 24 hours of preparation.

Note: If samples are received unpreserved, preservation upon receipt at the laboratory is not performed. A 48-hour holding time is applied.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives and/or de-chlorination agents.

8.1.1 Preservation Checks

8.1.1.1 pH Verification

For each sample,
- Place a piece of pH paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the pH paper.
- If the pH is <12, initiate a Nonconformance Memo. Adjust the sample pH to >12 using 50% NaOH. Do not add more preservative than 1% of the volume of the sample. For example, if the sample volume is 500mL, do not add more than 5mL of preservative.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the pH paper into the sample container. The pH paper dye may bleed into the sample and affect sample results.

8.1.1.2 Residual Chlorine Check

8.1.1.2.1 Residual Chlorine Check Strips

For each sample,
- Place a piece of starch-iodide paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the paper.
- If the paper turns blue or black, residual chlorine is present. Initiate a Nonconformance Memo. Dechlorinate the sample with sodium arsenite.

Note: To avoid cross-contamination, use a separate medicine cup and residual chlorine strip per sample. Do not dip the strip into the sample container.

8.1.1.2.2 Residual Chlorine Powder Pillows - This is the required method for drinking water samples.
- Place the appropriate volume of sample (5mL or 10mL) for the powder pillow that you are using into a disposable medicine cup.
- Add one of the DPD-Free Chlorine Reagent Powder Pillows to the sample in the cup and swirl to mix

- Allow sufficient time for color development – usually 5-10 minutes – according to the manufacturer's recommendation
- If the solution turns pink in color then chlorine is present. Initiate a Nonconformance Memo and dechlorinate the sample with sodium arsenite

8.1.1.3 Sulfide Check

Upon arrival in the laboratory, the sample must be checked with lead acetate paper for the presence of sulfides. Pour a small aliquot of the sample into a plastic cup. Wet a strip of lead acetate paper with acetic acid and test the aliquot. If the lead acetate paper turns black, add cadmium carbonate to the sample and shake the container to mix. Check the sulfide content again with the lead acetate paper. Continue adding cadmium carbonate to the sample until the lead acetate paper no longer turns black when exposed to the sample. Samples treated for sulfide must be filtered immediately to remove the cadmium sulfide (CdS) precipitate from the matrix.

8.1.1.4 Nitrate/Nitrite Check

If nitrates and nitrites are suspected, prior to analysis (but not necessarily upon receipt), samples must be screened for nitrates and nitrites. Pour a small aliquot of the sample into a plastic cup. Test the aliquot with a Nitrate/Nitrite test strip. If the strip indicates the presence of Nitrate/Nitrite, add 2g of reagent grade sulfamic acid to 50mL of sample. Note the addition is performed at the beginning of the distillation process.

8.2 Soil Samples

Soil samples are routinely collected in 250mL plastic containers.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. SW-846 Methods 9012A and 9012B require samples to be prepared within 14 days of collection and do not specify an analysis holding time. The laboratory has adopted EPA Region IV guidance (as stated per SC DHEC) for cyanide distillates and requires analysis of the sample within 24 hours of distillation. Therefore, samples must be prepared within 14 days of collection and analyzed within 24 hours of preparation.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

A preparation batch consists of up to 20 environmental samples and the associated QC items. The minimum QC items required for each digestion batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), a matrix spike duplicate (MSD), and a sample duplicate.

If there is insufficient sample to perform the MS/MSD or sample duplicate, the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated to denote this situation.

Batch QC must meet the criteria given in Attachment 4 of this SOP.

Note: The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water compliance samples, another LCS spiked at the reporting limit must be prepared with each batch.

9.2 Instrument QC

9.2.1 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves.* This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 3 standards and a blank. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

The initial calibration standard concentrations currently in use in the laboratory are defined in Section 7.5. Refer to Section 7.0 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-41.

The regression coefficient (r^2) of the regression curve must be greater than 0.995 for the initial calibration curve to be acceptable.

9.2.2 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The ICV must be within 10% to be acceptable.

Refer to Section 7.0 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.3 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed at the beginning of each day. Continuing calibration blanks must be analyzed after every 10 injections.

Initial and continuing calibration blanks must be <1/2RL to be acceptable.

9.2.4 Continuing Calibration Verification

The initial calibration curve must be verified after every 10 injections (or 2 hours, whichever comes first) with a mid-level standard.

The CCV must be within 10% to be acceptable.

Refer to Section 7.0 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

Remove the samples from the refrigerator and allow them to come to room temperature.

10.1.1 Chlorination Step for Amenable Cyanide

Note: The steps for the chlorination of the samples must be performed under a properly functioning fume hood.

Transfer 50mL of a water sample or 50mL of a soil leachate (Section 10.1.2) to a beaker. A smaller volume of sample or leachate may be used if the cyanide concentration is known to be high.

Place the beaker onto a magnetic stir plate in a fume hood. Add a Teflon stir bar to the beaker and stir the sample.

Check the pH of sample with pH paper. The pH of the sample must be maintained at >11 for the duration of the chlorination procedure.

Test the chlorine level in the sample using potassium iodide-starch paper. If the paper turns blue, residual chlorine is present in the sample. If the test paper is clear, add 0.5mL of calcium hypochlorite solution to the stirring sample. Test the sample again with the potassium iodide-starch paper. If the test paper turns blue, enough calcium hypochlorite solution has been added. If the paper remains clear, add calcium hypochlorite solution until the paper turns blue. An excess of chlorine must be maintained throughout this procedure.

Check the sample every 15 minutes with potassium iodide-starch paper and wide range pH paper. If the KI paper is blue, check the sample again in 15 minutes. If the paper is clear, add a 0.5mL of calcium hypochlorite solution to the sample and check the sample

again with the test paper. Continue adding small volumes of calcium hypochlorite solution until the test paper remains blue.

If the pH >11, check the sample again in 15 minutes. If the pH <11, add a few drops of 50% NaOH and check the pH again. Continue adding small aliquots of 50% NaOH until the pH remains >11.

Continue stirring the sample for a total of 1 hour, checking the chlorine level and pH every 15 minutes and adjusting as needed.

After 1 hour, add approximately 0.5g of sodium arsenite to the stirring sample. Test the sample with potassium iodide-starch paper. If the test paper remains white, add a second 0.5g portion of sodium arsenite to the sample. If the test paper turns blue, add sodium arsenite in 0.5g increments until the test paper remains white. Add approximately 0.5g excess of sodium arsenite to the sample.

The sample is now ready to be distilled and analyzed.

10.1.2 Soil Leaching Procedure

Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Compositing, Homogenization, and Segregation of Samples*.

The pH of the sample must be maintained at pH >10 throughout the leaching procedure. In most cases, the addition of 200mL of 0.25N NaOH will be sufficient to maintain the pH.

Transfer 10g (+/-0.5g) of a homogenized soil sample to a labeled, 250mL plastic container. Record the weight of the sample to the nearest 0.1g.

Add 200mL of 0.25N sodium hydroxide to the container. Cap the container and mix thoroughly. Check the pH with narrow range pH paper. If the pH is not greater than 10, add small aliquots of 50% NaOH to bring the pH above 10.

Securely cap the container and place the container in a rotary spinning device for 16 hours.

Remove the containers from the rotator and allow the samples to settle. Allow the sample leachate to settle and decant into a separate labeled container. Check the pH of the leachate. If the pH is greater than 10, the sample is ready for distillation. If the pH is less than 10, the leaching procedure is repeated with a smaller aliquot of solid.

Note: If the leachate pH is less than 10, the pH of the sample should be determined. If the sample pH is highly acidic the sample is not likely to contain cyanide amenable to the leaching procedure.

10.1.3 Sample Distillation – Midi Distillation

The distillation batch for cyanide may include both soils and liquids. The same method blank and LCS (distilled standards) can be used for both matrices. MS/MSD are required at a frequency of 5% for all matrices.

Remove the samples from the storage refrigerator and allow the samples to come to room temperature. Assemble the distillation apparatus as shown in the manufacturer's manual. Place 50mL of 0.25N NaOH into each absorber tube.

Add the samples to the distillation tubes. Add sulfamic acid if nitrates are present.

Mix the liquid sample by inverting the container several times and transfer 50mL of a liquid sample, the cyanide-amenable-to-chlorination sample, or soil leachate to the distillation tube.

Note: If cyanide-amenable-to-chlorination is requested on a soil matrix, the total cyanide must also be determined on the soil leachate.

Homogenize soil samples by stirring with a stainless steel spatula. Add 1g of the well-mixed soil sample to the distillation tube. Add 50mL of 0.25N sodium hydroxide (dilution solution) to the distillation tube. Record the weight of the sample to the nearest 0.1g on the cyanide distillation log.

Connect the glassware and the tubing. Turn on the pump and the condenser water. Inspect each unit to ensure that there are no leaks in the glassware or in the tubing.

If the sample contains nitrate, add 2g of reagent grade sulfamic acid to the tube before adding the sample.

> If performing total cyanide or amenable cyanide, add 2mL of the magnesium chloride solution followed by 5mL of 1:1 sulfuric acid to each flask through the distillation head. Rinse the inlet tube with a small aliquot of reagent water.
>
> If performing weak acid dissociable cyanide, add 2mL of the acetic buffer and 2mL of the zinc acetate buffer solution to each flask through the distillation head. Add 6-10 drops of the methyl red indicator solution to the sample, followed by approximately 2mL 1:9 acetic acid. Rinse the inlet tube with a small aliquot of reagent water. (Note: sample should turn orange/red in color when methyl red indicator is added. If sample does not change color, add more acetate buffer and re-test.)

Set the timer to 100 minutes and the heating block temperature to approximately 125°C.

After the samples have been distilled, turn off the pump and allow tubes to cool for approximately 20 minutes.

Pour the scrubber solution into a labeled 100mL storage container.

Store the distillate in the dark in the refrigerator until ready to perform the colorimetric analysis. The distillate must be analyzed within 24 hour of distillation and 14 days of collection.

10.1.4 Sample Distillation – Micro-Distillation

Preheat the heater block to 120°C (±3°C). Add 6 mL (±0.1 mL) of sample to the sample tube. The sample shall not be diluted prior to distillation. If the pre-filled collector tubes

are not being used, add 1.5mL (±0.1 mL) of the 1.0N NaOH to each collector tube. Add 0.75mL of the (7.11M/0.79M) sulfuric acid/magnesium chloride solution to each sample tube and immediately cap with a collector tube and press to seal.

Place the assembled tubes into the heater block and heat for approximately 30 minutes. After approximately 30 minutes, remove each tube from the block and immediately pull off the sample tube.

Invert each collector tube and allow it to cool. Mix the distillate and detach the upper portion. Dilute the distillate to 6mL (±0.1 mL) with DI water and mix. The distillate is now sufficiently diluted to 0.25N NaOH and is ready for analysis. Seal the distillate until analysis.

10.2 QC Sample Preparation

The method blank is performed using only the reagents used for the distillation; that is, add 50mL of 0.25N NaOH to the empty distillation unit and assume a sample weight of 1.0g.

Add 0.15mL of the KCN cyanide intermediate solution (10mg/L) to each matrix spike (MS) and matrix spike duplicate (MSD) sample.

The concentration of cyanide added to the liquid sample is:

$$\frac{0.15\,mL \otimes 10\,mg/L}{50\,mL} = \frac{0.00015\,L \otimes 10\,mg/L}{0.050\,L} = 0.030\,mg/L = 30ug/L$$

The concentration of cyanide added to the soil/solid sample is:

$$\frac{0.15\,mL \otimes 10\,mg/L}{(1\,g)(solids)} = \frac{0.00015\,L \otimes 10\,mg/L}{(0.0010\,kg)(solids)} = 1.5\,mg/kg\ (if\ \%\ solids = 100)$$

Where:
(solids) is the decimal equivalent of the percent solids (percent solids/100)

Every day that samples are distilled, two calibration standards are distilled and analyzed. Refer to the standardization section (Section 7) for calculations.

10.3 Analysis

10.3.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

Set up the manifold as shown in the Lachat manual. Fill water containers with fresh DI water.

Place the GRY/GRY line into the pyridine-barbituric acid reagent, the ORN/ORN line into the chloramine-T reagent, the other ORN/ORN line in the phosphate buffer reagent, and the YLW/YLW line into the 0.25N NaOH.

Clamp down the pump platens and turn on the pump. Allow a lag time of 10 minutes to assure a good reagent mix.

Input data system parameters. Place standards and samples into the autosampler and start analysis. After a tray is complete, pump DI water through the manifold for 10 minutes.

10.3.2 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2. Once the calibration has been established and verified with an ICV in accordance with Section 9.2, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.

10.3.3 Sample Analysis

Remove the distillates from the refrigerator and allow them to come to room temperature.

The samples must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to include QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the clock.

10.3.4 Example Analytical Sequence

An example analytical sequence is listed below.

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
ICB	
Samples & Batch QC Items	Up to 10 injections, including QC. Not to exceed 2 hours.
CCV	
CCB	
Samples & Batch QC Items	Up to 10 injections, including QC. Not to exceed 2 hours.
CCV	
CCB	

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review.*

11.1.2 Dilutions

Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the target analyte is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags must be used or qualification in a case narrative provided to the client.

11.1.3 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.1.4 Chemical Relationships

When available, the following chemical relationships must be evaluated for each sample. If these relationships are not met the Department Manager must be contacted immediately.

- Total Cyanide $\geq$ Amenable Cyanide
- Total Cyanide $\geq$ Weak Acid Dissociable Cyanide

11.1.5 Drinking Water Compliance Evaluation

Public water suppliers (PWS) are governed by EPA-specified Maximum Contaminant Levels (MCL) above which indicates noncompliance. The MCL associated with this procedure is 0.20mg/L. Notify the PM immediately via a Nonconformance Memo if any drinking water sample contains a detection above this level.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample
F = Final volume/weight
I = Initial volume/weight
D = Dilution factor
dw = % Moisture decimal equivalent

Note: All dry weight corrections are performed automatically in LIMS.

11.2.4 The concentration of amenable cyanide for liquids is the total cyanide concentration minus the cyanide concentration of the sample after treatment with chlorine as detailed in Section 7.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and annually thereafter, and verified annually in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs).*

12.2 Reporting Limit Verification (RLV)

Reporting limit verifications must be performed initially, and then annually thereafter, for non-routine matrices in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

12.3 Determination of the Instrument Detection Limit (IDL)

The instrument detection limit (IDL) is the concentration of analyte that can be statistically distinguished from the background noise of the instrument. The IDL limit must be determined annually, at a minimum, for each analyte in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs).*

The IDL is defined as three times the average of the standard deviation of seven replicate analyses of the IDL solution performed over three non-consecutive days. The IDL may be elevated above the background noise (blank levels). The current IDL associated with this procedure is given in the Equipment Limit Group (ELG) in LIMS.

12.4 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS, MS/MSD, and SD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data*.

12.5 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), or via acceptable results on a PT study. The CDOC must be documented and routed to the QA Department for filing.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Alkaline distillates – Neutralize before disposal in the sanitary sewer system.

- Pyridine waste for reagents and waste stream from instrument – isolate and transfer to the waste department for disposal as pyridine waste.

- Metals bearing waste – samples (distillation residues) that have had cadmium carbonate and sodium arsenite added to them must be transferred to a waste container and disposed of as metal bearing waste.

15.0 References / Cross-References

- SOP SA-AN-41: *Reagent and Standard Materials Procedures*
- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs)*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual

- Lachat QuickChem Method 10-2004-00-1-A Determination of Cyanide in Water; Revision Date: 6 June 1996.
- *Standard Methods for the Examination of Water and Wastewater*; Online Edition; American Public Health Association: Washington, DC
    - SM4020: *Quality Assurance/Quality Control*
    - SM4500-CN^- C: Cyanide, *Total Cyanide After Distillation*; 1999
    - SM4500-CN^- E: *Cyanide, Colorimetric Method*; 1999
    - SM4500-CN^- G: *Cyanide, Cyanides Amenable to Chlorination after Distillation*; 1999
- *Methods for Chemical Analysis of Water and Wastes*; U.S. EPA Office of Research and Development: Cincinnati, OH, March, 1983
    - EPA 335.1: *Cyanide, Amenable to Chlorination (Titrimetric; Spectrophotometric)*; 1974
    - EPA 335.4: *Determination of Total Cyanide by Semi-Automated Colorimetry*; Revision 1.0, August 1993
- *Test Methods for Evaluating Solid Waste, Third Edition On-line*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC
    - EPA 9012A: *Total and Amenable Cyanide (Automated Colorimetric with Off-line Distillation)*; Revision 1, December 1996
    - EPA 9012B: *Total and Amenable Cyanide (Automated Colorimetric with Off-line Distillation)*; Revision 2, November 2004
    - EPA 9013: *Cyanide Extraction Procedure for Solids and Oils, Automated Ferricyanide AAII)* ; Revision 0, July 1992

16.0 Method Modifications and Clarifications

16.1 This procedure may be modified to analyze other matrices based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project. Wipe, waste, and tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.), and soil QC limits to evaluate wipe, waste, and tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. Ottawa sand is used as the blank matrix for tissue samples unless a "true" tissue matrix is required by the project.

16.2 SW-846 Methods 9012A and 9012B require samples to be prepared within 14 days of collection and do not specify an analysis holding time. The laboratory has adopted EPA Region IV guidance (as stated per SC DHEC) for cyanide distillates and requires analysis of the sample within 24 hours of distillation.

16.3 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory defaults to 50-150%.

16.4 Currently, only total cyanide water samples are prepared using the Micro distillation procedure. Total cyanide soil samples, amenable cyanide samples, and WAD cyanide samples are prepared using the MIDI distillation procedure.

16.5 The reagent volumes utilized have been modified from the reference methods to accommodate the reduced volumes needed for the MIDI distillation and the micro distillation procedures. Method-specified reagent ratios have been maintained.

16.6 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires residual chlorine in cyanide samples be removed with ascorbic acid. Standard Methods 4500 CN^- B advises against the use of ascorbic acid because it can form cyanide during the distillation process. For this reason, the laboratory has chosen to use sodium arsenite as the dechlorination agent as recommended in both SM 4500 CN^- B and EPA 335.4.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting

Attachment 1:
SOP Summary

Sample Preparation and Analysis Summary

When total cyanide is requested, the sample is refluxed with a strong acid. The cyanide (as HCN) is released and distilled into an absorber-scrubber containing NaOH solution. The cyanide ion in the absorbing solution is then determined colorimetrically at a wavelength of 570nm. The cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at pH <8 without hydrolyzing to the cyanate ion. After the reaction is complete, a colored complex is formed upon the addition of pyridine-barbituric acid reagent.

When amenable cyanide is requested, the sample is treated with residual chlorine (calcium hypochlorite) for one hour. After one hour, the excess chlorine is destroyed and the sample is distilled and analyzed for cyanide. The cyanide amenable to chlorination is the difference between the total cyanide and the cyanide measured in the sample after treatment with chlorine. If cyanide amenable to chlorination is requested for a soil sample, the sample is extracted with a sodium hydroxide solution. A portion of the leachate is distilled and reported as the extractable cyanide, and a portion of the leachate is treated with chlorine and distilled. The leaching procedure is required because the direct chlorination of the sample may solubilize metal cyanides that will not be recovered by the direct distillation of the soil.

When weak acid dissociable cyanide is requested, the analysis is performed in the same manner as total cyanide except the sample is refluxed with a weak acid (i.e., acetic acid) and buffered with zinc acetate.

Analytical Sequence

An example analytical sequence is listed below.

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
ICB	
Samples & Batch QC Items	Up to 10 injections, including QC. Not to exceed 2 hours.
CCV	
CCB	
Samples & Batch QC Items	Up to 10 injections, including QC. Not to exceed 2 hours.
CCV	
CCB	

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Listed below are the routine sample collection containers, preservatives, and holding times:

Matrix	Sample Container	Minimum Sample Size	Preservation	Dechlorination Agent	Holding Time[1]
Water (Non-DW)	250mL Plastic	50mL – MIDI 6mL – Micro	NaOH	None	14 Days
Water (DW)	250mL Plastic	50mL – MIDI 6mL - Micro	NaOH	Sodium Arsenite	14 days
Soil	8oz	1g	NA	NA	14 days

[1] Inclusive of preparation and analysis.

Note: Analysis must occur within 24 hours of preparation.

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration (ICAL) - Minimum 4 stds and 1 blank	Daily	$r^2 \geq 0.995$	Recalibrate
Initial Calibration Verification (ICV) - Second Source	After each ICAL	Within ±10% of the true value	Recalibrate
Continuing Calibration Verification (CCV)	At the beginning and end of the analysis, and after every 10 samples (or 2 hours, whichever comes first)	Within ±10% of the true value	Terminate the analysis, fix the problem and reanalyze the affected samples.
Calibration Blank (ICB/CCB)	After every ICV and CCV	Result < MDL	Terminate the analysis, correct problem and reanalyze the previous 10 samples.
Batch Definition	No more than 20 field samples, prepared together within a 24 hour time period	Not Applicable	Not Applicable
Method Blank	One per batch	Result < MDL	Evaluate according to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	One per batch, when insufficient sample is provided for MS/MSD/SD	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Low-Level Laboratory Control Sample (LLCS)	Drinking Water Only: One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike (MS)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17 *Low recovery may indicate presence

QC Item	Frequency	Criteria	Corrective Action
			of residual chlorine. Recheck fresh portion of sample with DPD pillows.
Matrix Spike Duplicate (MSD)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17 *Low recovery may indicate presence of residual chlorine. Recheck fresh portion of sample with DPD pillows.
Sample Duplicate (SD)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Method Detection Limit Study (MDL)	Upon method/instrument set-up, per analyte/method/matrix combination, and then annually thereafter (Includes MDLV)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Reporting Limit Verification (RLV)	Upon analyte set-up, per analyte/method/matrix combination, and then annually thereafter (for non-routine analytes where MDL Study is not performed)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:
- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE

EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Flow Cell	X							Flush with water, prior to initial analysis and after shutdown.
Pump Tubes	X							Verify none have collapsed. Replace as needed.
Pump Oil	X							Verify sufficient level. Change as needed.
Tubing	X							Inspect daily. Change as needed and is reagent gets into lines.

D=daily; W=Weekly; M=monthly; Q=Quarterly; SA=semi-annually; A=annually; AN=as needed

Contingency Plan
Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual

colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Glassware Cleaning:

Rinse the glassware thoroughly with reagent water to remove all traces of soap. Soap residue that remains in the glassware may cause foaming in the distillation apparatus. The glassware should be rinsed with 10% nitric acid after rinsing with water to remove traces of cyanide and basic active sites and rinsed with deionized water to remove the acid residue.

18.0 Revision History

Summary of Changes from Previous Revision:

GE40:02.27.09:6 (eff. date: 03/27/09) to SA-GE-040, Rev. 7 (eff. date: 04/12/10):

- Updated to new TestAmerica SOP template. Significant formatting and content changes made. Minor editorial changes made. Significant amount of new text has been added.
- Performed comparison of method versus SOP versus laboratory procedures and made revisions and/or notations as needed. SOP has updated to reflect current instrument configuration, standards and reagents and applicable recipes, etc. Expanded method modification and clarification section.
- Revised title of SOP.
- Incorporated Micro Distillation procedures.
- Incorporated WAD cyanide procedures.
- Revised method references to reflect current methods performed.
- Changed the chlorination solution for amenable cyanide (as stated in method and required by SC DHEC). Samples were previously chlorinated with Clorox. They are now chlorinated with calcium hypochlorite.
- Holding time for 9012A/9012B to analyze the distillates was revised to match EPA Region 4 guidance (as required by SC DHEC). The sample must be analyzed within 24 hours of distillation instead of 14 days of collection.
- Added the use of DPD Free Chlorine pillows as the required procedure for drinking water samples. Included information to incorporate this check if MS/MSD fails.
- Revised ICB/CCB criteria to be <1/2RL.
- Changed TWA for sodium arsenite from 0.2mg to 0.010mg.
- Added requirement that if samples are received unpreserved, then a 48-hour holding time is applied.

Summary of Changes:

SA-GE-040, Rev. 7 (eff. date: 04/12/10) to SA-GE-040, Rev. 7A (eff. date: 04/12/10):

- Revised holding time in Section 10.1.3 to reflect 24 hours from distillation in addition to 14 days from collection.

Approval Signature:

Andrea Teal April 13, 2010

Andrea Teal Date
Quality Assurance Manager

SULFIDE: TITRIMETRIC PREPARATION AND ANALYSIS

(Total, Dissolved, Acid Soluble, and Acid Insoluble)

(Methods: EPA 376.1, 9030B, and 9034 and SM 4500-S^{2-} F)

Approvals (Signature/Date):

Andrea Teal December 1, 2009
Andrea Teal Date
Quality Assurance Manager

Benjamin Gulizia November 30, 2009
Benjamin Gulizia Date
Laboratory Director/Lead Technical Director

Ernest B. Walton December 11, 2009
Ernest Walton Date
EH&S Coordinator / Technical Manager

Jerry Lanier December 3, 2009
Jerry Lanier Date
Department Manager

Facility Distribution No. 1 **Distributed To:** QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of total and dissolved sulfide in water and soil samples by titration. This procedure can also be used to determine the acid soluble and insoluble sulfide concentrations of a water and soil samples that have undergone the EPA 9030B distillation procedure.

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

2.1 Sample Preparation

Total Sulfide: treat the sample with zinc acetate and sodium hydroxide. The sulfide is precipitated as zinc sulfide. The precipitate is captured by centrifugation or filtration and reconstituted in reagent water.

Dissolved Sulfide: the insoluble matter (suspended solids, particulates, color) may be removed from an unpreserved sample by pre-treatment with sodium hydroxide and aluminum chloride. The flocculation is allowed to settle and the liquid fraction is decanted and titrated for sulfide.

Note: The sample pre-treatment should be performed in the field.

Acid Soluble Sulfides (distillation): a known volume or weight of sample is placed in a specially designed reaction vessel. The vessel is swept with nitrogen to remove oxygen. The vessel is heated to 70 ± 5°C, and concentrated sulfuric acid is added to the sample under a nitrogen atmosphere which prevents the oxidation of sulfide to sulfate or other sulfur oxides not detected by this procedure. The liberated hydrogen sulfide is swept by the nitrogen flow into a scrubber solution containing zinc acetate. The presence of sulfide is evidenced by a white flocculation, zinc sulfide, in the scrubber solution. The acid soluble fraction includes dissolved hydrogen sulfide, unionized hydrogen sulfide, and acid soluble metal sulfides.

Insoluble Sulfides (distillation): a known volume or weight of sample is placed in a specially designed reaction vessel. The vessel is swept with nitrogen to remove oxygen. The vessel is heated to 100°C and concentrated hydrochloric acid is added to the sample under a nitrogen atmosphere. The liberated hydrogen sulfide is swept by the nitrogen flow into a scrubber solution containing zinc acetate. The presence of sulfide is evidenced by a white flocculation, zinc sulfide, in the scrubber solution. The insoluble sulfide digestion is more rigorous and includes metal sulfides such as iron and tin sulfides.

Note: The laboratory's default procedure will be to use the acid soluble digestion unless both acid soluble and insoluble sulfides are requested.

2.2 Sample Analysis

Sulfide is oxidized to sulfate in the presence of an excess of standardized iodine in an acidic medium. The mass of sulfide present in a sample is proportional to the amount of iodine required to oxidize the sulfide to sulfate. The excess iodine is back titrated with standardized sodium thiosulfate. The addition of starch indicator near the endpoint provides a clear endpoint.

The scrubber solutions are titrated in the same manner as routine samples. These solutions are basic and may require additional 6N HCl to bring the pH into the proper range for the titration. Samples that have undergone the preliminary preparation steps generally do not have matrix interferences or require zinc acetate separation or aluminum chloride flocculation.

This SOP is based on the following methods: EPA 376.1, EPA 9030B, EPA 9034, and SM4500-S^{2-} F. Note: Based on the 2007 Method Update Rule, EPA Method 376.1 is not approved for NPDES work. Standard Methods 4500-S^{2-} F is the approved NPDES method.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.1.5 Aqueous samples must be collected with a minimum of aeration to avoid the oxidation of sulfide to certain sulfur compounds that are not detected by this method.

4.1.6 Highly colored samples may impair the endpoint determination. Color may be diluted out by the addition of Reagent water (which will not affect the titration), or the sulfide can be precipitated with ZnAc and NaOH.

4.1.7 If the starch indicator is added too early in the titration, the iodine will bind with the starch and the titration will yield high bias results. The starch indicator must be added when a pale yellow color remains.

4.1.8 Reducing substances such as thiosulfate, sulfite and various organic compounds interfere with the iodometric titration by reacting with the iodine

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Sulfite, thiosulfate, and hydrosulfite in concentrations which exceed 10mg/L decompose in acid to form sulfur dioxide which will be adsorbed in the zinc acetate scrubber solution. Sulfur dioxide will react with the iodine to yield false positive results. The addition of formaldehyde to the scrubber solution will prevent the sulfur dioxide from reacting with the iodine.

4.2.4 If a substantial amount of solids are present, they may interfere with the stir bar during the reaction time, causing low recoveries due to insufficient stirring.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

Sodium hydroxide is a severe corrosive. Skin contact can cause irritation or severe burns and scarring. Contact with the eyes can instantly cause irritation, burns, permanent vision impairment or blindness. Contact will destroy unprotected clothing.

Acetic acid is a corrosive. Contact with concentrated acetic acid can cause damage to the skin and eyes. Inhalation of concentrated vapors may cause damage to the lining of the nose, throat, and lungs.

Sulfuric acid is an oxidizer, a corrosive, a poison, and is reactive. Contact with the skin can cause severe burns, redness, and pain. Acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage. Contact will destroy unprotected clothing.

Hydrochloric acid is extremely hazardous as an oxidizer, a corrosive, a poison, and is reactive. It must always be handled under a properly functioning fume hood. It has a strong suffocating odor and inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage. Contact will destroy unprotected clothing.

Hydrogen sulfide (H_2S) gas is extremely poisonous. Exposure to large amounts of hydrogen sulfide gas can cause nausea, headaches, diarrhea, and even death. Although very high levels of hydrogen sulfide rarely occur in environmental samples, the analyst must be careful when handling these potentially dangerous samples.

The odor threshold for hydrogen sulfide is between 0.025ug/L and 0.25ug/L. This means you will smell hydrogen sulfide gas (a rotten egg smell) at levels that are not considered toxic -- only bothersome. If the "rotten egg" smell is present when the sample is opened, the analysis of the sample should take place under a ventilation hood, or at a minimum, in a well ventilated area. Do not perform this analysis alone or in an isolated area-make sure that another lab employee is nearby.

The employee needs to follow all guidelines for glassware handling. Hand protection must be utilized when trying to separate ground glass fittings. Latex gloves do not provide protection from cuts from glassware.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS

can be found using the "MSDS Online" button on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Acetic Acid	Corrosive Poison Flammable	10ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Formaldehyde	Poison	260 mg/m^3 -TWA	Inhalation of vapors may cause respiratory irritation leading to frequent bronchial infection. Eye contact causes redness, watering, and itching. Skin contact causes itching, scaling, and reddening or blistering.
Iodine	Poison Corrosive Oxidizer	0.1ppm – Ceiling	Vapors severely irritate and can burn the mucous membranes and respiratory tract. Liquid contact may cause blistering burns, irritation, and pain. Vapors may be severely irritating to the skin. Vapors are severely irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Hydroxide	Corrosive	2mg/m^3 – Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Sulfide	Corrosive	10ppm – TWA 15ppm – STEL	Will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3 – TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5ppm – Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
Note: Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Analytical Balance – Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*

Thermometers – Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*

Centrifuge

10mL burette with 0.02mL increments – Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use)*

Gas evolution apparatus (Attachment 5) consisting of the following:

- 500mL three neck round bottom flask with 24/40 standard taper joints.
- 125mL dropping funnel with Teflon stopcock
  - Rubber stopper
  - Oval stir bars and elongated stir bars
  - Purge gas outlet arm
  - Gas scrubbing bottles
- Tubing: Nalgene, 5/16" ID
- Heating stir plate
- Nitrogen gas with regulator
- Glass dishes for water baths

Note: If insoluble sulfides are to be determined, the glass tubing leading to the scrubber is replaced by Teflon or propylene tubing.

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use).*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use).*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Support Equipment (Verification and Use).*

pH paper (narrow range) – provides a quick and easy way to approximate the pH of a sample to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step.

Lead Acetate (PbAc) Paper

Disposable eyedroppers

Stir Plate

Teflon Stir Bars

Suction bulb

Desiccator

50mL disposable centrifuge tubes

Detergent – used for washing non-disposable labware.

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are purchased with a Certificate of Analysis attesting to purity and are as follows:

Water Samples:

- Total Sulfide: 250mL plastic, containing 2N zinc acetate and NaOH
- Dissolved (Soluble) Sulfide: 300mL glass BOD bottles containing 0.60mL 6N NaOH and 0.60mL $AlCl_3$ solution.

Soil Samples: 4oz glass containers

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

Unless listed elsewhere in this SOP, the expiration dates given below apply.

7.1.1 The expiration date for unopened standards and reagents is the manufacturer's expiration date.

7.1.2 The expiration date for opened stock reagents is the manufacturer's expiration date or 5 years from the date opened, whichever is sooner.

7.1.3 The expiration date for prepared reagents is 6 months from the date prepared or the expiration date of the parent reagent, whichever is sooner.

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.*

Hydrochloric acid and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

Unless otherwise listed, all reagents are stored at room temperature.

7.2.1 Blank Matrix – Ottawa sand; Used for the preparation of soil QC samples

7.2.2 Laboratory Reagent Water – ASTM Type II

7.2.3 Glacial Acetic Acid (CH_3COOH) – reagent grade

7.2.4 Zinc Acetate [$Zn(CH_3COO)_2 \cdot 2H_20$] – reagent grade

7.2.5 Zinc Acetate (2N) – Dissolve 44g of zinc acetate in 80mL of reagent water in a 100mL volumetric flask. Dilute to 100mL with reagent water. Transfer this solution to a glass or plastic container for storage.

7.2.6 Zinc Acetate (0.5M) – Dissolve 110g zinc acetate in 800mL reagent water. Add 1mL of concentrated HCl and dilute to 1L with reagent water. Transfer this solution to a glass or plastic container.

Note: HCl is added to this reagent to prevent the precipitation of zinc hydroxide simultaneously with the zinc sulfide.

7.2.7 Sodium Hydroxide (NaOH) – reagent grade.

7.2.8 Sodium Hydroxide (6N) – In a 100mL volumetric flask, dissolve 24.0g NaOH in 80mL reagent water. Place a stir bar in the volumetric flask, and stir the solution on a stir plate until all of the NaOH has dissolved. Remove the stir bar and dilute to 100mL with reagent water. Transfer this solution to a plastic container for storage.

7.2.9 Formaldehyde (37% solution) – reagent grade

7.2.10 Sulfuric Acid (H_2SO_4) – concentrated; reagent grade

7.2.11 Hydrochloric Acid (HCl) – concentrated; reagent grade

7.2.12 Hydrochloric Acid (6N) – Under a ventilation hood, in a 1L glass beaker, place approximately 400mL of reagent water. Place the beaker on a stir plate. Place a large stir bar in the beaker and begin stirring the water. Slowly add 400mL of concentrated HCl.

Allow this solution to mix until cooled to room temperature. Carefully transfer this solution to a glass or plastic container for storage.

7.2.15 Potassium Iodide (KI) – reagent grade

7.2.16 Starch Solution – reagent grade, commercially prepared. Transfer starch solution to a plastic squirt bottle.

7.2.17 Potassium Iodate (KIO_3) – reagent grade

7.2.18 Potassium Iodate Solution

7.2.18.1 Dry 3-4g of KIO_3 at 180°C for a minimum of two hours. Allow to cool. Transfer to an airtight container, and store in a dessicator until needed for the standardization of the Sodium Thiosulfate Solution.

7.2.18.2 Using an analytical balance, weigh out 1.2 -1.5g of dried KIO_3, measured to the nearest 0.0001g. Quantitatively transfer the weighed KIO_3 to a 250mL volumetric flask, using several aliquots of reagent water to completely transfer the KIO_3. Dilute to volume with reagent water. Mix this solution and transfer to a glass or plastic container.

Calculate the normality of the KIO_3 as follows:

$$N(KIO3) = \frac{A}{35.67 g/eq \otimes 0.25L}$$

Where:
A = weight of KIO_3 (in grams)
35.67g/eq = equivalent weight of KIO_3

Record the normality of the KIO_3 on the Standardization Log.

7.2.19 Sodium Thiosulfate ($Na_2S_2O_3$) Solution (0.025N) – commercially prepared

Note: This solution must be standardized weekly against the Potassium Iodate Solution as detailed below.

7.2.19.1 Rinse a 10mL burette with the Sodium Thiosulfate Solution ($Na_2S_2O_3$). Fill the burette with the $Na_2S_2O_3$.

7.2.19.2 Weigh approximately 3.0g KI (potassium iodide) into each of three 250mL Erlenmeyer flasks. Add approximately 50mL reagent water and a stir bar to each flask. Begin stirring this solution. Add 2mL 6N HCl to the KI solution in each flask. Mix this solution until the KI dissolves.

Treat each flask individually from this point on.

7.2.19.3 Using a volumetric pipette, transfer 2.5mL of the KIO_3 solution to the KI-acid solution.

7.2.19.4 Titrate with 0.025N $Na_2S_2O_3$ to a pale yellow color. Add 1mL of starch indicator solution (the solution will turn blue) and titrate drop-wise to a colorless endpoint. Record the $Na_2S_2O_3$ titer in the Standardization Log.

Note: It is critical the analyst titrate to the palest yellow color distinguishable BEFORE adding the starch indicator otherwise the starch will bind with the excess iodine and cause biased high results.

Titrate the other two standardization aliquots, recording all three titers in the log.

7.2.19.5 Calculate the normality (N) of the $Na_2S_2O_3$ as follows:

$$N = \frac{A \otimes B}{V}$$

Where:
A = mL of KIO_3 titrated
B = N of KIO_3
V = mL $Na_2S_2O_3$ required to reach the endpoint

7.2.19.6 Record the normality of each solution in the Standardization Log.

Calculate the average of the three standardization analyses. Use the average normality in the calculation of the normality of the Iodine Solution.

7.2.20 Iodine (I_2) Solution (0.10N) – commercially prepared

Note: This solution must be standardized weekly and whenever a new bottle is opened as detailed below.

7.2.20.1 Rinse the 10mL burette with the standardized $Na_2S_2O_3$. Fill the burette with the standard $Na_2S_2O_3$ to prepare for titration.

7..2.20.2 Using a volumetric pipette, transfer 2.5mL of 0.10N I_2 to each of three 250mL Erlenmeyer flasks.

7.2.20.3 Add 2mL of 6N HCl and approximately 50mL of reagent water to each of the flasks.

7.2.20.4 Place the flask on a stir plate and add a stir bar. While stirring, titrate the iodide solution with the standardized $Na_2S_2O_3$ to a pale yellow color. Add approximately 1mL of the starch indicator solution, and titrate to a colorless endpoint.

Note: It is critical the analyst titrate to the palest yellow color distinguishable BEFORE adding the starch indicator otherwise the starch will bind with the excess iodine and cause biased high results.

Titrate each of the flasks containing the iodide solution and record the volume (mL) of $Na_2S_2O_3$ required for each standardization in the Standardization Log.

7.2.20.5 Calculate the normality (N) of the I_2 solution as follows:

$$N(I2) = \frac{A \otimes B}{V}$$

Where:
A = mL of standard $Na_2S_2O_3$
B = normality of standard $Na_2S_2O_3$
V = mL of I_2

Record the normalities determined for the I_2 along with the average normality of the iodine solution in the Standardization Log.

Use the average normality in the calculation of the sulfide concentration.

7.2.21 Dessicant – Drierite

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

Unless otherwise listed, all standards are stored at room temperature.

Sodium Sulfide Nonahydrate ($Na_2S \cdot 9H_2O$) – reagent grade. This solid must be stored in a dessicator at all times.
Storage: Dessicator
Expiration:
Unopened: Manufacturer's expiration date or five years from receipt
Opened: Manufacturer's expiration date or five years from receipt

Sulfide Stock Standard (approximately 10,000mg/L S) – In a 100mL volumetric flask, dissolve 7.51g of $Na_2S \cdot 9H_2O$ in 80mL reagent water. Place a stir bar in the solution, and stir on a stir plate until the solid is dissolved. Remove the stir bar and dilute to 100mL with reagent water. Test the solution with narrow range pH paper. The pH must be >9. If the pH is >9, then additional NaOH is added until pH >9 is achieved.
Storage: Room temperature, in 125mL plastic bottle
Expiration: Standardize weekly

Note: This stock solution must be standardized after preparation using the titration procedure given in Section 10. Transfer 0.25mL of the stock standard to a flask containing 2.5mL of 0.10N iodine and 2mL of 6N HCl. Perform the standardization in triplicate and use the average for the preparation of intermediate, spiking, and calibration standards.

8.0 Sample Collection, Preservation, Shipment, and Storage

Refer to Attachment 2 for a summary of bottles types, preservatives, and holding time requirements.

8.1 Aqueous Samples

8.1.1 Total Sulfide

Aqueous samples are routinely collected in 250mL plastic containers containing 2N zinc acetate and NaOH. Samples should be collected with zero headspace.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation and/or analysis. Samples must be prepared and analyzed within 7 days of collection.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives. NCMs must be initiated for samples that are received containing headspace.

8.1.1.1 Preservation Checks

8.1.1.1.1 Sulfide Verification

For each sample, upon sample receipt,
- Visually inspect the sample for a white precipitate indicating the presence of zinc sulfide (ZnS).
- Place a piece of lead acetate (PbAc) paper in a disposable medicine cup.
- Wet the PbAc paper with concentrated acetic acid.
- Pour a few drops of sample into the medicine cup and note the color change of the PbAc paper.
  - If the PbAc paper remains white the sample is properly preserved with zinc acetate (ZnAc).
- If the PbAc paper turns black the sample contains un-precipitated sulfide. Initiate a Nonconformance Memo. Add a small aliquot of 2N ZnAc to the sample container. Shake the sample gently to mix the ZnAc with the sample. Allow the precipitate to settle. Check for the presence of sulfide again and repeat as necessary until all of the sulfide in solution has been precipitated.
- Record the approximate volume of 2N ZnAc added to the sample.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the PbAc paper into the sample container. The PbAc paper dye may bleed into the sample and affect sample results.

8.1.1.1.2 pH Verification

For each sample, upon sample receipt,
- Place a piece of pH paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the pH paper.
- If the pH is not greater than 9, initiate a Nonconformance Memo. Adjust the sample pH to >9 using 6N NaOH.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the pH paper into the sample container. The pH paper dye may bleed into the sample and affect sample results.

8.1.2 Dissolved (Soluble) Sulfide

Aqueous samples are routinely collected in 300mL glass BOD bottles containing 0.60mL 6N NaOH and 0.60mL $AlCl_3$ solution. Samples should be collected with zero headspace.

Note: The sodium hydroxide and aluminum chloride should be added in the field when the sample is taken from its source. If this is not possible, the reagents must be added to the sample upon arrival in the lab and the analysis started as soon as possible.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation and/or analysis. Samples must be analyzed within 7 days of collection.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives. NCMs must be initiated for samples that are received containing headspace.

8.2 Soil Samples

Soil samples are routinely collected in 4oz glass containers. The soil container must be filled completely to avoid any exposure to air.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation and/or analysis. Samples must be analyzed within 14 days of collection.

NCMs must be initiated for samples that are received containing headspace.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

Batch QC must meet the criteria given in Attachment 3 of this SOP.

A preparation / analysis batch consists of up to 20 environmental samples and the associated QC items analyzed together within a 24 hour period.

9.1.1 EPA Method 376.1 – Aqueous Samples

This method does not specify any QC items. The laboratory's minimum default QC items required for each analytical batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). If there is insufficient sample to perform the MS/MSD, this situation must be noted in the Batch Information section of the extraction log.

The routine container supplied for this method is a 250mL container. 250mL is required for analysis. If there is insufficient sample to perform the required matrix spike(s) and/or

sample duplicates, an NCM must be initiated on all affected samples to denote this situation and the LCS must be performed in duplicate (i.e., LCSD). Insufficient sample volume is defined as receiving less than a total of 750g.

MRL LCS for DW
The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples, an LCS at the RL must also be included in the required batch QC.

9.1.2 Standard Methods 4500-S^{2-} F – Aqueous Samples
The minimum QC items required for each analytical batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), a matrix spike duplicate (MSD), and a sample duplicate. If there is insufficient sample to perform the MS/MSD or sample duplicate, this situation must be noted in the Batch Information section of the extraction log.

The routine container supplied for this method is a 250mL container. 250mL is required for analysis. If there is insufficient sample to perform the required matrix spike(s) and/or sample duplicates, an NCM must be initiated on all affected samples to denote this situation and the LCS must be performed in duplicate (i.e., LCSD). Insufficient sample volume is defined as receiving less than a total of 750g.

MRL LCS for DW
The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples, an LCS at the RL must also be included in the required batch QC.

9.1.3 EPA Methods 9030B and 9034 – Aqueous Samples
The minimum QC items required for each analytical batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate. If there is insufficient sample to perform the MS/MSD, this situation must be noted in the Batch Information section of the extraction log.

The routine container supplied for this method is a 250mL container. 250mL is required for analysis. If there is insufficient sample to perform the required matrix spike(s) and/or sample duplicates, an NCM must be initiated on all affected samples to denote this situation and the LCS must be performed in duplicate (i.e., LCSD). Insufficient sample volume is defined as receiving less than a total of 750mL.

9.1.4 EPA Methods 9030B and 9034 – Soil Samples
The minimum QC items required for each analytical batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate. If there is insufficient sample to perform the MS/MSD, this situation must be noted in the Batch Information section of the extraction log.

The routine container supplied for these methods is a 4oz container. 10g is required for analysis. If there is insufficient sample to perform the required matrix spike(s) and/or sample duplicates, an NCM must be initiated on all affected samples to denote this situation and the LCS must be performed in duplicate (i.e., LCSD). Insufficient sample volume is defined as receiving less than a total of 15g.

9.2 Instrument QC

There are no instrument QC items associated with this procedure.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Compositing, Homogenization, and Segregation of Samples*.

10.1.1 Total Sulfide Sample Preparation

Allow samples to come to room temperature before titration. No other sample preparation is required prior to titration unless samples are highly colored or interferences are present.

For highly colored samples and samples with known or suspected interferences, the sulfide must be separated from the interference as follows. The sample must have been properly preserved upon arrival in the lab. The sulfide in a properly preserved sample will be precipitated as zinc sulfide.

10.1.1.1 Draw a line on the sample container indicating the sample level in the container, using a water-proof marker.

10.1.1.2 Shake the sample container vigorously. Pour the sample into centrifuge tubes, cap, and centrifuge at 3/4 speed for approximately 3-5 minutes.

10.1.1.3 Decant the supernatant and discard. Add approximately 25-30mL of DI water to each centrifuge tube and shake vigorously to loosen the precipitate in the bottom of the centrifuge tube.

10.1.1.4 Pour the contents of each centrifuge tube back into the original sample container. Dilute the precipitate back to the volume of the original sample indicated by the black line on the sample container.

10.1.1.5 The prepared sample is titrated as in Section 10.3.

10.1.2 Dissolved (Soluble) Sulfide Sample Preparation – Un-distilled

The dissolved (soluble) sulfide sample should have been prepared in the field prior to arrival in the laboratory. If the dissolved (soluble) sulfide sample was treated in the field

with NaOH and $AlCl_3$, allow the precipitate to settle and decant the supernatant liquid for titration (Section 10.3).

If the sample was not prepared in the field, initiate an NCM. Add 0.6mL of 1N NaOH and 0.6mL of $AlCl_3$ solution to 300mL unpreserved sample. Cap the container, and rotate the container vigorously for 1 minute. Test the pH of the solution with wide range pH paper. The pH should be between 6 and 9. If the pH is not between 6 and 9, add 1N NaOH drop-wise until the proper pH is obtained. Allow the sample to settle 15 minutes or until a clear supernatant can be withdrawn. Withdraw the clear supernatant and titrate as in Section 10.3.

10.1.3 Dissolved (Soluble) Sulfide Sample Preparation – Distilled

10.1.3.1 Distillation Apparatus Set-up

Prepare the distillation apparatus as shown in Attachment 5.

10.1.3.1.1 Fill glass dishes 3/4 full with water and place on the heating/stir plate. Set heating/stir plate setting between 2 and 3. Allow the water to heat for one hour.

10.1.3.1.2 Check the temperature of each water bath to ensure a temperature of 70°C ± 5°C. Adjust each water bath within this range. Record water bath temperatures in the distillation log.

10.1.3.1.3 Using clamps, suspend the 500mL three-neck flask in the water bath. Place an oval stir bar in the three-neck flask.

10.1.3.1.4 With the stopcock closed, carefully fill 125mL dropping funnels with 50mL concentrated sulfuric acid (H_2SO_4). Place the rubber stopper in the top of the dropping funnel. Place the dropping funnel in the center neck of the three-neck flask. Use a clamp to provide support for the dropping funnel.

10.1.3.1.5 Into each of two scrubbing bottles, add 10 ± 0.5mL of 0.5M zinc acetate, 5.0 ± 0.1mL of 37% formaldehyde and 100mL DI water.

10.1.3.1.6 Attach prepared gas scrubbing bottles as shown in Attachment 5.

10.1.3.1.7 Connect the inlet nitrogen tube.

10.1.3.2 Sample Preparation – Soils

10.1.3.2.1 Weigh 10g of the homogenized sample in a weigh boat or into a small beaker. Record the sample ID and the weight of the sample to the nearest 0.1g in the distillation log.

10.1.3.2.2 Remove the nitrogen inlet tube and transfer each sample into separate, labeled reaction vessels. Reagent water is used to completely transfer the samples into the reaction vessels. Replace the nitrogen inlet tube.

10.1.3.2.3 Remove the nitrogen inlet tube and add approximately 250mL of reagent water to each distillation flask. Replace the nitrogen inlet tube.

10.1.3.3 Sample Preparation – Liquids

10.1.3.3.1 Shake the sample vigorously to homogenize the sample.

10.1.3.3.2 Using a volumetric flask or graduated cylinder, quickly measure 250mL of sample. Remove the nitrogen inlet tube and pour the sample aliquot into the three-neck flask. Replace the nitrogen inlet tube. Record the sample ID and sample volume in the distillation log.

10.1.3.4 Distillation Procedure

10.1.3.4.1 Turn nitrogen gas on at the tank. Adjust the regulator so that 3-5 bubbles per second are being produced in each of the gas scrubbers. Purge the system for 15 minutes to remove all oxygen.

10.1.3.4.2 Open the stopcock on the dropping funnel so that the H_2SO_4 is flowing at a rate of about 1 drop/second. When all of the H_2SO_4 has been dropped into the sample, close the stopcock.

10.1.3.4.3 Purge, stir and maintain a temperature of 70 ±5°C for a total of 90 minutes. Record the start time (the time at which the acid began to drop) in the distillation log.

10.1.3.4.4 After 90 minutes, turn off the nitrogen flow, and turn off the heat source. Record the end time (time the nitrogen supply and heat source are turned off) in the distillation log.

10.1.3.4.5 Remove the gas scrubbers from the distillation apparatus. Pour scrubber solutions containing the sample distillate into a 250mL volumetric flask. Rinse the scrubbers with small quantities of reagent water and add to the sample distillate. Dilute the distillate to 250mL using reagent water.

10.1.3.4.6 Transfer the sample to a 250mL plastic container. Label sample container with the sample ID, batch ID, date prepped, and analyst's initials.

10.1.3.4.7 Distillates should be analyzed as soon as possible after distillation. If this is not possible, store distillates at 4°C (less than 6 but not frozen) until analysis.

10.1.3.4.8 Using narrow range pH paper, test the pH of the sample remaining in the distillation flask. Record the pH in the distillation log.

10.1.3.4.9 If the pH is greater than 1, the sample must be redistilled using an amount of acid sufficient to bring the pH to less than 1.

The amount of acid required to bring the pH to less than 1 can be determined by taking an aliquot of sample equivalent to the weight of sample contained in the distillation flask and adding concentrated H_2SO_4 until the pH is less than 1. Record the amount of acid required. When redistilling the sample, add the amount of concentrated acid determined from the aliquot of sample and an excess of 10mL.

10.1.3.4.10 The prepared sample is titrated as in Section 10.3.

10.1.4 Insoluble Sulfide Sample Preparation – Distilled

If both soluble and insoluble sulfides are requested, the sample is prepared according to the procedures in this section. This is a more rigorous digestion that will liberate and collect soluble and insoluble sulfides from the sample. If the sample is to be analyzed only for insoluble sulfides, the sample may be dried (soils or solids) or evaporated (aqueous) prior to the digestion and distillation. Insoluble sulfides are not volatile.

The digestion procedure for the soluble + insoluble or insoluble sulfide is the same as used for the soluble sulfide with the following exceptions:

1) the digestion acid is concentrated hydrochloric
2) the temperature of the digestion is increased to 100°C
3) the tubing between the digestion vessel and the scrubber is changed to Teflon or propylene

10.1.4.1 Distillation Apparatus Set-up

Prepare the distillation apparatus as shown in Attachment 5.

10.1.4.1.1 Fill glass dishes 3/4 full with water and place on the heating/stir plate. Set heating/stir plate setting between 2 and 3. Allow the water to heat for one hour.

10.1.4.1.2 Check the temperature of each water bath to ensure a temperature of 100°C ± 5°C. Adjust each water bath within this range. Record water bath temperatures in the distillation log.

10.1.4.1.3 Using clamps, suspend the 500mL three-neck flask in the water bath. Place an oval stir bar in the three-neck flask.

10.1.4.1.4 With the stopcock closed, carefully fill 125mL dropping funnels with 50mL concentrated hydrochloric acid (HCl). Place the rubber stopper in the top of the dropping funnel. Place the dropping funnel in the center neck of the three-neck flask. Use a clamp to provide support for the dropping funnel.

10.1.4.1.5 Into each of two scrubbing bottles, add 10 ± 0.5mL of 0.5M zinc acetate, 5.0 ± 0.1mL of 37% formaldehyde and 100mL DI water.

10.1.4.1.6 Attach prepared gas scrubbing bottles as shown in Attachment 5.

10.1.4.1.7 Connect the inlet nitrogen tube.

10.1.4.2 Sample Preparation – Soils

10.1.4.2.1 Weigh 10g of the homogenized sample in a weigh boat or into a small beaker. Record the sample ID and the weight of the sample to the nearest 0.1g in the distillation log.

10.1.4.2.2 Remove the nitrogen inlet tube and transfer each sample into separate, labeled reaction vessels. Reagent water is used to completely transfer the samples into the reaction vessels. Replace the nitrogen inlet tube.

10.1.4.2.3 Remove the nitrogen inlet tube and add approximately 250mL of reagent water to each distillation flask. Replace the nitrogen inlet tube.

10.1.4.3 Sample Preparation – Liquids

10.1.4.3.1 Shake the sample aliquot submitted vigorously to homogenize the sample.

10.1.4.3.2 Using a volumetric flask or graduated cylinder, quickly measure 250mL of sample. Remove the nitrogen inlet tube and pour the sample aliquot into the three-neck flask. Replace the nitrogen inlet tube. Record the sample ID and sample volume in the distillation log.

10.1.4.4 Distillation Procedure

10.1.4.4.1 Turn nitrogen gas on at the tank. Adjust the regulator so that 3-5 bubbles per second are being produced in each of the gas scrubbers. Purge the system to remove all oxygen for 15 minutes.

10.1.4.4.2 Open the stopcock on the dropping funnel so that the HCl is flowing at a rate of about 1 drop/second. When all of the HCl has been added into the sample, close the stopcock.

10.1.4.4.3 Purge, stir and maintain a temperature of 70°C for a total of 90 minutes. Record the start time (the time at which the acid began to drop) in the distillation log.

10.1.4.4.4 After 90 minutes, turn off the nitrogen flow, and turn off the heat source. Record the end time (time the nitrogen supply and heat source are turned off) in the distillation log.

10.1.4.4.5 Remove the gas scrubbers from the distillation apparatus. Pour scrubber solutions containing the sample distillate into a 250mL volumetric flask. Rinse the scrubbers with small quantities of DI water and add to the sample distillate. Dilute the distillate to 250mL using DI water.

10.1.4.4.6 Transfer the sample to a 250mL plastic container. Label sample container with the sample ID, batch ID, date prepped, and analyst's initials.

10.1.4.4.7 Distillates should be analyzed as soon as possible after distillation. If it is not possible to analyze right away, store distillates at 4°C (less than 6 but not frozen) until analysis.

10.1.4.4.8 Using narrow range pH paper, test the pH of the sample remaining in the distillation flask. Record the pH in the distillation log.

10.1.4.4.9 If the pH is greater than 1, the sample must be redistilled using an amount of acid sufficient to bring the pH to less than 1.

The amount of acid required to bring the pH to less than 1, can be determined by taking an aliquot of sample equivalent to the weight of sample contained in the distillation flask and adding concentrated HCl until the pH is less than 1. Record the amount of acid required. When redistilling the sample, add the amount of concentrated acid determined from the aliquot and an excess of 10mL.

10.1.4.4.10 The prepared sample is titrated as in Section 10.3.

10.2 QC Sample Preparation

All QC samples are prepared in the same manner as samples using the appropriate steps from Section 10.1.

10.3 Analysis

10.3.1 Remove the samples or distillates from the refrigerator and allow them to come to room temperature. The default procedure is to include QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the batch.

10.3.2 Rinse the 10mL burette with the standardized $Na_2S_2O_3$. Fill the burette with the $Na_2S_2O_3$ to prepare for titration.

10.3.3 Using a volumetric pipette, transfer 2.5mL of standardized I_2 solution into a 500mL or 1000mL glass beaker (beaker size is dependent upon sample size). Place this solution on a stir plate. Add a large stir bar.

10.3.4 Add 2mL of 6N HCl.

10.3.5 Using a permanent marker, mark a line on the sample bottle at the liquid level BEFORE removing any sample.

10.3.6 Remove the beaker from the stir plate. Pipette the entire sample under the surface of the Iodine/HCl mixture using an automated pipetter and 50mL disposable pipettes. Rinse the sample container with DI water and pour washings in the iodine-acid mixture also. Place the beaker back on the stir plate and continue stirring.

10.3.7 Note: If only one sample container was submitted for sulfide analysis, a sample aliquot may be analyzed instead of the entire sample. If this is the case, the sample must be shaken well to mix the sample liquid with the precipitated sulfide.

10.3.8 If the solution turns colorless upon the addition of the sample, check the pH of the solution with pH paper. Place a drop of the sample on the pH paper. Do not dip the pH paper into the sample. If the pH is greater than 2, add 6N HCl in 2mL increments until the pH is less than 2. If the pH is less than 2 and the solution has turned colorless, add 0.10N I_2 in 1mL increments until an orange color persists.

10.3.9 Record the sample ID, method number, matrix, LIMS batch ID, and total amount of I_2 added to the solution in the sulfide run log.

10.3.10 Turn on the stir plate to allow for mixing during titration.

10.3.11 Titrate the sample solution with $Na_2S_2O_3$ to a pale yellow color.

10.3.12 Add 1mL of starch indicator. The solution will turn blue.

Note: It is critical that the analyst titrate to the palest yellow color distinguishable BEFORE adding the starch indicator solution because the starch will bind with the iodine and cause biased high results.

10.3.13 Continue to titrate drop-wise until the sample solution turns colorless. Record the titer in the sulfide run log.

10.3.14 Fill the sample bottle with tap water to the previously marked level. Measure the volume of water in the sample container with a graduated cylinder. The volume of water measured will equal the volume of sample actually titrated if the entire sample aliquot was measured. Record the sample volume titrated in the sulfide run log.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review*.

11.1.1 MS/MSD Evaluation

If the concentration of a target analyte in the un-spiked (native) sample is more than four times the theoretical concentration of the matrix spike, the recovery is not reported and the data is flagged.

11.1.2 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculation to determine final concentration is given as follows:

Liquids

$$\frac{mg\ S}{L} = \frac{(A \otimes B) - (C \otimes D)}{V} \otimes \frac{32.06\ mg\ S}{2\ meq\ I_2} \otimes \frac{1000\ mL}{1\ L}$$

Where:
A = mL of standardized I_2
B = N of I_2
C = mL of standardized $Na_2S_2O_3$
D = N of $Na_2S_2O_3$
V = volume of sample (mL)

Soils

$$\frac{mg\ S}{kg}, dw = \frac{(A \otimes B) - (C \otimes D)}{\frac{W \otimes solids}{FV} \otimes Vt} \otimes \frac{32.06\ mg\ S}{2\ meq\ I_2} \otimes \frac{1000\ g}{1\ kg}$$

Where:
A = mL of standardized I_2
B = N of I_2
C = mL of standardized $Na_2S_2O_3$
D = N of $Na_2S_2O_3$ from Section
W = weight of sample (g)
FV = final volume of the distillate (mL)
Vt = volume of distillate titrated (mL)
solids = (percent solids)/100

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

Method detection limits as generated in accordance with 40CFR Part 136 Appendix B are not applicable to this procedure. The reporting limit is based on the lowest discernable value achievable by the instrument/labware.

The reporting limit must be verified annually (i.e., RLV) in accordance with the procedures outlined in SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

12.2 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (e.g., LCS, MS/MSD, SD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.3 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration

standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.4 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the TestAmerica Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample

disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Acidic residue from the distillation flasks must be neutralized before disposal into the sewer system.

- Non-hazardous acidic and alkaline wastewater and samples must be neutralized before disposal into the sewer system.

15.0 References / Cross-References

- SOP SA-AN-41: *Reagent and Standard Materials Procedures*
- SOP SA-AN-100: *Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06*: Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- *Standard Methods for the Examination of Water and Wastewater*; Online Edition; American Public Health Association: Washington, DC
    - SM4020: *Quality Assurance/Quality Control*
    - SM4500-S^{2-} F: *Sulfide, Iodometric Method*; 2000
- *Methods for Chemical Analysis of Water and Wastes*; U.S. EPA Office of Research and Development: Cincinnati, OH, March, 1983
    - EPA 376.1: *Sulfide (Titrimetric, Iodine)*; 1978
- *Test Methods for Evaluating Solid Waste, Third Edition On-line*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC
    - EPA 9030B: *Acid-Soluble and Acid-Insoluble Sulfides: Distillation*; Revision 2, December 1996
    - EPA 9030B: Titrimetric Procedure for *Acid-Soluble and Acid-Insoluble Sulfides*; Revision 0, December 1996

16.0 Method Modifications and Clarifications

16.1 This procedure may be modified to analyze other matrices (e.g., waste or tissue samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project. Wipe, waste, and tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.), and soil QC limits to evaluate wipe, waste, and tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. Ottawa sand is used as the blank matrix for tissue samples unless a "true" tissue matrix is required by the project.

16.2 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory defaults to 50-150%.

16.3 The laboratory has incorporated the minimum batch QC items as outlined in Section 9.1. Some additional QC items are routinely performed above those required in the reference methods (i.e., LCSD and MS/MSD) to satisfy common regulatory and/or client requests for precision data and/or to facilitate scheduling and data evaluation.

16.4 Based on the 2007 Method Update Rule, EPA Method 376.1 is not approved for NPDES work. Standard Methods 4500-S^{2-} F is the approved NPDES method.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Gas Evolution Apparatus

Attachment 1:
SOP Summary

Sample Preparation Summary

Total Sulfide: treat the sample with zinc acetate and sodium hydroxide. The sulfide is precipitated as zinc sulfide. The precipitate is captured by centrifugation or filtration and reconstituted in reagent water.

Dissolved Sulfide: the insoluble matter (suspended solids, particulates, color) may be removed from an unpreserved sample by pre-treatment with sodium hydroxide and aluminum chloride. The flocculation is allowed to settle and the liquid fraction is decanted and titrated for sulfide.

Note: The sample pre-treatment should be performed in the field.

Acid Soluble Sulfides (distillation): a known volume or weight of sample is placed in a specially designed reaction vessel. The vessel is swept with nitrogen to remove oxygen. The vessel is heated to 70 ± 5°C, and concentrated sulfuric acid is added to the sample under a nitrogen atmosphere which prevents the oxidation of sulfide to sulfate or other sulfur oxides not detected by this procedure. The liberated hydrogen sulfide is swept by the nitrogen flow into a scrubber solution containing zinc acetate. The presence of sulfide is evidenced by a white flocculation, zinc sulfide, in the scrubber solution. The acid soluble fraction includes dissolved hydrogen sulfide, unionized hydrogen sulfide, and acid soluble metal sulfides.

Insoluble Sulfides (distillation): a known volume or weight of sample is placed in a specially designed reaction vessel. The vessel is swept with nitrogen to remove oxygen. The vessel is heated to 100°C and concentrated hydrochloric acid is added to the sample under a nitrogen atmosphere. The liberated hydrogen sulfide is swept by the nitrogen flow into a scrubber solution containing zinc acetate. The presence of sulfide is evidenced by a white flocculation, zinc sulfide, in the scrubber solution. The insoluble sulfide digestion is more rigorous and includes metal sulfides such as iron and tin sulfides.

Note: The laboratory's default procedure will be to use the acid soluble digestion unless both acid soluble and insoluble sulfides are requested.

Sample Analysis Summary

Sulfide is oxidized to sulfate in the presence of an excess of standardized iodine in an acidic medium. The mass of sulfide present in a sample is proportional to the amount of iodine required to oxidize the sulfide to sulfate. The excess iodine is back titrated with standardized sodium thiosulfate. The addition of starch indicator near the endpoint provides a clear endpoint.

The scrubber solutions are titrated in the same manner as routine samples. These solutions are basic and may require additional 6N HCl to bring the pH into the proper range for the titration. Samples that have undergone the preliminary preparation steps generally do not have matrix interferences or require zinc acetate separation or aluminum chloride flocculation.

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Matrix	Methods	Sample Container	Minimum Sample Size	Preservation	Dechlorination Agent	Holding Time [1]
Water: Total Sulfide	EPA 376.1 SM4500S2-F EPA 9034	250mL plastic	250mL	2N ZnAc/NaOH	None	7 days
Solid: Total Sulfide	EPA 9034	4oz glass	5g	None	None	14 days
Water: Dissolved Sulfide	EPA 376.1 SM4500S2-F EPA 9034	300mL glass BOD bottles	250mL	0.60mL 6N NaOH / 0.60mL $AlCl_3$	None	7 days
Solid: Dissolved Sulfide	EPA 9034	4oz glass	5g	None	None	14 days
Water: Acid Soluble	EPA 9030/9034	250mL plastic	250mL	2N ZnAc/NaOH	None	7 Days[2] 8 Hours[3]
Solid: Acid Soluble	EPA 9030/9034	4oz glass	5g	None	None	14 Days[2] 8 Hours[3]
Water: Acid Insoluble	EPA 9030/9034	250mL plastic	250mL	2N ZnAc/NaOH	None	7 Days[2] 8 Hours[3]
Solid: Acid Insoluble	EPA 9030/9034	4oz glass	5g	None	None	14 Days[2] 8 Hours[3]

[1]Unless noted, holding time is from collection to analysis
[2]From collection to distillation (or analysis, if undistilled)
[3]From distillation to analysis

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Batch Definition	Prepared/Analyzed together w/in 24-hr timeframe; not to exceed 20 field samples	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	result <1/2 RL	Evaluate according to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Low-Level Laboratory Control Sample (LLCS)	One per batch (Drinking Water only)	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike (MS)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Sample Duplicate (SD)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Initial Demonstration of Capability (IDOC)	Initially; Per analyst	Within limits listed in the MLG	Refer to SOP SA-QA-06
Continuing Demonstration of Capability (CDOC)	Annually; Per analyst	Within limits listed in the MLG	Refer to SOP SA-QA-06
Reporting Limit Verification (RLV)	Annually, at a minimum	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Inspect the glass joints and connections for leaks and cracks each time the apparatus is used. Replace or repair parts that are defective.

The apparatus should be observed while the distillation and purging process is going on. The presence of a steady stream of bubbles indicates that the system is leak-tight. A distillation unit that does not have a steady stream of bubbles should be inspected for leaks.

Desiccator Maintenance

Upright Desiccators with Doors

The following checks must be performed daily:

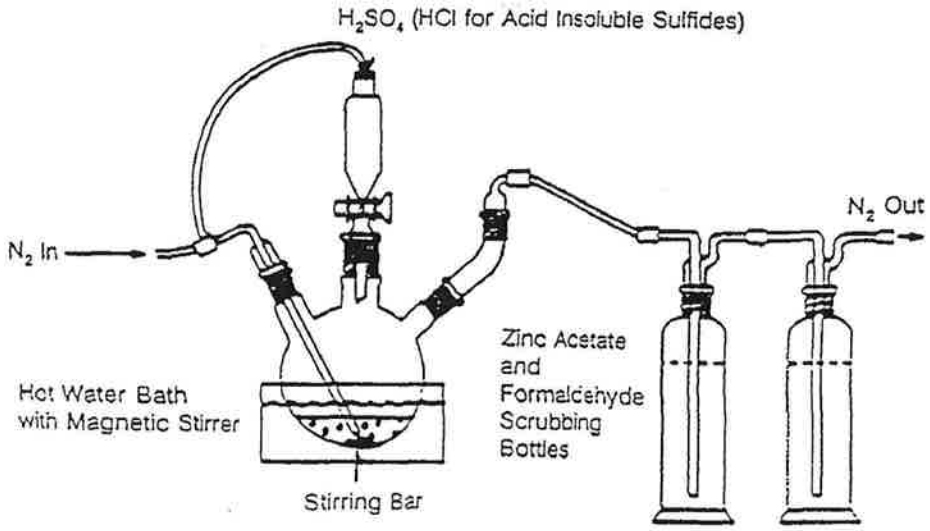
- Desiccant is active
- Hygrometer is in the low humidity zone
- Door is making an air tight seal

The desiccator door must remain closed and seated whenever possible.

When the desiccant turns from blue to light purple, discard desiccant, in accordance with the TestAmerica Savannah Addendum to the EHSM, and refill pan with fresh desiccant.

Contingency Plan
In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
Gas Evolution Apparatus



18.0 Revision History

Summary of Changes from Previous Revision:

- Updated to new TestAmerica SOP template. Significant formatting and content changes made. Minor editorial changes made. Performed review of SOP versus method versus laboratory procedure and made changes as applicable. Updated standards and reagents information/recipes/storage/expiration to reflect current practice. Included additional information into Method Modifications and Clarifications Section.
- Incorporated SOP GE100: *Sulfide by Iodometric Titration.* SOP GE100 has been made obsolete.
- Incorporated information from SOP AN22: *Desiccator Maintenance and Use.* This SOP is now obsolete.
- Revised title of SOP to clarify target analytes.
- Removed method modification allowing pouring the scrubber solution into the beaker as opposed to using a pipette. This modification is no longer allowed, and a pipette must be used. (Per SC DHEC Desk Audit response, 2009)
- Changed routine sample collection container from ZnAc to ZnAc/NaOH.
- Removed reference to pH/Pb/Ac Screening Log. No longer used.
- Revised required batch QC items and included information on determination of insufficient sample for MS/MSD. Added requirement to perform LCS/LCSD if MS/MSD cannot be performed.
- Added Low-Level LCS requirement for drinking water samples.
- Added requirement to perform annual RLV.
- Changed temperature requirements in distillation procedure.
- Added reference to MUR and note that EPA 376.1 is not approved for NPDES.

LIQUID PREPARATION PROCEDURES FOR ICP AND ICP/MS

(Methods: EPA 200.7, 200.8, 3005A, 3010A, SM3030C, and Filtration)

Approvals (Signature/Date):

Andrea Teal September 17, 2009
Andrea Teal Date
Quality Assurance Manager

Benjamin Gulizia September 16, 2009
Benjamin Gulizia Date
Laboratory Director/Lead Technical Director

Ernest B. Walton October 5 2009
Ernest Walton Date
EH&S Coordinator / Technical Manager / Department Manager

Facility Distribution No. 1 **Distributed To:** QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the preparation of metals in water and leachate samples prior to analysis by ICP (SOP SA-ME-070: *Elements by ICP*) or ICP/MS (SOP SA-ME-074: *Elements by ICP/MS*).

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

2.1 Total Recoverable Metals: A known volume of sample, usually 50mL, is transferred to a digestion vessel. The sample is refluxed with dilute nitric acid and hydrochloric acid at approximately 95°C. After the sample has evaporated to approximately 10-20mL, the sample is brought up to the original volume with reagent water. The laboratory utilizes two versions of the Total Recoverable preparation procedure. One version is equivalent to the EPA 3005A procedure and the second procedure is equivalent to the EPA 200.7 and 200.8 procedures.

2.2 Total Metals and TCLP/SPLP Leachates: A known volume of sample, usually 50mL, is transferred to a digestion vessel. The sample is refluxed with nitric acid at approximately 95°C. After the sample has digested, as evidenced by a clear, pale yellow color, HCl is added and the sample is brought up to the original volume with reagent water. This procedure is equivalent to EPA 3010A, and is utilized as the total metals preparation procedure for the EPA 200.7 and EPA 200.8.

2.3 Acid Extractable Metals: A known volume of sample, usually 50mL, preserved with nitric acid, is transferred to a digestion vessel. Hydrochloric acid is added and the sample is heated on a hot block for 15 minutes. The sample is filtered and the final volume adjusted to the original volume. This procedure is equivalent to Standard Methods 3030C.

2.4 Silica Samples for EPA 200.7 and EPA 6010C: Liquid samples are filtered. The filtered liquid samples are analyzed by ICP.

2.5 Drinking water samples for EPA 200.7 and EPA 200.8 with a turbidity concentration of less than 1NTU may be analyzed with no digestion. The exception to this rule is silver, which requires sample digestion prior to analysis. If the sample turbidity is >1NTU, then the EPA 200.7 or the EPA Method 200.8 preparation procedure is used.

2.6 Samples filtered for the determination of dissolved metals do not require digestion if the following criteria are met:

1) The sample has a low COD (<20mg/L);
2) The sample has a turbidity <1NTU ;
3) The sample is colorless with no significant odor ; ***and***
4) The sample is of one liquid phase and is free of suspended particulates or precipitates after acidification.

Note: Generally the lab will digest samples for dissolved metals, even if the above criteria are met, as the presence of organics in the native sample may lead to false positives for arsenic and selenium.

2.7 This SOP is based on the following methods: EPA 200.7, EPA 200.8, EPA 3005A, EPA 3010A, and Standard Methods 3030C.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid and nitric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Turbidity Matrix Interferences

4.2.3.1 The presence of floating debris and coarse sediments which settle out rapidly will give a low reading. Air bubbles will affect the results positively.

4.2.3.2 The presence of true color, that is the color of water which is due to dissolved substances that absorb light, will cause turbidities to be low, although this effect is generally not significant with drinking waters.

4.2.3.3 Light absorbing materials such as activated carbon in significant concentrations can cause low readings.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable latex or nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

Nitric and hydrochloric acids are extremely hazardous as oxidizers, corrosives, poisons, and are reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Nitric acid can cause deep ulcers, and staining of the skin to a yellow or yellow-brown color. These acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Samples that contain high concentrations of carbonates or organic matter, or samples that are at elevated pH can react violently when acids are added. Acids must be added to samples under a hood to avoid splash/splatter hazards and/or possibly toxic vapors that will be given off when the samples are acidified.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS

can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Hydrochloric Acid[2]	Corrosive Poison	5ppm - Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid[2]	Corrosive Oxidizer Poison	2ppm - TWA 4ppm - STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
[2]Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Digestion block – capable of maintaining a sample digestion temperature of 95±5°C. The temperature of the digestion block must be monitored and recorded for each batch. The temperature is measured in a beaker or digestion vessel containing reagent water.

Turbidimeter – Hach Model 2100AN

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

pH paper – provides a quick and easy way to approximate the pH of a sample to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step. pH paper should be checked upon receipt, as follows, to make sure that it is functioning properly.

- Examine the pH paper. If the paper is discolored or looks worn, it may be defective.
- Place a piece of pH paper on a watch glass or other suitable surface and add a few drops of a certified buffer solution onto the paper.
- Compare the color of the pH paper to the reference colors. If the colors match, the paper can be used. If not, acquire new paper.

Detergent – Alconox or equivalent, used for washing non-disposable labware.

Digestion vessels – appropriate volume for use with digestion block. Verify for volume accuracy per lot in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

0.45um polypropylene filters and syringes

Sample Cells for Turbidimeter – clear and colorless. The cells must be kept clean, and discarded when they become scratched or etched.

Disposable Medicine Cups

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

250mL plastic – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP *SA-AN-41: Reagent and Standard Materials Procedures.*

Hydrochloric acid and nitric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

Laboratory Reagent Water – ASTM Type I

Nitric acid (HNO_3): reagent grade. Stable under ordinary conditions of use and storage.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date of opening

Hydrochloric acid (HCl): reagent grade. Stable under ordinary conditions of use and storage.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date of opening

7.3 Standards

Standards must be prepared and documented in accordance with SOP *SA-AN-41: Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

7.3.1 Turbidity Standards

7.3.1.1 Formazin Stock Standard – 7500NTU Hach Ampoule
Storage: Store at room temperature
Expiration: Manufacturer's expiration date

7.3.1.2 Formazin Stock Standard – 4000NTU Hach Solution
Storage: Store at room temperature
Expiration: Manufacturer's expiration date

7.3.1.3 Formazin Calibration Standards

Concentration of Formazin Standard (NTU)	Volume of Formazin Standard (mL)	Final Volume (mL)	Concentration of CAL STD (NTU)
4000	0.50	100	20
4000	5.0	100	200
4000	25	100	1000
4000	30	30	4000

7500	30	30	7500

Expiration and storage: These standards must be prepared fresh on each day of use.

7.3.1.4 Second Source Calibration Verification Standards

Gelex turbidity standards, one standard for each instrument range – Stray Light, 0-2NTU, 0-20NTU, 0-200NTU, and 200-4000NTU.
Storage: Store at room temperature
Expiration: Manufacturer's expiration date

7.3.2 ICP Spiking Solutions

7.3.2.1 ICP Spiking Solution 1 is a solution purchased from SPEX (catalogue number SPIKE-1). The concentrations of the analytes in this solution are listed on the accompanying certificate of analysis.
Storage: Store this solution at room temperature.
Expiration: Replace this solution by the manufacturer's expiration date or sooner if needed or required.

7.3.2.2 Single Element Stock Standards – purchased from CPI, Inorganic Ventures, or equivalent vendor, at the concentrations listed below.

Arsenic (As) – 1000mg/L
Barium (Ba) – 1000mg/L
Boron (B) – 1000mg/L
Cadmium (Cd) – 1000mg/L
Calcium (Ca) – 10000mg/L
Chromium (Cr) – 1000mg/L
Lead (Pb) – 1000mg/L
Magnesium (Mg) – 10000mg/L
Molybdenum (Mo) – 1000mg/L
Potassium (K) – 10000mg/L
Selenium (Se) – 1000mg/L
Silver (Ag) – 1000mg/L
Sodium (Na) – 10000mg/L
Strontium (Sr) – 1000mg/L
Tin (Sn) – 1000mg/L
Titanium (Ti) – 1000mg/L

Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Manufacturer's expiration date.

7.3.2.3 ICP Spiking Solution 2 – Add 1mL of nitric acid and 5mL of hydrochloric acid to a 100-mL volumetric flask containing about 50mL of laboratory reagent water. Add the appropriate volume of each single element stock standard to the flask. Dilute to volume with reagent water, and mix thoroughly. Transfer the spiking solution to a labeled storage container.

Element	Parent Standard	Volume Added	Final Volume	Final Concentration

	Concentration (mg/L)	(mL)	(mL)	(mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Prepare this solution every 180 days or sooner as needed or required. The expiration date must not exceed the expiration date of any of the components.

7.3.2.4 Silica/Silicon Standards

Silicon (Si) stock solutions are usually purchased for this procedure. The following conversion is used to adjust any volumes or concentrations appropriately:

$$Si = \frac{SiO_2}{2.14}$$

7.3.2.4.1 Stock SiO_2 Standard, 10000mg/L Si / 21400mg/L SiO_2 – purchased from CPI. Store at room temperature. This standard must be used by the manufacturer's expiration date or within 6 months from the date of opening, whichever comes first.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Prepare this solution every 180 days or sooner as needed or required. The expiration date must not exceed the expiration date of any of the components.

Silicon (Si) stock solutions are usually purchased for this procedure. The following conversion is used to adjust any volumes or concentrations appropriately:

$$Si = \frac{SiO_2}{2.14}$$

7.3.2.4.2 Intermediate SiO_2 Standard, 467mg/L Si / 1000mg/L SiO_2 – Add 20mL to 30mL of reagent water to a clean, plastic 100-mL volumetric flask. Add the volume of the Stock SiO_2 Standard given in the table below to the volumetric flask. Dilute to volume with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

Element	Conc. Stock SiO_2 Std	Volume Stock SiO_2 Std	Final Volume	Final Conc.

	(mg/L)	(mL)	(mL)	(mg/L)
Silica (SiO_2) [Silicon (Si)]	21400 [10000]	4.67	100	1000 [467]

Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Prepare this solution every 180 days or sooner as needed or required. The expiration date must not exceed the expiration date of any of the components.

7.3.3 ICP/MS Spiking Solutions

7.3.3.1 Single Element Stock Standards – purchased from CPI, Inorganic Ventures, or equivalent vendor, at the concentrations listed below.

Aluminum (Al) – 10000mg/L
Antimony (Sb) – 1000mg/L
Arsenic (As) – 1000mg/L
Barium (Ba) – 1000mg/L
Beryllium (Be) – 1000mg/L
Boron (B) – 1000mg/L
Cadmium (Cd) – 1000mg/L
Calcium (Ca) – 10000mg/L
Chromium (Cr) – 1000mg/L
Cobalt (Co) – 1000mg/L
Copper (Cu) – 1000mg/L
Iron (Fe) – 10000mg/L
Lead (Pb) – 1000mg/L
Magnesium (Mg) – 10000mg/L
Manganese (Mn) – 1000mg/L
Mercury (Hg) – 1000mg/L
Molybdenum (Mo) – 1000mg/L
Nickel (Ni) – 1000mg/L
Potassium (K) – 10000mg/L
Selenium (Se) – 1000mg/L
Silver (Ag) – 1000mg/L
Sodium (Na) – 10000mg/L
Strontium (Sr) – 1000mg/L
Thallium (Tl) – 1000mg/L
Tin (Sn) – 1000mg/L
Titanium (Ti) – 1000mg/L
Vanadium (V) – 1000mg/L
Zinc (Zn) – 1000mg/L

Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Manufacturer's expiration date.

7.3.3.2 ICP/MS Spiking Solution 1 – Add 2mL of nitric acid and 0.5mL of hydrochloric acid to a 100-mL volumetric flask containing about 50mL of laboratory reagent water. Add the

appropriate volume of each single element stock standard to the flask. Dilute to volume with reagent water, and mix thoroughly. Transfer the spiking solution to a labeled storage container.

Element	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Aluminum (Al)	10000	1	100	100
Antimony (Sb)	1000	1		10
Arsenic (As)	1000	0.4		4
Barium (Ba)	1000	2		20
Beryllium (Be)	1000	0.5		5
Boron (B)	1000	2		20
Cadmium (Cd)	1000	0.5		5
Calcium (Ca)	10000	1		100
Chromium (Cr)	1000	2		20
Cobalt (Co)	1000	2		20
Copper (Cu)	1000	2.5		25
Iron (Fe)	10000	1		100
Lead (Pb)	1000	0.5		5
Magnesium (Mg)	10000	1		100
Manganese (Mn)	1000	5		50
Molybdenum (Mo)	1000	2		20
Nickel (Ni)	1000	2		20
Potassium (K)	10000	1		100
Selenium (Se)	1000	0.5		5
Sodium (Na)	10000	1		100
Strontium (Sr)	1000	2		20
Thallium (Tl)	1000	0.5		5
Tin (Sn)	1000	2		20
Titanium (Ti)	1000	2		20
Vanadium (V)	1000	2		20
Zinc (Zn)	1000	2		20

Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Prepare this solution every 180 days or sooner as needed or required. The expiration date must not exceed the expiration date of any of the components.

7.3.3.3 ICP/MS Spiking Solution 2 – Add 10mL of hydrochloric acid to a 100-mL volumetric flask containing about 50mL of laboratory reagent water. Add the appropriate volume of each single element stock standard to the flask. Dilute to volume with reagent water, and mix thoroughly. Transfer the spiking solution to a labeled storage container.

Element	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)

Mercury (Hg)	1000	0.05	100	0.5
Silver (Ag)	1000	0.5		5

Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Due to mercury requirements, prepare this solution every 28 days or sooner as needed. The expiration date must not exceed the expiration date of any of the components.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

8.1.1 Total Metals

Aqueous samples are routinely collected in 250mL plastic containers containing 3mL of a 1:3 nitric acid preservative. The preservative should be sufficient to achieve a sample pH of less than 2.

Although no temperature preservation is required, samples are routinely iced at the time of collection at 4°C (less than 6°C but not frozen). Samples are stored at room temperature until the time of digestion. Samples must be digested and analyzed within 180 days of sample collection. If mercury is requested the samples must be digested and analyzed within 28 days of collection. Digestates are stored at room temperature until the time of analysis.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives.

Note: The holding time for samples from North Carolina that require Standard Method 3030C digestion is 72 hours; that is, the digestion must be initiated within 72 hours of collection.

8.1.2 Dissolved Metals

Aqueous samples for dissolved metals are routinely filtered at the time of sampling and collected in 500-mL plastic containers containing 3mL of a 1:3 nitric acid preservative. The preservative should be sufficient to achieve a sample pH of less than 2.

Although no temperature preservation is required, samples are routinely iced at the time of collection at 4°C (less than 6°C but not frozen). Samples are stored at room temperature until the time of digestion. Samples must be digested and analyzed within 180 days of sample collection. If mercury is requested the samples must be digested and analyzed within 28 days of collection. Digestates are stored at room temperature until the time of analysis.

Note: If the sample is to be filtered in the laboratory, the sample must be collected in 500-mL plastic container with no preservatives. The sample must be stored at 4°C (less than 6°C but not frozen) until filtered. Once filtered, the laboratory will add nitric acid to obtain

a pH of less than 2.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives.

Note: The holding time for samples from North Carolina that require Standard Method 3030C digestion is 72 hours; that is, the digestion must be initiated within 72 hours of collection.

8.1.3 Silica Samples

Aqueous samples for silica are routinely collected in 500-mL plastic containers.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of filtration and analysis. Samples must be filtered and analyzed within 180 days of collection.

NCMs must be initiated for samples collected in improper containers.

Note: Acid preserved samples routinely collected for ICP analyses and acid digested samples should not be used for the analysis of silica. Also note that glass containers should be avoided.

8.1.4 Preservation Checks – pH Verification

For each sample, prior to sample preparation,
- Place a piece of pH paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the pH paper.
- If the pH is outside the range of less than 2, initiate a Nonconformance Memo. Adjust the sample pH to less than 2 using 1:1 nitric acid.
- Mix well and hold for 24 hours. If pH is still greater than 2 repeat the process.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the pH paper into the sample container. The pH paper dye may bleed into the sample and affect sample results.

NOTE: Samples that are not at pH <2 upon arrival in the lab may contain cyanide or sulfide or may be highly buffered. Working under a hood minimizes the hazard that may be caused by the evolution of hydrogen cyanide or hydrogen sulfide upon acidification of the sample. Be aware that acid/base neutralization reaction may be violent and evolve a significant amount of heat.

8.2 TCLP/SPLP Leachate Samples

Once the TCLP/SPLP extraction procedure has been performed, the leachate is transferred to a plastic container and refrigerated at 4°C (less than 6°C with no frozen samples). TCLP/SPLP leachates must be stored at 4°C (less than 6°C with no frozen samples) until the time of preparation and/or analysis. The leachate sample must be digested and analyzed within 180 days of completion of the TCLP/SPLP extraction. If mercury is requested, the leachate sample must be digested and analyzed within 28 days

of completion of the TCLP/SPLP extraction.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 of the associated analytical SOPs provide requirements for evaluating QC data.

9.1 Batch QC

EPA 200.7 and EPA 200.8 – Drinking Water

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The minimum QC items required for each extraction batch are: a method blank and a laboratory control sample (LCS), and a matrix spike (MS) to be performed on a minimum of 10% of samples or one per batch – whichever is greater.

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, and 1 matrix spike.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), and another matrix spike (from sample 11-20).

The routine container supplied for this method is a 250mL container. 50mL is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 25mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 100mL.

Note: There is no method-defined batch precision requirement for this method. For clients who require precision to be reported, the matrix spike must be prepared in duplicate (i.e., MS/MSD). If precision is required for the project and insufficient sample volume is provided to perform the MS/MSD, the LCS must be prepared in duplicate (LCS/LCSD). An NCM must be initiated on all samples within the batch to denote this situation

Note: The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples by EPA Methods 200.7 or 200.8, an LCS at the RL must also be included in the required batch QC.

Batch QC must meet the criteria given in Attachment 3 of the associated analytical SOP.

EPA 200.7 and EPA 200.8 – Clean Water Act

An extraction batch consists of up to 20 environmental samples and the associated QC

items extracted together within a 24 hour period.

The minimum QC items required for each extraction batch are: a method blank and a laboratory control sample (LCS), a matrix spike (MS) to be performed on a minimum of 10% of samples or one per batch – whichever is greater, and a matrix spike duplicate.

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, 1 matrix spike, and a matrix spike duplicate.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), another matrix spike (from sample 11-20), and a matrix spike duplicate.

The routine container supplied for this method is a 250mL container. 50mL is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 25mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 100mL.

Note: There is no method-defined batch precision requirement for this method; however, the EPA does require precision for all samples analyzed under the Clean Water Act. If insufficient sample volume is provided to perform the MS/MSD, the LCS must be prepared in duplicate (LCS/LCSD). An NCM must be initiated on all samples within the batch to denote this situation

Batch QC must meet the criteria given in Attachment 3 of the associated analytical SOP.

EPA Methods 3005A and 3010A and Standard Methods 3030C

A digestion batch consists of up to 20 environmental samples and the associated QC items. The minimum QC items required for each digestion batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD) or a sample duplicate. If there is insufficient sample to perform the MS/MSD or sample duplicate, this situation must be noted in the Batch Information section of the extraction log.

The routine container supplied for this method is a 250mL container. 50mL is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 25mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s) and/or sample duplicates, an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 100mL.

Note: If insufficient sample volume is provided to perform the MS/MSD or MS/SD, the LCS must be prepared in duplicate (LCS/LCSD). An NCM must be initiated on all samples within the batch to denote this situation

Batch QC must meet the criteria given in Attachment 3 of the associated analytical SOP.

9.2 Instrument QC

Details on instrument QC are given in the associated analytical SOPs listed in Section 1.

9.2.1 Turbidimeter Instrument QC

9.2.1.1 Turbidimeter Initial Calibration (ICAL)

The instrument must be calibrated quarterly (every 3 months) in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves*. This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 5 standards and a blank. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

The initial calibration standard concentrations currently in use in the laboratory are as follows:

Standard Level	Concentration (NTU)
1	20
2	200
3	1000
4	4000
5	7500

Refer to Section 7.3 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-41.

Fill the sample cell with 30mL turbidity-free DI water. Apply a thin bead of silicone oil to the cell and spread uniformly. Remove excess oil with a Kimwipe. Place the sample cell in the instrument and press 'enter'. The instrument will give a result after 60 seconds. Repeat for each Formazin calibration standard.

9.2.1.2 Turbidimeter Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

Determine the turbidity of the Gelex standards by applying silicone oil to the prepared standard and placing in instrument. Place lowest NTU Gelex standard in the instrument

first and press 'enter'. The value displayed is used to calculate the true value of the standard. The turbidity of each Gelex standard must be determined three times. The average of these three readings will be used as the true value for the upcoming quarter. The average must be within 15% of the first true value calculated. Repeat for each Gelex standard.

9.2.1.3 Turbidimeter Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed immediately following the initial calibration. Continuing calibration blanks are analyzed after each CCV.

Initial and continuing calibration blanks must be <RL to be acceptable.

If the blank is significantly above 0.50 NTU, the sample cell may be scratched and may need to be replaced.

9.2.1.4 Turbidimeter Continuing Calibration Verification

The initial calibration curve must be verified initially, after every ten samples, and at the end of the analysis with low level Gelex standard (0-2NTU) standard.

The CCV must be within 10% of the true value to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is the low level Gelex standard (0-2NTU) standard.

Note: This continuing calibration verification (CCV) is a second source standard and can also be referred to as the quality control sample (QCS) or the laboratory control sample (LCS).

9.2.1.5 Turbidimeter Reporting Limit Check Standard

The instrument must be verified at the beginning of each batch with a reporting limit check standard.

The RL check standard must be within 50% of the true value to be acceptable.

The RL check standard concentration currently in use in the laboratory is 0.1NTU. Refer to Section 7.3.5 for the standard preparation instructions. Another standard concentration may be used provided the reporting limit for the associated samples are elevated and the standard is fully documented in accordance with SOP SA-AN-41.

9.2.1.6 Turbidimeter Linear Calibration Range

For EPA Method 180.1, the linear calibration range (LCR) must be determined initially as part of an analyst's initial demonstration of capability and verified every 6 months thereafter. The initial demonstration of linearity uses as many standards as necessary to insure the curve is linear. The continued demonstration of linearity consists of a minimum of 3 standards and a blank.

For the linearity to be verified the standards must be within +/- 10% of the initial value to be acceptable. If this criterion is not met, the initial demonstration of linearity must be performed.

Note: This study is not meant to extend the linear range of the calibration. If turbidity is measured at a concentration greater than 40NTU, the sample must be analyzed at a dilution to bring the target analyte into the range of the initial calibration.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 3 of the associated analytical SOP. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample and QC Sample Preparation

Unless otherwise requested, groundwater and surface waters are to be prepared using the total recoverable metals procedure given in Section 10.1.3. TCLP/SPLP samples must be digested for total metals (Section 10.1.4). Note that there are different spiking solutions for routine and TCLP/SPLP matrix spikes.

10.1.1 Dissolved Metals

10.1.1.1 Results reported as "dissolved metals" are defined as the concentrations of analytes in a liquid sample that will pass through a 0.45um membrane filter prior to acidification/preservation. The filtration step can occur in the field or in the laboratory. In either case, the sample must be unpreserved prior to filtration and then filtered using a 0.45um filter.

10.1.1.2 Field filtered samples are usually preserved in the field, immediately after filtration. Unpreserved samples sent to the laboratory for lab filtration must be preserved immediately after filtration.

10.1.1.3 If the laboratory filters the samples, the reagent water used to prepare the method blank and laboratory control samples associated with the "dissolved metals" samples must be filtered through the same type of filter used to filter the field samples.

Note: The LCS should be spiked prior to filtration.

10.1.1.4 A comparison between total and dissolved results is good practice, and logic should follow that total results should be equal or greater than dissolved results, especially if the dissolved metals are lab filtered. Comparable hits with less than 20% RPD should be considered equal. Any other discrepancies should be

discussed with the Department Manager or Supervisor, Technical Manager, or the Project Manager.

10.1.1.5 The laboratory's standard practice is to digest all non-silica liquid samples; however, samples filtered for the determination of dissolved metals do not require digestion if the sample:
- has a low COD (<20mg/L);
- has a turbidity <1 NTU;
- is colorless with no significant odor; ***and***
- is of one liquid phase and free of suspended particulates or precipitates after acidification

10.1.2 Turbidity Determination for Drinking Water Samples

Drinking water samples with a turbidity concentration of less than 1NTU may be analyzed without digestion. The exception to this rule is silver, which requires sample digestion prior to analysis. The turbidity of drinking water samples is checked using the procedures outlined in this section. If the turbidity of the sample is not checked, the digestion procedure must be performed.

10.1.2.1 Turn on turbidimeter and allow it to warm up 15-30 minutes.

10.1.2.2 Verify the instrument is operating properly by the analysis of a continuing calibration verification sample initially, after every 25 samples, and at the end of the run with the lowest available Gelex standard (0-2). The Gelex standard must recover within ±10% of the true value to be acceptable.

10.1.2.3 Analyze a DI water blank (CCB). The DI water blank must be less than 1NTU to be acceptable. If the DI water blank is greater the 1NTU, check to be certain the sample cell is clean. If the blank is significantly above 1NTU, the sample cell may be scratched and may need to be replaced.

10.1.2.4 Determine the turbidities for all samples by filling the cell with sample and placing the cell in the sample well of the turbidimeter. Record these turbidities in the Metals Turbidity Logbook. Be certain to rinse the cells between samples with DI water to avoid contamination.

10.1.3 Total Recoverable Metals (EPA 3005A)

This digestion procedure is used to prepare aqueous samples for total recoverable metals determination by ICP and ICP/MS.

10.1.3.1 Transfer a 50mL aliquot (or an appropriate volume diluted to 50mL with reagent water) of a well-mixed sample to a 50mL digestion block vial.

Note: If there is not sufficient volume to use a 50mL aliquot, the lab can use a smaller volume of sample, proportional volumes of reagents, and adjust the final digestate volume back to the original volume of the sample used. For example, if 25mL of sample is digested, one half of the routine volumes of reagent are used and the final volume of the digestate is brought back to 25mL. When a smaller

aliquot is used, the digestion analyst must be careful not to allow the sample digest to evaporate completely.

10.1.3.2 Add 50mL of reagent water to a digestion block vial to serve as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for contamination that may be due to glassware, reagents, or sample handling.

10.1.3.3 Add 0.50mL of the appropriate spiking solutions to a 50-mL aliquot of reagent water to serve as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 50-mL aliquot of reagent water with 0.50mL of the appropriate spiking solutions.

Analytical Method	Matrix	QC	Spiking Solutions
6010	Aqueous	LCS/MS/MSD	(Spex) ICP Spike 1 ICP Spike 2
6020	Aqueous	LCS/MS/MSD	ICP/MS Spike 1 ICP/MS Spike 2

10.1.3.4 Add 0.50mL of the appropriate spiking solutions to each of two 50mL aliquots of the client sample designated as the matrix spike samples (MS and MSD).

10.1.3.5 Add 2.5mL of concentrated HCl and 1.0mL of concentrated HNO_3 to each sample. Gently heat the digestion vessel until the sample refluxes. The sample must not be heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the digestion vessel. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the sides of the digestion vessel and fall back into the digestion vessel. Evaporate the sample until the volume is approximately 15mL. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

Note: If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

10.1.3.7 Wash down the inside of the digestion vessel with reagent water. Dilute the sample digestate to 50mL with reagent water.

Note: The digestate may be diluted to a volume less than the original volume if sample pre-concentration is required to meet lower reporting limits. The pre-concentration must be limited to a factor of four.

10.1.3.8 The sample is now ready for analysis via the appropriate analytical SOP.

10.1.4 Total Metals (EPA 3010, EPA 200.7, and EPA 200.8)

This digestion procedure is used for the preparation of aqueous samples for total metal determination by ICP and ICP/MS.

10.1.4.1 Transfer a 50mL aliquot (or an appropriate volume diluted to 50mL with reagent water) of a well-mixed sample to a 50mL digestion block vial.

Note: If there is not sufficient volume to use a 50mL aliquot, the lab can use a smaller volume of sample, proportional volumes of reagents, and adjust the final digestate volume back to the original volume of the sample used. For example, if 25mL of sample is digested, one half of the routine volumes of reagent are used and the final volume of the digestate is brought back to 25mL. When a smaller aliquot is used, the digestion analyst must be careful not to allow the sample digest to evaporate completely.

10.1.4.2 Add 50mL of reagent water to a digestion block vial to serve as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for contamination that may be due to glassware, reagents, or sample handling.

10.1.4.3 Add 0.50mL of the appropriate spiking solutions to a 50-mL aliquot of reagent water to serve as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 50-mL aliquot of reagent water with 0.50mL of the appropriate spiking solutions.

Analytical Method	Matrix	QC	Spiking Solutions
6010 / 200.7	Aqueous	LCS/MS/MSD	(Spex) ICP Spike 1 ICP Spike 2
6020 / 200.8	Aqueous	LCS/MS/MSD	ICP/MS Spike 1 ICP/MS Spike 2

10.1.4.4 Add 0.50mL of the appropriate spiking solutions to two 50mL aliquots of the client sample designated as the matrix spike samples (MS and MSD).

10.1.4.5 Add 1.5mL of concentrated HNO_3 to each sample. Gently heat the digestion vessel until the sample refluxes. The sample must not be heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the digestion vessel. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the sides of the digestion vessel and fall back into the digestion vessel. Evaporate the sample until the volume is approximately 5-10mL. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

Note: If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

10.1.4.6 Remove the digestion vessels from the digestion block and cool the digestion vessels to room temperature. Add another 1.5mL portion of concentrated HNO_3. Continue heating the sample on the digestion block. Again, at the proper temperature, the sample should gently reflux in the digestion vessel. Do not allow the sample to boil.

10.1.4.7 Continue heating the sample and adding additional 1.5mL portions of concentrated HNO_3 until the digestate is light in color or does not change in appearance after subsequent additions of HNO_3. If a sample requires more than 6mL of acid to digest, contact the Department Manager for guidance.

10.1.4.8 Evaporate the digestate until the volume is approximately 5-10mL.

10.1.4.9 Add 2.5mL of concentrated HCl and warm the sample digestate for 15 minutes.

10.1.4.10 Wash down the inside of the digestion vessel with reagent water. Dilute the sample digestate to 50mL with reagent water.

Note: The digestate may be diluted to a volume less than the original volume if sample pre-concentration is required to meet lower reporting limits. The pre-concentration should be limited to a factor of four.

10.1.4.11 The sample is now ready for analysis via the appropriate analytical SOP.

10.1.5 Total Metals and TCLP/SPLP Samples (EPA 3010)

This digestion procedure is used for the preparation of TCLP/SPLP leachate samples for total metal determination by ICP. Note that the LCS is spiked with the routine analytes to allow the TCLP/SPLP samples to be digested along with aqueous samples.

10.1.5.1 Transfer a 5mL aliquot (diluted to 50mL) for TCLP or a 50mL aliquot for SPLP of a well-mixed sample to a clean 50mL digestion vessel. Larger volumes may be digested at the discretion of the lab. The volume of spike solution added should be adjusted proportionately.

10.1.5.2 Add 5mL of extraction fluid diluted to 50mL for TCLP or 50mL for SPLP to a digestion vessel to serve as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for contamination that may be due to glassware, reagents, or sample handling. A blank for each type of extraction fluid must be digested and analyzed.

10.1.5.3 Add 0.50mL of the appropriate spiking solutions to a 5mL aliquot of extraction fluid diluted to 50mL for TCLP or to a 50mL aliquot of extraction fluid for SPLP. This is designated as the laboratory control spike (LCS). If required, perform a LCSD by following the same procedure as the LCS. The routine ICP spiking solution is used for the TCLP/SPLP LCS because of frequent client requests for reporting more analytes from the TCLP/SPLP leachate than are currently regulated. Preparing an LCS with all of the target analytes eliminates re-digestion and provides QC for the requested analytes.

Note: If both Extraction Fluid 1 and Extraction Fluid 2 are included in the batch, use Extraction Fluid 1 for the LCS and LCSD. Refer to SOP EX15: *Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP)* for information on the TCLP/SPLP extraction fluids.

Analytical Method	Matrix	QC	Spiking Solutions
6010	TCLP/SPLP	MS	(Spex) ICP Spike 1 ICP Spike 2
6010	TCLP/SPLP	LCS	(Spex) ICP Spike 1 ICP Spike 2

10.1.5.4 For the matrix spike, add 0.50mL of each ICP spiking solution (1 and 2) to a separate 5mL aliquot of the client sample (diluted to 50mL) for TCLP or to a

separate 50mL aliquot of the client sample for SPLP designated as the matrix spike.

Note: The TCLP/SPLP digestion batch consists of twenty or fewer field samples and the associated QC items. A TCLP/SPLP digestion batch must not exceed 20 field samples. Every TCLP/SPLP digestion batch will have a method blank (MB), a laboratory control sample (LCS), and a matrix spike (MS).

10.1.5.5 Add 1.5mL of concentrated HNO_3 to each sample. Gently heat the digestion vessel until the sample refluxes. The sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the digestion vessel. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the sides of the digestion vessel and fall back into the digestion vessel. Evaporate the sample until the volume is approximately 5mL. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

Note: If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

10.1.5.6 Remove the digestion vessels from the digestion block and cool the digestion vessels to room temperature. Add another 1.5mL portion of concentrated HNO_3. Continue heating the sample on the digestion block. Again, at the proper temperature, the sample should gently reflux in the digestion vessel. Do not allow the sample to boil.

10.1.5.7 Continue heating the sample and adding additional 1.5mL portions of concentrated HNO_3 until the digestate is light in color or does not change in appearance after subsequent additions of HNO_3. If a sample requires more than 6mL of acid to digest, contact the Department Manager for guidance.

10.1.5.8 Evaporate the digestate until the volume is approximately 5-10mL.

10.1.5.9 Add 2.5mL of concentrated HCl and warm the sample digestate for 15 minutes.

10.1.5.10 Wash down the inside of the digestion vessel with reagent water. Dilute the sample digestate to 50mL with reagent water.

10.1.5.11 The sample is now ready for analysis by ICP.

10.1.6 Acid-Extractable Metals (SM3030C)

This digestion procedure is used for the preparation of aqueous samples for acid-extractable metals by ICP and ICP/MS.

10.1.6.1 Transfer a 50mL aliquot (or an appropriate volume diluted to 50mL with reagent water) of a well-mixed sample to a 50mL digestion block vial.

Note: If there is not sufficient volume to use a 50mL aliquot, the lab can use a smaller volume of sample, proportional volumes of reagents, and adjust the final digestate volume back to the original volume of the sample used. For example, if 25mL of sample is digested, one half of the routine volumes of reagent are used

and the final volume of the digestate is brought back to 25mL. When a smaller aliquot is used, the digestion analyst must be careful not to allow the sample digest to evaporate completely.

10.1.6.2 Add 50mL of reagent water to a beaker that has been designated as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for contamination that may be due to glassware, reagents, or sample handling.

10.1.6.3 Add 0.50mL of the appropriate spiking solutions to a 50mL aliquot of reagent water designated as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 50mL aliquot of reagent water with 0.50mL of the appropriate spiking solutions.

Analytical Method	Matrix	QC	Spiking Solutions
6010	Aqueous	LCS/MS/MSD	(Spex) ICP Spike 1 ICP Spike 2
6020	Aqueous	LCS/MS/MSD	ICP/MS Spike 1 ICP/MS Spike 2

10.1.6.4 Add 0.50mL of the appropriate spiking solutions to each of two 50mL aliquots of the client sample designated as the matrix spikes sample (MS and MSD).

10.1.6.6 Add 2.5mL of 1:1 HCl to each sample and QC item.

Note: If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

10.1.6.7 Heat for 15 minutes on a hot block.

10.1.6.8 Allow the digest to cool and filter through a 0.45um filter. Adjust the final volume to 50mL or to the original volume.

10.1.6.9 The sample is now ready for analysis by ICP or ICP/MS.

10.1.7 Total Recoverable Metals (EPA 200.8 and EPA 200.7)

This digestion procedure is used for the preparation of water and drinking water samples for total recoverable metal determination by ICP and ICP/MS.

10.1.7.1 Transfer a 50mL aliquot (or an appropriate volume diluted to 50mL with reagent water) of a well-mixed sample to a clean 50mL block digestion vial.

Note: If there is not sufficient volume to use a 50mL aliquot, the lab can use a smaller volume of sample and bring the final digestate volume back to the original volume of the sample used. That is, if 25mL of sample is digested, the final volume of the digestate should be brought back to 25mL. If a smaller aliquot is used, the digestion analyst must be careful not to allow the sample digest to evaporate completely.

10.1.7.2 Add 50mL of reagent water to a block digestion vial that has been designated as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for contamination that may be due to glassware, reagents, or sample handling.

10.1.7.3 Add 0.50mL of the appropriate spiking solutions to a 50-mL aliquot of reagent water designated as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 50mL aliquot of reagent water with 0.50mL of the appropriate spiking solutions.

Analytical Method	Matrix	QC	Spiking Solutions
200.7 DW and TR	Aqueous	LCS/MS/MSD	(Spex) ICP Spike 1 ICP Spike 2
200.8 DW and TR	Aqueous	LCS/MS/MSD	ICP/MS Spike 1 ICP/MS Spike 2

10.1.7.4 Add 0.50mL of the appropriate spiking solutions to each of two 50mL aliquots of the client sample designated as the matrix spikes sample (MS and MSD).

10.1.7.6 Add 1.0 mL of (1:1) HNO_3 and 0.5 mL of (1:1) HCl to each sample. Gently heat the block digestion vial and reduce the sample volume to about 10mL without boiling; that is, bubbles are not formed in the liquid in the bottom of the block digestion vial. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

Note: If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

10.1.7.7 Wash down the inside of the block digestion vial with reagent water. Dilute the sample digestate to 50mL with reagent water. Transfer the digest to a labeled storage container, usually a 125mL plastic vial. Allow any undissolved material to settle out or centrifuge the sample to remove particulate matter. A portion of the sample may be filtered, if necessary, to remove particulates but care must be taken to avoid contamination of the sample during filtration.

Note: The digestate may be diluted to a volume less than the original volume if sample concentration is required to meet lower reporting limits. The pre-concentration should be limited to a factor of four.

10.1.7.8 The sample is now ready for analysis by ICP and ICP/MS.

10.1.8 Silica Samples

10.1.8.1 Samples are prepared by filtration of an unpreserved aliquot through a 0.45um syringe filter. The sample must be kept refrigerated until time of analysis. Note: The same number of syringe filters should be used for the method blank, LCS, and the samples.

10.1.8.3 The method blank is prepared by filtering an amount of reagent water equal to the volume of sample that is filtered.

10.1.8.4 The LCS is prepared by spiking 10mL of reagent water with 0.10mL of SiO_2 Intermediate Standard, and passing it through a 0.45um syringe filter. The SiO_2 spike concentration in the LCS is 10mg/L.

10.1.8.5 The matrix spike and/or matrix spike duplicate (MS/MSD) are prepared by adding 0.10mL of SiO_2 Intermediate Standard solution to two separate 10mL aliquots of the sample to be spiked and filtering through a 0.45um filter. The SiO_2 spike concentration in the MS/MSD is 10mg/L.

10.2 Analysis

Details on sample analysis are given in the associated analytical SOPs listed in Section 1.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review.*

11.1.1 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.1.2 Chemical Relationships

When available, the following chemical relationships must be evaluated for each sample. If these relationships are not met the Department Manager must be contacted immediately.

- Total Results are ≥ Dissolved results (e.g. metals)

11.2 Calculations

Details on sample calculations are given in the associated analytical SOPs listed in Section 1.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and annually thereafter, and verified annually in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

12.2 Determination of the Instrument Detection Limit (IDL)

The instrument detection limit (IDL) is the concentration of analyte that can be statistically distinguished from the background noise of the instrument. The IDL limit must be determined annually, at a minimum, for each analyte in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

The IDL is defined as three times the average of the standard deviation of seven replicate analyses of the IDL solution performed over three non-consecutive days. The IDL may be elevated above the background noise (blank levels). The current IDL associated with this procedure is given in the Equipment Limit Group (ELG) in LIMS.

12.3 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS, MS/MSD, SD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.4 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.5 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Acidic sample digestions: Neutralize before disposal into drain/sewer system.

15.0 References / Cross-References

- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-AN-41: *Reagent and Standard Materials Procedures*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06*: Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual

- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- Methods 3005A and 3010A: *Test Methods for Evaluating Solid Waste*, Third Edition, SW-846; vs. EPA Office of Solid Waste and Emergency Response: Washington, DC.
- Methods 200.7 and 200.8 (Drinking Water): Methods for the Determination of Metals in Environmental Samples, May 1994, Supplement 1. (EPA 600/R-94/111).
- Standard Methods for the Examination of Water and Wastewater, Online Edition; American Public Health Association: Washington, DC 2004.

16.0 Method Modifications

The EPA 200.7 and EPA 200.8 reference methods were written specifically for drinking water and source water samples; however, the laboratory may perform other types of water samples using this procedure.

The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each EPA Method 200.7 and 200.8 batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory requires qualitative detection of the LL-LCS to be acceptable.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Turbidity Curve Form
Attachment 6: Turbidity Form

Attachment 1: SOP Summary

Sample Preparation Summary
Total Metals and TCLP/SPLP leachates: A known volume, usually 50mL, of sample is transferred to a digestion vessel. The sample is refluxed with nitric acid at approximately 95°C. After the sample has digested, as evidenced by a clear, pale yellow color, HCl is added and the sample is brought up to the original volume with reagent water. The laboratory utilizes two versions of the Total Recoverable preparation procedure. One version is equivalent to the EPA 3005A procedure and the second procedure is equivalent to the EPA 200.7 and 200.8 procedures.

Total Recoverable Metals: A known volume, usually 50mL, of sample is transferred to a digestion vessel. The sample is refluxed with dilute nitric acid and hydrochloric acid at approximately 95°C. After the sample has evaporated to approximately 10-20mL, the sample is brought up to the original volume with reagent water. This procedure is equivalent to EPA Method 3005A, and the EPA Methods 200.7 and 200.8 prep procedures for total recoverable metals.

Acid Extractable Metals: A known volume, usually 50mL of sample preserved with nitric acid, is transferred to a digestion vessel. Hydrochloric acid is added and the sample is heated on a hot bloack for 15 minutes. The sample is filtered and the final volume adjusted to the original volume. This procedure is equivalent to Standard Methods 3030C.

Silica samples for EPA Methods 200.7 and 6010C: Liquid samples are filtered. The filtered liquid samples are analyzed by ICP.

Drinking water samples for EPA Methods 200.7 and 200.8 with a turbidity concentration of less than 1NTU may be analyzed with no digestion. The exception to this rule is silver, which requires sample digestion prior to analysis. If the sample turbidity is >1NTU, then the EPA Method 200.7 preparation procedure or the EPA Method 200.8 preparation procedure is used.

Samples filtered for the determination of dissolved metals do not require digestion if the sample:
5) has a low COD(<20mg/L);
6) has a turbidity <1NTU ;
7) is colorless with no significant odor ; ***and***
8) is of one liquid phase and free of suspended particulates or precipitates after acidification.

Sample Analysis Summary
ICP: Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and excited to a higher energy level. As the elements fall to a lower energy level, radiation characteristic of the elements present in the plasma is emitted. The light is directed through an entrance slit, dispersed by the diffraction grating, and projected on to the photomultiplier tube (PMT). The PMTs, located behind the exit

slits, convert the light energy to an electrical current. This signal is then digitized and processed by the data system. Background correction is required for trace element determination.

ICP/MS: Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and excited to a higher energy level. The ions that are produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions are sorted according to their mass to charge ratios and quantified with a channel mass spectrometer.

Analytical Sequence
See the appropriate analytical SOP for information on the analytical sequence.
ICP: SOP SA-ME-070: *Elements by ICP*
ICP/MS: SOP SA-ME-074: *Elements by ICP/MS*

Attachment 2: Sample Collection, Preservation, and Holding Time Table

Listed below are the holding times and preservation requirements:

Matrix	Routine Laboratory Container	Minimum Sample Size	Preservation	Holding Time [1]
Water	250mL plastic	100mL	1:1 HNO_3 to pH<2	180 days from collection Hg – 28 days from collection
Water (Silica)	250mL plastic	100mL	<6°C but not frozen	180 days from collection
Leachate	100mL or 250mL plastic	10mL	1:1 HNO_3 to pH<2	180 days from leaching Hg – 28 days from leaching

[1] Inclusive of digestion and analysis.

Attachment 3: QC Summary

QC Item	Frequency	Criteria	Corrective Action
Method Blank	One per batch of twenty samples or less	Refer to analytical SOP	Refer to analytical SOP
Lab Control Sample	One per batch of twenty samples or less	Refer to analytical SOP	Refer to analytical SOP
Matrix Spikes and Duplicates (MS/MSD/SD)	EPA 200.7/EPA 200.8: 1 MS per 10% of samples SW-846: MS/MSD pair, or one MS and 1 SD, per batch of twenty samples or less	Refer to analytical SOP	Refer to analytical SOP
Demonstration of Capability (IDOC/CDOC)	Initially, per analyst, and then annually thereafter	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Method Detection Limit (MDL)	Upon method/instrument set-up, and then annually thereafter	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4: Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

The temperature of the hot plate or digestion block must be monitored with each batch. If the temperature required for sample preparation cannot be maintained, the heating device must be removed from service and repaired or replaced.

Contingency Plan
Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs, consisting of thermocouples, digestion tubes, and turbidimeter cells, and other common instrumentation components. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5: Turbidity Curve Form

TURBIDITY CURVE
Method EPA 180.1 / SM 2130B

Analyst Initials: _____ Date: _____ Instrument ID: _____

Formazin Primary Standards Calibration

Check the box when the standard is analyzed and write the LIMS ID # in the blank.

☐ 20NTU _____ ☐ 200NTU _____

☐ 1000NTU _____ ☐ 4000NTU _____

☐ 7500NTU _____

Gelex Secondary Standards Calibration

Each Gelex standard is analyzed in triplicate and the average is used as the true value.

Gelex Criterion: Percent Difference <15%

1. Gelex Concentration: Stray Light LIMS ID #: _____
   a_____NTU First True Value =_____NTU
   b_____NTU Average = _____NTU
   c_____NTU Percent Difference = _____

2. Gelex Concentration: 0 – 2 NTU LIMS ID #: _____
   a_____NTU First True Value =_____NTU
   b_____NTU Average = _____NTU
   c_____NTU Percent Difference = _____

3. Gelex Concentration: 0 – 20 NTU LIMS ID #: _____
   a_____NTU First True Value =_____NTU
   b_____NTU Average = _____NTU
   c_____NTU Percent Difference = _____

4. Gelex Concentration: 0 – 200 NTU LIMS ID #:_____
   a_____NTU First True Value =_____NTU
   b_____NTU Average = _____NTU
   c_____NTU Percent Difference = _____

5. Gelex Concentration: 200 – 4000 NTU LIMS ID #: _____
   a_____NTU First True Value =_____NTU
   b_____NTU Average = _____NTU
   c_____NTU Percent Difference = _____

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Attachment 6: Turbidity Form

Turbidity for Metals Drinking Water Samples

Date:

Analyst Initials:

CCV LIMS Standard Number:

CCV True Value: NTU

CCV criteria: ±10% of True Value
CCB criteria: <1 NTU
If sample turbidity is <1 NTU and silver is not requested, the sample does not require digestion.

Job Number	Turbidity (NTU)	Comments
CCV		
CCB		
CCV		
CCB		

FME158:09.19.07:1

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18.0 Revision History

Summary of Changes from Previous Revision:

- Some minor editorial and grammatical changes made.
- Revised all referenced SOP titles/numbers to be consistent with current revisions.
- Revised Standards and Reagents section to reflect those currently used by the laboratory. Removed reference to TCLP Spike Mix.
- Included the requirement to analyze an MSD with each batch of Clean Water Act samples. Section 9.1
- Included information on filtering the water used to prepare QC samples for dissolved metals, as is common laboratory practice. Also noted that the LCS should be spiked prior to filtration. Section 10.1.1.3
- Revised sections on TCLP preparation procedures to require a minimum of a matrix spike in the digestion batch.

SOIL PREPARATION PROCEDURES FOR ICP AND ICP/MS

(Methods: SW-846 3050B and DI Leach)

Approvals (Signature/Date):

Andrea Teal — April 23, 2010
Andrea Teal — Date
Quality Assurance Manager

Benjamin Gulizia — April 15, 2010
Benjamin Gulizia — Date
Laboratory Director / Lead Technical Director

Ernest B. Walton — April 28, 2010
Ernest Walton — Date
EH&S Coordinator / Technical Director

C Eaton — April 29, 2010
Cliff Eaton — Date
Department Manager

Facility Distribution No. 1 Distributed To: QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the digestion soil samples for the determination of total metals prior to analysis by ICP (SOP SA-ME-070: *Elements by ICP*) or ICP/MS (SOP SA-ME-074: *Elements by ICP/MS)*.

Note: The routine matrix for this procedure is soil; however, this procedure may be adapted to accommodate other matrices as outlined in Section 16.1.

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

A known weight (approximately 1g) of the well-mixed sample is transferred to a suitable digestion vessel. The sample is digested with aliquots of nitric acid and hydrogen peroxide to break down the organics present in the sample. After the sample has been digested, as evidenced by a clear, pale yellow digestate, HCl is added to give an approximate acid concentration of 10% HCl and 5% HNO_3. Then the sample digest is diluted to 100mL with reagent water.

A smaller weight of sample may be digested and the sample brought to a final volume that is proportional to the 1g sample to 100mL final volume ratio. For example, if 0.50g is digested, the final volume of the digestate must be 50mL to achieve the same reporting limits.

Note: For silica samples for EPA Methods 200.7 and 6010C, solid samples are extracted with reagent water using a DI Leach procedure and then filtered. The filtered solid extracts are analyzed by ICP.

This SOP is based on the following methods: SW-846 Method 3050B. Silica soil preparation guidance is taken from ASTM Method D3987-85.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid, hydrogen peroxide, and nitric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile or latex gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

Nitric and hydrochloric acids are extremely hazardous as oxidizers, corrosives, poisons, and are reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Nitric acid can cause deep ulcers and staining of the skin to a yellow or yellow-brown color. These acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Samples that contain high concentrations of carbonates or organic matter, or samples that are at elevated pH can react violently when acids are added. Acids must be added to samples under a hood to avoid splash/splatter hazards and/or possibly toxic vapors that will be given off when the samples are acidified.

Hydrogen Peroxide is a strong oxidizer that can cause a fire when it comes into contact with materials. Contact with the skin or eyes can cause irritation and burns.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Hydrochloric Acid[2]	Corrosive Poison	5ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns or permanent eye damage.
Nitric Acid[2]	Corrosive Oxidizer Poison	2ppm TWA 4ppm STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen Peroxide	Corrosive Oxidizer	1ppm TWA	Danger! Strong oxidizer. Contact with other material may cause a fire. Corrosive. Light sensitive. May be harmful if swallowed. May cause central nervous system effects. Eye contact may result in permanent eye damage. May cause severe respiratory tract irritation with possible burns. Causes eye and skin irritation and possible burns. May cause severe digestive tract irritation with possible burns.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
[2]Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Digestion Block – capable of maintaining a sample temperature of 95 ± 5°C – The temperature of the digestion block must be monitored and recorded for each batch. The temperature is measured in a digestion vessel containing reagent water.

Agitation/Leaching Equipment – capable of holding the sample containers and rotating around a central axis at 23-35rpm.

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Digestion Vessels – appropriate volume for use with digestion block – verify for volume accuracy per lot in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*.

Plastic Disposable Syringes

0.45um Syringe Filters

Plastic Sample Containers

Detergent – Alconox or equivalent, used for washing non-disposable labware.

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

8oz plastic soil jar – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.*

Hydrochloric acid, hydrogen peroxide, and nitric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Blank Matrix – Teflon chips, Ottawa sand, or equivalent. Used for the preparation of soil QC samples.
LIMS Name: P_TEFLONCH_xxxxx
Storage: Room Temperature
Expiration: Unopened: Manufacturer's expiration date; Opened: 5 years from date opened

7.2.2 Laboratory Reagent Water – ASTM Type I; The conductivity must be checked daily in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*.

7.2.3 Nitric acid (HNO_3) – reagent grade.
LIMS Name: ME_HNO3_XXXX
Storage: room temperature in the acid cabinet. Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials. Stable under ordinary conditions of use and storage.
Expiration:
Unopened: Manufacturer's expiration date or 5 years, whichever is sooner
Opened: Manufacturer's expiration date or 5 years, whichever is sooner

7.2.5 Hydrochloric acid (HCl) – reagent grade.
LIMS Name: ME_HCL_XXXX
Storage: room temperature in the acid cabinet. Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials. Stable under ordinary conditions of use and storage.
Expiration:
Unopened: Manufacturer's expiration date or 5 years, whichever is sooner
Opened: Manufacturer's expiration date or 5 years, whichever is sooner

7.2.7 Hydrogen peroxide (H_2O_2), 30% – reagent grade.
LIMS Name: ME_PEROX_XXXX
Storage: refrigerated between 0 °C and 6°C. Separate from incompatibles.
Expiration:
Unopened: Manufacturer's expiration date
Opened: Manufacturer's expiration date

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-*AN-041: Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

7.3.1 ICP Spiking Solution 1 – a purchased solution containing the following elements: aluminum, arsenic, barium, selenium, thallium at 200mg/L; iron at 100mg/L; cobalt, magnesium, nickel, lead, strontium, vanadium, antimony at 50mg/L; copper at 25mg/L; chromium at 20mg/L; and silver, beryllium, cadmium at 5mg/L.
LIMS Name: P_Spikel_XXXX

Storage: room temperature
Expiration: opened and unopened containers are given the manufacturer's expiration date

7.3.2 Stock Standards – purchased from CPI, Inorganic Ventures, or equivalent vendor, at the concentrations listed below.

Aluminum – 10000mg/L; LIMS Reagent Name: Alspx10000
Antimony – 1000mg/L; LIMS Reagent Name: Sbcpi1000
Arsenic – 1000mg/L; LIMS Reagent Name: Ascpi1000
Barium – 1000mg/L; LIMS Reagent Name: Bacpi1000
Beryllium – 1000mg/L; LIMS Reagent Name: Becpi1000
Boron – 1000mg/L; LIMS Reagent Name: Bcpi1000
Cadmium – 1000mg/L; LIMS Reagent Name: Cdcpi1000
Calcium – 10000mg/L; LIMS Reagent Name: Caspx10000
Chromium – 1000mg/L; LIMS Reagent Name: Crcpi1000
Cobalt – 1000mg/L; LIMS Reagent Name: Cocpi1000
Copper – 1000mg/L; LIMS Reagent Name: Cucpi1000
Iron – 10000mg/L; LIMS Reagent Name: Fecpi10000
Lead – 1000mg/L; LIMS Reagent Name: Pbcpi1000
Magnesium – 10000mg/L; LIMS Reagent Name: Mgspx10000
Manganese – 1000mg/L; LIMS Reagent Name: Pbcpi1000
Mercury – 1000mg/L; LIMS Reagent Name: Hgspex1000
Molybdenum – 1000mg/L; LIMS Reagent Name: Mocpi1000
Nickel – 1000mg/L; LIMS Reagent Name: Nicpi1000
Potassium – 10000mg/L; LIMS Reagent Name: Kcpi10000
Selenium – 1000mg/L; LIMS Reagent Name: Secpi1000
Silver – 1000mg/L; LIMS Reagent Name: Agcpi1000
Sodium – 10000mg/L; LIMS Reagent Name: Nacpi10000
Strontium – 1000mg/L; LIMS Reagent Name: SrABS1000
Thallium – 1000mg/L; LIMS Reagent Name: Tlcpi1000
Tin – 1000mg/L; LIMS Reagent Name: Sncpi1000
Titanium – 1000mg/L; LIMS Reagent Name: Ticpi1000
Vanadium – 1000mg/L; LIMS Reagent Name: Vcpi1000
Zinc – 1000mg/L; LIMS Reagent Name: Zncpi1000

Storage: room temperature. Store away from sunlight, heat, water, and incompatible materials.
Expiration: opened and unopened containers are given the manufacturer's expiration date

7.3.2 ICP Spiking Solution 2 – Add approximately 20mL reagent water to a clean 100-mL volumetric flask. Add 1mL of concentrated nitric acid and 5mL of concentrated hydrochloric acid to the volumetric flask. The standard will have an acid concentration of 1% HNO_3 and 5% HCl when diluted to volume.

Add the volumes of the stock standards given in the following table to the volumetric flask:

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

Dilute to volume with reagent water.

LIMS Name: P_SpikeII_xxxxx
Storage: room temperature
Expiration: 6 months of preparation or sooner based on the manufacturer's expiration date.

7.3.4 Silica/Silicon Standards

Silicon (Si) stock solutions are usually purchased for this procedure. The following conversion is used to adjust any volumes or concentrations appropriately:

$$Si = \frac{SiO_2}{2.14}$$

7.3.4.1 Stock SiO_2 Standard, 10000mg/L Si / 21400mg/L SiO_2 – purchased from CPI.
LIMS Name: Sicpi10000_xxxxx
Storage: Store at room temperature in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: This standard must be used by the manufacturer's expiration date.

Silicon (Si) stock solutions are usually purchased for this procedure. The following conversion is used to adjust any volumes or concentrations appropriately:

$$Si = \frac{SiO_2}{2.14}$$

7.3.4.2 Intermediate SiO_2 Standard, 467mg/L Si / 1000mg/L SiO_2 – Add 20mL to 30mL of reagent water to a clean, plastic 100-mL volumetric flask. Add the volume of the

Stock SiO_2 Standard given in the table below to the volumetric flask. Dilute to volume with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Silica (SiO_2) [Silicon (Si)]	21400 [10000]	4.67	100	1000 [467]

LIMS Name: P_SiO2_INT_xxxxx
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Prepare this solution every 180 days or sooner as needed or required. The expiration date must not exceed the expiration date of any of the components.

7.3.5 ICP/MS Spiking Solution 1 – Add approximately 50mL reagent water to a clean 100-mL volumetric flask. Add 2mL of concentrated nitric acid and 0.5mL of concentrated hydrochloric acid to the volumetric flask. The standard will have an acid concentration of 2% HNO_3 and 0.5% HCl when diluted to volume.

Add the volumes of the stock standards given in the following table to the volumetric flask:

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Aluminum (Al)	10000	1	100	100
Antimony (Sb)	1000	1		10
Arsenic (As)	1000	0.4		4
Barium (Ba)	1000	2		20
Beryllium (Be)	1000	0.5		5
Boron (B)	1000	2		20
Cadmium (Cd)	1000	0.5		5
Calcium (Ca)	10000	1		100
Chromium (Cr)	1000	2		20
Cobalt (Co)	1000	2		20
Copper (Cu)	1000	2.5		25
Iron (Fe)	10000	1		100
Lead (Pb)	1000	0.5		5
Magnesium (Mg)	10000	1		100
Manganese (Mn)	1000	5		50
Molybdenum (Mo)	1000	2		20
Nickel (Ni)	1000	2		20
Potassium (K)	10000	1		100
Selenium (Se)	1000	0.5		5
Sodium (Na)	10000	1		100
Strontium (Sr)	1000	2		20

Thallium (Tl)	1000	0.5		5
Tin (Sn)	1000	2		20
Titanium (Ti)	1000	2		20
Vanadium (V)	1000	2		20
Zinc (Zn)	1000	2		20

Dilute to volume with reagent water.

LIMS Name: MS lcs1cpi_xxxxx
Storage: room temperature
Expiration: 6 months of preparation or sooner based on the manufacturer's expiration date.

7.3.6 ICP/MS Spiking Solution 2 – Add approximately 50mL reagent water to a clean 100-mL volumetric flask. Add 10mL of concentrated hydrochloric acid to the volumetric flask. The standard will have an acid concentration of 10% HCl when diluted to volume.

Add the volumes of the stock standards given in the following table to the volumetric flask:

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Mercury (Hg)	1000	0.05	100	0.5
Silver (Ag)	1000	0.5		5

Dilute to volume with reagent water.

LIMS Name: MS_lcs2_wk_xxxxx
Storage: room temperature
Expiration: 28 days of preparation or sooner based on the manufacturer's expiration date.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Soil Samples

Soil samples are routinely collected in 8oz plastic soil containers.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of digestion/leaching. Samples for mercury must be digested/leached and analyzed within 28 days of collection. All other samples must be digested and analyzed within 6 months of collection. Digestates may be stored at room temperature until the time of analysis.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

A digestion batch consists of up to 20 environmental samples and the associated QC

items. The default QC items performed for each digestion batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD) or sample duplicate (SD).

The routine container supplied for this method 8oz (soil) container. 1g is required for digestion. It is unlikely that insufficient sample would be provided to meet the batch QC frequency. If insufficient sample is provided, reduced sample initial weights may be used to achieve the required batch matrix spike frequency; however, the minimum extraction weight to be used for the matrix spike samples is 0.5g.

Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample to perform the required matrix spike(s) and/or sample duplicates, the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample is defined as receiving less than a total of 2g.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

The instrument QC for the analytical procedures associated with this digestion procedure are given in SOP SA-ME-070: *Elements by ICP* or SOP SA-ME-074: *Elements by ICP/MS.*

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

10.1.1 EPA 3050B Sample Preparation

10.1.1.1 Remove the samples from the refrigerator and allow them to come to room temperature.

10.1.1.2 Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples.*

10.1.1.3 Weigh 1.0 - 1.2g (wet weight) of each homogeneous sample into a 100mL digestion vessel. The lab may weigh a larger aliquot equal to 1.0g of sample on a dry weight basis, if required.

Note: A smaller weight of sample may be digested and the sample brought to a final volume that is proportional to the 1g sample to 100mL final volume ratio. For example, if 0.50g is digested, the final volume of the digestate must be 50mL to achieve the same reporting limits; if 0.1g is digested, the final volume of the digestate must be 10mL. If the sample weight to final volume ratio is less than 1:100, the reporting limits will be higher than those listed in the LIMS MLGs. Adjust the volumes of spikes and reagents proportionately to compensate for the sample weight/final volume. For example, if 0.5g is digested, use ½ of the spike and reagent volumes listed above.

10.1.1.4 Add 5mL of reagent water and 5mL of concentrated HNO_3 to each digestion vessel and swirl the vessel to mix the contents.

10.1.1.5 Place the digestion vessels on the digestion block. The water in the digestion block must be 95°C +/- 5°C. Carefully heat the vessel until a gentle reflux is achieved. The sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the digestion vessel. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the sides of the digestion vessel and fall back into the digestion vessel. Do not allow the samples to boil. Reflux for 0-15 minutes.

10.1.1.6 Remove the digestion vessels from the digestion block, and allow them to cool to room temperature. Add 5mL of concentrated HNO_3 to each sample. Return the digestion vessels to the digestion block. Carefully heat the digestion vessels until a gentle reflux is achieved. Reflux the samples for at least 30 minutes. Do not allow the samples to boil.

10.1.7.1 Repeat the procedure in Section 10.1.6 with a second 5mL portion of concentrated HNO_3 if brown fumes are given off. Repeat Section 10.1.6 until no brown fumes are given off.

10.1.1.8 Evaporate the sample digestate to approximately 10mL. Do not allow the bottom of the digestion vessels to go dry during the evaporation. Remove the samples from the digestion block, and allow the samples to cool to room temperature before continuing onto the next step.

Note: If the sample is still warm when the 30% hydrogen peroxide (H_2O_2) is added in the next step, the sample may "boil over" and the entire process must be started over.

10.1.1.9 Add 2mL of reagent water to each digestion vessel. Slowly and carefully add 3mL of 30% H_2O_2 to each digestion vessel. It is very important to add the hydrogen peroxide slowly to prevent loss of sample due to vigorous effervescence. Return the digestion vessels to the digestion block, and heat until the effervescence subsides. Cool the digestion vessels after the effervescence subsides.

10.1.1.10 Continue to add 30% H_2O_2 in 1-3mL aliquots to the sample digestate until the effervescence is minimal or until the general appearance of the digestate is unchanged. Warm the sample digestate after each addition of H_2O_2 on the digestion block.

Note: Do not add more than 10mL of hydrogen peroxide to each sample.

10.1.1.11 After the last addition of peroxide, reduce the volume of the digestate to 5-10mL without boiling and without allowing the bottom of the digestion vessel to go dry. Add 10mL of concentrated HCl to each sample digestate. Return the digestion vessels to the digestion block, and reflux the sample digestates for 10-15 minutes.

10.1.1.12 Wash down the inside of the digestion vessels with reagent water. Dilute the sample digestate to 100mL with reagent water.

10.1.2 Silica (DI Leach) Sample Preparation

Solid and waste samples for silica are extracted by performing a DI leaching procedure. Note: Any QC samples which need the DI leach procedure (i.e. LCS, MS/MSD, IDOCs/CDOCs, MDL studies, etc.) need to be appropriately spiked prior to the leaching procedure.

10.1.2.1 Remove the samples from the refrigerator and allow them to come to room temperature.

10.1.2.2 Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*.

10.1.2.3 To a 125mL plastic container weigh a 4.5-5.5g portion of homogenized sample. Note: Different initial weights may be used as long as the extraction fluid to sample ratio remain the same.

10.1.2.4 Add 100mL of reagent water to each sample container (or a volume equal to 20 times the weight of the samples used).

10.1.2.5 Agitate (leach) continuously for 18 ± 2 hours at 23-35rpm.

10.1.2.6 After the extraction period, allow the sample to settle and filter a portion for analysis through a 0.45um filter. The sample may be allowed to settle, centrifuged, decanted, or filtered through coarse filter paper before the final filtration to remove the solid phase. The method blank and laboratory control sample must be treated the same as the samples (i.e., same volumes and same number of filter pads) so that an adequate background, contamination, and recovery checks can be made.

10.2 QC Sample Preparation

10.2.1 EPA Method 3050B QC Sample Preparation

10.2.1.1 Method Blank – Weigh a 1.0-1.2g aliquot of blank matrix into a labeled digestion vessel and prepare as listed in Section 10.1.1.

10.2.1.2 Laboratory Control Sample – Weigh a 1.0-1.2g aliquot of blank matrix into a labeled digestion vessel, add 1.0mL of each spiking solution (ICP Spike I and ICP Spike II or ICP/MS Spike I and ICP/MS Spike II) and prepare as listed in Section 10.1.1.

10.2.1.3 Matrix Spike / Matrix Spike Duplicate – Weigh out 2 separate 1.0 -1.2-g aliquots of the sample chosen for the matrix spike into a labeled digestion vessel. Add 1.0mL of each spiking solution (ICP Spike I and ICP Spike II or ICP/MS Spike I and ICP/MS Spike II) and prepare as listed in Section 10.1.1.

10.2.2 Silica (DI Leach) QC Sample Preparation

10.2.2.1 Method Blank – Weigh a 4.5-5.5g aliquot of blank matrix into a labeled 125mL plastic container and continue as outlined in Section 10.1.2.4 through Section 10.1.2.6.

10.2.2.2 Laboratory Control Sample – Weigh a 4.5-5.5g aliquot of blank matrix into a labeled 125mL plastic container, add 1.0mL of the SiO_2 Intermediate Standard and continue as outlined in Section 10.1.2.4 through Section 10.1.2.6.

10.2.2.3 Matrix Spike / Matrix Spike Duplicate – Weigh out 2 separate 4.5-5.5g aliquots of the sample chosen for the matrix spike into a labeled 125mL plastic container. Add 1.0mL of the SiO_2 Intermediate Standard and continue as outlined in Section 10.1.2.4 through Section 10.1.2.6.

10.3 Analysis

The analytical procedures associated with this digestion procedure are given in SOP SA-ME-070: *Elements by ICP* or SOP SA-ME-074: *Elements by ICP/MS.*

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review.*

The data reduction procedures associated with this digestion procedure are given in SOP SA-ME-070: *Elements by ICP* or SOP SA-ME-074: *Elements by ICP/MS.*

11.1.1 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.1.2 Chemical Relationships

When available, the following chemical relationships must be evaluated for each sample. If these relationships are not met the Department Manager must be contacted immediately.

- Total Results are ≥ Dissolved results (e.g. metals)

11.2 Calculations

The calculations for the determination of metals by ICP and ICP/MS are given in the associated analytical SOPs (SOP SA-ME-070 or SOP SA-ME-074).

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and verified in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs).*

12.2 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS, MS/MSD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.3 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.4 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess soil samples from homogenization procedure - Transfer to TCLP container for characterization in hazardous waste department.
- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.
- Acidic sample digestions – Neutralize before disposal into drain/sewer system.

- Excess oil samples – Transfer to waste department for storage/disposal.

15.0 References / Cross-References

- SOP SA-AN-041: *Reagent and Standard Materials Procedures*
- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs)*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- *Test Methods for Evaluating Solid Waste,* Third Edition, SW-846; EPA Office of Solid Waste and Emergency Response: Washington, DC. (including Updates III and IV)
    - Method 3050B Revision 2: Acid Digestion of Sediments, Sludges, and Soils
- ASTM Method D3987-85: *Shake Extraction for Solid Waste with Water*

16.0 Method Modifications/Clarifications

16.1 Incorporation of Other Matrices

16.1.1 This procedure may be modified to analyze other matrices (e.g., wipe, waste, tissue, and filter samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project.

16.1.2 Wipe, waste, filter, and tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and soil QC limits to evaluate wipe, waste, filter, and tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. Teflon chips, Ottawa sand, or equivalent is used as the blank matrix for these non-routine matrices unless specifically requested otherwise by the project.

16.1.3 Waste samples may be collected in 8oz plastic soil jars. However, it should be noted that an alternate container may be required as some organic wastes (oils) may not be conducive to plastic. Tissue samples may be collected in 8oz plastic soil jars. Wipes and filters may be collected in a variety of different containers.

16.1.4 Wipe, waste, and filter samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of digestion/leaching. Samples for mercury must be digested/leached and analyzed within 28 days of collection. All other samples must be digested and analyzed within 6 months of collection. Digestates may be stored at room temperature until the time of analysis.

16.1.5 Tissue samples must be iced at the time of collection and maintained at -10°C to -20°C for up to 6 months. Samples for mercury must be digested/leached and analyzed within 28 days of thawing. All other samples must be digested and analyzed within 6 months of thawing. Digestates may be stored at room temperature until the time of analysis.

16.1.6 Wipe, waste, filter, and tissue matrices are prepared in the same manner as soil samples with the following exceptions:

- The initial amount for wipe or filter samples is 1 wipe or 1 filter.
- The initial amount for tissue and waste samples is 1.0-1.2g.

16.2 Other Considerations

16.2.1 As allowed by EPA 3050B, an alternative determinative technique has been employed for samples analyzed by ICP/MS. The preparation procedures in the method are identical for ICP and ICP/MS samples up to the addition of concentrated HCl. SW-846 Method 3050B only requires this step for samples to be analyzed by ICP. The laboratory has adopted this procedure for both ICP and ICP/MS samples. All field samples and quality control samples (including MDLs, DOCs, and PT samples) have been prepared using this alternative technique.

16.2.2 The analyte list in Section 1.0 of EPA 3050B has been expanded to include all analytes currently performed by the laboratory.

16.2.3 EPA 3050B requires only a method blank, matrix spike, and matrix spike duplicate with each preparation batch; however, the analytical methods also require the analysis of a laboratory control sample taken through the entire preparation process. For this reason the laboratory includes the LCS as part of the required batch QC for SW-846 Method 3050B. The analytical methods also allow a sample duplicate to be performed in lieu of a matrix spike duplicate. The laboratory's procedures allow for this option.

16.2.4 EPA 3050B requires a method blank be analyzed prior to use of nitric acid, hydrochloric acid, and hydrogen peroxide with results less than the MDL for all analytes of interest. The laboratory does not perform this analysis in advance. The vendor certificate of analysis is reviewed and approved prior to use. Method blanks are also analyzed with each batch as a check on the cleanliness of the reagents.

16.2.5 EPA 3050B includes a final filtration step prior to establishing the final volume. The laboratory does not routinely encounter interferences that could be eliminated by this step. Additionally, this filtration step introduces another source of contamination. Therefore, this step has not been included in this procedure.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting

Attachment 1:
SOP Summary

Sample Preparation Summary

A known weight (approximately 1g) of the well-mixed sample is transferred to a suitable digestion vessel. The sample is digested with aliquots of nitric acid and hydrogen peroxide to break down the organics present in the sample. After the sample has been digested, as evidenced by a clear, pale yellow digestate, HCl is added to give an approximate acid concentration of 10% HCl and 5% HNO_3. Then the sample digest is diluted to 100mL with reagent water.

A smaller weight of sample may be digested and the sample brought to a final volume that is proportional to the 1g sample to 100mL final volume ratio. For example, if 0.50g is digested, the final volume of the digestate must be 50mL to achieve the same reporting limits.

Silica samples for EPA Methods 200.7 and 6010C: Solid samples are extracted with reagent water using a DI Leach procedure and then filtered. The filtered solid extracts are analyzed by ICP.

Sample Analysis Summary

Prior to analysis by ICP, the sample must be digested using the sample preparation method appropriate to the matrix. Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and excited to a higher energy level. As the elements fall to a lower energy level, radiation characteristic of the elements present in the plasma is emitted. The light is directed through an entrance slit, dispersed by the diffraction grating, and projected on to the photomultiplier tube (PMT). The PMTs, located behind the exit slits, convert the light energy to an electrical current. This signal is then digitized and processed by the data system. Background correction is required for trace element determination.

Prior to analysis by ICP-MS, the sample must be solubilized or digested using the sample preparation method appropriate to the matrix. Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and excited to a higher energy level. The ions that are produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions are sorted according to their mass to charge ratios and quantified with a channel mass spectrometer.

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Matrix	Routine Container	Routine Sample Size	Minimum Sample Size	Chemical Preservation	Thermal Preservation	Dechlorination Agent	Holding Time [1]
Soils	8oz plastic soil jar	1g 5g (Silica)	0.5g 2.5g (Silica)	None	<0-6°C	None	6 months (except for Hg which is 28 days)

[1] Inclusive of digestion and analysis.

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Batch Definition	Up to 20 field samples, prepared together w/in 24-hour time period	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Lab Control Sample (LCS)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Matrix Spike (MS)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Matrix Spike Duplicate (MSD) Or Sample Duplicate (SD)	One per batch	Refer to analytical SOP	Refer to analytical SOP
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per method/analyte combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06 (Unsupervised work cannot begin until acceptable IDOC is obtained.)
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per method/analyte combination	Refer to SOP SA-QA-06	Re-perform CDOC
Method Detection Limit (MDL)	Upon method/instrument set-up, and then annually thereafter	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
MDL Verification (MDLV)	Initially, with MDL Study, and quarterly thereafter (Note: Quarterly frequency is DOD QSM requirement. Annual frequency is NELAC requirement.)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

The temperature of the hot plate or digestion block must be monitored with each batch. If the temperature required for sample preparation cannot be maintained, the heating device must be removed from service and repaired or replaced.

Contingency Plan
In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial changes made and boilerplate text added.
- Specified types of gloves to be used for this procedure (nitrile or latex). Section 5.0
- Added information to Safety Section on hydrogen peroxide. Section 5.1 and Section 5.2
- Incorporated LIMS Reagent IDs for all standards and reagents. Section 7
- Added note that hydrogen peroxide must be stored away from incompatibles. Section 7.2.7
- Revised stock standards and concentrations to reflect current practice. Section 7.3.2
- Removed requirement to perform MDL Studies annually. As allowed by NELAC and DOD QSM, MDLVs can be performed in lieu of the annual study. Section 12.1
- Updated References/Cross-References Section to include SW-846 Update IV. Section 16

ELEMENTS BY ICP-MS

(Methods: EPA 200.8, EPA 6020, and EPA 6020A)

Approvals (Signature/Date):

Andrea Teal September 17, 2009
Andrea Teal Date
Quality Assurance Manager

Benjamin Gulizia September 16, 2009
Benjamin Gulizia Date
Laboratory Director/Lead Technical Director

Ernest B. Walton October 19, 2009
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Facility Distribution No. 1 **Distributed To:** QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of various metals by inductively coupled plasma mass spectrometry (ICP-MS).

Note: The routine matrices for this procedure are waters and soils; however, this procedure may be adapted to accommodate other matrices as outlined in Section 16.1.

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

Prior to analysis by ICP-MS, the sample must be solubilized or digested using the sample preparation method appropriate to the matrix. Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and excited to a higher energy level. The ions that are produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions are sorted according to their mass to charge ratios and quantified with a channel mass spectrometer.

This SOP is based on the following methods: EPA Method 200.8, SW-846 Method 6020, and SW-846 Method 6020A.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid and nitric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup such as filtration or dilution prior to analysis to reduce or eliminate the interferences.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Isobaric elemental interferences in the ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the target analyte. These can be managed by the selection of an alternate isotope or by the use of elemental interference equations. Most isobaric interferences that could affect the ICP-MS analysis for elements in this SOP have been identified. The basic elemental interference equations are based on natural isotopic abundances. The most precise coefficients for an instrument must be determined from the ratio of the net isotope signals that are observed for a known standard solution at a concentration sufficient to produce suitable counting statistics.

4.2.4 Physical interferences are effects associated with the sample nebulization and transport processes as well as ion-transmission efficiencies. Changes in viscosity can cause significant inaccuracies, especially in samples containing high concentrations of dissolved solids or high acid concentrations. These changes in matrix can cause significant signal suppression or enhancement. Dissolved solids can deposit on nebulizer tips and interface cones (reducing the orifice size and the instrument's performance). Internal standards can be used to correct for physical interferences if they are carefully matched to the analyte so that both elements react similarly to the matrix changes.

4.2.5 Memory interferences can occur when analytes from a previous sample contribute to signals measured from subsequent samples. The memory effects can result from analyte deposition of sample on the sample tubing, joints, nebulizer, spray chamber, torch, and/or interface cones. Routine maintenance on the sample introduction system is necessary in order to minimize the memory interferences. The memory effects must be taken into account when setting up a suitable rinse times. The evaluation of a minimum of three replicate integrations will help to determine memory problems.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

Nitric and hydrochloric acids are extremely hazardous as oxidizers, corrosives, poisons, and are reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Nitric acid can cause deep ulcers, and staining of the skin to a yellow or yellow-brown color. These acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Samples that contain high concentrations of carbonates or organic matter, or samples that are at elevated pH can react violently when acids are added. Acids must be added to samples under a hood to avoid splash/splatter hazards and/or possibly toxic vapors that will be given off when the samples are acidified.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS Online" button on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and symptoms of exposure
Hydrochloric Acid[2]	Corrosive Poison	5 ppm - Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid[2]	Corrosive Oxidizer Poison	2 ppm - TWA 4 ppm - STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
[2]Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Agilent 7500CE equipped with an Octopole Reaction System (ORS). The ORS is a small enclosed chamber that can be pressurized with a collision/reaction gas and mounted on-axis to the quadrapole for high ion transmission. The reaction gases used are:

Helium (UHP grade) - reduces both matrix based interferences, such as chlorides, and simple plasma based interferences, such as argon oxide or the doubly charged argon argon+, attributed from the argon plasma.

Hydrogen (UHP grade) - reduces the intense plasma-based interferences which the helium mode may not be efficient enough to correct for, such as argon hydride, argon gas, or argon oxide.

The ORS corrects for most of the interferences associated with a non-collision cell ICP-MS, but there are a few analytes that are evaluated in a "no gas" or normal mode that still require an interference equation. They are typically:

Cd 111: (1 * 111) - (0.00124 * 95)

Sn 115: (1 * 115) - (118 * 0.016)
Pb 208: (1 * 206) + (1 * 207) + (1 * 208)

If analyzing drinking water samples in "normal" mode only (no collision or reaction gas), then the following interference equations are recommended by the EPA. These equations are guidelines and can differ from instrument to instrument.

As 75: (1 * 75) - [(3.127 * 77) - (0.815 * 82)]
Cd 111: (1 * 111) - [(1.073 * 108) - (0.712 * 106)]
Pb 208: (1 * 206) + (1 * 207) + (1 * 208)
Mo 98: (1 * 98) - (0.146 * 99)
V 51: (1 * 51) - [(3.127 * 53) - (0.113 * 52)]
In 115: (1 * 115) - (0.016 * 118)

Data System: Chemstation and MARRS software are used to acquire, store, reduce, and output ICP mass spectral data. This software has the capability of processing stored ICPMS data. The software allows for the calculation of concentrations of analytes using the calibration curve.

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*

Argon gas supply and appropriate fittings

Cooling water supply

Hydrogen gas (UHP)

Helium gas (UHP)

Detergent – Citranox or comparable cleaner, used for washing non-disposable labware.

Filters – 0.45um syringe filters, used to filter samples for dissolved metals in the lab. Also used to remove particulates from sample digestions.

Syringes – 10mL luer lock syringes, used to filter samples

6.3 Sample Collection Containers
All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

Waters:
Total Metals:
250mL plastic with nitric acid – purchased with Certificate of Analysis attesting to purity.

Dissolved Metals:
250mL plastic – purchased with Certificate of Analysis attesting to purity.

Soils:
8oz plastic soil jar – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41*: Reagent and Standard Materials Procedures.*

Hydrochloric acid and nitric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

Laboratory Reagent Water – ASTM Type II or better; water from the Modulab filtration system (i.e., ASTM Type I) should be used as the default.

Nitric acid (HNO_3) - trace metal grade.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials. Stable under ordinary conditions of use and storage.
Expiration: Manufacturer's expiration date

Hydrochloric acid (HCl) - trace metal grade.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials. Stable under ordinary conditions of use and storage.
Expiration: Manufacturer's expiration date

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41*: Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

7.3.1 Calibration Stock Standards

The following individual analytes are purchased at the concentrations listed:
Aluminum – 10000mg/L
Antimony – 1000mg/L
Arsenic – 1000mg/L
Barium – 1000mg/L
Beryllium – 1000mg/L
Boron – 1000mg/L
Cadmium – 1000mg/L
Calcium – 10000mg/L
Chromium – 1000mg/L
Cobalt – 1000mg/L
Copper – 1000mg/L
Iron – 10000mg/L
Lead – 1000mg/L
Magnesium – 10000mg/L
Manganese – 1000mg/L
Mercury – 1000mg/L
Molybdenum – 1000mg/L
Nickel – 1000mg/L
Potassium – 10000mg/L
Selenium – 1000mg/L
Silver – 1000mg/L
Sodium – 10000mg/L
Strontium – 1000mg/L
Thallium – 1000mg/L
Tin – 1000mg/L
Titanium – 1000mg/L
Vanadium – 1000mg/L
Zinc – 1000mg/L

Storage: room temperature
Expiration: opened and unopened containers are given the manufacturer's expiration date

7.3.2 Initial Calibration Verification Stock Standards

The following individual analytes are routinely purchased from Absolute standards (this standard must be purchased from a vendor different than the vendor of the calibration standards) at the concentrations listed:
Aluminum – 10000mg/L
Antimony – 1000mg/L
Arsenic – 1000mg/L
Barium – 1000mg/L
Beryllium – 1000mg/L
Boron – 1000mg/L
Cadmium – 1000mg/L
Calcium – 10000mg/L
Chromium – 1000mg/L
Cobalt – 1000mg/L

Copper – 1000mg/L
Iron – 10000mg/L
Lead – 1000mg/L
Magnesium – 10000mg/L
Manganese – 1000mg/L
Mercury – 100mg/L
Molybdenum – 1000mg/L
Nickel – 1000mg/L
Potassium – 10000mg/L
Selenium – 1000mg/L
Silver – 1000mg/L
Sodium – 10000mg/L
Strontium – 1000mg/L
Thallium – 1000mg/L
Tin – 1000mg/L
Titanium – 1000mg/L
Vanadium – 1000mg/L
Zinc – 1000mg/L

Storage: room temperature
Expiration: opened and unopened containers are given the manufacturer's expiration date

7.3.3 Interference Check Standard

A/B Stock Standards:

Solution Component	Concentration Solution A (mg/L)	Concentration Solution B (mg/L)
Aluminum (Al)	1000	
Calcium (Ca)	1000	
Iron (Fe)	1000	
Magnesium (Mg)	1000	
Sodium (Na)	1000	
Phosphorus (P)	1000	
Potassium (K)	1000	
Sulfur (S)	1000	
Carbon (C)	2000	
Chloride (Cl)	10000	
Molybdenum (Mo)	20	
Titanium (Ti)	20	
Arsenic (As)		10
Cadmium (Cd)		10
Chromium (Cr)		10
Cobalt (Co)		10
Copper (Cu)		10
Manganese (Mn)		10
Nickel (Ni)		10
Silver (Ag)		10
Zinc (Zn)		10

Storage: room temperature
Expiration: opened and unopened containers are given the manufacturer's expiration date

7.3.3 Internal Standard Stock Standard
The following elements are used as the internal standards: Bi, In, Li6, Sc, Tb, Y and Ge. A mixed standard containing all elements is purchased from a vendor at a concentration of 10mg/L.

Storage: room temperature
Expiration: opened and unopened containers are given the manufacturer's expiration date

7.3.4 Prepared Standards
Refer to Attachment 7 for information on prepared standards.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Water Samples

8.1.1 Total Metals

Water samples are routinely collected in 250mL plastic containers containing 3mL of a 1:3 nitric acid preservative. The preservative should be sufficient to achieve a sample pH of less than 2.

Although no temperature preservation is required, samples are routinely iced at the time of collection at 4°C (less than 6°C but not frozen). Samples are stored at room temperature until the time of digestion. Samples must be digested and analyzed within 6 months of collection, unless mercury is requested. Samples for mercury analysis must be digested and analyzed within 28 days of sample collection. Digestates are stored at room temperature until the time of analysis.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives.

8.1.2 Dissolved Metals

Water samples for dissolved metals are routinely filtered at the time of sampling and collected in 250mL plastic containers containing 3mL of a 1:3 nitric acid preservative. The preservative should be sufficient to achieve a sample pH of less than 2.

Note: If the sample is to be filtered in the laboratory, the sample must be collected in 250mL plastic container with no preservatives. Once filtered, the laboratory will add nitric acid to obtain a pH of less than 2. Unpreserved water samples that are to be filtered in the laboratory must be iced at the time of collection at 4°C (less than 6°C but not frozen). The samples must be kept refrigerated until the time of filtration and preservation.

Although no temperature preservation is required when the samples are preserved with nitric acid, samples are routinely iced at the time of collection at 4°C (less than 6°C but not frozen). Samples are stored at room temperature until the time of digestion. Samples must be digested and analyzed within 6 months of collection, unless mercury is

requested. Samples for mercury analysis must be digested and analyzed within 28 days of sample collection. Digestates are stored at room temperature until the time of analysis.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives.

8.2 Soil Samples

Soil samples are routinely collected in 8oz plastic soil containers.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of digestion and analysis. Samples must be digested and analyzed within 6 months of collection, unless mercury is requested. Samples for mercury analysis must be digested and analyzed within 28 days of sample collection. Digestates are stored at room temperature until the time of analysis.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

9.1.1 EPA 200.8 – Drinking Water

A digestion batch consists of up to 20 environmental samples and the associated QC items digested together within a 24 hour period.

The minimum QC items required for each digestion batch are: a method blank, a laboratory control sample (LCS), and a matrix spike (MS) to be performed on a minimum of 10% of samples or one per batch – whichever is greater.

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, and 1 matrix spike.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), and another matrix spike (from sample 11-20).

The routine container supplied for this method is a 250mL container. 50mL is required for digestion. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum digestion volume to be used for the matrix spike samples is 25mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 100mL.

Note: There is no method-defined batch precision requirement for this method. For clients who require precision to be reported, the matrix spike must be prepared in

duplicate (i.e., MS/MSD). If precision is required for the project and insufficient sample volume is provided to perform the MS/MSD, the LCS must be prepared in duplicate (LCS/LCSD). An NCM must be initiated on all samples within the batch to denote this situation

Note: The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples by EPA 200.8, an LCS at the RL must also be included in the required batch QC.

The sample preparation and digestion procedures are listed in the following SOPs:

Matrix	SOP
Aqueous samples	SA-ME-050

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.1.2 EPA 200.8 – Clean Water Act

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The minimum QC items required for each extraction batch are: a method blank and a laboratory control sample (LCS), a matrix spike (MS) to be performed on a minimum of 10% of samples or one per batch – whichever is greater, and a matrix spike duplicate.

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, 1 matrix spike, and a matrix spike duplicate.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), another matrix spike (from sample 11-20), and a matrix spike duplicate.

The routine container supplied for this method is a 250mL container. 50mL is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 25mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 100mL.

Note: There is no method-defined batch precision requirement for this method; however, the EPA does require precision for all samples analyzed under the Clean Water Act. If insufficient sample volume is provided to perform the MS/MSD, the LCS must be prepared in duplicate (LCS/LCSD). An NCM must be initiated on all samples within the batch to denote this situation.

Batch QC must meet the criteria given in Attachment 3 of the associated analytical SOP.

9.1.3 EPA 6020 and EPA 6020A

A digestion batch consists of up to 20 environmental samples and the associated QC items. The minimum QC items required for each digestion batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD) or a sample duplicate. If there is insufficient sample to perform the MS/MSD or sample duplicate, an NCM must be initiated on all affected samples to denote this situation.

The routine container supplied for this method is a 250mL container. 50mL is required for digestion. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum digestion volume to be used for the matrix spike samples is 25mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s) or sample duplicate, an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 100mL.

The sample preparation and digestion procedures are listed in the following SOPs:

Matrix	SOP
Water samples	SA-ME-050
Soil samples	SA-ME-051

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

9.2.1 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves*. This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of a single standard and a blank; however a multi-point calibration is used for most analytes.

Note: During method development for the EPA 200.8 drinking water procedure (which does not permit use of the collision cell technology), it was determined that a single point calibration (i.e., a blank and a high standard) was more accurate at low concentrations for the majority of the elements. Therefore, the laboratory's default procedure for drinking water samples is to quantitate results using a single point calibration for the majority of the elements and a multi-point calibration curve for copper and magnesium only. A multi-point calibration curve is analyzed for all the elements due to the fact that the standards mixes include every element; however, the software is directed to evaluate only the blank and a high standard for those elements utilizing a single point calibration (i.e., all elements

except copper and magnesium). This evaluation is built into the software set-up and is not being made at the time of calibration using analyst discretion.

Refer to Attachment 7 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-41.

Tabulate the concentrations and corresponding responses for each analyte. Establish a calibration curve by plotting the concentration along the x-axis and the corresponding response along the y-axis.

The regression coefficient (r^2) of the regression curve must be greater than 0.998 for the initial calibration curve to be acceptable.

9.2.2 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The ICV must be within +/-10% to be acceptable.

Refer to Attachment 7 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.3 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed at the beginning of each analytical run immediately following the ICV. Continuing calibration blanks are analyzed every 10 analyses immediately following each CCV.

Initial and continuing calibration blanks must be <1/2RL to be acceptable.

9.2.4 Continuing Calibration Verification

The initial calibration curve must be verified every 10 analyses with a mid-level standard.

The CCV must be within +/-10% to be acceptable.

Refer to Attachment 7 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.5 Internal Standard (ISTD)

This procedure utilizes internals standards. See Attachment 7 for the concentrations and masses of the internal standard elements.

The internal standard solution is added to all standards, samples, and QC items by way of a peristaltic pump, a "T" connector, and a mixing coil at the instrument. The solution used

is 1mg/L for each of the internal standard elements. Other concentrations may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.5.1 EPA 200.8

The response of the internal standard in all samples and QC items must be within 60-125% of the response of the internal standard in the calibration blank. If the response is outside this range, flush the instrument with rinse blank and re-analyze the calibration blank. If the responses are within limits, re-analyze the samples at a dilution of 2.

9.2.5.2 EPA 6020

The response of the internal standard for CCV and CCB must be within 80-120% of the response of the internal standard in the original calibration solution. If the response is outside this range, terminate the analysis, correct the problem, and re-calibrate.

The response of the internal standard for samples and batch QC must be within 30-120% of the response of the internal standard in the initial calibration standard. If the response is outside this range, re-analyze the sample at a dilution of 5.

9.2.5.3 EPA 6020A

The response of the internal standard in all samples and QC items must not fall below 70% of the response of the internal standard in the initial calibration standard. If the response is outside this range for instrument QC, terminate the analysis, correct the problem, and re-calibrate. If the response is outside this range for samples, re-analyze the sample at a dilution of 5.

9.2.6 Post Digestion Spike

A post-digestion spike is performed on one sample per analytical batch to determine if matrix interferences are present. This post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration is not at least 50 times the instrument detection limit. This should be the same sample selected for the serial dilution in Section 10.4, above.

9.2.6.1 Transfer 10mL of a digestate to a suitable vial.

9.2.6.2 Spike the sample with appropriate volumes of the ICP-MS LCS/Matrix Spike Solution. The theoretical concentration of the post digestion spike is the same as the LCS or MS if the volume of spiking solution is discounted.

9.2.6.3 Analyze the spiked aliquot and an un-spiked aliquot (the un-spiked may have been analyzed previously and does not need to be reanalyzed).

9.2.6.4 Calculate the percent recovery of the post digestion spike as follows:

$$\%REC = \frac{C_{ps} - C_s}{C_2} \times 100$$

Where: C_{ps} = concentration of post digestion spike (ug/L)
C_s = concentration of un-spiked sample (ug/L)

C_2 = theoretical concentration of spike (ug/L)
(Refer to Section 10.2.5.2)

9.2.6.5 Evaluate the recovery using the following decision matrix. Limits for post digestion spikes are 80-120%.

Result of Post Digestion Spikes	Action
Within 80-120% limits	None
>120% recovery	Repeat analysis. Remake spiking solutions, re-spike, and reanalyze. Reanalyze un-spiked sample.
<80% recovery but >50% recovery	1) Dilute and re-spike. Elevate RL accordingly (for all associated samples). 2) Spike and evaluate all associated samples. 3) Spike and evaluate all associated samples by single point MSA. 4) Qualify all associated samples.
<50% recovery	Dilute digestate and repeat spike. ***Treat all samples associated with spike in the same manner as the spiked sample (i.e., spike or dilute samples).*** If recoveries are not 80-120%, analyze all associated samples by single point MSA. Note – high level of target analytes may inhibit spike recovery. Consult the supervisor in events where high levels of targets appear to be interfering.

Note: The >50% recovery of the post digestion spike is a benchmark below which samples may be biased high if corrected for spike recovery.

9.2.6.6 The post digestion spike and the method of standard additions must not be applied to samples analyzed at a dilution that produces a significant negative response. The analyst must use good judgment when evaluating data where the sample response is negative. Where a significant negative response is present, the digestate should be diluted and reanalyzed to determine the extent of the matrix interferences. If necessary, adjust the interference corrections and reanalyze the samples.

9.2.6.7 Single Point Method of Standard Additions

Two identical aliquots of the sample digest, V_x, are taken. One aliquot is spiked with a solution of known concentration, C_s. The second aliquot is analyzed un-spiked (the small volume of standard added to the spiked sample should be disregarded). The concentration of both aliquots is measured and the sample concentration, C_x, is calculated as follows:

$$C_x = \frac{S_2 V_s C_s}{(S_1 - S_2) V_x}$$

Where: S_1 = absorbance or concentration of the spiked aliquot
S_2 = absorbance or concentration of the un-spiked aliquot
Vs = volume of spike solution

Example:		
	Sample concentration (S_2):	523ug/L.
	Spike solution concentration (C_s):	50,000ug/L
	Volume of spike solution (V_s):	0.10mL
	Volume of sample aliquots (V_x):	10mL
	Spiked sample concentration (S_1):	95ug/L

C_x = [(523)*(0.10)*(50,000)] / [(951-523)*10)] = [2,615,000]/[4280] = 611 ug/L

9.2.7 Dilution Test (Serial Dilution)

A 1/5 dilution is prepared and analyzed on one sample per batch (one for every ten samples for EPA 200.8, or whichever is greater) to determine if matrix interferences are present.

9.2.7.1 Select a sample digestate that contains one or more target analytes at concentrations greater than 10X the reporting limit.

9.2.7.2 Dilute the digestate by a factor of 5, and analyze the dilution using the same procedures used for the un-diluted aliquot.

9.2.7.3 Compare the results of the diluted and un-diluted aliquots of sample digestate.

9.2.7.4 If the results of the dilution are within +/-10% of the results of the undiluted sample, no matrix interference is present. If the results differ by greater than +/-10%, matrix interference should be suspected and the sample digestate should be subjected to a post-digestion spike (refer to Section 10.5).

If the concentration of the analyte in the sample is not at least 50 times the instrument detection limit, evaluate the post-digestion spike.

9.2.8 Determination of Linear Range of the ICP-MS

If the instrument is not calibrated over its entire linear range for a particular element, a linear range standard must be analyzed daily to validate the linear range.

9.2.8.1 The ICSA solution is utilized as a linear range standard for those elements included in the solution. For elements not contained in the ICSA solution, a linear range standard must be prepared and analyzed.

9.2.8.2 Prepare the standard at concentrations that are expected to define the linear range of the instrument. The calibration standards and the linear range standards must be matrix matched; that is, they have the same percentage of hydrochloric and nitric acids.

9.2.8.3 Analyze the standard(s) after the initial calibration is validated.

9.2.8.4 Compare the concentration of the linear range standard with its true concentration using the following equation:

$$PercentDifference = \left| \frac{Ccal - Ctrue}{Ctrue} \right| \otimes 100$$

Where:
Ccal = concentration determined from analysis
Ctrue = true concentration of the standard

If the percent difference is less than or equal to 10%, the linear range is confirmed at that concentration. If the percent difference is greater than 10%, repeat the analysis with a lower concentration. For elements validated in this manner, data may be reported up to 90% of that linear range before a dilution is required.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

The sample preparation procedures are given in the following SOPs:

Matrix	SOP #
Aqueous Samples	SA-ME-050
Soil Samples	SA-ME-051

10.2 QC Sample Preparation

The QC sample preparation procedures are given in the following SOPs:

Matrix	SOP #
Aqueous Samples	SA-ME-050
Soil Samples	SA-ME-051

10.3 Analysis

10.3.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP. Turn the ICP-MS on and initiate the tune screen. Start the tune screen to allow the instrument to become thermally stable before analyzing the calibration standards. While the instrument is warming up, if the sample and skimmer cones are new or have been cleaned, aspirate the interference check solution (or similar solution) for about 15 minutes to pre-condition the cones.

10.3.1.1 Aspirate a 1ppb solution containing Lithium 7, Cesium, Yttrium, and Thallium and check the tune parameters for the following conditions:

Sensitivity: should yield counts greater than 1500 for Li7 and 2500 for Y and Tl
Precision: should be less than 10% RSD of 200 replicates
Oxides: must be less than 3% as CeO
Doubly charged ions: must be less than 10%

After the instrument is tuned to the above specifications then a P/A (pulse to analog) factor must be established for the dual-mode detector. Aspirate a 100ppb solution containing the analytes used in the calibration and the internal standards used for the method. Under the "tune" pull-down menu select P/A factor, and the software will calculate a factor used when the detector switches from analog to pulse due to high concentration.

Note: If an analyte does not have a factor and the concentration in the sample causes the detector to switch to pulse, the software will use the closest factor available in the calculation.

10.3.1.2 Analyze the calibration standards and calibrate the ICP-MS in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves.*

Note: During method development for the EPA 200.8 drinking water procedure (which does not permit use of the collision cell technology), it was determined that a single point calibration (i.e., a blank and a high standard) was more accurate at low concentrations for the majority of the elements. Therefore, the laboratory's default procedure for drinking water samples is to quantitate results using a single point calibration for the majority of the elements and a multi-point calibration curve for copper and magnesium only. A multi-point calibration curve is analyzed for all the elements due to the fact that the standards mixes include every element; however, the software is directed to evaluate only the blank and a high standard for those elements utilizing a single point calibration (i.e., all elements except copper and magnesium). This evaluation is built into the software set-up and is not being made at the time of calibration using analyst discretion.

10.3.2 Internal Standard (ISTD)

Prior to analysis, internal standards must be added to all standards, samples, and QC items. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. The internal standard solution is added at the time of analysis by using a peristaltic pump, a "T" connection, and a mixing coil that is inserted in the sample uptake line before the instrument's nebulizer. The concentration of the internal standard solution is listed in Attachment 7 of this document.

10.3.3 Initial and Continuing Calibration Verifications

Calibrate the instrument using the standards and criteria described given in Section 9.2. Once the calibration has been established and verified with an ICV in accordance with Section 9.2, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.

10.3.4 Sample Analysis

The samples/digestates must be analyzed using the same procedures as those used for the calibration standards.

The default procedure is to include QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the clock.

10.3.5 Example Analytical Sequence

An example analytical sequence is listed below.

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
ICB	
Samples & Batch QC Items	RL check standard, ICSA, ICSAB, up to 7 additional analyses.
CCV	
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	
CCB	

Analytical Sequence for samples not immediately following an initial calibration:

Description	Comments
CCV	
CCB	
Samples & Batch QC Items	ICSA, ICSAB (minimum of every 12 hours) Up to 8 additional analyses.
CCV	
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	
CCB	

Note: If the analysis run proceeds for more than 12 hours after the ICV, the analyst must repeat the analysis of the ICSA and ICSAB solutions.

The "up to 10 analyses" includes analysis of all analytical and batch QC items with the exception of the CCV and CCB analyses.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review.*

11.1.1 Dilutions

If the concentration of a sample is above the calibration range (or linear range for single point curves) of the instrument the sample digestate must be diluted and reanalyzed.

11.1.2 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.1.3 Chemical Relationships

When available, the following chemical relationships must be evaluated for each sample. If these relationships are not met the Department Manager must be contacted immediately.

- Total Results are $\geq$ Dissolved results (e.g. metals)

11.1.4 Drinking Water Compliance Evaluation

Public water suppliers (PWS) are governed by EPA-specified Maximum Contaminant Levels (MCL) above which indicates noncompliance. Many analytes also have a Maximum Contaminant Level Goal (MCLG), which is often lower than the MCL. The

MCLs and MCLGs associated with this procedure are given in Attachment 8. Notify the PM immediately via a Nonconformance Memo if any sample contains a detection above these levels.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

Regression Curve:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample
F = Final volume/weight
I = Initial volume/weight
D = Dilution factor
dw = % Solids decimal equivalent

Note: All dry weight corrections are performed automatically in LIMS.

Note: This calculation assumes all applicable unit correction factors are applied.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and annually thereafter, and verified annually in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

12.2 Reporting Limit Verification (RLV) / Lower Limit of Quantitation Check (QCS)

EPA 6020A requires a Lower Limit of Quantitation Check to be performed after establishing the lower laboratory and on an as needed basis to demonstrate sensitivity. As such, the laboratory requires a Low-Level LCS (spiked at the reporting limit) to be performed annually, at a minimum. The recovery of the LLCS must be within 70-130% of

the true value, or the reporting limit must be re-evaluated and elevated accordingly.

12.3 Determination of the Instrument Detection Limit (IDL)

The instrument detection limit (IDL) is the concentration of analyte that can be statistically distinguished from the background noise of the instrument. The IDL limit must be determined annually, at a minimum, for each analyte in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

The IDL for EPA 6020 and EPA 6020A is defined as three times the standard deviation of seven replicate analyses of a standard analyzed over three non-consecutive days. The IDL for EPA 200.8 is defined as the concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the selected mass(es). The IDL may be elevated above the background noise (blank levels). The current IDL associated with this procedure is given in the Equipment Limit Group (ELG) in LIMS.

The difference between the MDL and the IDL is the *digestion step*. The MDL samples are prepared and digested prior to analysis.

12.3 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS, MS/MSD, SD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.4 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the

QA Department for filing. Note: LCS CDOCs from the *same* source as the calibration standards are permitted.

12.5 Training Requirements
All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual (EHSM) and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Acidic sample digestions – Neutralize before disposal into drain/sewer system.

15.0 References / Cross-References

- SOP SA-AN-10: *Balance Calibration and Use*
- SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*
- SOP SA-AN-41: *Reagent and Standard Materials Procedures*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06*: Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- *Methods for Chemical Analysis of Water and Waste*; U.S EPA Office of Research and Development: Cincinnati, OHIO, March 1983.
- *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., November 1986 (Revision III and IV).
  - SW-846 Method 6020, Revision 0: Inductively Coupled Plasma – Mass Spectrometry, September 1994
  - SW-846 Chapter 3, Revision 3: Inorganic Analytes, December 1996
  - SW-846 Method 6020A, Revision 1: Inductively Coupled Plasma – Mass Spectrometry, February 2007
  - SW-846 Chapter 3, Revision 4: Inorganic Analytes, February 2007
- *Methods for the Determination of Metals in Environmental Samples*; US EPA Office of Research and Development. Washington, DC, May 1994.
- EPA Method 200.8, Revision 5.4: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry, 1994

16.0 Method Modifications

16.1 Incorporation of Other Matrices

This procedure may be modified to analyze other matrices (e.g., wipe, waste, tissue, filter, and TCLP/SPLP leachate samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project.

Wipe, waste, filter, and tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and soil QC limits to evaluate wipe, waste, filter, and tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and soil QC limits to evaluate TCLP/SPLP leachate samples. Water DOCs can be used to satisfy analyst demonstrations of capability for TCLP/SPLP matrices. Teflon chips, Ottawa sand, or equivalent is used as the blank matrix for wipes, wastes, filters, and tissues unless specifically requested otherwise by the project.

16.1.1 Collection and Handling Procedures for Non-Routine Matrices

Waste samples may be collected in 8oz plastic soil jars; however, it should be noted that an alternate container may be required as some organic wastes (oils) may not be conducive to plastic. Tissue samples may be collected in 8oz plastic soil jars. Wipes and filters may be collected in a variety of different containers.

Wipe, waste, and filter samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of digestion/leaching. Samples for mercury must be digested/leached and analyzed within 28 days of collection. All other samples must be digested and analyzed within 6 months of collection. Digestates may be stored at room temperature until the time of analysis.

Tissue samples must be iced at the time of collection and maintained at -10°C to -20°C for up to 6 months. Samples for mercury must be digested/leached and analyzed within 28 days of thawing. All other samples must be digested and analyzed within 6 months of thawing. Digestates may be stored at room temperature until the time of analysis.

Wipe, waste, filter, and tissue matrices are prepared in the same manner as soil samples with the following exceptions:

- The initial amount for wipe or filter samples is 1 wipe or 1 filter.
- The initial amount for tissue and waste samples is 1.0-1.2g.

Once the TCLP/SPLP extraction procedure has been performed, the TCLP/SPLP leachate must be transferred to a 500mL plastic container and preserved with 1.0mL nitric acid to a pH <2. Preserved TCLP/SPLP leachates are stored at room temperature until the time of digestion. The leachate sample must be digested within 6 months of completion of the TCLP/SPLP extraction. Digestates are stored at room temperature until the time of analysis and must be analyzed within 6 months of completion of the TCLP/SPLP extraction.

16.1.2 Preparation and Analytical Procedures for Non-Routine Matrices

Wipe, waste, filter, and tissue samples are prepared in the same manner as routine soil samples as outlined in SOP SA-ME-051. TCLP/SPLP matrices are prepared in the same manner as routine water samples as outlined in SOP SA-ME-050. Refer to the applicable preparation SOPs for more information.

Wipe, waste, filter, tissue, and TCLP/SPLP matrices are analyzed in the same manner as routine samples as outlined in this SOP.

16.2 Other Considerations

16.2.1 EPA 6020A notes to use gold as a preservative for mercury; however, the laboratory has not implemented this preservative. The instrument manufacturer's recommendations do not include this reagent if HCl is used in standards and samples. Additionally, initial method validation did not indicate this preservative was necessary to prevent carryover as intended by the method.

16.2.3 EPA 6020 and EPA 200.8 require the regression coefficient (r^2) of the regression curve to be greater than 0.995 for the initial calibration curve to be acceptable. EPA 6020A

requires the r^2 of the regression curve to be greater than 0.998 for the initial calibration curve to be acceptable. The laboratory has adopted the 0.998 criteria for all three methods.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Analysis Masses, Internal Standards, and Tune Steps
Attachment 6: Element-specific Masses and Concentrations
Attachment 7: Standard Preparation
Attachment 8: Drinking Water MCLGs and MCLs

Attachment 1:
SOP Summary

Sample Preparation Summary

Prior to analysis by ICP-MS, the sample must be solubilized or digested using the sample preparation method appropriate to the matrix.

Samples should be prepared according to the appropriate matrix-specific SOP.

Matrix	SOP
Aqueous Samples	SA-ME-050
Soil Samples	SA-ME-051

Sample Analysis Summary

Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and excited to a higher energy level. The ions that are produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions are sorted according to their mass to charge ratios and quantified with a channel mass spectrometer.

Analytical Sequence

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
ICB	
Samples & Batch QC Items	RL check standard, ICSA, ICSAB, up to 7 additional analyses.
CCV	
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	
CCB	

Analytical Sequence for samples not immediately following an initial calibration:

Description	Comments
CCV	
CCB	
Samples & Batch QC Items	ICSA, ICSAB Up to 8 additional analyses.
CCV	
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	
CCB	

Note: If the analysis run proceeds for more than 12 hours after the ICV, the analyst must repeat the analysis of the ICSA and ICSAB solutions.

The "up to 10 analyses" includes analysis of all analytical and batch QC items with the exception of the CCV and CCB analyses.

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Listed below are the holding times and preservation requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time [1]
Water	250-mL plastic	50 mL	3 mL 1:3 nitric acid to pH<2	Mercury = 28 days Other metals = 6 months
Soil	8-oz plastic soil jar	10g	Less than 6°C with no frozen samples	Mercury = 28 days Other metals = 6 months

[1] Inclusive of digestion and analysis.

Note: If dissolved metals are requested, the sample must be filtered prior to the acid being added to the sample.

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration: minimum 1 standard and 1 blank	Daily	Correlation ≥0.998 (for multipoint curves)	Recalibrate
Initial Calibration Verification Standard (ICV)	At the beginning of the analysis	Within ±10%	Recalibrate
Continuing Calibration Verification Standard (CCV)	At the beginning and end of the analysis, and every 10 samples	Within ±10% of the true value	Terminate the analysis, fix the problem and reanalyze the previous 10 samples.
Calibration Blank (ICB/CCB)	After ICV and every CCV	<½ RL	Terminate the analysis, correct problem and reanalyze the previous 10 samples
Internal Standard	All samples and QC items	Refer to Section 9.2.5	Refer to Section 9.2.5
Method Blank	One per batch of twenty samples or less	|result| <½ RL	Redigest and reanalyze batch
Laboratory Control Sample (LCS)	One per batch of twenty samples or less	LIMS MLG	Redigest and reanalyze batch
Low-Level Laboratory Control Sample (LLCS) – spiked at the RL	EPA 200.8 DW: One per batch of 20 samples or less	Qualitatively identified	If the "regular" LCS meets criteria, initiate NCM and report data If the "regular" LCS does not meet criteria, redigest and reanalyze batch
Lower Limit of Quantitation Check (LLQC)	EPA 6020A: Annually, at a minimum, and as needed thereafter	70-130%	Re-evaluate RL and elevate accordingly

QC Item	Frequency	Criteria	Corrective Action
– spiked at the RL			
Matrix Spike (MS)	EPA 200.8: 10% of samples prepared; i.e., 2 separate matrix spikes per batch of twenty samples EPA 6020 & EPA 6020A: 5% of samples prepared; i.e., 1 matrix spike per batch of twenty samples	LIMS MLG	Flag and report data
Matrix Spike Duplicate (MSD) or Sample Duplicate	EPA 200.8 (Clean Water Act), EPA 6020 & EPA 6020A: One MSD or sample duplicate per batch of twenty samples or less	LIMS MLG	Flag and report data
Serial Dilution (1/5 Dilution)	One per batch of twenty samples or less	Refer to Section 9.2.7	Refer to Section 9.2.7
Post Digestion Spike	One per batch of twenty samples or less	Refer to Section 9.2.6	Refer to Section 9.2.6
Reporting Limit Check Solution	At the beginning of analysis run	Recovery +/-50% of the true concentration (if the instrument is not calibrated at or below the RL).	Stop the analysis, fix the problem and reanalyze the affected samples.
Demonstration of Capability (IDOC/CDOC)	Initially, per analyst, and then annually thereafter	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Method Detection Limit (MDL)	Upon method/instrument set-up, and then annually thereafter	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:
- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	**Service Interval**							**SERVICE LEVEL**
	D	**W**	**M**	**Q**	**SA**	**A**	**AN**	
Cones							X	Clean, as needed.
Intake							X	Wipe down as needed.
Lenses							X	Clean or replace as needed.
Nebulizer							X	Clean, as needed.
Pump oil							X	Replace as needed.
Pump Tubing							X	Change as needed

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually; AN = as needed

Contingency Plan

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs, consisting of detectors, pump tubing, cones, lenses, torches, and other common instrumentation components. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
Analysis Masses, Internal Standards, and Tune Steps

The following are the recommended analysis masses, internal standards, and tune steps:

Element	IS	Tune Step	Element	IS	Tune Step
Be 9	Li 6	3	Cu 63	Ge 74	2
B 11	Li 6	3	Zn 66	Ge 74	3
Na 23	Sc 45	1	As 75	Ge 74	2
Mg 24	Sc 45	1	Se 78	Ge 74	1
Al 27	Sc 45	1	Sr 88	Y 89	3
K 39	Ge 74	2	Mo 95	In 115	3
Ca 40	Sc 45	1	Ag 107	In 115	3
Ti 47	Sc 45	3	Cd 111	In 115	3
V 51	Ge 74	2	Sn 118	In 115	3
Cr 52	Ge 74	2	Sb 121	In 115	3
Mn 55	Ge 74	3	Ba 137	In 115	3
Fe 56	Sc 45	1	Hg 202	Bi 209	3
Co 59	Ge 74	3	Tl 205	Tb 159	3
Ni 60	Ge 74	2	Pb 208*	Tb 159	3

* Pb 208 = Pb 208 + Pb 207 + Pb 206

Note: Different masses and internal standards may be utilized, as matrix issues deem necessary.

Tune Steps:
1. H_2 reaction mode, typical flows of 3.8 to 5.8 mL/min of Hydrogen gas
2. He collision mode, typical flows of 3.8 to 5.8 mL/min of Helium gas
3. Normal mode

Tune Check Criteria:
Instrument tunes must be performed before each calibration. A solution at ~1ppb of Be, Mg, Co, In, and Pb is analyzed, and the precision, mass calibration, and resolution are checked.

The following limits are used to evaluate the tune:
Mass calibration: +/- 0.1amu
Resolution check: <0.9 amu at 10% peak height (baseline resolution)
Stability (5 reps): <5%

Attachment 6:
Element-specific Masses and Concentrations

Element	Mass/ Mode #	Calibration Conc. (ug/L)	ICV/CCV Conc. (ug/L)	RL Std. Conc. (ug/L)	Linear Range Std. Conc. (ug/L)*	Matrix Spike / Post Spike Conc.	
						Water (ug/L)	Soil (mg/kg)
Aluminum (Al)	27 / #1	1000,500,10, 5	400/500	10	100000	5000	500
Antimony (Sb)	121 / #3	100,50,1,0.5	40/50	0.50	Not Applicable Use Cal Range	50	5
Arsenic (As)	75 / #2	100,50,1,0.5	40/50	0.50	2000	100	10
Barium (Ba)	137 / #3	100,50,1,0.5	40/50	1.0	2000	100	10
Beryllium (Be)	9 / #3	100,50,1,0.5	40/50	0.10	Not Applicable Use Cal Range	50	5.0
Boron (B)	11 / #3	200,100,2,1	80/100	20	2000	200	20
Cadmium (Cd)	111 / #3	100,50,1,0.5	40/50	0.50	Not Applicable Use Cal Range	50	5.0
Calcium (Ca)	40 / #1	10000,5000, 100,50	4000/5000	50	100000	5000	500
Chromium (Cr)	52 / #2	100,50,1,0.5	40/50	1.0	2000	100	10
Cobalt (Co)	59 / #3	100,50,1,0.5	40/50	0.10	2000	50	5
Copper (Cu)	65 / #2	100,50,1,0.5	40/50	0.50	Not Applicable Use Cal Range	100	10
Iron (Fe)	56 / #1	10000,5000, 100,50	4000/5000	20	100000	5000	500
Lead (Pb)	208 / #3	100,50,1,0.5	40/50	0.30	2000	50	5.0
Magnesium (Mg)	24 / #1	10000,5000, 100,50	4000/5000	50	100000	5000	500
Manganese (Mn)	55 / #3	1000,500,10, 5	400/500	1.0	2000	500	50
Mercury (Hg)	202 / #3	5,2.5,0.05,0. 025	2.0/2.5	0.10	Not Applicable Use Cal Range	5.0	0.50
Molybdenum (Mo)	95 / #3	100,50,1,0.5	40/50	1.0	2000	100	10
Nickel (Ni)	60 / #2	100,50,1,0.5	40/50	0.20	2000	100	10
Potassium (K)	39 / #2	10000,5000, 100,50	4000/5000	50	100000	5000	500
Selenium (Se)	78 / #1	100,50,1,0.5	40/50	0.50	Not Applicable Use Cal Range	100	10
Silver (Ag)	107 / #3	100,50,1,0.5	40/50	0.20	Not Applicable Use Cal Range	50	5.0
Sodium (Na)	23 / #1	10000,5000, 100,50	4000/5000	50	100000	5000	500
Strontium (Sr)	88 / #3	100,50,1,0.5	40/50	0.20	2000	100	10
Thallium (Tl)	205 / #3	20,10,0.2,0.1	8/10	0.20	Not Applicable Use Cal Range	40	4.0

Element	Mass/ Mode #	Calibration Conc. (ug/L)	ICV/CCV Conc. (ug/L)	RL Std. Conc. (ug/L)	Linear Range Std. Conc. (ug/L)*	Matrix Spike / Post Spike Conc.	
						Water (ug/L)	Soil (mg/kg)
Tin (Sn)	118 / #3	100,50,1,0.5	40/50	1.0	2000	100	10
Titanium (Ti)	47 / #3	100,50,1,0.5	40/50	1.0	2000	100	10
Vanadium (V)	51 / #2	100,50,1,0.5	40/50	1.0	2000	100	10
Zinc (Zn)	66 / #3	100,50,1,0.5	40/50	4.0	2000	100	10

*For guidance only - instrument sensitivity will vary.

Attachment 7:
Standard Preparation

Note: All standards must be stored at room temperature and have an expiration date of 6 months from date prepared.

All calibration standards should contain 0.5% hydrochloric acid and 2% nitric acid by volume. The following table lists the volume of each acid needed to prepare the desired final volume of standard.

Standard Final Volume (mL)	Hydrochloric acid (mL)	Nitric Acid (mL)
100	0.5	2.0
200	1.0	4.0
500	2.5	10
1000	5.0	20

For example, to prepare 500mL of a standard:

- Add 100mL to 200mL of reagent water to a clean 500mL volumetric flask.
- Add 10mL of concentrated nitric acid (HNO_3) and 2.5mL of hydrochloric acid (HCl) to the volumetric flask.
- Add the volumes of the stock standards given in the table to the volumetric flask:
- Dilute to a final volume of 500mL with reagent water. Store the standard at room temperature.

CALIBRATION STANDARDS

Calibration Standard Stock Solution

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Volume (mg/L)
Aluminum (Al)	10000	1.0	100	100
Antimony (Sb)	1000	1.0		10
Arsenic (As)	1000	1.0		10
Barium (Ba)	1000	1.0		10
Beryllium (Be)	1000	1.0		10
Boron (B)	1000	2.0		20
Cadmium (Cd)	1000	1.0		10
Calcium (Ca)	10000	10		1000
Chromium (Cr)	1000	1.0		10
Cobalt (Co)	1000	1.0		10
Copper (Cu)	1000	1.0		10
Iron (Fe)	10000	10		1000
Lead (Pb)	1000	1.0		10
Magnesium (Mg)	10000	10		1000
Manganese (Mn)	1000	10		100
Mercury (Hg)	1000	0.050		0.50
Molybdenum (Mo)	1000	1.0		10
Nickel (Ni)	1000	1.0		10
Potassium (K)	10000	10		1000
Selenium (Se)	1000	1.0		10
Silver (Ag)	1000	1.0		10
Sodium (Na)	10000	10		1000
Strontium (Sr)	1000	1.0		10
Thallium (Tl)	1000	0.2		2.0
Tin (Sn)	1000	1.0		10
Titanium (Ti)	1000	1.0		10
Vanadium (V)	1000	1.0		10
Zinc (Zn)	1000	1.0		10

The above standards may be grouped together into more than one stock standard to maximize the stability of the standards. For example, silver may need to be kept as a separate stock due to the stability of the silver in solution.

WORKING CALIBRATION STANDARDS

Calibration Blank (ICB, CCB) – All standards are made up to the same acid concentrations as the calibration blank

Add 500mL to 600mL of reagent water to a clean 1-L volumetric flask. Add 20mL of concentrated nitric acid (HNO_3) and 5.0mL of hydrochloric acid (HCl) to the volumetric flask. Dilute to a final volume of 1000mL with reagent water. Store the standard at room temperature. Other volumes may be prepared at the discretion of the lab. The nitric acid concentration must be 2% by volume and the hydrochloric acid concentration must be 0.5% by volume.

Calibration Standards concentration (ug/L) – example for a final volume of 1000mL

Element	Standard 4 – 10mL of stock	Standard 3 – 5.0mL of stock	Standard 2 – 0.10mL of stock	Standard 1 – 0.050mL of stock
Aluminum (Al)	1000	500	10	5.0
Antimony (Sb)	100	50	1.0	0.50
Arsenic (As)	100	50	1.0	0.50
Boron (B)	200	100	2.0	1.0
Barium (Ba)	100	50	1.0	0.50
Beryllium (Be)	100	50	1.0	0.50
Cadmium (Cd)	100	50	1.0	0.50
Calcium (Ca)	10000	5000	100	50
Cobalt (Co)	100	50	1.0	0.50
Chromium (Cr)	100	50	1.0	0.50
Copper (Cu)	100	50	1.0	0.50
Iron (Fe)	10000	5000	100	50
Lead (Pb)	100	50	1.0	0.50
Magnesium (Mg)	10000	5000	100	50
Manganese (Mn)	1000	500	10	5.0
Mercury (Hg)	5.0	2.5	0.050	0.025
Molybdenum (Mo)	100	50	1.0	0.50
Nickel (Ni)	100	50	1.0	0.50
Potassium (K)	10000	5000	100	50
Selenium (Se)	100	50	1.0	0.50
Silver (Ag)	100	50	1.0	0.50
Sodium (Na)	10000	5000	100	50
Strontium (Sr)	100	50	1.0	0.50
Thallium (Tl)	20	10	0.20	0.10
Tin (Sn)	100	50	1.0	0.50
Titanium (Ti)	100	50	1.0	0.50
Vanadium (V)	100	50	1.0	0.50
Zinc (Zn)	100	50	1.0	0.50

Note: The Standard 4 listed above is utilized when calibrating with a single standard and a blank.

CONTINUING CALIBRATION VERIFICATION (CCV) STANDARD

The calibration standard 3 is used as the continuing calibration verification standard.

INITIAL CALIBRATION VERIFICATION (ICV) SOLUTION

All standards must be from a different source than those used for the calibration standards.

Preparation of the ICP-MS initial calibration verification solution

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Aluminum (Al)	10000	0.40	100	40
Antimony (Sb)	1000	0.40		4.0
Arsenic (As)	1000	0.40		4.0
Boron (B)	1000	0.80		8.0
Barium (Ba)	1000	0.40		4.0
Beryllium (Be)	1000	0.40		4.0
Cadmium (Cd)	1000	0.40		4.0
Calcium (Ca)	10000	4.0		400.0
Cobalt (Co)	1000	0.40		4.0
Chromium (Cr)	1000	0.40		4.0
Copper (Cu)	1000	0.40		4.0
Iron (Fe)	10000	4.0		400.0
Lead (Pb)	1000	0.40		4.0
Magnesium (Mg)	10000	4.0		400.0
Manganese (Mn)	1000	1.0		40.0
Mercury (Hg)	100	0. 40		4.0
Molybdenum Mo)	1000	0.40		4.0
Nickel (Ni)	1000	0.40		4.0
Potassium (K)	10000	4.0		400.0
Selenium (Se)	1000	0.40		4.0
Silver (Ag)	1000	0.40		4.0
Sodium (Na)	10000	4.0		400.0
Strontium (Sr)	1000	0.40		4.0
Thallium (Tl)	1000	0.20		0.8
Tin (Sn)	1000	0.40		4.0
Titanium (Ti)	1000	0.40		4.0
Vanadium (V)	1000	0.40		4.0
Zinc (Zn)	1000	0.40		4.0

Preparation of Initial Calibration Verification Working Standard

Dilute 1.0mL of the ICP-MS initial calibration verification solution to a final volume of 100mL using the same matrix solution as the calibration blank.

The final concentrations of the various elements are the same as listed in Table 1.

REPORTING LIMIT (RL) CHECK STANDARD

RL/PQL Stock A

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Aluminum (Al)	10000	1.0	100	100
Antimony (Sb)	1000	0.50		5.0
Arsenic (As)	1000	1.0		10
Boron (B)	1000	5.0		50
Barium (Ba)	1000	1.0		10
Beryllium (Be)	1000	0.10		1.0
Cadmium (Cd)	1000	0.50		5.0
Calcium (Ca)	10000	5.0		500
Cobalt (Co)	1000	1.0		10
Chromium (Cr)	1000	1.0		10
Copper (Cu)	1000	1.0		10
Iron (Fe)	10000	0.50		50
Lead (Pb)	1000	0.30		3.0
Magnesium (Mg)	10000	5.0		500
Manganese (Mn)	1000	1.0		10
Molybdenum Mo)	1000	1.0		10
Nickel (Ni)	1000	1.0		10
Potassium (K)	10000	5.0		500
Selenium (Se)	1000	0.50		5.0
Silver (Ag)	1000	1.0		10
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	1.0		10
Thallium (Tl)	1000	0.20		2.0
Tin (Sn)	1000	1.0		10
Titanium (Ti)	1000	1.0		10
Vanadium (V)	1000	1.0		10
Zinc (Zn)	1000	1.0		10

* Other standard concentrations may be used to verify higher or lower reporting limits.

RL/PQL Stock B

Element	Parent Standard (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Mercury (Hg)	1000	0.10	100	1.0

Preparation of RL/PQL Working Standard

Dilute 10uL of the RL/PQL stock solutions A and B to a final volume of 100mL using the same matrix solution as the calibration blank.

ICP INTERFERENCE CHECK SOLUTIONS (for SW846 6020/6020A)

Preparation of ICP Interference Check Solution A

Element	Parent Standard (mg/L)	Volume Stock A (mL)	Final Volume (mL)	Final Concentration (mg/L)
Aluminum (Al)	1000	50	500	100
Calcium (Ca)	1000			100
Iron (Fe)	1000			100
Magnesium (Mg)	1000			100
Sodium (Na)	1000			100
Phosphorus (P)	1000			100
Potassium (K)	1000			100
Sulfur (S)	1000			100
Carbon (C)	2000			200
Chloride (Cl)	10000			1000
Molybdenum (Mo)	20			2.0
Titanium (Ti)	20			2.0

Preparation of ICP Interference Check Solution AB

Element	Parent Concentration (mg/L)	Volume Stock A (mL)	Volume Stock B (mL)	Final Volume (mL)	Final Concentration (mg/L)
Aluminum (Al)	1000	50	1.0	500	100
Calcium (Ca)	1000				100
Iron (Fe)	1000				100
Magnesium (Mg)	1000				100
Sodium (Na)	1000				100
Phosphorus (P)	1000				100
Potassium (K)	1000				100
Sulfur (S)	1000				100
Carbon (C)	2000				200
Chloride (Cl)	10000				1000
Molybdenum (Mo)	20				2.0
Titanium (Ti)	20				2.0
Arsenic (As)	10				0.020
Cadmium (Cd)	10				0.020
Chromium (Cr)	10				0.020
Cobalt (Co)	10				0.020
Copper (Cu)	10				0.020
Manganese (Mn)	10				0.020
Nickel (Ni)	10				0.020
Silver (Ag)	10				0.020
Zinc (Zn)	10				0.020

ICP-MS LCS/MATRIX SPIKE SOLUTION

Preparation of the ICP-MS Matrix Spiking / Post Digestion Spiking Solution

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Aluminum (Al)	10000	5.0	100	500
Antimony (Sb)	1000	0.5		5
Arsenic (As)	1000	1.0		10
Boron (B)	1000	2.0		20
Barium (Ba)	1000	1.0		10
Beryllium (Be)	1000	0.5		5.0
Cadmium (Cd)	1000	0.5		5.0
Calcium (Ca)	10000	5.0		500
Cobalt (Co)	1000	1.0		5.0
Chromium (Cr)	1000	1.0		10
Copper (Cu)	1000	1.0		10
Iron (Fe)	10000	5.0		500
Lead (Pb)	1000	0.50		5.0
Magnesium (Mg)	10000	5.0		500
Manganese (Mn)	1000	5.0		50
Mercury (Hg)	1000	0.050		0.50
Molybdenum Mo)	1000	1.0		10
Nickel (Ni)	1000	1.0		10
Potassium (K)	10000	5.0		500
Selenium (Se)	1000	1.0		10
Silver (Ag)	1000	0.50		5.0
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	1.0		10
Thallium (Tl)	1000	0.4		4.0
Tin (Sn)	1000	1.0		10
Titanium (Ti)	1000	1.0		10
Vanadium (V)	1000	1.0		10
Zinc (Zn)	1000	1.0		10

Separate mixtures can be utilized for stability considerations.

IDL/MDL SOLUTION

The IDL/MDL solution is used in this procedure for two purposes:

1) To determine the Instrument Detection Limit (IDL) of each target compound on a quarterly basis (SOP SA-QA-07); and
2) To determine the Method Detection Limit (MDL) of each target compound on an annual basis (SOP SA-QA-07).

Preparation of Recommended IDL/MDL Intermediate Stock Solution

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Antimony (Sb)	1000	2.0	100	20
Arsenic (As)	1000	5.0		50
Barium (Ba)	1000	5.0		50
Beryllium (Be)	1000	0.50		5.0
Cadmium (Cd)	1000	1.0		10
Cobalt (Co)	1000	0.30		3.0
Chromium (Cr)	1000	5.0		50
Copper (Cu)	1000	5.0		50
Lead (Pb)	1000	1.0		10
Magnesium (Mg)	10000	3.0		300
Manganese (Mn)	1000	2.0		20
Mercury (Hg)	1000	0.40		4.0
Molybdenum Mo)	1000	1.5		15
Nickel (Ni)	1000	1.0		10
Selenium (Se)	1000	1.0		10
Silver (Ag)	1000	0.50		5.0
Strontium (Sr)	1000	1.0		10
Thallium (Tl)	1000	0.5		5.0
Tin (Sn)	1000	2.0		20
Titanium (Ti)	1000	4.0		40
Vanadium (V)	1000	2.0		20

Preparation of IDL/MDL Working Stock Solution

Element	Parent Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Intermediate Stock Solution	See above	1.0	100	Varied
Aluminum (Al)	10000	0.10		10
Boron (B)	1000	0.20		2.0
Calcium	10000	0.10		10
Iron (Fe)	10000	0.10		10
Potassium (K)	10000	0.30		30
Sodium (Na)	10000	0.15		15
Zinc	1000	0.30		3.0

Preparation of the IDL Check Solution:

The IDL solution is made by diluting the IDL/MDL working stock solution by a factor of 1/1000. The solution should be diluted in the same matrix as the calibration standards.

The IDL Check Solution contains the following elements at the given concentrations:

Element	Concentration(ug/L)
Co	0.030
Hg	0.040
Be, Ag	0.050
Se, Cd, Pb, Ni, Sr	0.10
Mo	0.15
Sb, Mn, Sn, V	0.20
Ti	0.40
As, Ba, Cr, Cu	0.50
Mg, Zn	3.0
B	8.0
Al, Ca, Fe	10
K	15
Na	30

Preparation of MDL Solutions:

For MDL solutions to be prepared for aqueous digestions (3005A, 3010A), dilute the IDL/MDL working stock solution by a factor of 1/200.

For MDL solutions to be prepared for 200.8 drinking water digestions (3005A, 3010A), dilute the IDL/MDL working stock solution by a factor of 1/1000.

For MDL solutions to be prepared for solid digestions, dilute the IDL/MDL working stock solution by a factor of 1/100. For solid digestions to be diluted to a final volume of 100mL, spike the digestions with 1mL of the IDL/MDL working stock solution.

Linearity Check Solutions:
The linearity check solutions are prepared individually according to the following equation:

$$Vs = \frac{Vlc \otimes Clc}{Cs}$$

Where: Vs = volume of stock standard (mL)
Cs = concentration of stock standard (mg/L)
Vlc = volume of linearity check standard to prepare (mL)
Clc = concentration of linearity check standard to prepare (mg/L)

The linearity check solutions are prepared at the concentrations specified in Attachment 6. Prepare sufficient volume to perform the linearity check, maintaining the hydrochloric acid concentration at 0.5% by volume and the nitric acid concentration at 1% by volume.

Internal Standards:
A solution at 1mg/L is prepared for all elements. That solution is added in-stream by the use of a T-fitting. The sample is pumped into the T-fitting with a white/white peristaltic pump tube and the internal standard is pumped in using a blue/orange pump tube.

Attachment 8:
Drinking Water MCLGs and MCLs

Element	Regulation	MCLG (mg/L)	MCL (mg/L)	Secondary Standard (mg/L)
Antimony	National Primary Drinking Water Regulations	0.006	0.0060	
Arsenic		0	0.010	
Barium		2.0	2.0	
Beryllium		0.0040	0.0040	
Cadmium		0.0050	0.0050	
Chromium		0.10	0.10	
Copper [1]		1.3	Action Level = 1.3	
Lead [1]		0	Action Level = 0.015	
Mercury		0.0020	0.0020	
Selenium		0.050	0.050	
Thallium		0.00050	0.0020	
Aluminum	National Secondary Drinking Water Regulations			0.05 – 0.2
Copper				1.0
Iron				0.30
Manganese				0.050
Silver				0.10
Zinc				5.0

[1] Lead and copper are regulated by a Treatment Technique that requires systems to control the corrosiveness of their water. If more than 10% of tap water samples exceed the action level, water systems must take additional steps. For copper, the action level is 1.3 mg/L, and for lead is 0.015 mg/L.

18.0 Revision History

Summary of Changes from Previous Revision:

- Included the requirement to analyze an MSD with each batch of Clean Water Act samples. Section 9.2.1 and Attachment 3
- Revised Resolution Check criteria from <1.0 amu with baseline separation to <0.9 amu at 10% peak height with baseline resolution. Attachment 5
- Revised EPA 6020 and EPA 6020A internal standard criteria to match criteria listed in the referenced methods. Section 9.2.5 and Attachment 3.
- Revised the requirement to change the pump oil from quarterly to on an as needed basis. Attachment 4.
- Revised EPA 6020A information to match the Revision 1 from February 2007 and not the Revision 1 from January 1998.
- Revised ICAL correlation coefficient criteria from 0.995 to 0.998.
- Added requirement to perform Lower Limit of Quantitation Check (i.e., low-level LCS) annually for EPA 6020A with criteria of +/-30% of true value. (SCDHEC application deficiency)

MERCURY: PREPARATION AND ANALYSIS

(Methods: EPA CLP ISM01.2)

Approvals (Signature/Date):

Andrea Teal January 29, 2010	Benjamin Gulizia January 28, 2010
Andrea Teal Date	Benjamin Gulizia Date
Quality Assurance Manager	Laboratory Director/Lead Technical Director
Ernest B. Walton February 1, 2010	C Eaton February 2, 2010
Ernest Walton Date	Cliff Eaton Date
EH&S Coordinator / Technical Manager	Department Manager

Facility Distribution No. 1 **Distributed To:** QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of mercury in water and soil samples by cold vapor atomic absorption (CVAA).

Attachment 5 contains the Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs) for this procedure. The complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

This procedure is based on the absorption of characteristic radiation at 253.7nm by mercury vapor. After digestion, to convert all forms of mercury to the same oxidation state, the mercury ions are reduced to mercury by the addition of stannous chloride and aerated from solution after passing through a mixing coil. The mixture passes through a gas/liquid separator and through a drying tube. The vapor is passed through a flow cell positioned in the light path of an atomic absorption spectrophotometer. Mercury concentration is measured as a function of absorbance.

This SOP is based on the following methods: EPA CLP ISM01.2.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

- CLP – Contract Laboratory Program
- Contract Required Quantitation Limits (CRQL) – the minimum level of quantitation acceptable under the contract Statement of Work (SOW).
- Validated Time of Sample Receipt (VTSR) – the time samples are received at the laboratory. The VTSR is used in lieu of the date and time sampled to calculate holding times.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in

accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid, nitric acid, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Potassium permanganate is added to eliminate the possibility of interference from sulfide and certain organic compounds.

4.2.4 High levels of residual chlorine (such as those produced when seawaters, brines, and industrial effluents high in chlorides are digested) are known to interfere with this analysis. Addition of extra potassium permanganate may be needed during the digestion of samples containing chloride. Also, the samples are not capped tightly during digestion so that excess chlorine can escape.

4.2.5 Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences. The concentration levels for interferants are difficult to define. This suggests that quality control procedures must be strictly followed.

4.2.6 Volatile materials (e.g., chlorine) which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the digestion vessel should be purged before addition of stannous chloride solution.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable latex or nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

Nitric and hydrochloric acids are extremely hazardous as oxidizers, corrosives, poisons, and are reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Nitric acid can cause deep ulcers, and staining of the skin to a yellow or yellow-brown color. These acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

Samples that contain high concentrations of carbonates or organic matter, or samples that are at elevated pH can react violently when acids are added. Acids must be added to samples under a hood to avoid splash/splatter hazards and/or possibly toxic vapors that will be given off when the samples are acidified.

The making of aqua regia can produce toxic fumes and heat. This procedure must be performed under a fume hood.

The exhaust of the mercury analyzer must be vented or trapped so that mercury vapors do not enter the laboratory.

The preparation of the samples for mercury analysis uses a water bath with a temperature of ~95°C. The water and the steam produced can cause burns to unprotected skin. Employees must use appropriate PPE when working with sample digestions.

Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analyses should be conducted in a laboratory exhaust hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Hydrochloric Acid	Corrosive Poison	5ppm Ceiling	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2ppm TWA 4ppm STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5mg/m^3 for Mn Compounds	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic, causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1mg/m^3 -TWA	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Exposure limit refers to the OSHA regulatory exposure limit.			
Note: Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Water bath or heating block capable of maintaining temperatures of 95 ± 3°C

Leeman Hydra AA or other suitable automated mercury analyzer

Mercury Hollow Cathode Lamp

Absorption Cell

Nitrogen or argon gas supply and appropriate fittings

Air Pump

Pump (Aeration) tubing of appropriate sizes for use on the Hydra AA

Drying Tube – Purchased pre-packed from Leeman Labs

Recorder

Data System – The raw data from the Hg Analyzer is manual checked for validity by a minimum of 2 analysts. Raw instrument data is uploaded to the LIMS (TALS) via the Environmental Information Systems Corporation (MARRS) program. Additionally, any quality control failures are flagged in LIMS, as appropriate.

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Test tubes of the two sizes to fit the Hydra AA autosampler

Digestion glassware – 4oz flint digestion vessels

Digestion vials – 50mL. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use).*

Flow meter – capable of measuring an air flow of 1L/min

pH paper – provides a quick and easy way to approximate the pH of a sample to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step. pH paper should be checked upon receipt, as follows, to make sure that it is functioning properly.

- Examine the pH paper. If the paper is discolored or looks worn, it may be defective.
- Place a piece of pH paper on a watch glass or other suitable surface and add a few drops of a certified buffer solution onto the paper.
- Compare the color of the pH paper to the reference colors. If the colors match, the paper can be used. If not, acquire new paper.

Detergent – Liquinox, used for washing non-disposable labware.

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

Water Samples:
250mL plastic, nitric acid – purchased with Certificate of Analysis attesting to purity.

Soil Samples:
8oz plastic soil jar, unpreserved – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.*

Note: All secondary bottles must be labeled with the LIMS reagent name, analyst initials, the date opened, and the expiration date.

Hydrochloric acid, nitric acid, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Purchased Reagents

7.2.1.1 Laboratory Reagent Water – ASTM Type II

7.2.1.2 Nitric Acid (HNO_3), concentrated, reagent grade – stable under ordinary conditions of use and storage
LIMS Reagent Name: ME_HNO3
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date opened

7.2.1.3 Hydrochloric Acid (HCl), concentrated-reagent grade – stable under ordinary conditions of use and storage
LIMS Reagent Name: ME_HCL
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration:
Unopened: Manufacturer's expiration date.
Opened: 5 years from date opened

7.2.1.4 Potassium permanganate ($KMnO_4$), mercury free – stable under ordinary conditions of use and storage.

LIMS Reagent Name: Hg_KMnO4

Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from heat and avoid storage on wood floors. Store away from incompatibles, combustibles, organics and other readily oxidizable materials.

Expiration:

Unopened: Manufacturer's expiration date

Opened: 5 years from date opened

7.2.1.5 Sodium Chloride (NaCl) – stable under ordinary conditions of use and storage.

LIMS Reagent Name: Hg_NaCl

Storage: Store in a tightly closed container in a cool, dry, ventilated area.

Expiration:

Unopened: Manufacturer's expiration date

Opened: 5 years from date opened

7.2.1.6 Hydroxylamine Sulfate ($(NH_2OH)•2H_2O$) – stable under ordinary conditions of use and storage.

LIMS Reagent Name: Hg_DROXSO4

Storage: Store in a tightly closed container in a cool, dry, ventilated area. Store away from incompatible materials.

Expiration:

Unopened: Manufacturer's expiration date

Opened: 5 years from date opened

7.2.1.7 Potassium persulfate ($K_2S_2O_8$) – stable under ordinary conditions of use and storage.

LIMS Reagent Name: Hg_K2S2O4

Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from heat and avoid storage on wood floors. Store away from incompatibles, combustibles, organics and other readily oxidizable materials.

Expiration:

Unopened: Manufacturer's expiration date

Opened: 5 years from date opened

7.2.1.8 Stannous chloride ($SnCl_2.2H_2O$) – reagent grade, suitable for mercury determination. Stable if stored in tightly closed containers.

LIMS Reagent Name: Hg_SnCl2

Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from incompatible materials. It will absorb air and form the insoluble oxychloride.

Expiration:

Unopened: Manufacturer's expiration date

Opened: 5 years from date opened

7.2.1.9 Sulfuric Acid (H_2SO_4), concentrated reagent grade – stable under ordinary conditions of use and storage.

LIMS Reagent Name: Hg_H2SO4

Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.

Expiration:

Unopened: Manufacturer's expiration date

Opened: 5 years from date opened

7.2.2 Prepared Reagents

7.2.1.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3. This reagent needs to be carefully prepared under a fume hood due to vapors that are produced. Properly dispose of any unused volume. For stability, 1:1 Aqua Regia may be used. Prepare using 4 volumes of reagent water, 3 volumes of concentrated HCl, and 1 volume of concentrated HNO3. **Always add the acid to water under a working fume hood.**

7.2.1.2 Potassium permanganate, mercury-free, 5% solution (w/v) – Dissolve 50g of $KMnO_4$ in 1000mL of reagent water. Stable under ordinary conditions of use and storage.
LIMS Reagent Name: H_KMnO4_R
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from heat and avoid storage on wood floors. Store away from incompatibles, combustibles, organics and other readily oxidizable materials.
Expiration: 1 year from date prepared

7.2.1.3 Sodium chloride hydroxylamine sulfate solution – Dissolve 120g NaCl and 120g hydroxylamine sulfate in reagent water in a 1L volumetric flask and dilute to volume. Stable under ordinary conditions of use and storage.
LIMS Reagent Name: H_NACLHYSO
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Store away from incompatible materials.
Expiration: 1 year from date prepared

7.2.1.4 Potassium persulfate, 5% solution (w/v) – Dissolve 50g potassium persulfate in 1000mL reagent water. Stable under ordinary conditions of use and storage.
LIMS Reagent Name: Hg_K2S2O8_R
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from heat and avoid storage on wood floors. Store away from incompatibles, combustibles, organics and other readily oxidizable materials.
Expiration: 1 year from date prepared

7.2.1.5 Rinse Water, 5% HCl / 1%HNO_3 – to a clean 2L bottle, add 1L of reagent water. Carefully add 100mL of concentrated hydrochloric acid. Carefully add 20mL of concentrated nitric acid. Dilute to a final volume of 2L. Other volumes may be utilized providing the reagent proportions remain the same. Stable under ordinary conditions of use and storage.
LIMS Reagent Name: Hg_rinse
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: 1 year from date prepared

7.2.1.6 Stannous chloride ($SnCl_2 \cdot 2H_2O$) solution – to a clean 2L volumetric flask, add 100g of stannous chloride. Add approximately 400mL of reagent water. Carefully add 500mL of concentrated hydrochloric acid. Add a stirring bar, and stir on a stir plate until the stannous chloride is dissolved. Remove the stirring bar and dilute to volume with reagent water. Stable under ordinary conditions of use and storage.
LIMS Reagent Name: Hg_SnCl2_R
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away

from incompatible materials.
Expiration: 1 year from date prepared

7.2.1.7 Nitric Acid (HNO_3), 1:1 – Slowly add 250mL of concentrated nitric acid to 250mL of laboratory reagent water in a 1L beaker. Mix well and transfer to a tightly closed container.
LIMS Reagent Name: Hg_HNO3_1:1
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: 2 years from date prepared

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures*. Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

7.3.1 Purchased Standards

7.3.1.1 Hg Stock Standard, 1000mg/L – currently purchased from SPEX.
LIMS Reagent Name: Hgspex1000
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage up to the manufacturer's expiration date.

7.3.1.2 Second Source Hg Stock Standard, 1000mg/L – currently purchased from Baker.
LIMS Reagent Name: Hgbak1000
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage up to the manufacturer's expiration date.

7.3.2 Prepared Standards

7.3.2.1 Calibration standards

7.3.2.1.1 Mercury Intermediate Standard, 500ug/L – Add 0.050mL of the purchased 1000mg/L Hg Stock Standard and 2.5mL of nitric acid to about 50mL of reagent water in a 100mL volumetric flask and dilute to volume with reagent water.
LIMS Reagent Name: Hg_int_cal
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage for up to 28 days. The expiration date cannot exceed the expiration of any of the components.

7.3.2.1.2 Mercury Calibration Standards (Aqueous) – Transfer 0.0, 0.02, 0.04, 0.1, 0.3, and 0.5mL portions of the Mercury Intermediate Standard to a series of 125mL glass bottles. Add reagent water from a graduated cylinder to each bottle to make a final volume of 50mL. (This results in calibration standard concentrations of 0.0, 0.2, 0.4,

1.0, 3.0, and 5.0ug/L mercury.) Mix well. Add 2.5mL of concentrated H_2SO_4, 1.25mL of concentrated HNO_3, and 7.5mL of $KMnO_4$ solution and let stand at least 15 minutes. Add 4mL of potassium persulfate and heat for ~2 hours in a water bath at 95°C+/- 3°C. Cool and add 3mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. The standards are now ready for analysis. Larger volumes of standards may be digested as needed as long as reagent ratios are kept the same.

LIMS Reagent Name: Hg_0.0_std; Hg_0.2_std; Hg_0.4_std; Hg_1.0_std; Hg_3.0_std; Hg_5.0_std
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage for up to 28 days. The expiration date cannot exceed the expiration date of any of the components.

7.3.2.1.3 Mercury Calibration Standards (Solids) – Transfer 0.0, 0.02, 0.04, 0.1, 0.3, and 0.5 mL portions of the Mercury Intermediate Standard to a series of 125-mL glass bottles. Add reagent water from a graduated cylinder to each bottle to make a final volume of 5.0mL. Add 5.0mL reagent water and 5.0mL aqua regia. Alternatively add 10mL of 1:1 aqua regia. Heat for at least 2 minutes in a water bath or digestion block at 95°C± 3°C. Allow the samples to cool to room temperature and add 20 mL reagent water and 15mL $KMnO_4$ solution to sample, cap, shake well, **loosen cap**, and place the samples in a water bath or block digestion apparatus at 95 ± 3°C for at least 30 minutes. Allow the samples to cool to room temperature. Add 6mL of sodium chloride-hydroxylamine sulfate solution to each bottle to neutralize excess $KMnO_4$. Add 12 mL reagent water to each sample, cap, and shake well. This should give a final volume of 68mL. All standards and samples must be at the same final volume.

LIMS Reagent Name: Hg_0.0_std; Hg_0.2_std; Hg_0.4_std; Hg_1.0_std; Hg_3.0_std; Hg_5.0_std
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage for up to 28 days. The expiration date cannot exceed the expiration date of any of the components.

7.3.2.2 Initial Calibration Verification Standards – Provided by the EPA. If not available, prepare as below.

7.3.2.2.1 Second Source Intermediate Standard, 1.0mg/L – Add 0.1mL of the 1000mg/L Second Source Hg Stock Standard, and 2.5mL of nitric acid to about 50mL of reagent water in a 100mL volumetric flask and dilute to volume with reagent water.

LIMS Reagent Name: Hg_icvint
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage for up to 28 days. The expiration date cannot exceed the expiration date of any of the components.

7.3.2.2.2 Second Source Initial Calibration Verification (ICV) Standard, 3.0ug/L – Add 0.15mL of the 1.0mg/L Second Source Intermediate Standard to a 125mL glass bottle. Add enough reagent water from a graduated cylinder to give a final volume of 50mL. The ICV is now ready to be digested. Other final volumes may be used as long as the reagent ratios are kept the same.

LIMS Reagent Name: Hg_ICV_std
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage for up to 28 days. The expiration date cannot exceed the expiration date of any of the components.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

Aqueous samples are routinely collected in 250mL plastic containers containing 3mL of a 1:3 nitric acid preservative. The preservative should be sufficient to achieve a sample pH of less than 2.

Samples must be iced at the time of collection and maintained at 4°C (+/-2°C) until the time of digestion. Samples must be digested within 26 days of the VTSR. Digestates may be stored at room temperature until the time of analysis. Digestates must be analyzed as soon as possible, but no more than 48 hours after digestion. After preparation, water samples may be stored at room temperature. Samples must be stored for a minimum of 60 days after submittal of the data package to the client.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives and/or de-chlorination agents.

8.1.1 Preservation Checks – pH Verification

For each sample, upon sample receipt,
- Place a piece of pH paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the pH paper.
- If the pH is outside the range of less than 2, initiate a Nonconformance Memo. Adjust the sample pH to less than 2 using 1:1 nitric acid.
- Mix well and hold for 24 hours. If pH is still greater than 2 repeat the process.

The pH verification must be recorded in the sample preservation method in LIMS.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the pH paper into the sample container. The pH paper dye may bleed into the sample and affect sample results.

Note: Samples that are not at pH <2 upon arrival in the lab may contain cyanide or sulfide or may be highly buffered. Working under a hood minimizes the hazard that may be caused by the evolution of hydrogen cyanide or hydrogen sulfide upon acidification of the sample. Be aware that acid/base neutralization reaction may be violent and evolve a significant amount of heat.

8.2 Soil Samples

Soil samples are routinely collected in 8oz plastic soil containers.

Samples must be iced at the time of collection and maintained at 4°C (+/-2°C) until the time of digestion. Samples must be digested within 26 days of the VTSR. Digestates may be stored at room temperature until the time of analysis. Digestates must be analyzed as soon as possible, but no more than 48 hours after digestion. After preparation, soil samples may be stored at room temperature. Samples must be stored for a minimum of 60 days after submittal of the data package to the client.

8.3 Sample Security

Security precautions are taken to ensure all samples are stored in such a manner as to eliminate sample tampering. In order to ensure the samples are secure, the laboratory requires key card access to enter all exterior doors. All samples are also tracked using the Internal Chain of Custody (ICOC) program in LIMS. Using the ICOC program, bar code readers are used to scan samples into each location as they are transferred throughout the building. Every transfer of location must be recorded to fully document sample receipt, storage, preparation, analysis, and disposal. Sample Digestates are tracked using a form external to LIMS.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

A digestion batch consists of up to 20 environmental samples and the associated QC items digested together within a 24 hour period.

> Note: All samples within an SDG must be prepped together.

The minimum QC items required for each digestion batch are: a method blank, a matrix spike (MS), and a sample duplicate.

> Note: The ISM01.2 reference method does not require a laboratory control sample (LCS) as part of the batch QC. The instrument QC (ICAL, ICV, and CCV) are prepared with each batch and prove the extraction procedure was valid.

The routine container supplied for this method is a 250mL/8oz. container. 100mL/1g is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 90mL/0.9g.

Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s) and/or sample duplicates, an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 200mL/2g.

Note: If insufficient sample volume is provided to perform the MS/MSD or MS/SD, the

LCS must be prepared in duplicate (LCS/LCSD). An NCM must be initiated on all samples within the batch to denote this situation.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

9.2.1 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves.* This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Note: The instrument must be re-calibrated every 24 hours, each time it is started up, or upon failure of the continuing calibration verification (CCV). Calibration standards must be prepared fresh with each calibration performed.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of at least five standards and a blank.

The initial calibration standard concentrations currently in use in the laboratory are as follows:

Standard Level	Concentration (ug/L)
1	0.0
2	0.2
3	0.4
4	1.0
5	3.0
6	5.0

Note: Other standard concentrations may be used provided they support the CRQL (Attachment 5) and are fully documented in accordance with SOP SA-AN-41.

Tabulate the concentrations and corresponding responses for each analyte. Establish a calibration curve by plotting the concentration (in ug/L) along the x-axis and the corresponding corrected instrument response along the y-axis.

The correlation coefficient (r) of the regression curve must be greater than 0.995 and the y-intercept must be less than the CRQL for each analyte for the initial calibration curve to be acceptable.

Note: The only types of equations allowed for calibration evaluation are a standard linear regression, a weighted linear regression, or a linear regression forced through zero. No other types of equations (e.g., quadratic) are to be used.

The responses from all of the calibration standards are read back using the calibration curve to determine the calculated concentration of the standards. All of the calculated concentrations must fall within 70-130% of the true value of the standards for the curve to be considered acceptable.

9.2.2 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source. The EPA will provide the ICV standard. Refer to Section 7.3.2.2.

The ICV must be within 15% of the true value to be acceptable.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to level 3.0ug/L of the ICAL. Refer to Section 7.3.2.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.3 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed immediately following the initial calibration verification (ICV). Continuing calibration blanks must be analyzed immediately following each continuing calibration verification (CCV).

The absolute value of the initial and continuing calibration blanks must be <CRQL (Attachment 5) to be acceptable.

9.2.4 Continuing Calibration Verification

The initial calibration curve must be verified initially, after every 10 determinations or one hour whichever is most frequent, and at the end of the analytical sequence with a mid-level standard.

The CCV must be within 15% of the true value to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to mid-level (2.5ug/L) of the ICAL. Refer to Section 7.3.2.1 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

Note: The CCV must be prepared from the same source as the ICAL and must be at or near the concentration of one of the mid-level standards.

Note: The same CCV standard must be used for all samples in an SDG.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* and the QC Summary Table in Attachment 3. SOP SA-QA-

05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

Remove the samples from the refrigerator and allow them to come to room temperature.

Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Compositing, Homogenization, and Segregation of Samples.*

10.1.1 Water Samples

10.1.1.1 Mix the sample thoroughly.

10.1.1.2 Using a 100mL digestion vial, add 100mL of sample or an aliquot of sample diluted to 100mL to a 125mL glass bottle. 50mL of sample may be used if the aliquot of reagents are proportionately reduced.

10.1.1.3 Add 2.5mL HNO_3, 5.0mL H_2SO_4, and 15mL of $KMnO_4$ solution to each sample. Mix well after each addition. Be sure the purple color of $KMnO_4$ persists for at least 15 minutes. If not, add 15mL of $KMnO_4$ solution up to three additional times.

Note: Equal quantities of $KMnO_4$ must be added to the calibration standards and MB.

10.1.1.4 Add 8mL of potassium persulfate to each sample, cap, shake well, **loosen cap**, and place the samples in a water bath or block digestion apparatus at 95 ± 3°C for at least 2 hours.

10.1.1.5 Remove the samples and allow them to cool. Add 6mL of sodium chloride-hydroxylamine sulfate solution to each bottle to neutralize excess $KMnO_4$. This should give a final volume of 136.5mL. All standards and samples must be at the same final volume.

Note: If additional volume(s) of $KMnO_4$ were added, compensate for the addition(s) by adding less DI water so that the final volume will remain constant.

10.1.2 Soil Samples

10.1.2.1 Homogenize the sample thoroughly. Weigh between 0.50-0.60g wet weight of sample into a 125-mL glass bottle.

10.1.2.2 Add 5.0mL reagent water and 5.0mL aqua regia. Alternatively add 10mL of 1:1 aqua regia. Heat for at least 2 minutes in a water bath or digestion block at 95°C± 3°C.

10.1.2.3 Allow the samples to cool to room temperature and add 20mL reagent water and 15mL $KMnO_4$ solution to sample, cap, shake well, **loosen cap**, and place the samples in a water bath or block digestion apparatus at 95 ± 3°C for at least 30 minutes.

Be sure the purple color of $KMnO_4$ persists for at least 15 minutes prior to placing samples in the water bath or block digestion apparatus. If not, add 15mL of $KMnO_4$ solution up to two additional times.

Note: Equal quantities of $KMnO_4$ must be added to the LCS and MB.

10.1.2.4 Allow the samples to cool to room temperature. Add 6mL of sodium chloride-hydroxylamine sulfate solution to each bottle to neutralize excess $KMnO_4$. Add 17mL reagent water to each sample or 12mL to each standard, cap, and shake well. This should give a final volume of 68mL. All standards and samples must be at the same final volume.

Caution: The addition of the sodium chloride-hydroxylamine sulfate solution should be performed under a hood as chlorine gas could be evolved.

Note: If additional volume(s) of $KMnO_4$ were added, compensate for the addition(s) by adding less DI water so that the final volume will remain constant.

10.2 Batch QC Sample Preparation

10.2.1 Water Samples

10.2.1.1 ICAL – Prepare according to instructions in Section 7.3.2.1.2.

10.2.1.2 ICV – Prepare according to the instructions provided by the supplier

10.2.1.3 Method Blank – Add 100mL of reagent water to a 125mL glass bottle. Prepare in accordance with Section 10.1.1.

Note: The method blank must be prepared using the same volume of each reagent as used for the field samples. If additional $KMnO_4$ was added to any of the field samples an equal volume must be added to the method blank.

10.2.1.4 Matrix Spike (MS) – Add 50mL of the sample selected for the batch matrix spike to a 125mL glass bottle. Add 0.1mL of the 500ug/L Hg Intermediate Standard to the sample. Prepare in accordance with Section 10.1.1.

10.2.1.5 Sample Duplicate – Add 50mL of the sample selected for the batch sample duplicate to a 125mL glass bottle. Prepare in accordance with Section 10.1.1.

10.2.2 Soil Samples

10.2.2.1 ICAL – Prepare according to instructions in Section 7.3.2.1.3

10.2.2.2 ICV – Prepare according to the instructions provided by the supplier

10.2.2.3 Method Blank – Use an empty digestion vessel and prepare in accordance with Section 10.1.2 for soils.

Note: The method blank must be prepared using the same volume of each reagent as used for the field samples. If additional $KMnO_4$ was added to any of the field samples an equal volume must be added to the method blank.

10.2.2.4 Matrix Spike (MS) – Add 0.5-0.6g of the soil sample selected for the batch matrix spike to a 125mL glass bottle. Add 0.50mL of the 500ug/L Hg Intermediate Standard to the sample. Prepare in accordance with Section 10.1.2.

10.2.2.5 Sample Duplicate – Add 0.5-0.6g of the soil sample selected for the batch sample duplicate to a 125mL glass bottle. Prepare in accordance with Section 10.1.2.

10.3 Analysis

10.3.1 Instrument Start-up and Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

Before analysis begins, inspect the system (pump tubes, mixing coil, gas/liquid separator) to see if any parts need to be cleaned or replaced.

Inspect the drying tube. Clean or replace as needed with a pre-made drying tube from Leeman Labs that has been inspected for discoloration. Caution should be used if moisture is visible in the tubing that follows the drying tube.

Fill the rinse tank with rinse water.

If the lamp is not already on and warmed up, turn on the lamp. The lamp must warm up for a minimum of 2 hours.

If the lamp is already on and warmed up, make sure the platens have the appropriate tension and turn on the pump. Allow a minimum of 20 minutes of pump time for the pump tubes to break in each day.

Rinse and fill the stannous chloride reagent bottle with stannous chloride solution. Switch the reagent line from the rinse bottle to the stannous chloride reagent bottle. Allow the reagent to reach the sample stream before starting an autosampler run.

Autosampler setup
Fill the standard tubes with the appropriate standards for the protocol being followed. (Refer to Section 10.3.4 for more information on method-specific analytical sequence and standards required.)

Fill the labeled sample test tubes with the samples and calibration verification standards in the proper order.

The method blank will be analyzed first. The LCS will follow immediately after the method blank. The samples, matrix spikes, and duplicates will then follow with a maximum of 10 analyses between CCVs/CCBs.

Enter the sample/QC IDs into the autosampler table giving each rack a unique name.

Load the rack(s) onto the autosampler.

10.3.2 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.1. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.2, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.4.

Calibration of the Mercury Analyzer
Call up the required protocol. Open a new data folder.

Go to CALIBRATION, RESET, and reset the calibration for a new calibration.

Go to CALIBRATION, STANDARDS, and ensure that calibration standards are entered at the proper concentrations.

Analyze the standards, beginning with standard 1 (Blank), proceeding from lowest to highest concentration.

When all calibration standards have been analyzed, go to CALIBRATION, LINE CALIBRATION. If calibration is within acceptable limits, accept the linear calibration and print the calibration curve.

10.3.3 Sample Analysis

The digestate must be analyzed using the same volume as that used for the calibration standards. Samples known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to include QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples between CCVs/CCBs.

Sample Analysis
Go to AUTOSAMPLER, SETUP. Enter the Rack IDs and the cup numbers to be analyzed.

Carryover from high concentration samples usually affects only the next one to two samples in the sequence. The two samples following an off-scale sample that is greater than 10ug/L must be reanalyzed to verify the presence or absence of mercury and the

quantitation of mercury. It is the responsibility of the analyst to clearly demonstrate that all mercury results are accurate and free from carry-over contamination.

10.3.4 Example Analytical Sequence

An example analytical sequence is listed below.

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
ICB	
CCV	Mid-Level (2.5ug/L)
CCB	
Up to 10 analyses including Batch QC Items	Up to 1 hour, including QC.
CCV	Mid-Level (2.5ug/L)
CCB	
Up to 10 analyses including Batch QC Items	Up to 1 hour, including QC.
CCV	Mid-Level (2.5ug/L)
CCB	

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review*.

11.1.1 Dilutions

If an analyte recovers outside the calibration range of the instrument, the sample must be diluted to bring the analyte into the top 75% of the calibrated range. If a multi-analyte method requires a sample dilution, unless the detection limit (adjusted for dilution and prep factors) is below the CRQL for all analytes the sample must also be analyzed and reported undiluted. The raw data from both the diluted and undiluted runs must be included in the package. The only time this can be avoided is if the laboratory can provide proof the undiluted analysis was not valid or would have damaged the ICP-MS instrument. Note: All metals sample dilutions must be made with appropriately acidified reagent water in order to maintain constant acid strength.

If the concentration of a sample is above the calibration range of the Hg analyzer, the sample digestate must be diluted and reanalyzed. The amount of digestate needed to prepare the desired dilution is determined from the following equation:

$$V_{digest} = \frac{V_{fv}}{DF}$$

Where:

V_{digest} = volume of sample digestate used to make the dilution
V_{fv} = final volume of diluted sample
DF = dilution factor

Note: Samples should be diluted with digested blank solution.

Note: This calculation assumes all applicable unit correction factors are applied.

The dilution factor is calculated as follows:

$$DF = \frac{V_{fv}}{V_{digest}}$$

Where:

V_{digest} = volume of sample digestate used to make the dilution
V_{fv} = final volume of diluted sample
DF = dilution factor

Note: This calculation assumes all applicable unit correction factors are applied.

11.1.2 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.1.3 Chemical Relationships

When available, the following chemical relationships must be evaluated for each sample. If these relationships are not met, the Department Manager must be contacted immediately.

- Total Results are $\geq$ Dissolved results (e.g. metals)

Note: If required, CVAA results can be confirmed via ICP/MS.

11.1.4 MARRS Data Reduction and Reporting

Savannah uses the Environmental Information Systems Corporation MARRS program for data reduction and reporting. The following is the procedure used:

An archive file is sent via the laboratory network to a second PC. The MARRS software uploads the archive file and compares the data to the quality control parameters that are built into the software. These parameters may be customized to meet specific project requirements.

11.1.4.1 When the data file is uploaded, the analyst reviews the data to ensure that the QC types are correct. The QC types are: samples, calibration standards, ICV, ICB, CRI, ICSA, ICSAB, CCV, CCB, prep blanks (liquid, solid), LCS (liquid, solid), serial dilutions, post-digestion spikes, MS/MSD, DUP, etc. If any typographical errors are noted by the

instrument analyst on the instrument's summary report, then these errors need to be corrected in the MARRS system.

11.1.4.2 The sample data are then compared to the tightest limits for the samples on the run. There are tables set up with the tightest criteria required. These tables are used for the initial data evaluation.

11.1.4.3 After the results are processed, a data review report is printed that shows the samples and QC that exceed the acceptable limits. When the report shows that acceptable limits are exceeded, the analyst will determine if the element is required for the project. If the element is not required, this is noted on the data review report. If the element is required, a reanalysis is initiated for that sample and element.

11.1.4.4 A report is printed that shows that the correct number of CCV/CCBs were analyzed with the samples. If more that 10 samples are analyzed between CCV/CCBs, then all affected samples are reanalyzed.

11.1.4.5 When the data reduction is complete, all compliant data are reported to the LIMS system.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

Regression Curve:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample
F = Final volume/weight
I = Initial volume/weight
dw = % Solids decimal equivalent
D = Dilution factor

Note: All dry weight corrections are performed automatically in LIMS.

Note: This calculation assumes all applicable unit correction factors are applied.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and annually thereafter, and verified annually in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs).*

The MDLs must be determined using the procedures in 40CFR Part 136 for each digestion procedure and each instrument used.

The MDL studies must be repeated any time major instrument maintenance is performed or there are changes in instrumentation or instrumental conditions.

Note: The MDL must be less than ½ the CRQL listed in Attachment 5.

12.2 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS, MS, SD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.3 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four

consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.4 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Acidic sample digestions – Neutralize before disposal into drain/sewer system.

15.0 References / Cross-References

- SOP SA-AN-41: *Reagent and Standard Materials Procedures*
- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06*: Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs)*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- USEPA Contract Laboratory Program Statement of Work for Inorganic Superfund Methods (Multi-Media, Multi-Concentration): ISM01.2, January 2010
  - Exhibit D – Part C: Analytical Methods for Cold Vapor Mercury Analysis
- Code of Federal Regulations Title 40 Subchapter D Water Programs Part 136 Guidelines for Establishing Test Procedures for the Analysis of Pollutants (40 CFR Part 136)

16.0 Method Modifications and Clarifications

The laboratory has adopted one-half the required volume (soils and waters) as the routine preparation volume since the method allows for one-half the volume to be prepared when insufficient sample is available.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs)
Attachment 6: Glassware Cleaning Posting

Attachment 1:
SOP Summary

Sample Preparation and Analysis Summary

This procedure is based on the absorption of characteristic radiation at 253.7nm by mercury vapor. After digestion, to convert all forms of mercury to the same oxidation state, the mercury ions are reduced to mercury by the addition of stannous chloride and aerated from solution after passing through a mixing coil. The mixture passes through a gas/liquid separator and through a drying tube. The vapor is passed through a flow cell positioned in the light path of an atomic absorption spectrophotometer. Mercury concentration is measured as a function of absorbance.

Analytical Sequence

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
ICB	
CCV	Mid-Level (2.5ug/L)
CCB	
Up to 10 analyses including Batch QC Items	Up to 1 hour, including QC.
CCV	Mid-Level (2.5ug/L)
CCB	
Up to 10 analyses including Batch QC Items	Up to 1 hour, including QC.
CCV	Mid-Level (2.5ug/L)
CCB	

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Listed below are the holding times and preservation requirements:

Matrix	Routine Sample Container	Minimum Sample Size	Preservation	Holding Time
Water	250mL or 500mL plastic	100mL	<6°C but not frozen 1:1 Nitric Acid to pH<2	Digest: 26 days of VTSR Analysis: 48 hours from digestion
Soil	8oz plastic or glass	1g	<6°C but not frozen	Digest: 26 days of VTSR Analysis: 48 hours from digestion

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration (ICAL)	Every 24 hours	1 blank and 5 standards Correlation coefficient ≥ 0.995 Read-back of standards must fall within +/- 30%	Recalibrate
Initial Calibration Verification (ICV)	At the beginning of the analysis	within ± 15%	Recalibrate
Continuing Calibration Verification (CCV)	At the beginning and end of the analysis and hourly.	within ±15%	Terminate the analysis. Correct the problem and reanalyze all samples since the last compliant CCV.
Calibration Blank (ICB/CCB)	After ICV and every CCV	Absolute value of the calibration blank must be <CRQL	Terminate the analysis. Correct the problem and reanalyze all samples since the last compliant CCB.
Method Blank (MB)	One per batch of twenty or fewer samples	Result <CRQL	Refer to SOP SA-QA-17
Matrix Spike (MS)	One MS per batch of twenty or fewer samples	75-125%	Refer to SOP SA-QA-17
Sample Duplicate (SD)	One per batch of twenty or fewer samples	For sample concentrations ≥5xCRQL, 20% RPD	Refer to SOP SA-QA-17
Demonstration of Capability (IDOC/CDOC)	Initially, per analyst, and then annually thereafter	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Method Detection Limit (MDL)	Upon method/instrument set-up, and then annually thereafter	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:
- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE							
Equipment Item	**Recommended Service Interval**						**Comments**
	D	**W**	**M**	**Q**	**SA**	**A**	
CVAA							
Pump Tubing	X						Inspect daily Replace as needed
Standard Cups	X						Inspect daily Clean or replace as needed
Drying Tube	X						Inspect daily dry drying tube and all connection tubes or replace as needed
Mixing Coil		X					Inspect weekly Clean or replace as needed
Sample Probe			X				Inspect monthly Clean or replace as needed
Mercury Lamp		X					Adjust weekly. Clean or replace as needed

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually

Contingency Plan
Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs, consisting of Hg lamps, drying tubes, flow cells,

tubing, and other common instrumentation components. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs)

Analyte	CAS Number	CVAA CRQL for Water (ug/L)	CVAACRQL for Soil [1] (mg/kg)
Mercury	7439-97-6	0.2	0.1

[1] The CRQLs for soils are based on 100% solids and on the exact weights and volumes specified in the method.

Note: The CRQL is the minimum level of quantitation acceptable under the contract Statement of Work (SOW).

Attachment 6:
Glassware Cleaning Posting

GLASSWARE CLEANING PROCEDURES
METALS DEPARTMENT

Graduated Cylinders

1. Scrub with hot, soapy H_2O and brush.
2. Rinse thoroughly with tap H2O.
3. Rinse with 10% HNO_3
4. Rinse thoroughly with DI H_2O.

Volumetric Flasks

1. Empty contents of flask
2. Squirt a small amount of cleaning detergent directly into volumetric flask
3. Fill flask 1/3 full with **HOT** H_2O
4. Replace top and shake flask.
5. Empty flask and rinse with **HOT** H_2O until no soap remains in flask.
6. Add approximately 10mL concentrated HNO_3 to 50mL, 100mL, and 250mL flasks --- replace top and shake well.

For 500mL or 1000mL flasks use 25mL and for 10mL flasks use 2 - 5mL of concentrated HNO_3.

7. Rinse 3 times with DI H_2O, filling flask 1/3 full and replacing top. Store until needed.

*** NEVER PLACE VOLUMETRIC FLASKS OR TOPS IN SINK OR DISHPAN WITH OTHER DIRTY DISHES.**

***Dispose of all acid waste in accordance with the TestAmerica Savannah Addendum to the Corporate Safety Manual.**

FME023:03.11.09:3

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

18.0 Revision History

Summary of Changes from Previous Revision:

- This SOP is a new SOP developed in conjunction with validation of this method. No version precedes this version.

ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS (PCBs) BY GC/ECD

(Methods: EPA 608, EPA 8081A, EPA 8081B, EPA 8082, and EPA 8082A)

Approvals (Signature/Date):

Andrea Teal — March 1, 2011
Andrea Teal — Date
Quality Assurance Manager

January 20, 2011
Benjamin Gulizia — Date
Laboratory Director / Lead Technical Director

Ernest B. Walton — February 3, 2011
Ernest Walton — Date
EH&S Coordinator / Technical Director

January 20, 2011
Josh Kellar — Date
Department Manager

Facility Distribution No. 1 **Distributed To:** QAN

1.0 Scope and Application

This SOP gives the procedures for the determination of organochlorine pesticides and polychlorinated biphenyls (PCBs) as Aroclors via gas chromatography/electron capture detection (GC/ECD).

The routine matrices performed by this procedure are waters and soils. Other matrices which may be performed include wipes, leachates, tissues, and wastes.

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

Liquid samples are extracted using continuous liquid-liquid extraction with methylene chloride. Approximately 1L of sample is extracted. The extract is concentrated, the solvent is exchanged to hexane, and the final volume of the extract is adjusted to 10mL.

Soil samples are extracted using the sonication extraction procedure. Approximately 15g of the homogenized sample is dried with anhydrous sodium sulfate and extracted with 1:1 acetone/hexane. The extract is concentrated to a final volume of 5mL.

The preparation procedures may also incorporate Florisil, copper (sulfur), acid (PCBs and selected pesticides only), or gel permeation chromatography (GPC) cleanups, as outlined in the applicable preparation SOP.

The extract is analyzed by gas chromatography using dual capillary columns (different phases) and dual electron capture (EC) detectors. This configuration allows for simultaneous detection and confirmation of the target compounds. Identification of the target compounds in samples is performed by comparing the retention times of the peaks with standards analyzed under the same GC conditions. Quantitation is performed using the internal standards calibration technique.

This SOP is based on the following methods: EPA Methods 608, 8081A, 8081B, 8082, and 8082A.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Acetone, hexane and methylene chloride must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. All possible cleanup procedures are listed below. If matrix interferences continue after a cleanup has been performed, the sample is diluted as needed for data analysis. If a cleanup is used, the method blank and laboratory control standard must also be subjected to the cleanup.

Clean-up Procedure	Application	Effectiveness
Florisil	Pest/PCBs	Eliminates polar non-target compounds
Sulfuric acid	PCBs	Eliminates polar and some unsaturated hydrocarbon interferences
Copper	Pest/PCBs	Eliminates elemental sulfur
GPC	Pest/PCBs	Eliminates high molecular weight non-target compounds and sulfur

Copper is effective at removing elemental sulfur, which elutes as a very large peak in the middle of the chromatogram. Treatment with sulfuric acid is a very effective means of removing polar compounds and unsaturated compounds from the sample matrix. These

two cleanups require fewer sample manipulations, which have less negative impact on the recoveries of the target compounds and surrogates than Florisil and GPC cleanups.

Florisil and GPC cleanups are generally not effective in removing non-target compounds that interfere with the analysis of the target compounds.

Florisil removes polar compounds, which are generally not soluble in n-hexane. Some municipal wastewaters or similar matrices may benefit from this cleanup but it is not effective in removing hydrocarbons that are similar in polarity to the target compounds.

GPC is not generally effective for the same reason as it removes high molecular compounds such as polymers and biological materials; that is, the compounds that interfere with the target compounds are of similar molecular weight and are not removed from the sample matrix. These two cleanups also require more sample concentrations and manipulations than are routinely employed, which negatively affects the recoveries of the spiked target compounds and surrogates.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

Acetone and hexane are flammable solvents. They can cause irritation to the respiratory tract. Overexposure can cause fatigue, confusion, headache, dizziness, and drowsiness.

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

Note: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS Online" button on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Acetone	Flammable	1000ppm TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500ppm TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Analytical Balance – Verify in accordance with SOP SA-AN-100 *Laboratory Support Equipment (Verification and Use)*

Top-loading Balance – Verify in accordance with SOP SA-AN-100 *Laboratory Support Equipment (Verification and Use)*

Data System – Target and Chemstation software are used to acquire, store, reduce, and output mass spectral data. This software has the capability of processing stored GC data by recognizing a GC peak within any given retention time window, comparing the retention time of the GC peak with retention time window of a known standard. The software also allows integration of the peak, calculation of response factors as or construction of a linear regression calibration curve, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the response factors.

Agilent Gas Chromatograph (5890II, 6890, or 6890N) – equipped with dual detectors (an ECD pair) and an autosampler.

Recommended column pairs:

CLP I fused silica capillary column 30 M x 0.32 mm ID x 0.50 μm film
CLP II fused silica capillary column 30 M x 0.32 mm ID x 0.25 μm film

The recommended configuration is to connect two capillary columns to a single injection port via a y-splitter and a length of guard column. The ends of each column are connected to separate detectors. A single injection is split between the two columns to provide simultaneous detection and confirmation of the target compounds.

Chemstation Data System – compatible with the GC and capable of detecting and storing chromatographic data.

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100 *Laboratory Support Equipment (Verification and Use)*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100 *Laboratory Support Equipment (Verification and Use)*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100 *Laboratory Support Equipment (Verification and Use)*

Disposable Transfer Pipettes – various sizes

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100 *Laboratory Support Equipment (Verification and Use)*

Detergent – FL70, used for washing non-disposable labware.

Autosampler Vials, Septa, and Caps – compatible with the autosampler

6.3 Sample Collection Containers

All sample collection containers are pre-cleaned, single-use disposable containers, which limits the potential for contamination. The routine sample collection containers supplied by the laboratory are:

1250mL amber without preservative (Part #: Daniels A131601)

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

Unless listed elsewhere in this SOP, the expiration dates given below apply.

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.*

Acetone, Hexane and methylene chloride must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

Hexane - residue grade or better; J.T. Baker 9262-03 (4L)
Storage: Room temperature, Flammable Solvent cabinet
Expiration: Unopened: Manufacturer's expiration date
Opened: Manufacturer's expiration date

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

Attachment 8 contains the recipes for the calibration standards for the routine target compounds.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

Aqueous samples are routinely collected in unpreserved 1-L amber glass containers.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 7 days of collection. Extracts must be stored separately at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

The samples must be checked for pH and for the presence of residual chlorine prior to preparation. NCMs must be initiated for samples collected in improper containers, for samples with extreme pH, or for sample containing residual chlorine. Refer to the applicable preparation SOP for sample preservation check information.

8.2 Soil Samples

Soil samples are routinely collected in 16oz glass soil jars.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 14 days of

collection. Extracts must be stored separately at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The minimum QC items required for each extraction batch are as follows:

EPA 608:
a method blank and a laboratory control sample (LCS), a matrix spike (MS) per 10% of samples analyzed, and a matrix spike duplicate (MSD).

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, 1 matrix spike, and 1 matrix spike duplicate.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), another matrix spike (from sample 11-20), and a matrix spike duplicate.

8000-series:
a method blank and a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD).

The routine container supplied for this method is a 1L container. 1L is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 500mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 2L.

If there is insufficient sample volume available to perform the batch MS/MSD, the LCS must be prepared in duplicate (i.e., LCSD). If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required. An NCM must be initiated on all samples within the batch to denote this situation

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

9.2.1 PEVAL Breakdown Standard

The column(s) must be evaluated prior to the analysis of the calibration standards and once every 12-hour clock for EPA 8081A and EPA 8081B. For EPA 608, this column evaluation is required once every 24-hour clock. The column evaluation is performed by injecting a PEVAL standard that contains Endrin and p,p'-DDT and calculating the percent breakdown of these compounds. The standard used for determining the percent breakdown must not contain any compounds that coelute with Endrin, DDT, or any of the corresponding breakdown products.

Note: This column evaluation does not have to be performed if PCBs are the only target compounds required. PCBs are stable and not subject to breakdown in the injection port.

Inject the Endrin/DDT breakdown standard. Check the peak integrations and calculate the breakdown as follows:

$$\%\text{Breakdown Endrin} = \frac{\text{Response(Endrin Aldehyde + Endrin Ketone)}}{\text{Response(Endrin + Endrin aldehyde + Endrin Ketone)}} \otimes 100$$

$$\%\text{Breakdown DDT} = \frac{\text{Response(DDE + DDD)}}{\text{Response(DDT + DDE + DDD)}} \otimes 100$$

The response (area) must be used to evaluate the breakdown. Do not use concentrations and do not "undetect" peaks that are below the RL or MDL. All peaks detected by the data system must be included in the percent breakdown calculation.

Breakdown Criterion

The breakdown for each compound must be less than 15% to be acceptable. If the breakdown exceeds 15%, the instrument requires column and/or injector port maintenance. The maintenance may include, but is not limited to, replacing the septum, clipping the front of the guard column, replacing the glass injector sleeve, and scrubbing (cleaning) the injector port.

Note: If 2,4'-DDT and its degradates, 2,4'-DDD and 2,4'-DDE, are target compounds, the system must be tested for breakdown of 2,4'-DDT. The same % breakdown criterion is used to evaluate the column. Calculate the breakdown as follows:

$$\%\text{Breakdown 2,4'-DDT} = \frac{\text{Response(2,4'-DDE + 2,4'-DDD)}}{\text{Response(2,4'-DDT + 2,4'-DDE + 2,4'-DDD)}} \otimes 100$$

9.2.2 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves.* This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 5 standards for the 8000-series methods and a minimum of 3 standards for EPA 608. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

Note: A minimum of 6 points is required for a quadratic curve. Higher order curves are not permitted. Some programs and agencies (e.g., SC DHEC) do not allow the use of quadratic curves. Refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited.

The initial calibration standard concentrations currently in use in the laboratory are listed in Attachment 8. Refer to Attachment 8 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-41.

9.2.2.1 ICAL Criteria

The preferred method of quantitation is the average response factor. The relative standard deviation (%RSD) of the calibration standards must be <20% for the 8000-series methods and <10% for EPA 608 for the initial calibration curve to be acceptable.

If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve. If the regression curve option is chosen, the regression coefficient (r^2) must be greater than or equal to 0.990 to be acceptable.

If these criteria are not met, then re-calibration is required before sample analysis can proceed.

9.2.2.1.1 Grand Mean Exception (8000-series methods only)

SW-846 allows the use of the "grand mean exception" as described below. This exception should only be applied to initial calibration curves in extraordinary circumstances because of the difficulty of maintaining and providing documentation on an on-going basis.

Grand Mean Exception (GME): If one or more analytes exceed the %RSD criteria, the calibration curve is acceptable if the average of the %RSDs for all of the analytes in the ICAL (i.e., the grand mean) is less than or equal to the ICAL %RSD criteria.

SW-846 does not place a cap on an individual analyte's %RSD as long as the average is within criteria; however, the laboratory has adopted the requirement that no individual analyte can exceed 3X the ICAL criteria. Therefore, the calibration curve is acceptable if the average of the %RSDs is less than or equal 20% with no individual analyte exceeding 60%.

Note: Some programs and agencies do not allow the use of the grand mean exception. Refer to the Project Requirement Summary and/or Project Plan to determine if GME is not allowed.

9.2.3 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified after the initial calibration is established, prior to any sample analyses, in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to Level 4 of the ICAL. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

EPA 608, EPA 8081A, and EPA 8082:
The ICV is acceptable if the average of the %RSDs for all of the analytes in the ICV is less than 15% with no single analyte's %RSD greater than 45%.

EPA 8081B and EPA 8082A:
The ICV is acceptable if the average of the %RSDs for all of the analytes in the ICV is less than 20% with no single analyte's %RSD greater than 60%.

Note: ICVs are not required for the non-Aroclor PCBs. The AR1660 ICV is used to satisfy this evaluation.

9.2.4 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed at the beginning of each sequence. Continuing calibration blanks are analyzed in each clock.

Initial and continuing calibration blanks must be <1/2RL to be acceptable.

9.2.5 Continuing Calibration Verification

For EPA 608, the initial calibration curve must be verified at the beginning of each 24-hour clock with a mid-level standard. The CCV must be within +/-15% to be acceptable.

For EPA 8081A and EPA 8082, the initial calibration curve must be verified at the beginning and end of each 12-hour clock with a mid-level standard. The CCV must be within +/-15% to be acceptable.

For EPA 8081B and EPA 8082A, the initial calibration curve must be verified at the beginning and end of each 12-hour clock with a mid-level standard. The CCV must be within +/-20% to be acceptable.

Refer to Attachment 8 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

- Note: The routine CCV standards are the Pest A/B mix and the AR1660 standard. Single points of the remaining Aroclors, technical chlordane, and toxaphene are analyzed at least every 72 hours (e.g., Monday, Wednesday, and Friday) to update the retention times and for pattern recognition. As long as the Pest A/B calibration

standard and the AR1660 standard meet the calibration acceptance criteria, the ICAL is deemed acceptable for all targets.

9.2.5.1 Grand Mean Exception (8000-series methods only)

SW-846 allows the use of the "grand mean exception" as described below.

Grand Mean Exception (GME): If one or more analytes exceed the %D criteria, the CCV is acceptable if the average of the %s for all of the analytes in the CCV (i.e., the grand mean) is less than or equal to the CCV %D criteria.

SW-846 does not place a cap on an individual analyte's %D as long as the average is within criteria; however, the laboratory has adopted the requirement that no individual analyte can exceed 3X the CCV criteria. Therefore, the CCV is acceptable if the average of the %Ds is less than or equal 15% with no individual analyte exceeding 45% (for EPA 8081A and EPA 8082) and less than or equal 20% with no individual analyte exceeding 60% (for EPA 8081B and EPA 8082A)

Note: Some programs and agencies do not allow the use of the grand mean exception. Refer to the Project Requirement Summary and/or Project Plan to determine if GME is not allowed.

9.2.6 Internal Standard (ISTD)

This procedure is an internal standard (ISTD) procedure. 1-Bromo-2-nitrobenzene (BNB) is the internal standard.

Prior to analysis, this internal standard must be added to all standards, samples, and QC items. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. A concentration of 0.1ug/mL is used.

The response of the ISTD in the ICV/CCV must be within 50% of the response of the ISTD in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the CCV must be repeated and any samples associated with the CCV must also be re-analyzed. Repeated failure of the ISTD response will require re-calibration.

The response of the ISTD in the samples and batch QC items must be within 50% of the response of the previous ICAL. If the response is outside of this range, corrective action must be taken which can include reanalysis of the extract, re-spiking extract with ISTD and re-analysis, or re-calibration of the analytical system. Obvious matrix interferences are qualified and noted in an NCM.

9.2.7 Surrogate

This procedure uses surrogates to evaluate the extraction process. Decachlorobiphenyl (DCB) and Tetrachloro-m-xylene (TCMX) are the surrogates. Prior to preparation, these surrogates are added to all samples and QC items. The concentration of the surrogate is the same in all field samples and QC samples. A concentration of 0.50ug/L for water samples and a concentration of 16.7ug/kg is used for soil samples.

The percent recovery of the surrogate in all field samples and QC samples must be within the limits listed in the Method Limit Groups (MLGs) in LIMS. If the percent recovery is outside of this range, the analysis of the sample must be repeated. Barring obvious matrix interferences, repeated failure of the surrogate percent recovery may indicate re-extraction is necessary.

Note: If one of the surrogates is within the acceptance limits and the other surrogate recovery is >10%, a field sample is deemed acceptable and re-extraction and re-analysis is not automatically performed.

9.2.7.1 Surrogate Dilution Factor Threshold

Due to the level of dilution required for samples, surrogates may be diluted out. As such, recoveries will be reported as "0D" in dilutions greater than DF5. Control limits will not apply to samples analyzed at dilutions of greater than DF5.

An NCM must be initiated to denote this situation.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

The sample preparation procedures are given in the following SOPs:

Matrix	SOP
Aqueous Samples	SA-EX-30
Soil Samples	SA-EX-40

10.2 Analysis

10.2.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

Two columns are connected to the injection port using a press-tight glass y-splitter and a guard column, a two-hole ferrule, or a glass tee to provide simultaneous detection and confirmation of the target analytes.

Example GC Parameters
Injector: 220-240°C
Detector: 300-320°C
Carrier Gas Flow: hydrogen or helium at 2-5mL/min (per column)
Make-up Gas Flow: Nitrogen at 50-100mL/min (per detector) – see manufacturer's recommended flows

Temperature Program:

Initial Temp:	160°C
Initial Hold:	4 min
Program Rate:	10°C/min
Final Temp:	270°C (hold for 10 minutes)
Injection Volume:	1-2uL per column (single injection into guard column and "Y" splitter)

Note: These conditions and parameters are given for guidance. The columns/phases, GC conditions, and instrument parameters may be modified to optimize each analytical system.

10.2.1.1 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in SOP SA-QA-08: *Evaluation of Chromatographic Data*. Retention time windows (RTW), i.e., the length of time the instrument will scan for the analyte, must be established initially upon instrument set-up and verified quarterly.

Retention times (RT), i.e., the elution time of the analyte, are verified daily with the analysis of the ICAL or CCV. The retention time for the CCV must fall within the daily retention time window as defined in SOP SA-QA-08.

10.2.2 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.2. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.3, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.5.

10.2.3 Sample Analysis

The term "clock time" defines the continuing calibration verification frequency. The clock time starts at the injection of the PEVAL. The analysis of samples and batch QC items may continue until the clock time expires. A new PEVAL and CCV (i.e., a new clock) is required

to proceed with the analysis of more samples and/or batch QC items. The clock time is defined as 12 hours for the 8000-series methods and 24 hours for EPA 608.

Remove the extracts from the refrigerator and allow them to come to room temperature.

Transfer 1.0mL of the extract to an autosampler vial and add 0.10mL of the internal standard solution to give an internal standard concentration of 0.10ug/mL. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples.

The sample extract must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to exclude QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the clock.

10.2.4 Example Analytical Sequence

Refer to Attachment 1 for an example analytical sequence.

Guidance for the evaluation of the calibration standards, field samples, and QC items are summarized in Section 9 and in Attachment 3, the QC Summary.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data evaluation must be performed in accordance with SA-QA-08: *Evaluation of Chromatographic Data.* This SOP includes specific information regarding the evaluation of chromatographic data, including the requirements for performing manual integrations and the evaluation of retention times.

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review.*

11.1.1 Target Analyte Identification

The judgment and experience of the analyst and his/her colleagues are important factors in the evaluation of chromatographic data. Inspect each chromatogram to ensure that the peaks are properly identified and that the correct areas have been associated with the corresponding standard peak RT in the data system tabulation.

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times); the recovery and retention time shift of the surrogate compounds, whether the peak response falls within the working range of the calibration; and the integration of the peaks. The analyst must also take into account the results from the

method blank and lab control sample before reporting quantitative data. SOP SA-QA-08: *Evaluation of Chromatographic Data* provides additional guidance for the evaluation of chromatographic data. This guidance is summarized in the following sections.

11.1.2 Manual Integrations

Manual integrations must be documented in accordance with SOP SA-QA-08. Data systems should be adjusted to minimize operator intervention. All chromatographic peaks must be evaluated for overall peak shape and "reasonableness" of integration. Under no circumstances should manual integrations be used to change reasonable data system integrations in order to meet calibration or QC criteria.

11.1.3 Dual Column Reporting

Refer to SOP SA-QA-08: *Evaluation of Chromatographic Data* for information on assessing and reporting data from dual columns.

11.1.4 Surrogate Evaluation

Two surrogates, TCMX and DCB, are spiked into each sample and QC item prior to preparation. Given the complicated nature of GC-ECD chromatograms, assessing surrogate recovery is frequently complicated by co-eluting positive and negative interferences. Evaluate the surrogates in the same manner as the target compounds using the guidance above.

Two surrogates are added to all samples and field samples. The laboratory's policy is:

- both surrogates must be within the recovery limits for method blanks and LCS
- one surrogate must fall within the recovery limits for all samples and the other surrogate must have a recovery of at least 10%.
- dilution cannot be used as a justification for not re-analyzing or re-extracting a field sample if the sample can be analyzed at a dilution factor of five or less.

TCX	DCB	Action
Within limits	Within limits	Evaluate and report data
Within limit	Below LCL but >10% recovery	Evaluate and report data
Below LCL but >10% recovery	Within limits	
Below LCL	Below LCL	-reanalyze -re-extract unacceptable samples
Above UCL	Above UCL	Evaluate and report data if not target compounds are detected and recovery is <50% above the UCL

LCL = lower control limit UCL = upper control limit

NOTE: For samples that contain Aroclor 1268, TCX is used to determine if the surrogate recovery is acceptable. DCB is a component of AR1268 and will bias the recovery high.

Refer to Section 11.1.5.1 for information on the surrogate dilution threshold factor.

11.1.5 Dilutions

If the response for an analyte exceeds the working range of the system, a dilution is required. Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags must be used or qualification in a case narrative provided to the client.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 5 to provide lower reporting limits.

Prepare dilutions for sample extracts where the target compounds exceed the calibration range as follows:

Dilution Factor (DF)	Volume of Sample Extract	Final Volume* (mL)
2	0.50	1.0
5	0.20	1.0
10	0.10	1.0
20	0.50	10
50	0.20	10
100	0.10	10
200	Perform DF10, then DF20	
500	Perform DF10, then DF50	
1000	Perform DF10, then DF100	
2000	Perform DF20, then DF100	
5000	Perform DF50, then DF100	
10000	Perform DF100, then DF100	
20000	Perform DF20, then DF1000	
50000	Perform DF50, then DF1000	
100000	Perform DF100, then DF1000	

* Final Solvent = Hexane

Transfer 1.0mL of the dilution to an autosampler vial and add 100uL of the internal standard.

11.1.5.1 Surrogate Dilution Threshold Factor

Surrogates may be diluted out if the concentration of target compounds is high or the presence of non-target compounds interferes with the quantification of the target compounds. Undetect surrogates in the sample when the dilution factor is greater than 5. As such, recoveries must be reported as "0D", and control limits will not apply.

An NCM must be initiated to denote this situation.

11.1.5.2 Dilutions and MS/MSD Recoveries

Matrix spike recoveries are not reported for dilutions of greater than 5. An NCM is generated for instances where the dilution prohibits evaluation of the MS/MSD recoveries. In instances where the unspiked sample concentration is more than four times the concentration of the target compound spiked into the MS and MSD, the results are qualified with "4" or other suitable flag.

An NCM must be initiated to denote this situation.

11.1.6 Chemical Relationships

The analyst must be aware of the following chemical relationships:

Alpha-BHC, beta-BHC, delta-BHC, and gamma-BHC are isomers and will generally be present together in a sample. Gamma-BHC is usually the predominant isomer present and the only BHC isomer on the regulated drinking water list.

When 4,4'-DDT (p,p;-DDT) is present in a sample, its breakdown products, 4,4'-DDD and 4,4'-DDE will usually be present, too.

11.1.7 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes and/or use the TALS Historical Data Tracker feature to determine if historical data is available for review.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample
F = Final volume/weight
I = Initial volume/weight
D = Dilution factor
dw = % Solids decimal equivalent

Note: All dry weight corrections are performed automatically in LIMS.

Note: This calculation assumes all applicable unit correction factors are applied.

12.0 Method Performance

12.1 Reporting Limit Verification (RLV)

At a minimum, RLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, RLVs must also be performed quarterly thereafter. For all other analytes and methods, RLVs must also be performed annually thereafter. Exceptions may be made for project-specific non-routine analytes.

12.2 Method Detection Limit (MDL) Study

The MDL is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDLs associated with this procedure are given in the Method Limit Group (MLG) in TALS.

At a minimum, MDL Studies must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

Note: MDL Studies are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.3 Method Detection Limit Verification (MDLV)

At a minimum, MDLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, MDLVs must also be performed quarterly thereafter. For all other analytes and methods, MDLVs must also be performed annually thereafter.

Note: MDLVs are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.2 QC Limit Generation, Control Charting, and Trend Analysis

12.2.1 EPA 608

The control limits for the batch QC items (LCS/LCSD and MS/MSD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

12.2.2 EPA 8081A, EPA 8081B, EPA 8082, and EPA 8082A

The control limits for the batch QC items (LCS/LCSD and MS/MSD) for this procedure are not specified by the reference method; therefore, the laboratory defaults to in-house and/or laboratory-derived limits for the evaluation of batch QC items.

12.2.3 Even when the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data*.

12.1 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.2 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Flammable waste (hexane and methanol from extracts, rinsings, and standards) - Transfer to a satellite container designated for flammable waste and transfer to waste disposal department when the container is full.

- Methylene chloride extracts - Dispose according to characterization on sample disposal sheets. If non-hazardous, transfer extract to chlorinated waste container. If hazardous, transfer to hazardous waste department for storage.

15.0 References / Cross-References

- SA-AN-100 *Laboratory Support Equipment (Verification and Use)*
- SOP SA-AN-41: Reagent and Standard Materials Procedures
- SOP SA-EX-15: Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP)
- SOP SA-EX-030: *Liquid Extraction Procedures: Continuous Liquid-Liquid and Separatory Funnel*
- SOP SA-EX-040: *Sonication Procedures*
- SOP SA-EX-42: *Waste Dilution Extraction*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-08: *Evaluation of Chromatographic Data*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual

- Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, December 1996 and February 2007.
  - Method 8000B: Determinative Chromatographic Separations, Revision 2; December 1996.
  - Method 8081A: Organochlorine Pesticides by Gas Chromatography, Revision 1; December 1996
  - Method 8081B: Organochlorine Pesticides by Gas Chromatography, Revision 2; February 2007
  - Method 8082: Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Revision 0; December 1996
  - Method 8082A: Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Revision 1; February 2007
- *Code of Federal Regulations, Title 40, Part 136*; U.S. Government Printing Office: Washington, DC, July 1, 1988.
  - Method 608: Organochlorine Pesticides and PCBs

16.0 Method Modifications

16.1 Incorporation of Other Matrices

This procedure may be modified to analyze other matrices (e.g., wipe, waste, tissue, and TCLP/SPLP leachate samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project.

Wipe, waste, and tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and default QC limits to evaluate wipe, waste, filter, and tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. The laboratory uses its routine aqueous RLs (converted for initial and final volumes, etc.) and default QC limits to evaluate TCLP/SPLP leachate samples. Water DOCs can be used to satisfy analyst demonstrations of capability for TCLP/SPLP matrices. Teflon chips, Ottawa sand, or equivalent is used as the blank matrix for wipes, wastes, and tissues unless specifically requested otherwise by the project.

16.1.1 Collection and Handling Procedures

Waste (Oil) Samples:
Waste (oil) samples are routinely collected in 8oz soil containers with PTFE-lined lids. Waste (oil) samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

Wipe Samples:
Wipe samples are routinely collected in 40mL VOA vials. Wipe samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until time of preparation. Samples must be prepared within 14 days of collection. Extracts must be

stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

Tissue Samples:
Tissue samples are routinely collected in plastic containers with the size dependent upon the type of tissue being collected. Plastic jars or plastic baggies can be used. Upon receipt, samples must be placed in the freezer at -10° to -20°C if extraction/digestion cannot be completed that day and must be kept frozen until the time of preparation. A holding time of six months from the date of collection for frozen fish fillets is recommended by Alabama Department of Environmental Management (ADEM) and will be used for all biological tissues. Once the tissue has been thawed it must be stored at 4°C (less than 6°C but not frozen) and preparation must take place within 14 days. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

TCLP/SPLP Leachate Samples
Once the TCLP/SPLP extraction procedure has been performed, the leachate is transferred to a 1L glass container. TCLP/SPLP leachates must be stored at 4°C (less than 6°C with no frozen samples) until the time of preparation. The leachate sample must be prepared within 7 days of completion of the TCLP/SPLP extraction. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

16.1.2 Preparation and Analytical Procedures

Wipe, waste, and tissue samples are prepared in the same manner as routine soil samples as outlined in SOP SA-EX-040. TCLP/SPLP matrices are prepared in the same manner as routine water samples as outlined in SOP SA-EX-030. Refer to the applicable preparation SOPs for more information.

Wipe, waste, filter, tissue, and TCLP/SPLP matrices are analyzed in the same manner as routine samples as outlined in this SOP.

16.2 Other Considerations

16.2.1 EPA Method 608 was written specifically for industrial and municipal wastewater samples; however, the laboratory may perform other types of water samples using this procedure.

16.2.2 The procedures for chlorinated pesticides (EPA 8081A and EPA 8081A) and PCBs (EPA 8082 and EPA 8082A) are given as separate methods in SW-846. The extraction and the analysis are combined in this SOP to reduce the time of extraction and analysis, and to reduce the amount of solvent used in the procedures (one extraction instead of two). If interferences or high levels of non-PCB compounds are present, a portion of the extract can be subjected to the acid cleanup and reanalyzed.

16.2.3 Although this procedure incorporates the use of internal standard quantitation and the NELAC Standard expressly states that capping CCVs are not required for internal standard methods, the laboratory's default procedure for continuing calibration verification is to perform a bracketing CCV every 12 hours (or 20 samples) and at the end of the analytical sequence for samples being analyzed by EPA 8081A, EPA 8081B, EPA 8082, and EPA

8082A. The only exception to this requirement is for samples requesting EPA 8082A only (i.e., PCBs only).

16.2.4 The laboratory incorporates the use of the grand mean exception, for the 8000-series methods, to evaluate calibration data according to the provisions outlined in SW-846 Method 8000B. EPA Method 8000B does not place a cap on an individual analyte's %D or %RSD when evaluating the grand mean exception. The laboratory has adopted more stringent in-house requirements as outlined in this SOP.

16.2.5 The reference methods do not require the analysis of an ICV. NELAC requires an ICV; however, it does not list specific criteria. The laboratory has adopted the default criteria listed in Section 9 for ICVs for these methods.

16.2.6 The laboratory allows one surrogate compound to be outside acceptance limits, in field samples and MS/MSD, provided their recovery is greater than 10%.

16.2.7 The reference methods do not require the analysis of an instrument blank; however, the laboratory routinely analyzes instrument blanks items and has adopted in-house criteria as outlined in this SOP.

16.2.8 The laboratory has incorporated the minimum batch QC items as outlined in Section 9.1. Some additional QC items are routinely performed to satisfy common regulatory and/or client requests for precision data and/or to facilitate scheduling and data evaluation.

16.2.9 The laboratory has incorporated the evaluation of the breakdown check standard (PEVAL) for both EPA 608 and the 8000-series methods. This standard is required by the 8000-series methods, but is only recommended for EPA 608.

16.2.10 EPA SW-846 Update IV Chapter 4 re-defined the holding times for PCBs as "NONE". The EPA Methods Update Rule re-defined holding times for PCBs as one year from collection to extraction and one year from extraction to analysis. The laboratory has not incorporated these extended holding times for PCBs, and uses an internal default holding time equivalent to the previously defined (shorter) method holding times as listed in Section 8.0.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Qualitative Analysis of Multiple Peak Compounds-Evaluation of Field and QC Samples for PCB as Aroclors
Attachment 6: Qualitative Analysis of Multiple Peak Compounds-Evaluation of Field and QC Samples for Toxaphene
Attachment 7: Qualitative Analysis of Multiple Peak Compounds-Evaluation of Field and QC Samples for Technical Chlordane
Attachment 8: Standard Preparation Recipes

Attachment 1: SOP Summary

Sample Preparation Summary

Liquid samples are extracted using continuous liquid-liquid extraction with methylene chloride. Approximately 1L of sample is extracted. The extract is concentrated, the solvent is exchanged to hexane, and the final volume of the extract is adjusted to 10mL.

Soil samples are extracted using the sonication extraction procedure. Approximately 15g of the homogenized sample is dried with anhydrous sodium sulfate and extracted with 1:1 acetone/hexane. The extract is concentrated to a final volume of 5mL.

The preparation may also incorporate Florisil, copper (sulfur), acid (PCBs only), or gel permeation chromatography (GPC) cleanups.

Samples should be prepared according to the appropriate matrix-specific SOP.

Matrix	SOP
Aqueous Samples	SA-EX-030
Soil Samples	SA-EX-040

Sample Analysis Summary

The extract is analyzed by gas chromatography using dual capillary columns (different phases) and dual electron capture (EC) detectors. This configuration allows for simultaneous detection and confirmation of the target compounds. Identification of the target compounds in samples is performed by comparing the retention times of the peaks with standards analyzed under the same GC conditions. Quantitation is performed using the internal standards calibration technique.

Example Analytical Sequence

PEVAL
Initial Calibration 5-pt single peak Pesticides 5-pt AR1660 5-pt Toxaphene 5-pt Technical Chlordane 1-pt remaining Aroclors 5-pt APIX or additional compounds, if requested
Instrument Blank
ICV - 2nd Source (Pesticides, AR1660, Toxaphene, Technical Chlordane, and APIX)
PEVAL – Clock Time Starts
Analyze sample and QC extracts until Clock Time expires
PEVAL – Clock Time Starts
CCV (Pesticides, AR1660, and APIX)
Instrument Blank
Analyze samples and QC extracts until Clock Time expires
CCV (Pesticides, AR1660, and APIX)
Instrument Blank
Analyze samples and QC extracts until Clock Time expires
CCV (Pesticides, AR1660, and APIX)
Instrument Blank

*Note 1 - A mixture of AR1016 and AR1260 will be used as the continuing calibration verification standard for all Aroclors. Mid-level CCV standards of the remaining Aroclors, toxaphene, and technical chlordane must be analyzed every 72 hours for pattern recognition and retention time.

*Note 2 – PEVAL Breakdown Check is not required for PCB-only analyses

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Matrix	Routine Sample Container	Routine Sample Size	Minimum Sample Size	Chemical Preservation	Thermal Preservation	Dechlorination Agent	Holding Time
Water	1L amber glass	1L	500mL	None	4°C[1]	None	7 days to extract[2] 40 days to analyze[3]
Soil	16oz glass soil jar	15g	15g	None	4°C[1]	None	14 days to extract[2] 40 days to analyze[3]

[1]Samples must be maintained at 0-6°C, with no frozen samples.
[2]From sample collection.
[3]From sample preparation.

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Clock Time	EPA 608: 24 hours EPA 8000-series: 12 hours (or 20 samples, whichever comes first)	Clock time starts with the injection of the PEVAL. Analysis of samples and QC items must conclude within expiration of clock time. Subsequent analysis requires new opening PEVAL and CCV.	Not Applicable
Breakdown Check (PEVAL)	At beginning of each clock	Breakdown <15% for both DDT and Endrin	-Re-analyze check solution -Perform injector port and/or column maintenance and re-analyze
Initial Calibration (ICAL)	Upon instrument set-up, and after unsuccessful CCV	EPA 608: 3-point minimum; RSD <10%; r^2>0.990 EPA 8000-series: 5-point point minimum; RSD <20%; r^2>0.990	Refer to SOP SA-QA-16
Initial Calibration Verification (ICV) - Second Source	After each ICAL	EPA 608 %D<15% EPA 8081A & EPA 8082: %D<15%; GME<15%, w/ no analyte >45% EPA 8081A & EPA 8082: %D<20%; GME<15%, w/ no analyte >60%	Refer to SOP SA-QA-16

QC Item	Frequency	Criteria	Corrective Action
Continuing Calibration Verification (CCV)	EPA 608: Initially, and every 24 hours thereafter 8000-series: Initially, after every 12 hours (or 20 samples, whichever comes first), and at the end of the sequence	EPA 608 %D<15% EPA 8081A & EPA 8082: %D<15%; GME<15%, w/ no analyte >45% EPA 8081A & EPA 8082: %D<20%; GME<15%, w/ no analyte >60%	Refer to SOP SA-QA-16
Calibration Blank (CCB/ICB)	After ICV and every CCV	<1/2 RL	- Terminate the analysis; correct problem; reanalyze affected samples.
Internal Standard (ISTD)	All field, batch QC, & instrument QC samples	CCV: - Response of the internal standard must be within a range of +/-50% of the ICAL mid-level std Samples: - Response within +/-50% of previous CCV - RT within window defined by previous CCV	-Evaluate chromatogram and integrations. -Reanalyze or dilute and reanalyze -Flag data
Extraction Batch Definition	Extracted together w/in 24-hr period; Not to exceed 20 field samples	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	<½ RL	Refer to SOP SA-QA-17

QC Item	Frequency	Criteria	Corrective Action
Laboratory Control Sample (LCS)	One per batch	Within MLG limits	Refer to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	One per batch, if insufficient sample for MS/MSD	Within MLG limits	Refer to SOP SA-QA-17
Matrix Spike (MS)	EPA 608: 10% of samples 8000-series: Per batch	Within MLG limits	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	Per batch	Within MLG limits	Refer to SOP SA-QA-17
Surrogates	All field, batch QC, & instrument QC samples	Within MLG limits Surrogate DTF = 5	Refer to SOP SA-QA-17
Retention Time Window (RTW) Determination	Annually, after major instrument maintenance, and with each new column	Refer to SOP SA-QA-08	Refer to SOP SA-QA-08
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06 Note: Unsupervised work must not begin until acceptable IDOC is obtained.
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06

QC Item	Frequency	Criteria	Corrective Action
Reporting Limit Verification (RLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Method Detection Limit Study (MDL)	Upon method/instrument set-up, per analyte/method/matrix combination	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
MDL Verification (MDLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
	Service Interval							
EQUIPMENT ITEM	D	W	M	Q	SA	A	AN	SERVICE LEVEL
Guard Column/Injector							X	Change sleeve and cut front of guard column, recommended daily
Septum							X	Replace , recommended daily
Splitless Disc							X	Replace , recommended daily
Autosampler							X	Syringe cleaned or replaced as needed
Column							X	Change column

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually; AN = as needed

Troubleshooting

Troubleshooting should be documented as outlined above. If possible, troubleshooting is best performed in a step-wise manner to systematically isolate instrument components. Refer to the instrument manufacturer's guides for specific information and strategies. Enlist assistance from technical and/or department management as needed.

Contingency Plan

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Maintenance Log

A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Instrument Labeling

Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Attachment 5:
Qualitative Analysis of Multiple Peak Compounds

Evaluation of Field and QC Samples for PCBs as Aroclors

PCBs are reported as Aroclors, which are mixtures of PCB congeners. The Aroclors are named by percentage of chlorine in each mixture with the prefix 12- to represent the biphenyl molecule.

Aroclor	% Chlorine by Weight
1221	21
1232	32
1016	41.5
1242	42
1248	48
1254	54
1260	60
1262	62
1268	68

The exception to this naming convention is AR1016, which is about 42% chlorine by weight. AR1016 and AR1242 have similar chromatograms - both Aroclors have almost the same weight of chlorine by weight and nearly the same PCB congeners.

Aroclors are identified by matching the pattern of the sample with standards analyzed under the same analytical conditions. Interference may occur due to the presence of non-target analytes or due to "weathering" or degradation of the Aroclor in the environment. The presence of multiple Aroclors will also complicate identification and quantitation. Many matrix interferences may be reduced or eliminated by treating the sample extract with copper and sulfuric acid prior to analysis. The applicable preparation SOPs detail this procedure.

Note: Do not use the acid cleanup **on the entire extract** if pesticides are also to be reported as many of the pesticides are not stable in acid or strong oxidizer. Use a separate aliquot of sample to subject to acid clean-up if pesticides and PCBs are required.

When a pattern matching an Aroclor is encountered, it is quantitated using 3-5 characteristic peaks Residues of either AR1016 or AR1260 are quantitated using the average RF/CF determined during initial calibration. The other Aroclors are quantitated against the RF/CF determined from their single-point analysis during initial calibration. Samples should be diluted when the amount of PCB in a sample extract exceeds the calibration range defined in initial calibration. Note that the AR1660 standard defines the working range for all the Aroclors. (i.e. if AR1660 was calibrated from 0.10µg/mL to 2.5µg/mL, and a sample extract was analyzed containing 10µg/mL of AR1232, that extract would require dilution to get the amount of AR1232 to be less than 2.5µg/mL.) If a sample contains any of the single point Aroclors (that is, Aroclors other than AR1016 and AR1260), then that associated standard must be run within 72 hours of the sample to determine retention time shifts and pattern recognition.

In the 3-5 peak approach, use each peak in the standard to calculate a calibration factor for that peak, using the total mass of PCB in the standard. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 3-5 resulting concentrations are averaged to provide the final result for the sample.

"Weathering" is the loss of part of the Aroclor pattern due to biological or chemical degradation of individual PCBs. When weathering is suspected, try to match the later eluting peaks first. Flag the results for a weathered Aroclor pattern as tentatively identified or make a note in the case narrative.

The presence of multiple Aroclors can be a problem to identify since most Aroclors have at least a few peaks in common. The easiest case would be to have early and late eluting Aroclors present. The most difficult cases will involve the presence of Aroclors with the same relative chlorine level.

Note: When choosing individual peaks for quantitation, compare their responses in the sample and standard. If the peaks chosen do not correlate well (i.e. ratios to other peaks are close) between the sample and standard, review the chromatograms for other possible peaks for quantitation.

Calibration/Quantitation Peaks

The Aroclors are routinely calibrated and quantified in samples using five peaks on each column over the retention time range. The default peaks are listed the tables below:

AR1221

Peak	Column 1 Restek CLPesticides			Column 2 Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.840	1.000		2.603	1.000	
1	4.453	1.568	1.0	4.633	1.780	1.0
2	4.713	1.660	0.46	4.877	1.873	0.70
3	4.787	1.685	2.4	4.980	1.913	2.6

AR1232

Peak	Column 1 Restek CLPesticides			Column 2 Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.840	1.000		2.607	1.000	
1	5.400	1.901	1.0	5.680	2.182	1.0
2	6.187	2.178	2.0	6.017	2.311	0.19
3	6.417	2.259	0.77	6.073	2.333	0.42
4	6.527	2.298	0.54	6.440	2.474	1.7
5	7.820	2.754	0.38	6.673	2.563	0.76

AR1016

Peak	Column 1 Restek CLPesticides			Column 2 Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.842	1.000		2.607	1.000	
1	5.400	1.899	1.0	5.667	2.174	1.0
2	6.187	2.176	2.2	6.017	2.308	0.25
3	6.417	2.257	0.85	6.073	2.330	0.50
4	6.527	2.295	0.61	6.437	2.469	1.9
5	7.820	2.750	0.47	6.673	2.560	0.89

AR1242

Peak	Column 1 Restek CLPesticides			Column 2 Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.843	1.000		2.607	1.000	
1	5.400	1.899	1.0	5.680	2.179	1.0
2	6.187	2.176	2.1	6.020	2.309	0.20
3	6.417	2.257	0.83	6.073	2.330	0.46
4	5.527	2.295	0.58	6.440	2.471	1.9
5	7.820	2.750	0.15	6.673	2.560	0.84

AR1248

Peak	Column 1 Restek CLPesticides			Column 2 Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.843	1.000		2.607	1.000	
1	5.397	1.898	1.0	5.667	2.174	1.0
2	5.743	2.020	0.39	6.437	2.469	2.6
3	6.187	2.176	2.4	7.727	2.964	2.1
4	6.420	2.258	1.0	8.007	3.072	0.51
5	6.527	2.295	0.67	8.083	3.101	1.2

AR1254

Peak	Column 1 Restek CLPesticides			Column 2 Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.840	1.000		2.603	1.000	
1	7.820	2.754	1.0	8.280	3.181	1.0
2	8.300	2.923	1.7	8.637	3.318	0.96
3	9.073	3.195	1.9	9.523	3.658	1.5
4	9.593	3.378	1.7	9.937	3.817	1.2
5	9.923	3.494	1.5	10.560	4.056	1.2

AR1260

Peak	Column 1 Restek CLPesticides			Column 2 Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.842	1.000	NA	2.607	1.000	NA
1	10.610	3.732	1.0	11.040	4.235	1.0
2	10.693	3.761	0.54	11.133	4.271	0.60
3	11.113	3.909	0.50	11.553	4.432	1.0
4	11.573	4.070	2.1	11.677	4.480	0.55
5	12.063	4.243	0.80	11.983	4.597	2.3

AR1262

Peak	Column 1 Restek CLPesticides			Column 2 Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.840	1.000		2.607	1.000	
1	10.610	3.736	1.0	11.040	4.241	1.0
2	11.040	3.887	0.76	11.553	4.438	0.87
3	11.573	4.075	1.8	11.983	4.603	1.8
4	13.127	4.622	0.60	13.623	5.233	0.71

AR1268

Peak	Column 1 Restek CLPesticides			Column 2 Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.843	1.000		2.607	1.000	
1	12.117	4.261	1.0	12.603	4.835	1.0
2	12.183	4.285	1.1	12.687	4.867	1.0
3	12.513	4.401	0.79	13.127	5.036	0.85
4	13.127	4.617	0.34	13.623	5.226	0.36
5	13.617	4.789	1.9	14.197	5.446	2.1

Calibration Standards
Apply this guidance to both columns/detectors.

Adjust the baseline using an overlay of the previous PIBLK as guidance.

Inspect the peaks used for quantitation to make sure that the peaks are properly distinguishable from closely eluting peaks. NOTE: This is important because as the column degrades resolution between the peaks may decrease and the integration parameters adjusted. Be sure to apply the same integration parameters to the calibration standards and samples.

ICAL: Update the method with the retention times and responses of the standards.

CCV: Update the method with the retention times of the standards.

Qualitative Identification
The Aroclors are subject to degradation in the environment; that is, exposure to the environment will cause loss of some of the peaks in the sample pattern that are present in the standard. In general, the peaks at the higher retention times re degraded by loss of chlorine from the PCB congeners, resulting in the loss of the peak and/or the formation of compounds with lower levels of chlorination, which elute at earlier retention times. Degradation may also occur as the lighter PCB congeners volatilize. Degradation of the Aroclor patterns makes qualitative identification difficult and biases the quantitation significantly if the peaks used for quantitation are if not present in the pattern.

Apply this guidance to both columns/detectors.

Adjust the baseline using an overlay of the previous PIBLK as guidance.

Compare the overall pattern of the sample to the most recently analyzed Aroclor standard. Since the AR1016/AR1260 mixture contains all of the PCB congeners in all of the other Aroclors and because it is analyzed in every clock, overlaying the sample with the AR1660 standard can help in the evaluation for the presence of PCB in the sample. If a substantial number of peaks line up with the AR1660 standard, locate the clock where the most recent Aroclor single points were analyzed to compare the sample with the patterns in the other Aroclors.

Evaluate the ratios of the 3-5 quantitation peaks identified by the data system and compare to the standard(s).

Inspect the peaks used for quantitation to make sure that the peaks are properly distinguishable from closely eluting peaks.

Manually integrate peaks where the data system did not integrate peaks in the same manner as the calibration standards. The most common types of manual integration involve "splitting peaks" that are not resolved by the current integration parameters or identifying peaks as targets because of loss of resolution of peak symmetry.

Identify the Aroclor that most resembles the pattern of the sample and un-detect (mark as "not detected") in the data system quant file.

Inspect the chromatogram for the presence of interfering peaks from other target compounds or from non-target matrix interferences. The most common interference peaks will be from other Aroclors present in the sample matrix. Refer to Attachment 9 for guidance on retention times and relative retention times of potential interfering peaks.

"Un-assign" the quantitation peaks that are subject to interference.

Compare the average concentration (of the five quantitation peaks) from column 1 with the average concentration from column 2 and evaluate and qualify according to the guidance in the table for evaluating dual column results.

Attachment 6:
Qualitative Analysis of Multiple Peak Compounds

Evaluation of Field and QC Samples for Toxaphene

Toxaphene is a mixture of chlorinated camphenes and has a complex and characteristic pattern when analyzed by GC/EC. This pattern will degrade in the environment with the most of the degradation coming from "reductive de-chlorination" where the higher molecular weight components lose chlorine and form components with lower molecular weights. This degradation makes identification and quantification of toxaphene residues very problematic as the pattern shifts "forward" as the lower molecular weight components become more prominent.

Calibration/Quantitation Peaks
Toxaphene is routinely calibrated and quantified in samples using five peaks on each column over the retention time range. The default peaks are provided in the table below:

Peak	Restek CLPesticides			Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.843	1.000		2.607	1.000	
1	10.460	3.679	1.0	10.633	4.079	1.0
2	10.883	3.810	1.1	11.093	4.256	1.1
3	11.560	4.066	1.6	11.970	4.592	0.92
4	12.170	4.280	1.1	12.647	4.852	0.51
5	12.433	4.373	0.65	12.977	4.978	0.38

Calibration Standards:
Apply the following guidance to both columns/detectors:

- Adjust the baseline using an overlay of the previous PIBLK as guidance.
- Inspect the peaks used for quantitation to make sure that the peaks are properly distinguishable from closely eluting peaks.

  Note: This is important because as the column degrades resolution between the peaks may decrease and the integration parameters adjusted. Be sure to apply the same integration parameters to the calibration standards and samples.

  ICAL: Update the method with the retention times and responses of the standards.
  CCV: Update the method with the retention times of the standards.

Qualitative Identification

Toxaphene is subject to degradation in the environment; that is, exposure to the environment will cause loss of some of the peaks in the sample pattern that are present in the standard. A procedure where the sample pattern matches the standard and a procedure where the sample pattern does not match the pattern but a "toxaphene-like" pattern is present are provided.

a. **Samples where pattern matches standard pattern**
   - Apply the following guidance to both columns/detectors:
   - Adjust the baseline using an overlay of the previous PIBLK as guidance.
   - Compare the overall pattern of the sample to the most recently analyzed toxaphene standard.
   - If the sample and standard chromatograms agree well, quantify toxaphene using the five characteristic peaks used for calibration as follows:
     - Inspect the peaks used for quantitation to make sure that the peaks are properly distinguishable from closely eluting peaks.
     - Inspect the chromatogram for the presence of interfering peaks from other target compounds or from non-target matrix interferences. The most common interference peak is 4,4'-DDT on column 1 (RTX CLPesticides column).
     - Manually integrate peaks where the data system did not integrate peaks in the same manner as the calibration standards. The most common types of manual integration involve "splitting peaks" that are not resolved by the current integration parameters or identifying peaks as targets because of loss of resolution of peak symmetry.
     - "Undetect" the toxaphene quantitation peaks that are subject to interference. Again, the most common interference peak is 4,4'-DDT on column 1 (RTX CLPesticides column). If 4,4-DDT is present, "undetect" toxaphene peak 1. In this case, the quantitation will be based on the average of the remaining quantitation peaks.
     - Compare the average concentration (of the five quantitation peaks) from column 1 with the average concentration from column 2 and evaluate and qualify according to the guidance in the table for evaluating dual column results.
     - Provide an NCM describing the interference peaks, if present, and how the quantitation of toxaphene was affected.

Example:

Sample X contained toxaphene and 4,4-DDT. Since 4,4-DDT coelutes with the first peak used to quantify toxaphene on column 1, that toxaphene peak was "undetected" and not included in the quantification of toxaphene on column 1. The concentration of 4,4-DDT was most likely biased high on column 1 because it co-elutes with a peak from toxaphene and was reported from Column 2.

b. **Samples where sample pattern does not matches standard pattern closely**
   - Apply the following guidance to both columns/detectors:
   - Adjust the baseline using an overlay of the previous PIBLK as guidance.
   - Compare the overall pattern of the sample to the most recently analyzed toxaphene standard.
   - If the sample and standard chromatograms do not agree well, that is, the pattern and ratios of the quantitation peaks are not similar, as is the case of degraded toxaphene, evaluate the data as follows:

     Note: Contact the supervisor, department manager, or Technical Director as soon as toxaphene is tentatively identified. The evaluation of samples for degraded toxaphene is difficult and will require the consultation of the most experienced analysts.

   - Inspect the chromatogram for the presence of the peaks used for quantitation. The presence of three or more quant peaks on both columns, especially the first three, indicates that toxaphene may be present.
   - Try to match all the peaks (not just peaks used for quantitation) in the sample to all the early peaks in the toxaphene standard. The ratios will not be the same but the presence of peaks in the sample eluting at the same RT as the peaks in the early part of the toxaphene chromatogram is additional evidence that degraded toxaphene is present.
   - Inspect the chromatogram for the presence of interfering peaks from other target compounds or from non-target matrix interferences. The most common interference peak will be from 4,4-DDT, which co-elutes with toxaphene peak 1 on Column 1 and is often associated with the presence of toxaphene in the environment. Refer to Attachment 9 for guidance on retention times and relative retention times of potential interfering peaks.
   - Identify the sample as containing degraded toxaphene if the overall pattern of the peaks is similar to the toxaphene standard but the peaks elute at earlier RT AND the peaks in the first part of the sample chromatogram correspond reasonably to the early eluting peaks in the toxaphene standard.
   - Quantify degraded toxaphene using the total response of all peaks eluting within the pattern in the sample against the total response of all peaks between the first and last eluting peaks in the toxaphene standard.
   - Compare the concentration from column 1 with the concentration from column 2 and evaluate and qualify according to the guidance in the table for evaluating dual column results.
   - Additionally, qualify the data in an NCM, noting that toxaphene was identified even though the patterns of peaks did not match the standard exactly and that toxaphene quantified against a single standard using total response.

Example:
A pattern similar to toxaphene was present on both columns. The sample's chromatograms contained peaks that match the peaks eluting in the first part of the toxaphene standard pattern. The sample was quantified by comparing the total area of the peaks in the sample with the total area of the peaks in the toxaphene standard. The results were qualified with "J" to indicate that the concentration was estimated because the sample pattern does not match the standard pattern but there was sufficient evidence to identify the presence of toxaphene in the sample.

Attachment 7:
Qualitative Analysis of Multiple Peak Compounds

Evaluation of Field and QC Samples for Technical Chlordane

Technical Chlordane is a mixture of at least 11 major components and 30 or more minor components that is used to prepare specific pesticide formulations. The following components are significant: α-chlordane and γ-chlordane, trans-nonachlor, and heptachlor. The α-chlordane and γ-chlordane isomers are the most prevalent and their detection as single components is a good indicator that technical chlordane may be present.

When the GC pattern of the sample resembles that of the Technical Chlordane standard, quantitate chlordane by comparing the area of 3 to 5 major peaks. Heptachlor and heptachlor epoxide should not be included in this quantitation but rather should be quantitated and reported separately.

Calibration/Quantitation Peaks
Technical chlordane is routinely calibrated and quantified in samples using five peaks on each column over the retention time range. The default peaks are provided in the tables below:

Peak	Restek CLPesticides			Restek CLPesticides II		
	RT	RRT	Response Ratio	RT	RRT	Response Ratio
ISTD	2.843	1.000		2.607	1.000	
1	6.387	2.246	1.0	6.353	2.437	1.0
2	7.323	2.576	1.4	7.483	2.871	1.4
3	8.443	2.970	3.7	8.637	3.313	3.5
4	8.693	3.057	5.4	8.927	3.425	3.0
5	10.130	3.563	0.92	10.570	4.055	0.94

Calibration Standards
Apply the following guidance to both columns/detectors:

- Adjust the baseline using an overlay of the previous PIBLK as guidance.
- Inspect the peaks used for quantitation to make sure that the peaks are properly distinguishable from closely eluting peaks.

  Note: This is important because as the column degrades resolution between the peaks may decrease and the integration parameters adjusted. Be sure to apply the same integration parameters to the calibration standards and samples.

ICAL: Update the method with the retention times and responses of the standards.
CCV: Update the method with the retention times of the standards.

Qualitative Identification

Technical chlordane is subject to degradation in the environment; that is, exposure to the environment will cause loss of some of the peaks in the sample pattern that are present in the standard. In general, if alpha chlordane and gamma chlordane are detected in the sample and technical chlordane is a target compound, report the sample as containing technical chlordane.

c. **Samples where pattern matches standard pattern**
   - Apply the following guidance to both columns/detectors:
   - Adjust the baseline using an overlay of the previous PIBLK as guidance.
   - Compare the overall pattern of the sample to the most recently analyzed technical chlordane standard.
   - If the sample and standard chromatograms agree well, quantify technical chlordane using the five characteristic peaks used for calibration as follows:
   - Inspect the peaks used for quantitation to make sure that the peaks are properly distinguishable from closely eluting peaks.
   - Inspect the chromatogram for the presence of interfering peaks from other target compounds or from non-target matrix interferences.
   - Manually integrate peaks where the data system did not integrate peaks in the same manner as the calibration standards. The most common types of manual integration involve "splitting peaks" that are not resolved by the current integration parameters or identifying peaks as targets because of loss of resolution of peak symmetry.
   - "Undetect" the technical chlordane quantitation peaks that are subject to interference.
   - Compare the average concentration (of the five quantitation peaks) from column 1 with the average concentration from column 2 and evaluate and qualify according to the guidance in the table for evaluating dual column results.

d. **Samples where sample pattern does not matches standard pattern closely**
   - Apply this guidance to both columns/detectors.
   - Adjust the baseline using an overlay of the previous PIBLK as guidance.
   - Compare the overall pattern of the sample to the most recently analyzed technical chlordane standard.
   - If the sample and standard chromatograms do not agree well, that is, the pattern and ratios of the quantitation peaks are not similar, as is the case of degraded technical chlordane, evaluate the data as follows:

     Note: Contact the supervisor, department manager, or Technical Director as soon as technical chlordane is tentatively identified. The evaluation of samples for degraded technical chlordane is difficult and will require the consultation of the most experienced analysts.

     - Inspect the chromatogram for the presence of the peaks used for quantitation. The presence of three or more quant peaks on both columns, especially peaks TCHLOR-3 (gamma chlordane) and TCHLOR-4 (alpha chlordane), indicates that technical chlordane is present.
     - Try to match all the peaks (not just peaks used for quantitation) in the sample to the peaks in the standard. The ratios will most likely not agree but the presence of peaks in the sample eluting at the same RT along with the presence of heptachlor and alpha and gamma chlordane is additional evidence that degraded technical chlordane is present.

- Inspect the chromatogram for the presence of interfering peaks from other target compounds or from non-target matrix interferences. Refer to Attachment 9 for guidance on retention times and relative retention times of potential interfering peaks.
- Identify the sample as containing technical chlordane if the overall pattern of the peaks is similar to the technical chlordane standard and peaks are present for alpha chlordane and gamma chlordane.

- Quantify technical chlordane as the average of the quantitation peaks present in the sample matrix. Alternatively, use the total response of all peaks eluting within the pattern in the sample against the total response of all peaks between the first and last eluting peaks in the technical chlordane standard.

- Compare the concentration from column 1 with the concentration from column 2 and evaluate and qualify according to the guidance in the table for evaluating dual column results.

- Additionally, qualify the data in an NCM, noting that technical chlordane was identified even though the patterns of peaks did not match the standard exactly and note how the quantitation was done: either by the average of the quantitation peaks present or that technical chlordane was quantified against a single standard using total response.

ATTACHMENT 8:
Standard Preparation Instructions

Column/Instrument Check Standard

Stock Standard Mixes

Stock/Mix	TALS ID	Vendor/ Part Number	Concentration (ug/mL)
PEVAL Stock	PEVAL_	Restek 32417	Endrin 100 p,p'-DDT 200
2,4'-DDT PEVAL Stock	2,4'-DDT_	Restek 32200	1000
508 Performance Check Mix	508 LPC_	Restek 32045	0.02-0.5
Pesticides Internal Standard (bromonitrobenzene (BNB))	BNBISTD_	Chemservice F2319S	1000

Expiration: Unopened ampuls: manufacturer's expiration date; Opened ampuls: 6 months from open date

Pest ISTD Working Standard (TALSID = SGBNB_wk)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Pesticide Internal Standard	1000	1000	1.0

Solvent: Hexane Expiration: 3 months from prep date

PEVAL Run Standard (TALSID = SG PEVAL_)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
PEVAL Stock	100	250	Endrin 0.040 P,p'-DDT 0.080
Dilute to final volume and then add 25mL of the Pesticide ISTD Working Standard			

Solvent: Hexane Expiration: 3 months from prep date

2,4-DDT PEVAL Run Standard (TALSID = SG24PEVAL_)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
2,4'-DDT PEVAL Stock	20	50	0.40
Dilute to final volume and then add 0.5mL of the Pesticide ISTD Working Standard			

Solvent: Hexane Expiration: 3 months from prep date

Storage:
glass container with Teflon-lined cap; in standards' refrigerator at <4°C

Routine Pesticides (Pest A/B Mix) Standards

PEST A/B Stock Standard Mixes

Stock/Mix	TALS ID	Vendor/ Part Number	Concentration (ug/mL)
Pest A/B Routine Pesticides	SG AB CAL	Accustandard S-18858	10-20
Pest A/B Routine Pesticides- 2nd Source	SGSTICVAB	Ultra CUS-5454	10-20
Pest Surrogate Stock	SGPESTSURR	Supelco 48460	200
Pest Internal Standard (bromonitrobenzene (BNB))	BNBISTD	Chemservice F2319S	1000

Expiration: Unopened ampuls: manufacturer's expiration date; Opened ampuls: 6 months from open date

Pest ISTD Working Standard (TALSID = SGBNB_wk)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Pesticide Internal Standard	1000	1000	1.0

Solvent: Hexane Expiration: 3 months from prep date

Pest A/B Calibration Standards

Cal Level	TALS ID	A/B Stock	Surrogate Stock Aliquot	Final Volume	Pest ISTD Working Std Volume (mL)
1	SG PEST-1	12.5uL	1.0uL	50mL	5.0
2	SG PEST-2	25uL	2uL	50mL	5.0
3	SG PEST-3	50uL	4uL	50mL	5.0
4	SG PEST-4	500uL	40uL	250mL	25
5	SG PEST-5	200uL	16ul	50mL	5.0
6	SG PEST-6	500uL	40uL	50mL	5.0
Dilute to the final volume and then add the Pesticide ISTD working Standard					

Solvent: Hexane Expiration: 3 months from prep date

Pest A/B ICV Standard (TALS = SG AB ICV)

Cal Level	A/B ICV Stock Aliquot	Surrogate Stock Aliquot	Final Volume (mL)	Pest ISTD Working Std Volume (mL)
4 ICV	500uL	40uL	250	25
Dilute to the final volume and then add the Pesticide ISTD working Standard				

Solvent: Hexane Expiration: 3 months from prep date

Pest A/B On-Column Concentrations (ug/mL)

Compound	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6
Bromonitrobenzene (ISTD)	0.10	0.10	0.10	0.10	0.10	0.10
Tetrachloro-m-xylene Decachlorobiphenyl	0.0040	0.0080	0.016	0.032	0.064	0.16
Alpha-BHC Gamma-BHC Beta-BHC Delta-BHC Heptachlor Aldrin Heptachlor epoxide Gamma-Chlordane Alpha-Chlordane Endosulfan I	0.0025	0.0050	0.010	0.020	0.040	0.10
4,4'-DDE Dieldrin Endrin 4,4'-DDD Endosulfan II 4,4'-DDT Endrin aldehyde. Methoxychlor Endosulfan sulfate Endrin ketone	0.0050	0.010	0.020	0.040	0.080	0.20

Storage:
glass container with Teflon-lined cap; in standards' refrigerator at <4°C

Technical Chlordane Standards

Stock Standard Mixes

Stock/Mix	TALS ID	Vendor/ Part Number	Concentration (ug/mL)
Technical chlordane	SGSTCHLOR_	Accustandard P-017S-10X	1000
Technical chlordane ICV (2nd Source)	SGSTICVCHR_	Ultra PP-151-1	100
Pesticide Internal Standard (bromonitrobenzene (BNB))	BNBISTD	Chemservice F2319S	1000

Expiration: Unopened ampuls: manufacturer's expiration date; Opened ampuls: 6 months from open date

Pest ISTD Working Standard (TALSID = SGBNB_wk)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Pesticide Internal Standard	1000 (1.0mL)	1000 (1.0L)	1.0

Solvent: Hexane Expiration: 3 months from prep date

Technical Chlordane Initial Calibration Standards

Cal Level	TALS ID	TCHLOR Stock	Final Volume	Pest ISTD Working Standard
1	SG TCHLR-1	2.5uL	50mL	5mL
2	SG TCHLR-2	5uL	50mL	5mL
3	SG TCHLR-3	12.5uL	50mL	5mL
4	SG TCHLR-4	25uL	50mL	5mL
5	SG TCHLR-5	50uL	50mL	5mL
6	SG TCHLR-6	125uL	50mL	5mL
Dilute to the final volume and then add the Pesticide ISTD working Standard				

Solvent: Hexane Expiration: 3 months from prep date

Technical Chlordane ICV Standard (TALS ID = SGCHLRICV_)

Cal Level	TCHLOR ICV Stock	Final Volume	Pest ISTD Working Standard
4 ICV	250uL	50mL	5mL
Dilute to the final volume and then add the Pesticide ISTD working Standard			

Solvent: Hexane Expiration: 3 months from prep date

Technical Chlordane On-Column Concentrations (ug/mL)

Compound	CAL AZ	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6
Bromonitrobenzene (ISTD)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Technical Chlordane	0.025	0.050	0.10	0.25	0.50	1.0	2.5

Storage: **Glass container with Teflon-lined cap; in standards' refrigerator at <4°C**

Toxaphene Standards

Stock Standard Mixes

Stock/Mix	TALS ID	Vendor/ Part Number	Concentration (ug/mL)
Toxaphene Calibration Stock	SGST TOX_	Restek 32205	1000
Toxaphene ICV (2nd Source)	SGSTICVTOX_	Accustandard P-093S-H-10X	1000
Pesticide Internal Standard (bromonitrobenzene (BNB))	BNBISTD_	Chemservice F2319S	1000

Expiration: Unopened ampuls: manufacturer's expiration date; Opened ampuls: 6 months from open date

Pest ISTD Working Standard (TALSID = SGBNB_wk)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Pesticide Internal Standard	1000	1000	1.0

Solvent: Hexane Expiration: 3 months from prep date

Toxaphene Initial Calibration Standards

Cal Level	TALS ID	TOX Stock Aliquot	Final Volume	Pest ISTD Working Standard
1	SG TOX-1	5uL	10mL	1.0mL
2	SG TOX-2	12.5uL	10mL	1.0mL
3	SG TOX-3	25uL	10mL	1.0mL
4	SG TOX-4	250uL	50mL	5.0mL
5	SG TOX-5	100uL	10mL	1.0mL
6	SG TOX-6	250uL	10mL	1.0mL
Dilute to the final volume and then add the Pesticide ISTD working Standard				

Solvent: Hexane Expiration: 3 months from prep date

Toxaphene ICV Standard (TALS ID = SG TOXICV_)

Cal Level	TOX ICV Stock Aliquot	Final Volume	Pest ISTD Working Standard
4 ICV	250uL	50mL	5.0mL
Dilute to the final volume and then add the Pesticide ISTD working Standard			

Solvent: Hexane Expiration: 3 months from prep date

Toxaphene On-Column Concentrations (ug/mL)

Compound	CAL 1	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6
Bromonitrobenzene (ISTD)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Toxaphene	0.10	0.50	1.25	2.5	5.0	10	25

Storage: Glass container with Teflon-lined cap; in standards' refrigerator at <4°C

AR1016/AR1260 Standards

Aroclor Stock Standard Mixes

Stock/Mix	TALS ID	Vendor/ Part Number	Concentration (ug/mL)
AR1660 Stock	SGST1660 (or AR1660)	Restek 32039	1000
AR1660 Stock-2nd Source	SGSTICVPCB	Ultra PPM-8082	1000
Pest Surrogate Stock	SGPESTSURR	Supelco 48460	200
Pesticide Internal Standard (bromonitrobenzene (BNB))	BNBISTD	Chemservice F2319S	1000

Expiration: Unopened ampuls: manufacturer's expiration date; Opened ampuls: 6 months from open date

Pest ISTD Working Standard (TALSID = SGBNB_wk)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Pesticide Internal Standard	1000 (1.0mL)	1000 (1.0L)	1.0

Solvent: Hexane Expiration: 3 months from prep date

AR1660 Initial Calibration Standards

Cal Level	TALS ID	AR1660 Stock	Surrogate Stock	Final Volume	Pest ISTD Working Standard
1	SG 1660-1	5uL	1.0uL	50mL	5.0
2	SG 1660-2	12.5uL	2uL	50mL	5.0
3	SG 1660-3	25uL	4uL	50mL	5.0
4	SG 1660-4	250uL	40uL	250mL	25
5	SG 1660-5	100uL	16ul	50mL	5.0
6	SG 1660-6	125uL	40uL	50mL	5.0
Dilute to the final volume and then add the Pesticide ISTD working Standard					

Solvent: Hexane Expiration: 3 months from prep date

AR1660 ICV Standard (TALS ID = SGPCBICV_)

Cal Level	AR1660 ICV Stock	Surrogate Stock	Final Volume	Pest ISTD Working Standard
4 ICV	250uL	40uL	250mL	25mL
Dilute to the final volume and then add the Pesticide ISTD working Standard				

Solvent: Hexane Expiration: 3 months from prep date

AR1660 On-Column Concentrations (ug/mL)

Compound	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6	CAL AZ
Bromonitrobenzene (ISTD)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Tetrachloro-m-xylene, DCB	0.0040	0.010	0.020	0.040	0.080	0.20	0.0006
Aroclor 1016	0.10	0.25	0.50	1.0	2.0	2.5	0.015
Aroclor 1260	0.10	0.25	0.50	1.0	2.0	2.5	0.015

Storage: Glass container with Teflon-lined cap; in standards' refrigerator at <4°C

Single Point PCB Standards

Aroclor Stock Standard Mixes

Stock/Mix	TALS ID	Vendor/ Part Number	Concentration (ug/mL)
AR1221	SGST1221	Accustandard C221S-H-10X	1000
AR2154	SGST1254	Accustandard C254S-H-10X	1000
AR1232	SGST1232	Accustandard C232S-H-10X	1000
AR1262	SGST1262	Accustandard C262S-H-10X	1000
AR1242	SGST1242	Accustandard C242S-H-10X	1000
AR1268	SGST1268	Accustandard C268S-H-10X	1000
AR1248	SGST1248	Accustandard C248S-H-10X	1000
Pesticide Internal Standard (bromonitrobenzene (BNB))	BNBISTD	Chemservice F2319S	1000

Expiration: Unopened ampuls: manufacturer's expiration date; Opened ampuls: 6 months from open date

Pest ISTD Working Standard (TALSID = SGBNB_wk)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Pesticide Internal Standard	1000	1000	1.0

Solvent: Hexane Expiration: 3 months from prep date

AR2154 Calibration Standard (TALS ID = SG 21/54-4)

Cal Level	AR1221 Stock	AR1254 Stock	Final Volume	Pest ISTD Working Standard	AR2154 Conc (ug/mL)	ISTD Conc (ug/mL)
4	50uL	50uL	5mL	50mL	1.0	0.10
Dilute to the final volume and then add the Pesticide ISTD working Standard						

Solvent: Hexane Expiration: 3 months from prep date

AR3262 Calibration Standard (TALS ID = SG 32/62-4)

Cal Level	AR1232 Stock	AR1262 Stock	Final Volume	Pest ISTD Working Standard	AR3262 Conc (ug/mL)	ISTD Conc (ug/mL)
4	50uL	50uL	5mL	50mL	1.0	0.10
Dilute to the final volume and then add the Pesticide ISTD working Standard						

Solvent: Hexane Expiration: 3 months from prep date

AR4268 Calibration Standard (TALS ID = SG 42/68-4)

Cal Level	AR1242 Stock	AR1268 Stock	Final Volume	Pest ISTD Working Standard	AR4268 Conc (ug/mL)	ISTD Conc (ug/mL)
4	50uL	50uL	5mL	50mL	1.0	0.10
Dilute to the final volume and then add the Pesticide ISTD working Standard						

Solvent: Hexane Expiration: 3 months from prep date

AR1248 Calibration Standard (TALS ID = SG 1248-4)

Cal Level	AR1248 Stock	Final Volume	Pest ISTD Working Standard	AR1248 Conc (ug/mL)	ISTD Conc (ug/mL)
4	50uL	5mL	50mL	1.0	0.10
Dilute to the final volume and then add the Pesticide ISTD working Standard					

Solvent: Hexane Expiration: 3 months from prep date

Storage: Glass container with Teflon-lined cap; in standards' refrigerator at <4°C

APIX and Additional Standards

APIX/Additions Standard Mixes

Stock/Mix	TALS ID	Vendor/ Part Number	Concentration (ug/mL)
Chlorobenzilate	SGCBENZ_	Supelco 48370	200
Kepone	SGKepone_	NSI 573	1000
Hexachlorobenzene	SGSTHEXA_	Ultra CH-151-1	100
Isodrin	Isodrin_	Ultra PP-430-1	100
Mirex	MIREXICV_	Accustandard P-066S	100
2,4-DDT, 2,4-DDD, 2,4-DDE	Organoicv_	Accustandard	250 each
Pesticide Internal Standard (bromonitrobenzene (BNB))	BNBISTD	Chemservice F2319S	1000

Expiration: Unopened ampuls: manufacturer's expiration date; Opened ampuls: 6 months from open date

Pest ISTD Working Standard (TALSID = SGBNB_wk)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Pesticide Internal Standard	1000 (1.0mL)	1000 (1.0L)	1.0

Solvent: Hexane Expiration: 3 months from prep date

APIX/Additions Working Standard (TALSID = SGADDNSINT_)

Parent Standard	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Chlorobenzilate	1000	50	20
Kepone	100		10
Hexachlorobenzene	500		5
Isodrin	100		1
Mirex	500		5
2,4-DDT, 2,4-DDD, 2,4-DDE	80		2

Solvent: Hexane Expiration: 3 months from prep date

APIX/Additions Calibration Standards

Cal Level	TALS ID	SGADDNINT Aliquot (uL)	Final Volume (mL)	Pest ISTD Working Std Volume (mL)
1	SGADDNS-1	25	10	1.0
2	SGADDNS-2	50	10	1.0
3	SGADDNS-3	100	10	1.0
4	SGADDNS-4	1000	50	5.0
5	SGADDNS-5	400	10	1.0
6	SGADDNS-6	1000	10	1.0

Solvent: Hexane Expiration: 3 months from prep date

APIX/Additions On-Column Concentrations (ug/mL)

Compound	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6
Bromonitrobenzene (ISTD)	0.10	0.10	0.10	0.10	0.10	0.10
Chlorobenzilate	0.050	0.10	0.20	0.40	0.80	2.0
Kepone	0.025	0.050	0.10	0.20	0.40	1.0
Hexachlorobenzene	0.0125	0.0250	0.050	0.10	0.20	0.50
Isodrin	0.0025	0.0050	0.010	0.020	0.040	0.10
Mirex	0.0125	0.0250	0.050	0.10	0.20	0.50
2,4-DDT, 2,4-DDD, 2,4-DDE	0.0050	0.010	0.020	0.040	0.080	0.20

Storage: Glass container with Teflon-lined cap; in standards' refrigerator at <4°C

Attachment 9
Example Retention Times and Relative Retention Times
(Potential Interference Compounds)

Compound	Column 1 Restek CLPesticides	
	Retention Time*	Relative Retention Time
Bromonitrobenzene (ISTD)	2.843	1.000
Tetrachloro-m-xylene (SURR)	4.153	1.461
AR1221-1	4.453	1.568
AR1221-2	4.713	1.660
AR1221-3	4.787	1.685
Hexachlorobenzene	4.843	1.705
Alpha-BHC	5.147	1.811
AR1248-1	5.397	1.898
AR1016-1	5.400	1.899
AR1232-1	5.400	1.901
AR1242-1	5.400	1.899
Gamma-BHC (Lindane)	5.700	2.006
AR1248-2	5.743	2.020
Beta-BHC	5.857	2.061
Delta-BHC	6.170	2.170
AR1016-2	6.187	2.176
AR1232-2	6.187	2.178
AR1242-2	6.187	2.176
AR1248-3	6.187	2.176
TCHLOR-1	6.387	2.246
AR1016-3	6.417	2.257
AR1232-3	6.417	2.259
AR1242-3	6.417	2.257
AR1248-4	6.420	2.258
AR1242-4	6.527	2.295
Heptachlor	6.527	2.295
AR1016-4	6.527	2.295
AR1232-4	6.527	2.298
AR1248-5	6.527	2.295
Aldrin	7.070	2.487
TCHLOR-2	7.323	2.576
Isodrin	7.687	2.707
AR1016-5	7.820	2.750
AR1254-1	7.820	2.754
AR1232-5	7.820	2.754
AR1242-5	7.820	2.750
2,4-DDE	8.183	2.881
Heptachlor epoxide	8.210	2.887
AR1254-2	8.300	2.923
Gamma-Chlordane	8.443	2.970

Compound	Column 1 Restek CLPesticides	
	Retention Time*	Relative Retention Time
TCHLOR-3	8.443	2.970
TCHLOR-4	8.693	3.057
Alpha-Chlordane	8.700	3.060
4,4'-DDE	8.853	3.114
Endosulfan I	8.973	3.156
AR1254-3	9.073	3.195
2,4-DDD	9.187	3.235
Dieldrin	9.430	3.317
AR1254-4	9.593	3.378
2,4-DDT	9.657	3.400
Endrin	9.857	3.467
Kepone	9.923	3.494
AR1254-5	9.923	3.494
4,4'-DDD	9.980	3.510
Chlorobenzilate	10.007	3.523
TCHLOR-5	10.130	3.563
Endosulfan II	10.260	3.608
TOX-1	10.460	3.679
4,4'-DDT	10.470	3.682
AR1260-1	10.610	3.732
AR1262-1	10.610	3.736
AR1260-2	10.693	3.761
TOX-2	10.833	3.810
Endrin aldehyde	11.000	3.869
AR1262-2	11.040	3.887
AR1260-3	11.113	3.909
Methoxychlor	11.317	3.980
Mirex	11.533	4.061
TOX-3	11.560	4.066
AR1260-4	11.573	4.070
AR1262-3	11.573	4.075
Endosulfan sulfate	11.750	4.132
AR1260-4	12.063	4.243
AR1268-1	12.117	4.261
TOX-4	12.170	4.280
AR1268-2	12.183	4.285
Endrin ketone	12.220	4.298
TOX-5	12.433	4.373
AR1268-3	12.513	4.401
AR1262-4	13.127	4.622
AR1268-4	13.127	4.617
AR1268-5	13.617	4.789
Decachlorobiphenyl (SURR)	13.943	4.904

Compound	Column 2 Restek CLPesticides II	
	Retention Time	Relative Retention Time
Bromonitrobenzene (ISTD)	2.607	1.000
Tetrachloro-m-xylene (SURR)	4.100	1.584
AR1221-1	4.633	1.780
AR1221-2	4.877	1.873
Hexachlorobenzene	4.967	1.908
AR1221-3	4.980	1.913
Alpha-BHC	5.220	2.003
AR1016-1	5.667	2.174
AR1248-1	5.667	2.174
AR1232-1	5.680	2.182
AR1242-1	5.680	2.179
Gamma-BHC (Lindane)	5.843	2.242
Beta-BHC	5.997	2.300
AR1016-2	6.017	2.308
AR1232-2	6.017	2.311
AR1242-2	6.020	2.309
AR1016-3	6.073	2.330
AR1232-3	6.073	2.333
AR1242-3	6.073	2.330
TCHLOR-1	6.353	2.437
AR1016-4	6.437	2.469
AR1248-2	6.437	2.469
AR1232-4	6.440	2.474
AR1242-4	6.440	2.471
Delta-BHC	6.513	2.499
Heptachlor	6.613	2.537
AR1016-5	6.673	2.560
AR1232-5	6.673	2.563
AR1242-5	6.673	2.560
Aldrin	7.200	2.762
TCHLOR-2	7.483	2.871
AR1248-3	7.727	2.964
Isodrin	7.930	3.046
AR1248-4	8.007	3.072
AR1248-5	8.083	3.101
Heptachlor epoxide	8.277	3.175
AR1254-1	8.280	3.181
AR1254-2	8.637	3.318
TCHLOR-3	8.637	3.313
Gamma-Chlordane	8.640	3.315
2,4-DDE	8.657	3.325
Alpha-Chlordane	8.890	3.426
TCHLOR-4	8.927	3.425
4,4'-DDE	9.037	3.467
Endosulfan I	9.270	3.556

Compound	Column 2 Restek CLPesticides II	
	Retention Time	Relative Retention Time
AR1254-3	9.523	3.658
Dieldrin	9.557	3.666
2,4-DDD	9.643	3.704
AR1254-4	9.937	3.817
Chlorobenzilate	10.107	3.882
Endrin	10.110	3.878
2,4-DDT	10.197	3.917
Kepone	10.307	3.959
4,4'-DDD	10.330	3.964
Endosulfan II	10.490	4.024
AR1254-5	10.560	4.056
TCHLOR-5	10.570	4.055
TOX-1	10.633	4.079
4,4'-DDT	10.883	4.175
AR1260-1	11.040	4.235
AR1262-1	11.040	4.241
Endrin aldehyde	11.083	4.252
TOX-2	11.093	4.256
AR1260-2	11.133	4.271
AR1260-3	11.553	4.432
AR1262-2	11.553	4.438
Endosulfan sulfate	11.560	4.435
AR1260-4	11.677	4.480
TOX-3	11.970	4.592
AR1260-4	11.983	4.597
AR1262-3	11.983	4.603
Methoxychlor	12.097	4.641
Mirex	12.393	4.761
Endrin ketone	12.473	4.785
AR1268-1	12.603	4.835
TOX-4	12.647	4.852
AR1268-2	12.687	4.867
TOX-5	12.977	4.978
AR1268-3	13.127	5.036
AR1262-4	13.623	5.233
AR1268-4	13.623	5.226
AR1268-5	14.197	5.446
Decachlorobiphenyl (SURR)	14.657	5.623

*Note: These retention times are listed as guidance and reflect the retention times of the target compounds at the time this SOP was released. Changes in instrument configuration, length of column, etc. will affect these values.

18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial, grammatical, and formatting changes made. Boilerplate text added. Updated SOP references to reflect current revisions.
- Added note that if an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries for both LCS and LCSD are required. Section 9.1
- Added note that some programs and agencies do not allow the use of quadratic curves and to refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited. Section 9.2.2
- Added reference to TALS Historical Data Tracker feature. Section 11.1.7
- Clarified requirements and frequency for RLVs, MDL Studies, and MDLVs to be consistent with SOP SA-QA-07 and to include the quarterly frequency as defined by DOD. Section 12.1 - 12.3 and Attachment 3
- Added note that unsupervised work must not begin until acceptable IDOC is obtained. Attachment 3
- Added section on troubleshooting. Attachment 4
- Expanded Attachment 2 to match SOP template.
- Removed reference to sample duplicate. Not typically performed. MSD is routinely performed in lieu of sample duplicate as allowed by the reference method.
- Clarified Method Reference section to reflect Update III (Rev. 1, December 1996) and Update IV (Rev. 2, February 2007)
- Revised Surrogate Dilution Factor Threshold to DF >5. Section 9.2.7.1 and Section 11.1.5
- Corrected 2,4-DDT standard preparation final volume and concentration. Attachment 8
- Removed reference to Arizona-specific standards. No longer certified by this agency. Attachment 8

CHLORINATED HERBICIDES BY GC/ECD: PREPARATION AND ANALYSIS

(Methods: EPA 515.1, EPA 615, and EPA 8151A)

Approvals (Signature/Date):

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Facility Distribution No. 1 **Distributed To:** QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of chlorinated herbicides by gas chromatography/electron capture detection (GC/ECD). The routine sample matrices associated with this procedure are waters and soils. Other, non-routine matrices may be incorporated as outlined in Section 16.0.

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

2.1 Sample Preparation

2.1.1 Water Samples – A known volume of aqueous sample, nominally 1000mL, is transferred to a Teflon separatory funnel. The sample is hydrolyzed with base to convert the herbicides present to their salt form. The hydrolyzed sample is extracted with methylene chloride to remove the non-phenoxy acid herbicide material. The sample is acidified and extracted with diethyl ether. The extract is dried, filtered, concentrated, esterified with diazomethane, dissolved in MTBE, and analyzed by GC/ECD.

2.1.2 Soil Samples – A known weight of a sample, approximately 30g wet weight, is acidified with hydrochloric acid (HCl) and combined with acidified sodium sulfate to form a free flowing, sandy mixture. Diethyl ether is added to the dried sample, and the sample is extracted using an ultrasonic disrupter for 9 minutes. The extract is transferred to a separatory funnel containing water that has been adjusted to pH$\geq$12. The sample is allowed to hydrolyze for one hour to convert the acid and ester forms of the herbicides to their salt forms. The solvent is discarded, and the aqueous phase, which contains the herbicides in their salt form, is acidified and extracted with diethyl ether. The extract is dried, concentrated, esterified with diazomethane, dissolved in MTBE, and analyzed by GC/ECD.

2.2 Sample Analysis

The extracted methyl derivatives are analyzed by a GC equipped with dual capillary columns (different phases) connected to dual electron capture (EC) detectors, allowing simultaneous detection and confirmation of the target compounds. Quantitation is performed using the external standard calibration technique.

2.3 This SOP is based on the following methods: EPA 515.1, EPA 615, and EPA 8151A.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

Note: The glassware used for herbicides must not be used to extract or concentrate dioxins and furans. Several of the herbicides are precursors to the formation of dioxins or are associated with the presence of dioxins in the environment

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid, methanol, methylene chloride, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.1.5 The base hydrolysis step removes interferences from the sample extract. Dinoseb, a phenolic herbicide, is very reactive and will have poor recoveries when subjected to the base hydrolysis step.

4.1.6 Injection port maintenance is very important for the consistent detection of the reactive herbicides such as dinoseb.

4.1.7 The acid forms of the analytes are strong organic acids which react readily with alkaline substances and can be lost during sample preparation. Glassware and glass wool must be acid-rinsed with 1N hydrochloric acid or acidified methanol and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid analyte losses due to adsorption.

4.1.8 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. Alkaline hydrolysis and subsequent extraction of the basic sample removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

4.1.9 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the ECD. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates, that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted

surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive purification of reagents and glassware may be required to eliminate background phthalate contamination.

4.1.10 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. The method provides a Florisil cleanup procedure to aid in the elimination of interferences that may be encountered. Refer to Attachment 9 for instructions.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily during the "base shake" to remove the non-target compounds. The extract may be filtered or stirred to remove the emulsion or may be "salted out" by the addition of sodium chloride.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

5.1.1 Sample Preparation

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard. Exposure to these chemicals should be minimized.

The use of separatory funnels to extract aqueous samples with solvents creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This step is considered a high-risk activity, and a face shield must be worn over safety glasses or goggles when performed.

Ultrasonic disrupters can produce high intensity noise and must be used in an area with adequate noise protection.

Diethyl ether is a flammable solvent that can cause drowsiness. The extraction analyst using diethyl ether must not work alone in an isolated area of the lab. A solvent such as diethyl ether can cause a burning sensation when it contacts the skin. The rapid evaporation of the solvent causes a rapid heat loss in the skin, which is similar to frost bite. If this occurs, rinse the exposed skin in cold water to reduce the solvent evaporation.

Due to the flammable nature of diethyl ether, if a mechanical device is used for sample extraction it should be equipped with an explosion-proof motor and placed in a hood to avoid possible damage and injury due to an explosion.

The lab should keep only the minimum supply of diethyl ether. Diethyl ether will form explosive peroxides if stored in the lab for long periods of time. Opened containers of diethyl ether must be checked monthly for peroxides using peroxide test strips using the following steps:

- *Remove 1 test strip and immediately close the test strip tube.*
- *Dip the test strip into the solution to be tested for 1 second, such that the reaction zone is completely wetted.*
- *Move the test strip slightly back and forth for 3-30 seconds until the solvent has evaporated from the reaction zone, then*
  - *Dip into distilled water for 1 second, shake off excess water, or*
  - *Breathe on test strip 4 times each for 3-5 seconds*
- *After 15 seconds, compare the reaction zone with the color scale.*
- *If the color scale indicates the presence of peroxides, then dispose of the contents of the container as directed in the TestAmerica Savannah Addendum to the EHSM.*

Hexane is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, lightheadedness, headache, dizziness, and blurred vision.

Hydrochloric acid is extremely hazardous as an oxidizer, a corrosive, a poison, and is reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Methanol is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, confusion, headache, dizziness, and drowsiness.

Sodium hydroxide is a severe corrosive. Contact with the skin can cause irritation or severe burns and scarring. Contact with the eyes can cause irritation, burns, permanent vision impairment or even blindness.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

Diazomethane is a toxic carcinogen which can explode under certain conditions. In order to minimize safety hazards the diazomethane generation apparatus used in the esterification procedure produces micromolar amounts of diazomethane. Even with this precaution, the following procedures should be followed: Use only a well ventilated hood (do not breath vapors) with a safety screen. Use mechanical pipetting aides. Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips. **EXPLOSION** may result if the following occur: heating above 90°C, grinding surfaces, ground glass joints, sleeve bearings, glass stirrers, or storage with alkali metals.

5.1.2 Sample Analysis

Hexane is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, lightheadedness, headache, dizziness, and blurred vision.

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Hexane	Flammable Irritant	500ppm TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Hydrochloric Acid	Corrosive Poison	5ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methanol	Flammable Poison Irritant	200ppm TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methyl Tert-Butyl Ether	Flammable Irritant Poison	50ppm TWA	Inhalation of vapor can irritate respiratory tract. Breathing high concentrations in air can cause lightheadedness, dizziness, weakness, nausea, and headache. Ingestion may cause vomiting with symptoms similar to inhalation. Can cause irritation to skin and eyes with possible damage to the eye tissue.
Ethyl Ether, Diethyl Ether	Flammable Irritant Peroxide Former	400ppm TWA	General anesthesia by inhalation can occur. Continued exposure may lead to respiratory failure or death. Early symptoms include irritation of nose and throat, vomiting, and irregular respiration, followed by dizziness, drowsiness, and unconsciousness. May cause irritation, redness and pain to the eyes. Irritating to the skin and mucous membranes by drying effect. Can cause dermatitis on prolonged exposure. May be absorbed through skin. **May form explosive peroxides on long standing or after exposure to air or light. This material must be disposed of with six months.**

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Sodium Hydroxide	Corrosive	2mg/m^3 Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1mg/m^3 TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
Note: Always add acid to water to prevent violent reactions.			
TWA – the time-weighted average exposure limit: the maximum average concentration of a chemical in air for a normal 8-hour working day and 40-hour week Ceiling – the concentration that should not be exceeded at any time STEL – short-term exposure limit: the maximum average concentration to which workers can be exposed for a short period (usually 15 minutes)			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

6.1.1 Sample Preparation

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Ultrasonic disrupter – Tekmar Model or equivalent with horn-type titanium-tipped sonication probe. The sonicator should be capable of operating in the pulse mode at full power.

Sonabox – the sonicator must be placed in the sonabox to reduce noise. The sonabox must be placed under a fume hood.

Diazomethane generator

NOTE: If the herbicide blank is contaminated, clean the generator tubing and vessels with methylene chloride, methanol, and diethyl ether, in that order, and purge the

apparatus with nitrogen to dry. Replace the Teflon tubing and vessels if the solvent cleaning does not improve the blank.

Kuderna-Danish apparatus – consists of the K-D body, three-ball Snyder column, and a graduated concentration tube with springs or clips to hold the concentration tube to the K-D body. Verify the concentration tube in accordance with SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification.*

Water bath – compatible with the K-D apparatuses, located under an operating fume hood

6.1.2 Sample Analysis

Gas Chromatograph (GC) – temperature programmable, equipped with dual electron capture (EC) detectors and a compatible autosampler. The laboratory currently uses an Agilent 6890 GC with dual micro-cell electron capture detectors and an Agilent 7683 autosampler.

The following column pairs are recommended. Other columns/phases may be used if the calibration and QC criteria are met and adequate separation of the target compounds is achieved.

J&W DB-XLB 30m x 0.32mm ID x 0.5um film
J&W DB-35MS 30m x 0.32mm ID x 0.5um film

6.2 Analytical Data System / Software / Hardware

Chemstation software is used on a Windows-based PC to schedule and acquire data. Target (UNIX and/or Windows) software is used on a Windows-based PC to store, reduce/evaluate, and output the data to the laboratory's LIMS system (i.e., TALS). Target software has the capability of processing stored GC data by recognizing a GC peak within any given retention time window and comparing the retention time of the sample to the retention times of the standards analyzed under the same conditions. The software also allows calculation integration of the peak responses, response factors, construction of a linear regression calibration curve, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the response factors.

6.3 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Transfer Pipettes – various sizes

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

6.1.3 Sample Preparation

Separatory Funnels – 1L and 2L, Teflon with Teflon stopcocks. Glass funnels may also be used.

Large Funnels

Pyrex Glass Wool – rinse with acidified methanol prior to use

Stainless Steel Spatulas

Pre-Cleaned 500mL Extraction Bottles – Discard after use.

1L Pre-Cleaned Containers – This is the same container used to collect the sample and can be used to collect the aqueous phase during the solvent wash. Discard after use.

Filter paper – grade 414, 18.5cm diameter

Extract Vials – 12mL vials with Teflon-lined caps

Peroxide Test Strips

Detergent – FL-70, used for washing non-disposable labware.

pH paper – provides a quick and easy way to approximate the pH of a sample to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step.

Residual (free) chlorine powder pillows – HACH; Catalogue #2105569

Medicine cups – 30mL, disposable

Stainless steel measuring cup – 1/3 cup

6.1.4 Sample Analysis

Autosampler Vials, Septa, and Caps – compatible with the autosampler

6.2 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

Waters
1L Amber Glass – purchased with Certificate of Analysis attesting to purity.

Soils

16oz. Soil Jar – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

Unless listed elsewhere in this SOP, the expiration dates given below apply.

7.1.1 The expiration date for unopened standards and reagents is the manufacturer's expiration date.

7.1.2 The expiration date for opened stock reagents is the manufacturer's expiration date or 5 years from the date opened, whichever is sooner.

7.1.3 The expiration date for opened stock standards is the manufacturer's expiration date or 6 months from the date opened, whichever is sooner.

7.1.4 The expiration date for prepared reagents is 6 months from the date prepared or the expiration date of the parent reagent, whichever is sooner.

7.1.5 The expiration date for prepared standards is 3 months from the date prepared or the expiration date of the parent standard, whichever is sooner.

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.*

Hydrochloric acid, methanol, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Purchased Reagents

7.2.1.1 Sample Preparation

7.2.1.1.1 Blank Matrix – Teflon chips, glass beads, or equivalent. Used for the preparation of soil QC samples.

7.2.1.1.2 Laboratory Reagent Water – ASTM Type II

7.2.1.1.3 Sodium Sulfate – powdered and granular, anhydrous
Storage: Consignment room; Store in a tightly closed container in a cool, dry, ventilated area. Separate from incompatibles.

7.2.1.1.4 Methanol – residue grade or better
Storage: Consignment room; Store in a flammable storage cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.

7.2.1.1.5 Diethyl Ether – residue grade or better. Check periodically for formation of peroxides as described in Section 5.1.1.
Storage: Consignment room; Store in a flammable storage cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.

7.2.1.1.6 Sodium Hydroxide (NaOH) – reagent grade
Storage: Consignment room; Store in a cool, dry, ventilated area, away from incompatibles (acids, organics).

7.2.1.1.7 Sulfuric Acid (H_2SO_4) – concentrated reagent grade
Storage: Consignment room; Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.

7.2.1.1.8 Hydrochloric Acid (HCl) – concentrated, reagent grade
Storage: Consignment room; Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.

7.2.1.1.9 Potassium Hydroxide (KOH) – reagent grade
Storage: Consignment room; Store in a cool, dry, ventilated area, away from incompatibles (acids, organics).

7.2.1.1.10 Diazald (N-methyl-N-nitroso-p-toluenesulfonamide) – reagent grade
Storage: 0-6°C; SM/EX refrigerator; Store in a tightly closed container, away from heat, sparks or open flames.

7.2.1.1.11 Carbitol – reagent grade or better
Storage: 0-6°C; SM/EX refrigerator

7.2.1.1.12 Silica Gel – reagent grade
Storage: Soil extractions room

7.2.1.1.13 MTBE – residue grade or better
Storage: Consignment room; Store in a flammable storage cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.

7.2.1.1.14 Sodium Chloride – granular, anhydrous
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Separate from incompatibles.

7.2.1.2 Sample Analysis

7.2.1.2.1 MTBE – residue grade or better
Storage: Consignment room; Store in a flammable storage cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.

7.2.2 Prepared Reagents

7.2.2.1 Sample Preparation

7.2.2.1.1 Baked Sodium Sulfate – purify the Sodium Sulfate by heating at 400°C for four hours in a shallow tray.
Storage: Soils lab
Expiration: 1 year from preparation date

7.2.2.1.2 Acidified Sodium Sulfate – Transfer purified sodium sulfate to a suitable glass container until the container is about ¾ full. Working under a hood, add enough diethyl ether to wet the sodium sulfate. Add 10mL of concentrated sulfuric acid for each kilogram of sodium sulfate and stir to mix the acid into the solvent and sodium sulfate. Add more diethyl ether to keep the sodium sulfate wet while stirring the sodium sulfate. The acid must be thoroughly mixed into the sodium sulfate and diethyl ether. Pour off the excess solvent and allow the diethyl ether to evaporate under a hood for 24 hours. Store in a glass container. Check the pH of the acidified sodium sulfate by mixing 1g and 5mL of water in a small container. The pH of the solution should be less than 4.
Storage: Glass container, at 130°C
Expiration: 3 months

7.2.2.1.3 Sodium Hydroxide Solution (10N) – Dissolve 400g of NaOH pellets into about 500mL reagent water contained in a 2-L beaker on a magnetic stirrer. Add the NaOH in small portions, with constant stirring, to minimize the time it takes to dissolve the pellets. A good deal of heat will be generated as the NaOH dissolves. After all 400g have been added, carefully dilute to 1000mL with reagent water. Mix the solution thoroughly and transfer to a storage container. Do not store sodium hydroxide solution in volumetric glassware or in containers with ground glass joints.
Storage: Liquid-Liquid extraction Room
Expiration: 1 year from preparation date

7.2.2.1.4 Potassium Hydroxide Solution (37%) – Weigh 37g of KOH into a 100-mL volumetric flask and dilute to volume with reagent water.
Storage: Liquid-Liquid extraction Room
Expiration: 1 year from preparation date

7.2.2.1.5 Acidified Methanol (approximately 0.12N) – Carefully add 10mL of concentrated HCl to the 4L methanol container.
Storage: Liquid-Liquid extraction Room
Expiration: 3 month from preparation date

7.2.2.1.6 Baked Blank Matrix – purify the blank matrix by heating at 400°C for four hours in a shallow tray.
Storage: Soils extraction lab
Expiration: 1 year from preparation date

7.2.2.1.7 Baked Sodium Chloride – purify the Sodium Chloride by heating at 400°C for four hours in a shallow tray.
Storage: Soils extraction
Expiration: 1 year from preparation date

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

Note: EPA 515.1 samples analyzed for the Wisconsin Department of Natural Resources (WI DNR) must be analyzed against standards prepared in accordance with the WI DNR Project Requirements Summary (PRS).

Note: The values present in the LIMS Reagent Program for the analytical standards do not directly match the COA from the vendors. The LIMS values are the values present on the vendor COA and are adjusted by the correction factor equation given below. This correction factor is needed since the standard is expressed as mass of ester per volume.

$$CF = \frac{MWacid}{MWester}$$

7.3.1 Purchased Standards

7.3.1.1 Sample Preparation

7.3.1.1.1 DCAA (1000ug/mL) – Surrogate, prepared in methanol, purchased from Accustandard
Storage: 0-6°C; EX/SM Refrigerator

7.3.1.1.2 Chlorinated Herbicides Mixture (varying concentrations) – prepared in methanol, purchased from Ultra
Storage: 0-6°C; EX/SM Refrigerator

7.3.1.1.3 Herbicide Additions Mix (200ug/mL) – prepared in methanol, purchased from Restek
Storage: 0-6°C; EX/SM Refrigerator

7.3.1.2 Sample Analysis

Note: Herbicide analysis standards are purchased as methyl esters; therefore, the concentration of the standard must be corrected to the free acid concentration. This will eliminate the need to correct the final concentration of the sample. The correction factors are given in Attachment 5.

7.3.1.2.1 Herbicide Methyl Ester Mix (MCPA/MCPP at 20000ug/mL; Dalapon at 1000ug/mL; 2,4-D, 2,4-DB, 2,4,5-T, 2,4,5-TP, Dicamba, Dichlorprop, and Dinoseb at 100ug/mL) – prepared in Hexane, purchased from NSI.

Storage: 0-6°C; SG Refrigerator

7.3.1.2.2 Pentachloroanisol (100ug/mL) – prepared in methanol, purchased from Accustandard
Storage: 0-6°C; SG Refrigerator

7.3.1.2.3 DCAA Methyl Ester (100ug/mL) – prepared in MTBE, purchased from Ultra
Storage: 0-6°C; SG Refrigerator

7.3.1.2.4 Picloram Methyl Ester (100ug/mL) – prepared in Methanol, purchased from Accustandard
Storage: 0-6°C; SG Refrigerator

7.3.1.2.5 DCPA (1000ug/mL) – prepared in Restek, purchased from Methanol
Storage: 0-6°C; SG Refrigerator

7.3.1.2.6 Herbicide Additions Mix (200ug/mL) – prepared in Methanol, purchased from Restek
Storage: 0-6°C; SG Refrigerator

7.3.1.2.7 Herbicide Methyl Ester Mix, Second Source (MCPA/MCPP at 10000ug/mL; Dalapon at 1000ug/mL; 2,4-D, 2,4-DB, 2,4,5-T, 2,4,5-TP, Dicamba, Dichlorprop, and Dinoseb at 100ug/mL) – prepared in methanol, purchased from Ultra
Storage: 0-6°C; SG Refrigerator

7.3.1.2.8 Pentachloroanisol, Second Source (100ug/mL) – prepared in methanol, purchased from Chemservice
Storage: 0-6°C; SG Refrigerator

7.3.1.2.9 Picloram Methyl Ester, Second Source (1000ug/mL) – prepared in methanol, purchased from Restek
Storage: 0-6°C; SG Refrigerator

7.3.1.2.10 DCPA (100ug/mL) , Second Source – prepared in methanol, purchased from Ultra
Storage: 0-6°C; SG Refrigerator

7.3.2 Prepared Standards

7.3.2.1 Sample Preparation

7.3.2.1.1 Herbicide Surrogate Spiking Solution

Herbicide Surrogate Spiking Solution

Stock Standard	Parent Concentration (ug/mL)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ug/mL)
DCAA	1000	1.0	500	2.0

Solvent: Methanol
Storage: 0-6°C; EX/SM Refrigerator

7.3.2.1.2 Herbicide Spiking Solution

Herbicide Spiking Solution

Stock Standard	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Chlorinated Herbicides Mixture	200/20,000	1	100	2.0/200

Solvent: Methanol
Storage: 0-6°C; EX/SM Refrigerator

Herbicide Spiking Solution

Stock Standard	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Herbicide Additions Mix	200	1	100	2.0

Solvent: Methanol
Storage: 0-6°C; EX/SM Refrigerator

7.3.2.2 Sample Analysis

7.3.2.2.1 Intermediate Calibration Stock Standard

Intermediate Calibration Stock Standard

Stock Standard	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Herbicide Methyl Ester Mix	*	125	10	2.5, 25, 500
Pentachloroanisol	100	175		1.75
DCAA Methyl Ester	100	250		2.5
Picloram Methyl Ester	100	250		2.5
DCPA	1000	40		4.0

* MCPA/MCPP at 20000ug/mL; Dalapon at 1000ug/mL; 2,4-D, 2,4-DB, 2,4,5-T, 2,4,5-TP, Dicamba, Dichlorprop, and Dinoseb at 100ug/mL.

Solvent: MTBE
Storage: 0-6°C; EX/SM Refrigerator

7.3.2.2.2 Calibration Standards

Cal Level	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Cal Level 1	See Section 7.3.2.2.1	100	10	0.025, 0.25, 5.0
Cal Level 2		200	10	0.050, 0.50, 10
Cal Level 3		400	10	0.10, 1.0, 20
Cal Level 4		3000	50	0.15, 1.5, 30
Cal Level 5		800	10	0.20, 2.0, 45
Cal Level 6		1000	10	0.25, 2.5, 50
Cal Level 7		2000	10	0.50, 5.0, 100

Solvent: MTBE
Storage: 0-6°C; EX/SM Refrigerator

7.3.2.2.3 Intermediate Calibration Stock Standard for Wisconsin DNR Samples

Stock Standard	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Chlorinated Herbicides Mixture	*	250	10	2.5, 25, 500

* MCPA/MCPP at 20000ug/mL; Dalapon at 1000ug/mL; 2,4-D, 2,4-DB, 2,4,5-T, 2,4,5-TP, 2,6-D, 2,4,6-T, Dicamba, Dichlorprop, Dinoseb, and picloram at 200ug/mL; Pentachloroanisole at 133ug/mL; DCPA at 320 ug/mL.

Solvent: MTBE
Storage: 0-6°C; EX/SM Refrigerator

7.3.2.2.4 Wisconsin DNR Calibration Standards

Cal Level	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Cal Level 1	See Section 7.3.2.2.3	100	10	0.025, 0.25, 5.0
Cal Level 2		200	10	0.050, 0.50, 10
Cal Level 3		400	10	0.10, 1.0, 20
Cal Level 4		3000	50	0.15, 1.5, 30
Cal Level 5		800	10	0.20, 2.0, 45
Cal Level 6		1000	10	0.25, 2.5, 50
Cal Level 7		2000	10	0.50, 5.0, 100

Solvent: MTBE
Storage: 0-6°C; EX/SM Refrigerator

Note: Wisconsin calibration standards are to be made using the free acids listed above. Once the working levels of the calibration have been made they are to be

esterified prior to analysis.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

Aqueous samples for EPA 615 and EPA 8151A are routinely collected in 1L amber glass containers. Aqueous samples for EPA 515.1 are routinely collected in 1L amber glass containers containing sodium thiosulfate de-chlorination agent. The dechlorination agent should be sufficient to remove residual chlorine from the sample.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples for EPA 615 and EPA 8151A must be prepared within 7 days of collection. Samples for EPA 515.1 must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis. Extracts for EPA 615 and EPA 8151A must be analyzed within 40 of extraction. Extracts for EPA 515.1 must be analyzed within 28 days of extraction.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives and/or de-chlorination agents.

8.1.1 Preservation Checks – Residual Chlorine

These checks can be performed upon receipt or prior to preparation.

8.1.1.1 Mix the sample by inverting and transfer 10mL to a small medicine cup.

8.1.1.3 Add a residual chlorine powder pillow to the sample in the cup and note the presence of a pink color, which indicates the presence of residual chlorine. If the sample tests positive for residual chlorine, initiate an NCM noting that residual chlorine was present. Add sodium sulfite in small aliquots to the sample container and retest 10mL portions of the sample until the sample is negative for residual chlorine.

8.2 Soil Samples

Soil samples are routinely collected in 16oz soil jars.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The laboratory's default QC items required for each extraction batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS) – to be performed on a minimum of 10% of samples in a batch (for EPA 515.1 and EPA 615) or 20% of samples in a batch (for EPA 8151A), and a matrix spike duplicate (MSD).

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, 1 matrix spike, and 1 matrix spike duplicate.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), another matrix spike (from sample 11-20, for EPA 515.1 or EPA 615 only), and a matrix spike duplicate.

The routine container supplied for this method is a 1L container for waters and a 16oz container for soils. 1L is the default extraction volume for waters, and 30g is the default extraction amount for soils. Reduced sample initial volumes and amounts may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 500mL for waters and 15g for soils. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 2L for waters and 60g for soils.

Note: If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required.

Note: The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples, an LCS at the RL must also be included in the required batch QC.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

9.2.1 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves.* This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve for EPA 8151A must consist of a minimum of 5 standards. The calibration curve for EPA 615 must consist of a minimum of 3 standards. The calibration curve for EPA 515.1 must consist of a minimum of 3 (recommend 5) standards. The

lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

The initial calibration standard concentrations currently in use in the laboratory are provided in Section 7.3.2.2. Refer to Section 7.3.2.2 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-41.

9.2.2.1 ICAL Criteria

For EPA 515.1 and EPA 8151A, the relative standard deviation of the calibration standards must be <20% for the initial calibration curve to be acceptable. For EPA 615, the relative standard deviation of the calibration standards must be <10% for the initial calibration curve to be acceptable.

The preferred method of quantitation is the average response or calibration factor. If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve.

The regression coefficient (r^2) of the regression curve must be greater than 0.990 for the initial calibration curve to be acceptable.

Note: A minimum of 5 points is required for a linear curve. A minimum of 6 points is required for a quadratic curve. Higher order curves are not permitted. Some programs and agencies (e.g., SC DHEC) do not allow the use of quadratic curves. Refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited.

Grand Mean Exception – EPA 8151A

SW-846 allows the use of the "grand mean exception" as described below. This exception should only be applied to initial calibration curves in extraordinary circumstances because of the difficulty of maintaining and providing documentation on an on-going basis.

Grand Mean Exception (GME): If one or more analytes exceed the %RSD criteria, the calibration curve is acceptable if the average of the %RSDs for all of the analytes in the ICAL (i.e., the grand mean) is less than or equal to the ICAL %RSD criteria.

SW-846 does not place a cap on an individual analyte's %RSD as long as the average is within criteria; however, the laboratory has adopted the requirement that no individual analyte can exceed 3X the ICAL criteria. Therefore, the calibration curve is acceptable if the average of the %RSDs is less than or equal 20% with no individual analyte exceeding 60%.

Note: Some programs and agencies do not allow the use of the grand mean exception. Refer to the Project Requirement Summary and/or Project Plan to determine if GME is not allowed.

9.2.2 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The ICV for EPA 515.1 must be within 20% to be acceptable.

The average %D for the ICV for EPA 615 and EPA 8151A must be within 15% with no single analyte greater than 45% to be acceptable.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to level 4 of the ICAL. Refer to Section 7.3.2.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

Note: This standard must be analyzed at least quarterly for EPA 515.1. If the instrument does not require calibration after 3 months, the ICV must be analyzed.

9.2.3 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed at the beginning of each clock. Continuing calibration blanks are analyzed after each CCV.

Initial and continuing calibration blanks must be <1/2RL to be acceptable.

9.2.4 Continuing Calibration Verification

9.2.4.1 EPA 515.1

The initial calibration curve must be verified initially, every 24 hours or 20 samples, and at the end of the sequence. The concentration of the CCV must be varied with each clock.

The CCV for EPA 515.1 must be within 20% to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to levels 4 and 3 of the ICAL. Refer to Section 7.3.2.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.4.2 EPA 615

The initial calibration curve must be verified initially and every 24 hours (each working shift) or 20 samples, with a mid-level standard.

The CCV for EPA 615 must be within 10% to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to level 4 and 3 of the ICAL. Refer to Section 7.3.2.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.4.3 EPA 8151A

The initial calibration curve must be verified initially, every 12 hours or 20 samples, and at the end of the sequence with a mid-level standard.

The CCV for EPA 8151A must be within 15% to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to level 4 and 3 of the ICAL. Refer to Section 7.3.2.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

Grand Mean Exception – EPA 8151A
SW-846 allows the use of the "grand mean exception" as described below.

Grand Mean Exception (GME): If one or more analytes exceed the %D criteria, the calibration curve is acceptable if the average of the %Ds for all of the analytes in the CCV (i.e., the grand mean) is less than or equal to the CCV %D criteria.

SW-846 does not place a cap on an individual analyte's %D as long as the average is within criteria; however, the laboratory has adopted the requirement that no individual analyte can exceed 3X the CCV criteria. Therefore, the CCV is acceptable if the average of the %Ds is less than or equal 15% with no individual analyte exceeding 45%.

Note: Some programs and agencies do not allow the use of the grand mean exception. Refer to the Project Requirement Summary and/or Project Plan to determine if GME is not allowed.

9.2.5 Surrogate

This procedure uses surrogates to evaluate the extraction process. DCAA is the surrogate.

Prior to preparation, this surrogate is added to all samples and QC items. The concentration of the surrogate is the same in all field samples and QC samples. A concentration of 2.0ug/L is used.

The percent recovery of the surrogate in all field samples and QC samples must be within the limits listed in the Method Limit Groups (MLGs) in LIMS. If the percent recovery is outside of this range, the analysis of the sample must be repeated. Repeated failure of the surrogate percent recovery may indicate re-extraction is necessary.

9.2.6 Laboratory Performance Check Sample (LPC)

EPA 515.1 requires the analysis of a Laboratory Performance Check (LPC) Sample daily. The LPC includes checks for instrument sensitivity (using dinoseb), chromatographic performance (using 4-Nitrophenol), and column performance (using 3,5-Dichlorobenzoic acid and 4-Nitrophenol).

The evaluation criteria for the LPC are included in Attachment 6.

If the criteria in Attachment 6 are not met, the instrument system will need to be re-evaluated. This can include routine maintenance and/or replacement of analytical columns.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* and the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Aqueous Sample Preparation

10.1.1 Inspect the samples. Determine if the samples have multiple layers such as a sediment or an oil layer. Samples with large amounts of sediments or particulates may clog the stopcock on the separatory funnel. Consult with the Department Manager or Technical Manager if the sample matrix is unusual or is difficult to categorize. An NCM must be initiated to denote any unusual sample preparation steps required prior to the extraction.

Mark the level of the sample on the outside of the container. This marking will be used to determine the original sample volume actually used in the extraction process as follows: after the sample has been added to the separatory funnel, fill the empty sample container with water to the mark. Pour the water into a graduated cylinder, and determine the volume. Record the volume log to the nearest 5mL.

10.1.2 Add 1000mL of reagent water to each of two separatory funnels to serve as the method blank and laboratory control sample (LCS). Add 1.0mL of surrogate to each sample, MS, and MSD (directly to the original sample container) as well as to the method blank and LCS. Add 1.0mL of spiking solution to all LCS, MS, and MSD.

10.1.3 Thoroughly mix the sample by inverting the container several times and pour the entire contents of the sample into a properly labeled 2L Teflon separatory funnel.

Add approximately 50mL methylene chloride to the sample container. Swirl the solvent around the inside of the container to thoroughly rinse the sample bottle and add this rinse to the separatory funnel.

Using a stainless steel measuring cup, add 1/3 cup of granular NaCl to each sample, MB, LCS, MS, and MSD.

10.1.4 Adjust the pH of the sample to >12 with 10N NaOH. Check the pH with narrow range pH paper. Allow the samples to stand for at least one hour with intermittent shaking or shake on the automatic shaker for one hour.

Note: This step is necessary to convert the acid and ester forms of the herbicides to the water-soluble salts. After the hydrolysis step, the non-target compounds are extracted out of the sample with methylene chloride. The rest of the extraction steps may be performed with manual or automatic shaking.

10.1.5 Add 100mL of methylene chloride to each separatory funnel.

10.1.6 Shake each separatory funnel for ten minutes with periodic venting to release any excess pressure. If an automatic shaker is used, shake the samples for ten minutes. Allow ten minutes for complete separation between the lower solvent and upper water phases.

Note: The separatory funnel should be vented under a hood to remove the solvent fumes from the lab.

10.1.7 Drain the lower layer (methylene chloride) into a designated waste container.

Note: Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily during the "base shake" to remove the non-target compounds. The extract may be filtered or stirred to remove the emulsion.

10.1.8 Adjust the pH of each of the samples and QC items to <2 with 10mL sulfuric acid. Add the acid slowly and gently swirl the separatory funnels to ensure that the acid and base have reacted. Acid/base neutralization reactions can be violent if mixed too quickly. Check the pH of the samples and QC items to ensure that the pH < 2.

10.1.9 Add 250mL of diethyl ether to each sample and QC item.

-If performing a "manual shake", shake the funnels for one minute, venting frequently to release any pressure.
-If using the automatic shaker, shake the samples continuously for thirty minutes, releasing the pressure periodically.

10.1.10 After the extraction, allow the layers to separate for at least ten minutes. Collect the water layer (lower layer) in a large beaker or flask and discard this layer.

10.1.11 Collect the extract (upper layer) into a 500-mL pre-cleaned extraction bottle containing 30g acidified sodium sulfate. Allow the extract and sodium sulfate to remain in contact at least two hours but preferably overnight.

10.1.12 Concentrate the extract to a final volume of approximately 10mL using the K-D apparatus in a water bath set at a temperature of approximately 70°C.

The extract may be left in the 10mL graduated concentrator tube or transferred to a labeled storage vial. The extract is now ready for the diazomethane esterification.

10.2 Soil Sample Preparation

10.2.1 Remove samples to be extracted from the storage refrigerator and allow the samples to reach room temperature while the extraction glassware is being prepared.

Check the "tune" of the sonicator using the procedure in SOP SA-EX-40: *Ultrasonic Extraction*.

10.2.2 Collect the appropriate glassware and rinse with acidified methanol and diethyl ether prior

to use.

10.2.3 Open the sample container and inspect the sample. Note any unusual characteristics such as the presence of rocks, sticks, leaves, or other materials. Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples.*

Note: If it is difficult to homogenize the sample or if the sample matrix is difficult to characterize, contact the Department Manager before proceeding with the extraction. A careful inspection of the sample at this point can save time and effort later on in the analysis. Any unusual sample preparation steps required prior to the extraction must be noted on a Nonconformance Report.

10.2.4 Weigh 30.0-31.0g of the homogenized sample into a pre-cleaned, labeled 500mL extraction bottle. Record the weight to the nearest 0.1g for all samples in this batch.

Weigh 30.0-31.0g of blank matrix into two separate beakers to serve as the method blank and laboratory control sample (LCS). Weigh additional 30.0-31.0g portions of the samples selected as the MS and MSD.

10.2.5 Working under a hood, acidify each sample and QC item with 0.1 to 0.2mL of concentrated hydrochloric acid. Add the acid to the sample slowly and carefully, stirring the sample with a stainless steel spatula, glass rod, or pipette. Continue to add acid until the pH <2 when read with narrow range pH paper.

10.2.6 Add sodium sulfate to each non-porous or wet sample (gummy or clay-type) and QC item. Stir with a glass rod or stainless steel spatula to form a sandy, free-flowing mixture. The sodium sulfate combines with the water in the sample to "dry" the sample (remove the water). More sodium sulfate may be required if the sample is very wet. Proceed to the next step as quickly as possible.

Add 1.0mL of the herbicide surrogate spiking solution to the method blank, LCS, MS, MSD, and each sample in the batch. Add 1.0mL of the herbicide spiking solution to the LCS, MS, and MSD. Transfer the extraction bottles to a hood near the sonicator.

10.2.7 Under a hood, add 250mL of diethyl ether to each sample and QC item. Stir the sample to break up any lumps that may have formed. Add more solvent until the solids are covered by about one inch.

10.2.8 Place the tip of the sonicator horn in the center of the beaker about ½ inch below the surface of the solvent but above the solid portion.

10.2.9 Sonicate for nine minutes with the output control knob set at 10, mode switch to pulse, and percent duty cycle set at 50%. If the sonication is properly performed, the solids and solvent will vigorously mix each time the sonicator pulses.

10.2.10 Add 500mL of reagent water to a 2L Teflon separatory funnel. Adjust the pH of the water to pH >=12 using 10N KOH. Transfer the entire extract to the separatory funnel, using several small aliquots of diethyl ether to rinse the bottle.

Check the pH with narrow range pH paper. Allow the sample to stand for at least one hour with intermittent shaking or shake on the automatic shaker for one hour.

Check the pH again after the one hour time period. If the pH <12, adjust the pH to >= 12 and allow to stand or shake for an additional hour. The pH must remain at or above 12 during the hydrolysis step.

Note: This step is necessary to convert the acid and ester forms of the herbicides to the water-soluble salts. After the hydrolysis step, the non-target compounds are contained in the diethyl ether layer.

Discard the diethyl ether layer and retain the water layer for additional preparation steps. The rest of the extraction steps may be performed with manual or automatic shaking. The sample extraction/preparation steps from this point forward are the same as described in Sections 10.1.3 through 10.1.11.

10.3 Esterification with Diazomethane

10.3.1 After sample concentration has been performed, the sample will need to be esterified with diazomethane. Concentrate the extracts to approximately 1mL under a gentle stream of nitrogen using the N-Evap apparatus.

10.3.2 After all of the extracts have been concentrated, prepare the diazomethane generation device for the esterification. Inspect the lines to ensure that there are no leaks or broken connections.

10.3.3 Place the extracts on the support. Replace all of the needles, and place the needles into the first extracts to be esterified.

10.3.4 Add diethyl ether to the first container on the diazomethane generation device until the container is about ¾ full.

10.3.5 Add the following to the second container to esterify approximately 20 samples:

50mL diethyl ether
50mL 37% potassium hydroxide
50mL Carbitol
5g Diazald

Note: Smaller volumes and weights of reagents may be used if the ratios above are maintained.

Quickly attach the container to the diazomethane device and start the nitrogen flow. Recall that the needles should already be placed in the samples that are to be esterified first. The gas flow should be steady but not so high that the sample is bubbled out of the concentrator tube or that the sample is evaporated before the esterification can take place.

10.3.6 Allow the diazomethane to flow through the sample extracts until a persistent yellow color remains. This will usually take two to three minutes. The esterification process will take longer as the diazomethane is exhausted.

Note: For dark extracts where the persistent yellow color cannot be distinguished, esterify the samples for 10 minutes.

10.3.7 After the persistent yellow color remains, remove the needle from the tube in that position and replace it with a new needle. Place the needle into the next sample to esterify. Repeat for all samples in the batch, replacing the needle for each new extract. If a yellow color cannot be formed in a clear extract, the diazomethane has most likely been exhausted. Pour the used reagents into a waste container (under a hood) and replenish the reagents in the second container. Add more diethyl ether to the first container if needed.

10.3.8 After all of extracts have been esterified, add a small amount (about 0.1g) of silica gel to each sample extract, cover the concentrator tubes with aluminum foil and allow the extracts to sit for 30 minutes. The silica gel will destroy any un-reacted diazomethane. Dilute to 10mL with MTBE and transfer the extract to a labeled storage vial. Store the extracts at 4°C until the time of analysis.

10.2 Analysis

10.3.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

Two columns are connected to the injection port using a press-tight glass y-splitter and a guard column, a two-hole ferrule, or a glass tee to provide simultaneous detection and confirmation of the target analytes.

Example GC Parameters
Injector: 240°C
Detector: 300°C
Carrier Gas Flow: Helium at ~2mL/min (per column) (pressure at 20psi, constant)
Make-up Gas Flow: Nitrogen at ~60mL/min (per detector)

Temperature Program:

Initial Temp:	50°C
Initial Hold:	0.50 min
Program Rate 1:	12°C/min to 100°C
Program Rate 2	15°C/min to 200°C
Program Rate 3:	80°C/min to 300°C
Final Temp:	300°C (hold for 1.25 minutes)
Total Time:	15.73 minutes
Injected Volume:	1uL per column (single injection into guard column and "Y" splitter)

10.3.1.1 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in SOP SA-QA-08: *Evaluation of Chromatographic Data.* Retention time windows (RTW), i.e., the length of time the instrument will scan for the analyte, must be established initially upon instrument set-up and verified quarterly.

Retention times (RT), i.e., the elution time of the analyte, are verified daily with the analysis of the ICAL or CCV. The retention time for the CCV must fall within the daily retention time window as defined in SOP SA-QA-08.

10.3.2 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.1. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.2, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.4.

10.3.3 Sample Analysis

Remove the extracts from the refrigerator and allow them to come to room temperature.

The sample extract must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to exclude QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the clock.

10.3.4 Example Analytical Sequence

An example analytical sequence is provided in Attachment 1.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data evaluation must be performed in accordance with SA-QA-08: *Evaluation of Chromatographic Data.* This SOP includes specific information regarding the evaluation of chromatographic data, including the requirements for performing manual integrations and the evaluation of retention times.

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review.*

11.1.1 Target Analyte Identification

The judgment and experience of the analyst and his/her colleagues are important factors in the evaluation of chromatographic data. Inspect each chromatogram to ensure that the peaks are properly identified and that the correct areas have been associated with the corresponding standard peak RT in the data system tabulation.

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times); the recovery and retention time shift of the surrogate compounds, whether the peak response falls within the working range of the calibration; and the integration of the peaks. The analyst must also take into account the results from the method blank and lab control sample before reporting quantitative data. SOP SA-QA-08: *Evaluation of Chromatographic Data* provides additional guidance for the evaluation of chromatographic data. This guidance is summarized in the following sections.

11.1.2 Manual Integrations

Manual integrations must be documented in accordance with SOP SA-QA-08. Data systems should be adjusted to minimize operator intervention. All chromatographic peaks must be evaluated for overall peak shape and "reasonableness" of integration. Under no circumstances should manual integrations be used to change reasonable data system integrations in order to meet calibration or QC criteria.

11.1.3 Dual Column Reporting

Refer to SOP SA-QA-08: *Evaluation of Chromatographic Data* for information on assessing and reporting data from dual columns.

11.1.4 Surrogate Evaluation

One surrogate, DCAA, is spiked into each sample and QC item prior to preparation. Given the complicated nature of GC-ECD chromatograms, assessing surrogate recovery is frequently complicated by co-eluting positive and negative interferences. Evaluate the surrogates in the same manner as the target compounds using the guidance above.

11.1.5 Dilutions

If the response for an analyte exceeds the working range of the system, a dilution is required. Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags must be used or qualification in a case narrative provided to the client.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 5 to provide lower reporting limits.

11.1.5.1 Surrogate Dilution Threshold Factor

Surrogates may be diluted out if the concentration of target compounds is high or the presence of non-target compounds interferes with the quantification of the target compounds. Undetect surrogates in the sample when the dilution factor is 6 or greater. As such, recoveries must be reported as "0D", and control limits will not apply.

An NCM must be initiated to denote this situation.

11.1.5.2 Dilutions and MS/MSD Recoveries

Matrix spike recoveries are not reported for dilutions of 5 or greater. An NCM is generated for instances where the dilution prohibits evaluation of the MS/MSD recoveries. In instances where the unspiked sample concentration is more than four times the concentration of the target compound spiked into the MS and MSD, the results are qualified with "4" or other suitable flag.

An NCM must be initiated to denote this situation.

11.1.6 Chemical Relationships and Compounds of Concern

Dalapon - this compound elutes very early in the run and may be subject to interference from co-eluting compounds and from artifacts from the extraction process.

MCPA and MCPP - these compounds have very low response in comparison to the other herbicides.

Dinoseb - this compound can be lost in the extraction process (hydrolysis step) but also may be lost if the injection port is not frequently and properly maintained.

11.1.7 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify TALS Worksheet Notes or use the TALS Historical Data Tracker feature to determine if historical data is available for review.

11.1.8 Drinking Water Compliance Evaluation

Public water suppliers (PWS) are governed by EPA-specified Maximum Contaminant Levels (MCL) above which indicates noncompliance. The MCLs associated with this procedure are given in Attachment 7. Notify the PM immediately via a Nonconformance Memo if any sample contains a detection above these levels.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard

deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample
F = Final volume/weight
I = Initial volume/weight
dw = % Solids decimal equivalent
D = Dilution factor

Note: This calculation assumes all applicable unit correction factors are applied.

Note: All dry weight corrections are performed automatically in LIMS.

Note: Methyl ester herbicide standards must be corrected to the free acid concentration. This is performed by comparing the molecular weight of the methyl ester to that of the acid to determine a correction factor. Attachment 5 gives the molecular weights of the acids and esters. It also lists the correction factors and illustrates how to perform the acid-ester correction.

12.0 Method Performance

12.1 Reporting Limit Verification (RLV)

At a minimum, RLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, RLVs must also be performed quarterly thereafter. For all other analytes and methods, RLVs must also be performed annually thereafter. Exceptions may be made for project-specific non-routine analytes.

12.2 Method Detection Limit (MDL) Study

The MDL is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDLs associated with this procedure are given in the Method Limit Group (MLG) in TALS.

At a minimum, MDL Studies must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

Note: MDL Studies are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.3 Method Detection Limit Verification (MDLV)

At a minimum, MDLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, MDLVs must also be performed quarterly thereafter. For all other analytes and methods, MDLVs must also be performed annually thereafter.

Note: MDLVs are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.4 QC Limit Generation, Control Charting, and Trend Analysis

EPA 515.1 and EPA 615
The control limits for the batch QC items (LCS, MS/MSD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

EPA 8151A
The control limits for the batch QC items (LCS, MS/MSD) for this procedure are not specified by the reference method; therefore, the laboratory defaults to in-house and/or laboratory-derived limits for the evaluation of batch QC items.

Control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.5 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures*.

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four

consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Flammable wastes (hexane, methanol, diethyl ether, diazald) – Transfer to flammable waste containers. Transfer to hazardous waste section when the satellite container is 95% full.

15.0 References / Cross-References

- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-AN-41: *Reagent and Standard Materials Procedures*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-08: *Evaluation of Chromatographic Data*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- *Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846*; including Updates III and IV. U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November, 1986.
  - Method 8000B: *Determinative Chromatographic Separations*, Revision 2; December 1996
  - Method 8151A: *Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization*, Revision 1; December 1996
- *Code of Federal Regulations, Title 40, Part 136*; U.S. Government Printing Office: Washington, DC, July 1, 1988.
  - Method 615: *the Determination of Chlorinated Herbicides in Municipal and Industrial Wastewater*
- *Code of Federal Regulations, Title 40, Part 141*; U.S. Government Printing Office: Washington, DC, July 1, 1988, and Part III, March 12, 2007.
- Method 515.1: *Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector,* Revision 4.0, U.S. EPA, Cincinnati, OH 45268

16.0 Method Modifications and Clarifications

16.1 Incorporation of Other Matrices

The EPA 515.1 reference method was written specifically for drinking water and source water samples; however, the laboratory may perform other types of water samples by this method.

This procedure may be modified to analyze other matrices (e.g., wipe, waste, and leachate samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project.

Wipe, waste, and leachate matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.), and soil QC limits to evaluate these types of samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for wastes and wipes.

16.1.1 Waste Samples

Waste samples are extracted as follows:
Weigh 1.0-1.2g of the homogenized sample into a calibrate 12mL vial. Fill to vial to the mark with diethyl ether. Proceed to Section 10.1.3 and complete the preparation.

16.1.2 Wipe Samples

Wipe samples are prepared as follows:
Add diethyl ether to the sample until the volume comes up to the shoulder of the vial, leaving some headspace between the top of the solvent and the vial cap. Shake the vials for 1-2 minutes.

Set up a 2L separatory funnel for each sample and QC item. Add 500mL of reagent water to each funnel. Adjust the pH of the water in each funnel to >=12 with 10N sodium hydroxide.

Transfer the entire contents of the vial to the separatory funnel. Rinse the vial with several small aliquots of ethyl ether and add to the funnel.

Shake for one hour on the automatic shaker. Check the pH of the sample. If the pH >=12, continue on to Section 10.1.4 and complete the sample preparation. If the pH<12, add more 10N sodium hydroxide and shake for an additional 15 minutes. Continue until the pH is >=12. Proceed to Section 10.1.4 and complete the preparation.

Note: Since the same site cannot be used to collect another wipe sample, MS and MSD are not applicable to this preparation.

16.1.3 Leachate Samples

TCLP and SPLP samples are prepared as follows:
Transfer 10mL of the leachate to a separatory funnel and dilute to 500mL with reagent water. Proceed to Section 10.1.3 and complete the preparation.

16.2 Other Considerations

16.2.1 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each EPA 515.1 batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory defaults to 50-150%.

16.2.2 EPA Method 515.1 requires a Quality Control Sample (QCS) obtained from a source external to the laboratory and different from the source of calibration standards to be analyzed quarterly. The laboratory uses the second source initial calibration verification (ICV) to meet this requirement.

16.2.3 The laboratory prepares water samples for EPA 515.1, EPA 615, and EPA 8151A in the same manner (i.e., as mandated in EPA 515.1). Both EPA 615 and EPA 815A and associated EPA Memoranda provide allowances to adjust sample preparation procedures in this fashion provided method-defined quality control criteria are met. Further

information on this change is provided below:

Diethyl ether is used as the extraction solvent for soils in place of 1:1 acetone/methylene chloride. This step was modified to improve recovery of chlorinated herbicides. Recoveries of the herbicides using acetone/methylene chloride were found to be less than 10%. The initial extract of soils is not concentrated prior to hydrolysis. The entire extract is transferred to a separatory funnel containing water that has been adjusted to pH >=12 for hydrolysis.

The extraction procedure has been modified from the guidance provided in EPA 8151A. The table below summarizes the differences.

Extraction Step	EPA 8151A	SOP
Extraction of non-targets from hydrolyzed (basic) sample (essentially a cleanup step)	3x60mL MeCl2. Shake each aliquot for 2 minutes.	1x100mL MeCl2. Shake for 10 minutes on automatic shaker.
Extraction of herbicides from acidified sample (post hydrolysis)	120mL ethyl ether, then 2x60mL ethyl ether Shake each aliquot for 2 minutes.	1x300mL ethyl ether. Shake for 30 minutes on automatic shaker.

The laboratory's procedures are adapted from Section 11.2 of EPA Method 515.1, Revision 4. These modifications minimize transfer of the sample between containers which minimizes the loss of target analytes due to absorption on the glassware.

All batch QC samples, MDL studies, DOCs, and PT samples have been performed utilizing the method modifications listed above. Acceptable recoveries/results have been obtained indicating these modifications do not have a negative impact on the performance of this method.

16.2.4 EPA 515.1 lists mercuric chloride as a preservative for EPA 515.1 but acknowledges extreme health hazards associated with this chemical. As such, the laboratory has not incorporated the use of this chemical.

16.2.5 Unless specifically required to do otherwise (i.e., WI DNR compliance samples), the laboratory's default procedure is to incorporate the use of purchased methyl ester calibration standards instead of the free acids forms. All method validation steps (e.g., MDLs, DOCs, PTs, etc.) have been performed in this manner, and adverse results have not been noted

16.2.6 The reference methods specify continuing calibration verifications to be performed either every 12 hours (EPA 8151A) or every 24 hours (EPA 515.1 and EPA 615). The laboratory requires a capping CCV to be performed every 20 field samples or 12 or 24 hours, whichever comes first.

16.2.7 The laboratory uses its in-house control limits to evaluate initial demonstrations of capability.

16.2.8 EPA 515.1 does not provide criteria for initial calibration curves (i.e., non-RSD evaluation). The laboratory has adopted a r^2 criteria of 0.990 which is consistent with EPA 8151A. EPA 615 and EPA 8151A do not require analysis of a 2nd source ICV. This standard has been adopted to meet NELAC requirements. A 20% D criteria has been imposed for these methods, which is equivalent to the CCV criteria in EPA 615.

16.2.9 EPA 515.1 specifies to add 250g of sodium chloride per sample during the extraction process. The laboratory uses 1/3 cup sodium chloride (equivalent to approximately 100g) as its default amount as previous tests have indicated excess sodium chloride can adversely affect recoveries. 100g is sufficient to change the polarity of the sample enough to allow the compounds of interest to be extracted into diethyl ether and to prevent emulsions from occurring.

16.2.10 In an effort to meet some client- and/or state-specific requirements for batch precision, the laboratory's default batch QC items have been expanded from those outlined in the reference methods (i.e., to include MSD and/or LCSD).

16.2.11 EPA 515.1 Revision 4.1 was released by the EPA and then recalled due to QC requirements mandated for dinoseb that could not routinely be achieved by laboratories. As instructed by EPA, the method cited by the laboratory is the earlier version (i.e., EPA 515.1 Revision 4.0).

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Herbicide Molecular Weights and Correction Factors
Attachment 6: EPA 515.1 Laboratory Performance Check (LPC) Evaluation Criteria
Attachment 7: EPA-specified Maximum Contaminant Levels (MCL)
Attachment 8: Glassware Cleaning
Attachment 9: Florisil Clean-up Procedures

Attachment 1:
SOP Summary

Sample Preparation Summary

Water Samples – A known volume of aqueous sample, nominally 1000mL, is transferred to a Teflon separatory funnel. The sample is hydrolyzed with base to convert the herbicides present to their salt form. The hydrolyzed sample is extracted with methylene chloride to remove the non-phenoxy acid herbicide material. The sample is acidified and extracted with diethyl ether. The extract is dried, filtered, concentrated, esterified with diazomethane, dissolved in MTBE, and analyzed by GC/ECD.

Soil Samples – A known weight of a sample, approximately 30g wet weight, is acidified with hydrochloric acid (HCl) and combined with acidified sodium sulfate to form a free flowing, sandy mixture. Diethyl ether is added to the dried sample, and the sample is extracted using an ultrasonic disrupter for 9 minutes. The extract is transferred to a separatory funnel containing water that has been adjusted to pH$\geq$12. The sample is allowed to hydrolyze for one hour to convert the acid and ester forms of the herbicides to their salt forms. The solvent is discarded, and the aqueous phase, which contains the herbicides in their salt form, is acidified and extracted with diethyl ether. The extract is dried, concentrated, esterified with diazomethane, dissolved in MTBE, and analyzed by GC/ECD.

Sample Analysis Summary

The extracted methyl derivatives are analyzed by a GC equipped with dual capillary columns (different phases) connected to dual electron capture (EC) detectors, allowing simultaneous detection and confirmation of the target compounds. Quantitation is performed using the external standard calibration technique.

This SOP is based on the following methods: EPA 515.1, EPA 615, and EPA 8151A.

Example Analytical Sequence

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
Instrument Blank	
Laboratory Performance Check (LPC)	EPA 515.1 Only
Samples & Batch QC Items	
CCV	
Instrument Blank	
Samples & Batch QC Items	
CCV	
Instrument Blank	

The sequence continues until all samples have been analyzed or until the calibration verification fails the acceptance criteria. All sample extract analyses must be bracketed by acceptable verification standards.

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Method	Matrix	Routine Sample Container	Routine Sample Size	Minimum Sample Size	Chemical Preservation	Thermal Preservation	Dechlorination Agent	Holding Time
EPA 515.1	Water	1L amber glass	1L	500mL	None	0-6°C	80mg sodium thiosulfate	Extraction: 14 days from collection Analysis: 28 days from extraction
EPA 615	Water	1L amber glass	1L	500mL	None	0-6°C	None	Extraction: 7 days from collection Analysis: 40 days from extraction
EPA 8151A	Water	1L amber glass	1L	500mL	None	0-6°C	None	Extraction: 7 days from collection Analysis: 40 days from extraction
EPA 8151A	Soil	16oz soil jar	30g	15g	None	0-6°C	None	Extraction: 14 days from collection Analysis: 40 days from extraction

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration (ICAL) - 5-pt minimum	Initially, prior to sample analysis, and when acceptable CCV cannot be obtained	EPA 615: %RSD <=10%; r^2 >0.990 EPA 515.1 and 8151A: <20%RSD; r^2 >0.990	Refer to SOP SA-QA-16
2nd Source Initial Calibration Verification (ICV)	After Initial Calibration. (Quarterly, at a minimum, for EPA 515.1)	EPA 515.1: Percent difference <=20% EPA 615 and 8151A: Percent difference <=15% with no single analyte >45%	Refer to SOP SA-QA-16
Laboratory Performance Check (LPC)	EPA 515.1 Only: Daily, prior to sample analyses	See criteria in Attachment 6.	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Continuing Calibration Verification (CCV)	EPA 515.1: At the beginning and end of the analysis, and every 24 hours or 20 samples	Within ±20% of the true value	Refer to SOP SA-QA-16
	EPA 615: At the beginning of the analysis, and every 24 hours or 20 samples	Within ±10% of the true value	
	EPA 8151A: At the beginning and end of the analysis, and every 12 hours or 20 samples	Within ±15% of the true value; GME with no single analyte >45%	

QC Item	Frequency	Criteria	Corrective Action
Calibration Blank (ICB/CCB)	After ICV and every CCV	<1/2 RL	Terminate the analysis, correct problem and reanalyze the previous samples.
Batch Definition	Up to 20 field samples, extracted together w/in 24-hour time period	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	<1/2 RL	Evaluate according to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	One per batch, when insufficient sample provided for MS/MSD	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Low-Level Laboratory Control Sample (LLCS)	EPA 515.1 Only: One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike (MS)	EPA 515.1 and 615: 10% of samples prepared; i.e., 2 separate MS per batch EPA 8151A: One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Surrogate	All samples and batch QC items	Recoveries within MLG limits	Evaluate according to SOP SA-QA-17
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06 Note: Unsupervised work must not begin until acceptable IDOC is obtained.
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06

QC Item	Frequency	Criteria	Corrective Action
Reporting Limit Verification (RLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Method Detection Limit Study (MDL)	Upon method/instrument set-up, per analyte/method/matrix combination	Refer to SOP SA-QA-07	Evaluate according to SOP SA-QA-07
MDL Verification (MDLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Evaluate according to SOP SA-QA-07
Retention Time Window Determination	Annually	Refer to SOP SA-QA-08	Refer to SOP SA-QA-08

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling

Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log

A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE	
EQUIPMENT ITEM	**SERVICE LEVEL**
Water	Change the water in the water bath, recommended weekly. Add 1-2 drops of Clear Bath to prevent bacteria and algae growth.
K-D apparatuses	Inspect periodically for leaks and cracks. Leaks will allow the infiltration of water into the extract and compromise the entire extraction procedure.
Snyder Columns	Inspect frequently. The balls in the condenser will sometimes stick, causing pressure from the evaporating solvent to build up and spew the extract out of the top of the column. Wetting the column with a small volume of solvent will help to keep the balls from sticking.

Note: Glassware with leaks, cracks, and broken joints must be repaired or replaced.

Note: If the herbicide blank is contaminated, clean the diazomethane generator tubing and vessels with methylene chloride, methanol, and diethyl ether, in that order, and purge the apparatus with nitrogen to dry. Replace the Teflon tubing and vessels if the solvent cleaning does not improve the blank.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Guard Column/Injector							X	Change sleeve and cut front of guard column, recommended daily
Septum							X	Replace , recommended daily
Splitless Disc							X	Replace , recommended daily
Autosampler							X	Syringe cleaned or replaced as needed
Column							X	Change column

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually; AN = as needed

Troubleshooting

Troubleshooting should be documented as outlined above. If possible, troubleshooting is best performed in a step-wise manner to systematically isolate instrument components. Refer to the instrument manufacturer's guides for specific information and strategies. Enlist assistance from technical and/or department management as needed.

Contingency Plan

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
Herbicide Molecular Weights and Correction Factors

Herbicide acid	MW_{acid}	$MW_{ester/ether}$	Correction factor
2,4-D	221.04	235.07	0.940
Dalapon	142.97	157.00	0.911
2,4-DB	249.09	263.12	0.947
Dicamba	221.04	235.07	0.940
Dichloroprop	235.07	249.09	0.944
Dinsoeb	240.22	254.24	0.945
MCPA	200.62	214.65	0.935
MCPP	214.65	228.67	0.939
2,4,5-TP(Silvex)	269.51	283.54	0.951
2,4,5-T	255.48	269.51	0.948
DCAA	205.04	219.07	0.936
Picloram	241.48	255.51	0.945
Pentachlorophenol	266.35	280.37	0.950
4-Nitrophenol	139.11	153.14	0.908
3,5-Dichlorobenzoic Acid	191.01	205.04	0.932
Acifluorfen	361.66	375.68	0.963
Chloramben	206.03	220.05	0.936
Bentazon	240.28	254.31	0.945

Example Calculation:

$$CF(2,4-D) = \frac{W_{acid}}{W_{ester\,/\,ether}} = \frac{221.04}{235.07} = 0.940$$

If the standard is expressed as mass of ester per volume, convert the concentration to the acid form by multiplying by the correction factor (CF).

Attachment 6:
EPA 515.1 Laboratory Performance Check (LPC) Evaluation Criteria

Test	Analytes	Concentration (ug/mL)	Criteria
Sensitivity	Dinoseb	0.004	S/N>3
Chromat performance	4-nitrophenol	1.6	0.70<PGF<1.05
Column performance	3,5-Dichlorbenzoic acid	0.6	Resolution >0.4
	4-nitrophenol	1.6	

The sensitivity of the instrument is measured by determining the signal to noise ratio of dinoseb. The signal to noise ratio must be greater than 3 in order to analyze samples.

S/N = a ratio of peak signal to baseline noise

Where:
S = peak signal – measured as height of peak
N = baseline noise – measured as maximum deviation in baseline (in units of height) over a width equal to the width of the base of the peak

The chromatographic performance is measured by determining the Peak Gaussian Factor (PGF) of 4-nitrophenol. The Peak Gaussian Factor (PGF) is a mathematical representation of the peak shape. The closer to 1 the PGF is the more "normal" or "bell-shaped" the curve is. The PGF must be between 0.70 and 1.05 in order to analyze samples.

$$PGF = \frac{1.83 \otimes W_1}{W_2}$$

Where:
W_1 = the peak width at 1/2 the height (in seconds)
W_2 = the peak width at 1/10 the height (in seconds)

The column performance is measured by determining the resolution between 3,5-Dichlorobenzoic acid and 4-nitrophenol. Resolution (R) is a measure of the degree of separation of two peaks under specific chromatographic conditions and must be greater than 0.4 in order to analyze samples.

$$R = \frac{t}{W_{avg}}$$

Where:
t = the difference in elution times between the two peaks
W_{avg} = the average peak width of the two peaks (measurements taken at baseline)

Attachment 7:
Maximum Contaminant Levels (MCL)

Primary Drinking Water Regulations		
Contaminant	MCLG (mg/L)	MCL (mg/L)
2,4-D	0.07	0.07
Dalapon	0.2	0.2
Dinoseb	0.007	0.007
Pentachlorophenol	0	0.001
Picloram	0.5	0.5
2,4,5-TP (Silvex)	0.05	0.05

Attachment 8:
Glassware Cleaning

ZYMARK TUBE AND CLLE ROUNDBOTTOM FLASK CLEANING PROCEDURES

PPE: **Lab coat**
Eye protection
Kevlar gloves or equivalent

1. Note the condition of the Zymark tube or receiving flask. If heavily contaminated, do not place into the sink. Keep this glassware separate and contact the supervisor or Department Manager to determine the best course of action to clean the glassware.

It is important to segregate heavily contaminated glassware from use until verified clean by the analysis of a method blank. Discard if the condition of the glassware cannot be verified or if the glassware is obviously not salvageable.

2. Rinse each tube or flask thoroughly with water and discard down the sink drain.

3. Fill dishpan with hot water and add about ¼ cup of FL-70 detergent per gallon of water.

4. For Zymark tubes, use a small brush to clean the tip of the tube and a larger brush to clean the walls of the tube.

For receiving flasks, use a brush that will allow you to scrub the inside walls of the flask.

5. Rinse each tube and flask thoroughly a minimum of three times with hot tap water until no traces of soap are present in the tube. It is important to remove all traces of soap at this point.

6. Rinse each tube and flask thoroughly with acetone and place on covered counter or rack to dry.

Discard acetone rinses down the sink drain with the cold tap water running.

7. Rinse each tube with a small aliquot of methylene chloride and place on covered counter or rack until ready for use.

Discard methylene chloride in the satellite waste container designated for chlorinated waste.

Attachment 9
Florisil Clean-up

- Place a small plug of glass wool into a 5 mL disposable glass pipette. Tare the pipette, and measure 1 g of activated Florisil into the pipette.
- Apply 5 mL of 5% methanol in MTBE to the Florisil. Allow the liquid to just reach the top of the Florisil. In this and subsequent steps, allow the liquid level to just reach the top of the Florisil before applying the next rinse, however, do not allow the Florisil to go dry. Discard eluate.
- Apply 5mL methylated sample to the Florisil leaving silicic acid in the tube. Collect eluate in K-D tube.
- Add 1mL of 5% methanol in MTBE to the sample container, rinsing walls. Transfer the rinse to the Florisil column leaving silicic acid in the tube. Collect eluate in a K-D tube. Repeat with 1 mL and 3 mL aliquots of 5% methanol in MTBE, collecting eluates in K-D tube.
- If necessary, dilute eluate to 10 mL with 5% methanol in MTBE.
- Seal the vial and store in a refrigerator if further processing will not be performed immediately.

18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial, grammatical, and formatting changes made. Boilerplate text added.
- Added note that unsupervised work must not begin until acceptable IDOC is obtained. Attachment 3
- Added section on troubleshooting. Attachment 4
- Clarified requirements and frequency for RLVs, MDL Studies, and MDLVs to be consistent with SOP SA-QA-07 and to include the quarterly frequency as defined by DOD. Section 12.1 - 12.3 and Attachment 3
- Added section to describe analytical data system, software, and hardware. Section 6.2
- Added note that if an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required. Section 9.1.1
- Added note that some programs and agencies do not allow the use of quadratic curves and to refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited. Section 9.2.2.1
- Added reference to TALS Historical Data Tracker feature. Section 11.1.7
- Added requirement to spike sample bottle with surrogate and spike mixes prior to any sample manipulation steps (i.e., pouring sample into separatory funnel apparatus). Section 10.1.2 (Corporate Internal Audit Finding, May 2010)

SEMI-VOLATILE COMPOUNDS BY GC/MS

(Methods: EPA 625, EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, EPA 8270D_LL_PAH, and SM6410B)

Approvals (Signature/Date):

Andrea Teal November 22, 2010
Andrea Teal Date
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November 15, 2010
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Facility Distribution No. 1 Distributed To: QA Navigator

1.0 Scope and Application

This SOP contains the procedures for the determination of extractable semi-volatile organic compounds (SVOC) by gas chromatography/mass spectrometry (GC/MS).

The routine matrices performed by this procedure are waters and soils. Other matrices which may be performed include wipes, leachates, tissues, and wastes.

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

2.0 Summary of Method

A measured volume or weight of sample is extracted using continuous liquid-liquid or sonication extraction procedures. The extract is then analyzed by GC/MS. Qualitative identification of the target compounds in the extract is based on the retention time and the relative abundance of the characteristic masses determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

This SOP is based on the following methods: EPA 625, EPA 8270C, EPA 8270D, and SM6410B.

Note: This SOP contains the procedures for several variations of the SW-846 methods. These variations include:

- EPA 8270C and EPA 8270D (i.e., routine 8270)
- EPA 8270C_LL and EPA 8270D_LL (i.e., low-level 8270)
- EPA 8270C_LL_PAH and EPA 8270D_LL_PAH (i.e., low-level 8270 for polynuclear aromatics hydrocarbons only)

These three sets of procedures incorporate slightly different standard concentrations, surrogate compounds, instrument configuration, and QC evaluation criteria, which are outlined separately in the applicable sections of this SOP.

This SOP also gives the procedures for analyzing and reporting samples using the MS in Selective Ion Monitoring (SIM) mode.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Acetone and methylene chloride must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. Sample extracts that contain high concentrations of non-volatile material such as lipids and high molecular weight resins and polymers may require the optional gel permeation chromatography (GPC) cleanup prior to analysis. The GPC cleanup is generally not effective in removing non-target material that is associated with common petroleum products like diesel. Refer to extraction SOPs for further information on the GPC procedure.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 If there is interference with the primary ion, then secondary ions may be used for quantification. If a secondary ion is used for quantification, the linearity of the secondary ion must be established by meeting the criteria in Section 11.

4.2.3 The basic conditions of the initial extraction may cause hydrolysis and degradation of some target compounds. The degradation may be pronounced in phthalate esters.

4.2.4 Refer to Section 11.1.5 for more information on the chemical relationships of these compounds.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; therefore, each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

Methylene chloride is a carcinogen and an irritant. It causes irritation to the respiratory tract and has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting, and headache. May be absorbed through the skin and can cause irritation and pain to the skin and eyes.

The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS

can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit [1]	Signs and Symptoms of Exposure
Acetone	Flammable	1000ppm TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methylene Chloride	Carcinogen Irritant	25ppm TWA 125ppm STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Gas chromatograph - Agilent 5890, 6890, 7890, or equivalent with compatible autosampler, split/splitless injector, and direct capillary interface.

Mass spectrometer- Agilent 5973, 5975, or equivalent

Top-loading Balance – Verify in accordance with SOP SA-AN-10: *Balance Calibration and Use*

6.2 Analytical Data System / Software / Hardware

Chemstation software is used on a Windows-based PC to schedule and acquire data. Target (UNIX and/or Windows) software is used on a Windows-based PC to store, reduce/evaluate, and output the data to the laboratory's LIMS system (i.e., TALS). Target software has the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectrum from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software also allows integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as or construction of a linear regression calibration curve, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the response factors.

6.3 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*

Disposable Transfer Pipettes and Bulbs – various sizes

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*

Column – Supelco SLB5-MS, 30m x 0.25mm ID, 0.25um film thickness or equivalent

Injector Liner – 4mm ID quartz or 4mm glass, deactivated

Autosampler Vials and Caps – various sizes

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard must not exceed the expiration date of the standard that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Traceability.*

Acetone and methylene chloride must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Methylene chloride: pesticide grade, for preparation of analytical standards
Storage: Room temperature
Expiration: Unopened and Opened - Manufacturer's expiration date

7.2.2 Acetone: pesticide residue grade, for cleaning glassware.
Storage: Room temperature
Expiration: Unopened and Opened - Manufacturer's expiration date

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Traceability.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

Refer to Attachment 9 for the laboratory's current standards and recipes.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

Aqueous samples are routinely collected in 1L amber glass containers with PTFE-lined lids.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 7 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

Note: In the presence of samples containing residual chlorine, phenol-d_6 has been known to react to form chlorinated phenolic compounds that are not detected as the original spiked surrogate. Therefore, aqueous samples must be evaluated for the presence of residual chlorine prior to extraction.

8.2 Soil Samples

Soil samples are routinely collected in 16oz soil containers with PTFE-lined lids.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

An extraction batch consists of up to 20 environmental samples and the associated QC items.

For EPA 625, the minimum QC items required for each extraction batch are: a method blank, a laboratory control sample (LCS), and a matrix spike (MS) per 10% of samples extracted.

For EPA 8270C, EPA 8270D, EPA 8270C_LL, EPA 8270D_LL, EPA 8270C_LL_PAH, EPA 8270D_LL_PAH, and SM6410B the laboratory's default QC items performed for each extraction batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD).

Note: LCS and LCSD are performed if insufficient sample is provided for MS/MSD. If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required.

Refer to applicable preparation SOP listed in Section 10.1 for further information on batch QC.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.1.1 Poor Performers

As indicated in SW-846 and/or via assessment of laboratory control sample (LCS) recoveries and control charts, the compounds listed in Attachment 11 are poor performers and/or behave erratically. These compounds will not be included in the LCS/LCSD/MS/MSD marginal exceedance count, as outlined in SOP SA-QA-17: *Evaluation of Batch QC Data,* provided they are qualitatively detected.

Note: An NCM must be initiated to denote this situation.

9.2 Instrument QC

9.2.1 DFTPP

A solution containing DFTPP (difluorotriphenyl phosphate) must be analyzed at the beginning of each analytical clock. The analytical clock begins with the injection of the DFTPP standard and is defined as 12 hours for EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, EPA 8270D_LL_PAH, and SM6410B and is defined as 24 hours for EPA 625.

Meeting the DFTPP tuning criteria demonstrates that the instrument is measuring the proper masses in the proper ratios. The DFTPP analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of DFTPP. All other instrument conditions including the mass range, scan rate, and multiplier voltage must be identical.

A 1uL aliquot of the 50ng/uL DFTPP/Column Evaluation solution is utilized for EPA 625, EPA 8270C, EPA 8270D, and SM6410B. A 1uL aliquot of the 5ng/uL DFTPP/Column Evaluation solution is utilized for EPA 8270C_LL, EPA 8270D_LL, EPA 8270C_LL_PAH, and EPA 8270D_LL_PAH.

The DFTPP solution must also contain benzidine, pentachlorophenol, and p,p'-DDT at the following concentrations:

EPA 625, EPA 8270C, EPA 8270D, and SM6410B – 50ug/mL
EPA 8270C_LL and EPA 8270D_LL – 5ug/mL
EPA 8270C_LL_PAH and 8270D_LL_PAH – 5ug/mL

9.2.1.1DFTPP Spectrum Criteria

The spectrum of the DFTPP must meet the criteria for each method listed in Attachment 6. Background subtraction must be straightforward, that is, no scan within the elution window of DFTPP may be subtracted from another scan within the elution window, and designed only to eliminate column bleed or instrumental background. Scans ± 2 scans from the apex can be evaluated for the DFTPP criteria. Consecutive scans within this range may be averaged to meet the criteria.

Note: The DFTPP analysis should be evaluated as to the relative size of the DFTPP peak under the m/z 198 profile. A benchmark area window should be established for each instrument and data system. Area outside of this window suggests instrumental problems such as a bad injection, clogged autosampler syringe, leaking injector, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open, etc.

If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

9.2.1.2 DFTPP Tailing Factor Criteria

The analysis of benzidine and pentachlorophenol serves as a check on the system performance. The tailing factor for pentachlorophenol and benzidine is calculated as outlined in Attachment 7 and must meet the following criteria:

EPA 625, EPA 8270C, EPA 8270C_LL, and SM6410B:
pentachlorophenol <5
benzidine <3

EPA 8270D and EPA 8270D_LL:
pentachlorophenol <2
benzidine <2

EPA 8270_LL_PAH and 8270D_LL_PAH:
There are no tailing factor criteria for these methods.

If the criteria above are not met, perform injector port and column maintenance and reanalyze the DFTPP standard.

9.2.1.3 DFTPP Percent Breakdown Criteria

DFTPP percent breakdown must be evaluated for EPA 8270C, EPA 8270C_LL, EPA 8270D, and EPA 8270D_LL.

Percent breakdown is calculated using the areas from the total ion chromatogram using following equation:

$$\%Breakdown = \frac{(areaDDE + areaDDD)}{(areaDDT + areaDDE + areaDDD)} x\,100$$

The percent breakdown of p,p'-DDT must not exceed 20% for the methods cited above.

There is no percent breakdown requirement for EPA 625, EPA 8270C_LL_PAH, EPA 8270D_LL_PAH, and SM6410B.

9.2.2 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves.* This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 3 standards for EPA 625 and SM6410B and a minimum of 5 standards for EPA 8270C, EPA 8270D, EPA 8270C_LL, EPA 8270D_LL, EPA 8270C_LL_PAH, and EPA 8270D_LL_PAH. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

Note: A minimum of 6 points is required for a quadratic curve. Higher order curves are not permitted. Some programs and agencies (e.g., SC DHEC) do not allow the use of quadratic curves. Refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited.

The initial calibration standard concentrations currently in use in the laboratory are as follows:

EPA 8270C / EPA 8270D / EPA 625 / SM6410B

Standard Level	Concentration (ug/mL)
1	10
2	20
3	50
4	80
5	100
6	200

EPA 8270C_LL / EPA 8270D_LL

Standard Level	Concentration (ug/mL)
1	0.20
2	0.50
3	1.0
4	2.0
5	5.0
6	10
7	20
8	50

EPA 8270C_LL_PAH / EPA 8270D_LL_PAH

Standard Level	Concentration (ug/mL)
1	0.20

2	0.50
3	1.0
4	2.0
5	5.0
6	10
7	20

Refer to Attachment 9 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-41.

ICAL evaluation steps and acceptance criteria vary between the methods. Refer to Attachment 1 for a summary of the method-specific requirements.

9.2.3 Instrument Blanks

The instrument must be shown to be free from contamination by the analysis of instrument blanks or method blanks. Instrument blanks are analyzed at the beginning of each clock before analysis of any samples. The instrument blanks should be analyzed following the ICV or CCV.

Instrument blanks or method blank must be <1/2RL to be acceptable

9.2.4 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to Level 4 of the ICAL for EPA 625, EPA 8270C, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL_PAH, and SM6410B and equivalent to Level 6 for EPA 8270C_LL and EPA 8270D_LL. Refer to Section 7.3.2.5 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

ICV evaluation steps and acceptance criteria vary between the methods. Refer to Attachment 1 for a summary of the method-specific requirements.

9.2.5 Continuing Calibration Verification (CCV)

The initial calibration curve must be verified at the beginning of each clock with a mid-level standard. The analytical clock is defined as 12 hours for EPA Method 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, EPA 8270D_LL_PAH, and SM6410B and is defined as 24 hours for EPA Method 625. The initiation of the clock begins with the injection of the DFTPP.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to Level 4 of the ICAL for EPA 8270C, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL_PAH, EPA 625, and SM6410B and is equivalent to Level 6 of the ICAL EPA 8270C_LL and EPA 8270D_LL. Refer to Section 7.3.2.2 for the standard

preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

Note: An additional, low-level (RL) CCV is incorporated into the procedure for EPA 8270D, EPA 8270D_LL, and EPA 8270D_LL_PAH. This low-level CCV is used to demonstrate sensitivity at the RL can be obtained. Refer to the applicable CCV section for more information on how this CCV is utilized.

Note: CCV evaluation steps and acceptance criteria vary between the methods. Refer to Attachment 1 for a summary of the method-specific requirements.

9.2.6 Isomer Resolution Criteria

Monitor GC resolution of structural isomers in the ICAL and CCV. In the ICAL use the calibration level that will be utilized as the CCV.

Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. This criteria is important for the identification of benzo(b)fluoranthene and benzo(k)fluoranthene.

Note: The resolution should be monitored utilizing the signal resolution of the extracted ion profiles for the quantitation ion for each analyte. Sufficient GC resolution is needed to identify the individual isomeric peaks by retention time. If target software is able to integrate and define separate peaks for the isomeric pairs, then sufficient resolution has been achieved. If there is sufficient evidence to support the identification of the individual component, then the component is identified, quantified, and reported.

9.2.7 Internal Standard (ISTD)

This procedure is an internal standard (ISTD) procedure. The internal standards used are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}.

Prior to analysis, this internal standard must be added to all standards, samples, and QC items. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. A concentration of 40ug/mL is used for EPA 8270C, EPA 8270D, EPA 625, and SM6410B. A concentration of 2.0ug/mL is used for EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D_LL, and EPA 8270D_LL_PAH.

9.2.7.1 ISTD Criteria

9.2.7.1.1 ICV/CCV ISTD Criteria - EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, and EPA 8270D_LL_PAH

The response of the ISTD in the ICV/CCVIS must be within a factor of 2 of the response of the ISTD in the CCV-level standard in the initial calibration sequence. Due to the number of analytes reported in this method, multiple CCVs can be analyzed. The primary CCV is defined as the CCVIS and used to monitor ISTD response in samples. If the

response is outside of this range, the analysis of the CCVIS must be repeated and any samples associated with the CCVIS must also be re-analyzed. Repeated failure of the ISTD response may require instrument maintenance, re-preparation of standards, and/or re-calibration.

9.2.7.1.2 ICV/CCV ISTD Criteria - EPA 625 and SM6410B

There are no ICV or CCV ISTD criteria for EPA 625 or SM6410B.

9.2.7.1.3 Sample and Batch QC ISTD Criteria - EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, and EPA 8270D_LL_PAH

The response of the ISTD in samples and batch QC items must be within a factor of 2 of the response of the previous CCVIS. If the response is outside of this range, corrective action must be taken. Corrective actions include re-analysis (for field samples) and/or re-extraction (if batch QC item).

9.2.7.1.4 Sample and Batch QC ISTD Criteria - EPA 625 and SM6410B

There are no specific ISTD criteria in EPA 625 and SM6410B. The laboratory has adopted the criteria outlined in EPA 8270C and EPA 8270D.

9.2.8 Surrogates

This procedure uses surrogates to evaluate the extraction process.

The surrogates currently used by the laboratory for EPA 625, EPA 8270C, EPA 8270C_LL, EPA 8270D, EPA 8270D_LL, and SM6410B are phenol-d6 (acid), 2-fluorophenol (acid), 2,4,6-tribromophenol (acid), nitrobenzene-d5(base), 2-fluorobiphenyl (base), and p-terphenyl-d14 (base),

The surrogate currently used by the laboratory for EPA 8270C_LL_PAH and EPA 8270D_LL_PAH is ortho-terphenyl (OTP).

Prior to preparation, the surrogate analytes are added to all samples and QC items. The concentration of the surrogate is the same in all field samples and QC samples. A concentration of 100ug/mL is used for EPA 625, EPA 8270C, EPA 8270C_LL, EPA 8270D, EPA 8270D_LL, and SM6410B. A concentration of 2.0ug/mL is used for EPA 8270C_LL_PAH and EPA 8270D_LL_PAH.

The percent recovery of the surrogate in all field samples and QC samples must be within the limits listed in the Method Limit Groups (MLGs) in LIMS.

9.2.8.1 Surrogate Dilution Factor Threshold

Due to the level of dilution required for samples, surrogates may be diluted out. As such, recoveries will be reported as "0D" in dilutions at 1:10 or greater. Control limits will not apply to samples analyzed at dilutions of 1:10 or greater.

An NCM must be initiated to denote this situation.

9.2.8.2 One Acid / One Base Surrogate Exception

The laboratory allows one acid and one base surrogate compound to be outside acceptance limits, in field samples and MS/MSD, provided their recovery is greater than 10%. All surrogate compounds must pass in method blanks and LCS/LCSD.

An NCM must be initiated to denote this situation.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* and the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Preparation

10.1.1 Aqueous Sample Preparation

For continuous liquid-liquid extraction, the sample is adjusted to a specific pH, as required by the analyte list, transferred to a continuous liquid-liquid extractor, and extracted using methylene chloride. The extract is concentrated to a 1mL final volume using the Zymark nitrogen blow-down concentrator procedure.

For separatory funnel extraction, the sample is placed into a separatory funnel, adjusted to a specific pH, as required by the analyte list, and extracted using methylene chloride. The extract is concentrated to a 1mL final volume using the Zymark nitrogen blow-down concentrator procedure.

The preferred method for preparing aqueous samples is the continuous liquid-liquid extraction procedure. When required by a client QAPP, the laboratory may prepare aqueous samples using the separatory funnel extraction procedure.

Refer to SOP SA-EX-030: *Liquid Extraction Procedures: Continuous Liquid-Liquid and Separatory Funnel* for specifics on the aqueous and leachate sample preparation process.

10.1.2 Soil Sample Preparation

For ultrasonic extraction, the sample is combined with anhydrous, purified sodium sulfate to form a free flowing, sandy mixture. A 1:1 acetone/methylene chloride mixture is added to the dried sample, and the sample is extracted using an ultrasonic disrupter for three minutes. The solvent is decanted, and the extraction is repeated two more times. The extract is filtered and concentrated to a 1mL final volume in methylene chloride using the Zymark nitrogen blow-down concentrator procedure.

Refer to SOP SA-EX-040: *Sonication Procedures* for specifics on the soil sample preparation process.

10.2 Analysis

10.2.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

Example GC Parameters
Injector: 250-280°C
Injector Mode:

- Split – EPA 8270C, EPA 8270D, EPA 625
- Splitless – EPA 8270C_LL, EPA 8270D_LL
- Pulsed Spitless (20psi at injection for 0.30 minutes) – EPA 8270C_LL_PAH, EPA 8270D_LL_PAH

Column – HP5 MS 30m x 0.25mm ID, 0.25um film thickness; or equivalent

Carrier Gas Flow: Helium at 0.5-1.0mL/min (column)
Mass spectrometer interface: 280-300°C
Mass spectrometer source temperature: 230°C
Mass spectrometer quad temp: 150C
Mass range: 35-500amu, with a minimum scan time of 1.0 scan per second

Temperature Program: EPA 8270C, EPA 8270D, EPA 625

Initial Temp:	55°C
Initial Hold:	1.5 min
Program Rate:	30°C/min to 190°C, 32°C/min to 320°C
Final Temp:	320°C (hold until elution time of Benzo(ghi)perylene or last eluting analyte)
Injected Volume:	1-2uL per column
Inlet Purge Time:	0.8 minutes

Temperature Program: EPA 8270C_LL, EPA 8270D_LL

Initial Temp:	55°C
Initial Hold:	1.5 min
Program Rate:	30°C/min to 190°C, 32°C/min to 320°C
Final Temp:	320°C (hold until elution time of Benzo(ghi)perylene or last eluting analyte)
Injected Volume:	1-2uL per column
Inlet Purge Time:	0.8 minutes

Temperature Program: EPA 8270C_LL_PAH, EPA 8270D_LL_PAH

Initial Temp:	60°C
Initial Hold:	1.0min
Program Rate:	25°C/min to 130°C, hold 0 minutes 16°C/min to 240°C, hold 0 minutes 2°C/min to 310°C, hold 4 minutes
Final Temp:	310°C
Injected Volume:	1uL
Inlet Purge Time:	0.8 minutes

The injection volume must be the same for all standards and sample extracts.

10.2.2 Internal Standard (ISTD)

Prior to analysis, a volume of internal standard must be added to all standards, samples, and QC items that provides a concentration of 40ug/mL for EPA 8270C, EPA 8270D, EPA 625, and SM6410B or 2.0ug/mL for EPA 8270_LL, EPA 8270D_LL, EPA 8270C_LL_PAH, and EPA 8270D_LL_PAH.

The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples.

A volume of 20uL of the ISTD spiking mix is used for EPA 8270C, EPA 8270D, EPA 625, and SM6410B for a final concentration of 40ug/mL.

A volume of 10uL of the ISTD spiking mix is used for EPA 8270C_LL, EPA 8270D_LL, EPA 8270C_LL_PAH, and EPA 8270D_LL_PAH for a final concentration of 2ug/mL.

10.2.3 DFTPP Evaluation

The DFTPP standard must be analyzed at the beginning of each clock. The analytical clock is defined as 12 hours for EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, EPA 8270D_LL_PAH, and SM6410B and is defined as 24 hours for EPA 625. The initiation of the clock begins with the injection of the DFTPP.

Evaluate the DFTPP in accordance with Section 9.2.1.

10.2.4 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.2. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.3, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.4.

10.2.5 Sample Analysis

Remove the extracts from the refrigerator and allow them to come to room temperature.

The sample extract must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The term "clock time" defines the continuing calibration frequency. The clock time starts at the injection of the DFTPP, followed by CCV. The analysis of samples and batch QC items may continue until the clock time expires. A new DFTPP and CCV (i.e., a new clock) is required to proceed with the analysis of more samples and/or batch QC items. The clock times are defined as outlined below:

- 12-hour clock for EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, EPA 8270D_LL_PAH, and SM6410B
- 24-hour clock for EPA 625

10.2.6 Example Analytical Sequence

Description	Comments
DFTPP	Clock time begins.
Initial Calibration	
ICV	
Instrument Blank	
Samples & Batch QC Items	EPA 625: Clock time ends at 24 hours from DFTPP EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, EPA 8270D_LL_PAH, and SM6410B: Clock time ends at 12 hours from DFTPP
DFTPP	Clock time begins.
CCV	
RL CCV	EPA 8270D, EPA 8270D_LL, and EPA 8270D_LL_PAH only
Instrument Blank	
Samples & Batch QC Items	EPA 625: Clock time ends at 24 hours from DFTPP EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, EPA 8270D_LL_PAH, and SM6410B: Clock time ends at 12 hours from DFTPP

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data evaluation must be performed in accordance with SA-QA-08: *Evaluation of Chromatographic Data.* This SOP includes specific information regarding the evaluation of chromatographic data, including the requirements for performing manual integrations and the evaluation of retention times.

Data review and reporting must be performed in accordance with SA-QA-02: *Data Generation and Review.*

11.1.1 Target Analyte Identification

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from the daily calibration standard or a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

The following criteria must be met in order to positively identify a compound:

1) Elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound. RRT is calculated as follows:

$$RRT = \frac{retention\ time\ of\ the\ target\ compound}{retention\ time\ of\ the\ associated\ internal\ standard}$$

2) Correspondence of the target compound spectrum and the standard component mass spectrum

All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. Ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

The relative intensities of the ions present in the sample component spectrum should agree within ±30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

3) The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

4) Q Test – The ratios of Quant to Qual ions are updated with the analysis of the CCV. The ratio of the quant to qual ions in samples should be within +/- 20% of the ratio in the CCV.

5) Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

If the above criteria are not met, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported. If there is not sufficient evidence to support identification of the component, then an NCM must be generated to note that the isomers should be identified as the isomeric pair.

6) Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible subtraction from the sample spectrum because of over-lapping or co-eluting peaks.

Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of coeluting peaks.

11.1.2 Evaluation of Tentatively Identified Compounds (TICs)

For samples containing components not associated with the calibration standards, a library search on a reference library, such as the NIST/NBS, may be conducted in order to identify the non-target compounds. Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification. Note: TICs can not be provided from a SIM analysis.

Refer to Attachment 13 for the laboratory's TIC procedures.

11.1.3 Dilutions

Unless otherwise specified by the Worksheet Note, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags must be used or qualification in a case narrative provided to the client.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower reporting limits.

Note: If samples are analyzed at a dilution factor of 1:10 or greater, report the surrogate result as 0%D, to denote a dilution above the Dilution Threshold. Control limits will not apply to samples analyzed at dilutions of 1:10 or greater.

Dilute samples according to the following table:

Dilution Factor	Extract Aliquot (uL)	ISTD Aliquot (uL)	Final Volume* (mL)
2	500	5	1.0
5	200	8	1.0
10	100	9	1.0
20	50	9.5	1.0
50	20	10	1.0
100	10	10	1.0

*Final solvent = methylene chloride

11.1.4 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify TALS Worksheet Notes and/or use the TALS Historical Data Tracker feature to determine if historical data is available for review.

11.1.5 Chemical Relationships

The analyst must be aware of the following chemical relationships:

- Several analytes reported as "total" are summed from the individual components. For example, Aramite, Diallate, and Total Cresols are summed as follows:

  Aramite = aramite peak 1 + aramite peak 2
  Diallate = diallate peak 1 + diallate peak 2
  Total cresols = m/p-cresols + o-cresol

  Note that o-cresol and m/p-cresol are also reported as individual analytes. Aramite and diallate are always reported as the sum of the component peaks.

- Chromatographically unresolved isomers are reported together since isomers cannot be resolved by differences in mass. For example, m-cresol and o-cresol are reported as cresols.

  It is important that closely eluting isomers be resolved chromatographically so that the analyte can be properly identified. The most critical separation is benzo(b)fluoranthene and benzo(k)fluoranthene.

- Acid/Base Compounds

  Basic Compounds: In aqueous samples, several target compounds are soluble in methylene chloride only at basic pH (>12). These compounds form methylene chloride insoluble salts at acidic pH and remain in the aqueous phase. When the pH is adjusted to basic, the ionic compound reverts to its original form and can be extracted out of aqueous solution. Examples of these compounds include pyridine (TCLP, AP9), benzidine (625PP), and a,a-dimethylphenethylamine (AP9). If acid-only extraction is performed, basic compounds will not be extracted and detected.

  Neutral Compounds: In aqueous samples, neutral compounds can extract into methylene chloride at either acidic pH (<2) or at basic pH (>12). That is, these compounds do not convert to salts or ionic forms at either acidic pH. If the acid pH is performed first, the compounds partition into the methylene chloride and would be detected in the acid fraction; if the basic pH extraction is performed first, these compounds partition into the methylene chloride and would be detected in the base fraction. Exceptions include the phthalate esters (e.g., dimethyl phthalate, diethyl phthalate) and other esters which may be irreversibly converted (hydrolyzed) to salts if subjected to the basic pH extraction first.

  Acid Compounds: In aqueous samples, the acidic compounds can be extracted into methylene chloride at acid pH (pH<2). The acidic compounds are the phenols and benzoic acid. At basic pH, the phenols forms water soluble salts which are not soluble in methylene chloride. When the pH is adjusted to <2 the salt is converted back to the phenol or acid form. Some phenols (2,4-dimethyl phenol and the cresols) do not completely ionize at basic pH and may be present in both the acid and base fractions of a dual pH extraction.

- Single pH (<2) Extractions

  Single pH extractions are performed at pH<2 and include the compounds that are soluble in methylene chloride at acidic pH. The primary application of the single pH extraction is for the routine target compound list (TCL), which includes most of the target compounds that are monitored for and are detected in field samples. The advantages of the single pH extraction are a shorter extraction time and efficient extraction of all phenolic compounds and compounds subject to hydrolysis under basic pH conditions. The drawback is that basic compounds are not extracted under single pH conditions.

- Dual pH Extractions

  Dual pH extractions may be performed with the basic pH extraction first followed by the acidic pH or the acidic pH extraction may be performed first followed by the basic pH extraction. The table below summarizes some of the positive and negative aspects of dual pH extractions.

Extraction	Pros	Cons
Acidic pH first followed by basic pH Examples: TCLP, Appendix IX	No hydrolysis of phthalate esters	Acid and base/neutral surrogates are both extracted into solvent at acidic pH. There is no surrogate to determine whether the sample pH was adjusted to basic pH, to determine the extraction efficiency of the basic pH extraction
Basic pH first followed by acidic pH Example: EPA 625 PP	Acid compounds (phenols) and base/neutral compounds can be separated into two extracts. The partitioning of the target analytes into separate extracts can sometimes help to minimize the effect of the sample matrix on the target compounds.	Some compounds may be partitioned into both the acid and base/neutral extracts. Examples include 2,4-dimethylphenol and the cresol compounds.
		Phthalate esters are converted (hydrolyzed) to salts under basic conditions which causes irreversible loss of the compounds. Dimethyl phthalate and diethyl phthalate are the most effected compounds.
		Some phenolic compounds may have reduced recoveries

- Compounds with similar structures and properties are often found together in a sample or in the samples from the same project or site. That is, when one of that type of compound is detected, the analyst should be looking for other compounds of that type. For example, when one PAH compound (e.g., naphthalene, phenanthrene, benzo(a)pyrene, etc.) is detected, the analyst should expect other PAH compounds to be present. When chlorinated benzenes (e.g., 1,2-DCB, 1,3-DCB, 1,4-DCB,are present, the analyst should be aware that other chlorinated benzenes may be present. When pentachlorophenol is detected, the analyst should also look for tetrachlorophenols and trichlorophenols.

11.1.6 Confirmation of GC Analyses

If required, GC/MS can be used to confirm some GC-only analytes. Based on the response of the standard, concentrate the SVOC GC extract to an appropriate final volume.

Note for SVOC: The pesticide extracts cannot be used to confirm the presence of herbicides since the extract has not been properly prepared.

- Add an appropriate volume of internal standard to the extract or sample to give the same concentration as in the calibration standard. Analyze the extract under the same conditions as the standard.

- Compare the retention time of the sample to the retention time of the standard.

If a peak is detected at the retention time of the target compound containing the selected masses in the same ratio as the standard, the peak is confirmed as the target compound and the concentration is calculated. The relative intensities of the ions in the sample should agree within ±20% of the intensities of the ions in the standard.

If a peak is not present at the appropriate retention time or if the ratios of the ions are not the same as the standard, the analyte is not confirmed.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample
F = Final volume/weight
I = Initial volume/weight
D = Dilution factor
dw = % Solids decimal equivalent

Note: All dry weight corrections are performed automatically in LIMS.

Note: This calculation assumes all applicable unit correction factors are applied.

12.0 Method Performance

12.1 Reporting Limit Verification (RLV)

At a minimum, RLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, RLVs must also be performed quarterly thereafter. For all other analytes and methods, RLVs must also be performed annually thereafter. Exceptions may be made for project-specific non-routine analytes.

12.2 Method Detection Limit (MDL) Study

The MDL is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDLs associated with this procedure are given in the Method Limit Group (MLG) in TALS.

At a minimum, MDL Studies must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

Note: MDL Studies are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.3 Method Detection Limit Verification (MDLV)

At a minimum, MDLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, MDLVs must also be performed quarterly thereafter. For all other analytes and methods, MDLVs must also be performed annually thereafter.

Note: MDLVs are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.4 QC Limit Generation, Control Charting, and Trend Analysis

12.4.1 EPA 625

The control limits for the batch QC items (LCS, MS/MSD, SD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data*.

12.4.2 EPA 8270C and EPA 8270D

The control limits for the batch QC items (LCS, MS/MSD, SD) for this procedure are not specified by the reference method; therefore, the laboratory defaults to in-house and/or laboratory-derived limits for the evaluation of batch QC items.

Control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.5 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the SOP criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess samples, reagents, and standards must be disposed in accordance with the TestAmerica Savannah Addendum to the EHSM.
- Flammable waste (acetone from extracts, rinsings, and standards) – Transfer to a satellite container designated for flammable waste and transfer to waste disposal department when the container is full.
- Methylene chloride extracts – Dispose according to characterization on sample disposal sheets. If non-hazardous, transfer extract to chlorinated waste container. If hazardous, transfer to hazardous waste department for storage.
- Methylene chloride used to rinse glassware, etc. – Transfer to chlorinated waste container.
- Excess aqueous samples – Dispose according to characterization on sample disposal sheets. If non-hazardous, dispose down drain/sewer. If hazardous, transfer to hazardous waste department for storage.
- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.
- Excess oil samples – Transfer to waste department for storage/disposal

15.0 References / Cross-References

- SOP SA-AN-10: *Balance Calibration and Use*
- SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*
- SOP SA-AN-41: *Reagent and Standard Materials Traceability*
- SOP SA-EX-015: *Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP)*
- SOP SA-EX-030: *Liquid Extraction Procedures: Continuous Liquid-Liquid and Separatory Funnel*
- SOP SA-EX-040: *Sonication Procedures*
- SOP SA-EX-042: *Waste Dilution Extraction*
- SOP SA-PS-025: *Wipe Tests: Sampling and Analysis*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-08: *Evaluation of Chromatographic Data*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*

- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- Method 8000C: *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846;* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.
- Method 8270C: *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846;* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.
- Method 8270D: *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846;* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.
- EPA Method 625*: Base/Neutrals and Acids,* 40 CFR Part 136, Appendix A, July 1, 1995.
- *Standard Methods for the Examination of Water and Wastewater, Online Edition;* American Public Health Association: Washington, DC.
  - SM6020: Quality Assurance/Quality Control
  - SM6410B: *Extractable Base/Neutrals and Acids; Liquid-Liquid Extraction and Gas Chromatographic/Mass Spectrometric Method; 2000*

16.0 Method Modifications

16.1 Incorporation of Other Matrices

This procedure may be modified to analyze other matrices (e.g., wipe, waste, tissue, and TCLP/SPLP leachate samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project.

Wipe, waste, and tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and default QC limits to evaluate wipe, waste, filter, and tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. The laboratory uses its routine aqueous RLs (converted for initial and final volumes, etc.) and default QC limits to evaluate TCLP/SPLP leachate samples. Water DOCs can be used to satisfy analyst demonstrations of capability for TCLP/SPLP matrices. Teflon chips, Ottawa sand, or equivalent is used as the blank matrix for wipes, wastes, and tissues unless specifically requested otherwise by the project.

16.1.1 Collection and Handling Procedures

Waste (Oil) Samples:
Waste (oil) samples are collected in 8-oz soil containers with PTFE-lined lids. Waste (oil) samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

Wipe Samples:
Wipe samples are routinely collected in 40-mL VOA vials. Wipe samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until time of preparation. Samples must be prepared within 14 days of collection. Extracts must be

stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction. Refer to SOP SA-PS-25: *Wipe Tests: Sampling and Analysis* for additional information on wipe procedures.

Tissue Samples:
Tissue samples are routinely collected in plastic containers with the size dependent upon the type of tissue being collected. Plastic jars or plastic baggies can be used. Upon receipt, samples must be placed in the freezer at -10° to -20°C if extraction/digestion cannot be completed that day. Samples must be prepared within 14 days of defrosting. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

TCLP/SPLP Leachate Samples
Once the TCLP/SPLP extraction procedure has been performed, the leachate is transferred to a 1L glass container. TCLP/SPLP leachates must be stored at 4°C (less than 6°C with no frozen samples) until the time of preparation. The leachate sample must be prepared within 7 days of completion of the TCLP/SPLP extraction. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

16.1.2 Preparation and Analytical Procedures

Wipe, waste, and tissue samples are prepared in the same manner as routine soil samples as outlined in SOP SA-EX-040. TCLP/SPLP matrices are prepared in the same manner as routine water samples as outlined in SOP SA-EX-030. Refer to the applicable preparation SOPs for more information.

Wipe, waste, filter, tissue, and TCLP/SPLP matrices are analyzed in the same manner as routine samples as outlined in this SOP.

16.2 Other Considerations

16.2.1 SW-846 allows alternate criteria to be used for DFTPP evaluation. As such the laboratory has incorporated criteria from the following methods:

- EPA 8270C, EPA 8270C_LL, EPA 8270D, and EPA 8270D_LL tune criteria is taken from CLP OLM04.0 (January 1998)
- EPA 8270C and EPA 8270C_LL tailing factor criteria is taken from EPA 625
- EPA 8270C_LL_PAH and EPA 8270D_LL_PAH tune criteria is taken from EPA 525.2

16.2.2 The laboratory allows one acid and one base surrogate compound to be outside acceptance limits, in field samples and MS/MSD, provided their recovery is greater than 10%. All surrogate compounds must pass in method blanks and LCS/LCSD.

16.2.3 EPA Method 625 and EPA Method 8270C do not require the analysis of an ICV. NELAC requires an ICV; however, it does not list specific criteria. The laboratory has adopted the default criteria listed in Section 9.2.3 for ICVs for these methods.

Additionally, EPA Method 8270D lists recommended criteria of 30%D for the ICV and acknowledges that alternative acceptance limits may be appropriate based on project-specific data quality objectives. The laboratory defaults to the criteria outlined in this SOP; however, more stringent, project-specific requirements can be accommodated upon client request.

16.2.4 The laboratory has defined the analytes listed in Attachment 11 as poor or erratic performers and allows for exceptions to the ICV, CCV, LCS, MS/MSD, and Sporadic Marginal Exceedance criteria for these analytes as outlined in this SOP.

16.2.5 EPA Method 8270C does not place a cap on an individual analyte's %D or %RSD when evaluating the grand mean exception. The laboratory has adopted more stringent in-house requirements as outlined in this SOP.

16.2.6 The reference methods do not require the analysis of an instrument blank; however, the laboratory routinely analyzes instrument blanks items and has adopted in-house criteria as outlined in this SOP.

16.2.7 EPA Method 8270C does not contain calibration verification criteria for non-CCC analytes nor does it require non-CCC analytes to be evaluated for response; however, the laboratory has adopted in-house criteria for non-CCC analytes as outlined in this SOP.

16.2.8 EPA Method 8270D does not place a cap on an individual analyte's %D or %RSD when evaluating the CCV. The laboratory has adopted more stringent in-house requirements as outlined in this SOP.

16.2.9 Due to maintenance procedures, the laboratory allows internal standard retention times in continuing calibration checks (CCVs) for EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, and EPA 8270D_LL_PAH to vary by more than 30 seconds when compared to the retention time of the internal standards in the most recent initial calibration. A component of column maintenance is to remove a portion of the front of the column to eliminate reactive spots caused by injection of field samples. As the column is shortened, the retention times of the internal standards are also shortened. As long as peak resolution and sensitivity are maintained by meeting the CCV criteria, calibration of the analytical system is not required.

Note: This modification is used for CCVs only. The laboratory has made no similar modification to sample ISTD evaluation.

16.2.10 EPA Method 8270D indicates indeno(1,2,3)pyrene and di-n-octylphthalate will be quantitated using ISTD Perylene-12. EPA 8270C indicates Chrysene-d12 will be utilized. The laboratory uses Chrysene-d12 for both methods as this compound is more stable.

16.2.11 EPA Method 8270D states the method blank must be less than the MDL, 5% of the regulatory limit, or 5% of the sample result, whichever is greater. The laboratory's criteria for the method blank is <1/2RL. More stringent, project-specific requirements can be accommodated upon client request.

16.2.12 Laboratory-specific RRF criteria have been defined as outlined in Attachment 12 and differ slightly from the method recommended criteria as indicated by the footnoted analytes.

16.2.13 EPA Method 8270D specifies a reporting limit standard quantitation criteria of 30% when utilizing a linear fit for the ICAL. With Technical Management approval, the laboratory allows analysis to proceed for analytes with recovery outside 30% of the expected value, provided reasonable sensitivity is achieved.

16.2.14 EPA Method 8270D states that structural isomer resolution should be verified in the initial calibration and continuing calibration verification. These criteria have been added to the EPA 8270C analysis since the same ICALs and CCVs may be used for both methods.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Preventative Maintenance and Troubleshooting
Attachment 5: EPA 8270C Calibration Criteria: SPCCs and CCCs
Attachment 6: DFTPP Criteria
Attachment 7: Example Tailing Factor Calculation
Attachment 8: Target Compound Information: Quant ions and ISTDs
Attachment 9: Standard Preparation Postings
Attachment 10: Procedures for SIM Analyses
Attachment 11: Poor Responder Information
Attachment 12: EPA 8270D Minimum RRF Table
Attachment 13: Procedures for Evaluation of Tentatively Identified Compounds (TICs)

Attachment 1:
SOP Summary

Sample Preparation Summary
Samples should be prepared according to the appropriate matrix-specific SOP.

Matrix	SOP
Aqueous samples	SA-EX-030
Soil samples	SA-EX-040

Aqueous Sample Preparation:
For continuous liquid-liquid extraction, the sample is adjusted to a specific pH, as required by the analyte list, transferred to a continuous liquid-liquid extractor, and extracted using methylene chloride. The extract is concentrated to a 1mL final volume using the Zymark nitrogen blow-down concentrator procedure.

For separatory funnel extraction, the sample is placed into a separatory funnel, adjusted to a specific pH, as required by the analyte list, and extracted using methylene chloride. The extract is concentrated to a 1mL final volume using the Zymark nitrogen blow-down concentrator procedure.

Soil Sample Preparation:
For ultrasonic extraction, the sample is combined with anhydrous, purified sodium sulfate to form a free flowing, sandy mixture. A 1:1 acetone/methylene chloride mixture is added to the dried sample, and the sample is extracted using an ultrasonic disrupter for three minutes. The solvent is decanted, and the extraction is repeated two more times. The extract is filtered and concentrated to a 1mL final volume in methylene chloride using the Zymark nitrogen blow-down concentrator procedure.

Sample Analysis Summary
The extract is analyzed by GC/MS. Qualitative identification of the target compounds in the extract is based on the retention time and the relative abundance of the characteristic masses determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

Example Analytical Sequence

Description	Comments
DFTPP	Clock time begins.
Initial Calibration	
ICV	
Instrument Blank	
Samples & Batch QC Items	EPA 625: Clock time ends at 24 hours from DFTPP EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, and EPA 8270D_LL_PAH: Clock time ends at 12 hours from DFTPP for
DFTPP	Clock time begins.
CCV	
RL CCV	EPA 8270D, EPA 8270D_LL, and EPA 8270D_LL_PAH only
Instrument Blank	
Samples & Batch QC Items	EPA 625: Clock time ends at 24 hours from DFTPP EPA 8270C, EPA 8270C_LL, EPA 8270C_LL_PAH, EPA 8270D, EPA 8270D_LL, and EPA 8270D_LL_PAH: Clock time ends at 12 hours from DFTPP for

Initial and Continuing Calibration Requirements Summary

1.0 EPA 8270C and EPA 8270C_LL

1.1 Initial Calibration (ICAL)

1.1.1 CCC and SPCC Criteria

The initial calibration must be evaluated specifically for the calibration check compounds (CCC) and the system performance check compounds (SPCC). The CCC and SPCC analytes are identified in Attachment 5.

The following steps outline the evaluation of the CCCs and SPCCs:

1. The %RSD for each CCC analyte must be <30%. This CCC %RSD criteria must be met before the analysis of sample extracts can begin. If the CCC %RSD criteria are not met, re-calibration is required.

2. The minimum average RRF for each SPCC analyte must be ≥0.050. This minimum average RRF for SPCC must be met before the analysis of sample extracts can begin. If the SPCC minimum RRF criteria are not met, re-calibration is required.

   After the CCC and SPCC evaluation items listed in #1 and #2, above, have been met, the following steps are taken:

3. If any CCC has %RSD >15% (i.e., between 15% and 30% RSD), a regression curve must be applied to that compound, in accordance with SOP SA-QA-16. The criteria for the regression coefficient is r^2>0.990. If the r^2 criteria are not met, the only remaining option is to utilize the grand mean exception, as outlined in Section 1.1.3, below.

4. If the grand mean exception is not acceptable, then recalibration is required.

1.1.2 Non-CCC Linearity Criteria

After the CCC and SPCC initial calibration criteria have been met, all other compounds must be evaluated for linearity. The following steps outline evaluation of the non-CCC compounds:

1. Determine the %RSD for each compound. The %RSD of each compound must be <15% for the average RF to be used for quantitation of samples. If the %RSD criteria are not met, the next option is to utilize a regression curve for that compound, in accordance with SOP SA-QA-16. If the %RSD is less than 15%, a regression curve may still be used if it provides a better calibration model over the calibration range than the average RF.

2. If the %RSD criteria are not met, the next option is to utilize a regression curve for that compound, in accordance with SOP SA-QA-16.

3. For a regression curve to be used, the regression coefficient (r^2) must be greater than 0.990. If the r^2 criteria are not met, the only remaining option is to utilize the grand mean exception, as outlined in Section 1.1.3, below.

4. If the grand mean exception is not acceptable, then recalibration is required.

1.1.3 Grand Mean Exception

EPA 8000B allows the use of the "grand mean exception" as described below. This exception should only be applied to initial calibration curves in extraordinary circumstances because of the difficulty of maintaining and providing documentation on an on-going basis.

Grand Mean Exception (GME): If one or more analytes exceed the %RSD criteria, the calibration curve is acceptable if the average of the %RSDs for all of the analytes in the ICAL (i.e., the grand mean) is less than or equal to the ICAL %RSD criteria.

SW-846 does not place a cap on an individual analyte's %RSD as long as the average is within criteria; however, the laboratory has adopted the requirement that no individual analyte can exceed 60% RSD. Therefore, the calibration curve is acceptable if the average of the %RSDs is less than or equal 15% with no individual analyte exceeding 60%.

Note: Some programs and agencies do not allow the use of the grand mean exception. Refer to the Project Requirement Summary and/or Project Plan to determine if GME is not allowed.

1.2 Second Source Initial Calibration Verification (ICV)

The initial calibration verification (ICV) is acceptable if the average %D of all the analytes in the ICV is less than or equal 20% with no individual analyte exceeding 60%.

If the %D criteria are not met, re-calibration is required.

1.2.1 ICV Poor Performers

Refer to Attachment 11 for the identification of poor and/or erratic performing analytes. These analytes may have a %D >60% if the average %D of all the analytes in the ICV is 20%.

1.3 Continuing Calibration (CCV)

1.3.1 CCC & SPCC Criteria

The CCC and SPCC criteria listed in Attachment 5 must be met for the CCV to be acceptable. If these criteria are not met, re-analysis is required.

Note: The SPCC criteria must be met even if the regression curve option is used for quantitation.

1.3.2 %D Criteria

The reference method requires only the CCC analytes to be evaluated for response; however, the laboratory has adopted stricter criteria. Therefore, in addition to the CCC and SPCC criteria listed in Attachment 5, the average %D of all analytes must be <20% with no single analyte's %D >60% for the CCV to be acceptable.

Refer to Attachment 11 for information on Poor Performers.

2.0 EPA 8270C_LL_PAH

2.1 Initial Calibration (ICAL)

2.1.1 Linearity Criteria

The %RSD for each analyte must be <30% for the average RF to be used for quantitation of samples. This %RSD criteria must be met before the analysis of sample extracts can begin. If the %RSD criteria are not met, re-calibration is required for the affected analytes.

Once all analytes have been evaluated against the 30% RSD criteria, the following additional step must be performed. If any analyte has %RSD >15% (i.e., between 15% and 30% RSD), a regression curve is applied to that compound, in accordance with SOP SA-QA-16. The criteria for the regression coefficient is r^2 >0.990. If the r^2 criteria are not met, re-calibration is required for the affected analytes.

If the %RSD is less than 15%, a regression curve may still be used if it provides a better calibration model over the calibration range than the average RF.

2.2 Second Source Initial Calibration Verification (ICV)

The initial calibration verification (ICV) is acceptable if the average %D of all the analytes in the ICV is less than or equal 20% with no individual analyte exceeding 60%.

If the %D criteria are not met, re-calibration is required.

2.3 Continuing Calibration Verification (CCV)

2.3.1 %D Criteria

All analytes in the CCV must be within 20% of the true value to be acceptable.

3.0 EPA 625

3.1 Initial Calibration (ICAL)

3.1.1 Linearity Criteria

All compounds must be evaluated for linearity. The following steps outline the evaluation:

1. The relative standard deviation (%RSD) of the calibration standards must be <35% for the initial calibration curve to be acceptable.

2. A minimum of 3 points is required. The lowest calibration point must at or lower than the reporting limit (RL).

3.2 Second Source Initial Calibration Verification (ICV)

3.2.1 ICV Criteria

The initial calibration verification (ICV) is acceptable if the average %D of all the analytes in the ICV is less than or equal 20% with no individual analyte exceeding 60%.

If the %D criteria are not met, re-calibration is required.

3.2.2 ICV Poor Performers

Refer to Attachment 11 for the identification of poor and/or erratic performing analytes. These analytes may have a %D >60% if the average %D of all the analytes in the ICV is 20%.

3.3 Continuing Calibration

3.1 %D Criteria

All analytes in the CCV must be within 20% of the true value to be acceptable.

4.0 EPA 8270D, EPA 8270D_LL, and EPA 8270D_LL_PAH

4.1 Initial Calibration (ICAL)

4.1.1 Minimum Relative Response Factor (RRF) Criteria

The minimum RRF criteria and control analytes are listed in Attachment 12. If the minimum RRF criteria for each compound in each level of the ICAL are not met, analysis of an RLCCV is required in each clock. An NCM is required to denote this situation.

4.1.2 Linearity Criteria

All compounds must be evaluated for linearity. The following steps outline the evaluation:

1. Determine the %RSD for each compound. The %RSD of each compound must be <20% to be acceptable.

2. If the %RSD criteria are not met, the next option is to utilize a linear regression curve for that compound, in accordance with SOP SA-QA-16. For a linear regression curve to be acceptable, the regression coefficient (r^2) must be greater than 0.990.

   Note: When a linear regression curve is used, the reporting limit standard must be re-quantitated as a sample and recover within 30% of the expected value. If these criteria are not met, the initial calibration curve may be evaluated utilizing a quadratic curve or the compound may be quantitated using the average response factor as outlined in Item #3, below.

For a quadratic curve to be acceptable, the regression coefficient (r^2) must be greater than 0.990.

3. If the r^2 criteria are not met, the only remaining option is to utilize the average response factor (i.e., %RSD) and report that compound as estimated. In this situation, an NCM must be initiated to describe the issue.

   Note: SW-846 does not put a cap on an individual analyte's %RSD; however, the laboratory has adopted the requirement that no individual analyte can exceed 60% RSD. Therefore, if any analyte's %RSD is >60%, then re-calibration is required.

4. If more than 10% of the analytes do not meet both the %RSD criteria and don't meet the r^2 criteria, then recalibration is required.

   Note: Several standard mixes are utilized to perform an initial calibration for the full list of target analytes (e.g., TCL, Appendix IX, etc). Each of these mixes constitutes its own initial calibration. Therefore, when evaluating the numbers of acceptable analytes, each mix will be evaluated separately. Re-calibration need only involve the affected mixes.

5. For any analyte associated with a calibration that does not meet 20% or 0.990 or minimum response factor, an RLCCV must be analyzed with each subsequent clock. An NCM must be initiated to denote this situation. Any positive results should be noted as estimated.

4.2 Second Source Initial Calibration Verification (CV)

The initial calibration verification (ICV) is acceptable if the %D of each analytes in the ICV is less than or equal 30%.

4.2.1 ICV Poor Performers

Refer to Attachment 11 for the identification of poor and/or erratic performing analytes. These analytes are allowed a %D >30% but must be <50%D to be acceptable. If there are poor performers that exceed 50%D, the data may be reported provided results are noted as estimated. An NCM must be initiated to denote this situation.

4.3 Continuing Calibration Verification (CCV)

4.3.1 Minimum RRF Criteria

The recommended minimum RRF for each compound is listed in Attachment 12.

If the minimum RRF criteria are not met, take corrective action to correct the problem. Possible problems can include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

Note: The RRF criteria for certain analytes have been modified for the EPA 8270D_LL method.

4.3.2 %D Criteria

The CCV %D criteria is <20%.

The reference method makes the exception, however, such that due to the large numbers of analytes in each CCV, some analytes may not meet these criteria.

- If more than 20% of the analytes in a CCV exceed the %D criteria, the CCV is unacceptable, and re-analysis is required.

- If less than 20% of the analytes in a CCV exceed the %D criteria, run an RLCCV (i.e., a CCV at the reporting limit). Analytes that do not meet CCV %D criteria may be reported if the affected analytes are qualitatively identified in the RL CCV.
  - If the affected analyte is not detected in the associated client sample, the result is reported without qualification.
  - If the affected analyte is detected in the associated client sample, the result must be reported as estimated.
  - Note: An NCM must be initiated to denote this situation.

Note: SW-846 does not put a cap on an individual analyte's %D; however, the laboratory has the requirement that no individual analyte can exceed 60%D. Therefore, if any analyte's %D is >60%, then corrective action is required. Corrective actions include instrument maintenance, re-injection, and/or re-calibration.

5.0 SM6410B

5.1 Initial Calibration (ICAL)

5.1.1 Linearity Criteria

All compounds must be evaluated for linearity. The following steps outline the evaluation:

1. The relative standard deviation (%RSD) of the calibration standards must be <35% for the initial calibration curve to be acceptable.
2. Alternatively, a regression curve may be performed. The criteria for the regression coefficient is r^2 >0.990. If a regression curve is performed, each level of the ICAL must be re-quantitated as a sample and fall within 20% of its true value to be acceptable.
3. A minimum of 3 points is required. The lowest calibration point must at or lower than the reporting limit (RL).

5.2 Second Source Initial Calibration Verification (ICV)

5.2.1 ICV Criteria

The initial calibration verification (ICV) is acceptable if the average %D of all the analytes in the ICV is less than or equal 20% with no individual analyte exceeding 60%.

If the %D criteria are not met, re-calibration is required.

5.2.2 ICV Poor Performers

Refer to Attachment 11 for the identification of poor and/or erratic performing analytes. These analytes may have a %D >60% if the average %D of all the analytes in the ICV is 20%.

5.3 Continuing Calibration

5.1 %D Criteria

All analytes in the CCV must be within 20% of the true value to be acceptable.

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Matrix	Routine Sample Container	Routine Sample Size	Minimum Sample Size	Chemical Preservation	Thermal Preservation	Dechlorination Agent	Holding Time
Water	1L amber glass	1L	500mL	None	4°C[1]	None	7 days to extract 40 days to analyze
Soil	16oz glass soil jar	30g	15g	None	4°C[1]	None	14 days to extract 40 days to analyze

[1]Samples must be maintained at 0-6°C, with no frozen samples.

Attachment 3:
QC Summary

QC Item	Method	Frequency	Criteria	Corrective Action
Clock Time	EPA 625	24 hours	Clock time starts with the injection of the DFTPP. Analysis of samples and QC items must conclude within expiration of clock time. Subsequent analysis requires new DFTPP.	Not applicable
	All Other Methods	12 Hours		
Tune/Column Evaluation Standard (DFTPP) - Spectrum Criteria	All Methods	At beginning of each clock	Spectrum Criteria: Refer to Attachment 6.	- Perform instrument maintenance - Re-tune.
Tune/Column Evaluation Standard (DFTPP) - Tailing Factor Criteria	EPA 625 EPA 8270C EPA 8270C_LL SM6410B	At beginning of each clock	Pentachlorophenol <5 Benzidine <3	- Perform instrument maintenance - Re-tune.
	EPA 8270D EPA 8270D_LL		Pentachlorophenol <2 Benzidine <2	
	EPA 8270C_LL_PAH EPA 8270D_LL_PAH		None	
Tune/Column Evaluation Standard (DFTPP) - Breakdown Criteria	EPA 8270C EPA 8270C_LL EPA 8270D EPA 8270D_LL	At beginning of each clock	<20%	- Perform instrument maintenance - Re-tune.
	EPA 625 EPA 8270_LL_PAH EPA 8270D_LL_PAH SM6410B		None	

QC Item	Method	Frequency	Criteria	Corrective Action
Initial Calibration (ICAL)	EPA 625 SM6410B	Upon instrument set-up, and after unsuccessful CCV	3-point Minimum %RSD < 35%	-Re-analyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Replace column and/or clean source, and reanalyze standards
	EPA 8270C EPA 8270C_LL		5-point Minimum CCC: %RSD < 30% SPCC: RRF_{avg} > 0.050 If %RSD >15%, use curve fit with r^2 > 0.990. GME: Avg %RSD <15%; No single analyte %RSD > 60%.	
	EPA 8270C_LL_PAH		5-point Minimum %RSD < 30% If %RSD >15%, use curve fit with r^2 > 0.990.	
	EPA 8270D EPA 8270D_LL EPA 8270D_LL_PAH		5-point Minimum RRF per Attachment 11. %RSD < 20%. If %RSD > 20%, use curve fit w/ r^2 > 0.990; If linear fit, RL Level: 30% of true; If r^2 < 0.990, use %RSD (allowed for <10% of total # analytes; no analyte >60% RSD).	
	SIM		3-point Minimum r^2 > 0.990	

QC Item	Method	Frequency	Criteria	Corrective Action
Initial Calibration Verification (ICV) - Second Source	EPA 625 EPA 8270C EPA 8270C_LL EPA 8270C_LL_PAH SM6410B	After each ICAL	Average %D < 20%. No analyte %D > 60%. Poor performers per Attachment 11.	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
	EPA 8270D EPA 8270D_LL EPA 8270D_LL_PAH		%D < 30%. Poor performers %D <50% as per Attachment 11.	
Continuing Calibration Verification (CCV)	EPA 625 EPA 8270C_LL_PAH SM6410B	Per clock (Analyze after DFTPP)	%D < 20%	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate Note 1: If <20% total # analytes >20%D, evaluate RL CCV. RL CCV must be qualitatively identified. - If client sample is ND for affected analyte, report unqualified result. - If client sample has detection for affected analyte, report result as estimated.
	EPA 8270C EPA 8270C_LL		CCC: %D < 20%. SPCC: RRF > 0.050. Average %D < 20%. No analyte %D > 60%. Poor performers per Attachment 11.	
	EPA 8270D EPA 8270D_LL EPA 8270D_LL_PAH		RRF per Attachment 11. %D < 20%. Poor performers per Attachment 11. See Note 1.	
	All Methods		Spectrum Criteria: Refer to Attachment 6.	

QC Item	Method	Frequency	Criteria	Corrective Action
Reporting Limit Continuing Calibration Verification (RL CCV)	EPA 8270D EPA 8270D_LL EPA 8270D_LL_PAH	Per clock, if needed. (Analyze after CCV) When RRF criteria is not met in ICAL, or CCV criteria not met.	Affected analytes must be qualitatively identified.	- Perform instrument maintenance - Reanalyze affected samples. - Recalibrate
Internal Standards (ISTD)	All Methods	Spiked in all CCVIS, samples, and batch QC items	CCVIS: Area within 50% to +200% of corresponding level in the ICAL. Samples & batch QC items: - Area within 50% to +200% of CCVIS. - RT within +/-30 seconds from previous CCVIS.	Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available
Surrogate Compounds	All Methods	Spiked (during extraction procedure) in all samples and batch QC items.	Within MLG limits 1 Acid / 1 Base Allowance: samples and MS/MSD, only, with %R >10% Surrogate Threshold Dilution Factor = 10	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract(s) -Re-extract and reanalyze if sufficient sample available
Extraction Batch Definition	All Methods	Extracted together w/in 24-hr timeframe; not to exceed 20 field samples	Not Applicable	Not Applicable
Method Blank (MB)	All Methods	One per extraction batch	<1/2RL	Refer to SOP SA-QA-17

QC Item	Method	Frequency	Criteria	Corrective Action
Laboratory Control Sample (LCS)	All Methods	One per extraction batch	Within TALS MLG Limits	Refer to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	All Methods	One per extraction batch, when insufficient sample is provided for MS/MSD/SD	Within TALS MLG Limits	Refer to SOP SA-QA-17
Matrix Spike (MS)	All Methods	One per extraction batch	Within TALS MLG Limits	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	All Methods	One per extraction batch	Within TALS MLG Limits	Refer to SOP SA-QA-17
Initial Demonstration of Capability (IDOC)	All Methods	Initially, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06 Note: Unsupervised work must not begin until acceptable IDOC is obtained.

QC Item	Method	Frequency	Criteria	Corrective Action
Continuing Demonstration of Capability (CDOC)	All Methods	Annually, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Reporting Limit Verification (RLV)	All Methods	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Method Detection Limit Study (MDL)	All Methods	Upon method/instrument set-up, per analyte/method/matrix combination	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

QC Item	Method	Frequency	Criteria	Corrective Action
MDL Verification (MDLV)	All Methods	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Preventative Maintenance and Troubleshooting

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Septum							X	Replace, recommended daily
Splitless Disc							X	Replace, recommended daily
Column/Injector							X	Change sleeve and cut front of column, recommended daily
Autosampler							X	Clean syringe as needed; replace syringe as needed
Injector Port							X	Replace injector port as needed
Lines							X	Flush lines as needed; replace lines as needed
Column							X	Change column as needed
Mass Spectrometer							X	Clean as needed
Rough Pump							X	Change oil as needed

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually; AN = as needed

Troubleshooting

Troubleshooting should be documented as outlined above. If possible, troubleshooting is best performed in a step-wise manner to systematically isolate instrument components. Refer to the instrument manufacturer's guides for specific information and strategies. Enlist assistance from technical and/or department management as needed.

Contingency Plan

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Maintenance Log

A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Instrument Labeling

Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Attachment 5:
EPA 8270C Calibration Criteria: SPCCs and CCCs

Initial Calibration	Continuing Calibration*
CCC: <= 30% RSD SPCC: RRFavg >= 0.050	CCC: <= 20% difference from initial calibration SPCC: RRF>= 0.050

*If CCC and/or SPCC do not meet the stated criteria, all targets that are reported must meet the CCC criteria.

Calibration Check Compounds (CCC):
Phenol, 1,4-Dichlorobenzene, 2-Nitrophenol, 2,4-Dichlorophenol, Hexachlorobutadiene, 4-Chloro-3-methylphenol, 2,4,6-Trichlorophenol, Acenapthene, N-Nitrosodiphenylamine, Pentachlorophenol, Fluoranthene, Di-n-octylphthalate, Benzo(a) pyrene

System Performance Check Compounds (SPCC)
N-Nitrosodi-n-propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, 4-Nitrophenol

Attachment 6:
DFTPP Criteria

EPA 625 and SM6410B

m/z	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1.0% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

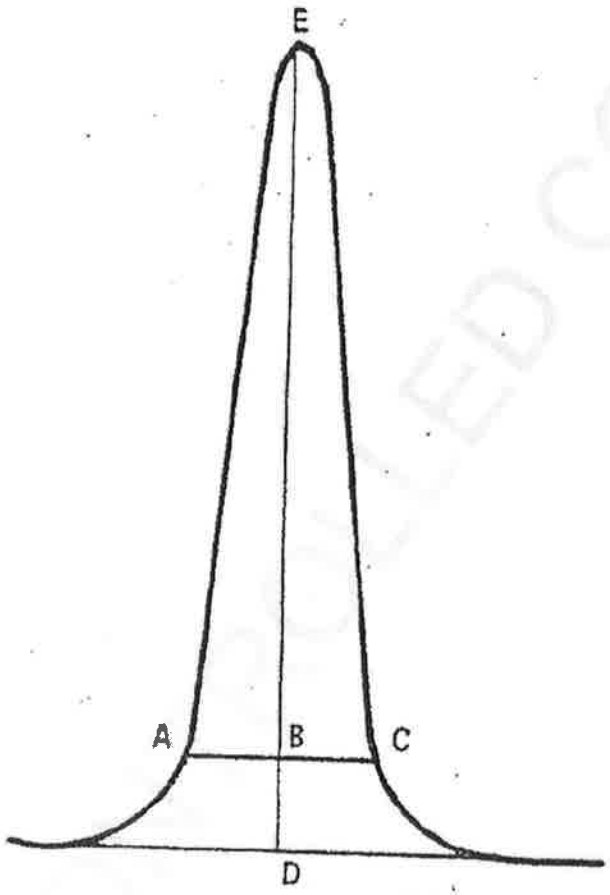
EPA 8270C, EPA 8270C_LL, EPA 8270D, and EPA 8270D_LL

m/z	Ion Abundance Criteria
51	30.0-80.0% of 198
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	25.0-75.0% of 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of mass 198
275	10.0-30.0% of 198
365	Greater than 0.75% of mass 198
441	Present but less than mass 443
442	40.0-110.0% of mass 198
443	15.0-24.0% of mass 442

EPA 8270C_LL_PAH and EPA 8270D_LL_PAH

m/z	Ion Abundance Criteria
51	10-80% of 442
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	10-80% of 198
197	Less than 2% of mass 198
198	>50% mass 442
199	5.0-9.0% of mass 198
275	10-60% of 442
365	Greater than1% of mass 442
441	0-100% of mass 443
442	Base peak, 100% relative abundance
443	15-24% of mass 442

Attachment 7:
Example Tailing Factor Calculation



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$

Attachment 8:
Target Compound Information: Quant Ions and ISTDs*

PARAMETER	Quant Ion	Secondary Ions			ISTD	pH 2 (Only)	pH2 or pH11
1,1'-Biphenyl	154	76		3	3	X	
1,2,3-Trichlorobenzene	216	214		1	1		X
1,2,4,5-Tetrachlorobenzene	216	214	179	3	3		X
1,2,4-Trichlorobenzene	180	182	145	2	2	X	
1,2-Dichlorobenzene	146	148		1	1	X	
1,2-Diphenylhydrazine	77	105	182	4	4	X	
1,3,5-Trichlorobenzene	180	145		1	1		X
1,3,5-Trinitrobenzene	213	74	120	4	4		X
1,3-Dichlorobenzene	146	148	111	1	1	X	
1,3-Dinitrobenzene	168	76	50	3	3		X
1,4-Dichlorobenzene	146	148	111	1	1	X	
1,4-Dioxane	88	58	45	1	1	X	
1,4-Naphthoquinone	158	104	76	3	3		X
1-Diallate	86	43	234	4	4		X
1-Methylnaphthalene	142	141		2	2	X	
1-Naphthylamine	143	115	116	3	3		X
2,2'-oxybis[1-chloropropane]	45	121		1	1	X	
2,3,4,5-Tetrachlorophenol	232	230	131	3	3		
2,3,4,6-Tetrachlorophenol	232	230	131	3	3	X	
2,3,5,6-Tetrachlorophenol	232	96	131	3	3	X	
2,3,6-Trichlorophenol	196	198		2	2	X	
2,3-Dimethylphenol	107	122	121	1	1	X	
2,4 & 2,5-Dimethylphenol	107	122	121	1	1	X	
2,4,5-Trichlorophenol	196	198	200	3	3	X	
2,4,6-Trichlorophenol	196	198	200	3	3	X	
2,4-Dinitrochlorobenzene	202	110	75	2	2		X
2,4-Dichlorophenol	162	164	98	2	2	X	
2,4-Dimethylphenol	122	107	121	2	2	X	
2,4-Dinitrophenol	184	63	154	3	3	X	
2,4-Dinitrotoluene	165	89	63	3	3	X	
2,5-Dimethylphenol	107	122	121	1	1	X	
2,5-Dinitrophenol	184	63		1	1	X	
2,6-Dichlorophenol	162	164	98	2	2	X	
2,6-Dimethylphenol	107	122	121	1	1	X	
2,6-Dinitrotoluene	165	89	63	3	3	X	
2-Acetylaminofluorene	181	180	223	5	5		X
2-Chloronaphthalene	162	164	127	3	3	X	
2-chloronitrobenzene/4-chloronitrobenzene	157	111	75	2	2		X
2-Chlorophenol	128	130	64	1	1	X	
2-Diallate	86	43	234	4	4		X
2-Mercaptobenzothiazole	167	108		5	5		X
2-Methylnaphthalene	142	141		2	2	X	
2-Methylphenol	107	108	77	1	1	X	
2-Naphthylamine	143	115	116	3	3		X

PARAMETER	Quant Ion	Secondary Ions			ISTD	pH 2 (Only)	pH2 or pH11
2-Nitroaniline	65	92	138	3	3	X	
2-Nitrobiphenyl	152	115		3	3		X
2-Nitrophenol	139	109	65	2	2	X	
2-Picoline	93	66		1	1		X
2-Toluidine	106	107	79	2	2		X
3 & 4 Methylphenol	107	108		1	1	X	
3,3'-Dichlorobenzidine	252	254	126	5	5	X	
3,3'-Dimethylbenzidine	212	196	106	5	5		X
3,4-Dichloronitrobenzene	109	133	191	2	2		X
3,4-Dimethylphenol	107	122	121	1	1	X	
3-Methylcholanthrene	268	252	253	6	6		X
3-Nitroaniline	138	108	92	3	3	X	
3-Nitrobiphenyl	152	199		4	4		X
3-Nitrochlorobenzene	157	111	75	2	2		X
3-Nitrophenol	139	65		1	1	X	
4,6-Dinitro-2-methylphenol	198	105	121	4	4	X	
4-Aminobiphenyl	169	168	170	4	4		X
4-Bromophenyl phenyl ether	248	250	141	4	4	X	
4-Chloro-3-methylphenol	107	144	142	2	2	X	
4-Chloroaniline	127	129	65	2	2	X	
4-Chloronitrobenzene	157	111	75	2	2		X
4-Chlorophenol	65	128		2	2	X	
4-Chlorophenyl phenyl ether	204	141	206	3	3	X	
4-Nitroaniline	138	108	92	3	3	X	
4-Nitrobiphenyl	152	199		4	4		X
4-Nitrophenol	65	109	139	3	3	X	
4-Nitroquinoline-1-oxide	174	101	128	4	4		X
5-Nitro-o-toluidine	152	77	106	3	3		
7,12-Dimethylbenz(a)anthracene	256	239	241	6	6		X
Acenaphthene	154	153	152	3	3	X	
Acenaphthylene	152	151	153	3	3	X	
Acetophenone	105	77	51	2	2	X	
alpha,alpha-Dimethyl phenethylamine	58	91	42	2	2		X
alpha-Pinene	93	121		1	1		X
Aniline	93	66		1	1		X
Anthracene	178	176	179	4	4	X	
Aramite, Total	185	191	319	5	5		X
Aramite-1	185	191	319	5	5		X
Aramite-2	185	191	319	5	5		X
Atrazine	200	173	215	4	4	X	
Benzaldehyde	77	105		1	1	X	
Benzidine	184	92	185	4	4		X
Benzo[a]anthracene	22	229	226	5	5	X	
Benzo[a]pyrene	252	125	253	6	6	X	
Benzo[b]fluoranthene	252	253	125	6	6	X	
Benzo[g,h,i]perylene	276	277	138	6	6	X	
Benzo[k]fluoranthene	252	253	125	6	6	X	

PARAMETER	Quant Ion	Secondary Ions			ISTD	pH 2 (Only)	pH2 or pH11
Benzoic acid	105	122		2	2	X	
Benzyl alcohol	108	79	77	1	1	X	
Bis(2-chloroethoxy)methane	93	123	95	2	2	X	
Bis(2-chloroethyl)ether	63	93	95	1	1	X	
Bis(2-ethylhexyl) phthalate	149	167	279	5	5	X	
Butyl benzyl phthalate	149	91	206	5	5	X	
Caprolactam	113	55		2	2	X	
Carbazole	167			4	4	X	
Catechol	110	64		1	1		X
Chrysene	228	226	229	5	5	X	
Di(2-ethylhexyl)adipate	129	57		3	3	X	
Diallate	86	43		4	4		X
Dibenz(a,h)anthracene	287	139	279	6	6	X	
Dibenzofuran	168	139		3	3	X	
Diethyl phthalate	149	177	150	3	3	X	
Dimethoate	87	93	125	4	4		X
Dimethyl phthalate	163	194	164	3	3	X	
Dimethyl terephthalate	194	135		2	2		X
Di-n-butyl phthalate	149	150	104	4	4	X	
Di-n-octyl phthalate	149	43		6	6	X	
Dinoseb	211	163	147	4	4	X	
Disulfoton	88	60		4	4		X
Ethyl methanesulfonate	79	109	97	1	1		X
Ethyl Parathion	109	97		4	4		X
Famphur	218	93	125	4	4		X
Fluoranthene	202	203	101	4	4	X	
Fluorene	166	165	167	3	3	X	
Hexachlorobenzene	284	142	249	4	4	X	
Hexachlorobutadiene	225	223	227	2	2	X	
Hexachlorocyclopentadiene	237	235	272	3	3	X	
Hexachloroethane	117	201	199	1	1	X	
Hexachlorophene	196	198		6	6		X
Hexachloropropene	213	211	215	2	2		X
Indeno[1,2,3-cd]pyrene	276	138		6	6	X	
Isophorone	82	95	138	2	2	X	
Isosafrole	162	104	131	2	2		X
Methapyrilene	97	58	191	4	4		X
Methyl Benzoate	105	77	51	1	1		X
Methyl methanesulfonate	80	79	65	1	1		X
Methyl parathion	109	125		4	4		X
Methyl Phenols, Total	107	108		1	1	X	
Monomethyl Terephthalate	149	121		3	3		X
Naphthalene	128	129		2	2	X	
Nitrobenzene	77	123	65	2	2	X	
N-Nitro-o-toluidine	152	77	106	3	3		X
N-Nitrosodiethylamine	102	42	44	1	1	X	

PARAMETER	Quant Ion	Secondary Ions			ISTD	pH 2 (Only)	pH2 or pH11
N-Nitrosodimethylamine	42	74		1	1		X
N-Nitrosodi-n-butylamine	84	57	41	2	2		X
N-Nitrosodi-n-propylamine	70	42		1	1	X	
N-Nitrosodiphenylamine	169	168	167	4	4	X	
N-Nitrosomethylethylamine	88	42	43	1	1		X
N-Nitrosomorpholine	56	86		1	1		X
N-Nitrosopiperidine	114	42	55	2	2		X
N-Nitrosopyrrolidine	100	41	42	2	2		X
o,o',o''-Triethylphosphorothioate	65	97	93	2	2		X
p-Dimethylamino azobenzene	120	225	77	5	5		X
Pentachlorobenzene	250	248	252	3	3		X
Pentachloronitrobenzene	237	295	142	4	4		X
Pentachlorophenol	266	264	268	4	4	X	
Phenacetin	108	109	179	3	3		X
Phenanthrene	178	176	179	4	4	X	
Phenol	94	66	65	1	1	X	
Phenyl ether	170	141		3	3		X
Phorate	75	121		4	4		X
p-Phenylene diamine	108	80	107	2	2		X
Pronamide	173	175	145	4	4		X
Pyrene	202	200	203	5	5	X	
Pyridine	79	52	51	1	1		X
Quinoline	129	102		1	1		X
Safrole, Total	162	104	135	2	2		X
Sulfotepp	97	65		4	4		X
Thionazin	107	96	97	4	4		X
Toluic acid	91	119	136	2	2		X
SURROGATES							
Nitrobenzene-d5[1]	82	128	54	2	2		
2-Fluorobiphenyl[1]	172	171		3	3		
Phenol-d5 [2]	99	71		1	1		
2-Fluorophenol [2]	112	64		1	1		
2,4,6-Tribromophenol [2]	330	332	144	3	3		
Terphenyl-d14[1]	244	122	212	5	5		
INTERNAL STANDARDS							
1,4-Dichlorobenzene-d4	152	150	115	1	1		
Naphthalene-d8	136	68		2	2		
Acenaphthene-d10	164	162	160	3	3		
Phenanthrene-d10	188	94	80	4	4		
Chrysene-d12	240	236	120	5	5		
Perylene-d12	264	265	260	6	6		

[1]Base Surrogate
[2]Acid Surrogate

For a complete list of target analytes for each method refer to the LIMS Method Limit Groups (MLGs).

Attachment 9:
Standard Preparation Information

SOURCE MIXES			
Vendor Name	Standard Description	Part number	Concentration (ug/mL)
Supelco	8270 Tuning Mix	47548-U	1000
Supelco	Internal Standard	5M07296	2000
Supelco	N-Nitrosodiphenylamine	46702-U	5000
Supelco	BNA CAL 1	506508	1000
Supelco	Cal Mix 5	8M61215	2000
Supelco	8270 Benzidines	48467	2000
Supelco	OLM 4.2	47514-U	2000
Supelco	Custom- CHT	CUSTOM	2000
Supelco	a'a-Dimethylphenethylamine	47448-U	2000
Supelco	Organophos	507202	2000
Supelco	Hexachlorophene	40323	5000
Supelco	Custom- Kingsford List	CUSTOM	2000
Supelco	Ap9 Mega Custom	CUSTOM	1000
Supelco	AP9 Short Custom	CUSTOM	2000
Supelco	Methylmethanesulfonate	21022012	2000
Supelco	8270 Surrogates	861155	4000
Supelco	1,4-Phenylenediamine	48298	2000
Supelco	PAH Mix 2	47543-U	2000
Restek	8270 Mega Mix	31850	1000
Restek	AP9 Mix 2	31806	1000
Restek	Benzoic Acid	31415	1000
Restek	Benzidines	31688	2000
Restek	Dinoseb	32251	1000
Restek	Organophos	32419	2000
Restek	Custom Phenols	562381	2000
Restek	O-Terphenyl	31066	2000
Restek	1,3-Dinitrobenzene	31662	1000
Restek	AP9 Mix 1	31625	2000
Restek	Custom Ap9	562586	2000
Restek	2,3,4,6-Tetrachlorophenol	31402	1000
Restek	Base Surrogates	31024	1000
Restek	Acid Surrogates	31025	2000
Restek	Hexachlorophene	31811	2000

Storage: 0°C to 6°C

Expiration:

Un-opened: Manufacturer's expiration date

Opened: 6 months from date opened or manufacturer's expiration date, whichever is sooner

8270/625 Standards

8270/625 DFTPP @ 50ug/mL

Mix	Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)
8270 Tuning Solution	1000	500	10

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

Primary BNA Mix @ 500ug/mL

Mixes	Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)
BNA CAL 1	1000	5000	10
N-nitrosodiphenylamine	5000	1000	
Cal Mix 5	2000	2500	
8270 Surrogates	4000	1250	

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

8270/625 BNA Working Standards, Final Volume = 2mL

Standards	BNA500 (uL) (500ug/mL)	Benzidines (uL) (2000 ug/mL)	OLM4.2 (uL) (2000ug/mL)	Internal Standard (uL)
BNA010	40	10	10	40
BNA020	80	20	20	40
BNA050	200	50	50	40
BNA080	320	80	80	40
BNA100	400	100	100	40
BNA200	800	200	200	40

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

8270/625 AP-9 Mix @ 500ug/mL, Final Volume = 5mL

Mix	Aliquot Volume (uL)
AP9-Mega Custom (1000mg/mL)	2500
AP9 Short Custom (2000mg/mL)	1250
KING (Kingsford) (2000mg/mL)	1250

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

8270/625 AP-9 Working Standards, Final Volume = 2mL

	AP-9 500 (uL)	Organophos Mix 2 (uL)	Hexaclorophene (uL)	a'a-Dimethylphenethylamine (uL)	Methyl Methanesulfonate (uL)	Internal Standard (uL)
Standards	(500ug/mL)	(2000ug/mL)	(5000ug/mL)	(2000ug/mL)		
AP9-010	40	10	50	10	20	40
AP9-020	80	20	100	20	40	40
AP9-050	200	50	200	50	100	40
AP9-080	320	80	300	80	160	40
AP9-100	400	100	400	100	200	40
AP9-200	800	200	500	200	0	40

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

RESTEK BNA ICV RECIPE

8270/625 BNAICV @ 80ug/mL, Final Volume = 1mL

Parent Standard	Restek Part Number	Aliquot Volume (uL)
8270 Mega Mix (1000ug/mL)	31850	80
AP9 Mix 2 (1000 ug/mL)	31806	80
Benzoic Acid (1000 ug/mL)	31415	80
Benzidines (2000 ug/mL)	31688	40
Dinoseb (1000 ug/mL)	32251	80
Base Surrogates (1000ug/mL)	31024	80
Acid Surrogates (2000 ug/mL)	31025	40
8270 ISTD		20

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

RESTEK AP-9 ICV

8270/AP-9 ICV @ 80ug/mL, Final Volume= 1mL

Parent Standard	Restek Part Number	Aliquot Volume (uL)
AP9 Mix 1 (2000ug/mL)	31625	40
AP9 Mix 2 (1000ug/mL)	31806	80
Hexachlorophene (2000ug/mL)	31811	400
Custom Phenols	562381	40
Custom Ap9	562586	40
8270 ISTD		20

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

8270LL Full Standards

Primary BNA Mix @ 50ug/mL

Mixes	Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)
BNA CAL 1	1000	500	10
N-nitrosodiphenylamine	5000	100	
Cal Mix 5	2000	250	
8270 Surrogates	4000	125	
OLM4.2	2000	250	
Benzidines	2000	250	

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

8270 BNA Working Standards, Final Volume = 2mL

Level	BNA50 (uL)	Internal Standard (uL)
LLBNA0.20	8	20ul
LLBNA0.50	20	20ul
LLBNA1.0	40	20ul
LLBNA2.0	80	20ul
LLBNA5.0	200	20ul
LLBNA10.0	400	20ul
LLBNA20.0	800	20ul
LLBNA50.0	2000	20ul

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

8270LL AP-9 Intermediate Mix @ 50ug/mL

Mixes	Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)
a'a-Dimethylphenethylamine	2000	125	5
Kingsford Custom	2000	125	
AP9 Mega Custom	1000	250	
AP9 Short Custom	2000	125	
Methyl Methanesulfonate	1000	250	
CHT Custom	2000	125	
Hexachlorophene	5000	500	

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

8270LL AP-9 Calibration @ 50ug/mL

Level	LLAP9 Intermediate (uL)	Internal Standard (uL)
LLAP91.0	40	20
LLAP92.0	80	20
LLAP95.0	200	20
LLAP910.0	400	20
LLAP920.0	800	20
LLAP950.0	2000	20

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

RESTEK LLBNA ICV RECIPE

LLBNAICV @ 10ug/mL, Final Volume = 2mL

Parent Standard	Restek Part Number	Aliquot Volume (uL)
8270 Mega Mix (1000ug/mL)	31850	20
AP9 Mix 2 (1000 ug/mL)	31806	20
Benzoic Acid (1000 ug/mL)	31415	20
Benzidines (2000 ug/mL)	31688	10
Dinoseb (1000 ug/mL)	32251	20
Base Surrogates (1000ug/mL)	31024	20
Acid Surrogates (2000 ug/mL)	31025	10
ISTD Solution		20

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

RESTEK AP-9 ICV

LLAP-9 ICV @ 10ug/mL, Final Volume= 1mL

Parent Standard	Restek Part Number	Aliquot Volume (uL)
AP9 Mix 1 (2000ug/mL)	31625	5
AP9 Mix 2 (1000ug/mL)	31806	10
Hexachlorophene (2000ug/mL)	31811	50
Custom Phenols	562381	5
Custom Ap9	562586	5
ISTD Solution		10

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

8270 LL_PAH Standards

Internal Standard Solution @ 200ug/ml

Mix	Concentration (ug/mL)	Aliquot	Final Volume (mL)
8270 Internal Standard Mix	2000 ug/ml	1000 uL	10

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

LLTuning Solution @ 5.0ug/ml

Mix	Concentration (ug/mL)	Aliquot	Final Volume (mL)
8270 Tuning Solution	1000	50	10

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

LLPAH Intermediate @ 20ug/ml

Mix	Concentration (ug/mL)	Aliquot	Final Volume (mL)
Supelco PAH Mix 2	2000	50	5
Supelco O-terphenyl	2000	50	

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

LLPAH Calibration

Level	Intermediate (uL)	Internal Standard (uL)	Final Volume (mL)
LLPAH0.2	20	20	2
LLPAH0.5	50	20	
LLPAH1.0	100	20	
LLPAH2.0	200	20	
LLPAH5.0	500	20	
LLPAH10.0	1000	20	
LLPAH20.0	2000	20	

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

LLPAH ICV

MIX	Concentration (ug/mL)	Aliquot	Final Volume (mL)
Restek 8270Mega	1000	4	2
Restek O-terphenyl	2000	2	
ISTD Solution	200	20	

Solvent: Methylene Chloride

Storage: 0°C to 6°C

Expiration: 3 months from date prepared or parent's expiration date, whichever is sooner

Attachment 10:
Procedures for SIM Analyses

Analytical Procedures for SIM Analysis

The mass spectrometer (MS) may be used in the selected ion monitoring mode to increase the sensitivity of the GC/MS analysis. In SIM mode, the MS is set to monitor for only a few selected ions; therefore, more ions of the selected mass(es) can be filtered and counted, resulting in an increase of sensitivity of 10 to 100 fold over scan monitoring, depending on the compound. SIM GC/MS analysis sacrifices selectivity for sensitivity since only a few characteristic ions are monitored. A spectral match cannot be made against a reference library and tentatively identified compounds (TICs) cannot be determined from a SIM run. In general, the SIM analysis should be used only when a few compounds are required to be monitored. SIM can also be used to confirm the presence of a target compound determined by GC when the routine GC/MS scan analysis cannot provide confirmation.

The following procedures are based on the guidance in SW-846 Method 8270D. The analytical sequence is the same as is given in the associated analytical SOPs, with mass tune criteria and calibration verification every 12 or 24 hours.

- Analyze the 50 ug/mL DFTPP in the scan mode. Evaluate the DFTPP against the acceptance criteria given in previous sections in the SOP.

- Determine the approximate retention time of the target by analyzing the target analyte(s) by GC/MS scan.

- Set the MS to monitor for the characteristic ions (minimum of two ions) for the target analyte(s) and internal standard(s). The ion dwell time should be set to give at least six integrations across the peak. A dwell time of 50-100ms is common.

- Prepare and analyze a minimum of three calibration standards for the target compounds. The lowest standard should be at the required quantitation limit and the other two standards should define the working range of the GC/MS. The internal standard(s) should be at a concentration of approximately 4ug/mL for SVOC.

- Evaluate the resulting calibration curve according to the initial calibration procedures given in SOP SA-QA-16. If r^2 is >0.990, the calibration curve is acceptable.

If the initial calibration criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the initial calibration must be repeated. The analyst must be aware of the 24-hour clock for the DFTPP analysis in 625 SIM and the 12-hour clock for the DFTPP analysis in 8270 SIM.

SIM Analysis of Target Compounds

- Add an appropriate volume of internal standard to the extract or sample to give the same concentration as in the calibration standards. Analyze the extract or sample under the same conditions as the standard.

Note: It is advised that the extract be split before addition of ISTD solution. One split can be utilized for scan analysis and second split reserved for SIM analysis.

- Compare the retention time of the sample to the retention time of the standard.

  If a peak is detected at the retention time of the target compound containing the selected masses in the same ratio as the standard, the peak is confirmed as the target compound and the concentration is calculated. The relative intensities of the ions in the sample should agree within ±20% of the intensities of the ions in the standard.

  If a peak is not present at the appropriate retention time or if the ratios of the ions are not the same as the standard, the analyte is not confirmed

- If the concentration of the target compound exceeds the highest calibration standard, analyze a more dilute aliquot of the sample or extract, maintaining the internal standard concentration at the same level as the calibration standards.

Attachment 11:
Poor Responder Information

The following analytes have been identified, in the reference method and/or via historical data, to be poor and/or erratic performers:

1-naphthylamine
1,4-Napthaquinone
2-naphthylamine
2-picoline (2-methylpyridine)
3,3'-dichlorobenzidine
3,3'-dimethylbenzidine
a,a-dimethylphenethylamine
Atrazine
Benzaldehyde
Benzidine
Benzoic acid
Dinoseb
Famphur
Hexachlorocyclopentadiene*
Hexachlorophene
Methyl Methanesulfonate
Methapyriline
o,o',o''-triethylphosphoro-thioate
p-Dimethylamino azobenzene
p-phenylenediamine

These analytes are exempt from the LCS, MS, MSD, Sporadic Marginal Exceedance, ICV, and CCV criteria as listed in this SOP.

*Exception applied to LCS, MS, MSD Only

Attachment 12:
EPA 8270D Minimum RRF Criteria

Analyte	Minimum RRF Criteria
1,2,4,5-Tetrachlorobenzene	0.010
1,1'-Biphenyl	0.010
2,3,4,6-Tetrachlorophenol	0.010
2,2'-Oxibis(1-chloroporopane)	0.010
2-Chloronaphthalene	0.800
2-Chlorophenol	0.800
2-Methylphenol	0.600[1]
2-Methylnaphthalene	0.400
2-Nitroaniline	0.010
2-Nitrophenol	0.100
2,4-Dichlorophenol	0.200
2,4-Dimethylphenol	0.200
2,4-Dintirophenol	0.010
2,4-Dinitrotoluene	0.200
2,4-Dinitrotoluene (Low-Level)[3]	0.100
2,4,5-Trichlorophenol	0.200
2,4,6-Trichlorophenol	0.200
2,6-Dinitrotoluene	0.200
2,6-Dinitrotoluene (Low-Level)[3]	0.100
3-Nitroaniline	0.010
3,3'-Dichlorobenzidine	0.010
4-Bromophenyl phenyl ether	0.100
4-Chloro-3-methylphenol	0.200
4-Chloroaniline	0.010
4-Chlorophenyl phenyl ether	0.400
4-Methylphenol	0.600
4-Nitroaniline	0.010
4-Nitrophenol	0.010
4,6-Dinitro-2-methylphenol	0.010
Acenaphthene	0.900
Acenaphthylene	0.900
Acetophenone	0.010
Atrazine	0.010
Anthracene	0.700
Benzaldehyde	0.010
Benzo(a)anthracene	0.700[2]
Benzo(a)pyrene	0.700
Benzo(a)pyrene (Low-Level)[3]	0.400
Benzo(b)fluoranthene	0.700
Benzo(b)fluoranthene (Low-Level)[3]	0.400
Benzo(g,h,i)perylene	0.500
Benzo(g,h,i)perylene (Low-Level)[3]	0.200
Benzo(k)fluoranthene	0.700
Benzo(k)fluoranthene (Low-Level)[3]	0.400

Analyte	Minimum RRF Criteria
Bis(2-choroethyl)ether	0.700
Bis (2-chloroethoxy)methane	0.300
Bis (2-ethylhexyl)phthalate	0.010
Butyl benzyl phthalate	0.010
Caprolactam	0.010
Carbazole	0.010
Chrysene	0.700
Dibenz(a,h)anthracene	0.400
Dibenz(a,h)anthracene (Low-Level)[3]	0.200
Dibenzofuran	0.800
Diethyl phthalate	0.010
Dimethyl phthalate	0.010
Di-n-butyl phthalate	0.010
Di-n-octyl phthalate	0.010
Fluoranthene	0.600
Fluorene	0.900
Hexachlorobenzene	0.100
Hexachlorobutadiene	0.010
Hexachlorocyclopentadiene	0.050
Hexachloroethane	0.300
Indeno(1,2,3-cd)pyrene	0.500
Indeno(1,2,3-cd)pyrene (Low-Level)[3]	0.200
Isophorone	0.400
Naphthalene	0.700
Nitrobenzene	0.200
N-Nitroso-di-n-propylamine	0.500
N-Nitroso-di-phenylamine	0.010
Pentachlorophenol	0.050
Pentachlorophenol (Low-Level)[3]	0.050
Phenanthrene	0.700
Phenol	0.800
Pyrene	0.600

[1]Minimum RF has been revised to be equivalent to 4-methylphenol.
[2]Minimum RF has been revised to be equivalent to chrysene.
[3]Minimum RF has been revised, as listed, for EPA 8270D_LL and EPA 8270D_LL_PAH methods.

Attachment 13
Procedures for Evaluation of Tentatively Identified Compounds (TICs)

Tentatively identified peaks (TICs) are defined by TestAmerica Savannah as:
1) a calibrated analyte that is not part of the list of analytes requested by the client; or
2) a non-calibrated analyte with a response of 10% or greater than the closest internal standard (ISTD).

The laboratory's default procedure is to report the top 20 TICs with the highest concentration.

Note: Internal standards or surrogates added to the sample, whether they are included in the ICAL or not, must not be identified as TICs. For example, the surrogate o-Terphenyl is added to the low-level 8270 surrogate spiking mix but is used as a surrogate only for LL PAH. This compound would be excluded as a TIC. Also, for semi-volatile analyses, routine target volatile analytes included on the EPA CLP OLM04.2 list (e.g., xylenes) are not included as TICs.

Data Evaluation Steps:
Identification of TICs is made by comparison of the mass spectrum to the reference spectrum (peaks with calibration) or by comparison of the mass spectrum to a reference library such as NIST (peaks without a calibration). Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification.

The unknown compounds are tentatively identified using a search of the reference library. If the library search produces a match at or above 85%, report that compound. If the library search produces more than one compound at or above 85%, report the first compound (the highest match quality). If the library search produces no matches at or above 85%, report the compound as unknown. If possible, provide a general classification of the unknown – for example, unknown aromatic, unknown hydrocarbon, etc.

TICs should be evaluated within the retention time range from the first eluting target or surrogate (whichever is first in the target list) to the elution of the last target compound.

Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum. The relative intensities of the major ions should agree within approximately ±20%.

Molecular ions present in the reference spectrum should be present in the sample spectrum. Note, however, that differences in the spectra may be attributed to over-lapping or co-eluting peaks. If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria are not met exactly, the peak may be considered tentatively identified. The analyst should consult the Department Manager if there are any questions concerning interpretation of spectra.

The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The concentration of TICs with a calibration is the concentration from the calibration curve at the dilution that the target list is reported, even if

the concentration is above the calibration range (an "E" value). The concentration of the non-calibrated TIC is as directed in the SOP and as calculated in the Target data system.

Data Processing Steps:

- Evaluate the peaks in the total ion chromatogram for:
  - correct integration
  - peaks that may not have been integrated, paying particular attention to large or odd-shaped peaks.
  - closely eluting peaks
- Manually integrate any peaks that were not detected by the data system and re-process the unknowns.
- Evaluate TICs in Target, as outlined above.
- Merge to TALS.
- Under the TIC tab, reject all "TGT" and "TIC" analytes.
- Right-click and select "Auto-Set TICs Primary". This should set the number of TICs and TGTs requested with the highest concentration to a "Primary" status.
- Highlight all TGT compounds (still under the TIC tab) and right-click.
- Choose "Result Conditions".
- Right-click and choose "Show Assigned Conditions".
- Uncheck all assigned conditions.
- Right-click and choose "Show Flag Suite Conditions".
- Select J, N, and T. Be sure to choose the J-flag defined as "Estimated Result TIC – Manual Flag".

18.0 Revision History

Summary of Changes:

- Minor editorial, grammatical, and formatting changes made. Boilerplate text added.
- Added section to describe analytical data system, software, and hardware. Section 6.2
- Added note that if an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries for both LCS and LCSD are required. Section 9.1
- Added note that some programs and agencies do not allow the use of quadratic curves and to refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited. Section 9.2.2
- Added reference to TALS Historical Data Tracker feature. Section 11.1.4
- Clarified requirements and frequency for RLVs, MDL Studies, and MDLVs to be consistent with SOP SA-QA-07 and to include the quarterly frequency as defined by DOD. Section 12.1 - 12.3 and Attachment 3
- Added note that unsupervised work must not begin until acceptable IDOC is obtained. Attachment 3
- Added section on troubleshooting. Attachment 4
- Updated TIC procedure for consistency with SOP SA-QA-08. Attachment 11
- Revised tuning criteria for EPA 8270C, EPA 8270C_LL, EPA 8270D, and EPA 8270D_LL. Attachment 6
- Updated column ID used in analysis from SLB5 MS to HP5 MS.
- Added information on instrument blanks to prescribe frequency. Section 9.2.4
- Added information on ICAL and CCV resolution criteria. Section 9.2.5.1 Added note that NCM must be initiated if resolution is not achieved for structural isomers and isomers must be reported as an isomeric pair. Section 11.1.1 Expanded Modifications section to note that isomeric resolution criteria have been adopted for EPA 8270C. Section 16.2.14 (2010 Corporate Internal Audit Finding.)
- Removed regression curve option for EPA 625. Attachment 1 and Attachment 3
- Updated Poor Performer list. Attachment 11
- Expanded Attachment 2 to match SOP template.
- Added note to Modifications Section that RRF criteria for certain analytes have been modified for the EPA 8270D_LL_PAH method.
- Added dilution factor table. Section 11.1.3
- Corrected typo in Attachment 3. Revised ISTD criteria for CCV listed in Attachment 3 to match that listed SOP text and actual laboratory practice.
- Revised EPA 8270D ICAL, ICV, and CCV criteria to be consistent with 05/17/10 Corporate Memo from Richard Burrows. Added requirement to perform RLCCV when RRF, ICAL, or CCV criteria are not met. Removed option to evaluate average RRF in ICAL as opposed to RRF for each compound in each level. Replaced 60% cap on poor performers with 50% cap. Attachment 1 and Attachment 3
- Removed reference to sample duplicate. Not typically performed. MSD is routinely performed in lieu of sample duplicate as allowed by the reference method.
- Incorporated procedures and criteria for method SM6410B.

VOLATILE COMPOUNDS BY GC/MS

(Methods: EPA 8260B, EPA 624, and SM6200B)

Approvals (Signature/Date):

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November 5, 2010
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1.0 Scope and Application

This SOP contains the procedures for the determination of volatile organic compounds (VOC) by purge and trap gas chromatography/mass spectrometry (GC/MS). This procedure is applicable to a wide variety of low molecular weight compounds that have low aqueous solubility and boiling points less than 200°C.

The routine matrices for this procedure are waters and soils (for EPA 8260B) and waters (for EPA 624 and SM6200B); however, this procedure may be adapted to accommodate other matrices as outlined in Section 16.1. This procedure may also be used to perform Custer Rule analyses for chloroform only (via a modified EPA 624 analysis).

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

2.0 Summary of Method

Volatile organic compounds (VOCs) are purged from the sample matrix with helium. The VOCs are transferred from the sample matrix to the vapor phase. The vapor is swept through a sorbent tube where the VOCs are trapped. After the purging is completed, the trap is heated and backflushed with helium to desorb the VOCs onto a GC column. The GC is temperature-programmed to separate the VOCs, which are then detected by a mass spectrometer. Qualitative identification of the target compounds in the sample is based on the relative retention time and the mass spectra of the characteristic masses (ions) determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

Water samples are routinely purged at ambient conditions; however, a heated purge may be used if required by the project. A 5mL purge volume is used as the default. The calibration standards and the associated QC must be analyzed under the same conditions and volume. This sample introduction procedure is based on EPA 5030B, EPA 624, and SM6200B.

Low-level (nominally<1mg/kg) soil samples are purged at 40°C in a purge and trap instrument designed to add water and internal standards to the vial containing the sample without breaking the seal. The sample is stirred during purging to thoroughly mix the soil and water. The calibration standards and associated QC are purged under the same conditions. This sample introduction procedure is based on EPA 5030A (for soil samples collected in bulk) and EPA 5035A (for soil samples collected via Encore/Terracore devices).

High level soils (nominally>1mg/kg) and waste samples are extracted with methanol (1mL of methanol per gram of sample). An aliquot of the methanol extract is injected into reagent water. The methanol extract/reagent water is purged at ambient temperature using the same instrument conditions and calibration used for aqueous samples.

This SOP is based on EPA 8260B, EPA 624, and SM6200B.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Methanol and Hydrochloric Acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.1.5 VOCs commonly used in the laboratory are potential sources of contamination. Methylene chloride, acetone, Freon-113, MEK, hexane, toluene, and isopropanol are used in the laboratory and tend to present the most problems.

4.1.5 The Teflon seals of the purge and trap device can absorb and outgas many of the compounds that are included in this method. These Teflon fittings should be periodically checked for integrity. If the contamination is suspected, the fittings may be heated at 105°C for one hour or replaced.

4.1.6 The addition of acid to the sample during collection will cause the degradation of several target compounds. Acrolein and acrylonitrile recovery may be reduced and 2-chloro-ethyl vinyl ether will be completely degraded. The recovery of 2-chloroethyl vinyl ether will also be reduced as the purge and trap lines become acidic. For this reason, unpreserved vials must be utilized if these analytes are requested.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are purged from the sample matrix.

Contamination by carryover can occur whenever high concentration samples and low concentration samples are analyzed sequentially. As such, samples known to be clean should be analyzed first. Where practical, high concentration samples should be followed by a blank to check for cross-contamination. If the targets found in the highly

concentrated sample are found in subsequent samples, the analyst must verify that the port and P/T system are not contributing contamination to the subsequent samples. If the target compound(s) are not present in subsequent samples, the analysis of a blank is not required but may be a prudent preventative measure. Frequent trap bakeout and purging of the entire purging system may be necessary when carry-over is suspected. Reagent blanks must be analyzed when contamination is suspected to ensure that the system is free from contamination.

A common type of contamination is from samples containing high concentrations of hydrocarbons such as gasoline or mineral spirits. At high concentrations, these compounds may cause elevated baselines that can obscure the mass ion signals of target compounds with masses similar to the hydrocarbons. For example, a common mass in hydrocarbons is mass 43, which is also present in many ketones. Mineral spirits at high concentrations can be very problematic as it contains hydrocarbons beyond C12, which can linger in the purge and trap unit and carryover for quite a few samples. High concentrations of hydrocarbons can also degrade the trap much more quickly than would be expected.

4.2.3 The volatiles laboratory must be kept as free from contamination as possible. Highly contaminated samples must be segregated from routine samples. Contact with sections of the laboratory where solvents are used should be minimized. Refrigerator and freezer blanks must be prepared, stored, and analyzed to evaluate the sample storage areas for possible contamination. Guidance is provided in SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples.*

4.2.4 Matrix interferences may be overcome by the use of the secondary ions for quantitation. An example of this is the use of mass 82 for quantitation with chlorobenzene-d5 internal standard when a potential co-eluter, 1,1,1,2-tetrachloroethane, is a target compound. One of the mass fragments of 1,1,1,2-tetrachloroethane is mass 117, which is the recommended quantitation ion for chlorobenzene-d5. The use of the secondary ions should be used for quantitation in such cases when the laboratory can clearly demonstrate matrix problems. Mass 58 is recommended for quantitation of acetone due to the elution of a hydrocarbon at the same retention time.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable gloves, and closed-toe,

nonabsorbent shoes when handling samples. Note: Cut-resistant gloves should be worn, or other hand protection material used, when opening and closing VOA vials.

5.1 Specific Safety Concerns or Requirements

The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst must be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

The exit vent of the split injector must have a carbon trap in-line to collect the volatile compounds that are vented during the injection of the sample. The traps should be changed a minimum of every three months and must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM.

Methanol is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, confusion, headache, dizziness, and drowsiness.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

Note: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Methanol	Flammable Poison Irritant	200ppm TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Hydrochloric Acid[2]	Corrosive Poison	5ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
[2]Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

A list of the instruments, with their basic configuration, is provided in Attachment 8. These instruments were in use at the time of SOP revision. Other instruments and configurations may be used provided they are fully documented and validated in accordance with laboratory procedures.

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

6.2 Analytical Data System / Software / Hardware

Chemstation software is used on a Windows-based PC to schedule and acquire data. Target (UNIX and/or Windows) software is used on a Windows-based PC to store, reduce/evaluate, and output the data to the laboratory's LIMS system (i.e., TALS). Target software has the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectrum from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software also allows integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as or construction of a linear regression

calibration curve, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the response factors.

6.3 Lab Supplies

Supelco Vocarb 3000 trap or equivalent – Other traps may be used as long as the target compounds can be detected at the required quantitation limit.

Recommended Column: J&W DB-624: 20m x 0.18mm ID, 1.8um film

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Pump-style Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

6.4 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination. Containers are received from vendors with a statement that the containers are suitable for the intended use and have been tested and certified to be free of contamination.

Refer to SOP SA-VM-021: *Preparation, Screening, and Storage of Volatiles Samples* for the containers routinely used to collect field samples.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard must not exceed the expiration date of the standard that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Traceability.*

Methanol and Hydrochloric Acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Reagent water – ASTM Type II; lab generated water

7.2.2 Blank sand – Accusands Industrial Quartz (50lb); used as blank matrix for soil samples; Purify by heating at 160°C for four hours or longer in a shallow tray.

7.2.3 Methanol – for purge and trap analysis; J.T. Baker 9077-02 (1L)

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Traceability.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

The recipes for the preparation of standards are provided in Attachment 9. The recipes contain the stock standards, preparation steps, storage, and expiration dates for the routine target compounds.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to Attachment 3 for a summary of the routine containers, holding times, preservation requirements, etc.

Refer to SOP SA-VM-021: *Preparation, Screening, and Storage of Volatiles Samples* for information on the preservation and dechlorination checks required for these methods.

Samples must be iced or refrigerated (at <6°C, with no frozen samples) from the time of collection until analysis.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the QC Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

All batch QC must meet the criteria given in Attachment 3 of this SOP.

9.1.1 Soil Samples

A batch consists of up to 20 environmental samples and the associated QC items. The laboratory defaults to the following as the minimum QC items required for each batch: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD).

If there is insufficient sample to perform the MS/MSD, the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample is defined as receiving less than 30g for bulk samples or less than 4 Encores/Terracores.

Note: If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required.

9.1.2 Aqueous Samples

A batch consists of up to 20 environmental samples and the associated QC items. The laboratory defaults to the following as the minimum QC items required for each batch:

EPA 8260B and SM6200B:
method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD).

EPA 624:
method blank, a laboratory control sample (LCS), a matrix spike (MS) performed per 10% of samples analyzed, and a matrix spike duplicate (MSD). This equates to 1 MS and 1MSD for a batch of 10 or less samples or equates to 1 MS (from sample 1-10), 1 MS (from sample 11-20), and 1 MSD for a batch of 11-20 samples.

If there is insufficient sample to perform the required MS and/or MSD, the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample is defined as receiving less than less than 4 vials.

Note: If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required.

9.1.3 Poor Performers / Erratic Compounds

As indicated in EPA 8260B and/or via assessment of laboratory control sample recoveries and control charts, the compounds listed in Attachment 10 are Poor Performers and/or behave erratically. These compounds will not be included in the LCS/LCSD/MS/MSD marginal exceedance count, provided their %R is >10%.

Note: An NCM must be initiated to denote this situation.

9.2 Instrument QC

The term "clock time" or "analytical clock" refers to the amount of time that can pass before additional instrument QC items must be performed. The analytical clock begins with the injection of the BFB, and all subsequent injections must be completed before the clock time expires - at which point new instrument QC is performed and a new clock is initiated.

The clock times are defined as follows:

- EPA 8260B and SM6200B= 12 hours
- EPA 624 = 24 hours
- EPA 624 Cluster Rule (chloroform only) = 8 hours

Note: Due to instrument configurations employing dual concentrators, most of the laboratory instruments can analyze more than 20 injections within the designated clock times. An analytical batch is still defined as 20 field samples; therefore, if more than 20 field samples are analyzed within a clock, additional batch QC is required (i.e., another method blank, LCS, and LCSD or MS/MSD must be performed).

9.2.1 BFB Tune Check

9.2.1.1 Fifty nanograms of 4-BFB must be analyzed at the beginning of each clock as a check on the "tune" of the mass spectrometer. Meeting the tuning criteria ensures that the instrument is measuring the proper masses in the proper ratios. The 4-BFB analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of 4-BFB. All other instrument conditions must be identical - the mass range, scan rate, and multiplier voltage.

If the instrument is configured for direct injection, 50ng of 4-BFB may be injected directly on to the column. If the purge and trap is used to analyze the 4-BFB, the purge and trap conditions must be the same as for the calibration standards and samples.

9.2.1.2 Evaluation of the 4-BFB peak

9.2.1.2.1 The chromatogram must exhibit acceptable baseline behavior and the 4-BFB peak must be symmetrical (i.e., Gaussian). A spectrum of the baseline that shows high abundances of mass 40 (Argon) and mass 44 (carbon dioxide) may indicate a leak or contaminated carrier gas.

9.2.1.2.2 The spectrum of the 4-BFB must meet the criteria listed in Attachment 6. Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans ±1 scan from the apex can be evaluated for the 4-BFB criteria. Consecutive scans within this range can be averaged to meet the criteria.

9.2.1.2.3 The 4-BFB analysis should be evaluated as to the relative size of the 4-BFB peak under the m/z 95 profile. A benchmark area window should be established for each instrument. Response outside of this window suggests instrumental problems such as a poor purge, clogged jet separator, leak in the Tekmar purging device, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open, or other anomalies.

9.2.1.2.4 If the 4-BFB fails to meet the acceptance criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the 4-BFB analysis, other corrective measures may include remaking the 4-BFB standard and/or cleaning the mass spectrometer source.

9.2.2 Trap Check Standard

The trap check standard is used to evaluate the condition of the trap by monitoring the formation of chloromethane and bromomethane. Chloromethane and bromomethane may be formed on a degraded trap by thermal decomposition of halogenated compounds.

9.2.2.1 Prepare the trap check standard by injecting 2uL of a 50ug/mL bromoform standard into 5mL of reagent water. Other sample volumes may be used but the sample must transfer 100ng of bromoform to the column. Add the internal standards and surrogates. Analyze the sample using the same analytical system conditions used for samples and standards.

9.2.2.2 Evaluate the chromatogram for the presence of chloromethane and bromomethane. Compare the response to the 1.0ug/L standard. The response must be less than or equal to one half of the response of the 1.0ug/L standard, and the trap check standard must quantify less than 0.5ug/L when compared to the initial calibration curve.

Note: Ensure sure that the spectra match the reference spectra and that the most abundant ions are present for both compounds - chloromethane (m/z 50, 52) and bromomethane (94, 96).

9.2.2.3 If the trap check standard does not meet the acceptance criteria, the trap must be replaced, conditioned, and the system re-calibrated prior to the analysis of samples.

9.2.3 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves.* This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 5 standards. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

The initial calibration standard concentrations currently in use in the laboratory are as follows:

EPA 8260B and SM6200B:

Standard Level	Concentration (ng)	Final Concentration – Waters (ug/L)	Final Concentration – Soils (ug/kg)
1	5	1.0	
2	25	5.0	5.0
3	50	10	10
4	100	20	20*
5	250	50*	50
6	500	100	100
7	1000	200	200

*CCV Level

EPA 624:

Standard Level	Concentration (ng)	Final Concentration – Waters (ug/L)
1	5	1.0
2	25	5.0
3	50	10
4	100	20*
5	500	100
6	1000	200

*CCV Level

Refer to Attachment 9 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-41.

9.2.3.2 ICAL Criteria

9.2.3.2.1 EPA 8260B

The initial calibration is evaluated specifically for the calibration check compounds (CCC) and the system performance check compounds (SPCC). The CCC and SPCC criteria are given in Attachment 5 of this SOP. The %RSD criteria for CCC and minimum RRF for SPCC must be met before the analysis of samples can begin.

After the CCC and SPCC initial calibration criteria have been met, each target must be evaluated for linearity. The relative standard deviation of the calibration standards must be <15% for the initial calibration curve to be acceptable.

If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve. The regression coefficient (r^2) of the regression curve must be greater than 0.990 for the initial calibration curve to be acceptable.

> Note: A minimum of 6 points is required for a quadratic curve. Higher order curves are not permitted. Some programs and agencies (e.g., SC DHEC) do not allow the use of quadratic curves. Refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited.

SW-846 allows the use of the "grand mean exception" as described below. This exception should only be applied to initial calibration curves in extraordinary circumstances due to the difficulty of maintaining and providing documentation on an on-going basis.

> Grand Mean Exception (GME): If one or more analytes exceed the %RSD criteria, the calibration curve is acceptable if the average of the %RSDs for all of the analytes in the ICAL (i.e., the Grand Mean) is less than or equal to the ICAL %RSD criteria.

SW-846 does not place a cap on an individual analyte's %RSD as long as the average is within criteria; however, the laboratory has adopted the requirement that no individual analyte can exceed 3X the ICAL criteria. Therefore, the calibration curve is acceptable if the average of the %RSDs is less than or equal 15% with no individual analyte exceeding 45%.

Note: Some programs and agencies do not allow the use of the Grand Mean Exception. Refer to the Project Requirement Summary and/or Project Plan to determine if GME is not allowed.

9.2.3.2.2 EPA 624

The relative standard deviation of the calibration standards must be <35% for the initial calibration curve to be acceptable. If one or more compounds do not meet the %RSD criterion of <35%, the next option is to evaluate a regression curve. The regression coefficient (r^2) of the regression curve must be greater than 0.990 for the initial calibration curve to be acceptable.

9.2.3.2.3 SM6200B

The relative standard deviation of the calibration standards must be <20% for the initial calibration curve to be acceptable. If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve. The regression coefficient (r^2) of the regression curve must be greater than 0.994 for the initial calibration curve to be acceptable.

Note: If a regression curve is used, all standards must be re-quantitated as samples. The concentration determined must be within +/-20% of the expected concentration to be acceptable.

9.2.4 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to the CCV concentration. Refer to Attachment 9 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.4.1 EPA 8260B ICV Criteria

The initial calibration verification (ICV) is acceptable if the average %D of all the analytes in the ICV is less than or equal 20% with no individual analyte exceeding 60%.

The analytes listed in Attachment 10 behave erratically and/or are poor performers; therefore, these analytes may exceed the ICV %D criteria such that their %D may be >60% if the average %D of all the analytes in the ICV is <20%. An NCM must be initiated to denote this situation.

9.2.4.2 EPA 624 ICV Criteria

The initial calibration verification (ICV) is acceptable if each analyte meets the criteria outlined in Attachment 12.

9.2.4.3 SM6200B ICV Criteria

The initial calibration verification (ICV) is acceptable if the average %D of all the analytes in the ICV is less than or equal 20% with no individual analyte exceeding 60%.

The analytes listed in Attachment 10 behave erratically and/or are poor performers; therefore, these analytes may exceed the ICV %D criteria such that their %D may be >60% if the average %D of all the analytes in the ICV is <20%. An NCM must be initiated to denote this situation.

9.2.5 Continuing Calibration Verification (CCV)

The initial calibration curve must be verified at the beginning of each clock with a mid-level standard.

For SM6200B, the CCV concentration should be varied throughout the range of the calibration curve and must also be performed at the end of the clock (i.e., capping CCV is required).

The continuing calibration verification standard concentration currently in use in the laboratory is specified in Section 9.2.3. Refer to Attachment 9 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.5.1 EPA 8260B CCV Criteria

For EPA 8260B, the CCC and SPCC criteria (Attachment 5) must be met for the CCV to be acceptable.

Note: EPA 8260B requires only the CCC analytes to be evaluated for response; however, the laboratory has adopted stricter criteria. Therefore, in addition to the CCC and SPCC criteria listed in Attachment 5, the average %D of all non-CCC and non-SPCC analytes must be <20% with no single analyte's %D >60% for the CCV to be acceptable.

Note: The SPCC criteria must be met even if the regression curve option is used for quantitation.

In addition to the response criteria given in this section, the CCV must be evaluated for internal standard response. The extracted ion current profile (EICP) area for each of the internal standards in the CCV must be within -50% to +100% from the last initial calibration sequence to be acceptable. If these criteria are not met, the analytical system must be inspected for problems and corrective action instituted.

The analytes listed in Attachment 10 behave erratically and/or are poor performers; therefore, these analytes may exceed the CCV %D criteria such that their %D may be >60% if the average %D of all the analytes in the ICV is <20%. An NCM must be initiated to denote this situation.

9.2.5.2 EPA 624 CCV Criteria

For EPA Method 624, all target analytes must meet the criteria outlined in Attachment 12 to be acceptable.

9.2.5.3 SM6200B CCV Criteria

For SM6200B, all gas compounds must be within 60-140%D and all other compounds must be within 70-130% to be acceptable.

9.2.6 Internal Standard (ISTD)

This procedure is an internal standard (ISTD) procedure. 1,2-dichloroethane-d4, 1,4-difluorobenzene, and chlorobenzene-d5 are the internal standards.

Prior to analysis, the internal standards must be added to all standards, samples, and QC items. The concentration of the internal standards must be the same in all calibration samples, field samples, and QC samples. A concentration of 50ug/L is used for each of the ISTD analytes.

EPA 8260B and EPA 624:
The response of the ISTD in the ICV/CCV must be within -50% to +100% of the response of the ISTD in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the CCV must be repeated and any samples associated with the CCV must also be re-analyzed. Repeated failure of the ISTD response will require re-calibration.

The response of the ISTD in the samples and batch QC items must be within -50% to +100% of the response of the previous CCV. If the response is outside of this range, corrective action must be taken.

SM6200B:
The response of the ISTD in the ICV/CCV must be within +/-30% of the response of the ISTD in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the CCV must be repeated and any samples associated with the CCV must also be re-analyzed. Repeated failure of the ISTD response will require re-calibration.

The response of the ISTD in the samples and batch QC items must be within +/-30% of the response of the previous CCV. If the response is outside of this range, corrective action must be taken.

9.2.7 Surrogates

This procedure uses surrogates to evaluate the analytical process. Dibromofluoromethane, toluene-d8, and p-BFB are the surrogates.

Prior to preparation, these surrogates must be added to all samples and QC items. The concentration of the surrogates must be the same in all field samples and QC samples. A concentration of 50ug/L is used for each of the surrogate analytes.

The percent recovery of the surrogate in all field samples and QC samples must be within the limits listed in the Method Limit Groups (MLGs) in LIMS. If the percent recovery is outside of this range, the analysis of the sample must be repeated. Repeated failure of the surrogate percent recovery may indicate re-extraction is necessary.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 4. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Preparation

10.1.1 Aqueous Sample Preparation

Remove the samples from the refrigerator and allow them to come to room temperature.

Using a 50uL syringe, add 43uL of the ISSU to the sample, injecting the solution through the vial septum. Invert the vial several times to mix. Transfer to the instrument.

10.1.2 Aqueous QC Preparation

The method blank and LCS are prepared in reagent water using a 50mL volumetric flask.

- For the method blank, add 50uL ISSU to 50mL reagent water. Pour into a VOA vial and place on the instrument.
- For the LCS, add 50uL ISTD, 50uL Mega Mix, and 150uL MeOH to 50mL reagent water. Pour into a VOA vial and place on the instrument.
- For the MS/MSD, add 43uL ISTD, 43uL Mega Mix, and 129uL MeOH into each sample vial selected for the MS and MSD. Place on the instrument.

10.1.3 Soil Sample Preparation

Refer to SOP SA-VM-021: *Preparation, Screening, and Storage of Volatiles Samples* for the soil specific sample preparation procedures. This information is summarized below.

Three Terracore/Encore devices and one bulk container are routinely received for each soil sample. Two of the Terracores/Encores are prepared for low level analysis and one is extracted in methanol for medium-level analysis to be used if the low-level samples exceed the calibration range. The bulk container is used for determining the type of preservation for the low-level samples and for screening.

At the time of analysis, the following steps are taken:

For low-level samples, 5mL reagent water and 5uL ISSU are added directly to the samples vial. The sample is then ready for analysis.

For medium-level samples, a dilution is prepared and analyzed. The default dilution is a DF40 (i.e., using 125uL of sample). 5uL VOA Surrogate Mix is added directly to the sample vial (if 5mL of MeOH were used) or 10uL VOA Surrogate Mix is added (if 10mL of MeOH were used). A aliquot of the sample is removed (to prepare the necessary dilution) and added to 10mL reagent water in VOA vial. 5uL ISTD is added. The sample is then ready for analysis.

10.1.4 Soil QC Preparation

For low-level samples, the method blank and LCS are prepared using blank sand directly in a VOA vial.

- For the method blank, add 5g sand, a stir bar, 10mL reagent water, and 5uL ISSU.
- For the LCS, add 5g sand, a stir bar, 10mL reagent water, 5uL ISTD, 5uL Mega Mix, and 15uL methanol.
- For the MS/MSD, add 5mL water, 5uL ISTD, 5uL Mega Mix, and 15uL methanol directly to the selected sample.

For medium-level samples, the method blank and LCS are prepared using Ottawa sand directly in a VOA vial.

- For the method blank, add 5g blank sand, 10uL methanol, and 10uL VOA Surrogate Mix. Remove a 125uL aliquot and add to 10mL reagent water spiked with 5uL ISTD.
- For the LCS, add 5g blank sand, 5uL methanol, 62.5uL Mega Mix, and 10uL VOA Surrogate Mix. Remove a 125uL aliquot and add to 10mL reagent water spiked with 5uL ISTD.
- For the MS/MSD, add 5g blank sand, 5uL methanol, 62.5uL Mega Mix, and 10uL VOA Surrogate Mix to the sample containers selected for the MS/MSD. Remove a 125uL aliquot and add to 10mL reagent water spiked with 5uL ISTD.

10.2 Analysis

10.2.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The purge time must be 11 minutes. All other parameters are optimized by the lab for the target compounds and documented in the maintenance log. Therefore, the actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

GC Parameters
Column: 20m x 0.18mm ID x 1.0um

Column: Flow: 0.5-1.0mL/min
Injector: Split/Splitless operated in the split mode with 1mm ID quartz insert
Split ratio (desorb to column flow): 40:1 or 80:1

MS Parameters
Mass spectrometer interface: 240°C (direct column interface)
Mass spectrometer source temperature: 250°C
Mass scan range: 35-300amu, with a minimum scan cycle of 1 scan per second
Injector: 100°C

Temperature Program:
Initial Temperature: 50°C
Program Rate: 18°C/minute
Final Temperature: 200°C

Example Purge and Trap Conditions
The purge and trap conditions listed in this section are for guidance. The lab must document the actual conditions used. The purge time must be 11 minutes. Other parameters may be varied to optimize the detection of the target compounds.

VOCARB 3000 trap
Purge Time: 11 minutes
Purge temperature: aqueous-ambient; soils-heated 40°C
Desorb time: 0.50 minutes
Desorb temperature: 250°C
Bake time: 8 minutes at 260°C
Purge flow: Approximately 30-40mL/minute
Valve temperature: 150°C
Transfer line: 150°C

The purge flow must be balanced for adequate sensitivity of the target compounds. If the purge flow is too high, the response of the gases will be low and not reproducible. The SPCC criteria for chloromethane may not be achieved if the purge flow is too high. If the purge flow is too low, the response of the more water-soluble targets - ketones, ethers, bromoform - may be low and the reporting limit may not be achieved on a routine basis.

10.2.2 Internal Standard (ISTD)

Prior to analysis, internal standard must be added to all standards, samples, and QC items. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. Instructions for the addition of the internal standard spiking mix is given in the previous sections.

10.2.3 BFB Tune Check

A BFB tune check must be analyzed at the beginning of each clock as a check on the "tune" of the mass spectrometer. This check must meet the criteria described given in Section 9.2.1.

If the instrument is configured for direct injection, inject 2uL of the 25ng/uL solution into the GC and analyze the 4-BFB using the instrument conditions listed in Section 10.1. A solvent delay should be set to allow the methanol to pass through the mass spectrometer while the MS is "off".

If the purge and trap is used to introduce the 4-BFB into the MS, add 1uL of the 50ng/uL solution to 5.0mL of reagent water. Transfer the 5.0mL to the purge and trap device and purge the sample using the same conditions used for sample analysis.

10.2.4 Trap Check Standard

The trap check standard is used to evaluate the condition of the trap by monitoring the formation of chloromethane and bromomethane. Chloromethane and bromomethane may be formed on a degraded trap by thermal decomposition of halogenated compounds. This check must meet the criteria described given in Section 9.2.2.

10.2.5 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.3. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.4, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.6.

10.2.6 Sample Analysis

The sample/extract must be injected using the same injection volume used for the calibration standards. The samples can only be analyzed after the tune, the trap check, the calibration (initial or continuing), and the method blank and LCS criteria have been met. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

10.2.7 Example Analytical Sequence

A typical example analytical sequence is listed below.

Description	Comments
Blank	
BFB	Clock time begins with injection of the BFB
Initial Calibration	
ICV	Second Source
BFB	Clock time begins with injection of the BFB
CCV	
LCS	
LCSD	If insufficient sample provided for MS/MSD
Trap Check	
MB	
Samples & Batch	

QC Items	
BFB	Clock time begins with injection of the BFB
CCV	
LCS	
LCSD	If insufficient sample provided for MS/MSD
Trap Check	
MB	
Samples & Batch QC Items	
CCV	Capping CCV required only for SM6200B

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data evaluation must be performed in accordance with SA-QA-08: *Evaluation of Chromatographic Data.* This SOP includes specific information regarding the evaluation of chromatographic data, including the requirements for performing manual integrations and the evaluation of retention times.

Data review and reporting must be performed in accordance with SA-QA-02: *Data Generation and Review.*

11.1.1 Target Analyte Identification

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1.1 Two criteria must be met in order to identify a target compound:

- Elution of the sample component within ±0.06 Relative Retention Time (RRT) units of the daily standard containing that compound. The RRT is calculated as follows:

$$RRT = \frac{retention\ time\ of\ the\ target\ compound}{retention\ time\ of\ the\ associated\ internal\ standard}$$

- Correspondence of the target compound spectrum and the standard component mass spectrum

11.1.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. The ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.1.3 The relative intensities of the ions present in the sample component spectrum should agree within ± 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or the Department Manager. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

1.1.2 Dilutions

Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags must be used or qualification in a case narrative provided to the client.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower reporting limits.

11.1.3 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify TALS Worksheet Notes or use the TALS Historical Data Tracker feature to determine if historical data is available for review.

11.1.4 Chemical Relationships

Benzene, toluene, ethylbenzene, and the xylenes are generally present together in samples and indicate the presence of gasoline

m/p-Xylenes are generally higher than o-xylene

Hydrocarbons present is samples containing gasoline generally contain mass 43 and may co-elute with target analytes with mass 43 as the quant or confirmation ion or may skew the spectrum of a compound with mass 43 as part of the spectrum.

Cis-isomers are generally more prevalent than the trans- isomers

Pay particular attention to the retention time of isomer because the only way to positively identify them is by retention time. The isomers are:

1,1-dichloroethane and 1,2-dichloroethane
1,1-dichloroethene, cis-1,2-dichloroethene, and trans-1,2-dichloroethene
1,1,1-trichloroethane and 1,1,2-trichloroethane
ethyl benzene, m/p-ylene, and o-xylene
1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2-dichlorobenzene

1,1-dichloropropene, cis-1,2-dichloropropene, and trans-1,2-dichloropropene
2-chlorotoluene and 4-chlorotoluene
1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene
1.3.5-trimethylbenzene and 1,2,4-trimethylbenzene
4-methyl-2-pentanone (MIBK) and 2-hexanone
n-butylbenzene, sec-butylbenzene, tert-butylbenzene, and isopropylbenzene

Higher chlorinated alkanes and alkenes may have lower chlorinated alkanes or alkenes present due to degradation. The following table lists some common chlorinated compounds and their degradation products. Look for the degradation product(s) when the concentration of the compound in the left column is present at high concentrations.

Analyte	Degration Product
1,1,2,2-tetrachloroethane	trichloroethene (TCE) cis-1,2-dichloroethene (c-1,2-DCE) trans-1,2-dichloroethene (t-1,2-DCE) vinyl chloride 1,1,2-trichloroethane (1,1,2-TCA) 1,2-dichloroethane (1,2-DCA) Chloroethane
1,1,2-trichloroethane (1,1,2-TCA)	1,2-dichloroethane (1,2-DCA) Chloroethane
1,1,1-trichloroethane (1,1,1-TCA)	1,1-dichloroethene (1,1-DCE) 1,1-dichloroethane (1,1-DCA) Chloroethane
Carbon tetrachloride	Chloroform Methylene chloride Chloromethane
Tetrachloroethene (PCE) (PCE = perchloroethylene which is a common name for tetrachloroethene)	trichloroethene (TCE) cis-1,2-dichloroethene (c-1,2-DCE) trans-1,2-dichloroethene (t-1,2-DCE) Chloroethene
1,2,4-trichlorobenzene	1,4-dichlorobenzene (1,4-DCB) 1,2-dichlorobenzene (1,2-DCB) Chlorobenzene

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample extract (at the instrument)
F = Final volume of the extract
I = Initial volume/weight
dw = % Solids decimal equivalent
D = Dilution factor

Note: All dry weight corrections are performed automatically in TALS.

Note: This formula assumes all unit conversion factors are applied.

12.0 Method Performance

12.1 Reporting Limit Verification (RLV)

At a minimum, RLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, RLVs must also be performed quarterly thereafter. For all other analytes and methods, RLVs must also be performed annually thereafter. Exceptions may be made for project-specific non-routine analytes.

12.2 Method Detection Limit (MDL) Study

The MDL is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDLs associated with this procedure are given in the Method Limit Group (MLG) in TALS.

At a minimum, MDL Studies must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

Note: MDL Studies are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

Note: For SM6200B, MDL Studies should be performed over 3-5 days.

12.3 Method Detection Limit Verification (MDLV)

At a minimum, MDLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, MDLVs must also be performed quarterly thereafter. For all other analytes and methods, MDLVs must also be performed annually thereafter.

Note: MDLVs are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.4 QC Limit Generation, Control Charting, and Trend Analysis

12.4.1 EPA 624 and SM6200B

The control limits for the batch QC items (LCS/LCSD and MS/MSD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.4.2 EPA 8260B

The control limits for the batch QC items (LCS/LCSD and MS/MSD) for this procedure are not specified by the reference method; therefore, the laboratory defaults to in-house and/or laboratory-derived limits for the evaluation of batch QC items.

Control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.5 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability (IDOC). The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Note: SM6200B requires IDOCs to be within 80-120% for the average recovery and <20%RSD.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or by the analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess samples, reagents, and standards must be disposed in accordance with the TestAmerica Savannah Addendum to the EHSM.
- Methanolic waste from rinsings and standards – Transfer to satellite container for methanolic (flammable) waste. Transfer to hazardous waste section when satellite container is full.
- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.
- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

15.0 References / Cross-References

- SOP SA-AN-41: *Reagent and Standard Materials Traceability*
- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06*: Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-08: *Evaluation of Chromatographic Data*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- SOP SA-VM-021: *Preparation, Screening, and Storage of Volatiles Samples*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- Method 8000C: *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846;* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.
- Method 8260B: *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846;* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.
- EPA Method 624*: Purgeables.* 40 CFR Part 136, Appendix A, July 1, 1995.
- *Standard Methods for the Examination of Water and Wastewater, Online Edition;* American Public Health Association: Washington, DC.
  - SM6020: Quality Assurance/Quality Control
  - SM6200B: *Volatile Organic Compounds; Purge and Trap Capillary-Column Gas Chromatographic/ Mass Spectrometric Method*; 1997

16.0 Method Modifications and Clarifications

16.1 Incorporation of Other Matrices

This procedure may be modified to analyze other matrices (e.g., wipe, waste, and TCLP/SPLP leachate samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project.

Wipe and waste matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and default QC limits to evaluate waste samples and its routine water RLs (converted for initial and final volumes, etc.) and default QC limits to evaluate wipe samples. Soil and/or water DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices, as applicable. The laboratory uses its routine aqueous RLs (converted for initial and final volumes, etc.) and default QC limits to evaluate TCLP/SPLP leachate samples. Water DOCs can be used to satisfy analyst demonstrations of capability for TCLP/SPLP matrices. Ottawa sand is used as the blank matrix for wipes and wastes unless specifically requested otherwise by the project.

16.1.1 Collection and Handling Procedures

Waste (oil) samples are routinely collected in 40mL VOA vials. Waste (oil) samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until

time of preparation. Samples must be analyzed within 14 days of collection.

Wipe samples are routinely collected in 40mL VOA vials. Wipe samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until time of preparation. Samples must be analyzed within 14 days of collection.

Once the TCLP/SPLP extraction procedure has been performed, the leachate is transferred to a Tedlar bag. TCLP/SPLP leachates must be stored at 4°C (less than 6°C with no frozen samples) until the time of preparation. The leachate sample must be analyzed within 14 days of completion of the TCLP/SPLP extraction.

16.1.2 Preparation and Analytical Procedures

Wipe samples are analyzed in the same fashion as water samples. Refer to Work Instruction FQA088: *Wipe Tests: Sampling and Analysis* for additional information on wipe procedures.

Waste samples are prepared and analyzed in the same fashion as medium-level soil samples. Note: Waste samples often require large dilutions.

TCLP/SPLP matrices are prepared and analyzed in the same manner as routine water samples; however, a default dilution factor of 20 is used.

16.2 Other Considerations

16.2.1 EPA Method 8260B does not contain calibration verification criteria for non-CCC analytes nor does it require non-CCC analytes to be evaluated for response; however, the laboratory has adopted in-house criteria for non-CCC analytes as outlined in this SOP.

16.2.2 EPA Method 8260B does not require the analysis of an ICV. NELAC requires an ICV; however, it does not list specific criteria. The laboratory has adopted in-house criteria for ICVs for EPA 8260B as outlined in this SOP. The SM6200B reference method requires an externally-prepared QCS to be performed quarterly. The laboratory satisfies this requirement via the ICV performed with each ICAL.

16.2.3 EPA Method 8260B allows alternate criteria to be used for the BFB evaluation. As such the laboratory has incorporated criteria the CLP OLMO4.0 (January 1998) method.

16.2.4 The laboratory has defined the analytes listed in Attachment 10 as poor or erratic performers and allows for exceptions to the ICV, CCV, LCS/LCSD, MS/MSD, and Sporadic Marginal Exceedance criteria for these analytes as outlined in this SOP.

16.2.5 EPA Method 8260B does not place a cap on an individual analyte's %D or %RSD when evaluating the Grand Mean Exception. The laboratory has adopted more stringent in-house requirements as outlined in this SOP.

16.2.6 It has been determined that increased methanol concentrations can suppress the response of the gas compounds, leading to erratic recovery and reduced linearity. As such, the laboratory normalizes the volume of methanol in all standards and QC items to minimize this effect. By introducing a constant volume of methanol to initial calibration

standards, CCV/ICV, LCS, and MS/MSD, better sensitivity and recovery of these analytes is achieved.

16.2.7 The 7-day holding time for samples with pH>2 is listed in EPA 624 and is not included in the SW-846 methods. The laboratory has adopted this as internal guidance for EPA Method 8260B as is common industry practice and will make every effort to analyze samples with pH>2 within 7 days.

16.2.8 Historical standard practice for most laboratories was to combine all analytes into one analysis using a single acid preserved container. This practice is still acceptable in those cases where the compounds of interest are not adversely affected by the addition of the hydrochloric acid (HCl) preservative; however, EPA 624 and EPA 8260B both list special preservation requirements for acrolein, acrylonitrile, and 2-chloroethylvinyl ether (2-CEVE). Although these analytes are rarely found in the environment, preservation at pH<2 (as achieved using HCl preservative) breaks down these analytes and may result in a significantly low bias and/or non-detect value.

The reference methods suggest to preserve these analytes to a pH between 4-5. Achieving this narrow pH range is problematic; therefore, the only other alternative is to use an unpreserved container for these analytes. As such, if acrolein, acrylonitrile, and/or 2-CEVE are on the requested target analyte list, the laboratory now defaults to using an unpreserved container. The other target analytes reported for these methods are not adversely affected by using an unpreserved container provided they are analyzed within the shorter, method-prescribed holding times (HT) defined for unpreserved samples. Specific information on VOA holding times, preservation requirements, and analyte-specific requirements is given in Attachment 2.

16.2.9 The 40mL VOA vials used by the laboratory have been demonstrated to actually contain approximately 43mL. As such, standard spiking amounts have been adjusted accordingly to accommodate for this volume (e.g., spiking 43uL instead of 40uL).

16.2.10 The laboratory has incorporated the batch QC items as outlined in Section 9.1. Some additional QC items are performed which differ from those specified in the reference methods (e.g., LCSD or MSD) to satisfy common state regulatory requirements and/or client requests for precision data and/or to facilitate scheduling and data evaluation. The method-specified batch QC items are as follows:

EPA 8260B:
Method blank, LCS, MS, and sample duplicate or MSD

EPA 624
Method blank, LCS, MS per 10% of samples analyzed
SM6200B:
Method blank, LCS, MS, and MSD

16.2.11 EPA Method 624 specifies a required concentration range criteria for the evaluation of QC items (i.e., the Q-Table). The laboratory has converted these values into percent recovery limits to be used to assess CCV, ICV, LCS/LCSD, and MS/MSD.

16.2.12 The EPA 8260B reference method specifies a 1-week expiration date for the gas standards. The laboratory prepares a 25mL volume of MegaMix standard and splits it

into five 5mL Mini-nert vials. Each vial is assigned a 1-week expiration date from the date that vial is opened, not to exceed 14 days from the preparation date of the 25mL volume. Note: This expiration date is a maximum. Shorter expiration dates may be used based on evidence of gas compound volatility as evaluated via CCVs.

16.2.13 The EPA 8260B reference method recommends 4 surrogates to be used but allows for other surrogates. Due to improved instrument conditions and shorter run times, the laboratory has incorporated the 3 surrogates specified in EPA Method 624.

16.2.14 Due to client requests, the analyte list utilized by the laboratory may be different than those listed in the reference methods.

16.2.15 The SM6200B reference method states that the MDL should be determined annually but does not specify the procedure to be used. The laboratory performs MDL Studies initially, in accordance with 40CFR Part 136B, and re-establishes the MDL annually or quarterly (as dictated by agency-specific requirements) via an MDLV study.

16.2.16 The SM6200B reference method states that the Method Quantitation Limit (MQL) must be 4 times the MDL. The laboratory typically defines the MQL (i.e., the RL) based on the low-point of the calibration curve as opposed to a factor of the MDL.

16.2.17 The SM6200B reference method states that internal standard areas must be within 30% of the ICAL mean. Due to a software limitation, the laboratory evaluates each CCV against the midpoint of the ICAL and all field samples and QC items to their associated CCV. This is consistent with the requirements outlined in SW846 Update IV.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Preventative Maintenance and Troubleshooting
Attachment 5: EPA 8260B Calibration Criteria: SPCCs and CCCs
Attachment 6: BFB Tune Criteria
Attachment 7: Target Compound Information: Ions and ISTDs
Attachment 8: Instrument Configurations
Attachment 9: Standard Information and Recipes
Attachment 10: Poor Performers
Attachment 11: Evaluation of TICs
Attachment 12: EPA 624 CCV & ICV Criteria (Q-Table)

Attachment 1:
SOP Summary

Sample Preparation Summary

Aqueous samples are routinely purged at ambient conditions; however, a heated purge may be used if required by the project. A 5mL purge volume is used as the default. The calibration standards and the associated QC must be analyzed under the same conditions and volume.

Low-level soil samples are purged at 40°C in a purge and trap instrument designed to add water and internal standards to the vial containing the sample without breaking the seal. The sample is stirred during purging to thoroughly mix the soil and water. The calibration standards and associated QC are purged under the same conditions.

High level soils and waste samples are extracted with methanol (1mL of methanol per gram of sample). An aliquot of the methanol extract is injected into reagent water. The methanol extract/reagent water is purged at ambient temperature using the same instrument conditions and calibration used for aqueous samples.

Sample Analysis Summary

VOCs are purged from the sample matrix with helium. The VOCs are transferred from the sample matrix to the vapor phase. The vapor is swept through a sorbent tube where the VOCs are trapped. After the purging is completed, the trap is heated and backflushed with helium to desorb the VOCs onto a GC column. The GC is temperature-programmed to separate the VOCs, which are then detected by a mass spectrometer. Qualitative identification of the target compounds in the sample is based on the relative retention time and the mass spectra of the characteristic masses (ions) determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

Description	Comments
Blank	
BFB	Clock time begins with injection of the BFB
Initial Calibration	
ICV	Second Source
BFB	Clock time begins with injection of the BFB
CCV	
LCS	
LCSD	If insufficient sample is provided for MS/MSD
Trap Check	
MB	
Samples & Batch QC Items	
BFB	Clock time begins with injection of the BFB
CCV	
LCS	
LCSD	If insufficient sample is provided for MS/MSD
Trap Check	
MB	
Samples & Batch QC Items	
CCV	Capping CCV required for SM6200B only

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Aqueous samples are routinely collected in 40mL VOA vials. The table below outlines the laboratory's default procedures for aqueous samples:

Method	Acrolein, Acrylonitrile, or 2-CEVE Requested?	Chemical Preservation	Thermal Preservation	Holding Time
EPA 8260B	Yes	None	<6°C	7 days
EPA 8260B	No	HCl (pH<2)	<6°C	14 days
EPA 624	Yes	None	<6°C	3 days*
EPA 624	No	HCl (pH<2)	<6°C	14 days
SM6200B	Yes	None	<6°C	7 days
SM6200B	No	HCl (pH<2)	<6°C	14 days

*Note: 3-day HT is specific to acrolein. If acrolein is not requested, 7 days is used for the remaining target compounds.

The table below outlines the laboratory's procedures for soil samples:

Sample Container	Chemical Preservation	Thermal Preservation	Holding Time
Terracore Kit: 5g Terracore sampler, 2 x pre-weighed 40-mL VOA w/ H2O, pre-weighed 40-mL VOA w/ MeOH, 2oz. bulk jar	H_2O & MeOH	<-10°C	48 hours to freeze, 14 days to analyze
Encore Kit: 3 x 5g Encore samplers, 4oz. bulk jar	$NaHSO_4$, H_2O, or MeOH (added in lab)	<6°C	48 hours to preserve, 14 days to analyze
Encore Kit: 3 x 5g Encore samplers, 2 x pre-weighed 40-mL VOA w/ NaHSO4, pre-weighed 40-mL VOA w/ MeOH, 4oz. bulk jar	$NaHSO_4$ or MeOH	<6°C	48 hours to preserve, 14 days to analyze

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Clock Time	EPA 8260B: 12 hours EPA 624: 24 hours EPA 624 Cluster Rule (Chloroform Only): 8 hours SM6200B: 12 hours or 20 samples, whichever occurs first	Clock time starts with the injection of the BFB. Analysis of samples and QC items must conclude within expiration of clock time. Subsequent analysis requires new BFB.	Not applicable
Tune Standard (BFB)	At beginning of each clock	Refer to Attachment 6.	- Perform instrument maintenance - Re-tune.
Trap Check Standard	At beginning of each clock	<0.5ug/L (Chloromethane & bromomethane)	- Perform instrument maintenance. - Change trap. - Recalibrate

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration (ICAL) - Minimum of 3 points for EPA 624. - Minimum of 5 points for EPA 8260B and SM6200B.	Upon instrument set-up, and after unsuccessful CCV	EPA 624: %RSD < 35% If %RSD > 35%, use curve fit w/ r^2>0.990. EPA 8260B: - CCC: %RSD < 30% - SPCC: RRF_{avg} > Attachment 5 - If %RSD >15%, use curve fit with r^2 > 0.990. - GME: Avg %RSD <15%; No single analyte %RSD > 45%. SM6200B: %RSD < 20% If %RSD > 20%, use curve fit w/ r^2>0.994. Requant all levels, w/ 20%D.	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Initial Calibration Verification (ICV) - Second Source	After each ICAL	EPA 624: Attachment 12 EPA 8260B and SM6200B: Avg %RSD <20%; No single analyte %RSD > 60%.	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate

QC Item	Frequency	Criteria	Corrective Action
Continuing Calibration Verification (CCV)	EPA 8260B and EPA 624: After BFB SM6200B: After BFB and at end of each clock	EPA 624: Attachment 12 EPA 8260B: - CCC: %D < 20% - SPCC: RRF > Attachment 5 - Non-CCC and non-SPCC: Avg %D <20%; No single analyte %D >60% SM6200B: %D < 20%	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Internal Standards (ISTD)	Spiked in all CCVIS, samples, and batch QC items	EPA 8260B & EPA 624: CCVIS: - Area -50% to +100% CCV in ICAL. - RT +/-30 seconds from ICAL. Samples & batch QC items: - Area within -50% to +100% of previous CCVIS. SM6200B: CCVIS: - Area +/-30% CCV in ICAL. Samples & batch QC items: - Area within +/-30% of previous CCVIS.	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available
Surrogate Compounds	Spiked in all samples and batch QC items.	Within MLG limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze sample, if sufficient sample available

QC Item	Frequency	Criteria	Corrective Action
Analytical Batch Definition	Analyzed together w/in 24-hr timeframe; not to exceed 20 field samples	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	<1/2RL	Refer to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per batch	Within TALS MLG Limits	Refer to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	One per batch, when insufficient sample is provided for MS/MSD	Within TALS MLG Limits	Refer to SOP SA-QA-17
Matrix Spike (MS)	EPA 8260B and SM6200B: One per batch EPA 624: 1 per 10% of samples	Within TALS MLG Limits	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per batch	Within TALS MLG Limits	Refer to SOP SA-QA-17
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06 Note: Unsupervised work must not begin until acceptable IDOC is obtained.
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06

QC Item	Frequency	Criteria	Corrective Action
Reporting Limit Verification (RLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Method Detection Limit Study (MDL)	Upon method/instrument set-up, per analyte/method/matrix combination	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
MDL Verification (MDLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Preventative Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:
- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
	Service Interval							
EQUIPMENT ITEM	D	W	M	Q	SA	A	AN	SERVICE LEVEL
Injector Port							X	Replace septum, sleeve, inlet seal, and washer (Recommend every 2 weeks)
Sparge Tubes							X	Clean (Recommend every 3 months)
Column							X	Change column (Recommend annually)

D=daily; W=Weekly; M=monthly; Q=Quarterly; SA=semi-annually; A=annually; AN=as needed

Troubleshooting
Troubleshooting should be documented as outlined above. If possible, troubleshooting is best performed in a step-wise manner to systematically isolate instrument components. Refer to the instrument manufacturer's guides for specific information and strategies. Enlist assistance from technical and/or department management as needed.

Contingency Plan
Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
EPA 8260B SPCC and CCC Criteria

Calibration Check Compounds (CCCs)

Initial Calibration	Continuing Calibration
<=30% RSD	<=20% difference from initial calibration

System Performance Check Compounds (SPCCs)

SPCC	Minimum RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Chlorobenzene	0.30
Bromoform	>0.10
1,1,2,2-Tetrachloroethane	0.30

Note: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

Calibration Check Compounds (CCCs)
Vinyl chloride
1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene

System Performance Check Compounds (SPCCs)
Chloromethane
1,1-Dichloroethane
Chlorobenzene
Bromoform
1,1,2,2-Tetrachloroethane

Attachment 6:
BFB Tune Criteria

EPA 8260B

m/e	Abundance Criteria
50	8.0-40.0% of mass 95
75	30.0-66.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0-9.0% of mass 95
173	< 2.0% of mass 174
174	50-120%% of mass 95
175	4.0-9.0% of mass 174
176	93.0-101.0% of mass 174
177	5.0-9.0% of mass 176

*8260 criteria taken from CLP OLMO4.0 (January 1998)

EPA 624 and SM6200B

m/e	Abundance Criteria
50	15.0-40.0% of mass 95
75	30.0-60.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0-9.0% of mass 95
173	<2.0% of mass 174
174	>50% of mass 95
175	5.0-9.0% of mass 174
176	95.0-101.0% of mass 174
177	5.0-9.0% of mass 176

Attachment 7:
Target Compound Information: Ions and ISTDs

Analyte	Quant Ion	Secondary Ions		ISTD
1,1,1,2-Tetrachloroethane	131	133	119	3
1,1,1-Trichloroethane	97	99	61	2
1,1,2,2-Tetrachloroethane	83	85	168	3
1,1,2-Trichloro-1,2,2-trifluoroethane	101	151	103	1
1,1,2-Trichloroethane	83	97	99	2
1,1-Dichloroethane	63	65	83	1
1,1-Dichloroethene	96	61	98	1
1,1-Dichloropropene	75	110	77	2
1,2,3-Trichlorobenzene	180	182		3
1,2,3-Trichloropropane	110	112		3
1,2,4-Trichlorobenzene	180	182	145	3
1,2,4-Trimethylbenzene	105	120	77	3
1,2-Dibromo-3-Chloropropane	157	75	155	3
1,2-Dichlorobenzene	146	148	111	3
1,2-Dichloroethane	62	49	64	2
1,2-Dichloroethene, Total	Sum of cis and trans isomers			
1,2-Dichloropropane	63	76	65	2
1,3,5-Trimethylbenzene	105	120	77	3
1,3-Dichlorobenzene	146	148	111	3
1,3-Dichloropropane	76	78	41	2
1,3-Dichloropropene, Total	Sum of cis and trans isomers			
1,4-Dichlorobenzene	146	148	111	3
1-Chlorohexane	41	43		3
1-Methylnaphthalene	142	141		3
2,2-Dichloropropane	77	41		1
2-Butanone (MEK)	43	72		1
2-Chloro-1,3-butadiene	53	88		1
2-Chloroethyl vinyl ether	63	65	106	2
2-Chlorotoluene	126	91	63	3
2-Hexanone	43	58		3
2-Methylnaphthalene	142	141		3
3-Chloro-1-propene	76	41		1
3-Methylhexane	43	71		2
4-Chlorotoluene	126	91	63	3
4-Isopropyltoluene	119	134	91	3
4-Methyl-2-pentanone (MIBK)	43	57	58	2
Acetone	58	43		1
Acetonitrile	41	40		1
Acrolein	56	55		1
Acrylonitrile	53	52	51	1
Amyl acetate	70	61		3

Analyte	Quant Ion	Secondary Ions		ISTD
Benzene	78	50		2
Benzyl chloride	91	63		3
Bromobenzene	156	77	158	3
Bromoform	173	171	175	3
Bromomethane	96	94	79	1
Butadiene	54	39		1
Carbon disulfide	76	78		1
Carbon tetrachloride	117	119	121	2
Chlorobenzene	112	77	51	3
Chlorobromomethane	49	128	130	1
Chlorodibromomethane	129	127	131	3
Chloroethane	64	66		1
Chloroform	83	85	47	1
Chloromethane	50	52		1
Chloroprene	53	88		1
cis-1,2-Dichloroethene	96	61	98	1
cis-1,3-Dichloropropene	75	77	110	2
Cyclohexane	56	69	84	2
Cyclohexanone	55	42	98	3
Dibromomethane	93	174	95	2
Dichlorobromomethane	83	85	129	2
Dichlorodifluoromethane	85	87	101	1
Dichlorofluoromethane	67	69		1
Ethyl acetate	43	61	70	1
Ethyl acrylate	55	73		1
Ethyl ether (diethyl ether)	59	74	45	1
Ethyl methacrylate	69	41	39	3
Ethylbenzene	91	106	51	3
Ethylene Dibromide	107	109		2
Ethylene oxide	43	44		1
Furan	68	39		1
Hexachlorobutadiene	225	223	190	3
Hexane	57	41	43	1
Iodomethane	142	127		1
Isobutyl alcohol	43	41		2
Isopropyl acetate	61	59	87	1
Isopropyl ether	45	43		1
Isopropylbenzene	105	120	77	3
m,p-Xylene	106	91	77	3
Methacrylonitrile	67	52		1
Methyl acetate	43	74		1
Methyl acrylate	55	85		1
Methyl methacrylate	69	41		2

Analyte	Quant Ion	Secondary Ions		ISTD
Methyl styrene	117	115	91	3
Methyl tert-butyl ether	73	57		1
Methylcyclohexane	83	55	98	2
Methylene Chloride	84	49	86	1
Naphthalene	128	102	51	3
n-Butyl acetate	43	56		2
n-Butyl acrylate	55	56		2
n-Butylbenzene	91	92	134	3
n-Heptane	43	57	71	1
N-Propylbenzene	120	91	65	3
o-Xylene	106	91	77	3
Pentachloroethane	167	130		3
Propene oxide	58	43		1
Propionitrile	54	55		1
sec-Butylbenzene	105	134	91	3
Styrene	104	78	103	3
Tert-amyl methyl ether	73	43		1
Tert-butyl alcohol	59	41		1
tert-Butylbenzene	119	91	134	3
Tert-butyl ethyl ether	59	87		1
Tetrachloroethene	164	166	168	3
Tetrahydrofuran	42	71		1
Toluene	92	91	65	2
trans-1,2-Dichloroethene	96	61	98	1
trans-1,3-Dichloropropene	75	77	110	2
trans-1,4-Dichloro-2-butene	53	88	89	3
Trichloroethene	130	95	132	2
Trichlorofluoromethane	101	103	105	1
Trichlorotrifluoroethane (Freon 113)	101	151	103	1
Trihalomethanes, Total	Sum of chloroform, dichlorobromomethane, dibromochloromethane, and bromoform			
Vinyl acetate	43	86		1
Vinyl chloride	62	64		1
Xylenes, Total	Sum of m/p- and o- isomers			

Analyte	Quant Ion	Secondary Ions		ISTD
Surrogates				
Dibromofluoromethane	113	81	111	1
Toluene-d8	98	100	70	2
p-Bromofluorobenzene	95	174	176	3
1,2-Dichloroethane-d4	65	67	102	1
Internal Standards				
1,2-Dichloroethane-d4	65	67	102	1
1,4-Difluorobenzene	114	63	88	2
Chlorobenzene-d5	82	117	119	3

Note: For a complete list of target analytes for each method, refer to the LIMS Method Limit Groups (MLGs).

Attachment 8:
Basic Instrument Configurations

System	GC	MS	P/T	Autosampler	Trap	GC/MS Data system	Methods
MSA	Agilent 6890	Agilent 5973	EST Encon (dual)	EST Centurion	Supelco VOCARB 3000	Agilent Chemstation	EPA 624 EPA 8260B (aqueous) SM6200B
MSB	Agilent 6890	Agilent 5973	Tekmar 3000	Tekmar Aquatek 70	Supelco VOCARB 3000	Agilent Chemstation	EPA 624 EPA 8260B (aqueous) SM6200B
MSL	Agilent 5890	Agilent 5972	Tekmar LSC 2000	Varian Archon	Supelco VOCARB 3000	Agilent Chemstation	EPA 8260B (soils)
MSM	Agilent 5890	Agilent 5972	Tekmar LSC 2000	Varian Archon	Supelco VOCARB 3000	Agilent Chemstation	EPA 8260B (soils)
MSO	Agilent 6890	Agilent 5973	EST Encon (dual)	EST Centurion	Supelco VOCARB 3000	Agilent Chemstation	EPA 624 EPA 8260B (aqueous) SM6200B
MSP	Agilent 6890	Agilent 5973	EST Encon (dual)	EST Centurion	Supelco VOCARB 3000	Agilent Chemstation	EPA 624 EPA 8260B (aqueous) SM6200B

Attachment 9
Standard Information and Recipes

Store standards in glass vials fitted with Teflon-lined caps in standards-only refrigerator at <-10C. Choose a container volume that will have minimal headspace when standard is added. Mark the level on the outside of the container so that evaporation of the solvent will be apparent.

The expiration dates represent the maximum time a standard can be maintained. Standards that exhibit obvious signs of degradation must be replaced sooner.

Routine Target Compounds

Stock Standard Mixes

Stock/Mix	TALS ID	Vendor/Part Number	Concentration (ug/mL)
O2SI 8260 Additional Compounds	8260 ADD	O2SI 120267-03-02	2500-5000
O2Si Custom VOA 57-1	8260VOA	O2SI 120315-01-02	2500-7500
8260B Surrogates from O2SI	O2SI Surr	O2SI 120005-05-02	2500
O2SI Custom Gases	O2SI-Gases	O2SI 120326-01-02	2500
O2SI 8260 Custom ISTD	O2SI-ISTD	O2SI 120192-02-02	2500

Expiration:
Un-opened ampuls: manufacturer's expiration date
Opened ampuls: 1 month (Note: These ampuls are used to prepare the Working Standards and are typically consumed/disposed open opening.)

8260 Working ISTD
(TALS ID: 8260 ISTD)

Stock/Mix	Initial Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
O2SI 8260 Custom ISTD	500	25	50

Solvent: P/T Methanol
Expiration: 1 Month

O2SI Primary MM + Butadiene/Methylstyrene
(Mega Mix Working Standard)
(TALS ID: O2SI MMix)

Stock/Mix	Initial Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
O2SI 8260 Additional Compounds	500	25	50-100
O2Si Custom VOA 57-1	500		50-150
8260B Surrogates from O2SI	500		50
O2SI Custom Gases	500		50

Solvent: P/T Methanol
Expiration: 2 weeks from date prepared
(Note: The 25mL final volume is split between five 5mL Mini-nert vials. Due to the volatility of the gas analytes, each vial is assigned a 1-week expiration date from the date that vial was opened, not to exceed 14 days from the preparation date.)

Calibration Standards

Stock/Mix	1	2	3	4	5	6	7
	Aliquot (uL) to prepare CAL standard						
O2SI MMix	20	100	200	400	1000	2000	4000
8260 ISTD	100	100	100	100	100	100	100
Volume of water (mL)	100	100	100	100	100	100	100
Target Compounds (ng)	5	25	50	100	250	500	1000
Internal Standards (ng)	250	250	250	250	250	250	250

Transfer to 40mL VOA vial containing preservatives.
Expiration: 24 hours

Appendix IX Target Compounds

Stock Standard Mixes

Stock/Mix	TALS ID	Vendor/Part Number	Concentration (ug/mL)
Appendix 9 Compounds	o2siAP_9	o2si 120314-01-02	1250-50000
Chloroprene Solution	o2siCPS	o2si 020315-030-02	1250
Pentachloroethane	o2siPENTA	o2si 020052-03-02	2500
Acrolein / Acrylonitrile	o2siA/A	o2si 120014-02	1000
Tetrahydrofuran / DEE Mix	o2siT/D	o2si 120312-02-02	2500-25000
O2SI 8260 Custom ISTD	O2SI-ISTD	O2SI 120192-02-02	2500

8260 Working ISTD
(TALS ID: 8260 ISTD)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
O2SI 8260 Custom ISTD	500	25	50

Solvent: P/T Methanol
Expiration: 1 month

AP9 Working Standard (TC2)
(TALS ID: o2si_TC2)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Appendix 9 Compounds	500	25	25-1000
Chloroprene Solution	500		25
Pentachloroethane	500		50

Solvent: P/T Methanol
Expiration: 1 month

THF/DEE Working Standard
(TALS ID: XXXXX)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Appendix 9 Compounds	500	25	25-1000
Chloroprene Solution	500		25
Pentachloroethane	500		50

Solvent: P/T Methanol
Expiration: 1 month

Calibration Standards

Stock/Mix	1	2	3	4	5	6	7
	Aliquot (uL) to prepare CAL standard						
O2SI A/A	1	5	10	20	50	75	100
O2SI TC2	2	10	20	40	100	150	200
THF DEE	1	5	10	20	50	75	100
8260 ISTD	5	5	5	5	5	5	5
Volume of water (mL)	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Target Compounds (ng)	5	25	50	100	250	500	1000
Internal Standards (ng)	250	250	250	250	250	250	250

Note: Record calibration standard preparation in A/D batch.
Expiration: 24 hours

Attachment 10
Poor Performers

As indicated in EPA 8260B and/or via assessment of laboratory control sample recoveries and control charts, the compounds listed below are poor performers and/or behave erratically. These compounds will not be included in the LCS/LCSD/MS/MSD marginal exceedance count, provided their %R is >10%.

Additionally, these analytes have exceptions to the routine ICV and CCV requirements as outlined in the applicable section of the SOP.

Note: An NCM must be initiated to denote this situation.

Poor Performer List
2-chloroethyl vinyl ether
Acrolein
Carbon disulfide
Methyl Acetate
Pentachloroethane
Vinyl Acetate

Attachment 11
Procedures for Evaluation of Tentatively Identified Compounds (TICs)

Tentatively identified peaks (TICs) are defined by TestAmerica Savannah as:
1) a calibrated analyte that is not part of the list of analytes requested by the client; or
2) a non-calibrated analyte with a response of 10% or greater than the closest internal standard (ISTD).

The laboratory's default procedure is to report the top 20 TICs with the highest concentration.

Note: Internal standards or surrogates added to the sample, whether they are included in the ICAL or not, must not be identified as TICs. For example, the surrogate o-Terphenyl is added to the low-level 8270 surrogate spiking mix but is used as a surrogate only for LL PAH. This compound would be excluded as a TIC. Also, for semi-volatile analyses, routine target volatile analytes included on the EPA CLP OLM04.2 list (e.g., xylenes) are not included as TICs.

Data Evaluation Steps:
Identification of TICs is made by comparison of the mass spectrum to the reference spectrum (peaks with calibration) or by comparison of the mass spectrum to a reference library such as NIST (peaks without a calibration). Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification.

The unknown compounds are tentatively identified using a search of the reference library. If the library search produces a match at or above 85%, report that compound. If the library search produces more than one compound at or above 85%, report the first compound (the highest match quality). If the library search produces no matches at or above 85%, report the compound as unknown. If possible, provide a general classification of the unknown – for example, unknown aromatic, unknown hydrocarbon, etc.

TICs should be evaluated within the retention time range from the first eluting target or surrogate (whichever is first in the target list) to the elution of the last target compound.

Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum. The relative intensities of the major ions should agree within approximately ±20%.

Molecular ions present in the reference spectrum should be present in the sample spectrum. Note, however, that differences in the spectra may be attributed to over-lapping or co-eluting peaks. If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria are not met exactly, the peak may be considered tentatively identified. The analyst should consult the Department Manager if there are any questions concerning interpretation of spectra.

The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area

of the nearest internal standard that has no interferences. The concentration of TICs with a calibration is the concentration from the calibration curve at the dilution that the target list is reported, even if the concentration is above the calibration range (an "E" value). The concentration of the non-calibrated TIC is as directed in the SOP and as calculated in the Target data system.

Data Processing Steps:

- Evaluate the peaks in the total ion chromatogram for:
  - correct integration
  - peaks that may not have been integrated, paying particular attention to large or odd-shaped peaks.
  - closely eluting peaks
- Manually integrate any peaks that were not detected by the data system and re-process the unknowns.
- Evaluate TICs in Target, as outlined above.
- Merge to TALS.
- Under the TIC tab, reject all "TGT" and "TIC" analytes.
- Right-click and select "Auto-Set TICs Primary". This should set the number of TICs and TGTs requested with the highest concentration to a "Primary" status.
- Highlight all TGT compounds (still under the TIC tab) and right-click.
- Choose "Result Conditions".
- Right-click and choose "Show Assigned Conditions".
- Uncheck all assigned conditions.
- Right-click and choose "Show Flag Suite Conditions".
- Select J, N, and T. Be sure to choose the J-flag defined as "Estimated Result TIC – Manual Flag".

Attachment 12
EPA 624 CCV and ICV Criteria
(Q Table)

Analyte	Criteria* (ug/L)
Benzene	12.8-27.2
Bromodichloromethane	13.1-26.9
Bromoform	14.2-25.8
Bromomethane	2.8-37.2
Carbon tetrachloride	14.6-25.4
Chlorobenzene	13.2-26.8
Chloroethane	7.6-32.4
2-chloroethyl vinyl ether	D-44.8*
Chloroform	13.5-26.5
Chloromethane	D-40.8
Dibromochloromethane	13.5-26.5
1,2-Dichlorobenzene	12.6-27.4
1,3-Dichlorobenzene	14.6-25.4
1,4-Dichlorobenzene	12.6-27.4
1,1-Dichloroethane	14.5-25.5
1,2-Dichloroethane	13.6-26.4
trans-1,2-Dichloroethene	13.9-26.1
1,1-Dichloroethene	10.1-29.9
1,2-Dichloropropane	6.8-33.2
cis-1,3-Dichloropropene	4.8-35.2
trans-1,3-Dichloropropene	10.0-30.0
Ethylbenzene	11.8-28.2
Methylene chloride	12.1-27.9
1,1,2,2-Tetrachloroethane	12.1-27.9
Tetrachloroethene	14.7-25.3
Toluene	14.9-25.1
1,1,1-Trichloroethane	15.-25.0
1,1,2-Trichloroethane	14.2-25.8
Trichloroethene	13.3-26.7
Trichlorotrifluoromethane	9.6-30.4
Vinyl chloride	0.8-39.2

*These values are given in ug/L (i.e., concentration ranges). The laboratory has converted these values into percent recovery limits to be used to assess CCV, ICV, LCS/LCSD, and MS/MSD.

18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial, grammatical, and formatting changes made. Boilerplate text added.
- Added note that cut-resistant gloves should be worn, or other hand protection material used, when opening and closing VOA vials. Section 5.0
- Added section to describe analytical data system, software, and hardware. Section 6.2
- Added note that if an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required. Section 9.1.1 and Section 9.1.2
- Clarified matrix spike frequency for EPA 624 to illustrate 10% frequency (i.e., this equates to 1 MS and 1MSD for a batch of 10 or less samples or equates to 1 MS (from sample 1-10), 1 MS (from sample 11-20), and 1 MSD for a batch of 11-20 samples.) Section 9.1.2
- Added note that some programs and agencies do not allow the use of quadratic curves and to refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited. Section 9.2.3.2.1
- Replaced reference to "Ottawa sand" with "blank sand". Section 7.2.2 and Section 10.1.4
- Clarified Example Analytical Sequence to include LCSD (if insufficient sample is provided for MS/MSD). Section 10.2.7 and Attachment 1
- Added reference to TALS Historical Data Tracker feature. Section 11.1.3
- Corrected equation for determination of final concentration. Note: this change simply corrects a typo in the SOP with regards to referencing % Solids versus % Moisture and does not reflect a change in procedure. Section 11.2.3
- Clarified requirements and frequency for RLVs, MDL Studies, and MDLVs to be consistent with SOP SA-QA-07 and to include the quarterly frequency as defined by DOD. Section 12.1 - 12.3 and Attachment 3
- Updated Method Modifications and Clarifications Section to include information on surrogates used by the laboratory. Section 16.2.13
- Revised expiration date for Gas Standards to be 1 week from the date of opening of each mini-Nert vial. Also added this information to Method Modifications and Clarifications Section. Attachment 9 and Section 16.2.12 (Corporate Internal Audit Finding, May 2010)
- Added note that unsupervised work must not begin until acceptable IDOC is obtained. Attachment 3
- Added section on troubleshooting. Attachment 4
- Updated TIC procedure for consistency with SOP SA-QA-08. Attachment 11
- Incorporated procedures and QC requirements for SM6200B.
- Removed the Instrument Blank section (9.2.5) from the SOP.

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: VOA CANISTER ANALYSIS

(SUPERSEDES: KNOX-MS-0001, Revision 11)

Prepared By: _____

Reviewed By: _____ 4/28/11
Technical Specialist

Approved By: _____ 04/29/11
Quality Assurance Manager

Approved By: _____ 4-28-11
Environmental, Health and Safety Coordinator

Approved By: _____ 4/29/11
Laboratory Director

1. Scope and Application

1.1. The purpose of this standard operating procedure is to define the procedures and quality control necessary to analyze samples collected in SUMMA®, TO-Can®, SilcoCan® or similarly passivated stainless steel canisters.

1.2. This procedure is applicable to the analysis of ambient air, indoor air, landfill gases, soil gases, vapor intrusion, and other gaseous samples. It is based on EPA Methods TO-14A and TO-15.

1.2.1. See Appendix I for the list of target analytes and reporting limits.

1.3. Responsibilities to perform this procedure in the lab are as follows:

Position	Responsibilities
Analyst	- Prepares and analyzes samples - Summarizes/assembles data package - Reviews the data package
Team/Group Leader	- Schedules/assigns analyses - Reviews data package

2. Summary of Method

2.1. Microscale Purge and Trap (MSPT): A precisely measured aliquot is removed from the canister or Tedlar bag and concentrated on a cryogenic trap. The cryogenic trap is desorbed. Polar and nonpolar compounds are quantitatively transferred to a subambient Tenax™ trap. Most of the water remains on the Cryotrap and CO2 passes through the Tenax trap and is vented. The Tenax™ trap is thermally desorbed to the on-column cryofocuser. Sample components are separated by temperature programmed gas chromatography and detected with a quadrupole mass spectrometer.

2.2. The compounds analyzed by this method are listed in Appendix I, Table 1.

3. Definitions

3.1. Canister - a stainless steel container, typically 6-liter volume, equipped with a stainless steel shut-off valve, suitable for use from vacuum to 40 psig. 1-L cans are available for reduced volume analysis.

3.2. SUMMA® Passivation - a proprietary treatment process used to deactivate stainless steel surfaces. It produces a pure chrome/nickel oxide surface that features a high level of inertness.

3.3. Absolute pressure - pressure measured with reference to absolute zero pressure, expressed as kpa, mmHg, or psia.

3.4. Gauge pressure - pressure above atmospheric pressure as measured by a standard gauge. Zero gauge pressure is equal to ambient atmospheric pressure, expressed as mmHg, inches Hg, or psig.

3.5. Polar compound - Oxygen-containing compound capable of forming hydrogen bonds in water; compound having significant solubility in water.

3.6. Batch – A batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same 24 hour time period. The Quality Control batch must contain a blank and a Laboratory Control Sample (LCS). Refer to the QC Program document (QA-003, current revision) for further details of the batch definition.

3.7. Additional definitions can be found in the TestAmerica Knoxville QAM glossary.

3.8. Tedlar bag - Tedlar bags are manufactured from PVF (Tedlar) film with a polypropylene valve and septum. Various volume capacities available.

4. Interferences

4.1. Only compounds having both a similar mass spectrum and GC retention time would be expected to interfere in the method. The most common occurrence of this would be with structural isomers.

4.2. Large concentrations of water, methane, or carbon dioxide may limit the size of the aliquot that can be effectively cryotrapped. This may elevate the quantitation limits obtainable for samples of this type.

4.3. Matrix interferences may be caused by non-target contaminants that are present in the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination, or evaluate the next sample for blank acceptance criteria. The autosampler and concentrator may require extensive bake-out and cleaning after a high-level sample.

5. Safety

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Procedures are carried out in a manner that protects the health and safety of all associates. Exposure to chemicals and samples will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made. The preparation of all standards, reagents and glassware cleaning procedures that involve solvents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.3. All work must be stopped in the event of a known or potential compromise to the health and safety of any associate. The situation must be reported **immediately** to a laboratory supervisor.

5.4. Specific Safety Concerns or Requirements

5.4.1. The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.4.2. The autosampler, concentrator, gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.4.3. The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.4.4. There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.4.5. Liquid Nitrogen is used to cool traps in the concentrator. The analyst needs to be aware of locations of those zones and warm them to room temperature prior to working on them. The effluent of the traps must be vented to a laboratory hood or outside the room.

5.5. Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in**

the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Acetonitrile	Flammable Poison	40 ppm-TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Acetone	Flammable	1000 ppm (TWA)	Inhalation may cause coughing, dizziness, dullness, and headache. Contact causes redness, pain, drying and cracking of the skin. Vapors cause eye irritation. Eye splashes may cause severe irritation, with stinging, tearing, redness and pain.
Benzene	Carcinogen Flammable Poison	1 ppm-TWA 5 ppm-STEL	Toxic by ingestion, inhalation and absorption. Causes headache, nausea, dizziness, weakness and breathing difficulties. This material is irritating on contact with the skin and eyes and may cause permanent eye damage.
Carbon Tetrachloride	Carcinogen Poison	10 ppm-TWA 200 ppm-STEL	Toxic by ingestion, inhalation and absorption. Causes headache, nausea, dizziness and narcosis. Contact with skin or eyes may cause irritation. Consumption of alcohol may increase toxic effects
Chloroform	Carcinogen Irritant	50 ppm Ceiling	Acts as a relatively potent anesthetic. Irritates respiratory tract and causes central nervous system effects, including headache, drowsiness, dizziness. Causes skin irritation resulting in redness and pain. Removes natural oils. May be absorbed through skin. Vapors cause pain and irritation to eyes. Splashes may cause severe irritation and possible eye damage.
1,4-Dichlorobenzene	Irritant	75 ppm-TWA	Can cause irritation by ingestion and inhalation. Causes nausea, vomiting and diarrhea. Contact with material or vapors can cause irritation to skin and eyes.
Vinyl Chloride	Carcinogen Flammable Poison	1 ppm TWA	Toxic by inhalation, ingestion and absorption. Can cause respiratory irritation, dizziness, weakness, fatigue, nausea and headache. Contact with the material can cause eye and skin irritation.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.6. Bulk Nitrogen Usage Procedures - All procedures require full time monitoring at work station and an audible O_2 monitor must be activated when any liquid nitrogen valve is open.

5.6.1. Priming lines for instrument analysis:

5.6.1.1. Turn on O_2 monitor.

5.6.1.2.Set timer to 2 minutes.

5.6.1.3. Open by-pass valve to cool the line (it will vent outside).

5.6.1.4. Activate Timer.

5.6.1.5. Close by-pass valve at end of timer or before (this may require gloves for protection).

5.6.1.6. Turn off O_2 monitor.

5.6.2. Filling of portable liquid N_2 Dewar flask:

5.6.2.1. Turn on O_2 monitor.

5.6.2.2. Set timer to 2 minutes.

5.6.2.3. Open by-pass valve to cool the line (it will vent outside).

5.6.2.4. Activate Timer.

5.6.2.5. Close by-pass valve at end of timer or before (this may require gloves for protection).

5.6.2.6. Position face shield on head.

5.6.2.7. Open valve to portable Dewar flask.

5.6.2.8. Close valve when portable Dewar flask has filled and seal lid with gloves.

5.6.2.9. Turn off O_2 monitor.

5.6.2.10. Open lid on portable Dewar flask and fill trap on canister cleaning apparatus with liquid N_2.

5.6.2.11. Remove face shield and gloves.

6. Equipment and Supplies

6.1. Canisters (SUMMA®, TO-Can®, SilcoCan®), 1, 6-, 15-, and 30-liter sizes, preferably equipped with two valves and integral vacuum/pressure gauge, Restek or equivalent.

6.2. Static gas dilution bottles (SGDB), nominally 2000 ml, with mininert valves, Entech Instruments Inc., or equivalent.

6.3. Syringes, gas-tight, 10 uL, 50 uL, 500 uL, 1000 uL, 2.5 mL, 50 mL, 500 mL, all side port needle, Hamilton, Inc., or equivalent.

6.4. Gas Chromatograph/Mass Spectrometer System, Agilent HP 6890 GC and 5973 MSD or equivalent.

6.5. Fused silica capillary column, 60 m x 0.32 x 1um film DB-5, J&W Scientific, or equivalent.

6.6. Vacuum pump, Model 726.3 TTP, KNF Newberger, or equivalent.

6.7. Canister concentrator system, Model 7100 or 7100A, Entech Instruments Inc., with a Model 7016CA, 16-position auto sampler.

6.8. Gauges: (certified annually):

6.8.1. Test gauge, 0 to 30 in. Hg vacuum, Ashcroft Co., or equivalent

6.8.2. Test gauge, 0-60 psi, Ashcroft Co., or equivalent

6.8.3. Test gauge, 0 to 100 in. Hg pressure, Ashcroft Co., or equivalent

6.8.4. Digital gauge 0 to 30” Hg vacuum, Dwyer or equivalent

6.8.5. Digital gauge 0 to -29.9” Hg vacuum, 0 to 99.9 psi, Dwyer or equivalent

6.9. Tedlar Bags: Variety of sizes. SKC or equivalent.

6.10. Fisherbrand traceable workstation digital barometer, or equivalent (use within certification date from manufacturer)

6.11. Mass flow controller: McMillan model 80SD-4 or equivalent (certified annually)

7. Reagents and Standards

7.1. Helium, ultra high purity, 99.999+%, Air Products, or equivalent.

7.2. Liquid nitrogen, Air Products, or equivalent.

7.3. Nitrogen, ultra high purity, Air Products or equivalent

7.4. Internal/Surrogate Standard (all at 50 ppb) in nitrogen, 2000 psig, Scott Specialty Gases, or equivalent:

CAS NUMBER	Internal Standards	MOLECULAR WEIGHT (ng/n mole)
74-97-5	bromochloromethane	129.4
540-36-3	1,4-difluorobenzene	114.1
3114-55-4	chlorobenzene-d5	117.6
	Surrogate	
460-00-4	4-bromofluorobenzene	175.0

7.4.1. Since there are no response factor requirements, no surrogate requirements, and no second source requirement for internal standards or surrogates from the reference methods, a 5-year expiration date is assigned from the manufacturer's preparation date.

7.4.2. A sufficient volume from the internal/surrogate standard cylinder is transferred to a canister to produce a positive pressure.

7.4.3. The working internal/surrogate standard may be used as long as the pressure in the canister remains above ambient pressure and is not past its expiration date.

7.4.4. The Entech is programmed to add 40 mL of the internal standard/surrogate can. This results in a concentration of 4 ppb/v of internal standard/surrogate (based on 500 mL volume).

7.5. Primary Target Initial Calibration/Laboratory Control Sample and Initial Calibration Verification Standard (2^{nd} source) Gaseous Standards: target compounds, 1000 ppb v/v, vendor-certified high-pressure aluminum cylinder.

7.5.1. An expiration date of one year from the date of vendor certification is assigned to the standard cylinder. This expiration date may be extended through comparison against an unexpired standard that meets the second source standard criteria in Section 10.4, or recertified by the vendor.

7.5.2. The initial calibration and the initial calibration verification standard (2^{nd} source) are from different lots provided by the manufacturer. See section 10.4 for ICV requirements.

7.6. Additional Standards: Neat materials, not contained in the certified cylinders, can be added to a SGDB either individually or as a mix.

7.6.1. If the desired compound is a gas at room temperature, a measured volume is injected into an evacuated canister and pressurized. See section 12.8 for calculation. If the desired compound is a liquid or solid at room temperature, the volume of each compound to be added to the SGDB is

back-calculated to the desired final concentration in the canister. See section 12.5 and 12.6 for calculation.

7.6.2. A cleaned SGDB is heated to approximately 60°C for 24 hours before use. Other SGDB and canister standards are stored at room temperature. If the analytes prove to be plating/condensing in the SGDB at room temperature, then the SGDB is heated to approximately 60°C before use.

7.6.3. Transfer from a SGDB to a canister is performed in a gas-tight syringe equipped with an on-off valve. The syringe is inserted into the SGDB and flushed (primed) several times by filling and evacuating the syringe without withdrawing the syringe from the bottle. The valve is closed after filling the syringe to the desired volume and before withdrawing the syringe from the bottle. The syringe is quickly removed from the SGDB and inserted into a canister capped with a septa. The valves to the syringe and the can are opened allowing the contents of the syringe to transfer. If using a heated syringe, this step must be completed quickly before the syringe cools.

7.7. Primary and Second Source “High” Standard (for a 15-L can; for a 6-L can, reduce the volume of standards appropriately).

7.7.1. 2 mL of reagent water is injected through a septum (inserted into a ¼ in. nut) into a clean evacuated (approx. -29" Hg) 15-L canister. A nitrogen line is attached and opened to blow the water from the valve area into the can, to the desired vacuum/pressure.

7.7.2. 200 ppb(v/v) example: 7.5 liters of a 1000 ppb(v/v) high pressure standard is added to the canister through a mass flow controller (for example, 107 min & 8 seconds at 70 mL/min.). The canister is then pressurized with nitrogen to 2.5 atm for a final volume of 37.5 L and a final concentration of 200 ppb(v/v).

7.8. Working Level Standard Preparation:

7.8.1. 100 uL of reagent water is injected through a septum (inserted into a ¼ in. nut) into a clean evacuated (approx. -29" Hg) 6-L canister. A nitrogen line is attached and opened to blow the water from the valve area into the can, to the desired vacuum/pressure.

7.8.2. 20 ppb(v/v) from a 200 ppb(v/v) example: 1.5 L of a 200 ppb(v/v) standard is added to a 6-L canister with a mass flow controller (for example, 21 min & 26 seconds at 70 mL/min.). The canister is pressurized

to 2.5 atm for a final volume of 15 L and a final concentration of 20 ppb(v/v).

7.9. Alternate concentrations of the high and working standards may be made as long as the calculations, concentrations and volumes are adjusted appropriately and preparation is clearly documented in the standard preparation logbook.

7.10. Approved SGDB and canister stock standards (section 7.6) may be used for 6 months from the date of preparation or the earliest expiration of parent standard, whichever comes first. Working canister standards (7.7 and 7.8) may be used for two months from the date of preparation or the earliest expiration of parent standard, whichever comes first.

7.11. Mixes and neat compounds (that are not in SGDB, cans, or cylinders) are stored at the manufacturer's recommended storage conditions.

8. Sample Collection, Preservation and Storage

8.1. Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, Receipt and Log-In of Commercial Samples, current revision.

Container Type	Preservative	Holding Time
Canister	None	30 days from sample collection to sample analysis.
Tedlar bag	None	The analyst must either analyze the sample in the tedlar bag within 72 hours from collection, or transfer the sample from the tedlar bag to a canister within 72 hours from sample collection. If the sample in the tedlar bag is transferred to a canister within 72 hours from collection, the holding time is 30 day from sample collection.

9. Quality Control

9.1. Internal/Surrogate Standards

9.1.1. Internal standards are added to each analytical standard, blank and sample. The acceptance criteria for each internal standard's area for every analysis must be $\pm$ 40% recovery of the internal standard area from the continuing calibration standard. The acceptance criteria for each internal standard's retention time in every analysis must be within $\pm$ 20 seconds (0.33

minutes) of the internal standard retention time from the continuing calibration standard. See Section 7.4 for preparation of the working internal standard/surrogate standard canister.

9.1.1.1. If the internal standard areas for a sample are outside their limits, the cause is determined. If it is a result of a system problem, then the problem must be corrected and the sample reanalyzed with acceptable results. If it is the result of a matrix effect, the sample must be reanalyzed to confirm this, unless the effect is caused by high levels of target or non-target compounds co-eluting with or interfering with the surrogate or internal standards. If there is not an obvious matrix effect, the sample must be reanalyzed without subsequent dilution unless a dilution is needed to bring target analytes within the instrument calibration range.

9.1.2. The reference methods do not require addition of surrogates. Bromofluorobenzene is used as a surrogate, and recovery must fall within 60% to 140%.

9.1.2.1. Since the concentration of the surrogate is constant in all initial calibration points, the response factor of the surrogates in the daily calibration may be substituted as a one-point calibration to calculate the recoveries in the samples and QC.

9.2. System Blanks (Method Blanks)

9.2.1. For each 24-hour tune in which samples are analyzed or every 20 samples, whichever is more frequent, an acceptable system blank must be analyzed before samples analysis.

9.2.1.1. A system blank is defined as a cleaned canister, humidified with reagent water and filled with UHP nitrogen.

9.2.1.2. Typically, a 30L canister, humidified with 200 uL of reagent water and pressurized to 25-30 psi with nitrogen is used for the blank. A lot check from the can cleaning system can be used as a system blank (See section 9.5).

9.2.1.3. An acceptable system blank is one with all target analytes less than 0.2 ppb/v. The data may still be reported if the concentration of the analyte is less than the laboratory reporting limit (see Table 1), and meets internal standard and surrogate requirements in section 9.1. Any samples associated with a method blank with results above 0.2 ppb/v are flagged in the data report. If a blank has a reportable result between

the RL and the MDL, the associated samples are also flagged with a B qualifier. A blank value above the RL may be accepted if the sample result is greater than 10 X the blank value or not detected above the RL.

9.2.2. If a system blank does not meet the above criteria, then the blank must be reanalyzed or a new blank prepared and analyzed with acceptable results.

9.3. Laboratory Control Standard (LCS)

9.3.1. The LCS is defined as a working standard made by the same method as analytical standards, using the same source materials. It is used to assess analytical control of this procedure. The LCS is analyzed every 24 hour tune or every 20 samples, whichever is more frequent. See Section 7.5, 7.7, 7.8, and 7.9 for details regarding the preparation of the LCS standard canister.

9.3.1.1. The daily calibration verification may also serve as the LCS as long as it meets the criteria of both the LCS and the daily calibration verification.

9.3.2. All target analytes requested are control analytes in the LCS. Sporadic marginal exceedances are allowed where more than 11 analytes are requested. See the table below. The recovery of all target analytes must be within 70-130%, with the marginal exceedence allowance of 60-140% recovery as indicated in Table 1. Provisory analytes must be within 60-140% recovery with the marginal exceedence allowance of 50-150% recovery. See Appendix I Table 1 for the provisory analytes. Naphthalene, n-Dodecane and 1,2,3-Trichlorobenzene have assigned control limits of 40-140%.

Number of target analytes in LCS	Allowable # of marginal exceedances of LCS control limits
>90	5
71 - 90	4
51 - 70	3
31 - 50	2
11 - 30	1
< 11	0

9.3.3. The internal standards and surrogate must pass criteria specified in section 9.1.

9.3.4. An LCS is considered to be “out of control” if any target analyte is outside marginal exceedance limits, or if the total number of marginal exceedances is more than the allowed number.

9.3.5. If marginal exceedances are observed, the analyst must review the previous LCS (e.g., review the control chart) for that instrument for each analyte marginally exceeding the control limits to determine if the marginal exceedance is a consecutive occurrence. If there are two consecutive marginal exceedances for the same analyte, the LCS is considered “out of control” and an NCM must be generated and corrective action taken.

9.3.5.1. When evaluating the control chart, the analyst should also check whether there was more than one out of the last three consecutive LCSs outside control limits. If more than one out of the last three LCSs was outside the LCS control limits but within the marginal exceedance limits, then the analyst should evaluate the system for non-random systematic trends.

9.3.6. Samples analyzed along with an LCS determined to be “out of control” shall be considered suspect and the samples reprocessed and re-analyzed or the data reported with appropriate data qualifying codes.

9.3.6.1. If the LCS recovery for a target analyte is biased high outside acceptance limits and that target analyte is not detected in any of the associated samples above the reporting limit, the sample data may be reported with qualification in the project narrative. Analytes that are biased high in the LCS and not detected in the associated samples are counted in the total number of allowable marginal exceedances.

9.4. Duplicate Analysis

9.4.1. A duplicate is analyzed with every 20 samples. It is not reported unless specifically requested

9.4.2. Selected samples for duplicates are rotated among client samples, and must not include trip blanks or field blanks.

9.4.3. The acceptance criteria for the duplicate analysis are $\leq$ 25% RPD for target compounds that are greater than 5 times the RL. No criteria for methanol and n-butanol. The calculations are given in section 12.18.

9.4.4. If the RPD is outside acceptance criteria for the duplicate, the sample is rerun once. If upon reanalysis, the duplicate does not meet acceptance criteria, the original sample data is qualified in the project narrative.

9.4.5. Due to limited sample volume, duplicates are not performed for Tedlar bags unless otherwise specified in the project requirements.

9.5. Canister Blank Checking

9.5.1. From each cleaned lot of canisters, a canister is selected, humidified with 40 μL reagent water, and pressurized with UHP nitrogen. (See SOP KNOX-SC-0001, current revision, "Canister Cleaning and Preparation").

9.5.2. A blank check is analyzed within 24 hours of a valid tune check and calibration. Alternatively, a calibration at the reporting limit may be used to quantitate results.

9.5.3. Note: If the CCV recovery for a target analyte is biased high outside acceptance limits and that target analyte is not detected in any of the associated samples above the reporting limit, the canister blank check sample data may be reported with qualification in the project narrative if submitted to the client.

9.5.4. A blank check passes if there are no target analytes above the reporting limit, and the internal standards pass criteria in section 9.1. Cans are considered certified "clean" if the result for all analytes are below 0.2 ppb/v. However the can may still be used to collect samples if the concentration of the target analyte is less than the reporting limit. If analytes are detected in the can being certified as clean above 0.2 ppb/v and below the reporting limit, this will be noted on the blank check quantitation report.

9.5.5. If a blank check canister does not pass, the can may be re-analyzed. If the acceptance criteria are still not met, the entire lot of canisters must be re-cleaned, and a blank check from the re-cleaned lot must pass.

9.6. Nitrogen check

9.6.1. Before a new nitrogen cylinder is used for pressurization of samples or standards, it must be analyzed as a blank and pass all the criteria in section 9.2.1.3.

9.7. Annual gauge calibration: The gauges and mass flow controllers that are used in calculations to measure cylinder and canister pressure or vacuum, and calibration standard flow rates must be certified annually. Digital barometers may be used

within the vendor assigned expiration date, then either calibrated annually or replaced.

10. Calibration and Standardization

10.1. Instrument Conditions: The following steps are part of the software's automatic tuning procedure and are performed as needed.

10.1.1. Mass assignments of the mass spectrometer are checked and adjusted using perfluorotributylamine (PFTBA FC43).

10.1.2. The mass spectrometer is tuned to meet the criteria for BFB (see Figure 1a and 1b).

10.1.3. The mass spectrometer is adjusted to minimize noise (see instrument manufacturer instruction manuals).

10.1.4. See Appendix III for examples of GC/MS and GC instrument parameters.

10.2. Daily Tune Check

10.2.1. 50 ng or less of BFB is analyzed for each 24-hour time tune period; the 24-hour time period begins at the moment of injection of BFB. All abundance criteria for BFB in Figure 1a or 1b must be met before the analysis of standards, QC samples or client samples. Figure 1a is the TO-14A method criteria, which is more stringent than the TO-15 method criteria (Figure 1b). The default criteria is the TO-14A tuning criteria (Figure 1a). However if the tune fails TO-14A criteria but meets TO-15 criteria, then samples logged in for TO-15 may be analyzed, but not samples for TO-14A.

10.2.2. The BFB must be acquired in the following manner: Three scans (the apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

10.2.3. Once the BFB passes criteria, the same mass spectral conditions used for the BFB must be used to acquire the data in that 24-hour tune period, until the next BFB event.

10.2.4. Correction Action: If the daily tune check does not meet acceptance criteria for the requested method, refer to Section 10.1 and retune the mass spectrometer. Also refer to Section 11.7 for guidance on instrument troubleshooting. An acceptable daily tune check must be obtained before initial calibration and daily calibration verification.

10.3. Initial Calibration

10.3.1. The GC/MS system must be calibrated with at least 5 concentrations that span the monitoring range of interest. The dynamic range of the curve is generally 0.2 ppb v/v to 40 ppb v/v based on 200 mL sample analysis for normal level reporting limits for most analytes, and 0.08 ppb v/v to 16 ppb v/v based on 500 mL sample analysis. The concentration of the low standard of the calibration must be at or below the reporting limit. If quadratic fit is required, there must be at least 6 points. See Appendix IV for the recommended calibration amounts.

10.3.2. See chart below to obtain the typical desired levels of quantitation. This is a typical schematic of the calibration; however the standard can concentration, calibration levels and calculated concentrations may be different, as long as the calibration rules in 10.3.10 and 10.3.12 are followed. See Appendix IV for the calibration table of analytes. If the actual standard amount trapped is greater than 5% from the programmed volume, the actual volume trapped is documented and used in calculations.

Example 8 standard canister calibration series for 200ml analysis (ppb/v/v)

Standard can concentration (ppbv/v)	0.2	0.2	0.4	0.8	2.5	5	10	20	40
# mLs analyzed	100	200	200	200	200	200	200	200	200
Calculated concentration (ppb v/v)	0.1	0.2	0.4	0.8	2.5	5	10	20	40

10.3.3. See Appendix I, Table 1 for suggested quantitation ions.

10.3.4. A calibration curve is valid for all target analytes if the relative standard deviation (RSD) of the relative response factors is $\leq$30% for each target analyte, with the following allowance: up to two target analytes may have an RSD $\leq$ 40%.

10.3.5. The internal standard area response at each calibration level must be within 40% of the mean area response over the initial calibration range for each internal standard.

10.3.6. The retention time (RT) shift for each of the internal standards at each calibration level must be within 20 seconds of the retention time of the mean calibration for each internal standard.

10.3.7. Each analyte at each level must be within 0.06 RRT units of the mean RRT.

10.3.8. If the curve is acceptable and there is time remaining in the 24-hour tune, blanks, LCS's and samples may be analyzed.

10.3.9. The concentrations in the samples, LCS's and blanks are calculated using the response factors from the initial calibration curve.

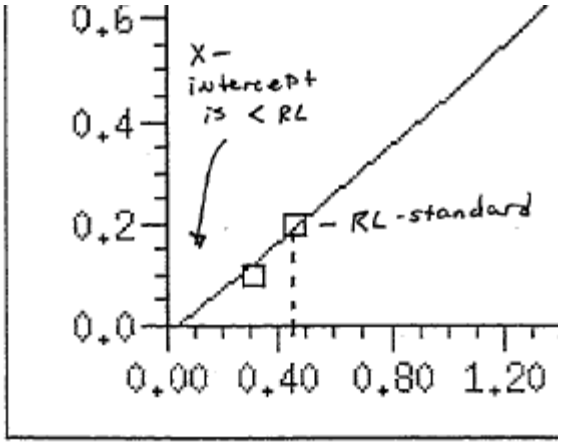
10.3.10. Linear or quadratic curve fits may be used. Use of 1/Concentration^2 weighting may be used to improve the accuracy of quantitation at the low end of the curve. The analyst should consider instrument maintenance to improve the linearity of response. The coefficient of determination (r^2) must be $\geq$ 0.990.

10.3.11. Analyst may elect to drop points from the calibration to improve subsequent quantitation. The rules for dropping points are:

- May drop points below the RL as long as there is a point remaining at or below the RL.
- May drop high points, decreasing linear range.
- May NOT drop a point between points.

10.3.12. Rules for curve use:

- The r^2 value obtained from Target must be $\geq$0.990.
- At least 5 points must be used for average or linear curve.
- At least 6 points must be used for a quadratic curve.
- For quadratic curves, the tangent line to the slope of the curve must be continuous and have either only positive or negative slopes (i.e., no parabolas or breaks in the curve). Quadratic curves cannot be used to extend the calibration range. Quadratic curves are only used if the compound has historically exhibited a nonlinear response.
- Forcing through zero is allowed. To activate "force through zero" in Target, select "Force" for "curve origin". "Include" zero for "curve origin" must NOT be used.
- If "forced through zero" is not used, the X and Y-intercept must be below the RL.
- To evaluate the Y-intercept, multiply the positive Y-intercept value by the internal standard amount. The resulting value must be less than the RL.
- Negative Y-intercepts indicate an X-intercept. To evaluate the X-intercept, the intercept from the slope must be less than the intercept of a vertical line from the reporting limit standard drawn down to the X-intercept. See example below:



10.3.13. The high point calibration standard is checked for saturation. If a quantitation ion saturates the mass spectrometer, the analyte will be removed from the calibration series, and the next highest concentration is checked for saturation as well. Saturation is present when an ion peak in Target reaches a Y axis maximum of 8.4×10^6.

10.3.14. Corrective Action: If the initial calibration fails to meet acceptance criteria a new instrument calibration must be analyzed that meets the acceptance criteria listed in Section 10.3.4. through 10.3.7. Also refer to Section 11.7. for guidance on troubleshooting the instrument. The initial calibration must meet acceptance criteria for all requested analytes prior to sample analysis.

10.4. Initial Calibration Verification (ICV)

10.4.1. The ICV is a second source standard containing all the target compounds in Appendix I, Table 1. The ICV is analyzed after the initial calibration and before any samples are analyzed.

10.4.2. A working standard from an independently prepared stock containing all analytes is also analyzed as the ICV for analytes not included in Table 1.

10.4.3. For each analyte, a percent recovery (%R) is calculated using the response factor from the initial calibration. The ICV is valid for all analytes if the %R is between 65% and 135% for each analyte

10.4.4. Corrective Action: If the ICV fails to meet acceptance criteria a new ICV calibration must be analyzed that meets the acceptance criteria listed in Section 10.4.3. Also refer to Section 11.7. for guidance on troubleshooting the instrument. The initial calibration verification must meet acceptance criteria for all requested analytes prior to sample analysis.

10.5. Daily Calibration Verification

10.5.1. A mid-level standard is analyzed following the daily tune check (section 10.2) as the calibration verification standard. Typically, this is 100 mL of the 5-ppb/v can. Alternate concentration/volumes may be analyzed.

10.5.2. For all target analytes, a percent difference (%D) or percent drift is calculated using the response from the calibration verification standard and compared to the current initial calibration curve.

10.5.3. A calibration verification standard is acceptable if the %D or % drift is $\leq$30% for all target analytes. However, data may be reported from a calibration verification standard outside 30% as long as the target analytes meet the LCS criteria stated in section 9.3.2. Analytes greater than 30% D in the CCV must be clearly noted in the data report.

10.5.4. The daily calibration verification may also serve as the LCS as long as it meets the criteria of both the LCS (section 9) and the daily calibration verification.

10.5.5. Corrective Action: If the calibration verification standard does not meet the above criteria, corrective action must be taken and/or a new initial calibration performed unless project specific analyte QC criteria are met. Corrective action may include a reanalysis of the calibration verification standard. If reanalysis of the standard does not meet acceptance criteria, further corrective action may include performing instrument maintenance, or preparation of a new working calibration verification standard. Also refer to Section 11.7. for guidance on troubleshooting the instrument. Either of these corrective actions must be followed by successful analysis of the calibration verification standard and reanalysis of any affected samples. If these corrective actions do not result in acceptable calibration verification, a new initial calibration must be performed.

10.5.6. If the recovery for a target analyte is biased high outside acceptance limits and that target analyte is not detected in any of the associated samples above the reporting limit, the sample data may be reported with qualification in the project narrative.

10.5.7. Since the concentration of surrogate is constant in all initial calibration points, the response factor of the surrogates in the daily calibration may be substituted as a one-point calibration to calculate the recovery in the samples and QC.

11. Procedure

11.1. Canister Preparation

11.1.1. Use the following guidelines when checking a sample upon receipt:

- Tedlar bags are inspected to ensure that the valve is closed and the bags are not leaking. Bags must be analyzed or transferred to a can within 72 hours of collection. Tedlar bags are analyzed directly from the bag or transferred to an evacuated can within 72 hours of sampling. If the entire bag is transferred to a can, the bag needle valve septum is pierced with a needle attached to a 1-L or a 6-L evacuated can, and the entire contents transferred. If only a portion of the bag is to be transferred, a measured aliquot of the bag is transferred via a clean syringe through a septum attached to the top of a 1-L or a 6-L humidified can. After transfer, the can is then pressurized to a positive pressure and the pressure is recorded. The lab default is to analyze Tedlar bags at a 20x dilution. Based on a default dilution factor at the bench, the RLs and MDLs will be 20 times higher for Tedlar bag analysis. (If a client requests lower RLs than 20x the standard this will need to be communicated to the lab via special instructions.) If a client requests RLs lower than 20x and the client is supplying the tedlar bags, the PM should request that the client send an unused bag to be logged in and analyzed along with their samples as a media blank check. If a client requests RLs lower than 20x and TestAmerica Knoxville is supplying the tedlar bags, the PM should have sample receiving set aside and log in a Tedlar bag from the same lot as a media check.

- For canisters, attach a vacuum/pressure gauge to the top of the can with a line attached to an evacuated cylinder. With the sample can closed, open the valve on the evacuated cylinder to remove air in the line and gauge. Observe that the vacuum is near -27” Hg or lower. If the vacuum is higher, evacuate the cylinder to lower than -27” Hg to prevent the contents of the cylinder from backflushing into the sample can. Close the evacuated cylinder valve and open the sample valve. Observe and record the vacuum/pressure reading of the sample.
- 1-L cans received between -10” Hg vacuum and a positive pressure are ready for a 20 mL analysis. If more volume is expected to be analyzed, the can will have to be pressurized in order to obtain more volume from the can.
- Cans received with a high positive pressure are assumed to have been collected with an active sampler and are analyzed as received.

Summary of Corrective Actions for 6 Liter Cans Collected Using Flow Controllers

Can Pressure	Lab Action	PM Action	NCM Needed?	Narrative Content
If can received open	Notify PM by email.	1. Inform client of the potential contamination. 2. If cancelled, initiate NCM and email Air Group. 3. If not cancelled, email Air Group to proceed with analysis.	Yes, if analysis cancelled	1. If cancelled, narrate. 2. If analyzed, narrate possibility of contamination.
Ambient to -9.9 (200 mL) Ambient to -7.5 (500 mL)	Proceed with analysis.	None	No	None
-10 to -23.9 (200 mL) -7.6 to -23.9 (500 mL) (inches Hg)	1. Pressurize to above ambient. 2. Proceed with analysis; if possible, analyze more volume to lower the dilution factor.	None	No	If RL not achieved due to insufficient volume, narrate dilutions that were necessary due to insufficient sample.
-24 to -25 (inches Hg)	1. Pressurize to above ambient. 2. Verify flow controller was working properly. 3. Notify PM by email, wait for client response.	1. Notify client that can pressure should have been higher if flow control was used properly and that there is not enough sample for analysis without dilution. 2. If cancelled, initiate NCM and email Air Group. 3. If not cancelled, email Air Group to proceed with analysis.	Yes, if analysis cancelled	1. If cancelled, narrate 2. Narrate dilutions that were necessary due to insufficient sample.
-26 or lower (inches Hg)	1. If trip blank, pressurize to above ambient, proceed with analysis using DF = 1. 2. Verify flow controller was working properly. 3. If not a trip blank, pressurize to above ambient. Notify PM by email, wait for client response.	1. Notify client that can pressure should have been higher if flow controller was used properly and that there is not enough sample for analysis without dilution. 2. If cancelled, initiate NCM and email Air Group. 3. If not cancelled, email Air Group to proceed with analysis.	Yes, if analysis cancelled	1. If cancelled, narrate. 2. Narrate dilutions that were necessary due to insufficient sample, dilution factor/results are estimated. "EST" flag on all detects

Summary of Corrective Actions for 6 Liter Cans Collected NOT Using Flow Controllers ("grab" sampling)

Can Pressure	Lab Action	PM Action	NCM Needed?	Narrative Content
If can received open	Notify PM by email.	1. Recommend to client that sample be cancelled due to possible contamination. 2. If cancelled, initiate NCM and email Air Group. 3. If not cancelled, email Air Group to proceed with analysis.	Yes, if analysis cancelled	1. If cancelled, narrate 2. If analyzed, narrate possibility of contamination.
Ambient to -9.9 (200 mL) inches Hg Ambient to -7.5 (500 mL) inches Hg	Proceed with analysis.	None	No	None
-10 to -23.9 (200 mL) -7.6 to -23.9 (500 mL) (inches Hg)	1. Pressurize to above ambient. 2. Proceed with analysis; if possible analyze more volume to lower the dilution factor.	None	No	If RL not achieved due to insufficient volume, narrate dilutions that were necessary due to insufficient sample
-24 to -25 (inches Hg)	1. Pressurize to above ambient. 2. Notify PM by email, wait for client response.	1. Notify client that can pressure should have been higher if grab can was used properly and that there is not enough sample for analysis without dilution. 2. If cancelled, initiate NCM and email Air Group. 3. If not cancelled, email Air Group to proceed with analysis.	Yes, if analysis cancelled	1. If cancelled, narrate 2. Narrate dilutions that were necessary due to insufficient sample.
-26 or lower	1. If trip blank, pressurize to above ambient, proceed with analysis using DF = 1. 2. If not a trip blank, pressurize to above ambient. Notify PM by email, wait for client response.	1. Notify client that can pressure should have been higher if grab can was used properly and that there is not enough sample for analysis without dilution. 2. If cancelled, initiate NCM and email Air Group. 3. If not cancelled, email Air Group to proceed with analysis.	Yes, if analysis cancelled	1. If cancelled, narrate 2. Narrate dilutions that were necessary due to insufficient sample, dilution factor/results are estimated. "EST" flag on all detects

11.1.2. If the sample must be pressurized, attach the nitrogen line to the can using a quick-connect fitting. Turn on the nitrogen, adjust the line pressure to approximate desired final pressure, and open the can. Remove the nitrogen line and connect a pressure gauge to obtain the pressure reading.

11.1.3. Measure the initial and final pressure/vacuum of the canisters using an NIST traceable, certified vacuum and/or pressure gauge.

11.1.4. The barometric pressure, initial pressure/vacuum and final pressure/vacuum are recorded in a laboratory worksheet and used to

calculate the dilution factor caused by pressurizing the can to working conditions.

11.1.5. The canister is allowed to equilibrate for approximately one hour before analysis. If the canister was pressurized to greater than 15 psig, pressure is released from the canister to bring the pressure below 15 psig. For autosampler volumes scheduled to be below 50 mL, the can pressure must be reduced to below 7 psig to more accurately measure the volume injected.

11.1.6. If necessary, this canister is further diluted by the dilution methods discussed in sections 11.3, 11.5, and 11.6.

11.2. Following a successful initial or calibration verification and prior to analysis of actual samples, an acceptable system blank and LCS must be analyzed (see sections 9.2 and 9.3). Following successful system blank and LCS analysis, actual sample analysis may begin. The LCS and blank are analyzed every 24 hour tune or every 20 samples, whichever is more frequent.

11.2.1. The desired sample size of each sample to be analyzed is determined by screening the cans according to SOP KNOX-MS-0010, current revision, Volatile Analyte Screening By Purge and Trap. The standard aliquot size is 200 mL for standard reporting limit work or 500 mL for low-level work. Sample volume injected can range from 10 mL to 1000 mL. For sample volumes below 50 mL, the can pressure must be reduced to below 7 psig to more accurately measure the volume injected. Volumes larger than 1000 mL can cause trap freeze-up when high humidity samples are trapped. If samples have been adequately pressurized with nitrogen, have been diluted, or only a small amount of sample collected in the can, then volumes larger than 1000 mL may be trapped, and the internal standards and surrogate monitored closely for breakthrough or freeze-up problems.

11.2.2. The pressure of each sample canister is checked. If the pressure is above 15 psig, the excess pressure is vented.

11.2.3. Each sample, volume (aliquot), method, and autosampler position are entered into the Entech sequence table.

11.2.4. If necessary, the automated flush function is used to sweep each autosampler line in the name list with helium.

11.2.5. The cans are then securely tightened onto the autosampler with the canister valves closed.

11.2.6. The sample work order numbers, and other pertinent information such as the GC method and the processing method are entered into the GC/MS sequence table.

11.2.7. The sample volume programmed, the can number, and the can's dilution factor are noted in the analytical run log. The Entech sequence, the GC/MS sequence table and the run log are verified to be in order.

11.2.7.1. If the actual sample amount trapped is greater than 5% from the programmed volume, the actual volume trapped is documented and used in calculating the results.

11.2.8. The Entech autosampler is started and the GC/MS acquisition program is started. (Note: The scan and GC parameters are controlled by the GC/MS method.)

11.2.9. 40 ml of the surrogate/internal standard is trapped on the Entech concentrator prior to sample introduction.

11.2.10. The analysis proceeds automatically for each name in the Entech autosampler program.

11.2.11. The internal standards and surrogate must pass all the criteria specified in section 9.1.

11.3. Autosampler Dilutions

11.3.1. Volumes of 10 to 1000 mL may be analyzed by the autosampler (see section 11.2.1). The standard aliquot is 200 mL for standard reporting limit work and 500 mL for low-level work.

11.3.2. If an analyte found in the sample is over the curve by less than a factor of twenty (based on 200 mL nominal volume) or fifty (based on 500 mL nominal volume), then the aliquot size of the sample may be reduced to a volume as low as 10 mL. This dilution factor is multiplied with all other dilution factors for this sample to obtain the final dilution factor.

11.3.3. If a dilution is performed to bring one or more analytes within the calibration range, the analyte having the highest concentration should not be diluted to less than 20% of the calibration range unless there are significant amounts of non-target compounds present.

11.3.4. If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non target peaks are less than five times the height of the internal standards, then the sample is

reanalyzed at a more concentrated dilution (up to the nominal volume). This requirement is approximate and subject to analyst judgment.

11.3.5. Only the most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4. Water addition

11.4.1. Humidity plays an important role in the recovery of certain target compounds, particularly polar compounds, and water is added to canisters where appropriate. The addition of water helps to stabilize the behavior of these compounds, which might otherwise interact with the interior surface of the canister or with the stainless-steel lines of the sample manifold.

11.4.2. Since it is not practical to know the relative humidity of all canisters received at the laboratory, canisters are assumed to be approximately 80 percent relative humidity. When making canister dilutions (see Sections 11.5, and 11.6), the analyst attempts to preserve the relative humidity of canisters at a level that will minimize recovery loss due to low canister relative humidity.

11.4.3. Under normal laboratory conditions, a 6 liter canister at ambient pressure will have a relative humidity of 100 percent if approximately 100 uL of water is in the canister.

11.4.3.1. The minimum relative humidity at which canisters containing polar analytes can be analyzed before polar target recovery is negatively affected is approximately 20 - 30 percent.

11.4.3.2. The minimum relative humidity at which canisters containing non-polar analytes can be analyzed before non-polar target recovery is negatively affected is approximately 10 percent.

11.5. Serial Dilution

11.5.1. High-level samples, for example, are those containing ppm levels of volatile organic compounds.

11.5.2. The original sample canister must have a positive pressure. If the pressure is less than 0 psig, then proceed to Section 11.1.2.

11.5.3. A septum cap is attached to the sample canister and a gas-tight syringe is purged with UHP nitrogen. A septum cap is attached to a clean evacuated 6-liter canister (the dilution canister).

11.5.4. 40 uL of deionized water is added to the canister through the septum of the evacuated can (See Section 11.4 for guidance on addition of water).

11.5.5. The syringe is inserted into the septum cap of the canister containing the sample and the canister valve is opened. The syringe is purged twice with sample and vented. The desired volume is then withdrawn and transferred into the dilution canister. The dilution canister is then pressurized using nitrogen.

11.5.6. The final pressure is measured in the serial dilution canister using a NIST traceable, certified gauge.

11.5.7. If the canister was pressurized to greater than 15 psig, pressure is released from the canister to bring the pressure below 15 psig.

11.5.8. The barometric pressure, the aliquot volume, final canister pressure and canister serial number are recorded in a laboratory worksheet. The serial dilution factor is calculated.

11.5.9. If a high level dilution is performed to bring one or more analytes within the curve, the analyte having the highest concentration should not be diluted to less than 20% of the upper calibration range, unless there are significant amounts of non-target compounds present. It is imperative that high levels of target and non-target analytes not contaminate the analytical system.

11.5.10. This serial dilution canister may be further diluted, if necessary, by another serial dilution, in-can dilution (see section 11.6), or on the autosampler (see section 11.3). The final dilution factor is the product of all the dilution factors for the sample.

11.6. In-canister Dilutions

11.6.1. If an analyte found or suspected to be in the sample is over the calibration range, to a level that an autosampler dilution would be insufficient, an in-canister dilution may be performed.

11.6.2. The canister vacuum/pressure is checked. If the can is under vacuum, then record the vacuum reading and proceed to section 11.6.3. If the canister is under pressure, then the can is bled to ambient pressure, then proceed to section 11.6.3.

11.6.3. The canister is pressurized to the desired pressure with nitrogen. The pressure must be no more than 40 psig.

11.6.4. The final pressure is measured using an NIST traceable, certified gauge.

11.6.5. The barometric pressure and the final pressures are recorded in a laboratory worksheet and the in-can dilution factor is calculated. (note: if multiple in-can dilutions are performed, record the final pressure of each pressurization before venting to perform the subsequent pressurization).

11.6.6. If the final pressure of the canister was greater than 15 psig, pressure is released from the canister to bring the pressure below 15 psig before loading on the autosampler.

11.6.7. If an in-canister dilution is performed to bring one or more analytes within the curve, the analyte having the highest concentration must not be diluted to less than 20% of the upper calibration range, unless there are significant amounts of non-target compounds present. Care must be taken to avoid over-dilution for in-canister dilutions since the original sample is affected.

11.6.8. This in-can dilution canister may be further diluted, if necessary, by another in-can dilution, or a serial dilution (see section 11.5), or on the autosampler (see section 11.3). This dilution factor is multiplied with all other dilution factors for this sample to obtain the final dilution factor.

11.7. Troubleshooting and Maintenance.

11.7.1. Troubleshooting is the identification and elimination of a problem or malfunction in a system or process. Troubleshooting is most effective when it is performed in a logical step by step sequence. (Refer to the instrument manufacturer's manual for specific guidance)

11.7.2. Basic Troubleshooting Principles

- Identify and analyze the problem and symptoms.
- Gather information that may help identify the problem such as prep information, system log, or output files.
- Evaluate the possibility that recent changes to the system caused the problem.
- Try to reproduce the problem if at all possible.
- Eliminate as many variables as possible.
- Document the system state then change variables one at a time and evaluate the effect on the problem

11.7.3. <u>Major Maintenance</u>

11.7.3.1. A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning or repairing the source, replacing filaments, changing

electronics, replacing the multiplier or changing moisture or Tenax traps.

11.7.4. Minor Maintenance

11.7.4.1. Minor maintenance includes cleaning the injector port, replacing filters, changing the pump oil, autotuning, switching filaments (instrument contains two filaments under vacuum), replacing valves or rotors, change/refill the calibration vial, changing seals and o-rings, ballasting pump, replacing fuses, replacing roughing pumps, changing pump oil, or replacing transfer lines.

11.8. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager and QA Manager. If contractually required, the client shall be notified.

11.9. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.10. Refer to TestAmerica Knoxville SOP KNOX-IT-0001, current revision, for requirements for computer hardware and software.

12. Data Analysis and Calculations

12.1. Refer to Figure 2 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2. Tentatively Identified Compounds (TICs): Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) are performed if required by the client. They are evaluated using the TestAmerica Knoxville SOP KNOX-MS-0014, current revision, “Determination of Tentatively Identified Compounds (TICs)”

12.3. Qualitative Identification: An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the most recent NIST library.

Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated). The characteristic ions from the reference mass spectrum are defined as the three ions with greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions are present in the reference spectrum (i.e. characteristic ions have relative intensity >30%).

- The sample component retention time must compare to within +0.2 minute of the retention time of the standard component. For reference, the standard must be run within the same 24 hours as the sample.
- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.
- The relative intensities of ions should agree to within +30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%).

If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst reports that identification and proceeds with quantitation.

12.4. Calculation legend:

A	=	amount of neat compound, uL
CB	=	concentration in SGDB, ug/mL
CC	=	concentration in canister, ppb v/v
CS	=	concentration in mix, ug/uL
Cx	=	the value determined by vendor certification analyses is used in the following calculations, ppb v/v (1000 ppb nominal)
d	=	density of neat compound, g/mL
DF	=	dilution factor, unitless
FV	=	final volume in a pressurized canister, L
GC	=	gas constant at 25^{o}C and standard pressure, 24.45 nL/n mole (or g/mol)
MW	=	molecular weight, ng/n mole
P_B	=	barometric pressure
P_F	=	final pressure, units specified
P_I	=	initial pressure, units specified
P_T	=	transfer pressure, units specified
Px	=	pressure in X = inches, psia or mmHg
TK	=	temperature in Kelvin
TV	=	transfer volume, L, mL or uL
Vbottle	=	volume of static gas dilution bottle, mL
Vmix	=	volume of mix, µL

Pmm Hg = P inches x 25.4

P inches = Ppsi * 2.036

Pmm Hg = P_{psi} x 51.7149

12.5. Calculations:

12.5.1. Final Canister Volume

$$FV = \frac{Canister\ size\,(L)\ x\ P_F(mm\ Hg\ Abs)}{P_B(mm\ Hg\ Abs)}$$

12.6. Stock standards in SGDB

12.6.1. Liquid formula

$$CB_{LIQUID}, \mu g/mL = \frac{\#\ \mu L * d * 1000ug / mg}{V_{bottle}}$$

12.6.2. Solid formula

$$CB_{SOLID}, \mu g/mL = \frac{\#\ mg * 1000ug / mg}{V_{bottle}}$$

12.7. Concentration of standards in primary target standard made from SGDB

$$CC, ppb\ v/v = \frac{TV, mL * CB\ x\ 1000(g / ug)(nL / L) * GC}{FV * MW * P_F atm(seenote)}$$

note:Atm = (“Hg gauge + 28.735 “Hg) / 28.735 “Hg
where 28.735 = barometric pressure based on STP corrected for Knoxville elevation of 305 m
STP = 760 mm Hg
Subtract 30.1 for elevation (from “Reduction of Barometer to Sea Level” pg 15-13, *Handbook of Chemistry and Physics*)
= 729.87 mm Hg
= 28.735 “Hg

12.8. Concentration of Analytes in Primary Target Standard (gauge method)

$$CC, ppb\ v/v = \frac{(P_T - P_I, inchesHg)(Cx\ or\ CC)}{(P_F, inchesHg + P_B, inchesHg)}$$

12.9. Concentration of Analytes in Primary Target Standard (syringe method)

$$CC, ppb\ v/v = \frac{(TV, mL)(CC\ or\ Cx)}{(FV, mL)}$$

12.10. Concentration of Analytes in Primary Target Standard (mass flow controller method)

12.10.1. The calculation is the same as 12.9 except to calculate *TV,mL*, through the mass flow controller:

TV,mL =flow rate (mL/min) * min

12.11. Dilution Factors of original sample canisters

12.11.1. In Can Dilution Factor

$$DF = \frac{P_{f(mmAbs)}}{P_{i(mmAbs)}}$$

12.11.2. Serial Dilution Factor

DF = FV/TV, (L)

12.11.3. Instrument Dilution Factor

$$\text{DF} = \frac{\text{Nominal Sample Volume}}{\text{Sample Volume Injected}}$$

12.12. Response Factor (RF)

$$RF = \frac{Ax * Cis}{Ais * Cx}$$

where:

x = area of the characteristic ion for the target compound.

Ais = area of the characteristic ion for the internal standard.

Cx = amount of the target compound.
Cis = amount of the internal standard.

12.13. Average Response Factor (ARF)

$$ARF = \frac{RF_1 + RF_2 + \ldots + RF_n}{n}$$

where:
n = the number of calibration points

12.14. Standard deviation of the ARF:

$$S = \sqrt{\frac{\sum_i^n (ARF - RF_n)^2}{n-1}}$$

12.15. Calibration Curve Evaluation Calculations

12.15.1. Relative standard deviation (RSD) of the ARF:

$$RSD = \frac{S}{ARF} * 100\%$$

12.15.2. Coefficient of Determination (r^2)

$$r^2 = \frac{\left(\sum_1^n \left[\left(y_{obs} - \overline{y_{obs}}\right) \times \left(y_{pred} - \overline{y_{pred}}\right)\right]\right)^2}{\sum_1^n \left[\left(y_{obs} - \overline{y_{obs}}\right)^2\right] \times \sum_1^n \left[\left(y_{pred} - \overline{y_{pred}}\right)^2\right]}$$

where
y_{obs} = Concentration of initial calibration standard (for standards 1 through n)
$\overline{y_{obs}}$ = Average of concentrations of initial calibration standards
y_{pred} = Predicated concentration of initial calibration standard (for standards 1 through n)
$\overline{y_{pred}}$ = Average of predicated concentrations of initial calibration standards

(For y_{pred} refer to calculation of Cpv found in Sections 12.19.1.2 and 12.19.1.3)

12.16. Calibration Verification: Percent deviation (% D) of the daily RF values as compared with the initial ARF values:

$$\% \ D = \frac{| \ RF \ - \ ARF \ |}{ARF} * 100\%$$

12.17. Surrogate and Laboratory Control Sample percent recovery (%R):

$$\% R \ = \ \frac{FoundAmount, ppb}{SpikeAmount, ppb} \ * \ 100\%$$

12.18. Duplicate relative percent difference (RPD):

$$RPD = \frac{| A_1 - A_2 |}{\overline{A}} \ x \ 100\%$$

where:

A_1 = amount determined in first analysis

A_2 = amount determined in second analysis

$\overline{A}$ = average determination, $(A_1 + A_2)/2$

12.19. Calibration verification percent drift and difference from the initial calibration:

$$\% \text{ Drift } = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100$$

Where

$C_{expected}$ = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

$$\%Difference = \frac{\overline{RF} - RF}{\overline{RF}} \times 100$$

$\overline{RF}$ = Average Analyte Response Factor from Initial Calibration

RF = Measured Analyte Response Factor from Calibration Verification

12.19.1. Target analyte concentrations in samples are typically calculated using the average response factor from the initial calibration. Quantitation may also be determined using linear or second order curves at the analyst's discretion to improve the quantitation of target analytes.

12.19.1.1. Calculation of concentration using Average Response Factors

$$C_{pv} = \frac{R_x C_{is}}{R_{is}\overline{RF}}$$

12.19.1.2. Calculation of concentration using Linear fit

$$C_{pv} = A + B\frac{(R_x C_{is})}{R_{is}}$$

C_{pv} = Concentration, ppb (v/v)
R_x = Response for analyte (area of quantitation ion)
R_{is} = Response for internal standard (area of quantitation ion)
C_{is} = Concentration of internal standard
A = Intercept
B = Slope

The corresponding Target software calculation is as follows:

$$Cpv = Cis(b + \frac{1}{m1} \times \frac{Rx}{Ris})$$

b = Concentration Ratio Intercept
m1 = Inverse of Slope

12.19.1.3. Calculation of concentration using Quadratic fit

$$Cpv = A + B\left(\frac{RxCis}{Ris}\right) + C\left(\frac{RxCis}{Ris}\right)^2$$

C = Curvature

The corresponding Target software calculation is as follows:

$$Cpv = Cis\left(b + m1 \times \frac{Rx}{Ris} + m2 \times \left(\frac{Rx}{Ris}\right)^2\right)$$

m1 = First order coefficient
m2 = Curvature (Second order coefficient)

12.20. Sample Quantitation: The amount of target compound detected is determined using the average RF or calibration curve values from the initial calibration (not the continuing calibration):

Amount = Cpv * DF

12.21. Unit conversions

12.21.1.

$$\text{Amount}, \mu g/m^3 = \frac{\text{Amount, ppb (v/v)} * \text{MW}}{\text{GC}}$$

12.21.2.

$$\text{Amount, ppm v/v} = \text{amount}, \frac{\text{ppb (v/v)}}{1000}$$

13. Method Performance

13.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP CA-Q-S-006 current revision based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit. MDL summaries are stored on the local area network.

13.2. Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in TestAmerica Knoxville SOP KNOX-QA-0009. Recovery limits must be 70-130% and RSD must be less than or equal to 25%. Recovery limits for methanol, butane and propene are 60-140% and RSD must be less than or equal to 30%.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009 current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

14. Pollution Prevention

14.1. All attempts will be made by laboratory personnel to minimize the use of solvents when performing this procedure.

15. Waste Management

15.1. All waste will be disposed of in accordance with all Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

15.2. The following waste streams are produced when this method is carried out.

- Expired solid and liquid standards are stored in metal closed-top containers.

16. References

16.1. Compendium Method TO-14, "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA® Passivated Canister Sampler and Gas Chromatographic Analysis," U.S. EPA 600/4-89/017, June 1988.

16.2. Compendium Method TO-14A, "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters With Subsequent Analysis by Gas Chromatography," U.S. EPA 625/R-96/010b, January 1999.

16.3. Compendium Method TO-15, "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GCMS)", U.S. EPA 625/R-96/010b, January 1999.

16.4. TestAmerica Quality Assurance Manual (QAM), current revision.

16.5. Entech Instruments Inc. 7100 Operators Manual. Version 2.0 for the 7100 Preconcentrator and Accessories

16.6. Agilent HP 5973 and 6890 Operation Manuals for GC and GC/MS.

17. Miscellaneous

17.1. Other SOPs cross-referenced in this SOP:

- KNOX-MS-0022, "Canister Cleaning and Preparation," latest revision.
- KNOX-MS-0010, "Volatile Analyte Screening by Purge and Trap," latest revision.

17.2. Modification from the referenced methods

17.2.1. The TO-14A tune limits are more stringent than the TO-15 limits. The default procedure is to use the TO-14A limits for both TO-14A and TO-15 samples. However if <u>all</u> the samples analyzed in the 24-hour tune batch are TO-15 samples, the analyst may elect to use the TO-15 limits. This SOP also allows for 50 ng or less of BFB to verify tuning of the instrument.

17.2.2. The continuing calibration listed in this procedure allows target analytes over 30% D as long as the target analytes meet the LCS criteria, with a narrative note of those target analytes that are over 30% D.

17.2.3. This procedure uses purified nitrogen in place of zero humid air specified in the reference methods. This must be noted in the case narrative.

17.2.4. TO-14 requires that the RT shift for the internal standards at each calibration level must be within 20 seconds of the RT of the mid-level calibration for each internal standard. TO-15 specifies that the comparison is made to the mean RT over the initial calibration range for each internal standard. This SOP uses the TO-15 criteria.

17.2.5. Section 7.13 Method TO-15 states that the working standard may be stored for 30 days. This laboratory experience has allowed the standard expiration date to be 2 months with no significant degradation of the standards.

17.2.6. Surrogates are not required by the reference methods. This SOP adds surrogate bromofluorobenzene (BFB) to every sample to help monitor for matrix effects and method performance.

17.2.7. The TO-15 method states that the scan time must give 10 scans per peak, not to exceed 1 second per scan. The GC/MS software is set for a sampling rate of 3, which corresponds to approximately 2 to 3 scans per second, depending on the instrument. See the GC/MS operator's manual or "help" on the software for more information about the sampling rate.

17.2.8. EPA Method TO-14A specifies that the relative accuracy of the field sampler or sample delivery system must meet 90-110% for a standard at 8 ppb v/v. The laboratory Control Sample (LCS) summary data is evaluated against alternate acceptance criteria based on this laboratory procedure for method TO-14A. When TO-14A work is performed, this must be noted in the case narrative.

17.3. List of Appendices

17.3.1. Appendix I: Target Analyte Tables

17.3.1.1.Table 1: Target Analytes - TO-14 and TO-15 Compounds

17.3.2. Appendix II: Figures

17.3.2.1.Figure 1: BFB Tuning Criteria

17.3.2.2. Figure 2: Example of a Data Review Checklist

17.3.2.3. Figure 3: Flow Chart

17.3.3. Appendix III: Example Instrument Parameters

17.3.4. Appendix IV: Recommended Calibration Levels (200 mL sample volume)

Appendix I: Table 1: Target Analytes

CAS NUMBER	TestAmerica Knoxville Compounds	MOLECULAR WEIGHT (ng/nmole)	conversion factor for ug/m3 = MW/24.45	200 mL REPORT-ING LIMIT (ppb(v/v)	200 mL REPORT-ING LIMIT (ug/m3)	500 mL REPORT-ING LIMIT (ppb(v/v)	500 mL REPORT-ING LIMIT (ug/m3)	SUGGESTED ION
71-55-6	1,1,1-Trichloroethane	133.4	5.45603	0.20	1.1	0.080	0.44	97
79-34-5	1,1,2,2-Tetrachloroethane	167.85	6.86503	0.20	1.4	0.080	0.55	83
79-00-5	1,1,2-Trichloroethane	133.4	5.45603	0.20	1.1	0.080	0.44	97
76-13-1	1,1,2-Trichlorotrifluoroethane [e]	187.37	7.66339	0.20	1.5	0.080	0.61	101
75-34-3	1,1-Dichloroethane	98.96	4.04744	0.20	0.81	0.080	0.32	63
75-35-4	1,1-Dichloroethene	96.94	3.96483	0.20	0.79	0.080	0.32	96
87-61-6	1,2,3-Trichlorobenzene	181.45	7.42127	1.0	7.4	0.40	3.0	180
96-18-4	1,2,3-Trichloropropane[l]	147.43	6.02986	0.50	3	0.20	1.2	110
120-82-1	1,2,4-Trichlorobenzene[l]	181.45	7.42127	1.0	7.4	0.40	3.0	180
95-63-6	1,2,4-Trimethylbenzene	120.19	4.91575	0.20	0.98	0.080	0.39	105
106-93-4	1,2-Dibromoethane (EDB)	187.86	7.68344	0.20	1.5	0.080	0.61	107
95-50-1	1,2-Dichlorobenzene	147	6.01227	0.20	1.2	0.080	0.48	146
107-06-2	1,2-Dichloroethane	98.96	4.04744	0.20	0.81	0.080	0.32	62
78-87-5	1,2-Dichloropropane	112.99	4.62127	0.20	0.92	0.080	0.37	63
76-14-2	1,2-Dichlorotetrafluoroethane [c,l]	170.92	6.99059	0.20	1.4	0.080	0.56	135
108-67-8	1,3,5-Trimethylbenzene	120.19	4.91575	0.20	0.98	0.080	0.39	120
106-99-0	1,3-Butadiene[l]	54.09	2.21227	0.40	0.88	0.16	0.35	54
541-73-1	1,3-Dichlorobenzene	147	6.01227	0.20	1.2	0.080	0.48	146
106-46-7	1,4-Dichlorobenzene	147	6.01227	0.20	1.2	0.080	0.48	146
123-91-1	1,4-dioxane[l]	88.11	3.60368	0.50	1.8	0.20	0.72	88
71-36-3	1-Butanol[l]	74.12	3.03149	2.0	6.1	0.80	2.4	31
540-84-1	2,2,4-Trimethylpentane	114.23	4.67198	0.50	2.3	0.20	0.93	57
78-93-3	2-Butanone[l]	72.11	2.94928	1.0	2.9	0.40	1.2	72
95-49-8	2-chlorotoluene	126.58	5.17710	0.40	2.1	0.16	0.83	126
591-78-6	2-Hexanone[l]	100.16	4.09652	0.50	2.0	0.20	0.82	58
78-78-4	2-Methyl butane	72.15	2.95092	0.50	1.5	0.20	0.59	43

CAS NUMBER	TestAmerica Knoxville Compounds	MOLECULAR WEIGHT (ng/nmole)	conversion factor for ug/m3 = MW/24.45	200 mL REPORT-ING LIMIT (ppb(v/v)	200 mL REPORT-ING LIMIT (ug/m3)	500 mL REPORT-ING LIMIT (ppb(v/v)	500 mL REPORT-ING LIMIT (ug/m3)	SUGGESTED ION
107-05-1	3-Chloropropene[(l)]	76.52	3.12965	0.20	0.63	0.080	0.25	39
622-96-8	4-ethyltoluene	120.19	4.91575	0.40	2.0	0.16	0.79	105
108-10-1	4-Methyl-2-Pentanone[(l)]	100.16	4.09652	0.50	2.0	0.20	0.82	43
67-64-1	Acetone[(l)]	58.08	2.37546	5.0	12	2.0	4.8	58
75-05-8	Acetonitrile[(l)]	41.05	1.67894	1.0	1.7	0.40	0.67	40
107-02-8	Acrolein[(l)]	56.06	2.29284	1.0	2.3	0.40	0.92	56
107-13-1	Acrylonitrile[(l)]	53.06	2.17014	2.0	4.3	0.80	1.7	53
98-83-9	alpha-Methylstyrene[(l)]	118.18	4.83354	0.40	1.9	0.16	0.77	118
71-43-2	Benzene	78.11	3.19468	0.20	0.64	0.080	0.26	78
100-44-7	Benzyl Chloride	126.58	5.17710	0.40	2.1	0.16	0.83	91
75-27-4	Bromodichloromethane	163.83	6.70061	0.20	1.3	0.080	0.54	83
75-25-2	Bromoform[(l)]	252.73	10.3366	0.20	2.1	0.080	0.83	173
74-83-9	Bromomethane	94.94	3.88303	0.20	0.78	0.080	0.31	94
75-15-0	Carbon Disulfide	76.14	3.11411	0.50	1.6	0.20	0.62	76
56-23-5	Carbon Tetrachloride	153.82	6.29121	0.20	1.3	0.080	0.50	117
108-90-7	Chlorobenzene	112.56	4.60368	0.20	0.92	0.080	0.37	112
75-45-6	Chlorodifluoromethane [(a,l)]	86.47	3.53661	0.20	0.71	0.080	0.28	67
75-00-3	Chloroethane	64.51	2.63845	0.20	0.53	0.080	0.21	64
67-66-3	Chloroform	119.38	4.88262	0.20	0.98	0.080	0.39	83
74-87-3	Chloromethane[(l)]	50.49	2.06503	0.50	1.0	0.20	0.41	52
156-59-2	cis-1,2-Dichloroethene	96.94	3.96483	0.20	0.79	0.080	0.32	96
10061-01-5	cis-1,3-Dichloropropene	110.97	4.53865	0.20	0.91	0.080	0.36	75
98-82-8	Cumene [(l)]	120.19	4.91575	0.40	2.0	0.16	0.79	105
110-82-7	Cyclohexane	84.16	3.44213	0.50	1.7	0.20	0.69	69
124-18-5	Decane[(l)]	142.28	5.81922	1.0	5.8	0.40	2.3	57
124-48-1	Dibromochloromethane	208.28	8.51861	0.20	1.7	0.080	0.68	129
74-95-3	Dibromomethane	173.83	7.10961	0.40	2.8	0.16	1.1	93

CAS NUMBER	TestAmerica Knoxville Compounds	MOLECULAR WEIGHT (ng/nmole)	conversion factor for ug/m3 = MW/24.45	200 mL REPORT-ING LIMIT (ppb(v/v)	200 mL REPORT-ING LIMIT (ug/m3)	500 mL REPORT-ING LIMIT (ppb(v/v)	500 mL REPORT-ING LIMIT (ug/m3)	SUGGESTED ION
75-71-8	Dichlorodifluoromethane[b,l]	120.91	4.94519	0.20	0.99	0.080	0.40	85
141-78-6	Ethyl acetate[l]	88.11	3.60368	2.0	7.2	0.80	2.9	43
60-29-7	Ethyl Ether[l]	74.12	3.03149	2.0	6.1	0.80	2.4	31
100-41-4	Ethylbenzene	106.17	4.34233	0.20	0.87	0.080	0.35	91
87-68-3	Hexachlorobutadiene[l]	260.76	10.6650	1.0	11	0.40	4.3	225
67-63-0	Isopropyl alcohol[l]	60.1	2.45808	2.0	4.9	0.80	2.0	45
136777-61-2	m/p-Xylene [g, h]	106.17	4.34233	0.20	0.87	0.080	0.35	91
67-56-1	Methanol [f,l]	32.04	1.31043	10	13	4.0	5.2	31
80-62-6	Methyl methacrylate[l]	100.12	4.09489	0.50	2.0	0.20	0.82	41
75-09-2	Methylene Chloride [f]	84.93	3.47362	0.50	1.7	0.20	0.69	84
1634-04-4	Methyl-tert-Butyl ether[l]	88.15	3.60532	1.0	3.6	0.40	1.4	73
91-20-3	Naphthalene	128.17	5.24213	0.50	2.6	0.20	1.0	128
106-97-8	n-Butane[l]	58.12	2.37710	0.40	0.95	0.16	0.38	43
104-51-8	n-Butylbenzene[l]	134.22	5.48957	0.40	2.2	0.16	0.88	91
112-40-3	n-Dodecane	170.33	6.96646	1.0	7.0	0.40	2.8	57
142-82-5	n-Heptane	100.2	4.09816	0.50	2.1	0.20	0.82	71
110-54-3	n-Hexane (f)	86.18	3.52474	0.50	1.8	0.20	0.70	56
111-65-9	n-Octane	114.23	4.67198	0.40	1.9	0.16	0.75	85
111-84-2	Nonane[l]	128.26	5.24581	0.50	2.6	0.20	1.0	57
103-65-1	n-Propylbenzene	120.19	4.91575	0.40	2.0	0.16	0.79	120
1120-21-4	n-Undecane[l]	156.31	6.39305	1.0	6.4	0.40	2.6	57
95-47-6	o-Xylene [h]	106.17	4.34233	0.20	0.87	0.080	0.35	91
99-87-6	p-Cymene [k]	134.22	5.48957	0.20	1.1	0.08	0.44	119
109-66-0	Pentane	72.15	2.95092	1.0	3.0	0.40	1.2	72
115-07-1	Propene[l]	42.08	1.72106	0.50	0.86	0.20	0.34	41
135-98-8	sec-butylbenzene	134.22	5.48957	0.40	2.2	0.16	0.88	105
100-42-5	Styrene	104.15	4.25971	0.20	0.85	0.080	0.34	104

CAS NUMBER	TestAmerica Knoxville Compounds	MOLECULAR WEIGHT (ng/nmole)	conversion factor for ug/m3 = MW/24.45	200 mL REPORT-ING LIMIT (ppb(v/v)	200 mL REPORT-ING LIMIT (ug/m3)	500 mL REPORT-ING LIMIT (ppb(v/v)	500 mL REPORT-ING LIMIT (ug/m3)	SUGGESTED ION
75-65-0	Tert-Butanol[l]	74.12	3.03149	2.0	6.1	0.80	2.4	59
98-06-6	tert-butylbenzene	134.22	5.48957	0.50	2.7	0.20	1.1	119
127-18-4	Tetrachloroethene	165.83	6.78241	0.20	1.4	0.080	0.54	129
109-99-9	Tetrahydrofuran[l]	72.11	2.94928	1.0	2.9	0.40	1.2	42
108-88-3	Toluene	92.14	3.76851	0.20	0.75	0.080	0.30	91
1330-20-7	Total-Xylenes	106.17	4.34233	0.40	1.7	0.16	0.70	91
156-60-5	trans-1,2-Dichloroethene	96.94	3.96483	0.20	0.79	0.080	0.32	96
10061-02-6	trans-1,3-Dichloropropene	110.97	4.53865	0.20	0.91	0.080	0.36	75
79-01-6	Trichloroethene	131.39	5.37382	0.20	1.1	0.040	0.22	130
75-69-4	Trichlorofluoromethane [d,l]	137.37	5.61840	0.20	1.1	0.080	0.45	101
108-05-4	Vinyl Acetate[l]	86.09	3.52106	1.0	3.5	0.40	1.4	43
593-60-2	Vinyl Bromide [j,l]	106.95	4.37423	0.20	0.87	0.080	0.35	106
75-01-4	Vinyl Chloride	62.5	2.55624	0.20	0.51	0.080	0.20	62

a) Freon 22
b) Freon 12
c) Freon 114
d) Freon 11
e) Freon 113, also 1,1,2-Trichloro-1,2,2-trifluoroethane
f) This is a common laboratory solvent
g) m-xylene and p-xylene coelute
h) Total xylenes (CAS # 1330-20-7) is the sum of m/p-xylenes and o-xylene
i) isopropylbenzene
j) bromoethene
k) isopropyltoluene
l) identified as provisory analyte. See Section 9.3.2.

Appendix II: Figures

Figure 1a: TO-14A BFB Tuning Criteria

Mass	Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	Less than 2% of mass 174
174	Greater than 50% of mass 95
175	5 to 9% of mass 174
176	Greater than 95% but less than 101% of mass 174
177	5 to 9 % of mass 176

Note: All ion abundances must be normalized to m/z 95, the nominal base peak, even though m/z 174 may be over 100 % of m/z 95.

Figure 1b: TO-15 BFB Tuning Criteria

Mass	Abundance Criteria
50	8.0 to 40.0 % of mass 95
75	30.0 to 66.0 % of mass 95
95	Base peak, 100% relative abundance
96	5.0 to 9.0 % of mass 95
173	Less than 2.0 % of mass 174
174	50.0 to 120.0 % of mass 95
175	4.0 to 9.0 % of mass 174
176	93.0 to 101.0 % of mass 174
177	5.0 to 9.0 % of mass 176

Note: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

Figure 2: Example Data Review Checklist

TestAmerica Knoxville GC/MS Air Initial Calibration Data Review / Narrative Checklist
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 12 & KNOX-MS-0023, Rev 0

Analysis Date:		Instrument::		ICAL Batch/Scan Name:		Scanned ◻

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd
1. Did BFB meet tune criteria?					
2. Were all standards injected within 24 hr of BFB?					
3. Was date/time of analysis verified and logbook as correct?					
4. Is low level std at or <RL and are the remaining points consecutive?					
5. Are the calibration levels correct? (Calculate standard concentration & amt. injected with quan rpt at each level)					
6. Was ICAL processed using correct methods and files?					
7. Are the ICAL start and end dates/times correct?					
8. Were at least 5 levels of each compound analyzed?					
9. At least 6 consecutive points used for quadratic curves, and at least 5 consecutive points for linear curves? Note: Ohio does not allow Quad					
10. Is %RSD for all target analytes ≤ 30%? (with up to 2 compounds with RSD ≤ 40%)					
11. If curves were used, is correlation coefficient ≥0.990?					
12. For quadratic: is a tangent's slope to the curve entirely positive or negative and continuous.					
13. For linear or quadratic: origin NOT "included"? (NOTE: OHIO does NOT allow "FORCE" through origin).					
14. Is the "Y" intercept less than the RL for each curve?					
15. RT for each IS ±20 sec avg. RT?					
16. Area for each IS ± 40% avg. area?					
17. Each analyte ± 0.06 RRT of avg. RRT?					
18. Have all peaks been auto identified? If not, list:					
19. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
20. Have alternate hits/manual integrations been verified as correct and are correct RFs listed in ICAL summary?					
21. Are all the active compounds listed on each quan report?					
22. High point checked for saturation and point removed if saturated?					
23. Elution order checked on isomeric pairs?					
• dichlorodifluoromethane / 1,2-dichlorotetrafluoroethane					
• trichlorofluoromethane / 1,1,2-trichlorotrifluoroethane					
• vinyl acetate / hexane					
• cis- and trans- isomers					
• ethyl benzene / m/p-xylene / o-xylene					
• n-propylbenzene/4-ethyl toluene/1,3,5-trimethylbenzene/1,2,4-trimethylbenzene					
• tert-butylbenzene/p-cymene					
• 1,2,4-trimethylbenzene/sec-butylbenzene					
• 1,3- , 1,4- , and 1,2-dichlorobenzene					
• 1,2,4-trichlorobenzene/1,2,3-trichlorobenzene					
24. Is the second source analysis of a reference standard within limits? (65-135% R)					
25. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
26. Does the ICAL folder contain complete data in the following order: Data review checklist, a complete runlog, BFB info, ICAL summary, curves, followed by [Quan reports, chromatograms, manual integrations], in increasing amount order, 2nd source info.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

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Figure 2: Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS Air Continuing Calibration Review / Narrative Checklist
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 12 & KNOX-MS-0023, Rev 0

Analysis Date:		CCAL Batch/ Scan Name:		Instrument:		ICAL Batch/ Scan Name:		Scanned □

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd
1. Did BFB meet tune criteria?				□ failed for TO-14A, but passes for TO-15	
2. Were all standards injected within 24 hr of BFB?					
3. Have the Entech position no. & vol. been verified with run log & sample vol. corrected if actual amount differs >5%?					
4. Was date/time of analysis in logbook correct?					
5. Was the CCAL compared to the correct ICAL (date & time on CCAL matches the ICAL)					
6. Is the %D ≤ 30% for all target analytes? (Narrative req'd.).				□ [ccal] analytes > 30% but passes LCS criteria.	
7. Have all peaks been auto identified? If not, list:					
8. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
9. Have alternate hits/manual integrations been verified as correct and are correct RFs listed in CCAL summary?					
10. Is the first IS documented correctly on the log?					
11. Elution order checked on isomeric pairs?					
• dichlorodifluoromethane / 1,2-dichlorotetrafluoroethane					
• trichlorofluoromethane / 1,1,2-trichlorotrifluoroethane					
• vinyl acetate / hexane					
• cis- and trans- isomers					
• ethyl benzene / m/p-xylene / o-xylene					
• n-propylbenzene/4-ethyl toluene/1,3,5-trimethylbenzene/1,2,4-trimethylbenzene					
• tert-butylbenzene/p-cymene					
• 1,2,4-trimethylbenzene/sec-butylbenzene					
• 1,3- , 1,4- , and 1,2-dichlorobenzene					
• 1,2,4-trichlorobenzene/1,2,3-trichlorobenzene					
12. Did the LCS meet criteria (70-130% with a limited # allowed 60-140% (see table) provisional analyte limit 60-140% with a limited # allowed 50-150%, and no two consecutive MEs). Note: Ohio does not allow for ME.				□ [lcs6] LCS analyte(s) flagged as being outside control limits but within marginal limits □ [lcs5] LCS outside marginal exceedences high, but analytes were not detected	
13. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
14. Does the CCAL folder contain **complete** data in the following order: data review checklist, a **complete** runlog, tune pass/fail page, m/z list, tune chromatogram, Target CCAL summary, Quan report, chromatogram, manual integrations.					

Number of target analytes in LCS	# marginal exceedances of LCS control limits allowed
>90	5
71 - 90	4
51 - 70	3
31 - 50	2
11 - 30	1
< 11	0

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

Figure 2: Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS Air Data Review / Narrative Checklist LOT/Project #_____
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 12 & KNOX-MS-0023, Rev 0

Instrument:				
Scanned File:				

Review Items **A. Tune / Continuing Calibration**	N/A	Yes	No	Why is data reportable?	2nd
1. Were all samples injected within 24 hr of BFB?					
2. Has a Continuing Calibration Checklist & run log been completed for each analytical batch **and scanned properly**?					
3. Was the correct ICAL used for quantitation?					
B. CLIENT SAMPLE AND QC SAMPLE Results	**N/A**	**Yes**	**No**	**Why is data reportable?**	
1. Were all special project requirements met?					
2. Were samples received in cans?				□ [Tedlar1] analyzed w/n 72 hours, □ [Tedlar2] X-fer within 72 hours.	
3. Can pressure/vac on receipt acceptable?				□ see narrative	
4. Were dilution factors/can prep information verified?					
5. Have the can number & lab ID been verified between the analysis log & sample prep log?					
6. Sample analyses done within analytical holding time (HT)? *If no, list samples:* _____				□ [ht2] Client requested analysis after HT expired. □ Other: _____	
7. Default sample volume verified?					
8. Are surrogates and internal standards within QC limits? (60-140% R for surr.; 60-140%R from CCAL for IS) *If no, list samples/reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____				□ [sur7] Obvious matrix effect □ **[sur12] high recovery, no hits.** □ [sur14] entire sample consumed □ **[is1] Per client, reanalysis was not performed *** □ [is2] Reanalysis confirmed a matrix effect.	
9. Were all positive results and false negatives on quan report verified to be correct in LIMS?					
10. For dilutions, is highest concentration hit ≥ 20% cal range and not above calibration range? *List samples and reason (e.g.,* **elev1***):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____				□ [elev1] Elevated RL for due to sample matrix interferences. □ [elev3] Elevated RLs for all analytes due to difficult sample matrix. □ [elev4] Elevated RLs based on screening □ [elev5] Elevated RLs for all analytes due to presence of non-target compounds. □ [elev7] Elevated RLs due to sample volume	
11. If manual integrations were performed, are they clearly identified, initialed, dated and reason given & alternate hits verified.				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
C. Preparation QC					
1. System blank run every 24 hours prior to samples?					
2. System blank surrogate recoveries within QC limits (60-140% R) ?				□ **[mb1] All sample surrogates OK and there is no analyte >RL in samples associated with blank.***	
3. Are all analytes present in the system blank < RL? (1/2 RL for DoD). *If no, list blank ID:* _____				□ **[mb3] No analyte > RL in associated samples.*** □ **[mb4] Sample results > 10x higher than blank.**	
4. DUP done per 20 samples and are all RPDs within limits? (for target analytes >5x RL, <25% RPD; no criteria for methanol and n-butanol) *If no, list DUP ID:* _____					
5. Did the LCS meet criteria (70-130% with a limited # allowed 60-140% (see table) provisional analyte limit 60-140% with a limited # allowed 50-150%, and no two consecutive MEs). Note: Ohio does not allow for ME.				□ [lcs6] LCS analyte(s) flagged as being outside control limits but within marginal limits □ [lcs5] LCS outside marginal exceedences high, but analytes were not detected LCS ID: _____	
D. Other					
1. Final report acceptable? (Results correct, RLs calculated correctly, units correct, surrogate %R correct, appropriate flags used, dilution factor correct, analysis dates correct.)					
2. Are all nonconformances documented appropriately and copy included with deliverable?					
4. Was a narrative prepared and all deviations noted?				□ [1pt6]; □ [1pt11]; □ [1ptsur] □ [Extras]	
5. TO14A Autotext included in narrative (for TO14A samples only).				□ [TO14]	
6. All target analytes on c.cal >30%D but passes LCS criteria noted in the narrative?				□ [ccal] The ccal exhibited a %D ICAL >30% but passes LCS…list analytes on narrative.	

Number of target analytes in LCS	# marginal exceedances of LCS control limits allowed
>90	5
71 - 90	4
51 - 70	3
31 - 50	2
11 - 30	1
< 11	0

Analyst:	**Date:**	**2nd Level Reviewer:**	**Date:**

□ see following page for comments.

*Such action must be taken in consultation with client.

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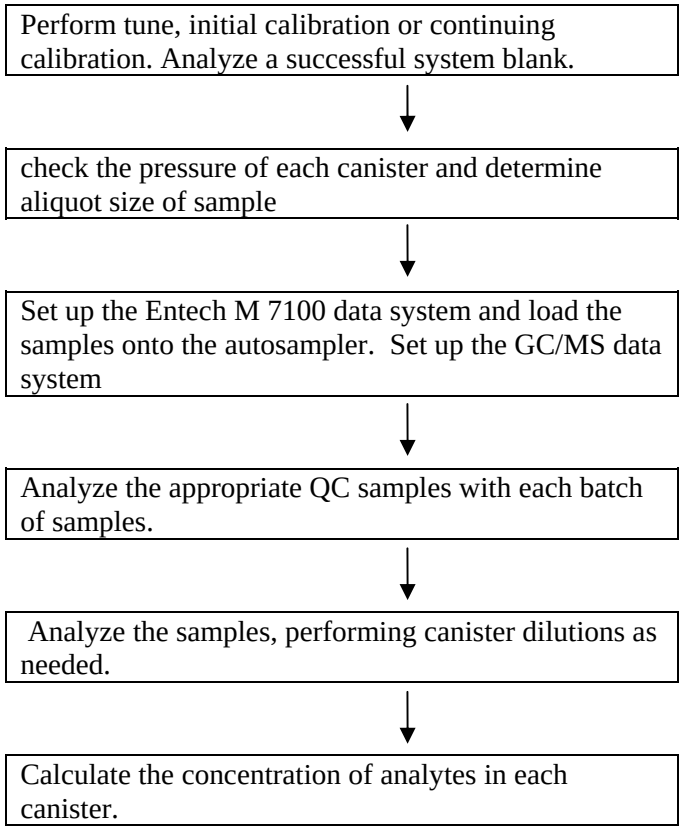
Figure 3: Flow Chart



Appendix III: Example Instrument parameters

```
                              TOPLEVEL PARAMETERS
                              -------------------

Method Information For: C:\MSDCHEM\1\METHODS\TO14.M

Method Sections To Run:

  ( ) Save Copy of Method With Data
  ( ) Pre-Run Cmd/Macro  =
  (X) Data Acquisition
  ( ) Data Analysis
  ( ) Post-Run Cmd/Macro =

Method Comments:
  TO14 METHOD USING HP-DB-5 60M X 0.32MM X 1.0 FILM THICKNESS

                              END OF TOPLEVEL PARAMETERS
                              --------------------------




                              INSTRUMENT CONTROL PARAMETERS
                              -----------------------------


Sample Inlet:       GC
Injection Source:   Manual
Injection Location: Front
Mass Spectrometer:  Enabled

================================================================================
                              HP6890 GC METHOD
================================================================================

OVEN
   Initial temp:  35 'C (On)                Maximum temp:  230 'C
   Initial time:  5.00 min                  Equilibration time:  0.00 min
   Ramps:
      #  Rate  Final temp  Final time
      1  6.00       65        0.00
      2 12.00      155        0.00
      3 25.00      220        7.00
      4   0.0(Off)
   Post temp:  35 'C
   Post time:  0.00 min
   Run time:  27.10 min

FRONT INLET (UNKNOWN)                    BACK INLET ()
   Mode:  Split
   Initial temp:  200 'C (On)
   Pressure:  7.89 psi (On)
   Split ratio:  2:1
   Split flow:  3.0 mL/min
   Total flow:  7.3 mL/min
   Gas saver:  Off
   Gas type:  Helium

COLUMN 1                                 COLUMN 2
   Capillary Column                         (not installed)
   Model Number:  HP 19091J-216
   HP-5 5% Phenyl Methyl Siloxane
   Max temperature:  325 'C
   Nominal length:  59.0 m
   Nominal diameter:  320.00 um
   Nominal film thickness:  1.00 um
   Mode:  constant flow
   Initial flow:  1.5 mL/min
   Nominal init pressure:  7.90 psi
   Average velocity:  31 cm/sec

Method: TO14.M            Wed Apr 30 14:03:13 2003            Page: 1
```

Appendix III: Example Instrument parameters (continued)

```
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR (NO DET)                 BACK DETECTOR (NO DET)

SIGNAL 1                                SIGNAL 2
   Data rate:  20 Hz                       Data rate:  20 Hz
   Type:  test plot                        Type:  test plot
   Save Data:  Off                         Save Data:  Off
   Zero:  0.0 (Off)                        Zero:  0.0 (Off)
   Range:  0                               Range:  0
   Fast Peaks:  Off                        Fast Peaks:  Off
   Attenuation:  0                         Attenuation:  0

COLUMN COMP 1                           COLUMN COMP 2
   (No Detectors Installed)                (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  150 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

                                        POST RUN
                                           Post Time: 0.00 min

TIME TABLE
   Time       Specifier                    Parameter & Setpoint

                            7673 Injector


     Front Injector:
         Injector not configured, use these parameters if it becomes configured
        Sample Washes                 2
        Sample Pumps                  4
        Injection Volume            1.0 microliters
        Syringe Size               10.0 microliters
        PostInj Solvent A Washes      4
        PostInj Solvent B Washes      0
        Viscosity Delay               0 seconds
        Plunger Speed              Fast

     Back Injector:
No parameters specified
                          MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File               : bfb.u
Acquistion Mode         : Scan


MS Information
-- -----------

Solvent Delay           : 3.80 min

EM Absolute             : False
EM Offset               : 0
Resulting EM Voltage    : 1858.8

[Scan Parameters]

Low Mass                : 28.5
High Mass               : 260.5
Threshold               : 200
Sample #                : 3       A/D Samples    8
Plot 2 low mass         : 28.5
Plot 2 high mass        : 260.5

[MSZones]

MS Quad                 : 106 C   maximum 200 C
MS Source               : 230 C   maximum 250 C

                            END OF MS ACQUISITION PARAMETERS

PostRun InstCntl macro(s) exist: msacq2.mac

                        END OF INSTRUMENT CONTROL PARAMETERS
```

Appendix IV: Recommended Calibration levels (based on 200 mL sample analysis)

		Level, ppb v/v[1]								
Compound	**IS Ref[2]**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Bromochlormethane (IS#1)	NA	10	10	10	10	10	10	10	10	10
1,4-Difluorobenzene (IS#2)	NA	10	10	10	10	10	10	10	10	10
Chlorobenzene-d5 (IS#3)	NA	10	10	10	10	10	10	10	10	10
4-Bromofluorobenzene	3	10	10	10	10	10	10	10	10	10
Chlorodifluoromethane	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Propene	1	-	-	0.4	0.8	2.5	5.0	10	20	40
Dichlorodifluoromethane	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Chloromethane	1	-	-	0.4	0.8	2.5	5.0	10	20	40
1,2-Dichlorotetrafluoroethane	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Vinyl Chloride	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
n-Butane	1	-	-	0.4	0.8	2.5	5.0	10	20	40
1,3-Butadiene	1	-	-	0.4	0.8	2.5	5.0	10	20	40
Bromomethane	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Chloroethane	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Vinyl Bromide	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
2-methyl butane	1	-	-	0.4	0.8	2.5	5.0	10	20	40
Trichlorofluoromethane	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Acrolein	1	-	-	0.4	0.8	2.5	5.0	10	20	40
Acetonitrile	1	-	-	-	0.8	2.5	5.0	10	20	40
Acetone	1	-	-	-	-	2.5	5.0	10	20	40
Pentane	1	-	-	-	0.8	2.5	5.0	10	20	40
Isopropyl Alcohol	1	-	-	-	0.8	2.5	5.0	10	20	40
Ethyl Ether	1	-	-	-	0.8	2.5	5.0	10	20	40
1,1-Dichloroethene	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Acrylonitrile	1	-	-	-	0.8	2.5	5.0	10	20	40
tert-butanol	1	-	-	-	0.8	2.5	5.0	10	20	40
1,1,2-Trichlorotrifluoroethane	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Methylene Chloride	1	-	-	0.4	0.8	2.5	5.0	10	20	40
3-Chloropropene	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Carbon Disulfide	1	-	-	0.4	0.8	2.5	5.0	10	20	40
trans-1,2-Dichloroethene	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Methyl-t-Butyl Ether	1	-	-	-	0.8	2.5	5.0	10	20	40
1,1-Dichloroethane	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Vinyl Acetate	1	-	-	-	0.8	2.5	5.0	10	20	40
Hexane	1	-	-	0.4	0.8	2.5	5.0	10	20	40
2-Butanone	1	-	-	-	0.8	2.5	5.0	10	20	40
cis 1,2-Dichloroethene	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Ethyl Acetate	1	-	-	-	0.8	2.5	5.0	10	20	40
Chloroform	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Tetrahydrofuran	1	-	-	-	0.8	2.5	5.0	10	20	40
1,1,1-Trichloroethane	1	-	0.2	0.4	0.8	2.5	5.0	10	20	40
1,2-Dichloroethane	2	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Benzene	2	-	0.2	0.4	0.8	2.5	5.0	10	20	40
1-Butanol	2	-	-	-	0.8	2.5	5.0	10	20	40
Cyclohexane	2	-	-	0.4	0.8	2.5	5.0	10	20	40
Trichloroethene	2	0.1	0.2	0.4	0.8	2.5	5.0	10	20	40
Dibromomethane	2	-	-	0.4	0.8	2.5	5.0	10	20	40

[1] See section 10.3.11.
[2] Internal standard quantitation reference.

Appendix IV: Recommended Calibration levels (based on 200 mL sample analysis), continued

		Level, ppb v/v[1]								
Compound	**IS Ref[2]**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Carbon tetrachloride	2	0.1	0.2	0.4	0.8	2.5	5.0	10	20	40
2,2,4-trimethyl pentane	2	-	-	0.4	0.8	2.5	5.0	10	20	40
n-heptane	2	-	-	0.4	0.8	2.5	5.0	10	20	40
1,2-dichloropropane	2	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Bromodichloromethane	2	-	0.2	0.4	0.8	2.5	5.0	10	20	40
1,4-dioxane	2	-	-	0.4	0.8	2.5	5.0	10	20	40
Methyl Methacrylate	2	-	-	0.4	0.8	2.5	5.0	10	20	40
4-Methyl-2-pentanone	2	-	-	0.4	0.8	2.5	5.0	10	20	40
cis-1,3-Dichloropropene	2	-	0.2	0.4	0.8	2.5	5.0	10	20	40
trans-1,3-Dichloropropene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Toluene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
1,1,2-Trichloroethane	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
2-Hexanone	3	-	-	0.4	0.8	2.5	5.0	10	20	40
Octane	3	-	-	0.4	0.8	2.5	5.0	10	20	40
Dibromochloromethane	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
1,2-Dibromoethane	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Tetrachloroethene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Chlorobenzene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Ethylbenzene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
m&p-Xylene	3	0.2	0.4	0.8	1.6	5.0	10	10	20	40
Bromoform	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Nonane	3	-	-	0.4	0.8	2.5	5.0	10	20	40
Styrene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
o-Xylene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
1,1,2,2-Tetrachloroethane	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
1,2,3-Trichloropropane	3	-	-	0.4	0.8	2.5	5.0	10	20	40
Cumene	3	-	-	0.4	0.8	2.5	5.0	10	20	40
n-Propylbenzene	3	-	-	0.4	0.8	2.5	5.0	10	20	40
2-chlorotoluene	3	-	-	0.4	0.8	2.5	5.0	10	20	40
4-Ethyltoluene	3	-	-	0.4	0.8	2.5	5.0	10	20	40
1,3,5-Trimethylbenzene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Alpha-Methylstyrene	3	-	-	0.4	0.8	2.5	5.0	10	20	40
Decane	3	-	-	-	0.8	2.5	5.0	10	20	40
Tert-butylbenzene	3	-	-	0.4	0.8	2.5	5.0	10	20	40
1,2,4-Trimethylbenzene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
sec-butylbenzene	3	-	-	0.4	0.8	2.5	5.0	10	20	40
1,3-Dichlorobenzene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
Benzyl chloride	3	-	-	0.4	0.8	2.5	5.0	10	20	40
1,4-Dichlorobenzene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
p-Cymene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
1,2-Dichlorobenzene	3	-	0.2	0.4	0.8	2.5	5.0	10	20	40
n-butylbenzene	3	-	-	0.4	0.8	2.5	5.0	10	20	40
Undecane	3	-	-	-	0.8	2.5	5.0	10	20	40
Dodecane	3	-	-	-	0.8	2.5	5.0	10	20	40
1,2,4-Trichlorobenzene	3	-	-	-	0.8	2.5	5.0	10	20	40
Napthalene	3	-	-	0.4	0.8	2.5	5.0	10	20	40
Hexachlorobutadiene	3	-	-	-	0.8	2.5	5.0	10	20	40
1,2,3-trichlorobenzene	3	-	-	-	0.8	2.5	5.0	10	20	40

[1] See section 10.3.11.

[2] Internal standard quantitation reference.

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE ATTACHMENT

TITLE: Determination of C5-C12 Total Petroleum Hydrocarbons (TPH) in Air as Octane

(SUPERSEDES: NONE)

Prepared By: _____

Reviewed By: _____ 12/6/10
Technical Specialist

Approved By: _____ 01/05/11
Quality Assurance Manager

Approved By: _____ 1-5-11
Environmental, Health and Safety Coordinator

Approved By: _____ 1-6-11
Laboratory Director

1. Scope and Application

1.1. This attachment describes additional procedures that are employed in order to quantitate total petroleum hydrocarbon (TPH) as octane in the C5-C12 range in samples analyzed by TO-14A or TO-15. See Appendix I, Table 1 for the list of target analytes and reporting limits.

2. Summary of Method

2.1. The TPH concentration is determined from all peak areas in the RIC summed from C5-C12 minus areas contributed by the surrogates and internal standards in the RIC. The final result is quantitated against the octane response factor obtained from the RIC in the TO-14/15 initial calibration.

2.2. The compounds analyzed by this method are listed in Appendix 1, Table 1.

3. Definitions

3.1. RIC: Reconstructed Ion Chromatogram

4. Interferences

4.1. Interferences in the RIC on the internal standard can cause a bias in the quantitation of TPH. The analyst must be intimately familiar with the internal standard and surrogate peak shape, retention time, and uninterfered height/area in order to determine matrix bias. Inspection of the RIC is required to ensure that there is no interference to the internal standards/surrogate in order to make appropriate decisions to remove or include the areas for calculation.

4.2. Non-TPH peaks can contribute to a bias in the results. Since it is not practical to examine every peak in the chromatogram, this method reports all peaks between C5 and C12. However, the advantage of TPH by GC/MS is that it allows the operator to tentatively identify extraneous peaks that could inflate the TPH values that may or may not be normally found in hydrocarbon mixtures. If the operator is aware of non-TPH peaks are present (e.g. chlorinated solvents), the operator may elect to remove the area of the non-TPH peaks to provide a lower-biased result. For example, a non-TPH peak may be present that would be cause to dilute a sample; in this case the non-TPH peak may be excluded and the sample would not have to be diluted.

4.3. Instances of obvious bias must be narrated in the project case narrative.

5. Safety

5.1. There are no additions to this section of the SOP.

6. Equipment and Supplies

6.1. There are no additions to this section of the SOP.

7. Reagents and Standards

7.1. Unleaded Gasoline Composite, Restek Catalogue Number 30205 or equivalent, 50000 ug/mL in methanol. (Other stock standard concentrations may be used.)

8. Sample Collection, Preservation and Storage

8.1. There are no additions to this section of the SOP.

9. Quality Control

9.1. Internal/Surrogate Standards

9.1.1. Internal standard 1,4-difluorobenzene RIC area is used for the quantitation of TPH. In addition to the $\pm$ 20 second RT time criteria in the SOP, the samples' internal standard RIC area is compared to the daily calibration's internal standard RIC area. The limit is $\pm$ 40% D. If the recovery is outside 40%, the internal standard RIC must be inspected for interferences. If in the TO-14A/TO-15 analysis (which uses the internal standard quantitation ion for calculation) the internal standard recovery is within control, then the analysis is within control and matrix interferences are likely on the RIC. If interferences are present, then the data is reported and narrated that matrix interferences are present which would bias the TPH results.

9.1.2. Surrogate recovery is calculated and reported from the quantitation ion analysis described in the SOP.

9.2. Laboratory Control Standard (LCS)

9.2.1. The LCS analytes of interest is the sum of the areas of toluene, octane, ethyl benzene, m/p-xylene, o-xylene and dodecane from the RIC of the daily calibration verification standard. The sum of these individual peak areas are quantitated against the response factor of octane. The recovery of TPH LCS must be within 50-150%.

10. Calibration and Standardization

10.1. Initial Calibration

10.1.1. Using the initial calibration standards and limits described in the SOP, octane is quantitated based on the response from the RIC. (Upon client request hexane can be used). See Appendix IV of the TO-14A & TO-15 SOP for the recommended calibration amounts.

10.1.2. The response factor of octane is obtained and entered into the appropriate Target processing methods for TPH in air.

10.2. Daily Calibration Verification

10.2.1. Using the daily calibration standard and limits described in the SOP, octane is quantitated based on the response from the RIC.

11. Procedure

11.1. The area of TPH is the sum of all the peaks in the RIC from pentane (- 0.05 minutes) to dodecane (+ 0.05 minutes) minus all peak areas of internal standards and surrogates from the TO-14A & TO-15 analysis.

11.2. Analyst must inspect the chromatograms for proper integration and interferences.

11.3. Any individual TPH area that exceeds the area of octane in the high point of the calibration curve is considered over range and must be diluted by procedures described in the SOP. Peaks that are determined not to be part of TPH (e.g. chlorinated solvents) are not reason to dilute the sample and the non-TPH area is subtracted from the total area for calculation.

11.4. Samples that are initially diluted to obtain on-scale TO-14A/15 results are not analyzed more concentrated if TPH are not detected above the reporting limit.

12. Data Analysis and Calculations

12.1. Response Factor (RF) octane to calculate TPH:

$$RF = \frac{Ax * Cis}{Ais * Cx}$$

where:

Ax	=	area of octane from the RIC.
Ais	=	area of 1,4-difluorobenzene for the internal standard from the RIC.
Cx	=	concentration amount of octane in ppb v/v.
Cis	=	amount of the internal standard (1,4-difluorobenzene) in ppb v/v.

12.2. TPH concentration in samples is calculated using the average response factor of octane from the initial calibration of the RIC.

In the formulas presented in the SOP, replace the following

R_x	= TPH RIC area of pentane (C5) -0.05 min. to dodecane (C12) + 0.05 min.
R_{is}	= internal standard RIC area
RF	= Response factor of octane obtained from initial calibration RIC

12.3. Estimated values below the reporting limit are not reported for TPH.

13. Method Performance

13.1. Reporting Limit (RL) - An RL standard must be analyzed for TPH on each instrument per year. A RL standard of gasoline of a known concentration in a canister must be no greater than 2X the reporting limit. The reporting limit standard must be at least 3X the area of the daily method blank.

13.2. Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) to performing the analysis independently. The IDOC is determined by analyzing four replicates of gasoline of a known concentration in a canister as detailed in TestAmerica Knoxville SOP KNOX-QA-0009. Recovery limits must be 50-150% and RSD must be less than or equal to 25%.

14. Pollution Prevention

14.1. There are no additions to this section of the SOP.

15. Waste Management

15.1. There are no additions to this section of the SOP.

16. References

16.1. Agency for Toxic Substances & Disease Registry, http://www.atsdr.cdc.gov/mhmi/mmg72.html

17. Miscellaneous

17.1. Appendix I: Table 1 Target Analyte

Appendix I: Table 1: Target Analytes

CAS NUMBER	TestAmerica Knoxville Compounds	MOLECULAR WEIGHT (ng/nmole)	conversion factor for ug/m3 = MW/24.45	200 mL REPORT-ING LIMIT (ppb(v/v)	200 mL REPORT-ING LIMIT (ug/m3)	500 mL REPORT-ING LIMIT (ppb(v/v)	500 mL REPORT-ING LIMIT (ug/m3)	SUGGESTED ION
n/a	TPH (as octane)[1]	108[2]	4.41718	10	44	4	17	RIC

1 – TPH may also be reported based on another reference peak, e.g., TPH as hexane.
2 – The average molecular weight of gasoline is taken from http://www.atsdr.cdc.gov/mhmi/mmg72.html

MERCURY PREPARATION AND ANALYSIS

(Methods: EPA 245.1, EPA 7470A, EPA 7471A, EPA 7471B, and SM3112B)

Approvals (Signature/Date):

Andrea Teal November 22, 2010
Andrea Teal Date
Quality Assurance Manager

November 29, 2010
Benjamin Gulizia Date
Laboratory Director / Lead Technical Director

Ernest B. Walton December 7, 2010
Ernest Walton Date
EH&S Coordinator / Technical Director

Charlton A. Riegner January 20, 2011
Charlton Riegner Date
Interim Department Manager

Facility Distribution No. 1 **Distributed To:** QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of mercury by cold vapor atomic absorption spectrophotometry (CVAA). The routine matrices performed by this procedure are waters and soils; however, this procedure may be adapted to accommodate other matrices as outlined in Section 16.1.

The reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

This procedure is based on the absorption of characteristic radiation at 253.7nm by mercury vapor. After digestion, to convert all forms of mercury to the same oxidation state, the mercury ions are reduced to mercury by the addition of stannous chloride and aerated from solution after passing through a mixing coil. The mixture passes through a gas/liquid separator and through a drying tube. The vapor is passed through a flow cell positioned in the light path of an atomic absorption spectrophotometer. Mercury concentration is measured as a function of absorbance.

This SOP is based on the following methods: EPA 7470A (liquids), EPA 7471A (solids), EPA 7471B (solids), SM3112B, and EPA 245.1.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid, nitric acid, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Potassium permanganate is added to eliminate the possibility of interference from sulfide and certain organic compounds.

4.2.4 High levels of residual chlorine (such as those produced when seawaters, brines, and industrial effluents high in chlorides are digested) are known to interfere with this analysis. Addition of extra potassium permanganate may be needed during the digestion of samples containing chloride. Also, the samples are not capped tightly during digestion so that excess chlorine can escape.

4.2.5 Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences. The concentration levels for interferants are difficult to define. This suggests that quality control procedures must be strictly followed.

4.2.6 Volatile materials (e.g., chlorine) which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the digestion vessel should be purged before addition of stannous chloride solution.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable latex or nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

Nitric and hydrochloric acids are extremely hazardous as oxidizers, corrosives, poisons, and are reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Nitric acid can cause deep ulcers, and staining of the skin to a yellow or yellow-brown color. These acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

Samples that contain high concentrations of carbonates or organic matter, or samples that are at elevated pH can react violently when acids are added. Acids must be added to samples under a hood to avoid splash/splatter hazards and/or possibly toxic vapors that will be given off when the samples are acidified.

The making of aqua regia can produce toxic fumes and heat. This procedure must be performed under a fume hood.

The exhaust of the mercury analyzer must be vented or trapped so that mercury vapors do not enter the laboratory.

The preparation of the samples for mercury analysis uses a water bath with a temperature of ~95°C. The water and the steam produced can cause burns to unprotected skin. Employees must use appropriate PPE when working with sample digestions.

Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analyses should be conducted in a laboratory exhaust hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Sulfuric Acid[2]	Corrosive Oxidizer Dehydrator Poison	1mg/m^3 TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid[2]	Corrosive Oxidizer Poison	2ppm TWA 4ppm STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid[2]	Corrosive Poison	5ppm - Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic, causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
[2]Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment: Verification and Use*

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment: Verification and Use*

Water bath or heating block capable of maintaining temperatures of 30 ± 3°C, 80 ± 3°C, and 95 ± 3°C

Leeman Hydra AA or other suitable automated mercury analyzer

Mercury Hollow Cathode Lamp

Absorption Cell

Nitrogen or argon gas supply and appropriate fittings

Air Pump

Pump (Aeration) tubing of appropriate sizes for use on the Hydra AA

Drying Tube – Purchased pre-packed from Leeman Labs

6.2 Analytical Data System / Software / Hardware

The Leeman software is used on a Windows-based PC to schedule and acquire data. The raw data from the Hg Analyzer is manually checked for validity by a minimum of 2 analysts. Raw instrument data are uploaded to the laboratory's LIMS (i.e., TALS) via the Environmental Information Systems Corporation Metals Analytical Review and Reporting System (MARRS) program. Additionally, any quality control failures are flagged in TALS, as appropriate.

6.3 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment: Verification and Use*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment: Verification and Use*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment: Verification and Use*

Test tubes of the two sizes to fit the Hydra AA autosampler

Digestion glassware – 4oz flint digestion vessels

Digestion vials – 50mL and 100mL. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment: Verification and Use*

pH paper

Detergent – Liquinox, used for washing non-disposable labware.

6.4 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

Waters or Field-Filtered Dissolved Mercury Samples:
250mL plastic, nitric acid – purchased with Certificate of Analysis attesting to purity.

Soil Samples:
8oz plastic soil jar, unpreserved – purchased with Certificate of Analysis attesting to purity.

Wipe Samples:
40mL VOA vial, Acetic acid in water, pH 4.93 +/- 0.05 – purchased with Certificate of Analysis attesting to purity.

Leachate Samples (originally aqueous):
1L amber glass, unpreserved – purchased with Certificate of Analysis attesting to purity.

Leachate Samples (originally solid):
16oz glass soil jar, unpreserved – purchased with Certificate of Analysis attesting to purity.

Lab-Filtered Dissolved Mercury Samples
250mL plastic, unpreserved – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

The standards and reagents listed are those in use at the time this SOP was updated. Other standard and reagent stocks, vendors, and concentrations may be used provided

they are fully documented and in compliance with method requirements.

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.*

Hydrochloric acid, nitric acid, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Blank Matrix – Teflon Chips, Ottawa Sand, or other suitable matrix. Used for the preparation of soil QC samples.

7.2.2 Laboratory Reagent Water – ASTM Type II

7.2.3 Nitric Acid (HNO_3), concentrated, reagent grade – stable under ordinary conditions of use and storage
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date opened

7.2.4 Hydrochloric Acid (HCl), concentrated-reagent grade – stable under ordinary conditions of use and storage
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration:
Unopened: Manufacturer's expiration date.
Opened: 5 years from date opened

7.2.5 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3. This reagent needs to be carefully prepared under a fume hood due to vapors that are produced. Properly dispose of any unused volume.

For greater stability 1:1 aqua regia may be prepared. To 4 volumes of reagent water, carefully add 3 volumes of concentrated HCl and 1 volume of concentrated HNO3. Store

this reagent away from incompatibles, combustibles, organics, and other readily oxidizable materials. This reagent will be stable for up to 3 months.

7.2.6 Potassium permanganate ($KMnO_4$), mercury free – stable under ordinary conditions of use and storage.
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from heat and avoid storage on wood floors. Store away from incompatibles, combustibles, organics and other readily oxidizable materials.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date opened

7.2.7 Potassium permanganate, mercury-free, 5% solution (w/v) – Dissolve 50g of $KMnO_4$ in 1000mL of reagent water. Stable under ordinary conditions of use and storage.
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from heat and avoid storage on wood floors. Store away from incompatibles, combustibles, organics and other readily oxidizable materials.
Expiration: 1 year from date prepared

7.2.8 Sodium Chloride (NaCl) – stable under ordinary conditions of use and storage.
Storage: Store in a tightly closed container in a cool, dry, ventilated area.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date opened

7.2.9 Hydroxylamine Sulfate ($(NH_2OH)•2H_2O$) – stable under ordinary conditions of use and storage.
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Store away from incompatible materials.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date opened

7.2.10 Sodium chloride hydroxylamine sulfate solution – Dissolve 120g NaCl and 120g hydroxylamine sulfate in reagent water in a 1-L volumetric flask and dilute to volume. Stable under ordinary conditions of use and storage.
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Store away from incompatible materials.
Expiration: 1 year from date prepared

7.2.11 Potassium persulfate ($K_2S_2O_8$) – stable under ordinary conditions of use and storage.
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from heat and avoid storage on wood floors. Store away from incompatibles, combustibles, organics and other readily oxidizable materials.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date opened

7.2.12 Potassium persulfate, 5% solution (w/v) – Dissolve 50g potassium persulfate in 1000mL reagent water. Stable under ordinary conditions of use and storage.
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from

heat and avoid storage on wood floors. Store away from incompatibles, combustibles, organics and other readily oxidizable materials.
Expiration: 1 year from date prepared

7.2.13 Rinse Water, 5% HCl / 1%HNO_3 – to a clean 2-L bottle, add 1-L of reagent water. Carefully add 100mL of concentrated hydrochloric acid. Carefully add 20mL of concentrated nitric acid. Dilute to a final volume of 2L. Other volumes may be utilized providing the reagent proportions remain the same. Stable under ordinary conditions of use and storage.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: 1 year from date prepared

7.2.14 Stannous chloride ($SnCl_2.2H_2O$) – reagent grade, suitable for mercury determination. Stable if stored in tightly closed containers.
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from incompatible materials. It will absorb air and form the insoluble oxychloride.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date opened

7.2.15 Stannous chloride ($SnCl_2 \cdot 2H_2O$) solution – to a clean 2-L volumetric flask, add 100g of stannous chloride. Add approximately 400mL of reagent water. Carefully add 500mL of concentrated hydrochloric acid. Add a stirring bar, and stir on a stir plate until the stannous chloride is dissolved. Remove the stirring bar and dilute to volume with reagent water. Stable under ordinary conditions of use and storage.
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Keep away from incompatible materials.
Expiration: 1 year from date prepared

7.2.16 Sulfuric Acid (H_2SO_4), concentrated reagent grade – stable under ordinary conditions of use and storage.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration:
Unopened: Manufacturer's expiration date
Opened: 5 years from date opened

7.2.17 Nitric Acid (HNO_3), 1:1 – Slowly add 250mL of concentrated nitric acid to 250mL of laboratory reagent water in a 1-L beaker. Mix well and transfer to a tightly closed container.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: 2 years from date prepared

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

7.3.1 Hg Stock Standard, 1000mg/L – currently purchased from SPEX.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage up to the manufacturer's expiration date.

7.3.2 Second Source Hg Stock Standard, 1000mg/L – currently purchased from Baker.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage up to the manufacturer's expiration date.

7.3.3 Calibration standards

7.3.3.1 Mercury Intermediate Standard, 500ug/L – Add 0.050mL of the purchased 1000mg/L Hg Stock Standard and 2.5mL of nitric acid to about 50mL of reagent water in a 100-mL volumetric flask and dilute to volume with reagent water.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage for up to 28 days. The expiration date cannot exceed the expiration of any of the components.

7.3.3.2 Mercury Calibration Standards – Transfer 0.0, 0.02, 0.04, 0.1, 0.3, and 0.5mL portions of the Mercury Intermediate Standard to a series of 125-mL glass bottles. Add reagent water from a graduated cylinder to each bottle to make a final volume of 50mL. (This results in calibration standard concentrations of 0.0, 0.2, 0.4, 1.0, 3.0, and 5.0ug/L mercury.) Mix well. Add 2.5mL of concentrated H_2SO_4, 1.25mL of concentrated HNO_3, and 7.5mL of $KMnO_4$ solution and let stand at least 15 minutes. Add 4mL of potassium persulfate and heat for ~2 hours in a water bath at 95°C+/- 3°C. Cool and add 3mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. The standards are now ready for analysis. Larger volumes of standards may be digested as needed as long as reagent ratios are kept the same.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage for up to 28 days. The expiration date cannot exceed the expiration date of any of the components.

7.3.4 Initial Calibration Verification Standards (also used as QCS and IPC standards)

7.3.4.1 Second Source Intermediate Standard, 1.0mg/L – Add 0.1mL of the 1000mg/L Second Source Hg Stock Standard, and 2.5mL of nitric acid to about 50mL of reagent water in a 100mL volumetric flask and dilute to volume with reagent water.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage for up to 28 days. The expiration date cannot exceed the expiration date of any of the components.

7.3.4.2 Second Source Initial Calibration Verification (ICV) Standard, 3.0ug/L – Add 0.15mL of the 1.0mg/L Second Source Intermediate Standard to a 125mL glass bottle. Add enough reagent water from a graduated cylinder to give a final volume of 50mL. The ICV is now

ready to be digested. Other final volumes may be used as long as the reagent ratios are kept the same.
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Stable under ordinary conditions of use and storage for up to 28 days. The expiration date cannot exceed the expiration date of any of the components.

7.3.5 QC Standards

7.3.5.1 Analytical Spike Standard, 73.26ug/L – Using a graduated cylinder, add 20mL of the 500ug/L Hg Intermediate Standard, and 5.0mL of nitric acid to about 50mL of reagent water and dilute to 136.5mL final volume with reagent water. Note: Since this standard is not digested the volume has been adjusted to compensate for the dilution that the other standards and samples undergo during the digestions.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

8.1.1 Total Mercury

Aqueous samples are routinely collected in 250mL plastic containers containing 3mL of a 1:3 nitric acid preservative. The preservative should be sufficient to achieve a sample pH of less than 2.

Although no temperature preservation is required, samples are routinely iced at the time of collection at 4°C (less than 6°C but not frozen). Samples are stored at room temperature until the time of digestion. Samples must be digested and analyzed within 28 days of sample collection. Digestates are stored at room temperature until the time of analysis.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives.

8.1.2 Dissolved Mercury

Aqueous samples for dissolved metals are routinely filtered at the time of sampling and collected in 250mL plastic containers containing 3mL of a 1:3 nitric acid preservative. The preservative should be sufficient to achieve a sample pH of less than 2.

Although no temperature preservation is required, samples are routinely iced at the time of collection at 4°C (less than 6°C but not frozen). Samples are stored at room temperature until the time of digestion. Samples must be digested and analyzed within 28 days of sample collection. Digestates are stored at room temperature until the time of analysis.

Note: If the sample is to be filtered in the laboratory, the sample must be collected in 250mL plastic container with no preservatives. The sample must be stored at 4°C (less than 6°C but not frozen) until filtered. Once filtered, the laboratory will add nitric acid to obtain a pH of less than 2.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives.

8.1.3 Preservation Checks – pH Verification

For each sample, prior to sample preparation,
- Place a piece of pH paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the pH paper.
- If the pH is outside the range of less than 2, initiate a Nonconformance Memo. Adjust the sample pH to less than 2 using 1:1 nitric acid.
- Mix well and hold for 24 hours. If pH is still greater than 2 repeat the process.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the pH paper into the sample container. The pH paper dye may bleed into the sample and affect sample results.

8.2 Soil Samples

Soil samples are routinely collected in 8oz plastic soil containers.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of digestion. Samples must be digested and analyzed within 28 days of collection. Digestates are stored at room temperature until the time of analysis.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

9.1.1 EPA 245.1 – Drinking Water

A digestion batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The laboratory's default minimum QC items performed for each digestion batch are: a method blank, a laboratory control sample (LCS), a low-level LCS (LLCS), a matrix spike (MS) to be performed on a minimum of 10% of samples or one per batch – whichever is greater, and a matrix spike duplicate (MSD).

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, an LLCS, 1 matrix spike, and 1 matrix spike duplicate (MSD).
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, an LLCS, 1 matrix spike (from sample 1-10), another matrix spike (from sample 11-20), and a matrix spike duplicate (MSD).

9.1.2 EPA 245.1 – Clean Water Act

A digestion batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The laboratory's default minimum QC items performed for each digestion batch are: a method blank and a laboratory control sample (LCS), a matrix spike (MS) to be performed on a minimum of 10% of samples or one per batch – whichever is greater, and a matrix spike duplicate (MSD).

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, 1 matrix spike, and 1 matrix spike duplicate.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), another matrix spike (from sample 11-20), and a matrix spike duplicate.

9.1.3 EPA 7470A, EPA 7471A, EPA 7471B, and SM3112B

A digestion batch consists of up to 20 environmental samples and the associated QC items. The laboratory's default minimum QC items performed for each digestion batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD).

The routine container supplied for this method is a 250mL (water) or 8oz (soil) container. 50mL or 1g is required for digestion. Reduced sample initial volumes or weights may be necessary to achieve the required batch QC frequency; however, the minimum digestion amount to be used is 10mL or 0.2g.

Note: Spike amounts must be adjusted to compensate for these reduced initial volumes or weights. Since final volumes are not easily reduced, elevated reporting limits will be provided when reduced initial volumes and weights are used

9.1.4 If there is insufficient sample volume to perform the required matrix spike(s), the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume or weight is defined as receiving less than a total of 50mL or 1g.

Note: If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required.

9.1.5 Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

9.2.1 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves*. This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 5 standards and a blank. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

The initial calibration standard concentrations currently in use in the laboratory are as follows:

Standard Level	Concentration (ug/L)
1	0.0
2	0.2
3	0.4
4	1.0
5	3.0
6	5.0

Refer to Section 7.3 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-041.

The correlation coefficient (r) of the regression curve must be greater than 0.995 for the initial calibration curve to be acceptable.

9.2.2 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

For EPA 245.1, the ICV must be within 5% of the true value to be acceptable. For EPA 7470A, EPA 7471A, EPA 7471B, and SM3112B, the ICV must be within 10% of the true value to be acceptable.

Note: The ICV is utilized to satisfy the EPA 245.1 requirement to analyze a QCS and IPC.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to level 5 of the ICAL. Refer to Section 7.3 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

9.2.3 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed immediately following the ICV. Continuing calibration blanks are analyzed immediately following each CCV.

The absolute value of the initial and continuing calibration blanks must be <½RL to be acceptable.

9.2.4 Continuing Calibration Verification

The initial calibration curve must be verified initially and after every 10 samples with a mid-level standard.

For SM3112B, the initial CCV must be within 5% of the true value and ongoing CCVs must be within 10% of the true value to be acceptable. For EPA 245.1, all CCVs must be within 10% of the true value to be acceptable. For EPA 7470A, EPA 7471A, and EPA 7471B, all CCVs must be within 20% of the true value to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to the 3.0 ug/L standard of the ICAL. Refer to Section 7.3 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

Note: The CCV is utilized to satisfy the EPA 245.1 requirement to analyze an IPC.

9.2.5 Reporting Limit Standard

SM3112B and certain project plans require the analysis of a reporting limit standard. If required, the reporting limit standard must be analyzed daily after the ICB, to verify the accuracy of the calibration curve at the reporting limit. The limits of recovery for the RL standard are 50-150%.

9.2.6 Quality Control Standard (QCS)

EPA 245.1 requires a second source QCS to be performed quarterly, at a minimum. The QCS must recover within 10% to be acceptable.

The laboratory uses the ICV to satisfy this QCS requirement.

9.2.7 Instrument Performance Check (IPC)

EPA 245.1 requires an IPC to be performed daily, after each calibration and after every tenth sample. The initial IPC must recover within 5% to be acceptable. Subsequent IPCs must recover within 10% to be acceptable.

The laboratory uses the ICV to satisfy the initial IPC requirement and the CCV to satisfy any subsequent IPC requirements.

9.2.8 Method of Standard Additions

Two identical aliquots of the sample digest, V_x, are taken. One aliquot is spiked with a known concentration, C_s. The second aliquot is analyzed un-spiked (the small volume of standard added to the spiked sample should be disregarded). The absorbance of both aliquots is measured and the sample concentration, C_x, is calculated as follows:

$$C_x = \frac{S_2 V_s C_s}{(S_1 - S_2) V_x}$$

Where:

S_1 = absorbance of the spiked aliquot
S_2 = absorbance of the un-spiked aliquot

The method of standard additions (MSA) must not be applied to samples analyzed at a dilution which produce a significant negative absorbance. The first point in the MSA (the un-spiked sample) should be greater than or equal to zero absorbance or the magnitude of the negative response should not exceed the reporting limit. Use good judgment when evaluating data where the absorbances are negative. The digestate should be diluted and reanalyzed to determine the extent of the matrix interferences.

9.2.9 Analytical Spike (Post Digestion Spike, PDS)

If the MS/MSD is not acceptable, an analytical spike (post digestion spike) must be prepared and analyzed on the sample used as the MS/MSD to determine if matrix interferences are present in the sample matrix. If the post digestion spike does not meet 85-115% recovery, proceed as outlined in the table below:

Result of Post Digestion Spikes	Corrective Action
Within 85-115% limits	None. PDS is acceptable.
>115% recovery	Repeat analysis. Remake spiking solutions, re-spike, and reanalyze. Reanalyze un-spiked sample.
<85% recovery but >50% recovery	Analyze all associated samples by single point method of standard addition and quantify by using MSA. Or qualify all associated samples on report. If sample concentration is less than the IDL, respike (to check for a spiking error), reanalyze, and re-evaluate.
<50% recovery	Dilute digestate and repeat spike. Perform the PDS procedure on all associated samples.

The >50% recovery of the post digestion spike is a benchmark below which samples may be biased high.

Note: If the sample used for MS/MSD exceeds 4x the spiking level, then the post digestion spike is not required.

Note: The post digestion spike must not be applied to samples which produce a significant negative absorbance. The analyst must use good judgment when evaluating data where the absorbances are negative.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

Remove the samples from the refrigerator, if refrigeration is required, and allow them to come to room temperature.

Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Compositing, Homogenization, and Segregation of Samples.*

10.1.1 Water Samples

10.1.1.1 Mix the sample thoroughly. Verify the sample pH as instructed in Section 8.1.3 and adjust as needed.

Note: If the pH is greater than 2 the sample must be held for 24 hours after pH adjustment and the pH re-verified.

10.1.1.2 Using a 50mL digestion vial, add 50mL of sample or an aliquot of sample diluted to 50mL to a 125-mL glass bottle.

10.1.1.3 Add 1.25mL HNO_3, 2.5mL H_2SO_4, and 7.5mL of $KMnO_4$ solution to each sample. Shake well after each addition. Be sure the purple color of $KMnO_4$ persists for at least 15 minutes. If not, add 7.5mL of $KMnO_4$ solution up to three additional times.

Note: Equal quantities of $KMnO_4$ must be added to the LCS and MB.

10.1.1.4 Add 4mL of potassium persulfate to each sample, cap, shake well, **loosen cap**, and place the samples in a water bath or block digestion apparatus at 95 ± 3°C for at least 2 hours.

10.1.1.5 Remove the samples and allow them to cool. Add 3mL of sodium chloride-hydroxylamine sulfate solution to each bottle to neutralize excess $KMnO_4$. This should give a final volume of 68.25mL.

Note: If a different final volume is obtained (due to additional $KMnO_4$ or other reason) a dilution factor must be calculated in order to correct the final result.

10.1.2 Soil Samples

10.1.2.1 Homogenize the sample thoroughly. Weigh between 0.50-0.60g wet weight of sample into a 125mL glass bottle.

10.1.2.2 Add 5.0mL DI water and 5.0mL aqua regia. Heat for at least 2 minutes in a water bath or digestion block at 95°C± 3°C.

Note: 10mL of 1:1 aqua regia may be utilized for this step.

10.1.2.3 Allow the samples to cool to room temperature and add 20mL DI water and 15mL $KMnO_4$ solution to sample, cap, shake well, **loosen cap**, and place the samples in a water bath or block digestion apparatus at 95 ± 3°C for at least 30 minutes.

Be sure the purple color of $KMnO_4$ persists for at least 15 minutes prior to placing samples in the water bath or block digestion apparatus. If not, add 7.5mL of $KMnO_4$ solution up to two additional times.

Note: Equal quantities of $KMnO_4$ must be added to the LCS and MB.

10.1.2.4 Allow the samples to cool to room temperature. Add 6mL of sodium chloride-hydroxylamine sulfate solution to each bottle to neutralize excess $KMnO_4$. Add 17mL DI water, cap, and shake well. This should give a final volume of 68mL.

Note: If additional volume(s) of $KMnO_4$ were added, compensate for the addition(s) by adding less DI water so that the final volume will remain constant.

10.2 Batch QC Sample Preparation

10.2.1 Water Samples

10.2.1.1 Method Blank – Add 50mL of reagent water to a 125mL glass bottle. Prepare in accordance with Section 10.1.1.

Note: The method blank must be prepared using the same volume of each reagent as used for the field samples. If additional $KMnO_4$ was added to any of the field samples an equal volume must be added to the method blank.

10.2.1.2 Laboratory Control Samples (LCS/LCSD) – Add 0.25mL of the 500ug/L Hg Intermediate Standard to a 125mL glass bottle. Using a disposable digestion vial, add 50mL reagent water. Prepare in accordance with Section 10.1.1.

Note: The LCS must be prepared using the same volume of each reagent as used for the field samples. If additional $KMnO_4$ was added to any of the field samples an equal volume must be added to the LCS.

10.2.1.3 Matrix Spikes (MS/MSD) – Add 50mL of the sample selected for the batch matrix spike to a 125mL glass bottle. Add 0.1mL of the 500ug/L Hg Intermediate Standard to the sample. Prepare in accordance with Section 10.1.1.

Note: For EPA 245.1 Clean Water Act, EPA 7470A, EPA 7471A, and EPA 7471B the matrix spike must be prepared in duplicate.

10.2.1.4 Low Level Laboratory Control Sample (LLCS) – Add 50mL of reagent water to a 125-mL glass bottle. Add 0.02mL of the 500ug/L Hg Intermediate Standard to the sample. Prepare in accordance with Section 10.1.1. Refer to Section 7.3.3.2 for additional information. (This is the same solution as the low level calibration standard, 0.2 ug/L.)

Note: The LCS must be prepared using the same volume of each reagent as used for the field samples. If additional $KMnO_4$ was added to any of the field samples an equal volume must be added to the LCS.

Note: The LLCS is only required for EPA 245.1 drinking water samples.

10.2.2 Soil Samples

10.2.2.1 Method Blank – Weigh out 0.5g of blank matrix and add to a 125mL glass bottle. Prepare in accordance with Section 10.1.2 for soils.

Note: The method blank must be prepared using the same volume of each reagent as used for the field samples. If additional $KMnO_4$ was added to any of the field samples an equal volume must be added to the method blank.

10.2.2.2 Laboratory Control Samples (LCS/LCSD) – Weigh out 0.5g of blank matrix and add to a 125mL glass bottle. Add 0.25mL of the 500ug/L Hg Intermediate Standard. Prepare in accordance with Section 10.1.2 for soil samples.

Note: The LCS must be prepared using the same volume of each reagent as used for the field samples. If additional $KMnO_4$ was added to any of the field samples an equal volume must be added to the LCS.

10.2.2.3 Matrix Spikes (MS/MSD) – Add 0.5-0.6g of the soil sample selected for the batch matrix spike to a 125mL glass bottle. Add 0.1mL of the 500ug/L Hg Intermediate Standard to the sample. Prepare in accordance with Section 10.1.2.

10.3 Analysis

10.3.1 Instrument Start-up and Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

Before analysis begins, inspect the system (pump tubes, mixing coil, gas/liquid separator) to see if any parts need to be cleaned or replaced.

Inspect the drying tube. Clean or replace as needed with a pre-made drying tube from Leeman Labs that has been inspected for discoloration. Caution should be used if moisture is visible in the tubing that follows the drying tube.

Fill the rinse tank with rinse water.

If the lamp is not already on and warmed up, turn on the lamp. The lamp must warm up for a minimum of 2 hours.

If the lamp is already on and warmed up, make sure the platens have the appropriate tension and turn on the pump. Allow a minimum of 20 minutes of pump time for the pump tubes to break in each day.

Rinse and fill the stannous chloride reagent bottle with stannous chloride solution. Switch the reagent line from the rinse bottle to the stannous chloride reagent bottle. Allow the reagent to reach the sample stream before starting an autosampler run.

Autosampler setup
Fill the standard tubes with the appropriate standards for the protocol being followed. (Refer to Section 10.3.4 for more information on method-specific analytical sequence and standards required.)

Fill the labeled sample test tubes with the samples and calibration verification standards in the proper order.

The method blank will be analyzed first. The LCS will follow immediately after the method blank. The samples, matrix spikes, and duplicates will then follow with a maximum of 10 analyses between CCVs/CCBs.

Enter the sample/QC IDs into the autosampler table giving each rack a unique name.

Load the rack(s) onto the autosampler.

10.3.2 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.1. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.2, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.4.

Calibration of the Mercury Analyzer
Call up the required protocol. Open a new data folder.

Go to CALIBRATION, RESET, and reset the calibration for a new calibration.

Go to CALIBRATION, STANDARDS, and ensure that calibration standards are entered at the proper concentrations.

Analyze the standards, beginning with standard 1 (Blank), proceeding from lowest to highest concentration.

When all calibration standards have been analyzed, go to CALIBRATION, LINE CALIBRATION. If calibration is within acceptable limits, accept the linear calibration and print the calibration curve.

10.3.3 Sample Analysis

The digestate must be analyzed using the same volume as that used for the calibration standards. Samples known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to include QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples between CCVs/CCBs.

Sample Analysis
Go to AUTOSAMPLER, SETUP. Enter the Rack IDs and the cup numbers to be analyzed.

Carryover from high concentration samples usually affects only the next one to two samples in the sequence. The two samples following an off-scale sample that is greater than 10ug/L must be reanalyzed to verify the presence or absence of mercury and the

quantitation of mercury. It is the responsibility of the analyst to clearly demonstrate that all mercury results are accurate and free from carry-over contamination.

10.3.4 Example Analytical Sequence

An example analytical sequence is listed below.

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
ICB	
RL Standard	Required for EPA 245.1 (Not a requirement for EPA 7470A, EPA 7471A, and EPA 7471B if calibrated to RL)
Samples & Batch QC Items	Up to 9 analyses, including QC.
CCV	Level 3.0ug/L
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	Level 3.0ug/L
CCB	

Analytical Sequence for samples not immediately following an initial calibration:

Description	Comments
CCV	Level 3.0ug/L
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	Level 3.0ug/L
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	Level 3.0ug/L
CCB	

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review.*

11.1.1 Dilutions

If the concentration of a sample is above the calibration range of the Hg analyzer, the sample digestate must be diluted and reanalyzed. The amount of digestate needed to prepare the desired dilution is determined from the following equation:

$$V_{digest} = \frac{V_{fv}}{DF}$$

Where:

V_{digest} = volume of sample digestate used to make the dilution
V_{fv} = final volume of diluted sample
DF = dilution factor

Note: Samples should be diluted with digested blank solution.

Note: This calculation assumes all applicable unit correction factors are applied.

The dilution factor is calculated as follows:

$$DF = \frac{V_{fv}}{V_{digest}}$$

Where:

V_{digest} = volume of sample digestate used to make the dilution
V_{fv} = final volume of diluted sample
DF = dilution factor

Note: This calculation assumes all applicable unit correction factors are applied.

If a sample exceeds the calibration range of the instrument by more than a factor of 10 (i.e., if the final, calculated result is greater than 50ug/L Hg at the instrument) the samples should be re-digested and reanalyzed with a smaller amount. This is a good check for possible positive bias of the sample by incomplete digestion of organic compounds. Initial weights or volumes of <0.2g or <1.0mL should be avoided, if possible, so that a representative sample can be achieved. If, due to the level of mercury in the samples, greater dilutions are required, consult with the Department Manager for further instructions.

11.1.2 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify the TALS Worksheet Notes and/or use the TALS Historical Data Tracker feature to determine if historical data is available for review.

11.1.3 Chemical Relationships

When available, the following chemical relationships must be evaluated for each sample. If these relationships are not met, the Department Manager must be contacted immediately.

- Total Results are $\geq$ Dissolved results (e.g. metals)

11.1.4 Drinking Water Compliance Evaluation

Public water suppliers (PWS) are governed by EPA-specified Maximum Contaminant Levels (MCL) above which indicates noncompliance. The MCL associated with this procedure is 0.002mg/L.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

Regression Curve:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample
F = Final volume/weight
I = Initial volume/weight
dw = % Solids decimal equivalent
D = Dilution factor

Note: All dry weight corrections are performed automatically in LIMS.

Note: This calculation assumes all applicable unit correction factors are applied.

12.0 Method Performance

12.1 Reporting Limit Verification (RLV)

At a minimum, RLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, RLVs must also be performed quarterly thereafter. For all other analytes and methods, RLVs must also be performed annually thereafter. Exceptions may be made for project-specific non-routine analytes.

12.2 Method Detection Limit (MDL) Study

The MDL is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDLs associated with this procedure are given in the Method Limit Group (MLG) in TALS.

At a minimum, MDL Studies must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

Note: MDL Studies are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.3 Method Detection Limit Verification (MDLV)

At a minimum, MDLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

For analytes and methods certified by DOD ELAP, MDLVs must also be performed quarterly thereafter. For all other analytes and methods, MDLVs must also be performed annually thereafter.

Note: MDLVs are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.4 Determination of the Instrument Detection Limit (IDL)

The instrument detection limit (IDL) is the concentration of analyte that can be statistically distinguished from the background noise of the instrument. The IDL limit must be determined annually, at a minimum, for each analyte in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs).*

The IDL is defined as three times the average of the standard deviation of seven replicate analyses of the IDL solution performed over three non-consecutive days. The IDL may be elevated above the background noise (blank levels). The current IDL associated with this procedure is given in the Equipment Limit Group (ELG) in LIMS.

12.5 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS, MS/MSD, Analytical Spike) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.6 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the

analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.7 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Acidic sample digestions – Neutralize before disposal into drain/sewer system.

- Excess oil samples – Transfer to waste department for storage/disposal.

15.0 References / Cross-References

- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-AN-041: *Reagent and Standard Materials Procedures*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs)*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- Method OB 10/90: Extraction and Analysis of Organics in Biological Tissue; U.S Environmental Protection Agency Environmental Services Division, Region IV Analytical Support Branch Athens, GA
- *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., November 1986 (SW-846 Update III).
  - Method 7000A, Revision 1: Atomic Absorption Methods; July 1992.
  - Method 7470A, Revision 1: Mercury in Liquid Waste (Manual Cold-Vapor Technique); September 1994.
  - Method 7471A, Revision 1: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique); September 1994.
- *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., February 2007 (SW-846 Update IV).
  - Method 7000B, Revision 2: Flame Atomic Absorption Spectrophotometry; February 2007.
  - Method 7471B, Revision 2: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique); February 2007.
- *Methods for Analysis of Water and Waste*; U.S. EPA Office of Research and Development: Cincinnati, OH, March 1983.
  - Method 245.1, Revision 3.0, EMMC Version: Determination of Mercury in Water by Cold Vapor Atomic Adsorption Spectrometry; 1994.
- *Methods for the Determination of Metals in Environmental Samples*; US EPA Office of Research and Development. Washington, DC.
  - Method 245.6, Revision 2.3, Determination of Mercury in Tissues by Cold Vapor Atomic Absorption Spectrometry, 1991

- *Standard Methods for the Examination of Water and Wastewater, Online Edition;* American Public Health Association: Washington, DC.
    - SM3020: Quality Assurance/Quality Control
    - SM3112B: *Metals by Cold vapor Atomic Absorption Spectrometry*; 1999

16.0 Method Modifications

16.1 Incorporation of Non-Routine Matrices

This procedure may be modified to analyze other matrices (e.g., waste (oil), wipe, tissue, and TCLP/SPLP leachate samples) upon client request. This will need to be arranged by the Project Manager at the initiation of the project.

Waste (oil), wipe, and tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and soil QC limits to evaluate wipe, waste, and tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. Teflon chips or blank sand are used as the blank matrix for tissues unless a "true" tissue matrix is required by the project. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and soil QC limits to evaluate TCLP/SPLP leachate samples. Water DOCs can be used to satisfy analyst demonstrations of capability for TCLP/SPLP matrices.

16.1.1 Collection and Handling Procedures for Non-Routine Matrices

Waste (oil) samples are collected in 8oz plastic soil containers. Waste (oil) samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of digestion. Waste (oil) samples must be digested and analyzed within 28 days of collection. Waste (oil) digestates are stored at room temperature until the time of analysis.

Wipe samples are routinely collected in 40mL VOA vials containing acetic acid in water, pH 4.93 +/- 0.05. Wipe samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of digestion. Wipe samples must be digested and analyzed within 28 days of collection. Wipe digestates are stored at room temperature until the time of analysis. Refer to the Work Instruction on *Wipe Tests: Sampling and Analysis* for additional information on wipe procedures.

Tissue samples are routinely collected in plastic containers with the size dependent upon the type of tissue being collected. Plastic jars or plastic baggies can be used. Upon receipt, tissue samples must be placed in the freezer at -10° to -20°C if extraction/digestion cannot be completed that day. Per the EPA Region 4 guidance document used for tissue analyses, tissue samples can be stored frozen for up to 6 months, and must be digested and analyzed within 28 days of thawing.

For TCLP and SPLP samples, once the TCLP/SPLP extraction procedure has been performed, the leachate is transferred to a plastic container and refrigerated at 4°C (less than 6°C with no frozen samples). TCLP/SPLP leachates must be stored at 4°C (less than 6°C with no frozen samples) until the time of preparation and/or analysis. The leachate

sample must be digested and analyzed within 28 days of completion of the TCLP/SPLP extraction.

16.1.2 Preparation and Analytical Procedures for Non-Routine Matrices

16.1.2.1 Waste (oil) samples are prepared in the same manner as routine soil samples, as outlined in Section 10.1 of this SOP. Waste (oil) QC samples are prepared in the same manner as routine soil samples, as outlined in Section 10.2 of this SOP.

16.1.2.2 Tissue samples are calculated on an "as is" basis and are prepared as outlined below. Tissue QC samples are prepared in the same manner as routine soil QC as outlined in Section 10.2 of this SOP.

Weigh between 1.0g and 1.2g of the sample and place into a 125-mL glass bottle. Add 2mL H_2SO_4 and 0.5mL HNO_3 to each sample and digest in the waterbath or heating block for at least 30 minutes at 80°C +/- 3°C or until the tissue is completely dissolved.

After samples are cooled, add 7.5mL of $KMnO_4$ (more $KMnO_4$ may be added if required), 4mL potassium persulfate solution, 25mL DI water and put samples back into water bath for an additional at least 90 minutes at 30°C +/- 3°C. Be sure the purple color of $KMnO_4$ persists for at least 15 minutes prior to placing samples in the water bath or block digestion apparatus. If not, add 7.5mL of $KMnO_4$ solution up to three additional times.

Remove the samples and allow them to cool. Add 3mL of sodium chloride-hydroxylamine sulfate solution to each bottle to neutralize excess $KMnO_4$. Add 26mL DI water and shake well. This should give a final volume of 68mL.

Note: If additional volume(s) of $KMnO_4$ were added, compensate for the addition(s) by adding less DI water so that the final volume will remain constant.

16.1.2.3 Wipe samples are prepared as outlined in the Work Instruction *Wipe Tests: Sampling and Analysis*.

16.1.2.4 Waste (oil), tissue, and wipe samples are analyzed in the same manner as routine matrices as outlined in Section 10.3.

16.2 Other Considerations

16.2.1 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each EPA 245.1 batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS (LLCS). The laboratory requires detection of this LLCS to be acceptable.

16.2.2 The reference methods state that the standards are to be made up daily and require the entire standard to be analyzed for the calibration; therefore, the standard had to be re-prepared for the next calibration. The newer technologies used by the laboratory require only a small amount of standard to be used (<10mL). Additionally, comparison studies have been performed, and the digested standards have been found to be stable for at

least 28 days. As such, a 28-day expiration date is used by the laboratory for these standards.

16.2.3 The referenced liquid preparation methods call for an initial volume of 100mL of sample. The reference methods utilize BOD bottles that required 100mL of sample to reach the required detection limit. The newer instrumentation utilized by the laboratory requires less than 10mL of the final digestion for analysis. Therefore, this SOP utilizes a 50mL initial volume and the reagents added for digestion are lowered proportionately.

16.2.4 EPA 245.1 specifies a 100mL initial volume but allows for reduced volumes as long as the reagent ratios and quality control are met. The laboratory uses 50mL as its default initial volume, and reagent ratios have been adjusted accordingly. All method detection limits, demonstrations of capability, and PTs have been performed in this same manner.

16.2.5 EPA 245.1 specifies the use of stannous chloride/sulfuric acid suspension used to reduce mercury to elemental mercury. EPA 7470A, EPA 7471A, and EPA 7471B specify stannous sulfate to be used to reduce elemental mercury to mercury; however, these methods also state stannous chloride dissolved in hydrochloric acid can be used as an option. In accordance with the instrument manufacturer's recommendations, the laboratory uses stannous chloride dissolved in hydrochloric acid as the stannous chloride/sulfuric acid suspension tend to clog the instrument's lines. All method detection limits, demonstrations of capability, and PTs have been performed in this same manner.

16.2.6 EPA 245.1 and SM3112B specify a Method Detection Limit (MDL) study to be performed annually and when a new analyst begins. The laboratory performs an MDL study initially, with MDL Verifications performed quarterly, and when a significant change is made to the equipment. The laboratory does not use analyst-specific MDLs; therefore, new analysts are required only to perform an initial demonstration of capability (IDOC) as described in Section 12.4.

16.2.7 EPA 245.1 specifies control criteria for the method blank as >10% the analyte concentration in the sample or 2.2 times the MDL, whichever is greater. The laboratory requires the method blank to be <1/2RL. The RL for this procedure is routinely within a factor of within ~3-5x the MDL; therefore, the 1/2RL criteria used for the method blank satisfies the method requirement.

16.2.8 EPA 245.1 and SM3112B specify a Linear Dynamic Range (LDR) to be performed initially and then annually thereafter, and these methods allow for samples to be reported without dilution provided they are no more than 90% greater than the LDR. The laboratory defines the LDR as the high point of the calibration curve and dilutes all samples with concentrations above the LDR such that the final concentration of the sample is within the LDR. As such, formal annual LDR studies are not performed. Re-evaluation of the calibration curve as samples is performed.

16.2.9 EPA 7470A states non-aqueous samples must be analyzed as soon as possible. EPA 7471B states non-aqueous samples must be analyzed as soon as possible but should be held no longer than 28 days. Therefore, the laboratory defaults to a 28-day holding time for these methods.

16.2.10 EPA 7471A states the waterbath temperature should be 90-95°C. EPA 7471B states the waterbath temperature should be 95 +/- 3°C. The laboratory has defaulted to the criteria listed in EPA 7471B.

16.2.11 EPA 7471A states to weigh triplicate portions of sample to obtain a final weight of 0.6g. EPA 7471B states to weigh an aliquot of sample equal to 0.5-0.6g. The laboratory weighs out 0.5-0.6 gram of wet sample. All PE studies, MDLs, and analyst demonstrations of capability are performed in this same manner.

16.2.12 EPA 245.1 and SM3112B do not contain a method-defined batch precision requirement. The laboratory's default QC items incorporate an MSD to satisfy the Clean Water Act requirements and those clients who batch require precision to be reported. Additionally, if insufficient sample volume is provided to perform the MS/MSD, the LCS is routinely prepared in duplicate (i.e., LCS/LCSD).

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Standard and Spike Solution Posting
Attachment 6: Glassware Cleaning Posting

Attachment 1:
SOP Summary

Sample Preparation and Analysis Summary

This procedure is based on the absorption of characteristic radiation at 253.7nm by mercury vapor. After digestion, to convert all forms of mercury to the same oxidation state, the mercury ions are reduced to mercury by the addition of stannous chloride and aerated from solution after passing through a mixing coil. The mixture passes through a gas/liquid separator and through a drying tube. The vapor is passed through a flow cell positioned in the light path of an atomic absorption spectrophotometer. Mercury concentration is measured as a function of absorbance.

Analytical Sequence

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
ICB	
RL Standard	Required for EPA 245.1 and SM4110B (Not a requirement for EPA 7470A, EPA 7471A, and 7471B if calibrated to RL)
Samples & Batch QC Items	Up to 9 analyses, including QC.
CCV	Level 3.0ug/L
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	Level 3.0ug/L
CCB	

Analytical Sequence for samples not immediately following an initial calibration:

Description	Comments
CCV	Level 3.0ug/L
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	Level 3.0ug/L (same as the 3.0ug/L calibration standard)
CCB	
Samples & Batch QC Items	Up to 10 analyses, including QC.
CCV	Level 3.0ug/L (same as the 3.0ug/L calibration standard)
CCB	

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Matrix	Routine Sample Container	Routine Sample Size	Minimum Sample Size	Dechlorination Agent	Chemical Preservation	Thermal Preservation	Holding Time[1]
Water	250mL plastic	50mL	10mL	Not Applicable	Nitric Acid pH<2	None[2]	28 days from collection
Soil	8oz plastic soil jar	10g	0.2g	Not Applicable	None	None[2]	28 days from collection

[1] Inclusive of digestion and analysis.
[2] Thermal preservation is not required; however, samples are routinely maintained at less than 6°C with no frozen samples.

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration	Daily	1 blank and 5 standards Correlation coefficient ≥ 0.995	Recalibrate
Initial Calibration Verification Standard (ICV)	At the beginning of the analysis	SW846 = within ± 10% 245.1 = within ± 5%	Recalibrate
Instrument Performance Check (IPC) (Note: ICV and CCV is used to satisfy IPC.)	EPA 245.1 only: After each ICAL and every 10 samples	Initial IPC = within 5% Subsequent IPC = within 10%	Recalibrate
2nd Source Quality Control (QCS) (Note: ICV is used to satisfy QCS.)	EPA 245.1 only: Quarterly	within 10%	Recalibrate
Continuing Calibration Verification (CCV)	At the beginning and end of the analysis and every 10 samples.	SW846 = within ± 20% 245.1 = within ±10%	Terminate the analysis. Correct the problem and reanalyze all samples since the last compliant CCV.
Calibration Blank (ICB/CCB)	After ICV and every CCV	Absolute value of the calibration blank must be < ½ RL	Terminate the analysis. Correct the problem and reanalyze all samples since the last compliant CCB.
RL Standard	After every calibration but not before the ICV. This standard is not a requirement of SW846, if a multi-point calibration encompassing the RL level is used.	50-150% of true value	Recalibrate
Method Blank (MB)	One per batch of twenty or fewer samples	Result < ½ RL	Refer to SOP SA-QA-17
Low-Level Laboratory Control Sample	EPA 245.1 Drinking Water Only:	Qualitatively identified	If the "regular" LCS meets criteria,

QC Item	Frequency	Criteria	Corrective Action
(LLCS)	One per batch of twenty or fewer samples		initiate NCM and report data If the "regular" LCS does not meet criteria, redigest and reanalyze batch
Laboratory Control Sample (LCS)	One per batch of twenty or fewer samples	MLG Limits	Refer to SOP SA-QA-17
Matrix Spike (MS)	EPA 245.1: One MS per 10% of samples (i.e., 2 MS per batch of 20 samples) Other Methods: One MS per 5% of samples (i.e., 1 MS per batch of 20 samples)	MLG Limits	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	1 per batch	MLG Limits	Refer to SOP SA-QA-17
Post Digestion Spikes (PDS)	When MS/MSD is unacceptable	Refer to Section 9.2.9 for guidance	Refer to Section 9.2.9 for guidance
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06 Note: Unsupervised work must not begin until acceptable IDOC is obtained.
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Reporting Limit Verification (RLV)	Upon method/instrument set-up, per analyte/method/matrix	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

QC Item	Frequency	Criteria	Corrective Action
	combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)		
Method Detection Limit Study (MDL)	Upon method/instrument set-up, per analyte/method/matrix combination	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
MDL Verification (MDLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Instrument Detection Limit (IDL)	Upon method/instrument set-up, and then quarterly thereafter	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:
- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Pump Tubing	X							Inspect daily, replace as needed
Standard Cups	X							Inspect daily, replace as needed
Drying Tube	X							Inspect daily, dry drying tube and all connection tubes or replace as needed
Mixing Coil		X						Inspect weekly, clean or replace as needed
Sample Probe			X					Inspect monthly, clean or replace as needed
Mercury Lamp							X	Clean or replace as needed

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually; AN = as needed

Troubleshooting
Troubleshooting should be documented as outlined above. If possible, troubleshooting is best performed in a step-wise manner to systematically isolate instrument components. Refer to the instrument manufacturer's guides for specific information and strategies. Enlist assistance from technical and/or department management as needed.

Contingency Plan
Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs, consisting of Hg lamps, drying tubes, flow cells, tubing, and other common instrumentation components. Since instrumentation is

standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
Standard and Spike Solution Posting

MERCURY STANDARDS AND SPIKE SOLUTIONS
PREPARATION INSTRUCTIONS / RECIPE

Standard	ICV standard, 2nd source	Calibration standards	CCV solution	LCS	MS/MSD	Analytical (post-digestion) spike
Source	Baker	SPEX	SPEX	SPEX	SPEX	SPEX

NOTES:
The purchased Baker stock (1000mg/L) will be used to create the 2nd Source (ICV) Intermediate standard (1.0 mg/L), which will then be used to create the ICV standard (3.0µg/L)

The purchased SPEX stock (1000mg/L) will be used to create the Hg Intermediate standard (0.50mg/L), which will then be used to directly create each of the calibration standards (including the CCV standard, 3.0µg/L), the LCS, and the MS/MSD

The Hg Intermediate standard (0.50mg/L) will also be used to make the analytical spike standard (73.26µg/L), which will then be used to create the analytical spike (1.0µg/L).

Standard Name	Source 1	Volume	Source 2	Volume	Final Volume*	Comments	Final Concentration
		mL		mL	mL		
2nd Source (ICV) Intermediate	Baker Stock *(1000mg/L)*	0.10	HNO3	2.5	100		*1.0 mg/L*
ICV solution	2nd Source (ICV) Intermediate	0.15			50	Digest	*3.0µg/L*
Hg Intermediate	SPEX Stock *(1000mg/L)*	0.050mL	HNO3	2.5	100		*0.50mg/L*
Calibration Standards	Hg Intermediate	0.0, 0.02, 0.04, 0.10, 0.30, and 0.50			50	Digest	*0.0, 0.2, 0.4, 1.0, 3.0, and 5.0µg/L*
CCV solution	Hg Intermediate	0.30			50	Digest	*3.0µg/L*
LCS	Hg Intermediate	0.25			50	Digest	*2.5µg/L*
MS/MSD	Hg Intermediate	0.10			50	Digest	*1.0µg/L*
Analytical Spiking standard	Hg Intermediate	20	HNO3	2.5	136.5	Use a graduated cylinder	*73.26µg/L*
Analytical (Post-digestion) spike	Analytical Spiking standard	0.10				Add to 10mL of digested sample	*1.0µg/L*

*DI water is used to dilute standards to final volume

****Note. This is a convenient reference for the basic instructions for the preparation of typical Hg standards and spike solutions, and should only be used in combination with a thorough understanding of Section 8 of SOP ME28.*

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Attachment 6:
Glassware Cleaning Posting

GLASSWARE CLEANING PROCEDURES
METALS DEPARTMENT

Graduated Cylinders

1. Scrub with hot, soapy H_2O and brush.
2. Rinse thoroughly with tap H2O.
3. Rinse with 10% HNO_3
4. Rinse thoroughly with DI H_2O.

Volumetric Flasks

1. Empty contents of flask
2. Squirt a small amount of cleaning detergent directly into volumetric flask
3. Fill flask 1/3 full with **HOT** H_2O
4. Replace top and shake flask.
5. Empty flask and rinse with **HOT** H_2O until no soap remains in flask.
6. Add approximately 10mL concentrated HNO_3 to 50mL, 100mL, and 250mL flasks ---- replace top and shake well.

For 500mL or 1000mL flasks use 25mL and for 10mL flasks use 2 - 5mL of concentrated HNO_3.

7. Rinse 3 times with DI H_2O, filling flask 1/3 full and replacing top. Store until needed.

*** NEVER PLACE VOLUMETRIC FLASKS OR TOPS IN SINK OR DISHPAN WITH OTHER DIRTY DISHES.**

***Dispose of all acid waste in accordance with the TestAmerica Savannah Addendum to the Corporate Environmental Health and Safety Manual.**

18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial, grammatical, and formatting changes made. Boilerplate text added. Updated referenced SOP titles and document control numbers to reflect current versions.
- Added section to describe analytical data system, software, and hardware. Section 6.2
- Added note that if an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required. Section 9.1
- Clarified requirements and frequency for RLVs, MDL Studies, and MDLVs to be consistent with SOP SA-QA-07 and to include the quarterly frequency as defined by DOD. Section 12.1 - 12.3 and Attachment 3
- Added note that unsupervised work must not begin until acceptable IDOC is obtained. Attachment 3
- Added section on troubleshooting. Attachment 4
- Revised batch QC frequency (i.e., default batch QC items). Section 9.1, Section 16, and Attachment 3
- Removed requirement to notify PM immediately via NCM for sample detections above the MCL. This notification is automatically generated via the Action Limit feature in TALS.
- Removed requirement to verify pH paper upon receipt.
- Incorporated method requirements from SM3112B.

ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS (PCBs) BY GC/ECD

(Method: EPA 508)

Approvals (Signature/Date):

Andrea Teal — April 29, 2010
Andrea Teal — Date
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April 15, 2010
Benjamin Gulizia — Date
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Ernest B. Walton — April 28, 2010
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Facility Distribution No. 1 Distributed To: QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of organochlorine pesticides and polychlorinated biphenyls (PCBs) as Aroclors in water samples by gas chromatography/electron capture detection (GC/ECD).

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

A known volume of sample is placed into a separatory funnel, buffered to pH 7, and extracted using methylene chloride. The extract is dried using anhydrous sodium sulfate and transferred to a glass Kuderna-Danish (K-D) concentration apparatus. The K-D is placed in a water bath that has been heated to 65-90°C. As the solvent evaporates, the target compounds are collected in the concentration tube. When the apparent volume of solvent reaches approximately 2mL, the K-D is removed from the water bath and allowed to cool. Approximately 20mL of MTBE is added to the K-D, and the K-D process is repeated. The extract is adjusted to a 5mL final volume with MTBE and transferred to a storage vial or container. The extract vials are stored at 4°C until the time of analysis.

Analysis of the extract is performed on a GC equipped with dual capillary columns (different phases) connected to dual electron capture (EC) detectors, allowing simultaneous detection and confirmation of the target compounds. Quantitation is performed using the internal standard calibration technique.

This SOP is based on the following methods: EPA Method 508.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Acetone, methylene chloride, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.1.5 After cleaning, glassware must be inspected for the presence of water, especially around the Snyder column balls. A thorough acetone rinsing will help to eliminate or minimize this problem.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. Also, note that all the analytes listed in the LIMS MLG are not resolved from each other on any one column, i.e., one analyte of interest may be an interferent for another analyte of interest. For this reason, analyte identifications are confirmed.

4.2.2 The sample extract may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. Drinking water samples rarely have complex matrices so cleanup is non-routine. Samples collected from groundwater, which may be used as a potential source of drinking water, may contain elemental sulfur and have more complex matrices than finished dirking water.

Copper may be added to the extract to eliminate or minimize interferences from elemental sulfur (EPA 3660B). Refer to Attachment 8 for sulfur clean-up instructions using copper. If copper (sulfur) cleanup is ineffective, the remaining option is to dilute the sample extract prior to analysis.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Samples with high levels of organic material (oils, particulates, etc.), which would be a rare and non-routine occurrence for drinking water samples, may cause the formation of emulsions during the extraction. Since the sample is buffered and adjusted to pH 7 prior to extraction, the possibility of emulsions is reduced. The extract may be filtered or stirred to remove the emulsion. Sodium sulfate may be also be used to break the emulsion by combining with the water in the emulsion.

4.2.4 Interferences by phthalate esters generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable latex or nitrile gloves, with thickness of 3mm or greater, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of chemicals used in this procedure has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

Methylene chloride is a carcinogen and an irritant. It causes irritation to the respiratory tract and has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting, and headache. Methylene chloride may be absorbed through the skin and can cause irritation and pain to the skin and eyes.

Acetone is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, lightheadedness, headache, dizziness, and blurred vision.

Sodium hydroxide is a severe corrosive. Contact with the skin can cause irritation or severe burns and scarring. Contact with the eyes can cause irritation, burns, permanent vision impairment or even blindness.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

This SOP contains procedures that are designed to reduce the exposure of lab personnel to solvent vapors, and to minimize the amount of solvent introduced into the lab air. All solvent transfer steps must be performed quickly and under a hood, if possible. Use the minimum amount of solvent to get the job done. Do not allow open containers of solvents or extracts to evaporate into the lab.

The gas chromatograph contains zones that have elevated temperatures. The analyst must be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Acetone	Flammable	1000ppm TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methyl Tert-Butyl Ether	Flammable Irritant Poison	50ppm TWA	Inhalation of vapor can irritate respiratory tract. Breathing high concentrations in air can cause lightheadedness, dizziness, weakness, nausea, and headache. Ingestion may cause vomiting with symptoms similar to inhalation. Can cause irritation to skin and eyes with possible damage to the eye tissue.
Methylene Chloride	Carcinogen Irritant	25ppm TWA 125ppm STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Sodium Hydroxide	Corrosive	2mg/m^3 Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid[2]	Corrosive Oxidizer Dehydrator Poison Carcinogen	1mg/m^3 TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
[2]Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Analytical Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Separatory funnels – 1L and 2L, glass with Teflon stopcocks or Teflon

Mechanical shaking device – the rotating (end-ever-end) extractor is used routinely to "shake" samples; the horizontal automatic shaker can also be used.

Kuderna-Danish apparatus – consists of the K-D body, three-ball Snyder column, and a graduated concentration tube with springs or clips to hold the concentration tube to the K-D body. Verify the concentration tube in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Water bath – compatible with the K-D apparatuses, located under an operating fume hood

Gas chromatograph (GC) – temperature programmable, equipped with single or dual electron capture (EC) detectors and a compatible autosampler. The instruments currently in

use are the Agilent 5890 and 6890 gas chromatographs equipped with dual electron capture detectors.

The following column pairs are recommended and are currently in use. Other columns/phases may be used if the calibration and QC criteria are met and adequate separation of the target compounds is achieved.

Restek CLP I fused silica capillary column 30m x 0.32mm ID x 0.50um film
Restek CLP II fused silica capillary column 30m x 0.32mm ID x 0.25um film

Data Systems – Instrument control and data acquisition are performed using Agilent Chemstation software. Once acquired, the data are electronically transferred to the Target data system. This software has the capability of processing stored retention time and response (area) data by recognizing a GC peak within a given retention time window and comparing the retention time of the sample to the retention times of standards analyzed under the same conditions. The Target software also allows integration of the peak responses, calculation of response factors as or construction of a linear regression calibration curve, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the response factors.

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Transfer Pipettes – various sizes

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

pH paper – used to provide a quick and easy way to approximate the pH of a sample to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step.

Peroxide Test Strips

DPD residual (free) chlorine reagent pillows – (currently purchased from HF Scientific; catalog # 10306)

Medicine cups – 30mL, disposable

Filter paper

Small funnels

Extract Vials – 10mL vials with Teflon lined screw caps

Autosampler Vials – 2mL vials with Teflon lined crimp caps or 2mL screw cap vials with PFTE-faced septa, compatible with the autosampler

Detergent – used for washing non-disposable labware.

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

1L amber glass fitted with a Teflon-lined cap containing 80mg of solid sodium thiosulfate (currently purchased from ESS; catalog # 1000-0150-SOTH-PC)

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.*

Acetone, methylene chloride, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Reagent water – lab-generated deionized water

7.2.2 Sodium sulfate, powdered and granular, anhydrous – currently purchased from J.T. Baker; catalog # 3375-07; 12kg
Purify by heating at 400°C for 4 hours in a shallow tray.

LIMS Name:EX_Na2SO4
Storage: Ambient in glass container - store in a tightly closed container in a cool, dry, ventilated area. Separate from incompatibles.
Expiration Date: 6 months

7.2.3 Hydrochloric acid (HCl) – concentrated (12N), reagent grade; currently purchased from Mallinkrodt; catalog # 5587-46; 2.5L
LIMS Name:EX_HCL
Storage: Ambient in acid cabinet - Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration Date: Manufacturer's date

7.2.4 Hydrochloric acid (0.10N) – Prepared by adding approximately 800mL reagent water to 1L volumetric flask. Add 8.3mL of concentrated HCl and dilute to volume with reagent water. Cap flask and invert to mix.
LIMS Name:EX_0.10NHCL
Storage: Ambient in acid cabinet
Expiration Date: One year

7.2.5 Dipotassium phosphate (K_2HPO_4) – reagent grade; currently purchased from Fisher; catalog # 3252-01; 500g.
LIMS Name:K2HPO4SALT
Storage: Ambient in reagent cabinet
Expiration Date: Manufacturer's date

7.2.6 Dipotassium phosphate (0.10M) – Prepared by transferring 17.44g of K_2HPO_4 to a 1L volumetric flask. Add 600mL reagent water to the container. Cap and invert to dissolve the solids and mix. Dilute to a final volume of 1 liter with reagent water.
LIMS Name:K2HPO4SOLN
Storage: Ambient in reagent cabinet
Expiration Date: Three months

7.2.7 Phosphate buffer – Prepared by adding 592mL of 0.10N HCl and 1000mL of 0.1M K_2HPO_4 to a 2L volumetric flask. Cap and invert to mix. Transfer to two 1L glass storage containers.
LIMS Name:508_BUFFER
Storage: Ambient, reagent cabinet
Expiration Date: Three months

7.2.8 Sodium hydroxide (NaOH) – reagent grade Mallinkrodt 7708-06 (2.5kg)
LIMS Name:EX-Naoh
Storage: Ambient, reagent cabinet - Store in a cool, dry, ventilated area, away from incompatibles (acids, organics).
Expiration Date: Manufacturer's date

7.2.9 Sodium hydroxide (1N) – Add about 500mL of reagent water to a 2L beaker. Add a magnetic stir bar and place on stir plate. Turn the stir bar to slow. Add 40g of sodium hydroxide in small portions slowly to the beaker. After all of the sodium hydroxide has been added and has dissolved, add another 500mL of reagent water to the beaker slowly. Allow the solution to cool and transfer to a glass storage container.
LIMS Name:EX10N_Naoh
Storage: Ambient, reagent cabinet
Expiration Date: Three months

7.2.10 Sulfuric acid (H_2SO_4) – concentrated (36N) reagent grade Mallinkrodt 5557-46 (2.5L)
LIMS Name:EX_h2so4c
Storage: Acid cabinet - Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration Date: Manufacturer's date

7.2.11 Sulfuric acid (1N) – Add 800mL reagent water to 1L volumetric flask. Add a magnetic stir bar and place on stir plate. Turn the stir bar to slow. Add 28mL of concentrated sulfuric acid slowly to the flask. Dilute to volume with reagent water. Continue to stir until the solution cools. Transfer to a 1L glass storage container.
LIMS Name:ex-1-on-h2so4
Storage: Ambient, in acid cabinet
Expiration Date: One year

7.2.12 Sodium chloride-reagent grade – J.T. Baker 3375-07 (12kg)
Purify by heating at 400°C for 4 hours in a shallow tray.
LIMS Name:ex_nacl
Storage: Ambient in glass container
Expiration Date: 6 months

7.2.13 Sodium thiosulfate – reagent grade Doe and Ingalls 395401 (500g)
LIMS Name:ex_na2s2o3
Storage: Ambient in reagent cabinet
Expiration Date: Manufacturer's date

7.2.14 Methanol – residue grade or better J.T. Baker 9093-03 (4L)
LIMS Name:meoh
Storage: Flammable solvents' cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.
Expiration Date: Manufacturer's date

7.2.15 Methylene Chloride – residue grade or better. J.T. Baker 9264-03 (4L)
LIMS Name:EX_MECL2
Storage: Chlorinated solvents' cabinet
Expiration Date: Manufacturer's date

7.2.16 Methyl tertiary butyl ether (MTBE) – residue grade or better. J.T. Baker 9043-02 (1L)
Check periodically for formation of peroxides.
LIMS Name: MTBESOL
Storage: Flammable solvents' cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.
Expiration Date: Manufacturer's date

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

The recipes for the preparation of the calibration standards and spiking standards are included in Attachment 6.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Containers

Drinking water samples are routinely collected in 1L amber glass containers fitted with Teflon-lined caps and containing 80mg sodium thiosulfate de-chlorination agent. This amount of dechlorination agent should be sufficient to remove residual chlorine from most routine drinking water samples.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be extracted within 7 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 14 days of extraction.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives and/or de-chlorination agents.

8.2 Preservation Checks (Sample pH and Residual Chlorine)

These checks can be performed upon receipt or prior to preparation. It is preferable to perform the checks upon receipt but the checks must be performed prior before sample preparation is initiated.

- Mix the sample by inverting several times.
- Pour 10mL of the sample into a 20mL medicine cup.
- Touch a piece of wide range pH paper to the sample in the cup and compare the pH to the colors on the side of the pH paper holder.
- Record the pH. Contact the Department Manager or Technical Manager if the sample pH is <5 or >9.
- Add a DPD powder pillow to the sample in the cup and gently swirl to mix the sample and the reagent.
- Wait approximately one minute for the color to develop and note the presence of any traces of a pink color on the prep sheet.
- If the sample is positive for residual chlorine (i.e., the sample turns pink), add 10mg of sodium thiosulfate to the 1L sample container, cap, and invert several times to dissolve the reagent.
- Recheck the sample for residual chlorine.
- Add up to two additional 10mg aliquots of sodium thiosulfate to the sample if it continues to test positive for residual chlorine.
- Stop and contact the Department Manager or Technical Manager if it the sample still tests positive for residual chlorine after three additional 10-mg aliquots of sodium thiosulfate have been added to the sample.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The default QC items performed for each extraction batch are: a method blank, a laboratory control sample (LCS), a low-level laboratory control sample (LLCS) spiked at the RL, a matrix spike (MS) to be performed on a minimum of 10% of samples or one per batch – whichever is greater, and a matrix spike duplicate (MSD).

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, an LLCS, and a matrix spike/matrix spike duplicate pair (MS/MSD).
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, an LLCS, a matrix spike/matrix spike duplicate pair (MS/MSD) from sample 1-10, and another matrix spike from sample 11-20.

The routine container supplied for this method is a 1000mL container. The routine RL and MDL are based on extraction of 1000mL and a final extract volume of 5.0mL. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 200mL with a final extract volume of 1.0mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), the LCS must be prepared induplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 2000mL.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

Refer to Section 10.1 for specifics on the preparation process.

9.2 Instrument QC

9.2.1 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves*. This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 3 standards. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

Note: A minimum of 6 points is required for a quadratic curve. Higher order curves are not permitted.

The initial calibration standard concentrations currently in use in the laboratory are listed in Attachment 6. Refer to Attachment 6 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-041.

9.2.2.1 ICAL Criteria

The preferred method of quantitation is the average response factor. The relative standard deviation (%RSD) of the calibration standards must be <20% for the initial calibration curve to be acceptable.

If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve. If the regression curve option is chosen, the regression coefficient (r^2) must be greater than or equal to 0.990 to be acceptable.

If these criteria are not met, then re-calibration is required before sample analysis can proceed.

9.2.2 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified after the initial calibration is established, prior to any sample analyses, in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The initial calibration verification standard concentration currently in use in the laboratory are summarized in the recipes in Attachment 6, which are equivalent to mid-level of the ICAL. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

The ICV must be within +/-20% to be acceptable.

9.2.3 Instrument blanks (Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB))

The instrument must be shown to be free from contamination by the analysis of instrument blanks (PIBLK). Instrument blanks are analyzed periodically throughout the sequence.

Initial and continuing calibration blanks must be <1/2RL to be acceptable.

9.2.4 Continuing Calibration Verification

The initial calibration curve must be verified at the beginning and end of each 12-hour clock with an alternating mid-level standard.

Refer to Attachment 6 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

The CCV must be within +/-20% to be acceptable.

Note: The routine CCV standards are the Pest A/B mix and the AR1660 standard. Single points of the remaining Aroclors, technical chlordane, and toxaphene are analyzed at least every 72 hours (e.g., Monday, Wednesday, and Friday) to update the retention times and for pattern recognition. As long as the Pest A/B calibration standard and the AR1660 standard meet the calibration acceptance criteria, the ICAL is deemed acceptable for all targets.

9.2.5 Internal Standard (ISTD)

This procedure is an internal standard (ISTD) procedure. Bromonitrobenzene is the internal standard.

Prior to analysis, this internal standard must be added to all standards, samples, and QC items. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples at a concentration of 0.10ug/mL.

The response of the ISTD in the ICV/CCV must be within 50% of the response of the ISTD in the CCV-level standard in the ICAL. If the response is outside of this range, the analysis of the CCV must be repeated and any samples associated with the CCV must also be re-analyzed. Repeated failure of the ISTD response will require re-calibration.

The response of the ISTD in the samples and batch QC items must be within 30% of the response of the previous CCV. If the response is outside of this range, corrective action must be taken to included reanalysis of the extract, re-spiking extract with ISTD and re-analysis, or re-calibration of the analytical system. Obvious matrix interferences are qualified and noted in an NCM.

9.2.6 Surrogates

This procedure uses two surrogates, tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB), to evaluate the extraction process. Prior to preparation, these surrogates are added to all samples and QC items. The concentration of the surrogate must be the same in all field samples and QC samples. The concentration of the surrogates added to the field samples and QC items is 0.25ug/L, which is equivalent to an extract concentration of 0.50ug/L, assuming a 1L extraction volume and a final extract volume of 5.0mL.

The percent recovery of the surrogates in all field samples and QC samples must be within the limits listed in the Method Limit Groups (MLGs) in LIMS (i.e., 70-130%R). If the percent recovery is outside of this range, the analysis of the sample must be repeated. Barring matrix interferences, repeated failure of the surrogate percent recovery indicates re-extraction is necessary.

Note: If one of the surrogates is within the acceptance limits and the other surrogate recovery is >10%, a field sample is deemed acceptable and re-extraction and re-analysis is not automatically performed.

9.2.7 Column Evaluation

9.2.7.1 Priming Standard

If the instrument has not been in use for more than one day, a "priming" analysis may be beneficial. The analysis of a relatively high concentration pesticide or PCB standard may help to stabilize the response of the very sensitive EC detector. Inject the high standard multiple times and allow the instrument to cycle through the temperature program. The baseline should be monitored before and after the priming analysis to gauge the condition of the detector. A hexane blank should be analyzed after the analysis of the priming standard and before the % breakdown check.

9.2.7.2 PEVAL Breakdown Evaluation Standard

The column(s) must be evaluated at the beginning of each 12-hour clock.

Note: This column evaluation does not have to be performed if PCBs are the only target compounds required. PCBs are stable and not subject to breakdown in the injection port.

The PEVAL evaluation is performed as follows:

- Inject the Endrin/DDT breakdown standard.
- Check the peak integrations and calculate the breakdown as follows:

$$\%\text{Breakdown DDT} = \frac{\text{Response(DDE + DDD)}}{\text{Response(DDT + DDE + DDD)}} \otimes 100$$

$$\%\text{Breakdown Endrin} = \frac{\text{Response(Endrin Aldehyde + Endrin Ketone)}}{\text{Response(Endrin + Endrin aldehyde + Endrin Ketone)}} \otimes 100$$

Note: The response (area) must be used to evaluate the breakdown. Do not use concentrations and do not "undetect" peaks that are below the RL or MDL. All peaks detected by the data system must be included in the percent breakdown calculation.

The breakdown for each compound must be less than 20%.
If the breakdown exceeds the criterion, the instrument will require column and/or injector port maintenance. The maintenance may include, but is not limited to, replacing the septum, clipping the front of the guard column, replacing the glass injector sleeve, and scrubbing (cleaning) the injector port.

9.2.7.3 Laboratory Performance Check (LPC)

The IPC must be analyzed every 12 hours to verify the instrument has adequate sensitivity and resolution. The IPC must be evaluated against the criteria given in Attachment 7.

If the IPC criteria cannot be met, the instrument will require column and/or injector port maintenance. The maintenance may include, but is not limited to, replacing the septum, clipping the front of the guard column, replacing the glass injector sleeve, and scrubbing (cleaning) the injector port.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

10.1.1 Remove the field samples from the storage refrigerator and allow them to come to room temperature.

10.1.2 Remove the surrogate and target compound spiking solutions from the storage refrigerator.

10.1.3 Prepare LIMS batch sheet and scan samples into the batch.

10.1.4 Gather and clean the glassware needed for the extraction:

1 Teflon separatory funnel for each field and QC sample
1 K-D apparatus for each field and QC sample
1 glass funnel for each field and QC sample
1 piece of filter paper for each field and QC sample
1 500mL jar for each field and QC sample
4 1L sample containers with sodium thiosulfate for MB, 2 LCS, and LLCS (these should be obtained from receiving)

10.1.5 If the extracts will be concentrated the same day as they are extracted, turn on the water bath.

10.1.6 Inspect the samples for the presence of solids. Solids will plug the separatory funnel stopcock. If solids are present, stop and contact the Department Manager or Technical Manager to determine a course of action. The option for samples with solids present is continuous liquid-liquid extraction.

10.1.7 Check the sample pH and check the sample for residual chlorine (in accordance with Section 8.2) if this was not checked upon receipt into the department.

10.1.8 Mark the level of the sample on the outside of the container with a marking pen.

10.1.9 Fill the four 1L containers for the MB, 2 LCS, and LLCS with reagent water. Label one LCS as the pesticide LCS and the other as the PCB LCS.

Note: The QC items must have the same preservative (sodium thiosulfate) as the field samples.

10.1.10 Add 0.50mL of the pesticide spiking solution to the pesticide LCS and 0.50mL of the PCB spiking solution to the PCB LCS. Cap and invert to mix.

For the pesticide LLCS, add 0.050mL of the pesticide spiking solution.
For the PCB LL-LCS, add 0.010mL of the PCB spiking solution.

Prepare MS/MSD in the same manner as the LCS, by adding the applicable amount of spiking mix to separate aliquots of the chosen sample.

10.1.11 Add 0.50mL of the surrogate spiking solution to each of the field samples and QC items. Cap and invert to mix.

Note: Add target compound and surrogate spiking solutions directly to the sample container.

If limited volume is available or you must use a smaller volume for MS or MS/MSD; reduce the volume of sample extracted, the volume of surrogate and target spiking solutions added, and the final volume of the extract proportionately as summarized in the following table:

Volume of sample (mL)	Volume of Surrogate (mL)	Volume of Target Compound Spike if MS or MSD (mL)	Final Volume of Extract (mL)
1000	0.50	0.50	5.0
500	0.25	0.25	2.5
200	0.10	0.10	1.0

Do not use less than 200mL of sample or concentrate the extract less than 1.0mL.

10.1.12 Pour the field samples and QC items into the 2L separatory funnels.

10.1.13 Add 50mL of phosphate buffer to each field sample and QC item. Cap the funnel and invert to mix.

10.1.14 Check the pH of each field sample and QC item as described previously (in accordance with Section 8.2). The pH should be 7 +/- 1 pH unit. If not, adjust to pH 7 with small aliquots of 1N NaOH or 1N H_2SO_4 and re-check the pH. Record any additions of acid or base on the prep sheet.

10.1.15 Add 100g of purified sodium chloride to each field sample and QC item. Cap and shake to dissolve the salt.

10.1.16 Add 70mL of methylene chloride to each sample and QC item container, seal, and shake for 30 seconds, venting under the hood. Transfer the methylene chloride to the separatory funnel corresponding to the sample or QC item.

10.1.17 Cap the separatory funnels and place on the automatic shaker for three minutes.

If using the shaker, remove the separatory funnels from the shaker and vent under the hood. Place the separatory funnels on the holding rack and remove the cap. Allow

the layers to separate for approximately ten minutes while the next set of separatory funnels is extracted on the shaker.

10.1.18 Collect the extract in a labeled 500mL jar. Add approximately 50g purified sodium sulfate to each collection jar to remove any water present.

10.1.19 Repeat the steps in Section 10.1.16 through Section 10.1.18 two more times with additional 70mL aliquots of methylene chloride, combining the three extracts for each field sample and QC item.

10.1.20 After all three of the extractions are completed, allow the combined extracts to sit for a minimum of 30 minutes or, if this is a good stopping point, overnight.

10.1.21 Make sure that the water bath is on. The temperature should be 65-90°C before starting the solvent evaporation/extract concentration. Attach the 10mL receiving tube to the 500mL KD flask and secure with clips. Label the flask and place in holder. Add a boiling stone to each flask.

10.1.22 Fit a piece of filter paper into the glass funnel and add about 10g of sodium sulfate to the filter. Rinse with methylene chloride, discarding the solvent in the chlorinated solvent waste container.

10.1.23 Position the filter/funnel over the K-D flask and pour the extract through the filter/funnel and collect in the K-D. Rinse the jar with several small aliquots of methylene chloride and pour through the filter/funnel into the KD. Rinse the filter/funnel with several small aliquots of methylene chloride.

10.1.24 Attach the Snyder column to the KD flask and add 1-2mL of methylene chloride to the top of the column to set the glass balls in the column.

10.1.25 Place the KD apparatus on to the water bath and evaporate the solvent to concentrate the extract. When the evaporation is proceeding properly, the glass balls in the Snyder column will "chatter" and the chamber holding the glass balls will not flood with solvent.

Lift the KD apparatus out of the water bath periodically and check the volume of the extract. When the apparent volume of the extract is 2mL, remove the KD apparatus from the water bath and place on the holder. Allow the KD apparatus to drain for approximately 10 minutes.

10.1.26 Remove the Snyder column and add 25mL of MTBE and a new boiling stone to the KD. Wet the Snyder column with 1-2mL MTBE and return the KD to the water bath maintained at 65-90°C.

Lift the KD apparatus out of the water bath periodically and check the volume of the extract. When the apparent volume of the extract is 2mL, remove the KD apparatus from the water bath and place on the holder. Allow the KD apparatus to drain for approximately 10 minutes.

10.1.27 Add 1-2mL of MTBE to the top of the Snyder column and allow the solvent to drain into the receiving flask, rinsing down the sides of the KD.

10.1.28 Repeat Sections 10.1.26 and 10.1.27 at least once, for a minimum of two solvent exchanges.

10.1.29 Remove the receiving tube from the KD flask, label, and cover with a small piece of aluminum foil. If the extract will not be concentrated further at this point (this is a good stopping point) label the tube, cover with a glass stopper, and transfer to the extract refrigerator until ready to concentrate the extract to the final volume.

10.1.30 Evaporate the solvent under a gentle stream on nitrogen on the N-Evap to a volume of about 1mL. Add 5mL of MTBE and evaporate again to about 1mL. Adjust the final volume to 5.0mL with MTBE and transfer the extract to a 12mL vial fitted with a Teflon-lined cap. Mark the volume on the side of the container with a Sharpie.

10.1.31 Transfer the samples to the storage refrigerator and record the storage box number on the prep sheet.

10.2 Analysis

10.2.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

Two columns are connected to the injection port using a press-tight glass y-splitter and a guard column, a two-hole ferrule, or a glass tee to provide simultaneous detection and confirmation of the target analytes.

Example GC Parameters
Column1: Restek CLPesticides 1 30m x 320um, x 0.5um
Column2: Restek CLPesticides 2 30m x 320um, x 0.25um
Injector: 220°C
Mode: Splitless
Pressure: 6psi hydrogen at 100C (Flow = 3-4mL/min)
Purge flow: 50.0mL/minute
Purge time: 0.50 minutes

Initial pressure: 10.00psi for 2.5 minutes
Pressure program 1: 20psi/min to 35psi, hold 0 minutes
Pressure program 2: 25psi/min to 45psi, hold 0 minutes
Pressure rate: 13.00psi/minute
Final pressure: 55psi for 0 minutes

Total flow: 60.1mL/min (hydrogen)

Temperature program
Initial Temp: 100°C
Initial Hold: 0.5 minutes
Program Rate1: 25°C per minute to 175°C, hold 0 minutes
Program Rate2: 10°C per minute to 250°C, hold 0 minutes
Program Rate3: 25°C per minute to 325°C, hold 1.0 minutes
Maximum Temp: 325°C

Run Time: Approximately 15 minutes

Detector: Dual electron capture
Detector temperature: 325°C
Makeup flow: 60-100mL/min (nitrogen)

Signal data rate: 20hz

Autoinjector
Sample washes: 0
Sample pumps: 4
Injection volume: 1.0uL
Syringe size: 10uL
PostInj(ection) Solvent A washes: 4
PostInj(ection) Solvent B washes: 4 (use hexane as wash solvent)
Viscosity delay: 0 seconds
Plunger speed: fast
Preinjection dwell: 0.00minutes
Postinjection dwell: 0.00minutes

10.2.2 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in SOP SA-QA-08: *Evaluation of Chromatographic Data*. Retention time windows (RTW), i.e., the length of time the instrument will scan for the analyte, must be established initially upon instrument set-up and verified annually.

Retention times (RT), i.e., the elution time of the analyte, are verified daily with the analysis of the ICAL or CCV. The retention time for the CCV must fall within the daily retention time window as defined in SOP SA-QA-08.

10.2.3 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.2. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.3, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.5.

10.2.4 Sample Analysis

The term "clock time" defines the continuing calibration verification frequency. The clock time starts at the injection of the IPC, followed by the PEVAL and ICAL, or CCV. The analysis of samples and batch QC items may continue until the clock time expires at which point a capping CCV is required. A new IPC, PEVAL, and CCV (i.e., a new clock) is required to proceed with the analysis of more samples and/or batch QC items. The clock time is defined as 12 hours.

Remove the extracts from the refrigerator and allow them to come to room temperature.

Transfer 1.0mL of the extract to an autosampler vial and add 0.10mL of the internal standard solution to give an internal standard concentration of 0.10ug/mL. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples.

The sample extract must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to exclude QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the clock.

10.2.5 Example Analytical Sequence

Refer to Attachment 1 for an example analytical sequence.

Guidance for the evaluation of the calibration standards, field samples, and QC items are summarized in Section 9 and in Attachment 3, the QC Summary.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data evaluation must be performed in accordance with SA-QA-08: *Evaluation of Chromatographic Data.* This SOP includes specific information regarding the evaluation of chromatographic data, including the requirements for performing manual integrations and the evaluation of retention times.

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review.*

11.1.1 Target Analyte Identification

The judgment and experience of the analyst and his/her colleagues are important factors in the evaluation of chromatographic data. Inspect each chromatogram to ensure that the peaks are properly identified and that the correct areas have been associated with the corresponding standard peak RT in the data system tabulation.

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times); the recovery and retention time shift of the surrogate compounds, whether the peak response falls within the working range of the calibration; and the integration of the peaks. The analyst must also take into account the results from the method blank and lab control sample before reporting quantitative data. SOP SA-QA-08: *Evaluation of Chromatographic Data* provides additional guidance for the evaluation of chromatographic data. This guidance is summarized in the following sections.

11.1.2 Manual Integrations

Manual integrations must be documented in accordance with SOP SA-QA-08. Data systems should be adjusted to minimize operator intervention. All chromatographic peaks must be evaluated for overall peak shape and "reasonableness" of integration. Under no circumstances should manual integrations be used to change reasonable data system integrations in order to meet calibration or QC criteria.

11.1.3 Dual Column Reporting

Refer to SOP SA-QA-08: *Evaluation of Chromatographic Data* for information on assessing and reporting data from dual columns.

11.1.4 Surrogate Evaluation

Two surrogates, TCMX and DCB, are spiked into each sample and QC item prior to preparation. Given the complicated nature of GC-ECD chromatograms, assessing surrogate recovery is frequently complicated by co-eluting positive and negative interferences. Evaluate the surrogates in the same manner as the target compounds using the guidance above.

Two surrogates are added to all samples and field samples. The laboratory's policy is:

- both surrogates must be within the recovery limits for method blanks and LCS
- one surrogate must fall within the recovery limits for all samples and the other surrogate must have a recovery of at least 10%.
- dilution cannot be used as a justification for not re-analyzing or re-extracting a field sample if the sample can be analyzed at a dilution factor of five or less.

TCX	DCB	Action
Within limits	Within limits	Evaluate and report data
Within limit	Below LCL but >10% recovery	Evaluate and report data
Below LCL but >10% recovery	Within limits	
Below LCL	Below LCL	-reanalyze -re-extract unacceptable samples
Above UCL	Above UCL	Evaluate and report data if not target compounds are detected and recovery is <50% above the UCL

LCL = lower control limit UCL = upper control limit

NOTE: For samples that contain Aroclor 1268, TCX is used to determine if the surrogate recovery is acceptable. DCB is a component of AR1268 and will bias the recovery high.

Refer to Section 11.1.5.1 for information on the surrogate dilution threshold factor.

11.1.5 Dilutions

If the response for an analyte exceeds the working range of the system, a dilution is required. Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags must be used or qualification in a case narrative provided to the client.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower reporting limits.

Prepare dilutions for sample extracts where the target compounds exceed the calibration range as follows:

Dilution Factor	Volume of Sample Extract (mL)	Final volume in MTBE* (mL)
2	0.50	1.0
5	0.20	1.0
10	0.10	1.0
20	0.50	10
50	0.20	10
100	0.10	10

*Transfer 1.0mL of the dilution to an autosampler vial and add 100uL of the internal standard.

11.1.5.1 Surrogate Dilution Threshold Factor

Surrogates may be diluted out if the concentration of target compounds is high or the presence of non-target compounds interferes with the quantification of the target compounds. Undetect surrogates in the sample when the dilution factor is 5 or greater. As such, recoveries must be reported as "0D", and control limits will not apply.

An NCM must be initiated to denote this situation.

11.1.5.2 Dilutions and MS/MSD Recoveries

Matrix spike recoveries are not reported for dilutions of 5 or greater. An NCM is generated for instances where the dilution prohibits evaluation of the MS/MSD recoveries. In instances where the unspiked sample concentration is more than four times the concentration of the target compound spiked into the MS and MSD, the results are qualified with "4" or other suitable flag.

An NCM must be initiated to denote this situation.

11.1.6 Chemical Relationships

The analyst must be aware of the following chemical relationships:

Alpha-BHC, beta-BHC, delta-BHC, and gamma-BHC are isomers and will generally be present together in a sample. Gamma-BHC is usually the predominant isomer present and the only BHC isomer on the regulated drinking water list.

When 4,4'-DDT (p,p;-DDT) is present in a sample, its breakdown products, 4,4'-DDD and 4,4'-DDE will usually be present, too.

11.1.7 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.1.8 Drinking Water Compliance Evaluation

Public water suppliers (PWS) are governed by EPA-specified Maximum Contaminant Levels (MCL) above which indicates noncompliance. The MCLs associated with this procedure are given in Attachment 5. Notify the PM immediately via a Nonconformance Memo if any sample contains a detection above these levels.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard

deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample (at the instrument)
F = Final volume/weight
I = Initial volume/weight
D = Dilution factor

Note: This calculation assumes all applicable unit correction factors are applied.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and annually thereafter, and verified annually in accordance with SOP SA-QA-07: *Determination and Verification of Reporting and Detection Limits.*

12.2 Reporting Limit Verification

Reporting limits must be verified annually in accordance with SA-QA-07: *Determination and Verification of Reporting and Detection Limits.*

12.3 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS, MS/MSD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.4 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with

SOP SA-QA-06*: Training Procedures*.

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.5 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Flammable extracts – Dispose according to characterization on sample disposal sheets. If non-hazardous, transfer to a satellite container designated for flammable waste and transfer to waste disposal department when the container is full. If hazardous, transfer to hazardous waste department for storage and disposal.

- Flammable wastes (acetone and MTBE) – Transfer to flammable waste containers.

- Methylene chloride waste – Transfer to chlorinated waste container.

15.0 References / Cross-References

- SOP SA-AN-041: *Reagent and Standard Materials Procedures*
- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs)*
- SOP SA-QA-08: *Evaluation of Chromatographic Data*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- EPA Method 508, "*Determination of Chlorinated Pesticides in Water by Gas Chromatography with an Electron Capture Detector*". Revision 3.1, 1995.
- EPA Method 3660B, "*Sulfur Cleanup*". Revision 2, December 1996.

16.0 Method Modifications and Clarifications

16.1 The reference method was written specifically for drinking water and source water samples; however, the laboratory may perform other types of water samples using this procedure.

16.2 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each EPA 508 batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory defaults to 50-150%.

16.3 EPA Method 508 recommends the use of pentachloronitrobenzene (PCNB) as the internal standard (ISTD); however, the method allows for an alternate ISTD to be used. As such the laboratory uses 1-Bromo-2-nitrobenzene as the ISTD.

16.4 EPA Method 508 only requires 1 surrogate (DCB); however, the method allows for an alternate surrogate to be used. The laboratory has incorporated 2 surrogates (TCMX and DCB). DCB is the primary surrogate, and TCMX is the secondary surrogate to be used when there are problems with DCB. If one of the surrogates is within the acceptance limits and the other surrogate recovery is >10%, the sample is deemed acceptable and re-extraction and re-analysis and/or re-extraction is not automatically performed. Both surrogates are reported, and qualified as applicable.

16.5 EPA Method 508 states that preservation data for the analytes chlorthalonil, alpha-HCH, delta-HCH, gamma-HCH, cis-permethrin, trans-permethrin, and trifluralin are nondefinitive and that if these are analytes of interest it is recommended that the samples be analyzed immediately. These analytes are not in the laboratory's routine target analyte list nor are they regulated drinking water analytes. Unless requested to do otherwise by the client, these analytes will be evaluated using the same holding time constraints as the routine target list.

16.6 EPA Method 508 acknowledges that no suitable preservation agent (biocide) has been found other than mercuric chloride; however, the use of mercuric chloride is not required due to its toxicity and potential harm to the environment. Due to the hazards associated with this preservative, the laboratory has not incorporated its use.

16.7 The EPA's drinking water regulations (i.e., 40 CFR) state that EPA 508 can only be used to screen for polychlorinated biphenyls (PCBs). If PCBs are detected in a sample, the sample must be re-analyzed using EPA Method 508A, the only approved PCB method. The laboratory does not currently perform EPA 508A. Although unlikely in drinking water samples, the detection of Aroclor PCBs requires samples to be subcontracted to a laboratory that performs EPA 508A.

16.8 EPA Method 508 defines continuing calibration frequency in terms of days and requires a CCV and LPC to be performed daily. The laboratory defines continuing calibration frequency in terms of hours and requires the CCV and LPC to be performed every 12 hours.

16.9 The calibration standards for EPA 508 are prepared in hexane. There is little or no difference in response for standards prepared in hexane versus standards prepared in MTBE. The following bullet points provide a rationale for this approach:

- all of the target compounds are fully soluble in both hexane and MTBE and many EPA methods make use of hexane as the solvent for these target compounds; an EPA-approved methods for chlorinated pesticides and PCB in drinking water (EPA 505) uses hexane as the calibration and extraction solvent for the same target compounds reported under this SOP, as do EPA method 608 and EPA Methods 8081 and 8082.
- since we prepare and use standards in relatively large quantities, using the same calibration standards for the various EPA methods for chlorinated pesticides and PCB decreases the use of MTBE, a suspected carcinogen
- the boiling points of both solvents are below the initial temperature of the column, mitigating the solvent effect and making the transfer of the target compounds from the injection port to the guard column the same
- the use of a 5m guard column also mitigates against the solvent effect, allowing the target compounds to fully volatilize before entering the analytical columns

- a side-by-side comparison performed by the lab showed good agreement between standards prepared in hexane and standards prepared in MTBE.

16.9 A specific temperature set-point for the water bath has not been established at this time, but rather a temperature range of 65-90°C is used. There should be little impact on the analyte recoveries provided the temperature is hot enough the boil the solvent.

16.10 The routine CCV standards are the Pest A/B mix and the AR1660 standard. Single point standards of the remaining Aroclors, technical chlordane, and toxaphene are analyzed at least every 72 hours (e.g., Monday, Wednesday, and Friday) to update the retention times and for pattern recognition. If the Pest A/B CCV and the AR1660 CCV meet the calibration acceptance criteria, the ICAL is deemed acceptable for all target analytes.

16.11 The second source ICV is performed for the pesticides, toxaphene, technical chlordane, and AR1660. Second source ICV is not performed for the remaining Aroclors.

16.12 The laboratory has incorporated the batch QC items as outlined in Section 9.1. Some additional QC items are performed (above those required in the reference methods) to satisfy common state regulatory and/or client requests for precision data and/or to facilitate scheduling and data evaluation. The method-specified batch QC items are as follows:

1 Lab Reagent Blank (method blank) per batch; 1 LCS per batch (Table II R+/-30%); 1 MS per 10% of samples or 1 per batch, whichever is greater (Table II R+/-35%).

EPA Manual for the Certification of Laboratories Analyzing Drinking Water: method blank per batch, LCS per batch, Low-Level LCS daily.

Note: Due to limited volumes supplied, there are occasions where the same sample may not be used for both the pesticide MS/MSD and PCB MS/MSD.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: EPA MLGs and MCLs
Attachment 6: Calibration Standards and Spiking Standards
Attachment 7: Laboratory Performance Check
Attachment 8: Sulfur Cleanup Procedures

Attachment 1:
SOP Summary

Sample Preparation Summary

A known volume of sample is placed into a separatory funnel, adjusted to a pH 7, and extracted using methylene chloride. The extract is dried using anhydrous sodium sulfate and transferred to a glass Kuderna-Danish (K-D) concentration apparatus. The K-D is placed in a water bath that has been heated to 60-90°C. As the solvent evaporates, the target compounds are collected in the concentration tube. When the apparent volume of solvent reaches 2mL, the K-D is removed from the water bath and allowed to cool. The extract is brought up to an approximate volume of 15mL with MTBE and the K-D process is repeated. The sample is adjusted to a 5mL final volume with MTBE and transferred to a storage vial or container. The vials are stored at 4°C until the time of analysis by GC/ECD.

Sample Analysis Summary

Analysis of the extract is performed on a GC equipped with dual capillary columns (different phases) connected to dual electron capture (EC) detectors, allowing simultaneous detection and confirmation of the target compounds. GC/MS confirmation can also be employed if analyte concentration is sufficiently high or if the sample extract is concentrated to an appropriate final volume. Quantitation is performed using the internal standards calibration technique.

Target Compounds Spikes and Surrogate Spike Concentrations

The following table summarizes the concentrations of the compounds spiked into the QC items:

Sample	Surrogate Concentration Spiked	Target Concentration Spiked
Field Sample	0.50ug/L	-
Method blank	0.50ug/L	-
LCS/MS/MSD (pest)	0.50ug/L	0.050-0.10ug/L
LCS/MS/MSD (PCB)	0.50ug/L	5.0ug/L
LLCS (pest)	0.50ug/L	0.025-0.050ug/L
LLCS (PCB)	0.50ug/L	0.50ug/L

Example Analytical Sequence

Initial Calibration - PEVAL - Endrin/p,p'-DDT Breakdown Check 5-pt single peak pesticides 5-pt AR1660 5-pt Toxaphene 5-pt Technical Chlordane 1-pt remaining Aroclors 5-pt APIX or additional compounds if requested
Instrument Blank
Laboratory Performance Check -12-hour clock starts
ICV - 2nd Source (pesticides, toxaphene, technical chlordane, and AR1660)
Analyze sample and QC extracts until 12-hour clock expires
Laboratory Performance Check -12-hour clock starts
PEVAL - Endrin/p,p'-DDT Breakdown Check
CCV - Alternate concentrations (Pesticides and AR1660)
Instrument Blank
Analyze sample and QC extracts until 12-hour clock expires
CCV - Alternate concentrations (Pesticides and AR1660)

*Note 1 - A mixture of AR1016 and AR1260 will be used to calibrate and verify the response for PCBs. Mid-level standards of the remaining Aroclors, toxaphene, and technical chlordane must be analyzed every 72 hours for pattern recognition and retention time.

*Note 2 – PEVAL Breakdown Check is not required for PCB-only analyses

EPA requires bracketing of samples with acceptable CCV.

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Listed below are the holding times and preservation requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Dechlorination Agent	Holding Time
Water	1L Amber glass fitted with a Teflon-lined cap	200mL	None	80mg sodium thiosulfate	7 days to extract; 14 days after extraction to analyze

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Clock Time	12 hours	Clock time starts with the injection of the IPC. Analysis of samples and QC items must conclude within expiration of clock time. Subsequent analysis requires new opening QC.	Not Applicable
Laboratory Performance Check (LPC)	At beginning of each 12-hour clock	Refer to Attachment 7	-re-analyze check solution -perform injector port and/or column maintenance and re-analyze
Breakdown Check (PEVAL)	At beginning of each 12-hour clock	<%20 breakdown for both endrin and DDT	-re-analyze check solution -perform injector port and/or column maintenance and re-analyze
Initial Calibration (ICAL) - Minimum 3 points	Initially prior to sample analysis, when major instrument maintenance performed, or when CCV fails	%RSD<20% r^2>0.990	Refer to SOP SA-QA-16
Initial Calibration Verification (ICV) - 2nd Source	After each ICAL	<20%D	Refer to SOP SA-QA-16
Continuing Calibration Verification (CCV)	Initially, after every 20 samples (not to exceed 12 hours), and at the end of the sequence - Concentration must be varied.	<20%D	Refer to SOP SA-QA-16

QC Item	Frequency	Criteria	Corrective Action
Calibration Blank (CCB/ICB)	After ICV and every CCV	<1/2 RL	- Terminate the analysis; correct problem; reanalyze affected samples.
Internal Standard (ISTD)	All field, batch QC, & instrument QC samples	CCV: - Response of the internal standard must be within a range of +/-50% of the ICAL mid-level std Samples: - Response within +/-30% of previous CCV - RT within window defined by previous CCV	-Evaluate chromatogram and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available
Surrogates	All field, batch QC, & instrument QC samples	Within TALS MLG limits (70-130%R)	Refer to SOP SA-QA-17
Batch Definition	Extracted together w/in 24-hr period; not to exceed 20 field samples	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	<1/2 RL	Refer to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per batch	Within limits listed in the MLG	Refer to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	One per batch, if insufficient sample for MS/MSD	Within limits listed in the MLG	Refer to SOP SA-QA-17
Low-Level Laboratory Control Sample (LLCS)	One per batch	Within limits listed in the MLG (50-150%R)	Refer to SOP SA-QA-17

QC Item	Frequency	Criteria	Corrective Action
Matrix Spike (MS)	10% of samples or 1 per batch, whichever is greater	Within limits listed in the MLG	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per batch	Within limits listed in the MLG	Refer to SOP SA-QA-17
Retention Time Window (RTW) Determination	Annually, after major instrument maintenance, and with each new column	Refer to SOP SA-QA-08	Refer to SOP SA-QA-08
Initial Demonstration of Capability (IDOC)	Initially; Per analyst / matrix / method / analyte combination	Within %R limits listed in the MLG <20% RSD	Refer to SOP SA-QA-06
Continuing Demonstration of Capability (CDOC)	Annually; Per analyst / matrix / method / analyte combination	Within limits listed in the MLG	Refer to SOP SA-QA-06
Method Detection Limit (MDL)	Upon method/instrument set-up, and then annually thereafter (Includes MDLV)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE

EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Guard Column/Injector							X	Change sleeve and cut front of guard column, recommended daily
Septum							X	Replace, recommended daily
Splitless Disc							X	Replace, recommended daily
Autosampler							X	Syringe cleaned or replaced as needed
Column							X	Change column

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually; AN = as needed

It is recommended to change the water in the water bath weekly. Add 1-2 drops of Clear Bath to prevent bacteria and algae growth. Methylene chloride that dissolves in the water bath will damage the sensors.

The K-D apparatuses must be inspected periodically for leaks and cracks. Leaks will allow the infiltration of water into the extract and compromise the entire extraction procedure. Glassware with leaks, cracks, and broken joints must be repaired or replaced.

Inspect the Snyder columns frequently. The balls in the condenser will sometimes stick, causing pressure from the evaporating solvent to build up and spew the extract out of the

top of the column. Wetting the column with a small volume of solvent will help to keep the balls from sticking.

Contingency Plan

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs,. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
EPA MCLGs and MCLs

Analyte	MCLG (mg/L)	MCL (mg/L)
Chlordane	0	0.002
Endrin	0.002	0.002
Heptachlor	0	0.0004
Heptachlor Epoxide	0	0.0002
Hexachlorobenzene	0	0.001
Hexachlorocyclopentadiene	0.05	0.05
Gamma-BHC (Lindane)	0.0002	0.0002
Methoxychlor	0.04	0.04
Polychlorinated Biphenyls	0	0.0005
Toxaphene	0	0.003

Note: EPA Method 508 can only be used to screen for polychlorinated biphenyls (PCBs). If PCBs are detected in a sample, the sample must be re-analyzed using EPA Method 508A, the only approved PCB method.

Attachment 6:
Standard Recipes

508/608/8081 PEST A/B Standard Preparation Recipe
Initial Calibration, Continuing Calibration Verification (CCV), and
Initial Calibration Verification (ICV)

PEST A/B Stock Standard Mixes

Stock/Mix	LIMS ID	Vendor/ Part Number	Concentration (ug/mL)
Pest A/B Routine Pesticides	SG AB CAL	Accustandard S-18858	10-20
Pest A/B Routine Pesticides 2nd Source	SGSTICVAB	Ultra CUS-5454	10-20
Pest Surrogate Stock	SGPESTSURR	Supelco 48460	200
Pest Internal Standard (bromonitrobenzene (BNB))	BNBISTD	Chemservice F2319S	1000

Expiration date: Unopened ampuls: manufacturer's date of expiration Opened ampuls: 6 months

Pest ISTD Working Standard (LIMS ID = SGBNB_wk)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Final Concentraton (ug/mL)
Pesticide Internal Standard	1000	1000	1.0

Solvent: hexane Expiration: 3 months

Pest A/B Calibration Standards

Cal Level	LIMS ID	A/B Stock Aliquot	Surrogate Aliquot	Final Volume (mL)	Pest ISTD Working Std Volume (mL)
1	SG PEST-1	12.5uL	1.0uL	50mL	5.0
2	SG PEST-2	25uL	2uL	50mL	5.0
3	SG PEST-3	50uL	4uL	50mL	5.0
4	SG PEST-4	500uL	40uL	250mL	25
5	SG PEST-5	200uL	16ul	50mL	5.0
6	SG PEST-6	500uL	40uL	50mL	5.0
AZ	SG PEST-AZ	10mL of SG PEST-1	0	25mL	1.5
Dilute to the final volume and then add the Pesticide ISTD working Standard					

Solvent: hexane Expiration: 3 months

Pest A/B ICV Standard (LIMS ID = SG AB ICV)

Cal Level	A/B ICV Stock	Surrogate Stock	Final Volume	Pest ISTD Working Std Volume (mL)
4 ICV	500uL	40uL	250mL	25mL
Dilute to the final volume and then add the Pesticide ISTD working Standard				

Solvent: hexane Expiration: 3 months

Pest A/B On-Column Concentrations (ug/mL)

Compound	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6	CAL AZ
Bromonitrobenzene (ISTD)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Tetrachloro-m-xylene Decachlorobiphenyl	0.0040	0.0080	0.016	0.032	0.064	0.16	0.0016
Alpha-BHC, Gamma-BHC, Beta-BHC, Delta-BHC, Heptachlor, Aldrin, Heptachlor epoxide, Gamma-Chlordane, Alpha-Chlordane Endosulfan I	0.0025	0.0050	0.010	0.020	0.040	0.10	0.001
4,4'-DDE, Dieldrin, Endrin 4,4'-DDD, Endosulfan II, 4,4'-DDT, Endrin aldehyde Methoxychlor, Endosulfan sulfate, ndrin ketone	0.0050	0.010	0.020	0.040	0.080	0.20	0.002

Storage: glass container with Teflon-lined cap; in standards' refrigerator at <4C

508/608/8081 AR1660 Standard Preparation Recipe
Initial Calibration, Continuing Calibration Verification (CCV), and
Initial Calibration Verification (ICV)

Aroclor Stock Standard Mixes

Stock/Mix	LIMS ID	Vendor/ Part Number	Final Concentration (ug/mL)
AR1660 Stock	SGST1660 (or AR1660)	Restek 32039	1000
AR1660 Stock-2nd Source	SGSTICVPCB	Ultra PPM-8082	1000
Pest Surrogate Stock	SGPESTSURR	Supelco 48460	200
Pesticide Internal Standard (bromonitrobenzene (BNB))	BNBISTD	Chemservice F2319S	1000

Expiration date: Unopened ampuls: manufacturer's date of expiration Opened ampuls: 6 months

Pest ISTD Working Standard (LIMS ID = SGBNB_wk)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
Pesticide Internal Standard	1000 (1.0mL)	1000 (1.0L)	1.0

Solvent: hexane Expiration: 3 months

AR1660 Initial Calibration Standards

Cal Level	LIMS ID	AR1660 Stock	Surrogate Stock	Final Volume	Pest ISTD Working Standard
1	SG 1660-1	5uL	1.0uL	50mL	5.0
2	SG 1660-2	12.5uL	2uL	50mL	5.0
3	SG 1660-3	25uL	4uL	50mL	5.0
4	SG 1660-4	250uL	40uL	250mL	25
5	SG 1660-5	100uL	16ul	50mL	5.0
6	SG 1660-6	125uL	40uL	50mL	5.0
AZ	SG 1660-AZ	0.75mL SG 1660-1	0	5mL	4.25mL
Dilute to the final volume and then add the Pesticide ISTD working Standard					

Solvent: hexane Expiration: 3 months

AR1660 ICV Standard (LIMS ID = SGPCBICV_)

Cal Level	AR1660 ICV Stock	Surrogate Stock	Final Volume	Pest ISTD Working Standard
4 ICV	250uL	40uL	250mL	25mL
Dilute to the final volume and then add the Pesticide ISTD working Standard				

Solvent: hexane Expiration: 3 months

AR1660 On-Column Concentrations (ug/mL)

Compound	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6	CAL AZ
Bromonitrobenzene (ISTD)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Tetrachloro-m-xylene, DCB	0.0040	0.010	0.020	0.040	0.080	0.20	0.0006
Aroclor 1016	0.10	0.25	0.50	1.0	2.0	2.5	0.015
Aroclor 1260	0.10	0.25	0.50	1.0	2.0	2.5	0.015

Storage: glass container with Teflon-lined cap; in standards' refrigerator at <4C

508/608/8081 Technical Chlordane Standard Preparation Recipe
Initial Calibration, Continuing Calibration Verification (CCV), and
Initial Calibration Verification (ICV)

Stock Standard Mixes

Stock/Mix	LIMS ID	Vendor/ Part Number	Concentration (ug/mL)
Technical chlordane	SGSTCHLOR_	Accustandard P-017S-10X	1000
Technical chlordane ICV (2nd Source)	SGSTICVCHR_	Ultra PP-151-1	100
Pesticide Internal Standard (bromonitrobenzene (BNB))	BNBISTD	Chemservice F2319S	1000

Expiration: Unopened ampuls: manufacturer's date of expiration Opened ampuls: 6 months

Pest ISTD Working Standard (LIMS ID = SGBNB_wk)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
Pesticide Internal Standard	1000 (1.0mL)	1000 (1.0L)	1.0

Solvent: hexane Expiration: 3 months

Technical Chlordane Initial Calibration Standards

Cal Level	LIMS ID	TCHLOR Stock	Final Volume	Pest ISTD Working Standard
1	SG TCHLR-1	2.5uL	50mL	5mL
2	SG TCHLR-2	5uL	50mL	5mL
3	SG TCHLR-3	12.5uL	50mL	5mL
4	SG TCHLR-4	25uL	50mL	5mL
5	SG TCHLR-5	50uL	50mL	5mL
6	SG TCHLR-6	125uL	50mL	5mL
AZ	SG TCHLR-AZ	12.5mL SG TCHLR-1	25mL	1.25mL
Dilute to the final volume and then add the Pesticide ISTD working Standard				

Solvent: hexane Expiration: 3 months

Technical Chlordane ICV Standard (LIMS ID = SGCHLRICV_)

Cal Level	TCHLOR ICV Stock	Final Volume	Pest ISTD Working Standard
4 ICV	250uL	50mL	5mL
Dilute to the final volume and then add the Pesticide ISTD working Standard			

Solvent: hexane Expiration: 3 months

Technical Chlordane On-Column Concentrations (ug/mL)

Compound	CAL AZ	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6
Bromonitrobenzene (ISTD)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Technical chlordane	0.025	0.050	0.10	0.25	0.50	1.0	2.5

Storage: Glass container with Teflon-lined cap; in standards' refrigerator at <4C

508/608/8081 Toxaphene Standard Preparation Recipe
Initial Calibration, Continuing Calibration Verification (CCV), and
Initial Calibration Verification (ICV)

Stock Standard Mixes

Stock/Mix	LIMS ID	Vendor/ Part Number	Concentration (ug/mL)
Toxaphene Calibration Stock	SGST TOX_	Restek 32205	1000
Toxaphene ICV (2nd Source)	SGSTICVTOX_	Accustandard P-093S-H-10X	1000
Pesticide Internal Standard (bromonitrobenzene (BNB))	BNBISTD_	Chemservice F2319S	1000

Expiration: Unopened ampuls: manufacturer's date of expiration Opened ampuls: 6 months

Pest ISTD Working Standard (LIMS ID = SGBNB_wk)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
Pesticide Internal Standard	1000 (1.0mL)	1000 (1.0L)	1.0

Solvent: hexane Expiration: 3 months

Toxaphene Initial Calibration Standards

Cal Level	LIMS ID	TOX Stock	Final Volume	Pest ISTD Working Standard
1	SG TOX-1	5uL	10mL	1.0mL
2	SG TOX-2	12.5uL	10mL	1.0mL
3	SG TOX-3	25uL	10mL	1.0mL
4	SG TOX-4	250uL	50mL	5.0mL
5	SG TOX-5	100uL	10mL	1.0mL
6	SG TOX-6	250uL	10mL	1.0mL
AZ	SG TOX-AZ	2mL SG TOX-1	10mL	0.80mL
Dilute to the final volume and then add the Pesticide ISTD working Standard				

Solvent: hexane Expiration: 3 months

Toxaphene ICV Standard (LIMS ID = SG TOXICV_)

Cal Level	TOX ICV Stock	Final Volume	Pest ISTD Working Standard
4 ICV	250uL	50mL	5.0mL
Dilute to the final volume and then add the Pesticide ISTD working Standard			

Solvent: hexane Expiration: 3 months

Toxaphene On-Column Concentrations (ug/mL)

Compound	CAL 1	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6
Bromonitrobenzene (ISTD)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Toxaphene	0.10	0.50	1.25	2.5	5.0	10	25

Storage: Glass container with Teflon-lined cap; in standards' refrigerator at <4C

508/608/8081 Single Point PCB Standard Preparation Recipe
Initial Calibration, Continuing Calibration Verification (CCV), and
Initial Calibration Verification (ICV)

Aroclor Stock Standard Mixes

Stock/Mix	LIMS ID	Vendor/ Part Number	Concentration (ug/mL)
AR1221	SGST1221	Accustandard C221S-H-10X	1000
AR2154	SGST1254	Accustandard C254S-H-10X	1000
AR1232	SGST1232	Accustandard C232S-H-10X	1000
AR1262	SGST1262	Accustandard C262S-H-10X	1000
AR1242	SGST1242	Accustandard C242S-H-10X	1000
AR1268	SGST1268	Accustandard C268S-H-10X	1000
AR1248	SGST1248	Accustandard C248S-H-10X	1000
Pesticide Internal Standard (bromonitrobenzene (BNB))	BNBISTD	Chemservice F2319S	1000

Expiration date: Unopened ampules: manufacturer's date of expiration Opened ampules: 6 months

Pest ISTD Working Standard (LIMS ID = SGBNB_wk)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
Pesticide Internal Standard	1000	1000	1.0

Solvent: hexane Expiration: 3 months

AR2154 Calibration Standard (LIMS ID = SG 21/54-4)

Cal Level	AR1221 Stock	AR1254 Stock	Final Volume	Pest ISTD Working Standard	AR2154 Conc (ug/mL)	ISTD Conc (ug/mL)
4	50uL	50uL	5mL	50mL	1.0	0.10
Dilute to the final volume and then add the Pesticide ISTD working Standard						

Solvent: hexane Expiration: 3 months

AR3262 Calibration Standard (LIMS ID = SG 32/62-4)

Cal Level	AR1232 Stock	AR1262 Stock	Final Volume	Pest ISTD Working Standard	AR3262 Conc (ug/mL)	ISTD Conc (ug/mL)
4	50uL	50uL	5mL	50mL	1.0	0.10
Dilute to the final volume and then add the Pesticide ISTD working Standard						

Solvent: hexane Expiration: 3 months

AR4268 Calibration Standard (LIMS ID = SG 42/68-4)

Cal Level	AR1242 Stock	AR1268 Stock	Final Volume	Pest ISTD Working Standard	AR4268 Conc (ug/mL)	ISTD Conc (ug/mL)
4	50uL	50uL	5mL	50mL	1.0	0.10
Dilute to the final volume and then add the Pesticide ISTD working Standard						

Solvent: hexane Expiration: 3 months

AR1248 Calibration Standard (TALS ID = SG 1248-4)

Cal Level	AR1248 Stock	Final Volume	Pest ISTD Working Standard	AR1248 Conc (ug/mL)	ISTD Conc (ug/mL)
4	50uL	5mL	50mL	1.0	0.10
Dilute to the final volume and then add the Pesticide ISTD working Standard					

Solvent: hexane Expiration: 3 months

Storage: glass container with Teflon-lined cap; in standards' refrigerator at <4C

508/608/8081 Column/Instrument Checks
DDT/Endrin breakdown
Laboratory Performance Check (IPC – 508 only)

Stock Standard Mixes

Stock/Mix	LIMS ID	Vendor/ Part Number	Concentration (ug/mL)
PEVAL Stock	PEVAL_	Restek 32417	Endrin 100 p,p'-DDT 200
2,4'-DDT PEVAL Stock	2,4'-DDT_	Restek 32200	1000
508 Performance Check Mix	508 LPC_	Restek 32045	0.02-0.5
Pesticides Internal Standard (bromonitrobenzene (BNB))	BNBISTD_	Chemservice F2319S	1000

Expiration date: Unopened ampules: manufacturer's date of expiration Opened ampules: 6 months

Pest ISTD Working Standard (LIMS ID = SGBNB_wk)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
Pesticide Internal Standard	1000 (1.0mL)	1000 (1.0L)	1.0

Solvent: hexane Expiration: 3 months

PEVAL Run Standard (LIMS ID = SG PEVAL_)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
PEVAL Stock	100 (0.100mL)	250	Endrin 0.040 P,p'-DDT 0.080
Dilute to final volume and then add 25mL of the Pesticide ISTD Working Standard			

Solvent: hexane Expiration: 3 months

2,4-DDT PEVAL Run Standard (LIMS ID = SG24PEVAL_)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
2,4'-DDT PEVAL Stock	20 (0.020mL)	5.0	0.040
Dilute to final volume and then add 0.5mL of the Pesticide ISTD Working Standard			

Solvent: hexane Expiration: 3 months

Laboratory Performance Check Standard (LPC)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
508 Performance Check Mix	100 (0.100mL)	250	Chlorpyrifos 0.002 DCPA 0.050 Chlorothaloni 0.050l Delta BHC 0.040
Dilute to final volume and then add 25mL of the Pesticide ISTD Working Standard			

Solvent: hexane Expiration: 3 months

Storage: glass container with Teflon-lined cap; in standards' refrigerator at <4C

508/608/8081 Surrogate and Spiking Solution Preparation Recipes

Stock Standard Mixes

Stock/Mix	LIMS ID	Vendor/ Part Number	Concentration (ug/mL)
Pesticides Mix A	Pest mix A_	NSI Q-2108	10-20
Pesticides Mix B	Pest mix B_	NSI Q-2109	10-20
AR 1016 / AR 1260 Mix	AR1660_	Restek 32038	1000
Pesticides Surrogate Stock (TCX and DCB)	PEST SURR_	Supelco 505935	200
Triphenyl phosphate (TPP) (OP Pesticide surrogate)	TPP STD_	Restek 32281	1000
Tetrachloro-m-xylene (508 surrogate)	TCMX STD_	Restek 32027	200

Expiration date: Unopened ampules: manufacturer's date of expiration Opened ampules: 6 months

NOTE: The organic-phosphorus pesticide surrogate is combined with the organic-chlorine pesticides surrogate so that the same extract can be used for both types of compounds.

608 Working Surrogate Standard (LIMS ID = PESTwkSURR_)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
Pesticides Surrogate Stock (TCX and DCB)	1250 (1.25mL)	500	0.50 each
Triphenyl phosphate (TPP)	2000 (2.0mL)		4.0

Solvent: methanol Expiration: 3 months

Pesticide Working Spiking Standard (LIMS ID = 608wkSPIKE_)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
Pesticides Mix A	1000 (1.0mL)	100	0.10-0.20
Pesticides Mix B	1000 (1.0mL)		0.10-0.20

Solvent: methanol Expiration: 3 months

1660 Working PCB Spiking Standard (LIMS ID = 1660wkSPIK_)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)	Conc. (ug/mL)
AR 1016 / AR 1260 Mix	500 (0.50mL)	50	10 each

Solvent: methanol Expiration: 3 months

Storage: glass container with Teflon-lined cap; in standards' refrigerator at <4C

Attachment 7:
Laboratory Performance Check

Test	Analyte / Concentration	Acceptance Criterion
Sensitivity	Chlorpyrifos 0.0020ug/mL	Detected; S/N >3
Column Performance:		
Peak shape/symmetry	DCPA 0.050ug/mL	PGF between 0.80 and 1.15
Resolution	Chlorothalanil 0.050ug/mL Delta-BHC 0.040ug/mL	Resolution > 0.50

PGF = peak Gaussian factor

$$PGF = \frac{1.83 \otimes W1}{W2}$$

W1 = peak width, in seconds, at half height
W2 = peak width, in seconds, at one-tenth height

$$\text{Re}solution = \frac{t}{W}$$

t = difference in time (in seconds) between the two peaks
W = average width (in seconds) of the two peaks at the baseline

Attachment 8:

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Work Instruction
FEX096:01.28.09.0
Page 1 of 1

Sulfur Cleanup Procedures

Method: 3660B

Summary of Procedure
This procedure is based on EPA Method 3660B and is used in conjunction with the following SOPs:

Method	SOP #
EPA 3510C / EPA 3520C	SA-EX-030
EPA 3550C	SA-EX-040
EPA 508	SA-SG-046
EPA 608 / EPA 8081B / EPA 8082A	SA-SG-045

The sulfur cleanup uses copper granules to eliminate elemental sulfur from PCB or pesticide extracts. Copper is added to the extract, and the vial is shaken. If sulfur is present, a black precipitate (copper sulfide) will form. The extract is treated with copper until no further precipitate is formed.

The method blank and LCS must be subjected to the same cleanup steps as the samples.

Perform all cleanup steps under a fume hood or in a well-ventilated area.

Reagents
Copper granules – the surface of the copper should be "shiny"

Cleanup Instructions
1. Ensure the sample extract has been exchanged into the applicable final solvent (e.g., MTBE for EPA 508, Hexane for EPA 608/8081B/8082A) prior to performing the sulfur cleanup procedure.

2. Add approximately 0.1g of "shiny" copper to the vial, and vortex for approximately two minutes.

   Note: If the extract is for EPA 614 or EPA 8141B in addition to one of the analytical methods listed above, transfer an aliquot of the extract to another vial for the copper cleanup.

3. If sulfur is present, a black precipitate will form. Allow the extract to sit for 2-3 minutes for any additional precipitate to form and settle out.

   If the precipitate does not settle out, additional copper treatments and/or filtration may be required. Contact the Technical Manager for instructions on how to proceed.

4. The sample is now ready for analysis as outlined in Section 10 of the associated analytical SOP.

18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial and formatting changes made. Added boilerplate text.
- Revised SOP titles and document control numbers to reflect current revisions.
- Updated Reagents and Standards Section to include more specific storage conditions and LIMS Reagent IDs. Section 7
- Corrected Phosphate Buffer reagents and recipes to correspond with those outlined in the reference method. Section 7.2.6 and Section 7.2.7 (PT CAR #328)
- Added reference to peroxide test strips to Equipment and Supplies Section. As states in Section 7.2.16, these should be used periodically to check MTBE for the presence of peroxides.
- Added note that due to due to limited volumes supplied, there are occasions where the same sample may not be used for both the pesticide MS/MSD and PCB MS/MSD. Section 16.12
- Removed reference to the rotation extractor. No longer used. Section 10.1.17
- Revised length of time to shake separatory funnels from 10 minutes to 3 minutes, as is consistent with current practice and allowed by the reference method). Section 10.1.17

MICROEXTRACTABLES BY GC/ECD

(Methods: EPA 504.1 and 8011)

Approvals (Signature/Date):

Andrea Teal September 13, 2010
Andrea Teal Date
Quality Assurance Manager

September 1, 2010
Benjamin Gulizia Date
Laboratory Director/Lead Technical Director

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Facility Distribution No. 1 Distributed To: QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of 1,2-Dibromoethane (Ethylene dibromide, EDB) and 1,2-Dibromo-3-chloropropane (Dibromochloropropane, DBCP) in water samples by microextraction and gas chromatography/electron capture detection (GC/ECD).

The reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

Thirty-five milliliters of sample are extracted with two milliliters of hexane. The extract is analyzed by gas chromatography utilizing dual capillary columns and dual electron capture (EC) detectors. Calibration standards are extracted and analyzed in the same manner as the samples.

This SOP is based on the following methods: EPA 504.1 and EPA 8011.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hexane and methanol must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require dilution prior to analysis to reduce or eliminate the interferences. Addition of sodium sulfate may be necessary to break up emulsions should they form during the extraction process.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Dibromochloromethane (DBCM) is a common disinfection byproduct in chlorinated drinking waters, often occurring in high concentrations. DBCM elutes closely to EDB, and, at high concentrations, may mask low concentrations of EDB. Adequate separation of DBCM and EDB must be demonstrated each day samples are analyzed.

4.2.4 High concentrations of non-target compounds may make detection and quantification of EDB, DBCP, and 1,2,3-TCP difficult. The electron capture detector is very sensitive to halogenated compounds and produces a very large response for concentrations as low as 1ppb. The results from the EPA 524.2 or EPA 8260 volatiles analysis can provide information about the compounds causing the interference. Some common volatile compounds that elute near the target compounds are tetrachloroethene, dibromochloromethane, chlorobenzene, bromoform, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene. Note that very large concentrations of any halogenated solvent may overwhelm the response of the electron capture detector, making detection of the target compounds impossible at the routine reporting limit.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

Hexane is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, lightheadedness, headache, dizziness, and blurred vision.

Methanol is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, confusion, headache, dizziness, and drowsiness.

Methanol is the primary solvent for standards. Hexane is used to extract the compounds from the samples. To minimize evaporation and the chance for exposure:

- store standards in methanol in glass containers with crimp-top caps and vials with Teflon-lined caps or septa
- store material with minimal headspace
- store materials at -10°C or lower
- work under a hood
- if no hood is available, work in a well ventilated area, work quickly, and minimize the number of times the standard container is opened
- wear proper PPE (Personal Protection Equipment). PPE for this procedure includes a laboratory coat, eye protection, and gloves when handling standards, samples, or reagents.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Hexane	Flammable Irritant	500ppm TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200ppm TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.

[1]Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Data System – Target and Chemstation software are used to acquire, store, reduce, and output mass spectral data. This software has the capability of processing stored GC data by recognizing a GC peak within any given retention time window and comparing the response of the peak to a reference standard. The software also allows calculation of response factors or construction of a calibration curve, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the response factors.

Agilent 6890 Gas Chromatograph with dual micro electron capture detectors and Agilent 7683 autosampler

Columns:
RTX CLP Pest, 30m x 0.32mm ID x 0.50um (Restek)
RTX CLP2, 30m x 0.32mm ID x 0.25um (Restek)
Guard Column Restek 5m x 0.32mm ID (Restek)

The columns are connected to a single injection port via a glass y-splitter and a 5m guard column. The ends of each column are connected to separate detectors. When properly configured, a single injection is split between the two columns to provide simultaneous detection and confirmation of the target compounds.

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Residual (free) chlorine powder pillows – HACH catalogue number 2105569 (for a 10-mL sample)

Medicine cups – 30mL, disposable

Auto sampler vials, septa, and caps

Screw cap vials equipped with PTFE-faced septa (40mL VOA vials)

Vials - 12mL with Teflon-lined screw caps

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

40mL VOA vial, with sodium thiosulfate dechlorination agent – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.*

Hexane and methanol must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Purchased Reagents

7.2.1.1 Laboratory Reagent Water – ASTM Type II

Note: If laboratory water is unsuitable for analysis of target compounds, purging the water with nitrogen for 30 minutes or boiling the water and purging with nitrogen may reduce contamination.

7.2.1.2 Hexane – residue grade
LIMS Name: Hexane(lot number)_
Storage: Room temperature
Expiration:
Unopened: 5 years or manufacturer's expiration date
Opened: 6 months

7.2.1.3 Methanol – residue grade
LIMS Name: EX_MEOH
Storage: Room temperature
Expiration:

Unopened: 5 years or manufacturer's expiration date
Opened: 6 months

7.1.4 Sodium Chloride (NaCl) - ACS reagent grade. Purify by heating at 400°C for four hours in a shallow tray.
LIMS Name: NACL
Storage: Room temperature
Expiration:
Unopened: 5 years or manufacturer's expiration date
Opened: 5 years or manufacturer's expiration date; 6 months from baking.

7.1.5 Sodium Sulfate - granular, anhydrous - Purify by heating at 400°C for four hours in a shallow tray.
LIMS Name: EX_na2SO4
Storage: Room temperature
Expiration:
Unopened: 5 years or manufacturer's expiration date
Opened: 5 years or manufacturer's expiration date; 6 months from baking.

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

The standard recipes are included in Attachment 5. This attachment includes stock standards (vendor and part number) used in this SOP, the preparation steps for the intermediate and working standards, and the instructions for assigning expiration dates to the stocks, intermediate, and working level standards.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

Samples are routinely collected in 40mL VOA vials containing 75uL of a 40mg/mL solution of sodium thiosulfate de-chlorination agent. The dechlorination agent should be sufficient to remove residual chlorine from the sample. Samples should be collected without headspace.

Note: 40mL VOA vials with HCl preservative may also be used for EPA 8011. This bottle type is consistent with the bottle type used commonly used for analysis of these particular analytes by EPA 8260.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 24 hours of extraction.

NCMs must be initiated for samples collected in improper containers and containing

improper or insufficient preservatives and/or de-chlorination agents. NCMs must be initiated for samples that are received containing headspace.

8.1.1 Preservation Checks – Residual Chlorine

These checks are performed prior to preparation.

8.1.1.1 Mix the sample by inverting and transfer 10mL to a small medicine cup.

8.1.1.2 Add a residual chlorine powder pillow to the sample in the cup and note the presence of a pink color, which indicates the presence of residual chlorine.

If the sample tests positive for residual chlorine, initiate an NCM noting that residual chlorine was present.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

9.1.1 For EPA 504.1, the laboratory's default minimum QC items performed for each extraction batch are: a method blank, laboratory control sample (LCS), a low-level LCS (LLCS), a matrix spike (MS), and a matrix spike duplicate (MSD). This frequency equates to the following:

- For a batch of 10 or fewer samples, the default minimum QC items are a method blank, an LCS, an LLCS, and 1 MS/MSD pair.
- For a batch of 11-20 samples, the default minimum QC items are a method blank, an LCS, an LLCS, 1 MS (from sample 1-10), another MS (from sample 11-20), and an MSD.

9.1.2 For EPA 8011, the laboratory's default minimum QC items performed for each extraction batch are: a method blank, laboratory control sample (LCS), matrix spike (MS), and matrix spike duplicate (MSD). This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, and 1 MS/MSD pair.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, and 1 MS/MSD pair.

9.1.3 The routine container supplied for this method is a 40mL container. 35mL is required for extraction. Due to the nature of this procedure, and the need to maintain zero headspace, reduced sample initial volumes may not be used to achieve the required batch matrix spike frequency (i.e., a separate vial is required for to perform each of the native sample, MS, and MSD analyses).

9.1.4 If there is insufficient sample volume to perform the required matrix spike(s), the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of three 40mL VOA vials for matrix spike/matrix spike duplicate and less than two 40mL VOA vials for the additional matrix spike required for batches having greater than 10 samples.

9.1.5 Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

9.2.1 Column Resolution / RL Check

The purpose of the Column Resolution / RL Check is check is to ensure that EDB can be resolved from a common chlorination by-product, dibromochloromethane (DBCM). DBCM is often present at concentrations that are much higher than EDB is expected to occur, and this check is intended to demonstrate that EDB can be detected at the RL of 0.020ug/L in the presence of DBCM at 1.0ug/L, a 50-fold difference in concentrations.

- Prepare, extract, and analyze the Column Resolution Check standard (Table 5).

- Evaluate the chromatogram, inspecting the resolution between DBCM and EDB on both columns.

- The peaks should be resolved at the baseline (a gap in the baseline from the end of the DBCM peak to the beginning of the EDB peak) on both columns.

- If EDB cannot be detected, prepare new standard and repeat the preparation and analysis. If the repeat analysis still does not meet the criterion, take steps to increase the resolution between these two compounds which may include decreasing the initial temperature and/or reducing the column flow rate.

Note: Do not proceed with the analysis is this check can be met.

9.2.2 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves*. This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 5 standards. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

Note: A minimum of 6 points is required for a quadratic curve. Higher order curves are not permitted.

The initial calibration standard concentrations currently in use in the laboratory are listed in Attachment 5. Refer to Attachment 5 for the standard preparation instructions. Other

standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-041.

9.2.2.1 ICAL Criteria

The preferred method of quantitation is the average response factor. The relative standard deviation (%RSD) of the calibration standards must be <10% for EPA 8011 and <20% for EPA 504.1 for the initial calibration curve to be acceptable.

If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve. If the regression curve option is chosen, the regression coefficient (r^2) must be greater than or equal to 0.990 to be acceptable.

If these criteria are not met, then re-calibration is required before sample analysis can proceed.

9.2.3 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified after the initial calibration is established, prior to any sample analyses, in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to level 5 of the ICAL. Refer to Attachment 5 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

The ICV must be within 30% of the true value to be acceptable.

Note: If the LCS is prepared from a second source standard it can be used to satisfy the ICV criteria.

9.2.4 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The method blank for this method is analyzed and evaluated in lieu of instrument or calibration blanks.

Additional instrument blanks may be analyzed after samples with high levels of target or non-target compounds to mitigate and evaluate the analytical system for carry-over.

9.2.5 Continuing Calibration Verification

The initial calibration curve must be verified at the beginning and end of every 12-hour clock for EPA 504.1 and at the before and after every 20 samples analyzed for EPA 8011.

The concentration of the standard should be varied, such that several points of the calibration range are verified.

The CCV must be within 30%D to be acceptable for EPA 504.1.

The CCV must be within 15%D to be acceptable for EPA 8011.

9.2.6 Surrogate

This procedure uses a surrogate compound to evaluate the extraction process. 1,2,3-trichloropropane is the surrogate used for this procedure. Other surrogate compounds may be used provided they produce consistent results within method-defined criteria.

Prior to preparation, this surrogate is added to all samples and QC items. The concentration of the surrogate is the same in all field samples and QC samples. A concentration of 0.50ug/L is used.

The percent recovery of the surrogate in all field samples and QC samples must be within the limits listed in the Method Limit Groups (MLGs) in LIMS. If the percent recovery is outside of this range, the analysis of the sample must be repeated. Repeated failure of the surrogate percent recovery may indicate re-extraction is necessary.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* and the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

Samples, calibration standards, and QC items are subjected to the same extraction and analytical procedures.

10.1.1 Remove the samples from storage and scan them into the SG department. Allow them to warm to room temperature.

10.1.2 Gather and label one 40mL VOA vial for each calibration standard and QC item. Add 35mL reagent water to each of the labeled VOA vials. Prepare the calibration standards in accordance with Attachment 5. Prepare the QC items in accordance with Section 10.2.

10.1.3 Scan each sample into the prep batch and complete the information for the calibration standards and the QC items for the batch.

10.1.4 Inspect the samples for large air bubbles, the presence of large amounts of sediment, and other anomalies and, if present, contact the supervisor to determine the course of action.

In the absence of any additional guidance, use the following:

If the sample contains air bubbles, notify the Project Manager via a Nonconformance Memo (NCM) and proceed with the analysis.

If the sample contains large amounts of sediment, pour off the liquid above the sediment into a tared 40mL vial and proceed with the analysis. Notify the Project Manager via an NCM.

10.1.5 Working with each sample in turn, invert the sample vial three times and open the cap. Pipette 6mL of sample from each 40mL sample vial and transfer to a labeled, 25mL plastic cup. Cap the vial. Repeat for the remaining samples.

Add a residual chlorine powder pillow to the 6mL of sample that was transferred to the plastic cup. Swirl to mix and note whether the residual chlorine test is positive (pink color forms) or negative (no color forms) on the prep sheet. If residual chlorine is present, an NCM must be initiated.

10.1.6 Weigh and record the weight of the capped sample vials (after removing 6mL) to the nearest 0.1 grams on the prep sheet.

10.1.7 Add the surrogate spiking solution to each sample and QC item as follows:

- draw 35uL of the surrogate spiking solution into a 50uL syringe
- remove the cap of the vial and quickly add the surrogate under the surface of the sample
- replace the cap and invert the sample once to mix
- repeat for the remaining samples and QC items.

10.1.8 Add the 504 Spike Solution to each LCS/LCSD and MS/MSD item as follows:

- draw 35uL of the surrogate spiking solution into a 50uL syringe
- remove the cap of the vial and quickly add the 504 Spike Solution under the surface of the sample
- replace the cap and invert the sample once to mix
- repeat for the remaining QC items.

10.1.9 Add 6g of purified sodium chloride (NaCl) to each standard, sample, and QC item. Recap the sample containers and gently swirl until the NaCl has dissolved.

10.1.10 Working with one vial at a time, quickly remove the cap, pipette 2.0mL hexane into the vial, and replace the cap. Repeat for all remaining samples, QC, and calibration standards.

10.1.11 Shake the vials for approximately three minutes.

10.1.12 Allow the hexane and water layers to separate.

10.1.13 Remove the cap and carefully transfer approximately 0.25mL of the extract (i.e., hexane; top layer) into a GC autosampler vial fitted with a 400uL insert. Cap the vial. The extract is now ready for analysis.

Note: If an emulsion forms in the solvent layer, add small amounts (~0.1g) of purified sodium sulfate to the extract, letting the crystals fall gently through the emulsion/solvent layer. Alternatively, prepare a small drying column by placing a small wad of glass wool in a Pasteur pipette and then added about 1 inch of

purified sodium sulfate to the pipette. Rinse the column with hexane. Transfer the solvent/emulsion layer to the drying column in 0.25-0.5mL aliquots and collect the solvent in a clear autosampler vial fitted with a 250uL insert. Add additional extract to fill the insert half to completely full and cap the vial. If water (from the emulsions) passes through the drying column, remove the top layer and transfer to a clean vial insert and cap.

If the sodium sulfate does not break the emulsion, centrifuge the sample. The centrifuge is located in the Metals Prep laboratory. If centrifugation does not clear up the emulsion freeze the sample to separate the water layer and solvent layer.

Invert the remaining sample and vials and stored at 4°C until analysis is completed. The extracts must be analyzed within 24 hours of extraction.

10.1.11 Determine the volume of sample as follows:

- remove the cap and discard the remaining water sample down the sink
- "flick" the sample vial several time to remove the remaining drops of water
- recap the vial, weigh the vial, and record the weight of the empty sample container on the prep sheet to the nearest 0.1g.

10.1.12 Calculate the volume of sample, assuming that 1.0gram of sample is equal to 1.0mL of sample.

$$V = (W_1 - W_2) \otimes \frac{1.0mL}{g}$$

Where:
V = volume of sample extracted (mL)
W_1 = weight of vial, cap, and sample (g) (Section 9.6)
W_2 =weight of empty vial and cap (Section 9.13)

Record the volume of sample on the prep sheet.

10.1.15 Complete the LIMS prep sheet.

10.2 QC Sample Preparation

Refer to Section 9.1 for the minimum QC items to be prepared with each preparation batch of twenty or fewer field samples. Additionally, the Resolution Check / RL Standard and a mid-level CCV (or multi-point ICAL) are also required.

Note: The LCS/LCSD are prepared using a source different from the source used to the calibration standards and also serve the initial calibration verification standards for an ICAL.

Batch QC samples are processed in the same manner as field samples.

10.3 Analysis

10.3.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

Two dissimilar columns are connected to the injection port using a press-tight glass y-splitter and a guard column which provides simultaneous detection and confirmation of the target analytes.

These conditions and parameters are given for guidance and for a starting point if the method is lost in the acquisition computer. The conditions and parameters may be modified to optimize the analytical system. The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

GC Parameters
Column1: Restek CLPesticides 30m x 320um, x 0.50um
Column2: Restek CLPesticides 2 30m x 320um, x 0.25um
Injector: 220°C
Mode: Pulsed Splitless
Pressure: 9.34psi (Flow = 2.0mL/min)
Pulse pressure: 30psi
Pulse time: 0.25 minutes
Purge flow: 50.0mL/minute
Purge time: 0.25 minutes
Total flow: 60.1mL/min (helium)

Temperature program
- Initial Temp: 55°C
- Initial Hold: 0.5 minute
- Program Rate: 25°C per minute to 100°C, hold 8 minutes
- Maximum Temp: 320°C

Run Time: Approximately 10.3 minutes

Detector: Dual electron capture
Detector temperature: 305°C
Makeup flow: 80mL/min (nitrogen)

Signal data rate: 10hz

Autoinjector
Sample washes: 1
Sample pumps: 3
Injection volume: 1.0uL
Syringe size: 10uL
PostInj(ection) Solvent A washes: 3
PostInj(ection) Solvent B washes: 3 (use hexane as wash solvent)
Viscosity delay: 0 seconds

Plunger speed: fast
Preinjection dwell: 0.00minutes
Postinjection dwell: 0.00minutes

10.3.1.1 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in SOP SA-QA-08: *Evaluation of Chromatographic Data*. Retention time windows (RTW), i.e., the length of time the instrument will scan for the analyte, must be established initially upon instrument set-up and verified quarterly.

Retention times (RT), i.e., the elution time of the analyte, are verified daily with the analysis of the ICAL or CCV. The retention time for the CCV must fall within the daily retention time window as defined in SOP SA-QA-08.

10.3.2 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.2. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.3, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.5.

10.3.3 Sample Analysis

Remove the extracts from the refrigerator and allow them to come to room temperature.

The sample extract must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to exclude QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the clock.

10.3.4 Example Analytical Sequence

Refer to Attachment 1 for an example analytical sequence.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data evaluation must be performed in accordance with SA-QA-08: *Evaluation of Chromatographic Data*. This SOP includes specific information regarding the evaluation of chromatographic data, including the requirements for performing manual integrations and the evaluation of retention times.

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review*.

11.1.1 Target Analyte Identification

The judgment and experience of the analyst and his/her colleagues are important factors in the evaluation of chromatographic data. Inspect each chromatogram to ensure that the peaks are properly identified and that the correct areas have been associated with the corresponding standard peak RT in the data system tabulation.

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times); the recovery and retention time shift of the surrogate compounds, whether the peak response falls within the working range of the calibration; and the integration of the peaks. The analyst must also take into account the results from the method blank and lab control sample before reporting quantitative data. SOP SA-QA-08: *Evaluation of Chromatographic Data* provides additional guidance for the evaluation of chromatographic data. This guidance is summarized in the following sections.

11.1.2 Manual Integrations

Manual integrations must be documented in accordance with SOP SA-QA-08. Data systems should be adjusted to minimize operator intervention. All chromatographic peaks must be evaluated for overall peak shape and "reasonableness" of integration. Under no circumstances should manual integrations be used to change reasonable data system integrations in order to meet calibration or QC criteria.

11.1.3 Dual Column Reporting

Refer to SOP SA-QA-08: *Evaluation of Chromatographic Data* for information on assessing and reporting data from dual columns.

11.1.4 Surrogate Evaluation

The surrogate, 1,2,3-trichloropropane, is spiked into each sample and QC item prior to preparation. Given the complicated nature of GC-ECD chromatograms, assessing surrogate recovery is frequently complicated by co-eluting positive and negative interferences. Evaluate the surrogates in the same manner as the target compounds using the guidance above.

Refer to Section 11.1.5.1 for information on the surrogate dilution threshold factor.

Note: Other surrogate compounds may be used provided they produce consistent results within method-defined criteria.

11.1.5 Dilutions

If the response for an analyte exceeds the working range of the system, a dilution is required. Prepare dilutions of the extract if the dilution can be analyzed within 24 hours of the time the sample was extracted. If not, extract a smaller aliquot of sample and repeat the analysis.

Dilution from Extract

Dilution Factor	Volume of Extract	Final Volume of Dilution in Hexane
2	500uL	1000uL
5	200uL	1000uL
10	100uL	1000uL
25	40uL	1000uL
50	20uL	1000uL
100	10uL	1000uL

Dilution from Sample

Dilution Factor	Volume of Sample	Final Volume of Dilution in Water
2	25mL	50mL
5	10mL	50mL
10	5.0mL	50mL
25	2.0mL	50mL
50	1.0mL	50mL
100	0.5mL	50mL

Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags must be used or qualification in a case narrative provided to the client.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower reporting limits.

11.1.5.1 Surrogate Dilution Threshold Factor

Surrogates may be diluted out if the concentration of target compounds is high or the presence of non-target compounds interferes with the quantification of the target compounds. Undetect surrogates in the sample when the dilution factor is 6 or greater. As such, recoveries must be reported as "0D", and control limits will not apply.

An NCM must be initiated to denote this situation.

11.1.5.2 Dilutions and MS/MSD Recoveries

Matrix spike recoveries are not reported for dilutions of 6 or greater. An NCM is generated for instances where the dilution prohibits evaluation of the MS/MSD recoveries. In instances where the unspiked sample concentration is more than four times the concentration of the target compound spiked into the MS and MSD, the results are qualified with "4" or other suitable flag.

An NCM must be initiated to denote this situation.

11.1.6 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes or use the TALS Historical Date tracker feature to determine if historical data is available for review.

11.1.7 Drinking Water Compliance Evaluation

Public water suppliers (PWS) are governed by EPA-specified Maximum Contaminant Levels (MCL) above which indicates noncompliance. The MCLs associated with this procedure are given in Attachment 6. Notify the PM immediately via a Nonconformance Memo if any sample contains a detection above these levels.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample (at the instrument)
F = Final volume/weight
I = Initial volume/weight
D = Dilution factor

Note: This calculation assumes all applicable unit correction factors are applied.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and verified quarterly in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs).*

Note: EPA 8011specifies that the MDL must be ≤0.03ug/L.

12.2 Reporting Limit Verification

Reporting limits must be verified annually in accordance with SA-QA-07: *Determination and Verification of Reporting and Detection Limits.*

12.3 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items for EPA 8011 and EPA 504.1 are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items. Although the laboratory must default to the method-defined QC limits, control charting should still be used as outlined below.

Control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.4 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision (i.e., 70-130%R and <20%RSD). The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 13 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.
- Flammable waste (acetone, hexane, and methanol from extracts, rinsings, and standards) -Transfer to a satellite container designated for flammable waste and transfer to waste disposal department when the container is full.
- Sample residue from the sample vials contains hexane - The samples are poured into a storage container that is used to separate the hexane layer from the aqueous layer. The aqueous layer is discarded and the hexane layer is contained in a flammable waste container.

15.0 References / Cross-References

- SOP SA-AN-041: *Reagent and Standard Materials Procedures*
- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs)*

- SOP SA-QA-08: *Evaluation of Chromatographic Data*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, December 1986 and February 2007.
  - Method 8011: 1,2-Dibromoethane and 1.2-Dibromo-3-Chloropropane by Microextraction and Gas Chromatography, Revision 0; July 1992
  - Method 8000B: Determinative Chromatographic Separations, Revision 2; December 1996.
- *Methods for the Determination of Organic Compounds in Drinking Water:*
  - EPA Method 504.1, 1,2-Dibromoethane (EDB), 1.2-Dibromo-3-Chloropropane (DBCP), and 1,2,3-Trichloropropan (123TCP) in Water by Microextraction and Gas Chromatography, Revision 1.1, Munch, J.W. 1995

16.0 Method Modifications and Clarifications

16.1 The reference method was written specifically for drinking water and source water samples; however, the laboratory may perform other types of water samples using this procedure.

16.2 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this frequency via the Low-level LCS required by both methods.

16.3 The amount of sodium chloride added to the samples differs between EPA 504.1 (6g) and EPA 8011 (7g). This SOP directs the analyst to use 6g per sample, calibration standard, and QC item. The addition of salt to the sample is to increase the polarity of the sample matrix, which increases the tendency for the target compounds to partition into the non-polar solvent (hexane). Six grams of salt is adequate to achieve this purpose. In addition, the laboratory believes this minor modification of the method to have no impact on sample results since the samples and calibration standards are processed in the same manner.

16.4 A calibration standard at one half the routine RL of 0.020ug/L is included in the initial calibration to support the RL of 0.010ug/L required by one or more state agencies.

16.5 The laboratory has incorporated the batch QC items as outlined in Section 9.1. Some additional QC items are performed (above those required in the reference methods) to satisfy common state regulatory and/or client requests for precision data and/or to facilitate scheduling and data evaluation. Additionally, some QC items are combined (such as the daily Low-level LCS required for the EPA Drinking Water Manual and the weekly Low-level LCS required by EPA 504.1; or for EPA 504.1, the CCV and the LCSD required for batches of 11-20) to facilitate analysis and performing both EPA 504.1 and EPA 8011 in the same batch.

The method-specified batch QC items are as follows:

EPA 504.1: Lab reagent blank and field reagent blank each day; 1 LCS per 10% of samples (70-130%R); Low-level LCS weekly (60-140%R); 1 MS per batch (65-135%).

EPA 8011: reagent and calibration blank per batch; check sample at 0.25ug/L for 5% of samples (60-140%R); QC reference sample at 0.10ug/L weekly (60-140%R); MS/MSD or sample duplicate daily.

EPA Manual for the Certification of Laboratories Analyzing Drinking Water: method blank per batch, LCS per batch, Low-Level LCS daily.

16.6 EPA 8011 does not give CCV acceptance criteria. The laboratory uses 15%D, which is consistent with the guidance given in EPA 8000B.

16.7 EPA 504.1 includes the use of Field Reagent Blanks (i.e., trip blanks). The laboratory does not normally include these in outgoing bottle kits; however, this task can be accommodated upon client request.

16.8 SW-846 does not specifically address bottle types for EPA 8011. The bottle type specified in EPA 504.1 (i.e., a 40mL VOA vial with sodium thiosulfate dechlorination agent) can be used for both EPA 504.1 and EPA 8011, or alternatively, the bottle type specified in EPA 8260 (i.e., a 40mL VOA vial with HCl preservative) or that specified in EPA 624 (i.e., a 40mL unpreserved VOA vial) can be used for this method.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Standard Preparation Recipes
Attachment 6: Maximum Contaminant Level (MCL) Table

Attachment 1:
SOP Summary

Sample Preparation and Analysis Summary

Thirty-five milliliters of sample are extracted with two milliliters of hexane. The extract is analyzed by gas chromatography utilizing dual capillary columns and dual electron capture (EC) detectors. Calibration standards are extracted and analyzed in the same manner as the samples.

Example Analytical Sequences

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
Instrument blank	Hexane
ICAL	Minimum of five points
Instrument blank	Hexane
ICV	Second source standard
Instrument blank	Hexane
Field and QC samples	Not to exceed 20 field samples
CCV	Mid-level
Instrument blank	Hexane
Field and QC	Not to exceed 20 field samples
CCV	Mid-level calibration standard
Instrument blank	Hexane

Analytical Sequence for samples not immediately following an initial calibration:

Description	Comments
Instrument blank	Hexane
RL Standard	Per batch
CCV	Mid-level calibration standard
Instrument blank	Hexane
Field and QC samples	Not to exceed 20 field samples
CCV	Mid-level
Instrument blank	Hexane
Field and QC samples	Not to exceed 20 field samples
CCV	Mid-level
Instrument blank	Hexane

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Listed below are the holding times and preservation requirements:

Matrix	Routine Sample Container	Routine Sample Size	Minimum Sample Size	Chemical Preservation	Thermal Preservation	Dechlorination Agent	Holding Time
Water	3 x 40mL VOA; no headspace	35mL	35mL	None	0-6°C	Sodium Thiosulfate	Extraction: 14 days from collection Analysis: 24 hours from extraction

Attachment 3: QC Summary

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration (ICAL) - Minimum 5 points	Initially prior to sample analysis, when major instrument maintenance performed, or when CCV fails	EPA 504.1: %RSD<20% r^2>0.990 EPA 8011: %RSD<10% r^2>0.990	Refer to SOP SA-QA-16
Initial Calibration Verification (ICV) - 2nd Source	After each ICAL and weekly thereafter. Note: LCS is used to satisfy since from a second source.	70-130% Recovery	Refer to SOP SA-QA-16
Continuing Calibration Verification (CCV)	Initially, after every 20 samples (not to exceed 12 hours), and at the end of the sequence - Concentration must be varied throughout the mid-range.	EPA 504.1: <30%D EPA 8011: <15%D	Refer to SOP SA-QA-16
Calibration Blank (CCB/ICB)	After ICV and every CCV	<MDL	Terminate the analysis; correct problem; reanalyze affected samples.
Surrogate	All field, batch QC, & instrument QC samples	Within TALS MLG limits	Refer to SOP SA-QA-17
Batch Definition	Extracted together w/in 24-hr period; not to exceed 20 field samples	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	<MDL	Refer to SOP SA-QA-17

QC Item	Frequency	Criteria	Corrective Action
Laboratory Control Sample (LCS)	One per batch	Within limits listed in the MLG	Refer to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	One per batch, when insufficient volume provided for MS/MSD	Within limits listed in the MLG	Refer to SOP SA-QA-17
Low-Level Laboratory Control Sample (LLCS)	EPA 504.1 One per batch	60-140%R	Refer to SOP SA-QA-17
Matrix Spike (MS)	One per batch	Within limits listed in the MLG	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per batch	Within limits listed in the MLG	Refer to SOP SA-QA-17
Column Resolution Check (DBCM Check)	One per batch	Baseline resolution between DBCM and EDB	- Perform column maintenance - Adjust column flow/temperature to attain resolution. - Install new column or columns.
Retention Time Window Determination	Annually	Refer to SOP SA-QA-16	Refer to SOP SA-QA-16
Initial Demonstration of Capability (IDOC)	Initially; Per analyst / matrix / method / analyte combination	70-130%R <20% RSD	Refer to SOP SA-QA-06 (Unsupervised work must not begin without successful completion of IDOC.)
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method/matrix combination	Within limits listed in the MLG	Refer to SOP SA-QA-06

QC Item	Frequency	Criteria	Corrective Action
Method Detection Limit (MDL)	Upon method/instrument set-up	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
MDL Verification (MDLV)	Upon method/instrument set-up, and quarterly thereafter	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Guard Column/Injector							X	Change sleeve and cut front of guard column, recommended daily
Septum							X	Replace, recommended daily
Splitless Disc							X	Replace, recommended daily
Autosampler							X	Syringe cleaned or replaced as needed
Column							X	Change column

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually; AN = as needed

Contingency Plan
Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
Standard Preparation Recipes

Stock Standard Mixes

Stock/Mix	LIMS ID	Vendor/ Part Number	Concentration (ug/mL)
504.1 Mixture	504.1 Mix_	Ultra DWM-514	200
552.2 Internal Standard (1,2,3-Trichloropropane Soln.)	552.2 Itsd_	Ultra PPS-251-1	1000
504.1 EDB/DBCP Spike Std (Second Source)	EDB/DBCP_	Accustandard M-504	200
Dibromochloromethane (Stock)	DBCM(504)_	Ultra HC-100	100

Storage: <-10°C
Expiration:
Unopened: Manufacturer's expiration date
Opened: 6 months from opening

504 Intermediate Standard (LIMS ID = 504 INT A)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)*	Final Concentration (ug/mL)
504.1 Mixture	140	2.0	14 (EDB/DBCP)
552.2 Internal Standard	112		70 (1,2,3-TCP)

(*) in methanol
Storage: <-10°C
Expiration: 1 month from prep date

504 Working Standard #1 (LIMS ID = 504 WS#1)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)*	Final Concentration (ug/mL)
504 Intermediate A	10	2.0	0.07 (EDB/DBCP) 0.35 (1,2,3-TCP)

(*) in methanol
Storage: <-10°C
Expiration: 1 month from prep date

504 ICV/LCS Spike Intermediate Standard (LIMS ID = 504 Spike_)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)*	Final Concentration (ug/mL)
504.1 EDB/DBCP Spike Std (Second Source)	5	10	0.10 (EDB/DBCP)

(*) in methanol
Storage: <-10°C
Expiration: 1 month from prep date

504 Surrogate Spiking Solution (LIMS ID: 504 SURR DL_)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)*	Final Concentration (ug/mL)
552.2 Internal Standard	5	10	0.50 (1,2,3-TCP)

(*) in methanol
Storage: <-10°C
Expiration: 1 month from prep date

Dibromochloromethane Intermediate Standard (LIMS ID = 504-DBCM_)

Stock/Mix	Aliquot Volume (uL)	Final Volume (mL)*	Final Concentration (ug/mL)
Dibromochloromethane (Stock)	140	2	7.0

(*) in methanol
Storage: <-10°C
Expiration: 1 month from prep date

504/8011 Calibration Standards (LIMS ID: enter in prep batch)

CAL STD	Volume 504 WS#1 (uL)	Volume of Reagent Water (mL)	EDB/DBCP		1,2,3-TCP	
			ug/mL[1]	ug/L[2]	ug/mL[1]	ug/L[2]
1	5	35	0.00018	0.010	0.00088	0.050
2	10	35	0.00035	0.020	0.00175	0.10
3	20	35	0.00070	0.040	0.00350	0.20
4	35	35	0.00122	0.070	0.00612	0.35
5	50	35	0.00175	0.10	0.00875	0.50
6	65	35	0.00228	0.13	0.01138	0.65
7	80	35	0.00280	0.16	0.01400	0.80
8	100	35	0.00350	0.20	0.01750	1.0

Storage: Not applicable; made fresh each day
Expiration: 24 hours

(1) Concentration in extract, final volume = 2.0mL
(2) Concentration in standard, initial volume = 35mL

504/8011 Initial Calibration Verification/LCS (LIMS ID: enter in prep batch)*

STD	Volume 504 Spike (uL)	Volume 504 Surr DL (uL)	Volume of Reagent Water (mL)	Final Concentration (EDB/DBCP) (ug/L)	Final Concentration (1,2,3-TCP) (ug/L)
ICV/LCS	35	35	35	0.10	0.50

Storage: Not applicable; made fresh each day
Expiration: 24 hours
*Also used to prepare the MS and MSD

504/8011 Column Resolution/RL Check (LIMS ID: enter in prep batch)

STD	Volume of Intermediate (uL)		Volume of Water	Concentration of RL/Resolution Check (ug/L)		
	504 INT A	504-DBCM		EDB/DBCP	1,2,3-TCP	DBCM
RL/ResCheck	5	5	35mL	0.010	0.050	1.0

Storage: Not applicable; made fresh each day
Expiration: 24 hours

Guidance for Preparing Intermediate and Working Standards in Methanol

- Clean and rinse volumetric flask with methanol.
- Add methanol to volumetric flask to approximately one half volume.
- Add standard to volumetric flask, inserting the syringe needle under the surface of the methanol.
- Dilute to volume with methanol, cap, and invert three times to mix.
- Transfer by gently pouring the newly made standard into a labeled storage with minimal headspace and seal with Teflon-lined screw or crimp cap.
- Store at -10C in freezer

Guidance for Preparing Calibration and Verification Standards in Water

- Add 35mL of reagent water to a 40mL VOA vial.
- Add standard to the vial, inserting the syringe needle under the surface of the water.
- Cap the vial and mix by inverting three times.
- Use immediately.

Attachment 6:
Maximum Contaminant Level (MCL) Table

Primary Drinking Water Regulations		
Contaminant	MCL (mg/L)	MCL (ug/L)
1,2-Dibromo-3-chloropropane (DBCP)	0.0002	0.2
Ethylene Dibromide (EDB)	0.00005	0.05

18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial and grammatical changes made. Boilerplate text added. Expanded tables in Attachment 2 and Attachment 3.
- Updated SOP references to reflect current versions.
- Added LIMS reagent names. Section 7
- Added reference to TALS Historical Data Tracker feature. Section 11.1.6
- Removed requirement to perform MDLs annually. Added requirement to perform MDLV quarterly. Section 12.1 and Attachment 3
- Added note that other surrogate compounds may be used for this procedure provided they produce consistent results and meet the method-defined recovery criteria. Section 9.2.6 and Section11.1.4
- Changed sample aliquot volume from 6mL to 5mL when performing residual chlorine check. Section 10.1.5 and 10.1.6
- Changed time required to shake vials from 1 minute to 3 minutes. Section 10.1.12
- Changed autosampler insert size from 250uL to 400uL. Section 10.1.13
- Added option of freezing samples to break up emulsions. Section 10.1.13
- Removed instructions to transfer a second aliquot of the extract to an autosampler vial in case an additional dilution or analysis is performed. This step is not typically performed as samples must be analyzed within 24 hours of extraction. Added note to invert remaining sample and store at 4°C until analysis is completed. Section 10.1.3
- Batch QC changes (Section 9.1, Section 16.5, and Attachment 3):
  - Added requirement to perform LCSD if insufficient sample is provided for MS/MSD.
  - Added information to Method Modifications and Clarifications Section that the laboratory has expanded the method's default batch QC items to include MSD and LCSD (if insufficient sample provided for MS/MSD).
  - Removed requirement to utilize reduced volumes for MS/MSD when insufficient sample is provided.

SEMIVOLATILE ORGANIC COMPOUNDS IN DRINKING WATER BY GC/MS

(Methods: EPA 525.2)

Approvals (Signature/Date):

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Andrea Teal Date
Quality Assurance Manager

August 24, 2010
Benjamin Gulizia Date
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Ernest B. Walton September 5, 2010
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Facility Distribution No. 1 **Distributed To:** QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of semivolatile organic compounds in water samples by GC/MS using liquid-solid extraction. This procedure is most applicable to drinking water samples, but because of the low reporting limits achieved, other sample matrices are often requested.

Attachment 5 provides a list of the routine target compounds with the quantitation ions and associated internal standards. The reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

Analytes are extracted from a sample by passing 1L of sample through a disk containing a solid matrix with a chemically bonded C-18 organic phase. This process is referred to as liquid-solid extraction or LSE. The organic compounds are eluted from the LSE disk with small quantities of ethyl acetate followed by methylene chloride, and a 1:1 mixture of ethyl acetate and methylene chloride. This extract is concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a gas chromatography/mass spectrometry (GC/MS) system.

Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a database. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

This SOP is based on the following method: EPA Method 525.2.

Due to the reporting levels required for some regulatory agencies (e.g., Arizona DHS), the laboratory has incorporated a Low-Level EPA 525.2 procedure into this SOP. For the purposes of this SOP, the term "Routine EPA 525.2" refers to the standard procedure; whereas, the term "Low-Level EPA 525.2" refers to the low level procedure.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Acetone, hydrochloric acid, methanol, and methylene chloride must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.1.5 Some polycyclic aromatic hydrocarbons (PAHs), including the labeled PAHs used in this method as internal standards, especially anthracene, benz[a]anthracene, and benzo[a]pyrene, are susceptible to photodegradation. Therefore, care should be taken to avoid exposing standards, samples, and extracts to direct light.

4.1.6 Low recoveries of some PAH compounds have been observed when the cartridge or disk was air dried longer than 10 minutes. Drying times longer than 10 minutes should be avoided, or nitrogen may be used to dry the cartridge or disk to minimize the possible oxidation of these analytes during the drying step.

4.1.7 Several of the nitrogen and/or phosphorus containing pesticides listed as method analytes are difficult to chromatograph and appear as broad, asymmetrical peaks. The method performance for these analytes is strongly dependent on chromatographic efficiency and performance. Poor peak shapes for these analytes will affect the linearity of the calibration curves and result in poor accuracy at low concentrations.

4.1.8 Phthalate esters and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured at levels below 2ug/L.

4.1.9 Low recoveries of metribuzin were observed in samples fortified with relatively high concentrations of additional method analytes. In samples fortified with approximately 80 analytes at 5ug/L each, metribuzin was recovered at about 50% efficiency. This suggests that metribuzin may break through the C-18 phase in highly contaminated samples resulting in low recoveries.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require dilution prior to analysis to reduce or eliminate the interferences.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Some polycyclic aromatic hydrocarbons (PAHs), including the labeled PAHs used in this method as internal standards, are rapidly oxidized and/or chlorinated in water containing residual chlorine. Therefore, any residual chlorine present in samples must be eliminated at the time of sampling.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analysis.

Acetone and methanol are flammable solvents. They can cause irritation to the respiratory tract. Overexposure can cause fatigue, confusion, headache, dizziness, and drowsiness.

Hydrochloric acid is extremely hazardous as an oxidizer, a corrosive, a poison, and is reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Acid vapors

are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Methylene chloride is a carcinogen and an irritant. It causes irritation to the respiratory tract and has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting, and headache. May be absorbed through the skin and can cause irritation and pain to the skin and eyes.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP.

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Acetone	Flammable	1000ppm TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Ethyl Acetate	Flammable	400ppm TWA	May cause eye, skin, and respiratory tract irritation. May cause digestive tract irritation. Ingestion of large amounts may cause central nervous depression, headache, nausea, fatigue, and dizziness. May be harmful if inhaled.
Hydrochloric Acid	Corrosive Poison	5ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methanol	Flammable Poison Irritant	200ppm TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25ppm TWA 125ppm STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
Note: Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Baker Extraction Manifold – Six-place manifold with Teflon bases, Teflon disk holders, Teflon sample funnels, Teflon and glass collection tubes, and appropriate tubing.

Vacuum Pump System with glass trap – Adjustable pump with sufficient capacity to maintain a minimum vacuum of approximately 25 inches of mercury, with appropriate tubing to connect pump to the glass trap and the trap to the extraction manifold.

Analytical Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Zymark Turbo II concentration device or equivalent: The instrument must be vented into an operating fume hood.

Standard EPA 525.2 GC/MS System – Agilent 6890 Gas Chromatograph (GC), Agilent 5973 Mass Spectrometer (MS) Analytical Column: Agilent HP-5MS, 0.25mm x 30m x 0.25um or equivalent.

The GC must be capable of temperature programming and be equipped for splitless/split injection. On-column capillary injection is acceptable if all the quality control specifications are met. The injection tube liner should be quartz or glass and about 4mm in diameter. The injection system must not allow the analytes to contact hot stainless steel or other metal surfaces that promote decomposition. The MS interface should allow the capillary column or transfer line exit to be placed within a few millimeters of the ion source.

The mass spectrometer must be capable of electron ionization at nominal electron energy of 70eV to produce positive ions. The spectrometer must be capable of scanning at a minimum from 45-450amu with a complete scan cycle time (including scan overhead) of 1.0 second or less. (Scan cycle time = total MS data acquisition time in seconds divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 2 when an injection of approximately 5ng of DFTPP is introduced into the GC. An average spectrum across the DFTPP GC peak may be used to test instrument performance.

Data System – Target and Chemstation software are used to acquire, store, reduce, and output mass spectral data. This software has the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectrum from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan

numbers. The software also allows integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as or construction of a linear regression calibration curve, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the response factors.

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Glass Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Transfer Pipettes – various sizes

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

pH paper – used to approximate sample pH to ensure samples have been properly preserved prior to preparation.

Residual (free) chlorine powder pillows – HACH catalogue number 2105569 (for a 10mL sample)

Medicine cups – 30mL, disposable

Detergent – FL-70, or equivalent, used for washing non-disposable labware.

Concentration tubes – 50mL with 1.0mL tip. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Vials – 2mL amber vials with Teflon-lined screw caps. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Glass wool – rinsed with methylene chloride prior to use.

Drying Funnels – Glass funnels containing a small amount of pre-cleaned glass wool

Liquid-Solid Extraction (LSE) Disks – Bakerbond LSE Speedisk, 50mm. The disks should not contain any organic compounds, either from the matrix or the bonded silica, which will leach into the ethyl acetate and methylene chloride eluent. One liter of reagent water should pass through the disks in 5-20 minutes using a vacuum of approximately 25in. of mercury.

40mL VOA Vials

Autosampler vials, amber, crimp-cap – approximately 2mL

1L Amber glass containers

1L Graduated Cylinder

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are 1L certified pre-cleaned amber glass bottles, fitted with Teflon-lined caps, containing 50mg granular sodium sulfite. Additionally, an 8mL vial containing 4mL 1:1 HCl is sent along with the sample container so that samples can be properly preserved by adjusting pH to <=2 at time of collection.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Traceability*.

Acetone, hydrochloric acid, methanol, and methylene chloride must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Reagent Water – ASTM Type II, purchased from JT Baker (Part number: 4218-03)

7.2.2 Methylene Chloride – residue grade, JT Baker 9264-03 (4L)
Storage: Room temperature, in solvent cabinet
Expiration: Manufacturer's expiration date

7.2.3 Ethyl Acetate – residue grade. JT Baker 9260-03 (4L)
Storage: Room temperature, in solvent cabinet
Expiration: Manufacturer's expiration date

7.2.4 Acetone – residue grade. JT Baker 9254-03 (4L)
Storage: Room temperature, away from incompatibles
Expiration: Manufacturer's expiration date

7.2.6 Methanol – residue grade. JT Baker 9093-03 (4L)
Storage: room temperature, in solvent cabinet

Expiration: Manufacturer's expiration date

7.2.7 Ethyl Acetate / Methylene Chloride (1:1) – In a 1L amber glass container, carefully add 500mL of ethyl acetate to 500mL of methylene chloride.
Storage: Room temperature, in solvent cabinet
Expiration: One year from preparation date, or manufacturer's expiration date, whichever occurs first.

7.2.8 Hydrochloric Acid – concentrated; reagent grade. Mallinckrodt 5587-46 (2.5L)
Storage: room temperature, in acid cabinet
Expiration: Manufacturer's expiration date

7.2.9 Hydrochloric Acid (6N) – Transfer 500mL of deionized water to a 2L beaker. Add a Teflon stir bar, place on a magnetic stir plate, and stir slowly. Transfer 500mL of concentrated HCl to a 1L graduated cylinder. Slowly and carefully add the acid to the beaker. Allow the acid and water to mix for ten minutes and then cool for thirty minutes. Transfer to a labeled one liter storage container.
Storage: Room temperature
Expiration: One year from preparation date, or manufacturer's expiration date, whichever occurs first.

> **Caution**: Use extreme caution when preparing this solution. Heat will be generated as the acid and water combine. This solution will cause skin burns and destroy unprotected clothing.

7.2.10 Sodium Sulfate, Anhydrous – reagent grade. JT Baker 3375-07 (12kg);
Storage: Room temperature in a glass or aluminum foil lined container
Expiration: Manufacturer's expiration date

7.2.11 Purified Sodium Sulfate – Heated to >400°C for a minimum of two hours in the oven used to purify salts.
Storage: Room temperature in porcelain mortar, covered with foil.
Expiration: One year from preparation date, or manufacturer's expiration date, whichever occurs first.

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-041 *Reagent and Standard Materials Traceability.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

7.3.1 Purchased Standards

7.3.1.1 Internal Standards and Surrogate Stock Standard (ISSU) – 500ug/mL in acetone, purchased from Ultra. Part number ISM-510.
The ISTDs are acenaphthene-D10, phenanthrene-D10, and chrysene-D12.
The surrogates are 2-nitro-m-xylene, perylene-D12, and triphenylphosphate.
Storage: Refrigerate at 4°C (0°C to 6°C).
Expiration:
Unopened: Manufacturer's expiration date; Opened: 6 months from open date, or

manufacturer's expiration date, whichever occurs first.

7.3.1.2 Recovery Standard – p-terphenyl-D14 at a concentration of 500ug/mL in methylene chloride; purchased from Accustandard Part number M-525-FS-2
Storage: Refrigerate at 4°C (0°C to 6°C).
Expiration:
Unopened: Manufacturer's expiration date; Opened: 6 months from open date , or manufacturer's expiration date, whichever occurs first.

7.3.1.3 GC/MS Performance Check Solution (Tuning Stock Standard) – DFTPP, Endrin, and 4,4'-DDT at 500ug/mL each in methylene chloride. Purchased from Accustandard (called Method 525.2 - Tuning Standard Mix) Part number M-525-2-TS
Storage: Refrigerate at 4°C (0°C to 6°C).
Expiration:
Unopened: Manufacturer's expiration date; Opened: 6 months from open date , or manufacturer's expiration date, whichever occurs first.

7.3.1.4 Calibration and LCS Stock Standards – Mixes purchased individually as follows:

Vendor	Part Number	Concentration (ug/mL)
Accustandard	M-526	1000
Accustandard	M-507A	1000
Accustandard	M-507B	1000
Accustandard	M-507C	1000
Accustandard	M-507D	1000
Accustandard	M-507E	1000
Accustandard	M-508P-A	1000
Accustandard	M-508P-B-R-2	1000
Accustandard	M-525-2-5X	500
Accustandard	M-525-4-R-5X	500
Ultra	NPM-109 (Simazine/Methylparaxon)	1000
Supelco	47543-U (525 PAH 2)	2000

Expiration:
Unopened: Manufacturer's expiration date; Opened: 6 months from open date, or manufacturer's expiration date, whichever occurs first.

7.3.1.5 Second Source Initial Calibration Verification (ICV) Stock Standard – Purchased from O2SI

- Part #: 132121-01 – 525 Custom Solution, 6-1. 1000ug/mL in acetone;
- Part #: 132129-03 – Chlorothanlonil, Benzo(ghi)perylene, Fenamiphos and Methyl Paraxon Solution; 500ug/mL in acetone
- Part #: 031004-04 – Metribuzin 1000ug/mL
- Part #: 132124-01 – Custom Pesticide Solution; 1000ug/mL

Expiration:
Unopened: Manufacturer's expiration date; Opened: 6 months from open date

7.3.1.6 Low-Level Laboratory Control Standard (LLCS) Stock Standard – Purchased from O2SI; contains all target analytes. Part #: 132114-05-2
Expiration:
Unopened: Manufacturer's expiration date; Opened: 6 months from open date, or manufacturer's expiration date, whichever occurs first.

For Routine EPA 525.2, 100uL is spiked. For Low-Level EPA 525.2, 5uL is spiked.

Note: For custom reagents, part numbers are subject to change as quotes are reissued.

7.3.2 Prepared Standards

7.3.2.2 Tuning Standard – DFTPP solution is prepared using 5uL of the Tuning Stock Standard.
Final concentration is 5ug/mL
Final volume: 5mL in methylene chloride
Storage: Transfer solution to an amber vial and refrigerate at 4°C (0°C to 6°C).
Expiration: 3 months from preparation date. Date not to exceed expiration date assigned when stock standard vial was opened or vendor expiration date.

7.3.2.3 Intermediate Calibration Standard Solution at 50ug/mL

Part Number	Concentration (ug/mL)	Aliquot (uL)
M-526	1000	500
M-507A	1000	500
M-507B	1000	500
M-507C	1000	500
M-507D	1000	500
M-507E	1000	500
M-508P-A	1000	500
M-508P-B-R-2	1000	500
M-525-2-5X	500	1000
M-525-4-R-5X	500	1000
47543-U	2000	250
NPM-109	1000	500

Final Volume: 10mL in ethyl acetate
Storage: Transfer solution to an amber vial and refrigerate at 4°C (0°C to 6°C).
Expiration: 3 months from preparation date. Date not to exceed expiration date assigned when stock vial(s) were opened.

7.3.2.4 Intermediate ICV; Prepared at 50ug/mL utilizing reagents from O2SI.

Part Number	Concentration (ug/mL)	Aliquot (uL)
031004-04 (Metribuzin)	1000	250
132121-01 (525 Custom 56.1)	1000	250
132129-03 (525 Custom)	500	500
132124-01 (Custom Pesticide)	1000	250

Final Volume: 5mL in ethyl acetate
Storage: Transfer solution to an amber vial and refrigerate at 4°C (0°C to 6°C).
Expiration: 3 months from preparation date. Date not to exceed expiration date assigned when stock vial(s) were opened.

7.3.2.4 Calibration/Working Standards

Routine EPA 525.2 Calibration:

Level	Volume Intermediate Standard (uL)	Volume ISSU Standard (uL)	Volume p-terphenyl-d14-Standard (uL)	Final Volume (mL)	Final Target Concentration* (ug/mL)
1	4	20	20	2	0.10
2	8	20	20	2	0.20
3	20	20	20	2	0.50
4	40	20	20	2	1.0
5	100	20	20	2	2.5
6	200	20	20	2	5.0
7	400	20	20	2	10
8	600	20	20	2	15

*Each level contains 5ug/mL ISSU and 5ug/mL p-terphenyld14.
Final Solvent: Ethyl Acetate
Storage: Transfer solution to an amber vial and refrigerate at 4°C (0°C to 6°C).
Expiration: 3 months from date prepared.

Low-Level EPA 525.2 Calibration:
- Prepared by performing 1:5 dilution of Routine EPA 525.2 curve

Standard Level	Volume Corresponding Routine 525 ICAL Standard (uL)	Final Volume (mL)	Final Concentration (ug/mL)
1	200	1	0.020
2	200	1	0.040
3	200	1	0.10
4	200	1	0.20
5	200	1	0.50
6	200	1	1.0
7	200	1	2.0
8	200	1	3.0

Solvent: Ethyl Acetate
Storage: Transfer solution to an amber vial and refrigerate at 4°C (0°C to 6°C).
Expiration: Same as the corresponding 525 Calibration solution.

7.3.2.5 Second Source Initial Calibration Verification Standards

Routine EPA 525.2 ICV:

Part Number	Concentration (ug/mL)	Aliquot (uL)
525ICV Intermediate	50	100
525ISSU	500	20
M-525-FS-2	500	20

Final Volume: 2mL
Solvent: Ethyl Acetate
Storage: Transfer solution to an amber vial and refrigerate at 4°C (0°C to 6°C).
Expiration: 3 months from date prepared.

Low-Level 525.2 ICV:
Perform a 1: 5 dilution of the Routine EPA 525.2 ICV.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

Aqueous samples are routinely collected in 1L amber glass containers containing 40-50mg of sodium sulfite de-chlorination agent. The pH of the sample is adjusted at the time of sampling with 4mL of 1:1 HCL preservative. The preservative should be sufficient to achieve a sample pH of less than 2. The dechlorination agent should be sufficient to remove residual chlorine from the sample.

Note: It is very important the sample be dechlorinated prior to adding acid to lower the pH of the sample. Adding sodium sulfite and HCl to the sample bottles prior to shipping to the sampling site is not permitted.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 30 days of extraction.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives and/or de-chlorination agents.

8.1.1 Preservation Checks – Residual Chlorine and pH

These checks can be performed upon receipt or prior to preparation.

8.1.1.1 Mix the sample by inverting and transfer 10mL to a small medicine cup.

Touch a piece of narrow range pH paper to the sample in the cup and note the pH. Record the pH in the preservation check batch in LIMS.

If the pH is greater than 2, initiate an NCM noting that the pH was outside of the preservation requirements. Adjust the pH to <2 using 1:1 HCL, AFTER the absence of chlorine is confirmed.

8.1.1.3 Add a residual chlorine powder pillow to the sample in the cup, wait approximately 10 seconds, and note the presence of a pink color, which indicates the presence of residual chlorine.

If the sample tests positive for residual chlorine, initiate an NCM noting that residual chlorine was present.

- If the sample pH was found to be <2.0, additional sodium sulfite can not be added and preparation can not proceed. Edit the NCM accordingly.
- If the sample pH was found to be >2.0, add sodium sulfite until chlorine is not present, then proceed to pH adjustment if necessary. Edit the NCM accordingly.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 12 hour period. Note: This 12-hour time period is shorter than most similar preparation methods, which allow 24 hours for a batch.

The default QC items performed for each extraction batch are: a method blank (MB), a laboratory control sample (LCS), a low-level LCS (LLCS, spiked at the RL), a matrix spike (MS), and a matrix spike duplicate (MSD).

The routine container supplied for this method is a 1L container. 1L is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike/matrix spike duplicate frequency; however, the minimum extraction volume to be used for the matrix spike samples is 500mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike and/or matrix spike duplicate, the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 2L.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

9.2.1 GC/MS Performance Check

Prior to each initial calibration and continuing calibration, the performance of the GC/MS is checked using DFTPP, endrin, and 4,4'-DDT. The GC/MS performance check standard is injected and a mass spectrum is acquired that includes data for m/z = 45-450. Use GC conditions that produce a narrow (at least five scans per peak) symmetrical peak. If the spectrum does not meet the criteria in Attachment 6, the MS must be retuned.

The analytes endrin and DDT are evaluated for breakdown. Evaluate the degradation products of Endrin (i.e., endrin ketone and endrin aldehyde) and 4'4-DDT (i.e., 4.4'-DDE and 4,4'-DDD). Breakdown must not exceed 20%.

The MS must meet the criteria in Attachment 6 and breakdown criteria prior to analysis of standards or samples.

9.2.2 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves*. This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 6 standards. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

Note: A minimum of 6 points is required for a quadratic curve. Higher order curves are not permitted.

The initial calibration standard concentrations currently in use in the laboratory are listed below. Refer to Section 7.3 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-041.

EPA 525.2 Routine

Standard Level	Concentration (ug/mL)
1	0.10
2	0.20
3	0.50
4	1.0
5	2.5
6	5.0
7	10
8	15

EPA 525.2 Low-Level

Standard Level	Concentration (ug/mL)
1	0.020
2	0.040
3	0.10
4	0.20
5	0.50
6	1.0
7	2.0
8	3.0

9.2.2.1 Mid-level Calibration Performance Criteria

9.2.2.1.1 GC Performance Criteria

Anthracene and phenanthrene should be separated by baseline.

Benzo[a]anthracene and chrysene must be separated by a valley whose height is less than 25% of the average peak height of these two compounds. If the valley between benzo[a]anthracene and chrysene exceeds 25%, the GC column requires maintenance.

The analyst must use good judgment in evaluating performance criteria. Use the extracted ion profile of the quantitation ion to determine baseline resolution. A visual inspection of the ion chromatogram must allow each individual analyte to be identified and quanted. Consult the supervisor or technical manager for guidance when criteria are not met.

9.2.2.1.2 MS Sensitivity Performance Criteria

The GC/MS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution, and make correct identifications. If fewer than 99% of the compounds are recognized, system maintenance is required.

9.2.2.2 The preferred method of quantitation is the average response factor. The relative standard deviation (%RSD) of the calibration standards must be <30% for the initial calibration curve to be acceptable.

If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve. If the regression curve option is chosen, the regression coefficient (r^2) must be greater than or equal to 0.990 to be acceptable.

If these criteria are not met, then re-calibration is required before sample analysis can proceed.

9.2.3 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified after the initial calibration is established, prior to any sample analyses, in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to Level 5 of the ICAL. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

The ICV must be within 30% of the true value to be acceptable.

Note: EPA Method 525.2 acknowledges that due to the large number of compounds on the analyte list, it is possible for a few analytes of interest to be outside the continuing calibration criteria. Analysis may proceed as long as no more than 10% of the analytes of interest are outside initial calibration criteria; *and* as long as the %D or %Drift is no more than 45% for each analyte.

If more than 10% of the analytes are outside the continuing calibration criteria the ICV must be re-analyzed. If an acceptable ICV cannot be achieved, then a new initial calibration curve is required.

9.2.4 Instrument Blank

The instrument must be shown to be free from contamination by the analysis of instrument blanks. Instrument blanks are analyzed at the beginning of each clock, following analysis of the CCV and prior to analysis of samples.

If any target analytes are present in instrument blanks, they must be present at <1/2RL to be acceptable.

9.2.5 Continuing Calibration Verification (CCV)

The initial calibration curve must be verified every 12 hours prior to sample analysis with a mid-level standard.

The CCV must meet the criteria listed below and be within 30% of the true value to be acceptable.

a) GC Performance Criteria

Anthracene and phenanthrene should be separated by baseline.

Benzo[a]anthracene and chrysene must be separated by a valley whose height is less than 25% of the average peak height of these two compounds. If the valley between benzo[a]anthracene and chrysene exceeds 25%, the GC column requires maintenance.

The analyst must use good judgment in evaluating performance criteria. Use the extracted ion profile of the quantitation ion to determine baseline resolution. A visual inspection of the ion chromatogram must allow each individual analyte to be identified and quanted. Consult the supervisor or technical manager for guidance when criteria are not met.

b) MS Sensitivity Performance Criteria
The GC/MS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution, and make correct identifications. If fewer than 99% of the compounds are recognized, system maintenance is required.

c) Internal standard areas must be within 50% of the corresponding level in the Initial Calibration.

Exception:
EPA Method 525.2 acknowledges that due to the large number of compounds on the analyte list, it is possible for a few analytes of interest to be outside the continuing calibration criteria. Analysis can proceed as long as the same analyte has not been outside the criteria for 3 or more consecutive analyses, no more than 10% of the analytes evaluated in the calibration standard are outside initial calibration criteria, *and* as long as the %D or %Drift is no more than 45% for each analyte.

If more than 10% of the analytes miss the continuing calibration check, or if the same analyte does not meet the calibration criteria for 3 consecutive analyses, remedial action must be taken. Some possible remedial actions include:

- Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.
- Clean or replace the splitless injection liner.
- Break off a short portion (about 1m) of the column from the end near the injector; or replace GC column. Prepare fresh CAL solutions, and repeat the initial calibration step.
- Clean the MS ion source. Replace the MS electron multiplier, or any other faulty components.
- Replace any components that allow analytes to come into contact with hot metal surfaces. (injection port, lines)

Major maintenance such as cleaning an ion source, replacing filament assemblies, changing the column, etc. require returning to the initial calibration step.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to Level 5 of the ICAL. Refer to Section 7.3.8 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

9.2.6 Recovery Standard

A recovery standard, p-terphenyl-D14, is used to quantitate the internal standard recoveries.

Prior to analysis, this recovery standard must be added to all standards and extracts. The concentration of the recovery standard must be the same in all calibration samples, field samples, and QC samples. A concentration of 5ug/mL is used for Routine EPA 525.2, and 1.0 ug/mL is used for Low-Level EPA 525.2.

The integrated areas of the recovery standard are monitored for gross failures.

9.2.7 Internal Standard (ISTD)

This procedure is an internal standard (ISTD) procedure. Acenaphthene-D10, phenanthrene-D10, and chrysene-D12 are the internal standards.

Prior to extraction, this internal standard must be added to all samples and QC items. Prior to analysis the internal standard must be added to all standards. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. A concentration of 5ug/mL is used for Routine EPA 525.2 and 1ug/mL is used for Low-Level EPA 525.2.

For samples and batch QC items, the ISTD must recover >70% when quanted against the recovery standard. If the percent recovery is outside of this range, the analysis of the sample must be repeated. Repeated failure of the ISTD percent recovery may indicate re-extraction is necessary.

For CCV the area of the ISTDs must be within 50% of the CCV level in the ICAL. If the area is outside this range, the analysis of the CCV must be repeated. Repeated failure of the ISTD recovery may indicate re-calibration is necessary.

9.2.8 Surrogate

This procedure uses surrogates to evaluate the extraction process. 2-nitro-m-xylene, perylene-D12, and triphenylphosphate are the surrogates.

Prior to preparation, this surrogate is added to all samples and QC items. The concentration of the surrogate is the same in all field samples and QC samples. A concentration of 5.0ug/mL is used for Routine EPA 525.2 and 1.0ug/mL for Low-Level EPA 525.2.

The percent recovery of the surrogate must be within 70-130 % recovery to be acceptable.

9.2.8.1 Surrogate Threshold Dilution Factor

Due to the level of dilution required for samples, surrogates may be diluted out. As such, recoveries will be reported as "0D" in dilutions at 1:10 or greater. Control limits will not apply to samples analyzed at dilutions of 1:10 or greater.

An NCM must be initiated to denote this situation.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action* the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

10.1.1 Remove the samples from the refrigerator and allow them to come to room temperature.

10.1.2 Perform the pH and residual chlorine checks as described in Section 8. Document the results of these checks in a preservation batch in LIMS.

10.1.3 Inspect each container. Mark the level of sample on the side of the container so that the volume of sample can be determined later.

10.1.4 Prepare the QC samples as described in Section 10.2.

10.1.5 For samples that will be analyzed using the routine EPA 525 analysis, add 10uL of the 500ug/mL ISSU standard to each QC item and sample. Mix by inverting the sample at least three times.

For samples that will be analyzed using the low-level preparation and analysis, add 20uL of the low-level 525.2 ISSU Spiking Solution (50ug/mL) to each QC item and sample. Mix by inverting the sample at least three times.

Note: Pre-rinse the syringe with acetone before using.

10.1.6 Add 5mL of methanol to each sample and QC item. Mix by inverting at least three times.

10.1.7 Attach an LSE C 18 Speedisk to the extraction manifold. Attach the funnel section on top of the filter holder. Inspect to ensure that the fittings are secure.

10.1.8 Close the manifold valve for each position. Add 10mL of ethyl acetate to each disk. Turn on the pump to about 5 inches Hg. Open the manifold valve and allow about half of the ethyl acetate to pass through the disk and then close the valve. There should be a layer of ethyl acetate on the surface of the disk. Allow the disk to soak for approximately two minutes. Repeat for all positions.

10.1.9 After approximately two minutes, open the manifold valve and allow most of the remaining ethyl acetate to pass through the disk to waste. A layer of solvent must be left on the

surface of the disk, which should not be allowed to go dry from this point until the end of the sample extraction. Note: This is a critical step for obtaining uniform flow and good recovery.

10.1.10 Repeat the steps in Sections 10.1.6 and Section 10.1.7 with the following:
10mL ethyl acetate
10mL methylene chloride
10mL methylene chloride
10mL methanol
10mL reagent water

10.1.11 Turn off the pump and dispose of solvents in a satellite waste container.

10.1.12 Working with each position, pour the water sample into the reservoir and apply vacuum (i.e., open the manifold valve and set pump to about 25 inches Hg) to begin the extraction. Invert the sample container and place on top of the funnel reservoir. The vacuum will draw sample from the container. Particulate-free water may pass through the disk in as little as five minutes without reducing analyte recoveries.

Note: It has been noted that a maximum flow of 50mL/min is needed to achieve acceptable recoveries.

Extract the entire sample, draining as much water from the sample container as possible. After all of the sample has passed through the disk, dry the disk by maintaining the vacuum for approximately 5 minutes (no longer than 8 minutes).

While the disk is drying, add 5mL of ethyl acetate to each container and rinse the inside walls thoroughly with the solvent.

10.1.13 Turn off the pump and close the manifold valve on each position. Place a VOA vial in each Teflon collection tube and attach them to the extraction manifold under the disk holder.

10.1.14 Adjust the pump pressure to about 5 inches Hg.

10.1.15 Invert the sample container with the ethyl acetate added and allow the container to rest on the disk apparatus. Allow to soak for approximately 2 minutes.

Note: From this point forward, the solvents, which contain the target analytes, will be collected in the VOA vial.

While the disk is soaking, add 5mL of methylene chloride to the sample container and rinse the inside walls of the container with the solvent.

10.1.16 Remove the container and draw the remaining ethyl acetate through the disk and collect in the VOA vial.

10.1.17 Invert the sample container with the methylene chloride added and allow the container to rest on the disk apparatus. Allow to soak for approximately 2 minutes.

10.1.19 Remove the container and draw the remaining methylene chloride through the disk and collect in the VOA vial.

10.1.20 Close the manifold valve. Using a disposable glass pipette, rinse the side walls of the funnel reservoir with two 3mL portions of 1:1 ethyl acetate/methylene chloride. Allow 1:1 ethyl acetate/methylene chloride to soak for approximately 2 minutes. Open the manifold valve and slowly collect the solvent in the collection vial. When there is no visible solvent on the disk, open the manifold valve completely to ensure that all of the solvent has been collected. Cap the vial and store in the refrigerator if extract concentration will not be performed immediately.

10.1.21 Prepare a drying column (Section 6.2) for each extract. Rinse the drying column with methylene chloride.

10.1.22 Add approximately 5g purified sodium sulfate to sample extracts in VOA vials. Shake vials vigorously for 30 seconds, then pour the extract through the drying column and collect in a Zymark tube. Rinse the vial with 10mLs of 1:1 ethyl acetate/methylene chloride and add the solvent to the top of the drying column. Repeat with an additional 5mL 1:1 ethyl acetate/methylene chloride.

10.1.23 Concentrate the extract in the Zymark apparatus according to the following procedure:

10.1.23.1 Ensure the incoming gas supply is turned on. The inlet pressure to the instrument must be at least 30psi. Confirm the water level in the water bath is at least as high as the initial solvent level in the sample tube.

10.1.23.2 Turn the unit on and select the TEMPERATURE display. Set to 45°C. Allow time for the water bath to come to temperature. (The temperature display stops blinking.) Place the concentrator tube (with sample) in the water bath and close the cover.

10.1.23.3 Begin adjusting the gas pressure as needed. The recommended pressure is 3psi.

- High pressure causes faster evaporation
- Excessively high pressure can cause loss of analyte. Do NOT operate over recommended psi.

10.1.23.4 The gas vortex shearing action automatically rinses the vertical side walls as evaporation occurs, but for optimum recoveries, the lower, angled portion of the concentrator tube should be rinsed with methylene chloride to recover any sample left behind.

10.1.23.5 When the concentration is completed, the button blinks and the beeper sounds briefly to alert that the sample has completed the concentration process. Promptly remove the concentrator tube from the bath, and, using a glass pipette, transfer concentrated sample extract to a labeled autosampler vial.

10.1.24 For samples that will be analyzed for routine EPA 525.2, the instrumental analyst will add 10uL of the recovery standard to the extract. For samples that will be analyzed by Low-level EPA 525.2, the instrumental analyst will add 2.0uL of the recovery standard to the extract.

10.1 QC Sample Preparation

Add 1.0L of reagent water to each of four 1L amber bottles. Label one as method blank (MB) and the others as LCS, LCSD (if needed), and LLCS.

Note: Do not add sodium sulfite or use a container that already has sodium sulfite in it to prepare the MB, LCS, LCSD, or LLCS. Sodium sulfite will interfere with the recoveries of several of the PAH target compounds. Refer to Section 16.0, Method Modifications, for more details.

Add 4mL of 6N HCl to the MB and to each LCS. Mix by inverting the containers three times and verify that the pH<=2 with narrow range pH paper. Add additional 6N HCl in 0.5mL increments if pH >2, mixing between additions, until pH<=2.

- Routine EPA 525.2
  For quality control samples for the routine EPA 525.2 method, add 100uL of the 525 Intermediate Calibration Solution (at 50ug/mL) to the LCS and any samples selected as matrix spikes. Mix by inverting the sample at least three times. For the LLCS, add 100uL of the LLCS spiking solution.

- Low-Level EPA 525.2
  For quality control samples to be run using the Low-Level EPA 525.2, add 20uL of the 525 Intermediate Calibration Solution to the LCS and any samples selected as matrix spikes. Mix by inverting the sample at least three times. For the LLCS, add 20uL of the LLCS spiking solution.

Prepare quality control samples using the procedures outlined in Section 10.1.

10.2 Analysis

10.3.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

10.3.1.1 Routine EPA 525.2

Column: Agilent HP-5MS, 0.25mm x 30m x 0.25um

Pulsed Splitless
Injector temperature: 250°C
Injection Volume: 1uL
Pulse Pressure: 25psi — Pulse Time: 0.50 minutes
Purge Flow: 50mL/min — Purge Time: 0.48 minutes

Helium carrier gas flow rate: 0.9mL/min (constant flow)
Following will change as column length changes in method:
Inlet Pressure: 8.09psi (this will change as column degrades and is clipped)
Total Flow: 53.9mL/min Gas Saver: ON
Save Flow: 20mL/min Saver Time: 4 minutes

Target Compounds Temperature Program
Initial Temperature: 80°C for 0.50minutes
Ramp1: 70°C/min to 160°C
Ramp2: 12°C/min to 280°C
Ramp3: 5°C/min to 311°C hold until last target compound elutes.

DFTPP/Column Check Temperature Program
Initial Temperature: 100°C for 0.50minutes
Ramp1: 30°C/min to 250°C
Ramp2: 12°C/min to 280°C
Ramp3: 5°C/min to 311°C

MS Settings:
Mass range: 45-450amu
Solvent Delay: 2.5 Minutes (this will change as the column degrades and is clipped)
Threshold: 150 Sample #: 1 A/D Samples: 2
MS Quad Temperature: 150°C MS Source Temperature: 230°C
EM Absolute: RELATIVE
Tune File: MSRTUNE.U

10.3.1.2 Low-Level EPA 525.2

Column: Agilent HP-5MS, 0.25mm x 30m x 0.25um

Target Compounds Temperature Program (Method name is 525AZ.M)
Initial Temperature: 80°C for 0.50minutes
Ramp1: 40°C/min to 160°C
Ramp2: 20°C/min to 280°C
Ramp3: 5°C/min to 310°C hold for 5.25 minutes
Pulsed splitless
Pulse Pressure: 25psi Pulse Time: 0.75 minutes
Purge Flow: 50mL/min Purge Time: 0.75 minutes
Helium carrier gas flow rate: 0.9mL/min (constant flow)
Injector temperature: 250°C
Injection Volume: 2uL

Following conditions will change as column length changes:
Inlet Pressure: 6.81psi
Total Flow: 54.4mL/min Gas Saver: OFF

MS Settings for method 525AZ.M

Tune file: 525AZ.U
Mass range: 45-450amu
Solvent Delay: 2.5 Minutes (this will change as the column degrades and is clipped)

Threshold: 50 Sample #: 3 A/D Samples: 8
MS Quad Temperature: 150°C MS Source Temperature: 230°C
EM Absolute: RELATIVE
(EM voltage set at AUTOTUNE + 200)

10.3.1.3 Retuning

If retuning of instrument is needed for analysis, run standard spectra autotune and store the parameters in the MSRTUNE.U file used in the acquisition of DFTPP and the EPA 525.2 analytes. The tune file MSRTUNE.U file must be used in the Chemstation methods used for the analysis of the DFTPP and the standards or samples.

The multiplier EM voltage should be set to the value acquired at tuning plus 200. This is achieved by setting voltage at "relative" in the MS parameters. This will usually give sufficient sensitivity to detect the target analytes at the required levels.

10.3.2 Recovery Standard

Prior to analysis the recovery standard must be added to all samples, QC items, and standards. The concentration of the recovery standard must be the same in all calibration samples, field samples, and QC samples. A concentration of 5.0ug/mL is used for the Routine EPA 525.2 and 1.0ug/mL is used for the Low-Level EPA 525.2.

10.3.3 Initial and Continuing Calibration

Analyze the GC/MS Performance Check standard prior to each ICAL and CCV. The criteria in Attachment 6 must be met before proceeding to the next step.

Calibrate the instrument using the standards and criteria described given in Section 9.2.2. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.3, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.5.

10.3.4 Sample Analysis

Remove the extracts from the refrigerator and allow them to come to room temperature.

The sample extract must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The term "clock time" defines the GC/MS tune frequency. The clock time is defined as 12 hours from the injection of the DFTPP. The analysis of samples and batch QC items may continue until the clock time expires. A new DFTPP and CCV (i.e., a new clock) is required to proceed with the analysis of more samples and/or batch QC items.

10.3.5 Example Analytical Sequence

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
DFTPP	12-hour clock starts with injection of the DFTPP
Initial calibration	
ICV	Second Source
Instrument Blank	
Samples and QC Items	Analyze until 12-hour clock expires; last injection must occur before 12 hours from DFTPP injection
DFTPP	12-hour clock starts with injection of the DFTPP
CCV	Level 5
Instrument Blank	
Samples and QC Items	Analyze until 12-hour clock expires; last injection must occur before 12 hours from DFTPP injection

Analytical Sequence for samples not immediately following an initial calibration:

Description	Comments
DFTPP	12-hour clock starts with injection of the DFTPP
CCV	Level 5
Instrument Blank	
Samples and QC Items	Analyze until 12-hour clock expires; last injection must occur before 12 hours from DFTPP injection
DFTPP	12-hour clock starts with injection of the DFTPP
CCV	Level 5
Instrument Blank	
Samples and QC Items	Analyze until 12-hour clock expires; last injection must occur before 12 hours from DFTPP injection

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data evaluation must be performed in accordance with SA-QA-08: *Evaluation of Chromatographic Data.* This SOP includes specific information regarding the evaluation of chromatographic data, including the requirements for performing manual integrations and the evaluation of retention times.

Data review and reporting must be performed in accordance with SA-QA-02: *Data Generation and Review.*

11.1.1 Target Analyte Identification

Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created database. The GC retention time of the sample component should be within five seconds of the retention time observed for that same compound in the most recently analyzed continuing calibration check standard.

In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Sufficient resolution is typically achieved if the height of the valley between the two isomer peaks is less than 25% of the average height of the two peak heights. If sufficient resolution can not be achieved (i.e., the instrument software cannot integrate distinct peaks), generate an NCM to denote the situation.

Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation

11.1.2 Evaluation of Tentatively Identified Compounds (TICs)

Refer to Attachment 8 for information on evaluation of TICs.

11.1.3 Dilutions

Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half of the calibration range.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower reporting limits.

Dilute samples according to the following table:

Dilution Factor	Extract Aliquot (uL)	ISTD Aliquot (uL)	Recovery Standard Aliquot (uL)	Final Volume* (mL)
2	500	5	5	1.0
5	200	8	8	1.0
10	100	9	9	1.0
20	50	9.5	9.5	1.0
50	20	10	10	1.0
100	10	10	10	1.0

*Final solvent = ethyl acetate

11.1.3.1 Surrogate Dilution Threshold Factor

Surrogates may be diluted out if the concentration of target compounds is high or the presence of non-target compounds interferes with the quantification of the target compounds. The Surrogate Dilution Threshold Factor associated with this procedure is equivalent to a dilution factor of 0; therefore, undetect surrogates in the sample when the dilution factor is 10 or greater. As such, recoveries must be reported as "0D", and control limits will not apply.

An NCM must be initiated to denote this situation.

11.1.3.2 Dilutions and MS/MSD Recoveries

Matrix spike recoveries are not reported for dilutions of 10 or greater. An NCM is generated for instances where the dilution prohibits evaluation of the MS/MSD recoveries.

In instances where the unspiked sample concentration is more than four times the concentration of the target compound spiked into the MS and MSD, the results are qualified with "4" or other suitable flag. An NCM must be initiated to denote this situation.

11.1.4 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes to determine if historical data is available for review.

11.1.5 Drinking Water Compliance Evaluation

Public water suppliers (PWS) are governed by EPA-specified Maximum Contaminant Levels (MCL) above which indicates noncompliance. Many analytes also have a Maximum Contaminant Level Goal (MCLG), which is often lower than the MCL. The MCLs and MCLGs associated with this procedure are given in Attachment 7. Notify the PM immediately via a Nonconformance Memo if any sample contains a detection above the MCL.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample on the instrument
F = Final volume/weight
I = Initial volume/weight
D = Dilution Factor

Note: This calculation assumes all applicable unit correction factors are applied.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and and verified quarterly in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

Note: The reference method recommends analyzing MDLs over 3-4 days to add more variability into the value.

12.2 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS, MS) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house nor laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends.

Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17.

12.3 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4-7 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP QA06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.4 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 13 of the

TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.
- Flammable waste – Transfer to a satellite container designated for flammable waste and transfer to waste disposal department when the container is full.
- Chlorinated waste – Transfer to a chlorinated waste container for storage / disposal.
- Sample extracts – Transfer autosampler vials to a storage container. When full, transfer container to the waste disposal department for crushing, and disposal of the liquid as flammable waste.

15.0 References / Cross-References

- SOP SA-AN-041: *Reagent and Standard Materials Traceability*
- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-08: *Evaluation of Chromatographic Data*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- EPA Method 525.2: Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry; Revision 2.0, 1995; J.W. Eichelberger, T.D. Behymer, W.L. Budde -- Method 525, Revision 1.0, 2.0, 2.1 (1988), J.W. Eichelberger, T.D. Behymer, and W.L. Budde -- Method 525.1, Revision 2.2 (July 1991), J.W. Eichelberger, J.W. Munch, and J.A. Shoemaker Method 525.2 -- Revision 1.0 (February, 1994).
- EPA Manual for the Certification of Laboratories Analyzing Drinking Water, 5th edition

16.0 Method Modifications and Clarifications

16.1 The reference method was written specifically for drinking water and source water samples; however, the laboratory may perform other types of water samples using this procedure.

16.2 EPA Method 525.2 recommends a field reagent blank (FRB), or trip blank, be processed with each sample collection event. The laboratory can perform this additional QC element upon client request; however, it is the laboratory's standard practice not to provide trip

blanks for non-volatile analytes. It should be noted that this procedure is used primarily for drinking water samples that should not contain the target analytes of interest.

16.3 EPA Method 525.2 acknowledges that due to the large number of compounds on the analyte list, it is possible for a few analytes of interest to be outside the continuing calibration criteria. The method allows for up to 10% of target analytes to be outside criteria. TestAmerica Savannah has placed a cap on the maximum %D or %Draft allowed such that analysis may proceed as long as no more than 10% of the analytes of interest are outside continuing calibration criteria *and* as long as the %D or %Drift is no more than 45% for each analyte.

16.4 There are several analytes contained in EPA Method 525.2 that the laboratory does not analyze for due to shortened holding times and/or different preservation and dechlorination techniques. Prior to bringing new analytes online, a careful review of the method must be performed to ensure holding times special requirements are met.

16.5 EPA Method 525.2 requires an initial demonstration of low disk or cartridge system background. The method blanks analyzed by the laboratory are used to satisfy this requirement.

16.6 EPA Method 525.2 requires a quality control sample (QCS) to be performed quarterly. The laboratory meets this requirement by analyzing a second source ICV with each initial calibration. If an initial calibration and ICV are not required at least once a quarter, a separate QCS must be analyzed. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

16.7 The laboratory has incorporated the minimum batch QC items as outlined in Section 9.1. There is no method-defined batch precision requirement for this method; however a matrix spike duplicate is routinely performed to satisfy common regulatory and/or client requests for precision data and/or to facilitate scheduling and data evaluation. Additionally, LCSD is routinely performed if insufficient sample volume is provided for batch MS/MSD.

16.8 As indicated in the EPA 525.2 reference method, bis(2-ethylhexyl)phthalate is a common laboratory contaminant and generally cannot be accurately measured below 2.0ug/L. Due to the low EPA-specified reporting limits for this analyte and the level of background contamination routinely found in laboratory blanks, the LCS recovery limit for this analyte has been broadened from 70-130% to 70-160% for the low-level EPA 525.2 method.

16.9 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each EPA 525.2 batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory defaults to 50-150%.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table

Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Quantitation Ions and Internal Standard References
Attachment 6: GC/MS Performance Check Criteria
Attachment 7: EPA Regulated Drinking Water Analytes, Maximum Contaminant Levels (MCLs), and Maximum Contaminant Level Goals (MCGLs)
Attachment 8: Procedures for Evaluation of Tentatively Identified Compounds (TICs)

Attachment 1:
SOP Summary

Sample Preparation Summary

Analytes are extracted from a sample by passing 1L of sample through a disk containing a solid matrix with a chemically bonded C-18 organic phase. This process is referred to as liquid-solid extraction or LSE. The organic compounds are eluted from the LSE disk with small quantities of ethyl acetate followed by methylene chloride and a 1:1 mixture of ethyl acetate and methylene chloride. This extract is concentrated further by evaporation of some of the solvent.

Sample Analysis Summary

The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a gas chromatography/mass spectrometry (GC/MS) system. The laboratory uses EI (electron ionization) GC/MS system for sample analysis.

Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a database. Retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard the concentration of the internal standard and the average response factor of the analyte generated from the initial calibration. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

Analytical Sequence

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
DFTPP	12-hour clock starts with injection of the DFTPP
Initial calibration	
ICV	Second Source
Instrument Blank	
Samples and QC Items	Analyze until 12-hour clock expires; last injection must occur before 12 hours from DFTPP injection

Analytical Sequence for samples not immediately following an initial calibration:

Description	Comments
DFTPP	12-hour clock starts with injection of the DFTPP
CCV	Level 5
Instrument Blank	
Samples and QC Items	Analyze until 12-hour clock expires; last injection must occur before 12 hours from DFTPP injection
DFTPP	12-hour clock starts with injection of the DFTPP
CCV	Level 5
Instrument Blank	
Samples and QC Items	Analyze until 12-hour clock expires; last injection must occur before 12 hours from DFTPP injection

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Matrix	Routine Sample Container	Routine Sample Size	Minimum Sample Size	Chemical Preservation	Dechlorination Agent	Thermal Preservation	Holding Time
Water	1L amber glass	1L	1L	4mL 1:1 HCl	50mg sodium sulfite	0-6 °C	Preparation: 14 days from sampling Analysis: 30 days from preparation

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Clock Time	12 hours	Clock time starts with the injection of the DFTPP. Analysis of samples and QC items must conclude within expiration of clock time. Subsequent analysis requires new DFTPP.	Not applicable
Tune/Column Evaluation Standard (DFTPP)	At beginning of each clock	<u>Spectrum Criteria:</u> Refer to Attachment 6. <u>Breakdown Criteria:</u> 20%	- Perform instrument maintenance - Re-tune.
Initial Calibration (ICAL) - Minimum of 6 points	Upon instrument set-up, and after 2 consecutive unsuccessful CCVs or 3 consecutive CCVs in which the same analyte fails method criteria.	1. Mid-Level Standard Performance Criteria 2. %RSD < 30% 3. If %RSD > 30%, use curve fit w/ r^2>0.990.	Refer to SOP SA-QA-16
Second Source Initial Calibration Verification (ICV) - Also called QCS	After each ICAL (Quarterly, at a minimum)	1. Mid-Level Standard Performance Criteria 2. %D<30% for >90% of target analytes w/ no analyte >45%.	Refer to SOP SA-QA-16
Continuing Calibration Verification (CCV)	After DFTPP	1. Mid-Level Standard Performance Criteria 2. %D<30% for >90% of target analytes w/ no analyte >45%. 3. The same analyte must not fail in 3 consecutive analyses.	Refer to SOP SA-QA-16

QC Item	Frequency	Criteria	Corrective Action
Mid-Level Standard Performance Criteria	Each ICAL, ICV, and CCV	GC Performance: 1. Baseline separation of anthracene and phenanthrene 2. Valley between benz(a)anthracene and chrysene less than 25% of the average heights of the two compounds MS Sensitivity: 1. Data system must detect and correctly identify 99% of all analytes	-Reanalyze standard -Prepare new standard and reanalyze -Perform instrument maintenance and reanalyze - Perform instrument maintenance and recalibrate - Install new column if resolution criterion cannot be readily met.
Internal Standards (ISTD)	Spiked in all standards, samples, and batch QC items	CCV: Area ± 50% of ICAL Samples & batch QC items: >70% Rec	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available and if samples are still in holding time. If samples are out of holding time, contact PM to determine how to proceed.
Surrogate Compounds	Spiked (during extraction procedure) in all samples and batch QC items. (Also included in all instrument QC items.)	70-130% - Surrogate Threshold Dilution Factor = 10	Refer to SOP SA-QA-17
Extraction Batch Definition	Extracted together w/in 12-hr timeframe; not to exceed 20 field samples	Not Applicable	Not Applicable

QC Item	Frequency	Criteria	Corrective Action
Method Blank (MB)	One per batch	<1/2RL	Refer to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per batch	70-130% R <30% RPD	Refer to SOP SA-QA-17; If affected analyte is not regulated, issue may be addressed with NCM.
Laboratory Control Sample Duplicate (LCSD)	One per batch, when insufficient sample provided for MS/MSD	70-130% R <30% RPD	Refer to SOP SA-QA-17; If affected analyte is not regulated, issue may be addressed with NCM.
Low-Level Laboratory Control Sample (LLCS)	One per batch	50-150% Rec, regulated analytes.	Refer to SOP SA-QA-17
Matrix Spike (MS)	One per batch	70-130% Rec, regulated analytes. <30% RPD	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per batch	70-130% Rec, regulated analytes. <30% RPD	Refer to SOP SA-QA-17
Initial Demonstration of Capability (IDOC)	Initially; Per analyst / matrix / method / analyte combination	MLG Limits	Refer to SOP SA-QA-06 (Unsupervised work may not begin until successful IDOC is obtained.)
Continuing Demonstration of Capability (CDOC)	Annually; Per analyst / matrix / method / analyte combination	MLG Limits	Refer to SOP SA-QA-06
Method Detection Limit Study (MDL)	Upon method/instrument set-up	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
MDL Verification (MDLV)	Upon method/instrument set-up, and then quarterly thereafter	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Reporting Limit Verification (RLV)	Upon analyte set-up, per analyte/method/matrix combination, and then annually thereafter (for non-routine analytes where	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

QC Item	Frequency	Criteria	Corrective Action
	MDL Study is not performed)		

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:
- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance, if non-routine.
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
Refer to the instrument manufacturer's guides for trouble-shooting items.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Septum							X	Replace, recommended daily
Splitless Disc							X	Replace, recommended daily
Column/Injector							X	Change sleeve and cut front of column, recommended daily
Autosampler							X	Clean syringe as needed; replace syringe as needed
Injector Port							X	Replace injector port as needed
Lines							X	Flush lines as needed; replace lines as needed
Column							X	Change column as needed
Mass Spectrometer							X	Clean as needed
Rough Pump							X	Change oil and replace carbon trap as needed

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually; AN = as needed

Zymark Maintenance Schedule:
It is recommended to change the water in the water bath weekly. Add 1-2 drops of Clear Bath to prevent bacteria and algae growth. Methylene chloride that dissolves in the water bath will damage the sensors.

The Zymark sensor diagnostic test must be performed weekly. If the sensors do not meet criteria the sensor may need replacing. Refer to the manufacturer's manual for replacement procedures if necessary.

Contingency Plan

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs, consisting of MS source parts, filaments, GC lines and injection ports, and other common instrumentation components.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
Quantitation Ions and Internal Standard References

Analytes	CAS #	Quant Ion	Quant Ion	Internal Standard
Recovery Standard				
Terphenyl-d14	1718-51-0	244		N/A
Terphenyl-d14 is used to quantify the internal standards, which are added to the samples prior to extraction.				
Internal Standards				
Acenaphthene-d10	15067-26-2	164		1
Chrysene-d12	1719-03-5	240		2
Phenanthrene-d10	1517-22-2	188		3
Surrogates				
2-Nitro-m-xylene	81-20-9	134		1
Perylene-d12	1520-96-3	264		3
Triphenylphosphate	115-86-6	326	325	3
Target Analytes				
2,4-Dinitrotoluene	121-14-2	165		1
2,6-Dinitrotoluene	606-20-2	165		1
2-Methylnaphthalene	91-57-6	142		1
4,4'-DDD	72-54-8	235	165	3
4,4'-DDE	72-55-9	318		3
4,4'-DDT	50-29-3	235	165	3
Acenaphthene	83-32-9	153		1
Acenaphthylene	208-96-8	152		1
Acetochlor	34256-82-1	223		2
Alachlor	15972-60-8	160		2
Aldrin	309-00-2	66		2
alpha-BHC	319-84-6	181		2
alpha-Chlordane	5103-71-9	375	373	3
Anthracene	120-12-7	178		2
Atrazine	1912-24-9	200	215	2
Benzo[a]anthracene	56-55-3	228		3
Benzo[a]pyrene	50-32-8	252		3
Benzo[b]fluoranthene	205-99-2	252		3
Benzo[g,h,i]perylene	191-24-2	276		3
Benzo[k]fluoranthene	207-08-9	252		3
beta-BHC	319-85-7	181		2
Bis(2-ethylhexyl) phthalate	117-81-7	149		3
Bromacil	314-40-9	205		2
Butachlor	23184-66-9	176	160	3
Butyl benzyl phthalate	85-68-7	149		3

Analytes	CAS #	Quant Ion	Quant Ion	Internal Standard
Butylate	2008-41-5	156	146	1
Chlorobenzilate	510-15-6	139		3
Chloroneb	2675-77-6	191		1
Chlorothalonil	1897-45-6	266		2
Chlorpropham	101-21-3	127		1
Chlorpyrifos	2921-88-2	197	199	2
Chrysene	218-01-9	228		3
cis-Permethrin	54774-45-7	183		3
Cycloate	1134-23-2	83	154	1
DCPA	1861-32-1	301		2
delta-BHC	319-86-8	181		2
Di(2-ethylhexyl)adipate	103-23-1	129		3
Dibenz(a,h)anthracene	53-70-3	278		3
Dichlorvos	62-73-7	109		1
Dieldrin	60-57-1	79		3
Diethyl phthalate	84-66-2	149		1
Dimethyl phthalate	131-11-3	163		1
Di-n-butyl phthalate	84-74-2	149		2
Diphenamid	957-51-7	72	167	2
Endosulfan I	959-98-8	204		3
Endosulfan II	33213-65-9	195		3
Endosulfan sulfate	1031-07-8	272		3
Endrin	72-20-8	263	265	3
Endrin aldehyde	7421-93-4	345		3
EPTC	759-94-4	128		1
Ethoprop	13194-48-4	158		1
Etridiazole	2593-15-9	211	213	1
Fenamiphos	22224-92-6	303	154	2
Fenarimol	60168-88-9	139		3
Fluoranthene	206-44-0	202		1
Fluorene	86-73-7	166		1
Fluridone	59756-60-4	328		3
gamma-BHC (Lindane)	58-89-9	181		2
gamma-Chlordane	5103-74-2	375		2
Heptachlor	76-44-8	100		2
Heptachlor epoxide	1024-57-3	81		2
Hexachlorobenzene	118-74-1	284		2
Hexachlorocyclopentadiene	77-47-4	237		1
Hexazinone	51235-04-2	171		3
Indeno[1,2,3-cd]pyrene	193-39-5	276		3
Isophorone	78-59-1	82		1

Analytes	CAS #	Quant Ion	Quant Ion	Internal Standard
Methoxychlor	72-43-5	227		3
Methyl paraoxon	950-35-6	109		2
Metolachlor	51218-45-2	162		2
Metribuzin	21087-64-9	198		2
Mevinphos	7786-34-7	127		1
MGK 264 - isomer a	113-48-4	164	66	2
MGK 264 - isomer b	113-48-4	164	66	2
Molinate	2212-67-1	126		1
Naphthalene	91-20-3	128		1
Napropamide	15299-99-7	72		3
Norflurazon	27314-13-2	145		3
PCB 1 (2-Chlorobiphenyl)	2051-60-7	188		1
PCB 154 2,2',4,4',5,6'-hexachlorobiphenyl	60145-22-4	360		3
PCB 171 2,2',3,3',4,4',6-heptachlorobiphenyl	52663-71-5	394	396	2
PCB 201 2,2',3,3',4,6-octachlorobiphenyl	40186-71-8	430	385	3
PCB 29 2,4,5-trichlorobiphenyl	15862-07-4	256		2
PCB 47 2,2',4,4'-tetrachlorobiphenyl	2437-79-8	292		2
PCB 5 2,3-dichlorobiphenyl	16605-91-7	222	224	2
PCB 98 2,2',3',4,6-pentachlorobiphenyl	60233-25-2	326		2
Pebulate	1114-71-2	72		1
Phenanthrene	85-01-8	178		2
Pronamide	23950-58-5	173		2
Propachlor	1918-16-7	120		1
Propazine	139-40-2	214	172	2
Pyrene	129-00-0	202		2
Simazine	122-34-9	201	186	2
Terbacil	5902-51-2	161		2
Tetrachlorvinphos (Stirophos)	961-11-5	109		2
trans-Nonachlor	39765-80-5	409		3
trans-Permethrin	51877-74-8	183		3
Triadimefon	43121-43-3	57		2
Tricyclazole	41814-78-2	189		3
Trifluralin	1582-09-8	306		2
Vernolate	1929-77-7	128		1

Attachment 6:
GC/MS Performance Check Criteria

(m/z)	Relative Abundance	Purpose of Checkpoint 1
51	10-80% of the base peak	low mass sensitivity
68	<2% of mass 69	low mass resolution
70	<2% of mass 69	low mass resolution
127	10-80% of the base peak	low-mid mass sensitivity
197	<2% of mass 198	mid-mass resolution
198	Base peak or >50% of 442	mid-mass resolution and sensitivity
199	5-9% of mass 198	mid-mass resolution and isotope ratio
275	10-60% of the base peak	mid-high mass sensitivity
365	>1% of the base peak	baseline threshold
441	Present and < mass 443	high mass resolution
442	Base peak or >50% of 198	high mass resolution and sensitivity
443	15-24% of mass 442	high mass resolution and isotope ratio

All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. The correct setting of the baseline threshold, as indicated by the presence of low intensity ions, is the next most important part of the performance test. Finally, the ion abundance ranges are designed to encourage some standardization to fragmentation patterns.

Locate any degradation products of endrin (endrin ketone and endrin aldehyde) and 4,4'-DDT (4,4'-DDE and 4,4'-DDD) at their appropriate retention times and quantitation ions (see Attachment 5). Endrin ketone can be located at approximately 1.1 to 1.2 times the endrin retention time with prominent m/z 67 and 317 ions in the mass spectrum.

Calculate percent breakdown using peak areas based on total ion current as follows:

$$\% \text{ 4,4'-DDT breakdown} = \frac{\text{Area of DDD + DDE}}{\text{Area of DDD + DDE + DDT}} \times 100$$

$$\% \text{ Endrin breakdown} = \frac{\text{Area of EA + EK}}{\text{Area of EA + EK + Endrin}} \times 100$$

If degradation of either endrin or DDT exceeds 20%, maintenance is required on the GC injection port and possibly other areas of the system before proceeding with analysis of standards or samples.

Attachment 7:
EPA Regulated Drinking Water Analytes, Maximum Contaminant Levels (MCLs), and Maximum Contaminant Level Goals (MCLGs)

Analyte	MCLG (ug/L)	MCL (ug/L)	EPA RDL* (ug/L)
Alachlor	0	2.0	0.20
Atrazine	3.0	3.0	0.10
Benzo(a)pyrene	0	0.20	0.020
Bis(2-ethylhexyl)adipate	400	400	0.60
Bis(2-ethylhexyl)phthalate	0	6.0	0.60
Endrin	2.0	2.0	0.010
Heptachlor	0	0.40	0.040
Heptachlor epoxide	0	0.20	0.020
Hexachlorobenzene	0	1.0	0.10
Hexachlorocyclopentadiene	50	50	0.10
gamma-BHC (Lindane)	0.20	0.20	0.020
Methoxychlor	40	40	0.10
Simazine	4.0	4.0	0.070

*Required as Reporting Limit for EPA 525.2 Low-Level

Attachment 8:
Procedures for Evaluation of Tentatively Identified Compounds (TICs)

Tentatively identified peaks (TICs) are defined by TestAmerica Savannah as:
1) a calibrated analyte that is not part of the list of analytes requested by the client; or
2) a non-calibrated analyte with a response of 10% or greater than the closest internal standard (ISTD).

The laboratory's default procedure is to report the top 20 TICs with the highest concentration.

Note: Internal standards or surrogates added to the sample, whether they are included in the ICAL or not, must not be identified as TICs. For example, the surrogate o-Terphenyl is added to the low-level 8270 surrogate spiking mix but is used as a surrogate only for LL PAH. This compound would be excluded as a TIC. Also, for semi-volatile analyses, routine target volatile analytes included on the EPA CLP OLM04.2 list (e.g., xylenes) are not included as TICs.

Data Evaluation Steps:
Identification of TICs is made by comparison of the mass spectrum to the reference spectrum (peaks with calibration) or by comparison of the mass spectrum to a reference library such as NIST (peaks without a calibration). Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification.

The unknown compounds are tentatively identified using a search of the reference library. If the library search produces a match at or above 85%, report that compound. If the library search produces more than one compound at or above 85%, report the first compound (the highest match quality). If the library search produces no matches at or above 85%, report the compound as unknown. If possible, provide a general classification of the unknown – for example, unknown aromatic, unknown hydrocarbon, etc.

TICs should be evaluated within the retention time range from the first eluting target or surrogate (whichever is first in the target list) to the elution of the last target compound.

Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum. The relative intensities of the major ions should agree within approximately ±20%.

Molecular ions present in the reference spectrum should be present in the sample spectrum. Note, however, that differences in the spectra may be attributed to over-lapping or co-eluting peaks. If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria are not met exactly, the peak may be considered tentatively identified. The analyst should consult the Department Manager if there are any questions concerning interpretation of spectra.

The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The concentration of TICs with a calibration is the concentration from the calibration curve at the dilution that the target list is reported, even if

the concentration is above the calibration range (an "E" value). The concentration of the non-calibrated TIC is as directed in the SOP and as calculated in the Target data system.

Data Processing Steps:

- Evaluate the peaks in the total ion chromatogram for:
  - correct integration
  - peaks that may not have been integrated, paying particular attention to large or odd-shaped peaks.
  - closely eluting peaks
- Manually integrate any peaks that were not detected by the data system and re-process the unknowns.
- Evaluate TICs in Target, as outlined above.
- Merge to TALS.
- Under the TIC tab, reject all "TGT" and "TIC" analytes.
- Right-click and select "Auto-Set TICs Primary". This should set the number of TICs and TGTs requested with the highest concentration to a "Primary" status.
- Highlight all TGT compounds (still under the TIC tab) and right-click.
- Choose "Result Conditions".
- Right-click and choose "Show Assigned Conditions".
- Uncheck all assigned conditions.
- Right-click and choose "Show Flag Suite Conditions".
- Select J, N, and T. Be sure to choose the J-flag defined as "Estimated Result TIC – Manual Flag".

Revision History

Summary of Changes from Previous Revision:

- Updated to new TestAmerica SOP template. Significant formatting and content changes made. Boilerplate text added. Minor editorial and/or grammatical changes made. Performed review of SOP versus method versus actual laboratory procedure and made changes and/or incorporated Method Modifications and Clarifications, as applicable.
    - Updated Instrument Parameters to reflect current practice.
    - Updated Equipment and Supplies to reflect current items/practice.
    - Updated Standard and Reagent information to reflect current practice.
    - Updated sample preparation procedures to reflect current practice.
- Revised title of SOP to include reference to "Drinking Water".
- Clarified procedures for removal of residual chlorine using sodium sulfite, to occur prior to pH adjustment. Section 8.1.1.3
- Changed regression curve criterion from 0.99 to 0.990.
- Revised CCV and ICV criteria to include the requirement for no single analyte to be greater than 45% and no single analyte can fail in 3 consecutive analyses.
- Clarified language regarding anthracene and phenanthrene separation. Previous language stated "must". New language states "should" and allows for analyst judgment with supervisor/TM approval when these criteria are not met. Section 9.2.
- Added ISTD criteria for CCV such that areas must be within 50% of the corresponding ICAL level. Clarified exception such that all analytes in CCV are evaluated, rather than only the "analytes of interest". Revised corrective actions (maintenance actions) to be taken should CCV not meet acceptance criteria. Section 9.2.5
- Removed requirement for CCV ISTD to be within +/-30% of the previous CCV. Section 9.2.8
- Revised batch QC frequency to incorporate MS/MSD. Included information for determination of insufficient volume for MS/MSD and the requirement to perform LCS/LCSD (and initiate NCM) should this occur.
- Removed requirement to preserve method blank and LCS samples with sodium sulfite.
- Added allowance to perform corrective action for regulated analytes only, in LCS/LCSD and MS/MSD.
- Added requirement to perform Low-Level LCS per the EPA Manual for the Certification of Drinking Water Laboratories.
- Revised extraction soak times to be approximately 2 minutes each. Section 10
- Added note that a layer of solvent must be left on the surface of the disk which is critical for achieving uniform flow and obtaining good recovery. Section 10.1.7
- Revised solvents used to repeat Steps 10.1.6 and 10.1.7. section 10.3.8
- Revised recommended pressure to 3psi. Section 10.1.23.3
- Included information on addition 5g sodium sulfate to sample extract vials. Section 10.3.8
- Updated MCL Table to include RDLs for EPA 508 compounds (i.e., endrin, g-BHC, heptachlor, heptachlor epoxide, and methoxychlor). Attachment 7
- Added Attachment 8 which includes new TIC reporting procedures.
- Added requirement to initiate NCM if adequate resolution is not achieved for structural isomers. Section 11.1.1
- Clarified type of reagent water used (purchased form JT Baker). Section 7.2.1

- Revised preservation and chlorine check procedures to clarify that pH may only be adjusted after the absence of residual chlorine is confirmed (i.e., additional sodium sulfite may not be added to samples with pH <2. Section 8.1.1
- Revised ICAL concentration levels associated with the EPA 525.2 Low-Level curve. Section 9.2.2
- Removed reference to Autotune procedures. Section 10.1.3.1.3
- Added note to Attachment 3 that re-calibration is required after 2 consecutive unsuccessful CCVs or 3 consecutive CCVs in which the same analyte fails method criteria.
- Revised corrective actions such that PM is contacted for instruction on how to proceed if internal standard exceeds criteria and sample holding time is expired. Attachment 3
- Removed reference to filter holders (attached to LSE C Speedisk). Section 10.1.7
- Corrected routine bottle types to correspond to current practice. Section 6.3, Section 8.1, and Attachment 2

VOLATILE COMPOUNDS IN DRINKING WATER BY GC/MS

(Methods: EPA 524.2)

Approvals (Signature/Date):

Andrea Teal May 10, 2011
Andrea Teal Date
Quality Assurance Manager

April 8, 2011
Benjamin Gulizia Date
Laboratory Director/Lead Technical Director

May 6, 2011
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Technical Director / EH&S Coordinator

Facility Distribution No. 1 **Distributed To:** QA Navigator

1.0 Scope and Application

This SOP gives the procedures for the determination of volatile organic compounds in water samples by gas chromatography/mass spectrometry (GC/MS).

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

Volatile organic compounds (VOC) are purged from the sample matrix with helium. The VOC are transferred from the sample matrix to the vapor phase. The vapor is swept through a sorbent tube where the VOC are trapped. After the purging is completed, the trap is heated and backflushed with helium to desorb the VOCs onto a GC column. The GC is temperature-programmed to separate the VOC, which are then detected by a mass spectrometer. Qualitative identification of the target compounds in the sample is based on the relative retention time and the mass spectra of the characteristic masses (ions) determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

This SOP is based on the following methods: EPA 524.2.

3.0 Definitions

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

THM (Trihalomethanes) - The four THM are chloroform, dichlorobromomethane, dibromochloromethane, and bromoform.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Methanol must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require dilution prior to analysis to reduce or eliminate the interferences.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 VOC commonly used in the laboratory may be a major source of contamination. Hexane, methylene chloride, acetone, freon, 2-butanone (MEK), toluene, and isopropanol are all common laboratory solvents and tend to cause the most interference. The analyses of highly concentrated samples (>1ppm) may also affect the succeeding runs. "Carryover" can occur when low concentration samples are analyzed after high level samples. Reagent blanks must be analyzed periodically to check for laboratory contamination and carryover. The VOC laboratory must be kept as free from contaminants as possible.

4.2.4 Samples containing chlorine must be treated with ascorbic acid. If excess chlorine is not destroyed, the concentration of some compounds formed when water is chlorinated (for example, trihalomethanes) may not reflect the analyte concentration at the time of sampling. Samples for trihalomethanes are dechlorinated using sodium thiosulfate.

4.2.5 Samples must be acidified, except samples where only trihalomethanes are requested, at the time of collection (after dechlorination) to prevent biological degradation of some VOC. The addition of acid also minimizes dehydrohalogenation of some chlorinated alkanes.

4.2.6 THM formation potential water samples should be relatively clean, as they are potential sources of potable water. Avoid exposure of the samples to volatile halocarbons, particularly chloroform, which may contaminate the samples.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves (or equivalent), and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

Methanol is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, confusion, headache, dizziness, and drowsiness.

The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

Hydrochloric acid is extremely hazardous as an oxidizer, a corrosive, a poison, and is reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage. Concentrated acids should be used in a fully functional fume hood.

Sodium hydroxide is a severe corrosive. Contact with the skin can cause irritation or severe burns and scarring. Contact with the eyes can cause irritation, burns, permanent vision impairment or even blindness.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

Note: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Methanol	Flammable Poison Irritant	200ppm TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Hydrochloric Acid	Corrosive Poison	5ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Hydroxide	Corrosive	2mg/m^3 Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Hypochlorite (Bleach)	Irritant	0.5ppm TWA 1.0ppm STEL	Harmful if swallowed or inhaled. Causes irritation to eyes and respiratory tract. Can cause substantial eye injury.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
Note: Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Analytical Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Agilent (HP) 5973 Mass spectrometer equipped with a capillary direct interface.

Agilent (HP) 6890 Gas chromatograph with spilt/splitless injector. The exit vent must have a carbon trap in-line to collect the volatile compounds that are vented during the transfer from the purge and trap device. The carbon traps should be changed a minimum of every three months.

Restek RTX-624 Column: 20m x 0.18mm ID, 1.0um film thickness, or equivalent.

EST Encon purge and trap concentrator with 5mL sparge vessel, or equivalent.

EST Centurion Autosampler, or equivalent.

Supelco Vocarb 3000 trap or equivalent. Other traps may be used as long as the target compounds can be detected at the required quantitation limit and the IDOC requirements (Section 12.2 and 12.3) are met.

6.2 Analytical Data System / Software / Hardware

Chemstation software is used on a Windows-based PC to schedule and acquire data. Target (UNIX and/or Windows) software is used on a Windows-based PC to store, reduce/evaluate, and output the data to the laboratory's LIMS system (i.e., TALS). Target software has the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectrum from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software also allows integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as or construction of a linear regression calibration curve, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the response factors.

6.3 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Transfer Pipettes – various sizes

Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

pH paper

Residual Chlorine Check Strips – starch iodide strips; provide a quick and easy way to verify if the sample was dechlorinated properly. Store in original, capped container and use within the manufacturer's expiration date.

Medicine cups – 30mL, disposable

Detergent – Liquinox used for washing non-disposable labware.

Mini-nert vials – used for standard storage (various sizes)

6.4 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:
40mL VOA vials – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

Unless listed elsewhere in this SOP, the expiration dates given below apply.

7.1.1 The expiration date for unopened standards and reagents is the manufacturer's expiration date.

7.1.2 The expiration date for opened stock reagents is the manufacturer's expiration date or 5 years from the date opened, whichever is sooner.

7.1.3 The expiration date for opened stock standards is the manufacturer's expiration date or 1 month from the date opened, whichever is sooner.

7.1.4 The expiration date for prepared reagents is 6 months from the date prepared or the expiration date of the parent reagent, whichever is sooner.

7.1.5 The expiration date for prepared standards is 1 month from the date prepared or the expiration date of the parent standard, whichever is sooner.

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.*

Methanol must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

Laboratory Reagent Water – ASTM Type II

Methanol – Purge and Trap grade
Storage: Flammable Cabinet

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.* Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

Refer to Attachment 6 for standard preparation information.

Unless noted elsewhere in this SOP, all standards must be stored in the freezer at <-10°C.

8.0 Sample Collection, Preservation, Shipment, and Storage

Aqueous samples are routinely collected in triplicate. Two vials are retained for analysis and the third vial is used to check the sample pH and for the presence of residual chlorine. This "sacrifice" vial should not be used for analysis unless all other vials have been consumed. If the "screening vial" is used for analysis, a Nonconformance Memo (NCM) must be initiated.

Samples are routinely collected with no headspace in 40mL vials equipped with Teflon-lined caps. The samples are dechlorinated with 25mg of ascorbic acid and acidified with about 1.0mL of 1:1 HCl per 40mL of sample at the time of collection. The preservative should be sufficient to achieve a sample pH of less than 2. The dechlorination agent should be sufficient to remove residual chlorine from the sample.

Note: If Total Trihalomethanes (THM) are the only analytes requested, the acid may be omitted and the samples may be dechlorinated with 4mg of sodium thiosulfate per 40mL of sample at the time of collection.

Samples must be iced at the time of collection and refrigerated at 4°C (less than 6°C with no frozen samples) in the lab until analysis. Samples must be analyzed within 14 days of collection. If the samples are unpreserved or if the pH >2, the samples must be analyzed within 24 hours of collection.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives and/or de-chlorination agents. NCMs must be initiated for samples that are received containing headspace.

Refer to SOP SA-VM-21: *Preparation, Screening, and Storage of Volatile Samples* for additional information.

8.1 Preservation Checks

These checks can be performed upon receipt or prior to preparation.

8.1.1 Mix the sample by inverting and transfer 10mL to a small medicine cup.

8.1.2 Touch a piece of narrow range pH paper to the sample in the cup and note the pH. Record the pH in the preservation check method in LIMS.

If the pH is greater than 2, initiate an NCM noting that the pH was outside of the preservation requirements.

Note: If the pH is greater than 2, a 24-hour holding time is enacted. Notify the project manager via a NCM if the 24-hour holding time is not met.

8.1.3 Touch a piece of starch iodide paper to the sample in the cup and note the color change of the paper.

If the paper turns blue or black, residual chlorine is present. Initiate a Nonconformance Memo.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

An analytical batch consists of up to 20 environmental samples and the associated QC items analyzed together within a 12 hour period. The minimum QC items required for each batch are: a method blank, a laboratory control sample (LCS), a low-level LCS (spiked at the reporting limit), and a matrix spike (MS), and a matrix spike duplicate (MSD)

If there is insufficient sample to perform the required MS and/or MSD, the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample is defined as receiving less than less than 4 vials.

Note: The LCS must be analyzed in duplicate at least once a quarter.

Note: If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required.

Note: The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples by EPA 524.2, an LCS at the RL must also be included in the required batch QC.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

The term "clock time" or "analytical clock" refers to the amount of time that can pass before additional instrument QC items must be performed. The analytical clock begins with the injection of the BFB, and all subsequent injections must be completed before the

clock time expires – at which point new instrument QC is performed and a new clock is initiated.

The clock time for EPA 524.2 is defined as 12 hours.

Note: Due to instrument configurations employing dual concentrators, most of the laboratory instruments can analyze more than 20 injections within the designated clock times. An analytical batch is still defined as 20 field samples; therefore, if more than 20 field samples are analyzed within a clock, additional batch QC is required (i.e., another method blank, LCS, and MS/MSD must be performed).

9.2.1 Tune Check

Inject 1uL of the 25ng/uL BFB standard.

Note: The analysis may be performed using purge and trap or by direct injection of the BFB standard. Mass spectrometer conditions must be the same as for the standard and sample analyses. The temperature programs may be different to allow for timely elution of BFB.

Evaluate the spectrum of the BFB peak. Test the apex of the peak first against the acceptance criteria. If the apex does not meet the criteria, evaluate the scans plus one and minus one scan from the apex. An average spectrum across the peak may also be evaluated against the criteria. If background subtraction is required, choose a spectrum at least ten scans before the elution of the peak for background.

TUNING AND MASS CALIBRATION ACCEPTANCE CRITERIA	
m/e	**Abundance Criteria**
50	15-40% of mass 95
75	30-80% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	Greater than 50% of mass 95
175	5-9% of mass 174
176	95-101% of mass 174
177	5-9% of mass 176

Note: The p-BFB analysis must meet the criteria before any standards or samples may be analyzed. Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. If there is any question about whether the BFB passes the criteria, contact the supervisor immediately before proceeding.

If the p-BFB fails to meet the acceptance criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the p-

BFB analysis, other corrective measures may include remaking the p-BFB standard, cleaning the instrument ion source, etc. Additionally, the chromatogram of the tuning analysis should be checked for acceptable baseline and the p-BFB peak should be symmetrical.

9.2.2 Trap Check Standard

Analysis of a trap check standard is recommended for this procedure. The trap check standard is prescribed in EPA Method 8260B and is used to evaluate the condition of the trap by monitoring the formation of chloromethane and bromomethane. Although not required in EPA 524.2, analysis of the Tarp Check Standard is useful as chloromethane and bromomethane may be formed on a degraded trap by thermal decomposition of halogenated compounds.

9.2.2.1 Prepare the trap check standard by injecting 2uL of a 50ug/mL bromoform standard into 5mL of reagent water. Other sample volumes may be used but the sample must transfer 100ng of bromoform to the column. Add the internal standards and surrogates. Analyze the sample using the same analytical system conditions used for samples and standards.

9.2.2.2 Evaluate the chromatogram for the presence of chloromethane and bromomethane. Compare the response to the 1.0ug/L standard. The response must be less than or equal to one half of the response of the 1.0ug/L standard, and the trap check standard must quantify less than 0.5ug/L when compared to the initial calibration curve.

Note: Ensure sure that the spectra match the reference spectra and that the most abundant ions are present for both compounds - chloromethane (m/z 50, 52) and bromomethane (94, 96).

9.2.2.3 If the trap check standard does not meet the acceptance criteria, the trap should be replaced, conditioned, and the system re-calibrated prior to the analysis of samples.

9.2.3 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves.* This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of a minimum of 3 standards. The lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

The initial calibration standard concentrations currently in use in the laboratory are as follows:

Standard Level	Concentration (ug/L)
1	0.5
2	1.0
3	2.0
4	5.0
5	10
6	20
7	50
8*	100

*Used for TTHMs only.

Refer to Attachment 6 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-041.

Note: EPA 524.2 requires a minimum of a 3-point calibration curve for a 20 fold concentration range, a 4-point calibration curve for a 50 fold concentration range, and a 5-point calibration curve for a 100 fold concentration range.

9.2.3.1 ICAL Criteria

The relative standard deviation of the calibration standards must be <20% for the initial calibration curve to be acceptable.

If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve. The regression coefficient (r^2) of the regression curve must be greater than 0.990 for the initial calibration curve to be acceptable.

Note: A minimum of 6 points is required for a quadratic curve. Higher order curves are not permitted.

9.2.4 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The ICV must be within 30% to be acceptable.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to level 6 of the ICAL. Refer to Attachment 6 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

Note: The LCS may be used to satisfy the ICV requirement if it is prepared from a second source and meets the criteria outlined above.

9.2.5 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed immediately following the initial calibration. Continuing calibration blanks are analyzed immediately following the continuing calibration verification (CCV).

Initial and continuing calibration blanks must be <1/2RL to be acceptable.

9.2.6 Continuing Calibration Verification

The initial calibration curve must be verified at the beginning of each clock with a mid-level standard.

The CCV must be within 30% to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to level 6 of the ICAL. Refer to Attachment 6 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-041.

9.2.7 Internal Standard (ISTD)

This procedure is an internal standard (ISTD) procedure. Fluorobenzene is the internal standard.

Prior to analysis, this internal standard must be added to all standards, samples, and QC items. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. A concentration of 10ug/L is used.

The response of the ISTD in the ICV/CCV must be within 30% of the response of the ISTD in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the CCV must be repeated and any samples associated with the CCV must also be re-analyzed. Repeated failure of the ISTD response will require re-calibration.

The response of the ISTD in the samples and batch QC items must be within 30% of the response of the previous CCV. If the response is outside of this range, corrective action must be taken.

9.2.8 Surrogate

This procedure uses surrogates to evaluate the analytical process. 1,2-Dichlorobenzene-d4 and 4-Bromofluorobenzene are the surrogates.

Prior to analysis, this surrogate is added to all samples and QC items. The concentration of the surrogate is the same in all field samples and QC samples. A concentration of 10ug/L is used.

The percent recovery of the surrogate in all field samples and QC samples must be within the limits listed in the Method Limit Groups (MLGs) in LIMS. If the percent recovery is

outside of this range, the analysis of the sample must be repeated. Repeated failure of the surrogate percent recovery may indicate instrumentation problems.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* and the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

Remove the samples from the refrigerator and allow them to come to room temperature.

Composite samples can be prepared using the guidance provided in SOP SA-QA-15: *Compositing, Homogenization, and Segregation of Samples.*

Refer to SOP SA-VM-021: *Preparation, Screening, and Storage of Volatiles Samples* for additional information.

10.2 QC Sample Preparation

10.2.1 Method Blank – The method blank is prepared as follows: Fill a 50mL volumetric with reagent water. Add 50uL of ISSU. Place on instrument to be analyzed.

10.2.2 Laboratory Control Sample – The LCS is prepared as follows: Fill a 50mL volumetric with reagent water. Add 20uL of Mega Mix, 20uL of Additional Mix, 50uL of ISSU, and 160uL of MeOH. Place on instrument to be analyzed.

10.2.3 Low-Level Laboratory Control Sample – The LLCS is prepared as follows: Fill a 50mL volumetric with reagent water. Add 0.5uL of Mega Mix, 0.5uL of Additional Mix, 50uL of ISSU, and 199uL of MeOH. Place on instrument to be analyzed.

10.2.4 Matrix Spike – Matrix spikes are prepared as follows: Spike 17.2uL of Mega Mix, 17.2uL of Additionals Mix, 43uL of ISSU, and 137.6uL of MeOH into a 43mL VOA vial containing the sample designated for the MS and MSD. Place in the instrument to be analyzed.

10.3 Analysis

10.3.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Note: The drinking water methods are prescriptive. For this reason, items such as purge volume, purge gas, purge time, carrier gas, etc. must match the EPA method.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

Note that the MS must be set to monitor ions between 35 and 260amu with a scan rate of 1 second or less. The purge time must be 11 minutes. All other parameters may be changed to optimize the system.

Column: J&W DB-624, 0.18mm x 20m x 1.0um, or equivalent

Helium carrier gas flow rate: 0.5mL/min (constant flow)
Inlet Pressure: 15.8 psi
Total Flow: 28.2mL/minute
Split Ratio: 50:1 (Routine and Tune Check)
Split Ratio: 25:1 (UCMR List 1 Compounds)
Split Flow: 25mL/min
Gas Saver: OFF

Routine Targets and UCMR List 1
Initial column temperature: 40°C for 1min
Column temperature program 1: 17°C/min
Final column temperature: 200°C for 7min
Run Time: 11.41 minutes

BFB Tune Check
Initial column temperature: 50°C for 1min
Column temperature program 1: 17°C/min
Final column temperature: 200°C for 7min
Run time: 8.82 minutes

Injector temperature: 250°C
Mass range: 35-260amu
Solvent Delay: 0.90 Minutes
Threshold: 150 Sample #: 2 A/D Samples: 4
MS Quad Temperature: 150°C MS Source Temperature: 250°C
EM Absolute: TRUE
Resulting EM Voltage: EM voltage set at AUTOTUNE + 200
Tune File: TUS.U

Purge and Trap Instrument Conditions

Purge Time: 11 min
Purge Temperature: Ambient
Desorb Time: 0.5 min
Desorb Temperature: 250°C
Bake Time: 8 min at 260°C
Purge Flow: Approximately 35 mL/min. Adjust to maximize response of chloromethane and bromoform.
Valve Temperatures: 150°C
Transfer Line: 150°C

10.3.1.1 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in SOP SA-QA-08: *Evaluation of Chromatographic Data.* Retention time windows (RTW), i.e., the length of time the instrument will scan for the analyte, must be established initially upon instrument set-up and verified quarterly.

Retention times (RT), i.e., the elution time of the analyte, are verified daily with the analysis of the ICAL or CCV. The retention time for the CCV must fall within the daily retention time window as defined in SOP SA-QA-08.

10.3.2 Internal Standard (ISTD)

Prior to analysis, 43uL of ISSU must be added to all standards, samples, and QC items. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. A concentration of 10ug/L is used.

10.3.3 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.2. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.3, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.5.

10.3.4 Sample Analysis

Remove the samples from the refrigerator and allow them to come to room temperature.

The sample must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to exclude QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the clock.

10.3.5 Example Analytical Sequence

See Attachment 1 for an example analytical sequence.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data evaluation must be performed in accordance with SA-QA-08: *Evaluation of Chromatographic Data.* This SOP includes specific information regarding the evaluation

of chromatographic data, including the requirements for performing manual integrations and the evaluation of retention times.

Data review and reporting must be performed in accordance with SA-QA-02: *Data Generation and Review.*

11.1 Qualitative Analysis of Target Compounds

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1 Two criteria must be met in order to identify a target-compound.

1) elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{retention\ time\ of\ the\ target\ compound}{retention\ time\ of\ the\ associated\ internal\ standard}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum

11.1.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. These ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.1.3 The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

11.1.1.5 MS/MSD Evaluation

If the concentration of a target analyte in the un-spiked (native) sample is more than four times the theoretical concentration of the matrix spike, the recovery is not reported and the data is flagged.

11.1.2 Evaluation of Tentatively Identified Compounds (TICs)

Refer to Attachment 11 of SOP SA-QA-08: *Evaluation of Chromatographic Data* for the laboratory's TIC processing procedures.

11.1.3 Dilutions

Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags must be used or qualification in a case narrative provided to the client.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower reporting limits.

11.1.4 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes and/or use the Historical Data Tracker feature to determine if historical data is available for review.

11.1.5 Chemical Relationships

When available, the following chemical relationships must be evaluated for each sample. If these relationships are not met the Department Manager must be contacted immediately.

Benzene, toluene, ethylbenzene, and the xylenes are generally present together in samples and indicate the presence of gasoline

m/p-Xylenes are generally higher than o-xylene

Hydrocarbons present is samples containing gasoline generally contain mass 43 and may co-elute with target analytes with mass 43 as the quant or confirmation ion or may skew the spectrum of a compound with mass 43 as part of the spectrum.

Cis- isomers are generally more prevalent than the trans- isomers

Pay particular attention to the retention time of isomer because the only way to positively identify them is by retention time. The isomers are:

1,1-dichloroethane and 1,2-dichloroethane
1,1-dichloroethene, cis-1,2-dichloroethene, and trans-1,2-dichloroethene
1,1,1-trichloroethane and 1,1,2-trichloroethane
ethyl benzene, m/p-xylene, and o-xylene
1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2-dichlorobenzene
1,1-dichloropropene, cis-1,2-dichloropropene, and trans-1,2-dichloropropene
2-chlorotoluene and 4-chlorotoluene
1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene

1.3.5-trimethylbenzene and 1,2,4-trimethylbenzene
4-methyl-2-pentanone (MIBK) and 2-hexanone
n-butylbenzene, sec-butylbenzene, tert-butylbenzene, and isopropylbenzene

Higher chlorinated alkanes and alkenes may have lower chlorinated alkanes or alkenes present due to degradation. The following table lists some common chlorinated compounds and their degradation products. Look for the degradation product(s) when the concentration of the compound in the left column is present at high concentrations.

Analyte	Degration Product
1,1,2,2-tetrachloroethane	trichloroethene (TCE) cis-1,2-dichloroethene (c-1,2-DCE) trans-1,2-dichloroethene (t-1,2-DCE) vinyl chloride 1,1,2-trichloroethane (1,1,2-TCA) 1,2-dichloroethane (1,2-DCA) Chloroethane
1,1,2-trichloroethane (1,1,2-TCA)	1,2-dichloroethane (1,2-DCA) Chloroethane
1,1,1-trichloroethane (1,1,1-TCA)	1,1-dichloroethene (1,1-DCE) 1,1-dichloroethane (1,1-DCA) Chloroethane
Carbon tetrachloride	Chloroform Methylene chloride Chloromethane
Tetrachloroethene (PCE) (PCE = perchloroethylene which is a common name for tetrachloroethene)	trichloroethene (TCE) cis-1,2-dichloroethene (c-1,2-DCE) trans-1,2-dichloroethene (t-1,2-DCE) Chloroethene
1,2,4-trichlorobenzene	1,4-dichlorobenzene (1,4-DCB) 1,2-dichlorobenzene (1,2-DCB) Chlorobenzene

Trihalomethanes are formed when water from a natural source (river, well, etc.) is chlorinated. Usually, THM will be present in the relative concentrations as follows:
chloroform >> dichlorobromomethane > dibromochloromethane >> bromoform.

11.1.6 Drinking Water Compliance Evaluation

Public water suppliers (PWS) are governed by EPA-specified Maximum Contaminant Levels (MCL) above which indicates noncompliance. The MCLs associated with this procedure are given in Attachment 8. Notify the PM immediately via a Nonconformance Memo if any sample contains a detection above these levels.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample
F = Final volume/weight
I = Initial volume/weight
D = Dilution factor

Note: This calculation assumes all applicable unit correction factors are applied.

12.0 Method Performance

12.1 Reporting Limit Verification (RLV)

At a minimum, RLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

For analytes and methods certified by DOD ELAP, RLVs must also be performed quarterly thereafter. For analytes and methods certified by NELAC, RLVs must also be performed annually thereafter. Exceptions may be made for project-specific non-routine analytes.

12.2 Method Detection Limit (MDL) Study

The MDL is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDLs associated with this procedure are given in the Method Limit Group (MLG) in TALS.

At a minimum, MDL Studies must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

In addition to the requirements in SOP SA-QA-07, EPA 524.2 also requires that MDL studies be performed over multiple days.

12.3 Method Detection Limit Verification (MDLV)

At a minimum, MDLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

For analytes and methods certified by DOD ELAP, MDLVs must also be performed quarterly thereafter. For analytes and methods certified by NELAC, MDLVs must also be performed annually thereafter.

Note: MDLVs are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.4 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS and MS/MSD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data.*

12.5 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06*: Training Procedures.*

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Note: The IDOC must meet 80-120% recovery and less than 20% RSD.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures.*

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Flammable waste (acetone, hexane, and methanol from extracts, rinsings, and standards) – Transfer to a satellite container designated for flammable waste and transfer to waste disposal department when the container is full.

15.0 References / Cross-References

- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-AN-041: *Reagent and Standard Materials Procedures*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits (RLs, MDLs, and IDLs)*
- SOP SA-QA-08: *Evaluation of Chromatographic Data*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- SOP SA-VM-021: *Preparation, Storage, and Screening of Volatiles Samples*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)

- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- US EPA 524.2 Revision 4.1: *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*; 1995

16.0 Method Modifications

16.1 The reference method was written specifically for drinking water and source water samples; however, the laboratory may perform other types of water samples using this procedure.

16.2 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each batch of samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory defaults to 50-150%. These criteria are required for THMs, as specified in the Disinfection By-Product Rule.

16.3 The laboratory has incorporated the minimum batch QC items as outlined in Section 9.1. Some additional QC items are routinely performed above those required in the EPA 524.2 reference method (i.e., MS/MSD and/or LCS/LCSD) to satisfy common regulatory and/or client requests for precision data and/or to facilitate scheduling and data evaluation.

16.4 The Trap Check Standard described in Section 9.2.2 is not included in EPA Method 524.2. This standard may be adopted and implemented by the laboratory as an internal check on the process; however, it is not required.

16.5 Due to the volatile nature of the analytes tested, the laboratory sacrifices a vial to be used for pH check, residual chlorine verification, and screening. The laboratory applies the pH and residual chlorine values identified on this vial to the remaining vials submitted for that sample (e.g., if the pH of the tested vial is acceptable, the remaining vials for that sample are assumed to be acceptable). The practice of checking pH prior to analysis allows for re-adjustment of holding times based on the preservation of the sample, as outlined in Attachment 2.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Standard Preparation
Attachment 6: List of Regulated Analytes and MCLs
Attachment 7: Quant Ions

Attachment 1:
SOP Summary

Sample Preparation and Analysis Summary

Volatile organic compounds (VOC) are purged from the sample matrix with helium. The VOC are transferred from the sample matrix to the vapor phase. The vapor is swept through a sorbent tube where the VOC are trapped. After the purging is completed, the trap is heated and backflushed with helium to desorb the VOCs onto a GC column. The GC is temperature-programmed to separate the VOC, which are then detected by a mass spectrometer. Qualitative identification of the target compounds in the sample is based on the relative retention time and the mass spectra of the characteristic masses (ions) determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

Analytical Sequence

Description	Comments
Blank	
Tune	12-hour clock begins with injection of the tune
Initial Calibration	
ICV	Second Source
ICB	
Samples & Batch QC Items	Not to exceed 12 hours; last injection must occur before 12 hours from BFB injection
Tune	12-hour clock begins with injection of the tune
CCV	20ug/L
CCB	
Samples & Batch QC Items	Not to exceed 12 hours; last injection must occur before 12 hours from BFB injection
Tune	12-hour clock begins with injection of the tune
CCV	20ug/L
CCB	

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Matrix	Routine Sample Container	Routine Sample Size	Minimum Sample Size	Dechlorination Agent	Chemical Preservation[1]	Thermal Preservation	Holding Time[3]
Water	3 x 40mL VOA vial	40mL	40mL	Ascorbic Acid	1:1 HCl	4 °C[2]	pH≤2: 14 days pH>2: 24 hours
Water (TTHM Only)	3 x 40mL VOA vial	40mL	40mL	Sodium Thiosulfate	Not Applicable	4 °C[2]	14 days

[1]Samples must be dechlorinated prior to acidification.
[2]Samples are collected on ice and maintained at <6 °C with no frozen samples.
[3]Holding time is from sample collection to analysis.

Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Clock Time	12 hours	Clock time starts with the injection of the BFB. Analysis of samples and QC items must conclude within expiration of clock time. Subsequent analysis requires new BFB.	Not applicable
Tune Standard (BFB)	At beginning of each clock	Refer to Section 9.2.1.	- Perform instrument maintenance - Re-tune.
Trap Check Standard	At beginning of each clock	<0.5ug/L (Chloromethane & bromomethane)	- Perform instrument maintenance. - Change trap. - Recalibrate.
Initial Calibration (ICAL) - Minimum 3 points	Upon instrument set-up, and after unsuccessful CCV	%RSD < 20% If %RSD > 20%, use curve fit w/ r^2>0.990.	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Initial Calibration Verification (ICV) - Second Source	After each ICAL	%RSD < 30%	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate

QC Item	Frequency	Criteria	Corrective Action
Continuing Calibration Verification (CCV)	After BFB	%RSD < 30%	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Calibration Blank (ICB/CCB)	After ICV and every CCV	<1/2RL	Refer to SOP SA-QA-17
Internal Standards (ISTD)	Spiked in all CCVIS, samples, and batch QC items	CCVIS: - Area within 30% of CCV in ICAL. Samples & batch QC items: - Area within 30% of previous CCVIS.	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available
Surrogate Compounds	Spiked in all samples and batch QC items.	70-130%	-Evaluate chromatogram, spectra, and integrations -Reanalyze sample, if sufficient sample available
Analytical Batch Definition	Analyzed together w/in 12-hr timeframe; not to exceed 20 field samples	Not Applicable	Not Applicable
Method Blank (MB)	One per analytical batch	<1/2RL	Refer to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per analytical batch	70-130% Rec	Refer to SOP SA-QA-17

QC Item	Frequency	Criteria	Corrective Action
Laboratory Control Sample Duplicate (LCSD)	One per analytical batch, when insufficient sample is provided for MS/MSD	70-130% Rec; <30%RPD	Refer to SOP SA-QA-17
Low-Level Laboratory Control Sample (LLCS)	One per analytical batch	50-150% Rec	Refer to SOP SA-QA-17
Matrix Spike (MS)	One per analytical batch	70-130% Rec	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per analytical batch	70-130% Rec; <30%RPD	Refer to SOP SA-QA-17
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per analyte/method/matrix combination	80-120% Rec; <20% RPD	Refer to SOP SA-QA-06 Note: Unsupervised work must not begin until acceptable IDOC is obtained.
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Reporting Limit Verification (RLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for NELAC)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

QC Item	Frequency	Criteria	Corrective Action
Method Detection Limit Study (MDL) - Must be performed over multiple days	Upon method/instrument set-up, per analyte/method/matrix combination	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
MDL Verification (MDLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for NELAC)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Injector Port							X	Replace septum, sleeve, inlet seal, and washer (Recommend every 2 weeks)
Sparge Tubes							X	Clean (Recommend every 3 months)
Column							X	Change column (Recommend annually)

Troubleshooting
Troubleshooting should be documented as outlined above. If possible, troubleshooting is best performed in a step-wise manner to systematically isolate instrument components. Refer to the instrument manufacturer's guides for specific information and strategies. Enlist assistance from technical and/or department management as needed.

Contingency Plan
Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation,

the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

Attachment 5:
Standard Preparation

Purchased Standards

Mega Mix, 2000 ug/mL – NSI Solutions

Mega Mix 2 (Secondary Standard), 2000ug/mL – Restek

Gases Mix, 2000ug/mL – Supelco

Gases Mix 2 (Secondary Standard), 2000ug/mL – Restek

California Oxygenates Mix 1, 2000-10000 ug/mL – Restek

California Oxygenates Mix 2 (Secondary Standard), 2000-10000 ug/mL – O2Si

Volatile Organics Calibration Mix, 5000ug/mL – Restek
Storage: In refrigerator (2 - 6°C)

Ketone 2 (Secondary Standard) 2000ug/mL – Supelco

Freon, 2000ug/mL – Supelco

Freon 2 (Secondary Standard), 2000ug/mL – Ultra Scientific

Internal Standard and Surrogate Mix, 2000 ug/mL – Purchased from Restek

Prepared Standards

524 Mega Mix (Working Standard), 50-150ug/mL – Prepared by adding 250uL of Mega Mix and 250uL of Gases Mix to 10mL of methanol.

524 Mega Mix 2 (Secondary Working Standard), 50-150ug/mL – Prepared by adding 250uL of Mega Mix 2 and 250uL of Gases Mix 2 to 10mL of Methanol.

524 Additions (Working Standard), 40-200ug/mL – Prepared by adding 200uL of California Oxygenates Mix 1, 200uL of Freon, and 200uL of Volatile Organics Calibration Mix to 10mL of methanol.

524 Additions 2 (Secondary Working Standard), 40-200ug/mL – Prepared by adding 200uL of California Oxygenates Mix 2, 200uL of Freon 2, and 500uL of Ketones 2 to 10mL of methanol.

524 ISSU (Working Standard), 10ug/mL – Prepared by adding 125uL of Internal Standard and Surrogate Mix to 25mL of ethanol.

ICAL Standards

Stock/Mix	1	2	3	4	5	6	7	8
	Aliquot to prepare CAL standard (uL)							
524 Mega Mix	0.5	1.0	2.0	5.0	10	20	50	100
524 Additionals	0.5	1.0	2.0	5.0	10	20	50	100
524 ISSU	50	50	50	50	50	50	50	50
Methanol	199	198	196	190	180	160	100	---
Volume of water (mL)	50	50	50	50	50	50	50	50
Concentration								
Target Compounds (ng)	2.5	5	10	25	50	100	250	500
Internal Standards (ng)	50	50	50	50	50	50	50	50

Attachment 6:
List of Regulated Analytes and MCLs

Analyte	MCL (ug/L)
Benzene	5
Carbon tetrachloride	5
Chlorobenzene	100
1,2-Dichlorobenzene	600
1,4-Dichlorobenzene	75
1,2-Dichloroethane	5
1,1-Dichloroethene	7
Cis-1,2-Dichloroethene	70
Trans-1,2-Dichloroethene	100
1,2-Dichloropropane	5
Ethylbenzene	700
Methylene chloride	5
Styrene	100
Tetrachloroethene	5
Toluene	1000
1,2,4-Trichlorobenzene	70
1,1,1-Trichloroethane	200
1,1,2-Trichloroethane	5
Trichloroethene	5
Vinyl chloride	2
Total Xylenes (Sum of o-xylenes and m/p-Xylenes)	10000
Trihalomethanes, total (Sum of chloroform, bromoform, dibromochloromethane, and dibromochloromethane)	100

Attachment 7:
Quant Ions

Compound	CAS	ISTD	Quant Ion	Secondary Ions	
1,1,1,2-Tetrachloroethane	630-20-6	1	131	133	119
1,1,1-Trichloroethane	71-55-6	1	97	99	61
1,1,2,2-Tetrachloroethane	79-34-5	1	83	85	168
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	1	101	51	43
1,1,2-Trichloroethane	79-00-5	1	97	83	99
1,1-Dichloroethane	75-34-3	1	63	65	83
1,1-Dichloroethene	75-35-4	1	61	96	98
1,1-Dichloropropene	563-58-6	1	75	110	77
1,2,3-Trichlorobenzene	87-61-6	1	180	182	109
1,2,3-Trichloropropane	96-18-4	1	110	112	
1,2,4-Trichlorobenzene	120-82-1	1	180	182	145
1,2,4-Trimethylbenzene	95-63-6	1	105	120	77
1,2-Dibromo-3-Chloropropane	96-12-8	1	75	157	155
1,2-Dichlorobenzene	95-50-1	1	146	148	111
1,2-Dichlorobenzene-d4 (Surrogate)	2199-69-1	1	152	115	150
1,2-Dichloroethane	107-06-2	1	62	49	64
1,2-Dichloropropane	78-87-5	1	63	76	65
1,3,5-Trimethylbenzene	108-67-8	1	105	120	77
1,3-Dichlorobenzene	541-73-1	1	146	148	111
1,3-Dichloropropane	142-28-9	1	76	78	41
1,4-Dichlorobenzene	106-46-7	1	146	148	111
2,2-Dichloropropane	594-20-7	1	77	41	
2-Butanone (MEK)	78-93-3	1	43	72	
2-Chlorotoluene	95-49-8	1	91	126	63
2-Hexanone	591-78-6	1	43	85	100
2-Methyl-2-propanol (TBA)	75-65-0	1	59	41	43
4-Bromofluorobenzene (Surrogate)	460-00-4	1	95	174	176
4-Chlorotoluene	106-43-4	1	91	126	63
4-Isopropyltoluene	99-878-6	1	119	134	91
4-Methyl-2-pentanone (MIBK)	108-10-1	1	43	85	100
Acetone	67-64-1	1	43	58	
Benzene	71-43-2	1	78	50	51
Bromobenzene	108-86-1	1	77	156	158
Bromoform	75-25-2	1	173	171	174
Bromomethane	74-83-9	1	94	96	79
Carbon tetrachloride	56-23-5	1	117	119	121
Chlorobenzene	108-90-7	1	112	77	51
Chlorobromomethane	74-97-5	1	49	130	

Compound	CAS	ISTD	Quant Ion	Secondary Ions	
Chlorodibromomethane	124-48-1	1	129	127	131
Chloroethane	75-00-3	1	64	66	
Chloroform	67-66-3	1	83	85	47
Chloromethane	74-87-3	1	50	52	
cis-1,2-Dichloroethene	156-59-2	1	61	96	98
cis-1,3-Dichloropropene	10061-01-5	1	75	77	110
Dibromomethane	74-95-3	1	93	174	95
Dichlorobromomethane	75-27-4	1	83	85	129
Dichlorodifluoromethane	75-71-8	1	85	87	101
Ethylbenzene	100-41-4	1	91	106	51
Ethylene Dibromide	106-93-4	1	107	109	
Fluorobenzene (Internal Standard)	17060-07-0	1	96	70	50
Hexachlorobutadiene	87-68-3	1	225	223	190
Isopropyl ether	108-20-3	1	45	59	87
Isopropylbenzene	98-82-8	1	105	120	77
Methyl tert-butyl ether	1634-04-4	1	73	57	
Methylene Chloride	75-09-2	1	49	84	86
m-Xylene & p-Xylene	136777-61-2	1	91	106	77
Naphthalene	91-20-3	1	128	102	51
n-Butylbenzene	104-51-8	1	91	92	134
Nitrobenzene	98-95-3	1	96	70	50
N-Propylbenzene	103-65-1	1	91	120	65
o-Xylene	95-47-6	1	91	106	77
sec-Butylbenzene	135-98-8	1	105	134	91
Styrene	100-42-5	1	104	78	103
Tert-amyl methyl ether	994-05-8	1	73	43	87
Tert-butyl ethyl ether	637-92-3	1	59	87	57
tert-Butylbenzene	98-06-6	1	119	91	134
Tetrachloroethene	127-18-4	1	166	164	168
Toluene	108-88-3	1	91	92	65
trans-1,2-Dichloroethene	156-60-5	1	61	96	98
trans-1,3-Dichloropropene	10061-02-6	1	75	77	110
Trichloroethene	79-01-6	1	130	95	132
Trichlorofluoromethane	75-69-4	1	101	103	105
Vinyl chloride	75-01-4	1	62	64	

18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial, grammatical, and formatting changes made. Boilerplate text added.
- Changed SOP Document Control Number. This was SOP SA-VM-015: *Volatile Compounds in Drinking Water by GC/MS.* SOP SA-VM-015 is now obsolete.
- Added note that if an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required. Section 9.1.1
- Clarified requirements and frequency for RLVs, MDL Studies, and MDLVs to be consistent with SOP SA-QA-07 and to include the quarterly frequency as defined by DOD. Section 12.1 - 12.3 and Attachment 3
- Added note that unsupervised work must not begin until acceptable IDOC is obtained. Attachment 3
- Added section on troubleshooting. Attachment 4
- Added section to describe analytical data system, software, and hardware. Section 6.2
- Removed references to and procedures Trihalomethane Formation Potential. This procedure is no longer performed.
- Added note to Safety Section that concentrated acids should be used in a fully functional fume hood. Section 5.0
- Removed requirement to perform inspection of pH paper prior to use. Section 6.3
- Removed procedures for Tentatively Identified Compounds (TICs) and added reference to SOP SA-QA-08, where these procedures are now housed. Section 11.1.2
- Added reference to LIMS Historical Data Tracker feature. Section 11.1.4
- Added note that 50-150% criteria for LLCS is specified in the Disinfection By-Product Rule. Section 16
- Removed reference to residual chlorine powder pillows. These are no longer used. Replaced residual chlorine powder pillows with residual chlorine check strips. Revised procedure for checking residual chlorine accordingly. Section 6.3 and Section 8.1
- Expanded/clarified sample collection information for consistency with SOP SA-VM-21. Section 8.0
- Added information to Method Modifications and Clarifications Section regarding using the sacrifice vial for pH checks and applying this value to all vials submitted for that sample. Section 16.5