EXHIBIT D

INTRODUCTION TO ORGANIC ANALYTICAL METHODS

THIS PAGE INTENTIONALLY LEFT BLANK

Exhibit D – Introduction to Organic Analytical Methods

Table of Contents

THIS PAGE INTENTIONALLY LEFT BLANK

1.0 INTRODUCTION

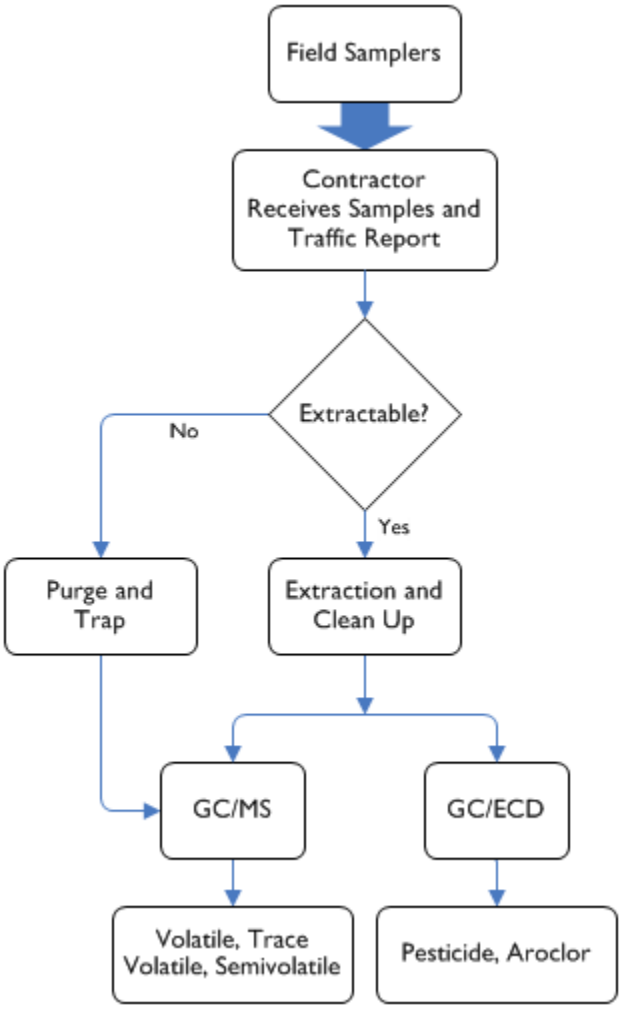
The organic analytical service provides a contractual framework for laboratories. This framework applies U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) analytical methods for the isolation, detection, and quantitative measurement of trace volatiles, low-medium volatiles, semivolatiles, pesticides, and aroclors in aqueous/water and soil/sediment samples.

The analytical methods that follow are designed to analyze aqueous/water, leachate, and soil/sediment samples from hazardous waste sites for the presence of organic analytes contained in the Organic Target Analyte List (TAL) (see Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits). The organic methods include alternative analysis procedures for some analytes, multiple preparation procedures, and Quality Control (QC) requirements. Analytical techniques in the organic methodologies include Gas Chromatography/Mass Spectrometry (GC/MS) and Gas Chromatography/Electron Capture Detection (GC/ECD).

2.0 ORGANIC METHODS FLOW CHART

Figure 1 outlines the general analytical scheme the Contractor shall follow in performing standard organic analyses under this contract.

Figure 1 - Organic Methods Flow Chart



3.0 GLASSWARE CLEANING

Laboratory glassware to be used within the organic analyses must be scrupulously cleaned according to the EPA's (SW-846) Chapter Four Organic Analytes, Section 4.1.4, Revision 4, 2007, or an equivalent procedure. Equivalent procedures are those which meet the Preparation Blank requirements in the Statement of Work (SOW). An electronic version of this manual can found at http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/chap4.pdf.

4.0 STANDARD STOCK SOLUTIONS

Stock solutions to be used for preparing instrument or method standards may be purchased or prepared as described in the individual methods of Exhibit D.

5.0 VERIFICATION OF AQUEOUS/WATER SAMPLE CONDITION

At the time of sample receipt, the Contractor shall check the condition of each sample container and its contents and note the condition in a sample receipt log if the condition is not acceptable. The Contractor shall determine if sufficient sample volume has been provided for all tests scheduled and listed on the Traffic Report/Chain of Custody (TR/COC) Record. Containers of water samples for volatile organic analysis should be completely filled without air bubbles. Preservation of samples, if required, should be noted on the label and TR/COC Record. The Contractor shall not adjust the pH of a volatiles sample if preservation is not documented.

6.0 SAMPLE CHARACTERIZATION

6.1 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil/sediment sample) are received by the Contractor, the Contractor shall contact the Sample Management Office (SMO) to apprise them of the type of sample received. SMO will contact the EPA Region.

6.1.1 If all phases of the sample are amenable to analysis, the EPA Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze one or more of the phases, separately. SMO will provide the EPA Sample Numbers for the additional phases, if required.
- Do not analyze the sample.

6.1.2 If all of the phases are not amenable to analysis (i.e., outside scope), the EPA Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is (are) amenable to analysis. SMO will provide the EPA Sample Numbers for the additional phases, if required.
- Do not analyze the sample.

6.1.3 The Contractor shall document the EPA Region's decision in the SDG Narrative.

7.0 SAMPLE MIXING

Unless instructed otherwise by the EPA Regional Laboratory Contracting Officer Representative (COR), all samples shall be mixed thoroughly prior to aliquoting for extraction. Decant and discard any water layer on a sediment sample. There is no specific procedure provided herein for homogenization of soil/sediment samples; however, an effort shall be made to obtain a representative aliquot. Coarse stones, twigs, or debris that are not representative of the soil/sediment shall be excluded from the aliquot.

8.0 SAMPLE DILUTIONS

The Contractor shall follow the requirements for sample dilutions as described in the individual methods of Exhibit D. The Contractor shall use the least dilution necessary to bring the analyte(s) concentrations within the calibration range. Unless the Contractor can submit proof that dilution was required to obtain valid results, or to avoid damage to Gas Chromatographs or detectors, both diluted and undiluted sample measurements must be contained in the raw data.

8.1.1 The sample and its associated Matrix Spike (MS) and Matrix Spike Duplicate (MSD) shall initially be run at the same dilution.

8.1.2 All volatile water sample dilutions must be made with laboratory reagent water.

8.1.3 All sample extracts must be diluted using the same solvent used in the final sample extract.

9.0 MANUAL INTEGRATIONS

If the Contractor analyzes samples or standards using manual integrations, the Contractor shall clearly identify the manual integrations used to calculate the final sample result and provide the raw data and refer to Exhibit B – Reporting and Deliverables Requirements, Section 2.4 for reporting manual integrations.

10.0 RAW DATA REQUIREMENTS

The Contractor is reminded and cautioned that the collection and reporting of raw data may or may not be referred to within the individual methods of Exhibit D or the Quality Assurance (QA) protocol of Exhibit F - Programmatic Quality Assurance/Quality Control Elements. The raw data deliverable requirements are specified in Exhibit B - Reporting and Deliverables Requirements, Section 2.4. Raw data collected and provided in association with the performance of analyses under this contract shall conform to the appropriate sections of Exhibit B.

11.0 ANALYTICAL STANDARDS REQUIREMENTS

The EPA will not supply analytical reference standards for either direct analytical measurements or the purpose of traceability. All contract laboratories shall be required to prepare, from materials or purchase from private chemical supply companies, those standards necessary to successfully and accurately perform the analyses required in this protocol.

11.1 Preparation of Chemical Standards from the Neat High Purity Bulk Material

11.1.1 If the laboratory cannot obtain analytical reference standards, the laboratory may prepare its own chemical standards. Laboratories shall obtain the highest purity possible when purchasing chemical standards. Standards purchased at less than 97% purity shall be documented as to why a higher purity could not be obtained.

11.1.2 The chemical standards shall be kept at manufacturer recommended conditions when not being used in the preparation of standard solutions. Proper storage of chemicals is essential to safeguard them from decomposition.

11.1.3 The Contractor is responsible for having analytical documentation demonstrating that the purity of each chemical is correctly stated. Purity confirmation, when performed, should use appropriate techniques. Use of two or more independent methods is recommended. The correction factor for impurity when weighing neat materials in the preparation of solution standards is determined using the following equation:

EQ. 1 Weight of Impure Compound

$$\text{Weight of Impure Chemical} = \frac{\text{weight of pure chemical}}{(\text{percent purity}/100)}$$

WHERE,

Weight of Pure Chemical = That required to prepare a specific volume of a solution standard of a specified concentration.

11.1.4 Logbooks are to be kept for all weighing and dilutions of standards and reagents. All subsequent dilutions from the primary standard and the calculations for determining their concentrations are to be reviewed and verified by a second person.

11.1.5 All solution standards are to be refrigerated, if required, when not in use.

11.1.6 All solution standards are to be clearly labeled to include the identity of the analyte or analytes, concentration, the standard ID number of the solution, date prepared, solvent, expiration date of the solution, special storage requirements (if any), and initials of the preparer.

11.2 Purchase of Chemical Standards Already in Solution

Solutions of analytical reference standards can be purchased by Contractors provided they meet the following criteria.

11.2.1 Contractors shall maintain documentation of the purity confirmation of the material to verify the integrity of the standard solutions they purchase.

11.2.2 The quality of the reference standards purchased shall be demonstrated statistically and analytically by a method of the supplier's choice.

11.3 Documentation of the Verification and Preparation of Chemical Standards

It is the responsibility of the Contractor to maintain the necessary documentation to show that the chemical standards used in the performance of the CLP analysis conform to the requirements previously listed.

11.3.1 In those cases where the documentation is supportive of the analytical results of data packages sent to the Government, such documentation is to be kept on-file by the Contractor for a period of one year.

11.3.2 Upon request by the EPA Regional Laboratory COR, the Contractor shall submit their most recent previous year's documentation (12 months) for the verification and preparation of chemical standards within 14 days of receipt of the request to the designated recipients.

12.0 SAFETY

The toxicity or carcinogenicity of each reagent used in this SOW has not been precisely defined; however, each chemical compound shall be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The Contractor is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of chemicals specified in these methods. A reference file of Material Safety Data Sheets (MSDS) shall be made available to all personnel involved in the chemical analysis.

13.0 POLLUTION PREVENTION

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the EPA recommends recycling as the next best option.

14.0 WASTE MANAGEMENT

The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The EPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with applicable environmental rules and regulations.

THIS PAGE INTENTIONALLY LEFT BLANK

EXHIBIT D

GENERAL ORGANIC ANALYSIS

THIS PAGE INTENTIONALLY LEFT BLANK

Exhibit D –General Organic Analysis

Table of Contents

THIS PAGE INTENTIONALLY LEFT BLANK

1.0 SCOPE AND APPLICATION

This Exhibit provides procedures for the use of General Analysis to determine the percent solids of soil/sediment samples and leaching samples by Toxicity Characteristic Leaching Procedure (TCLP) (SW-846 Method 1311) or Synthetic Precipitation Leaching Procedure (SPLP) (SW-846 Method 1312).

2.0 SUMMARY OF METHOD

These methods describe the determination of sample characteristics by gravimetry, or the leaching of samples for subsequent analysis by the other analytical methods in this Statement of Work (SOW).

3.0 DEFINITIONS

See Exhibit G - Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

Not applicable.

5.0 SAFETY

See Section 12.0 in Exhibit D - Introduction to Organic Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, a demonstration of equivalent performance meeting the requirements of this SOW is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Percent Solids Determination

6.1.1 Disposable weigh boats with covers

6.1.2 Oven capable of maintaining a temperature of 105°C (±5°C). Oven shall be in a well-ventilated area.

6.1.3 Balance – Top loader, 300 grams (g) capacity with a minimum sensitivity of ±1.0 milligrams (mg)

The balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±50% of the expected measured mass) for each balance and be accurate to ±1.0 mg. The masses that are used to check the balances daily must be checked on a monthly basis using NIST (National Institute of Standards and Technology)-traceable known reference masses (Class '1' or '2') as defined by ASTM E617-97 (2008) or equivalent (e.g., earlier Class 'S' defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must be recertified every five years or sooner if there is reason to believe damage (corrosion, nicks) has occurred. The Contractor shall maintain documentation that demonstrates that these criteria have been met.

6.2 TCLP and SPLP Leaching

6.2.1 Agitation Apparatus – Capable of rotating the extraction vessel(s) in an end-over-end fashion at 30 ±2 rpm.

6.2.2 Extraction Vessels – Jar with sufficient capacity to hold sample and extraction fluid. Vessels shall be constructed of polytetrafluoroethylene (PTFE), stainless steel, or borosilicate glass.

NOTE: PTFE, borosilicate glass, or stainless steel are the only materials suitable when TCLP extracts will be analyzed for organic constituents.

6.2.3 Filters – Borosilicate glass with no binder material with an effective pore size of 0.6–0.8 µm. Acid wash with 1N nitric acid prior to use, followed by three consecutive rinses with reagent water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

6.2.4 Filtration Device – Capable of exerting pressures up to 50 psi. Use of units having an internal volume of 1.5 L and capable of accommodating a 142 mm filter is recommended.

6.2.5 Beaker – 500 mL.

6.2.6 Balance – Any laboratory balance accurate to within ±0.01 grams may be used (all weight measurements are to be within ±0.1 grams). All requirements in Section 6.1.3 shall be met.

6.2.7 Zero-Headspace Extraction (ZHE) Vessel – For volatile analytes, it allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel while effectively excluding headspace. The vessel must be made of inert type 316 stainless steel which will not leach or adsorb sample components. The vessel shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm diameter, 0.6-0.8 µm glass fiber filter. The device contains VITON® O-rings which should be replaced frequently.

6.2.8 An in-line glass fiber filter may be used to filter the material within the ZHE vessel when it is suspected that the glass fiber filter has been ruptured.

NOTE: The ZHE vessel must be free of contaminants and cleaned between TCLP samples. Manufacturer-recommended testing procedures shall be performed to ensure the apparatus is functioning properly before proceeding with the extraction.

6.2.9 ZHE Extract Collection Devices – TEDLAR® bags or glass, stainless steel, or PTFE gas-tight syringes to collect the initial liquid phase and the final TCLP extract from the ZHE device.

6.2.10 ZHE Extraction Fluid Transfer Devices - Capable of transferring the extraction fluid into the ZHE vessel without changing the nature of the extraction fluid (e.g., a positive displacement or peristaltic pump, a gas-tight syringe).

6.2.11 pH meter with reference electrode accurate to at least ±0.05 units at 25°C. The pH meter/probe should be equipped with a means of temperature compensation either manually or automatically.

6.2.12 Magnetic stirrer with fluoropolymer-coated stir bar.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-06). Use this water for all reagents, standards, and dilutions.

7.1.2 Hydrochloric acid, (1N) - Add 83.5 mL conc. hydrochloric acid, 32-38% (specific gravity 1.19) to 400 mL reagent water and dilute to 1 L.

7.1.3 Nitric acid, (1N) – Add 62 mL conc. nitric acid, 67-70% (specific gravity 1.41) to 400 mL reagent water and dilute to 1 L.

7.1.4 Sodium Hydroxide, (1N) - Add 40 g reagent grade NaOH to 400 mL reagent water and dilute to 1 L.

7.1.5 Glacial Acetic Acid – reagent grade.

7.1.6 Sulfuric Acid/Nitric Acid, (60/40 weight percent mixture) – Cautiously mix 60 g (approximately 33 mL)of conc. sulfuric acid, 95-98% (specific gravity 1.84) with 40 g (approximately 28 mL) conc. nitric acid. The Contractor may prepare a more diluted version of this reagent for ease in adjusting extraction fluid pH.

7.1.7 Extraction Fluids

Extraction fluids should be monitored for impurities and the pH checked prior to use. If impurities are found or the pH is not within specifications, the fluid shall be discarded and fresh extraction fluid prepared. Solutions are unbuffered and exact pH may not be attained.

7.1.7.1 TCLP Extraction Fluid #1 – Add 5.7 mL of glacial acetic acid to 500 mL of reagent water, add 64.3 mL of 1N NaOH solution, and dilute to 1 L. The pH of this solution should be 4.93 ±0.05. For ZHE, use TCLP Fluid #1.

7.1.7.2 TCLP Extraction Fluid #2 (do not use Fluid #2 for ZHE) – Dilute 5.7 mL of glacial acetic acid with reagent water to a final volume of 1 L. The pH of this solution should be 2.88 ±0.05.

7.1.7.3 SPLP Extraction Fluid #1 – Use this solution with samples from east of the Mississippi River. Add sufficient 60/40 Sulfuric/Nitric acid solution to reagent water until the pH is 4.20 ±0.05.

7.1.7.4 SPLP Extraction Fluid #2 - Use this solution with samples from west of the Mississippi River. Add sufficient 60/40 Sulfuric/Nitric acid solution to reagent water until the pH is 5.00 ±0.05.

7.1.7.5 SPLP Extraction Fluid #3 – This fluid is reagent water and is used to determine volatiles leachability.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All aqueous/water and soil/sediment samples must be collected in glass or polyethylene containers. ZHE samples must be collected in PTFE-lined septum-capped vials. All aqueous/water and soil/sediment samples must be iced or refrigerated at a temperature of ≤6°C, but not frozen, from the time of collection until receipt at the laboratory.

8.2 Sample Storage

All aqueous/water and soil/sediment samples must be stored at ≤6°C, but not frozen, from the time of sample receipt until preparation. ZHE samples should be opened just prior to extraction to minimize the loss of volatiles.

8.2.1 Unused Sample Storage

Following preparation for percent solids determination or sample characterization, the remaining unused portion of aqueous/water and soil/sediment samples must be returned to storage at a temperature of ≤6°C, but not frozen, and protected from light. After all applicable leaching procedures and/or extractions have been completed, the remaining unused portion of the aqueous/water and soil/sediment samples must be stored within the laboratory until 60 days after delivery of a complete, reconciled data package to the U.S. Environmental Protection Agency (EPA). The Contractor may store these samples at room temperature. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 Leachate Sample Storage

The remaining unused portion of the preserved TCLP or SPLP leachates must be stored within the laboratory until 180 days after delivery of a complete, reconciled data package to the EPA. The Contractor may store these samples at room temperature.

8.2.3 Container Storage

The Contractor shall retain the empty sample containers for 60 days after delivery of a complete, reconciled data package to the EPA. The sample container may be photographed in lieu of retention.

8.2.4 Temperature Records

8.2.4.1 The temperature of all sample and sample extract storage refrigerators and freezers shall be recorded daily.

8.2.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

8.2.4.3 Corrective action SOPs shall be posted on the refrigerators and freezers.

8.3 Contract Required Holding Time

The holding time for ZHE extraction of volatile soil samples or waste samples containing $\geq$ 0.5% solids is 10 days from Validated Time of Sample Receipt (VTSR). The holding time for TCLP/SPLP extraction of non-volatile soil samples or waste samples containing $\geq$ 0.5% solids is 10 days from VTSR. TCLP/SPLP holding time for aqueous samples is 5 days from VTSR.

9.0 CALIBRATION AND STANDARDIZATION

Not applicable.

10.0 PROCEDURE

10.1 Percent Solids Determination

Percent Solids determination is based on Standard Method (SM) 2540G, approved 1997.

10.1.1 Transfer 5–10 g of sample to a tared weighing boat and record the total weight to the nearest 0.01 g. Sample handling and drying should be conducted in a well-ventilated area.

10.1.2 Dry the sample in an oven maintained at 105°C (±5°C) for at least 12 hours, but no more than 24 hours. At the start of drying and at the end of drying, record the oven temperature and date/time.

10.1.3 Remove the sample from the oven and allow it to cool in a desiccator.

10.1.4 Weigh the sample to the nearest 0.01 g and calculate the percent solids using Equation 1. This value will be used for calculating analytical concentration on a dry weight basis.

EQ. 1 Percent Solids

$$\% \text{ Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

10.1.5 For samples scheduled for semivolatile, pesticide, or aroclor analysis, if the sample contains less than 30% solids, the Contractor shall notify the Sample Management Office (SMO) immediately of the samples impacted. SMO will contact the EPA Region for instructions. This requirement does not apply to 7-day turnaround or Preliminary Results samples. The EPA Region may require the Contractor to do any of the following:

- Use a higher mass of soil/sediment sample (up to 50 g)
- Separate the phases by centrifugation or settling and analyze one or more of the phases separately. SMO will provide EPA Sample Numbers for the additional phases, if required.
- Do not analyze the sample

10.2 TCLP and SPLP Extraction Procedures

Extraction methods are based on EPA SW-846 Method 1311, Toxicity Characteristic Leaching Procedure (TCLP), Revision 0, July 1992 or EPA SW-846 Method 1312, Synthetic Precipitation Leaching Procedure (SPLP), Revision 0, September 1994.

TCLP vessel and devices must be free of contaminants and cleaned between TCLP samples. Testing procedures shall be performed to ensure the apparatus is functioning properly before proceeding with the extraction.

10.2.1 Preliminary Evaluation

Perform preliminary evaluation on a minimum 100 g sample aliquot. This aliquot will not undergo extraction. These preliminary evaluations include: (1) determination of percent solids by pressure filtration; (2) determination of whether the sample contains insignificant (<0.5%) solids and is therefore its own extract after filtration; (3) determination of whether the solid portion of the sample requires particle size reduction; and for TCLP samples, (4) determination of the appropriate extraction fluid.

10.2.1.1 Preliminary determination of percent solids – For these samples, percent solids is defined as that fraction of a sample (as a percentage of the total sample) from which no liquid can be forced out by applied pressure.

10.2.1.1.1 If a sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids), proceed to extraction.

10.2.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required.

10.2.1.1.2.1 Pre-weigh the filter and the container that will receive the filtrate.

10.2.1.1.2.2 Assemble the filter holder and filter per the manufacturer's instructions. Place the filter on the support screen and secure.

10.2.1.1.2.3 Weigh out at least 100 g of the sample and record the weight.

10.2.1.1.2.4 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered, followed by filtration of the solid portion of the sample through the same filtration system.

10.2.1.1.2.5 Quantitatively transfer the sample to the filter holder (both liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at a temperature of ≤6°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering. If waste material (greater than 1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 10.2.1.1.2.7 to determine the weight of sample that will be filtered.

10.2.1.1.2.6 Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to

move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration. Note that instantaneous application of high pressure can damage the filter and may cause premature plugging.

10.2.1.1.2.7 The material retained on the filter is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase. Note that certain oily wastes and paint wastes will contain material that appears to be a liquid. However, this material may not filter under pressure filtration. In this case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

10.2.1.1.2.8 Determine the weight of the liquid phase by subtracting the weight of the filtrate container from the total weight of the filtrate-filled container. Determine the weight of the solid phase by subtracting the weight of the liquid phase from the total weight of the sample. Record the weights of the liquid and solid phases. Calculate the percent solids using the following equation:

EQ. 2 Extraction Percent Solids

$$\% \text{ Solids} = \frac{\text{Weight of solid}}{\text{Total Weight of Sample}} \times 100$$

10.2.1.1.2.9 If the percent solids determined above is equal to or greater than 0.5%, then determine if the solid material requires particle size reduction.

10.2.1.1.2.10 If it is noticed that a small amount of the filtrate is entrained in wetting of the filter, remove the solid phase and filter from the filtration apparatus. Dry the filter and solid phase at 100°C (±20°C) until two successive weighings yield the same value (within ±1%) and record the weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

10.2.1.1.2.11 Calculate the Percent Dry Solids using the following equation:

EQ. 3 Percent Dry Solids

$$\text{Percent Dry Solids} = \frac{(\text{Wt. of dry waste and filter}) - \text{Tared wt. of filter}}{\text{Initial wt. of waste}} \times 100$$

10.2.1.2 If the percent dry solids is less that 0.5%, then treat the filtrate as the extract. Store this extract at a temperature of ≤6°C.

10.2.1.3 To determine if particle size reduction is required, using a fresh portion of sample, examine the solid portion for particle size. If the material is less than 1 centimeter (cm) in its narrowest dimension (i.e., is capable of passing through a 9.5 mm standard sieve), no particle size reduction is required. Otherwise, prepare the solid portion for extraction by crushing, cutting, or grinding the sample to meet the above criterion.

10.2.1.3.1 Special precautions must be taken when processing solid samples for organic volatiles extraction. Wastes and appropriate reduction equipment should be refrigerated, if possible, to ≤ 6°C prior to particle size reduction. The means used to affect particle size reduction must not generate heat. If reduction the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be minimized.

10.2.1.4 For samples that are scheduled for extraction with percent solids greater than 0.5%, the appropriate extraction fluid is determined as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1. Therefore, if TCLP extraction only for volatiles is required, please proceed to Section 10.2.3.

10.2.1.4.1 For samples scheduled for TCLP extraction of non-volatile constituents, remove a small aliquot of the sample and reduce the particle size to less than 1 mm. Transfer 5 g of this material to a 500 mL beaker or Erlenmeyer flask.

10.2.1.4.1.1 Add 96.5 mL of reagent water, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH.

10.2.1.4.1.1.1 If the pH is less than 5.0, use TCLP Extraction Fluid #1 (Section 7.1.7.1).

10.2.1.4.1.1.2 If the pH is greater than or equal to 5.0, add 3.5 mL 1N HCl (Section 7.1.2), slurry briefly, cover with the watchglass, and heat to 50°C for 10 minutes. Let the solution cool to room temperature and measure the pH. If the pH is less than 5.0, use TCLP Extraction Fluid #1 (Section 7.1.7.1), otherwise use TCLP Extraction Fluid #2 (Section 7.1.7.2).

NOTE: DO NOT USE FLUID #2 FOR ZHE SAMPLES.

10.2.1.4.2 Use the SPLP extraction fluid appropriate to the information provided on the scheduling document.

10.2.1.4.2.1 For soil samples from east of the Mississippi River, use SPLP Extraction Fluid #1. For samples west of the Mississippi River, use SPLP Extraction Fluid #2.

10.2.1.4.2.2 For samples scheduled for SPLP ZHE extraction, use SPLP Extraction Fluid #3 (Section 7.1.7.5).

10.2.2 TCLP Sample Extraction

Follow this procedure for TCLP leachates that will be analyzed for non-volatile organic target analytes. For volatile organic analysis, use ZHE in Section 10.2.3.

10.2.2.1 A minimum sample size of 100 g is required; however, enough solids shall be extracted to yield a sufficient volume of extract to support all required analyses. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample, and whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid. See Section 10.2.2.3 to determine the approximate amount of extract that will be generated for a given mass with the percent solids determined in Section 10.2.1.1.2.7.

10.2.2.1.1 If the sample is 100% solids, then weigh out 100 g of sample and proceed to Section 10.2.2.3.

10.2.2.1.2 If the sample is less than 0.5% solids, filter enough sample to yield a sufficient volume of extract to support all required analyses if the preliminary percent solids determination did not yield sufficient volume.

10.2.2.1.3 For multiphasic samples with percent solids greater than or equal to 0.5%, but less than 100%, weigh out enough sample to generate a sufficient volume of extract to support all required analyses. Filter the sample using the procedure described in Section 10.2.1. Store the filtrate at ≤6°C, but not frozen.

10.2.2.2 Prepare the solid portion of the sample for extraction by reducing the particle size as described in Section 10.2.1.3. Quantitatively transfer the material into an extractor bottle and include the filter used to separate the initial liquid from the solid phase.

10.2.2.3 Determine the amount of extraction fluid to add to the extractor bottle using the following equation:

EQ. 4 Weight of Extraction Fluid

$$\text{Weight of Extraction Fluid} = \frac{20 \times \%\ \text{solids} \times \text{Weight of sample filtered}}{100}$$

10.2.2.4 Add this amount of the appropriate extraction fluid (Section 10.2.1.4) to the extractor bottle. Close the bottle tightly (Teflon tape may be used to ensure a tight seal) and secure it in the rotary agitation apparatus. Rotate the samples at 30 rpm (±2 rpm) for 18 hours (±2 hours). Maintain a temperature of 23°C (±2°C) in room where extraction is performed.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of samples (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

10.2.2.4.1 Following the 18-hour extraction, separate the material in the extractor bottle into its component liquid and solid phase by filtering through a new glass filter as described in Section 10.2.1.1. For the final filtration of the extract, the glass fiber filter may be changed as necessary during filtration.

10.2.2.4.2 If the sample was 100% solids, this filtered liquid is the extract.

10.2.2.4.3 For multiphasic samples, combine this extract with the filtrate generated in Section 10.2.2.1.3 if the two liquids are miscible. If the two liquids are not miscible, they shall be prepared and analyzed separately and the results combined.

10.2.2.4.4 Record the pH of the final extract. If organic and inorganic analyses are required on the sample, separate approximately 3/4 of the sample extraction fluid for organic analysis and store in an amber glass bottle.

10.2.2.4.5 DO NOT ACIDIFY OR PRESERVE ANY PORTION OF AN EXTRACT INTENDED FOR ORGANIC ANALYSIS. Do not acidify any non-aqueous portion of the sample.

CAUTION: Nitric acid should not be mixed with organic compounds because of the possibility of dangerous reaction.

10.2.3 Zero Headspace Extraction

Use ZHE for the TCLP sample extraction for analysis of volatile organic target analytes. For non-volatile organic target analytes, follow the TCLP Sample Extraction procedure in Section 10.2.2. Follow manufacturer's instructions for operation of the ZHE apparatus.

10.2.3.1 Maintaining the ZHE Apparatus

10.2.3.1.1 The ZHE vessel and devices must be free of contaminants and cleaned between TCLP samples. Manufacturer-recommended testing procedures shall be performed to ensure the apparatus is functioning properly before proceeding with the extraction.

10.2.3.1.2 Disassemble and clean the ZHE parts using laboratory detergent. Rinse with methanol and water until there is no visible contamination when surfaces are wiped with a clean paper towel. Bake ZHE metal parts overnight in an oven at 170°C.

10.2.3.1.3 Reassemble the ZHE and check that it is clean by adding 250 mL of laboratory reagent water, pressurizing the unit, and tumbling for about 1 hour, making sure it is pressure tight. Collect the laboratory reagent water and analyze as a check sample by Gas Chromatography/Mass Spectrometry (GC/MS) to determine if the ZHE is clean. If any target analytes are detected, disassemble the ZHE and repeat the cleaning.

10.2.3.1.4 Record the date, time, and results of each cleaning check in a ZHE laboratory log.

10.2.3.1.5 Disassemble, clean, and check the ZHE, and allow the parts to air dry. Cover the ZHE components in aluminum foil and store in the volatile organics analysis laboratory until use.

10.2.3.1.6 Check the ZHE for leaks after every extraction. Pressurize the ZHE to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the ZHE device does not have a pressure gauge, submerge the pressurized ZHE in water and check for air leaks. If the ZHE is leaking, check all fittings, inspect O-rings, and replace if necessary. Retest the device. If the leakage cannot be solved, the ZHE should be taken off-line and sent to the manufacturer for repairs.

10.2.3.1.7 The piston within the ZHE device must be movable with approximately 15 psi or less. If more than 15 psi is required to move the piston, replace the O-rings. If this does not free up the piston, the ZHE should be taken off-line and sent to the manufacturer for repairs.

10.2.3.2 Zero Headspace Extraction of Volatile Compounds

10.2.3.2.1 The ZHE has a 500 mL internal capacity and accommodates a maximum of 25 g solid based on the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase (fraction of sample from which no additional liquid may be forced out when 50 psi is applied).

10.2.3.2.2 Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

10.2.3.2.3 Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary.

10.2.3.2.4 Pre-weigh the evacuated filtrate collection container and set aside.

10.2.3.2.5 Place the ZHE piston within the body of the ZHE. Adjust the height of the piston to minimize the travel distance once the ZHE is charged with the sample. Secure bottom flanges. Secure the glass fiber filter between the support screens and set top flanges according to manufacturer's instructions.

10.2.3.2.6 If the sample is 100% solids, then weigh a maximum of 25 g and proceed to Section 10.2.3.2.9.

10.2.3.2.7 If the sample is less than 0.5% solids, filter enough sample to yield a sufficient volume of extract to support all volatile analyses required.

For samples containing ≥0.5% solids, use the percent solids determination in Section 10.2.1.1.2.7 to determine the sample size to add to the ZHE using the following equation:

EQ. 5 Sample Size

$$\text{Weight} = \frac{25}{\%\ \text{solids}} \times 100$$

10.2.3.2.8 For multiphasic samples, weigh out enough sample to generate a sufficient volume of extract to support all required analyses. Filter the sample using the procedure described in Sections 10.2.1.1.7 – 10.2.1.1.9. Store the filtrate at a temperature of ≤6°C.

10.2.3.2.9 Prepare the solid portion of the sample for extraction by reducing the particle size as described in Section 10.2.1.3.

10.2.3.2.10 Determine the amount of TCLP Extraction Fluid #1 to add to the ZHE using the following calculation:

EQ. 6 Weight of Extraction Fluid

$$\text{Weight of Extraction Fluid} = \frac{20 \times \%\ \text{solids} \times \text{Weight of sample filtered}}{100}$$

10.2.3.2.11 Quickly transfer the entire sample (liquid and solid phases) quantitatively to the ZHE. Secure the filter and support screens onto the top flange of the device. Secure the top flange. Tighten all ZHE fittings according to the manufacturer's instructions. Place the ZHE device in vertical position with the gas inlet/outlet flange on the bottom. Do not attach the extract collection device to the top plate at this stage.

10.2.3.2.12 Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At

the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

10.2.3.2.13 Attach the evacuated pre-weighed filtrate collection container (Section 10.2.3.2.4) to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

10.2.3.2.14 The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase.

NOTE: Oily samples and some paint samples may contain material that appears to be a liquid. If after applying pressure filtration the material will not filter, it shall be defined as a solid and is carried through the TCLP extraction as a solid. If the original sample contained <0.5% dry solids, this filtrate shall be defined as the TCLP extract and analyzed directly.

10.2.3.2.15 With the ZHE device in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. Add the appropriate amount of the TCLP Extraction Fluid #1 to solid material within the ZHE device.

10.2.3.2.16 The line used must contain fresh TCLP Extraction Fluid #1 and shall be pre-flushed with fluid to eliminate any air in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue introducing extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

10.2.3.2.17 Close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. The bleeding must be done quickly and stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

10.2.3.2.18 Secure the ZHE device in the rotary agitation apparatus. Rotate the samples at 30 rpm (±2 rpm) for 18 hours (±2 hours). Maintain a temperature of 23°C (±2°C) in room where extraction is performed.

10.2.3.2.19 Following the 18-hour extraction period, check that the ZHE is not leaking by quickly opening and closing the gas inlet/outlet valve, and noting the escape of gas. There will be no escape of gas if the device is leaking. If the ZHE device was leaking, perform the extraction again with a new sample.

10.2.3.2.20 If the pressure within the device has been maintained, the material in the extractor vessel shall be once again separated into its component liquid and solid phases. If the sample contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container holding the initial liquid phase of the sample.

10.2.3.2.21 A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed. All extracts shall be filtered and collected in the collection container if the extract is multiphasic, or if the sample contained an initial liquid phase.

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

If the original sample contained no initial liquid phase, the filtered liquid material obtained from ZHE procedure shall be defined as the TCLP extract. If the sample contained an initial liquid, the filtered liquid material obtained from the ZHE procedure and the initial liquid phase shall be collectively defined as the TCLP extract.

10.2.3.2.22 Following collection of the TCLP extract, immediately prepare the extract for analysis, and store with minimal headspace at a temperature of ≤6°C until analyzed.

If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

EQ. 7 Final Concentration

$$\text{Final Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

WHERE,

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

10.2.4 SPLP Sample Extraction

The Contractor shall follow the procedures in Section 10.2.2 using the appropriate extraction fluid specified in Section 10.2.1.4.2.

11.0 DATA ANALYSIS AND CALCULATIONS

See individual procedures in Section 11.0 for data analysis and calculations.

12.0 QUALITY CONTROL

12.1 Leachate Extraction Blank

12.1.1 The Leachate Extraction Blank (LEB) shall contain all the reagents and in the same volumes as used in extracting the samples. The LEB shall be carried through the complete extraction procedure.

12.1.2 At least one LEB, consisting of reagent water processed through the extraction procedure, shall be extracted with every SDG scheduled for TCLP or SPLP.

12.1.3 Each Complete SDG File (CSF) shall contain the results of all LEB analyses associated with the samples in that SDG.

12.1.4 The LEB(s) result(s) is (are) to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination.

12.2 Summary of Quality Control Operations

The Quality Control (QC) operations performed are summarized in Section 17.0, Table 1 – Quality Control Operations.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 13.0 in Exhibit D - Introduction to Organic Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 14.0 in Exhibit D - Introduction to Organic Analytical Methods.

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 1311, Revision 0, Update III, July 1992.

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 1312, Revision 0, Update III, September 1994.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QUALITY CONTROL OPERATIONS

QC Operation	Frequency
Leachate Extraction Blank (LEB)	For each SDG, an LEB for each extraction procedure.

EXHIBIT D

TRACE CONCENTRATIONS OF
VOLATILE ORGANIC COMPOUNDS ANALYSIS

THIS PAGE INTENTIONALLY LEFT BLANK

Exhibit D – Trace Concentrations of
Volatile Organic Compounds Analysis

Table of Contents

Exhibit D – Trace Concentrations of
Volatile Organic Compounds Analysis

Table of Contents

1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze water samples containing trace concentrations of the volatile analytes listed in the Target Analyte List (TAL) for trace volatiles in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits. The majority of the samples are expected to be obtained from drinking water and well/groundwater type sources around Superfund sites. The method is based on the U.S. Environmental Protection Agency (EPA) Method 524.2. The sample preparation and analysis procedures included in this method are based on purge-and-trap (P/T) Gas Chromatograph/Mass Spectrometer (GC/MS) techniques.

1.2 Problems that have been associated with the following analytes analyzed using this method include:

- Chloromethane, vinyl chloride, bromomethane, and chloroethane may display peak broadening if the analytes are not delivered to the GC column in a tight band.
- Acetone, hexanone, 2-butanone, and 4-methyl-2-pentanone have poor purge efficiencies and may be lost if purge flow is too slow.
- 1,1,1-Trichloroethane and all of the dichloroethanes may dehydrohalogenate during storage or analysis.
- Tetrachloroethane and 1,1-dichloroethane may be degraded by contaminated transfer lines in P/T systems and/or active sites in trapping materials.
- Chloromethane and other gases may be lost if the purge flow is too fast.
- Bromoform is one of the analytes most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by the tuning of 4-bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio within the specified Quality Control (QC) limits may improve bromoform response.
- Due to the lower quantitation limits required by this method, extra caution must be exercised when identifying compounds.

2.0 SUMMARY OF METHOD

2.1 Water

An inert gas is bubbled through a 25 milliliter (mL) sample contained in a specially designed purging chamber at ambient temperature. Higher purge temperatures may be used, provided that all technical acceptance criteria are met for all standards, samples, and blanks. The same purge conditions must be used for all associated standards, samples, and blanks. The purgeable compounds are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeable compounds are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a GC capillary column. The GC is temperature-programmed to separate the purgeable compounds, which are then detected with an MS.

2.2 Soil/Sediment

Not applicable to this method.

2.3 Wipes

Not applicable to this method.

2.4 Waste

Not applicable to this method.

2.5 Non-Target Compounds

Non-target compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the NIST (2011 release or later), Wiley (2011 release or later), or equivalent mass spectral library. Non-target compounds are quantitated by comparing the area response from the total Reconstructed Ion Chromatogram (RIC) for the non-target compound peaks to the area response produced by the nearest internal standard compound. A Relative Response Factor (RRF) of 1 is assumed.

3.0 DEFINITIONS

See Exhibit G – Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

4.1.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing laboratory method and instrument blanks as described in Section 12.0. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.1.2 Samples can be contaminated by diffusion of purgeable organics (particularly methylene chloride, fluorocarbons, and other common laboratory solvents) through the septum seal into the sample during storage and handling. Therefore, these samples must be stored separately from other laboratory samples and standards, and must be analyzed in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis.

4.1.3 Contamination by carryover can occur whenever high-level and trace-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it must either be followed by analysis of an instrument blank, or the next sample must be closely monitored to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required.

4.1.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to

determine the presence of methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all Gas Chromatography (GC) carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken. At the time of sample receipt, the Contractor must prepare a 40 mL VOA vial containing reagent water to be stored as a storage blank with each group of samples (Section 12.1.4).

4.2 Matrix Interferences

Matrix interferences may be caused by compounds that are purged or co-extracted from the sample. The extent of matrix interferences will vary considerably depending on the nature of the site being sampled.

5.0 SAFETY

See Section 12.0 of Exhibit D – Introduction to Organic Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 General Laboratory Equipment

6.1.1 Bottle - 15 milliliters (mL), screw-cap, with PTFE cap liner.

6.1.2 Pasteur Pipettes - Disposable.

6.1.3 pH Paper - Wide range.

6.1.4 Syringes - 25 mL, gas-tight with shut-off valve.

6.1.5 Micro syringes – 10 microliters (µL) and larger, 0.006 inch [0.15 millimeter (mm)] ID needle. All micro syringes shall be visually inspected and documented monthly.

6.1.6 Syringe Valve - Two-way, with Luer ends (three each), if applicable to the purging device.

6.1.7 Vials and Caps - Assorted sizes.

6.1.8 Volumetric Flasks - Class A with ground-glass stoppers.

6.2 Glassware/Extraction/Cleanup Equipment

Not applicable to this method.

6.3 Analytical Instrumentation

6.3.1 Gas Chromatograph

The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout desorption and temperature program operations. The system must include or be interfaced to a P/T system as specified in Section 6.3.4 and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants, or flow controllers with rubber components, are not to be used.

6.3.2 Gas Chromatography Columns

Recommended column: Minimum length 30 meter (m) x 0.53 mm ID fused silica wide-bore capillary column with a 6% Cyanopropylphenyl 94% Dimethyl Polysiloxane phase having a 3 micrometer (µm) film thickness (i.e., VOCOL, Rtx®-502.2, DB-624, Rtx®-624, CP-Select 624CB, or equivalent fused silica wide-bore capillary column). A description of the GC column used for analysis shall be provided in the SDG Narrative. Packed GC columns cannot be used.

The column shall be able to accept up to 1000 nanograms (ng) of each analyte listed in Exhibit C- Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits without becoming overloaded.

6.3.2.1 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits.
- The analytical results generated using the column meet the initial calibration and continuing calibration verification (CCV) technical acceptance criteria (Sections 9.3.5 and 9.4.5) and the CRQLs listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits. Sufficient chromatographic resolution is achieved when the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights.
- The column provides equal or better resolution of the analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits than the columns listed in Section 6.3.2.
- As applicable, follow the manufacturer’s instructions for use of its product.

6.3.2.1.1 The Contractor must maintain documentation that the column met the criteria in Section 6.3.2.1. The minimum documentation is as follows:

6.3.2.1.1.1 Manufacturer provided information concerning the performance characteristics of the column.

6.3.2.1.1.2 Reconstructed ion chromatograms (RICs) and data system reports generated on the GC/MS used for Contract Laboratory Program (CLP) analyses:

- From instrument blanks that demonstrate that there are no contaminants that interfere with the volatile analysis when using the alternate column; and
- From initial calibration and CCV standards analyzed using the alternate column.

6.3.2.1.2 Based on the Contractor-generated data described above, the Contractor shall complete a written comparison/review, signed by the Laboratory Manager, certifying that:

- The alternate column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the volatile CRQLs;
- The high-point initial calibration standard analysis was not overloaded; and
- The column does not introduce contaminants that interfere with the identification and/or quantitation of analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits.

6.3.2.1.3 The documentation must be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional Laboratory Contracting Officer Representative (COR).

6.3.3 Mass Spectrometer

The MS must be capable of scanning from 35-300 atomic mass units (u) every 2 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the BFB GC/MS performance check technical acceptance criteria in Table 2 – 4-Bromofluorobenzene Key Ions and Abundance Criteria, when 50 ng of BFB is injected through the GC inlet. The instrument conditions required for the acquisition of the BFB mass spectrum are given in Section 9.2.4.

NOTE: To ensure sufficient precision of mass spectral data, the MS scan rate should allow acquisition of at least five spectra while a sample compound elutes from the GC. The purge-and-trap GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis. The instrument must be vented to the outside of the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.3.3.1 Gas Chromatograph/Mass Spectrometer Interface

Any GC/MS interface may be used that gives acceptable calibration points at 12.5 ng or less per injection for each of the purgeable non-ketone target analytes and Deuterated Monitoring Compounds (DMCs), and achieves all acceptable performance criteria. GC/MS interfaces constructed of all-glass or glass-lined materials are

recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.3.4 Purge-and-Trap Device

The P/T device consists of three separate pieces of equipment: the sample purge chamber, the trap, and the desorber. The analyst either manually or automatically (through an automated P/T device separate or integral with the GC) samples an appropriate volume (e.g., 25 mL) from the vial; adds DMCs, matrix spikes (MS), and internal standards to the sample; and transfers the sample to the purge device. The device also purges the volatile organic compounds (VOCs) using an inert gas stream and traps the released VOCs for subsequent desorption into the GC. Such systems shall meet the following specifications:

6.3.4.1 The sample purge chamber must be designed to accept 25 mL samples with a water column at least 10 centimeters (cm) deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.

6.3.4.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inches (2.667 mm). The trap must be packed to contain (starting from the inlet) 0.5 cm silanized glass wool, and the following minimum lengths of adsorbent:

- 8 cm of 2,6-diphenylene oxide polymer (60/80 mesh chromatographic grade Tenax GC or equivalent).
- 1 cm methyl silicone packing, 3.0% OV-1 on Chromasorb W, 60/80 mesh (or equivalent).
- 8 cm of silica gel, 35/60 mesh (or equivalent).
- 7 cm of coconut charcoal.

6.3.4.3 Alternate sorbent traps may be used if:

- The trap packing materials do not introduce contaminants that interfere with identification and quantitation of the analytes listed in Exhibit C - Organic Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs), Table 1 – Trace Volatiles Target Analyte List and Contract Required Quantitation Limits;
- The analytical results generated using the trap meet the initial calibration and CCV technical acceptance criteria listed in the analytical method and the CRQLs listed in Exhibit C - Organic Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs), Table 1 – Trace Volatiles Target Analyte List and Contract Required Quantitation Limits; and
- The trap must be capable of accepting up to 1000 ng of each analyte listed in Exhibit C - Organic Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs), Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits without becoming overloaded.

6.3.4.3.1 Before use of any trap other than the one specified in Section 6.3.4.2, the Contractor must first meet the criteria listed in Section 6.3.4.3. Once this has been demonstrated, the Contractor must document its use in each SDG Narrative by specifying the trap composition (packing material/brand name, amount of packing material). Other sorbent traps include, but are not limited to: Tenax/Silica Gel/Carbon Trap from EPA Method 524.2, Tenax - GC/Graphpac-D Trap (Alltech) or equivalent, and Vocarb 4000 Trap (Supelco) or equivalent.

6.3.4.3.2 The Contractor must maintain documentation that the alternate trap meets the criteria listed in Section 6.3.4.3. The minimum documentation requirements are as follows:

6.3.4.3.2.1 Manufacturer-provided information concerning the performance characteristics of the trap.

6.3.4.3.2.2 RICs and data system reports generated on the Contractor's GC/MS used for CLP analyses:

- From instrument blank analyses that demonstrate that there are no contaminants that interfere with the volatile analysis when using the alternate trap; and
- From initial calibration and CCV standards analyzed using the trap specified in Section 6.3.4.2.

6.3.4.3.2.3 Based on Contractor-generated data described above, the Contractor must complete a written comparison/review that has been signed by the Laboratory Manager, certifying that:

- The alternate trap performance meets the technical acceptance criteria listed in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the volatile CRQLs;
- The high-point initial calibration standard analysis was not overloaded; and
- The alternate trap materials do not introduce contaminants that interfere with the identification and/or quantitation of the analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits.

6.3.4.3.2.4 The documentation must be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request of the EPA Regional Laboratory COR.

6.3.4.3.2.5 A description of the trap used for analysis shall be provided in the SDG Narrative.

6.3.4.4 The P/T apparatus may be assembled as a separate unit or be an integral unit coupled with a GC.

6.3.4.5 The desorber shall be capable of rapidly heating the trap to the desorb temperature recommended for the trap in use. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bake-out mode.

6.4 Data System/Data Storage

A computer system must be interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching of any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows comparing sample spectra against reference library spectra. The NIST (2011 release or later), Wiley (2011 release or later), or equivalent mass spectral library shall be used as the reference library. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

7.0 REAGENTS AND STANDARDS

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit D – Introduction to Organic Analytical Methods, Section 4.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1 Reagents

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the CRQL for each analyte of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g [1 pound (lb)] of activated carbon.

7.1.1.2 Reagent water may also be generated using a water purification system.

7.1.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle, seal with a PTFE-lined septum, and cap.

7.1.2 Methanol - High Performance Liquid Chromatography (HPLC) quality or equivalent - Each lot of methanol used for analysis under the contract must be purged with nitrogen and must be demonstrated to be free of contaminants that interfere with the measurement of purgeable analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits.

7.2 Standards

7.2.1 Stock Standard Solutions

Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be in methanol from pure standard materials or purchased as pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if standard has degraded or evaporated.

7.2.2 Working Standards

7.2.2.1 Initial and Continuing Calibration Solutions

Prepare working calibration standard solution(s) containing all of the purgeable target analytes (Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits) in methanol. Prepare fresh calibration standard solution(s) every month, or sooner if the solution has degraded or evaporated.

NOTE: The Contractor may prepare a calibration standard containing all of the non-ketones and a separate standard containing ketones.

7.2.2.1.1 Add a sufficient amount of each working standard to a 25 mL aliquot of reagent water to produce the desired calibration standard concentrations listed in Section 7.2.2.1.2 or 7.2.2.1.4.

7.2.2.1.2 Prepare five aqueous initial calibration standard solutions containing all of the purgeable target analytes, and the DMCs at the suggested following levels: all non-ketone target analytes and associated DMCs at 0.50, 1.0, 5.0, 10 and 20 µg/L (in Table 3 – Trace Volatile Deuterated Monitoring Compounds and the Associated Target Analytes); all ketones and their associated DMCs (see Table 3 - Trace Volatile Deuterated Monitoring Compounds and the Associated Target Analytes) at 5.0, 10, 50, 100, and 200 µg/L. All three xylene isomers (o-, m-, and p-xylene) must be present in the calibration standards. The o-xylene calibration standard concentrations must be at 0.50, 1.0, 5.0, 10 and 20 µg/L, while the concentration of the m- plus the p-xylene isomers must total 0.50, 1.0, 5.0, 10, and 20 µg/L.

7.2.2.1.3 Calibration standards must be prepared in a volumetric flask or in the syringe used to inject the standard into the purging device.

7.2.2.1.4 For CCV (opening and closing CCVs), the standard shall be at a concentration equivalent to the mid-level calibration standards: 5.0 µg/L for non-ketones and 50 µg/L for ketones.

7.2.2.1.5 The methanol contained in each of the aqueous calibration standards must not exceed 1% by volume.

7.2.2.2 Instrument Performance Check Solution

Prepare the instrument performance check solution containing BFB in methanol. If the BFB solution is added to the mid-level calibration standard (5.0 µg/L for non-ketones and 50 µg/L for ketones), add a sufficient amount of BFB to result in a 2.0 µg/L concentration of BFB (50 ng on-column). The BFB must be analyzed

using the same GC and MS analytical conditions as is used for the calibration analysis.

7.2.2.3 Deuterated Monitoring Compound Spiking Solution

7.2.2.3.1 Prepare a DMC spiking solution in methanol (or in deuterated methanol) containing the compounds listed in Table 3 - Trace Volatile Deuterated Monitoring Compounds and the Associated Target Analytes.

7.2.2.3.2 DMCs are to be added to each sample and blank, as well as initial calibration standards and CCV standards.

7.2.2.3.3 For samples and blanks, add sufficient amount of the DMC spiking solution to each 25 mL of sample to result in 0.125 µg for each non-ketone DMC and 1.25 µg for each ketone DMC.

7.2.2.3.4 For calibration standards, add sufficient amounts of the DMC spiking solution to each 25 mL aliquot of calibration standard to result in the concentrations listed in Section 7.2.2.1.2 (initial calibration) and Section 7.2.2.1.4 (CCV).

7.2.2.3.5 Prepare a fresh DMC spiking solution every month, or sooner if the standard has degraded or concentrated.

7.2.2.4 Matrix Spiking Solution

If Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis is requested at the time of scheduling, prepare a spiking solution in methanol that contains the following analytes at a concentration of 12.5 µg/mL: 1,1-dichloroethene; trichloroethene; chlorobenzene; toluene; and benzene. Prepare fresh spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.2.5 Internal Standard Spiking Solution

Prepare an internal standard spiking solution containing 1,4-dichlorobenzene-d_4, chlorobenzene-d_5, and 1,4-difluorobenzene in methanol. Add a sufficient amount of the internal standard spiking solution to 25 mL of samples including MS/MSDs, blanks, and calibration standards to result in a 5.0 µg/L concentration or the addition of 0.125 µg for each internal standard. Prepare a fresh internal standard spiking solution every month, or sooner if the standard had degraded or evaporated.

7.2.3 Storage of Standard Solutions

7.2.3.1 Store the stock standards in PTFE-sealed screw-cap bottles with zero headspace at -10°C to -20°C.

7.2.3.2 Aqueous standards may be stored for up to 24 hours if held in PTFE-sealed screw-cap vials with zero headspace at ≤6°C, but not frozen. If not stored as such, the standards must be discarded after 1 hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept up to 12 hours in purge tubes connected via the autosampler to the P/T device.

7.2.3.3 Standard solutions purchased from a chemical supply company as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from the preparation date. The

expiration date of the ampulated standards, upon the breaking of the glass seal, is 6 months (or sooner if the standard has degraded or evaporated).

7.2.3.4 Protect all standards from light.

7.2.3.5 Purgeable standards must be stored separately from other standards, samples, and blanks.

7.2.3.6 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. Storage of standard solutions in the freezer may cause some standards to precipitate. This means that standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution.

7.2.3.6.1 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases may be replaced after 1 month for working standards and 6 months for opened stocks, or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

7.2.4 Temperature Records for Storage of Standards

7.2.4.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.

7.2.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.2.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in glass containers having a total volume of at least 40 mL with a PTFE-lined septum and an open top screw-cap.

8.1.2 The containers should have been filled in such a manner that no air bubbles are entrained to create a headspace in the vial.

8.1.3 The samples are preserved to a pH of ≤2 at the time of collection.

8.1.4 A total of three vials per field sample is the recommended amount the Contractor should receive.

NOTE: If MS/MSD analysis is required for a particular sample, two additional vials should be sent by the field samplers. Contact the Sample Management Office (SMO) if insufficient sample for MS/MSD analysis has been provided.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at ≤6°C, but not frozen, from the time of receipt until 60 days after delivery of a complete, reconciled data package to the EPA.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants and in a refrigerator used only for storage of volatile samples received under the contract.

8.2.3 All volatile samples in an SDG must be stored together in the same refrigerator.

8.2.4 Storage blanks shall be stored at ≤6°C, but not frozen, with samples within an SDG until all such samples are analyzed.

8.3 Contract Required Holding Times

Analysis of water samples must be completed within 10 days of Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Initial Instrument Set-up

9.1.1 Purge-and-Trap

9.1.1.1 The recommended P/T analytical conditions are provided in Table 5 – Purge-and-Trap Analytical Conditions. The conditions are suggested, but other conditions may be used, provided that all technical acceptance criteria are met for all standards, samples, and blanks:

9.1.1.2 Assemble a P/T device that meets the specifications in Section 6.3.4 and that is connected to a GC/MS system.

9.1.1.3 P/T instrumentation that allows internal standards and DMCs to be automatically added to each sample is widely available. Some of this instrumentation may be set-up by the manufacturer to add only 1 µL of internal standard or DMCs. The 1 µL addition of standards will be allowed if the addition is done solely in an automated manner, and if the final concentration of the following standards in the 25 mL water samples and blanks can be met: 5 µg/L for internal standards; the concentrations listed in Section 7.2.2.1.2 for DMCs in the initial calibration; and the concentrations listed in Section 7.2.2.1.4 for DMCs in the CCV.

9.1.1.4 Before initial use, condition the trap overnight at 180°C by backflushing with at least 20 mL/minute flow of inert gas according to the manufacturer's recommendations. Do not vent the trap effluent onto the analytical column. Prior to daily use, condition the trap by heating at 180°C for 10 minutes while backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be conditioned through the temperature program prior to the analysis of samples and blanks.

9.1.1.5 Optimize P/T conditions for sensitivity and to minimize cross-contamination between samples. Once optimized, the same P/T conditions must be used for the analysis of all standards, samples, and blanks.

9.1.1.6 A moisture reduction/water management system may be used to improve the chromatographic performance by controlling moisture if:

- The system does not introduce contaminants that interfere with identification and quantitation of target analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits;
- The analytical results generated when using the moisture reduction/water management system meet the initial calibration

and continuing calibration verification technical acceptance criteria listed in the analytical method and the CRQLs listed in Exhibit C- Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte and Contract Required Quantitation Limits;

- All calibration standards, samples, and blanks are analyzed under the same conditions; and
- The Contractor performs acceptably on the Performance Evaluation (PE) samples using this system.

9.1.2 Gas Chromatograph

9.1.2.1 The recommended GC analytical conditions are provided in Table 6 – Gas Chromatograph Analytical Conditions. The conditions are recommended unless otherwise noted. GC conditions must achieve all performance criteria required for initial and continuing calibration.

9.1.2.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and MS/MSDs.

9.1.2.3 Target analytes that are isomers (e.g., dichlorobenzenes) must be at least 50% resolved from each other. For xylene isomers, the two peaks representing o-xylene, m- and p-xylene, respectively, must be at least 50% resolved.

9.1.2.4 If the gaseous analytes chloromethane, bromomethane, vinyl chloride, and chloroethane fail to exhibit narrow, symmetrical peak shape, are not separated from the solvent front, or are not resolved greater than 90.0% from each other, then a subambient oven controller must be used, and the initial temperature must be less than or equal to 10°C.

9.1.3 Mass Spectrometer

The recommended MS analytical conditions are provided in Table 7 – Mass Spectrometer Analytical Conditions.

9.2 Instrument Performance Check

9.2.1 Summary of GC/MS Instrument Performance Check

9.2.1.1 The GC/MS system must be tuned to meet the manufacturer’s specifications, using a suitable calibrant such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.2.2).

9.2.1.2 Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing BFB.

9.2.2 Frequency of GC/MS Instrument Performance Check

The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples, blanks, or standards are to be analyzed. The 12-hour period for the GC/MS instrument performance check, calibration standards (initial calibration or CCV), blank, and sample analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. However,

in cases where a closing CCV can be used as an opening CCV for the next 12-hour period, then an additional BFB tune is not required, and the 12-hour period begins with the injection of the CCV. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for GC/MS Instrument Performance Check

The analysis of the instrument performance check solution shall be performed as follows:

- As an injection of up to 50 ng of BFB into the GC/MS.
- By adding a sufficient amount of BFB solution (Section 7.2.2.2) to 25 mL of reagent water to result in a 2.0 µg/L concentration of BFB.
- By adding a sufficient amount of BFB solution to the mid-level calibration standard to result in a 2 µg/L concentration of BFB.

9.2.4 Technical Acceptance Criteria for GS/MS Instrument Performance Check

9.2.4.1 The GC/MS system must be tuned at the frequency described in Section 9.2.2.

9.2.4.2 The abundance criteria listed in Table 2 – 4-Bromofluorobenzene Key Ions and Abundance Criteria, must be met for a 25 ng injection of BFB. The mass spectrum of BFB must be acquired in the following manner:

9.2.4.2.1 Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.

9.2.4.2.2 Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the beginning of the elution of BFB. Do not background subtract part of the BFB peak.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must be analyzed under identical GC/MS instrument analytical conditions.

9.2.5 Corrective Action for GC/MS Instrument Performance Check

9.2.5.1 If the BFB technical acceptance criteria are not met, retune the GC/MS system. It may also be necessary to clean the ion source or take other corrective actions to achieve the technical acceptance criteria.

9.2.5.2 Any samples or required blanks analyzed when tuning technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples (including MS/MSDs) and required blanks, and after the instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.2.1.2) to determine instrument sensitivity and the linearity of GC/MS response for the purgeable target analytes and DMCs.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be calibrated prior to analyzing samples, whenever the Contractor takes corrective action that may change

or affect the initial calibration criteria (i.e., ion source cleaning or repair, column replacement, etc.), or if the CCV technical acceptance criteria have not been met.

9.3.2.2 If time remains in the 12-hour period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed (Section 9.3.1). It is not necessary to analyze another CCV standard. A method blank is required.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Set up the GC/MS system as described in Section 9.1.

9.3.3.2 All standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.3.3.3 Add sufficient amount of the internal standard solution (Section 7.2.2.5) to each of the five aqueous calibration standard solutions (Section 7.2.2.1.2) containing the DMCs (Section 7.2.2.3.1) at the time of purge. Analyze each calibration standard according to Section 10.0 and outlined in Section 9.3.1. The initial calibration sequence is listed below.

Initial Calibration Sequence

1. GC/MS Instrument Performance Check
2. CS1 Initial Calibration Standard
3. CS2 Initial Calibration Standard
4. CS3 Initial Calibration Standard
5. CS4 Initial Calibration Standard
6. CS5 Initial Calibration Standard

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the RRF for each purgeable target analyte and DMC using Equation 1. The primary characteristic ions used for quantitation are listed in Table 8 – Characteristic Ions for Trace Volatile Target Analytes, Deuterated Monitoring Compounds and Internal Standards. If an interference prevents the use of a primary ion for a given internal standard, use a secondary ion listed in the same table. Assign the target analytes and DMCs to an internal standard according to Table 9 – Trace Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation.

NOTE: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 1 Relative Response Factor

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

WHERE,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (Table 8 – Characteristic Ions for Trace Volatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards)

A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (Table 8 – Characteristic Ions for Trace Volatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards). The target analytes are listed with their associated internal standards in Table 9 - Trace Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation

C_{is} = Concentration or amount of the internal standard

C_x = Concentration or amount of the analyte to be measured

9.3.4.2 Calculating the RRFs of the xylenes requires special attention. Report an RRF for m,p-xylene and one for o-xylene. On the available capillary columns, the m,p-xylene isomers coelute. Therefore, when calculating the RRF in the equation below, use the area response (A_x) and concentration (Cx) of the peak from o-xylene, and A_X and C_X of the peak from the m,p-xylene isomers respectively.

9.3.4.3 The Mean ($\overline{RRF}$) must be calculated for all analytes according to Equation 2.

9.3.4.4 Calculate the Percent Relative Standard Deviation (%RSD) of the RRF values for each purgeable target analyte and DMC over the initial calibration range using Equation 3 in conjunction with Equations 2 and 4.

9.3.4.4.1 Equation 2 is the general formula for the mean of a set of values.

EQ. 2 Mean Value

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

WHERE,

X_i = Value

$\overline{X}$ = Mean value

n = Number of values

9.3.4.4.2 Equation 3 is the general formula for the relative standard deviation.

EQ. 3 Percent Relative Standard Deviation

$$\%RSD = \frac{SD_{RRF}}{\overline{X}} \times 100$$

WHERE,

SD_{RRF} = Standard deviation of initial calibration RRFs (per compound) from EQ. 4

$\overline{X}$ = Mean value of the initial calibration RRFs (per compound)

9.3.4.4.3 Equation 4 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 4 Standard Deviation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{(n-1)}}$$

WHERE,

X_i = Each individual value used to calculate the mean

$\overline{X}$ = The mean of n values

n = Total number of values

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentrations described in Section 7.2.2.1.2, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the BFB technical acceptance criteria (Section 9.2.4).

9.3.5.2 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.3.5.3 The RRF at each calibration concentration for each target analyte and DMC that has a required minimum RRF value must be greater than or equal to the compound's minimum RRF listed in Table 4 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Trace Volatile Organic Compounds.

9.3.5.4 The %RSD for each target analyte or DMC listed in Table 4 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Trace Volatile Organic Compounds must be less than or equal to that value listed.

9.3.5.5 Up to two target analytes and DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Table 4 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Trace Volatile Organic Compounds. Up to two target analytes and DMCs (excluding those with maximum %RSD requirements of 40.0%) may fail to meet the criteria listed in Table 4 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Trace Volatile Organic Compounds, but these compounds must still meet the maximum %RSD requirements of 40.0%.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, service the P/T device, or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 It may be necessary to adjust the purge gas (helium) flow rate (normal in the range of 25-40 mL/minute). Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

9.3.6.3 Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Continuing Calibration Verification

Prior to the analysis of samples and required blanks, and after instrument performance check and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing an opening CCV (containing all the purgeable target analytes, DMCs, and internal standards) to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method. A closing CCV using the same standard conditions as for the opening CCV is required after all samples and blanks have been analyzed and before the end of the 12-hour period (refer to the analytical sequence provided in Section 9.4.2.3).

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 The calibration for each GC/MS system used for analysis must be verified at the beginning and end of every 12-hour period of operation. The 12-hour period begins with the injection of BFB, followed by the injection of the opening CCV solution. BFB may be added to the CCV solution, in which case only one injection is necessary. If a closing CCV meets the technical acceptance criteria for an opening CCV (Section 9.4.5.2) and samples are analyzed within that subsequent 12-hour period, then an additional BFB tune is not required and the 12-hour period begins with that calibration verification. If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then a BFB tune, followed by an opening CCV, is required and the next 12-hour period begins with the BFB tune (Section 9.2.2).

9.4.2.2 If time remains in the 12-hour period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. A method blank is required.

9.4.2.3 After the injection of all samples and required blanks, and before the end of the 12-hour period, another injection of the CCV solution is required (closing CCV). The closing CCV used to bracket the end of a 12-hour analytical sequence may be used as the opening CCV for a new 12-hour analytical sequence, provided that all technical acceptance criteria are met for an opening CCV in Section 9.4.5.

Time	**Injection #**	**Material Injected**
0 hr	1st - 6th - GC/MS Instrument Performance Check followed by CS1 – CS5 calibration standards	BFB then CS1–CS5 First 6 steps of the initial calibration
	7th - blanks, samples, MS/MSD	Blanks, samples, and MS/MSD
	8th - Subsequent Samples	
End 12 hr	Closing CCV (meeting Closing CCV criteria, but not Opening CCV)	CS3 – Closing CCV

Time	Injection #	Material Injected
New 12 hr	1st GC/MS Instrument Performance Check	BFB Instrument Performance Check
	2nd - Analysis past 12 Opening CCV	CS3 - Opening CCV
		Blank, MS/MSD, subsequent samples
		Subsequent Samples
		Last Sample
End 12 hr	Closing CCV (meeting Closing CCV criteria but not Opening CCV)	CS3 – Closing CCV
New 12 hr	1st Analysis Instrument Performance Check	BFB Instrument Performance Check
	2nd Analysis Opening CCV	CS3 – Opening CCV
		Blank, MS/MSD, subsequent samples
		Subsequent Samples
		Last Sample
		Storage Blank if previous sample is the last sample in SDG
End of 12 hr begins next 12 hr	Closing CCV (meeting Opening CCV criteria) Instrument Performance Check not required	CS3 – Closing CCV meeting Opening CCV
		Blank, MS/MSD, subsequent samples
		Subsequent Samples
		Last Sample
		Storage Blank (after last sample in SDG)
End of 12 hr	Closing CCV meeting criteria	CS3 – Closing CCV meeting Opening CCV

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 All standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.4.3.2 Add sufficient amount of internal standard solution (Section 7.2.2.5) to the CCV (Section 7.2.2.1.4) and the DMC solution (Section 7.2.2.3). Analyze the CCV Standard according to Section 10.0.

9.4.4 Calculations for Continuing Calibration Verification

9.4.4.1 Calculate an RRF for each target analyte and DMC according to Section 9.3.4.1.

9.4.4.2 Calculate the Percent Difference (%D) between the CCV RRF_c and the most recent initial calibration $\overline{RRF_i}$ for each purgeable target analyte and DMC using the following equation:

EQ. 5 Internal Standard Calibration Percent Difference

$$\%D = \frac{RRF_C - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

WHERE,

RRF_c = Relative Response Factor from current CCV standard

$\overline{RRF_i}$ = Mean Relative Response Factor from the most recent initial calibration

9.4.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.4.5.1 The concentration of the trace volatile organic target analytes and DMCs in the opening and closing CCV must be at or near the mid-point concentration of the calibration standards (5.0 µg/L for non-ketones and 50 µg/L for ketones). The opening and closing CCV must be analyzed at the frequency described in Section 9.4.2, on a GC/MS system meeting the BFB (Section 9.2.4) and the initial calibration (Section 9.3.5) technical acceptance criteria.

9.4.5.2 For an opening or closing CCV, except as noted in Section 9.4.5.4, the RRF for each target analyte and DMC must be greater than, or equal to, the compound's minimum RRF listed in Table 4 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Trace Volatile Organic Compounds.

9.4.5.3 For an opening CCV, the %D for each target analyte and DMC listed in Table 4 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Trace Volatile Organic Compounds must be in the inclusive range of the compound's %D values listed. For a closing CCV, the %D for each target analyte and DMC must be in the inclusive range of the compound's %D values listed. Up to two target analytes and/or DMC's in the closing CCV are allowed to exceed the %D values listed.

9.4.5.4 For an opening CCV, up to two target analytes and/or DMCs (excluding those compounds with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Table 4 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Trace Volatile Organic Compounds. For a closing CCV, all target analytes and DMCs must meet the requirements listed.

9.4.5.5 No quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Continuing Calibration Verification

9.4.6.1 If the opening CCV technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3. If the closing CCV technical acceptance criteria are not met, then all samples and blanks analyzed within that 12-hour period must be reanalyzed at no additional cost to the EPA.

9.4.6.2 The Contractor shall follow the procedure in Section 10.2.12.1 if it cannot meet the control criteria after the analysis of an original undiluted or minimally diluted sample due to matrix interference. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the CCV technical acceptance criteria.

9.4.6.3 Any samples or required blanks analyzed when opening CCV technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

10.0 PROCEDURE

10.1 Introduction to Sample Analysis

10.1.1 Samples shall be analyzed only after the GC/MS system has met the technical requirements. The same instrument conditions must be employed for the analysis of samples as were used for calibration. All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

NOTE: Contact SMO if sample vials have bubbles entrained resulting in headspace.

10.2 Procedure for Sample Analysis

10.2.1 If time remains in the 12-hour period (as described in Section 9.2.2), samples may be analyzed without analysis of a CCV standard.

10.2.2 If the autosampler can automatically sample the appropriate volume, then Sections 10.2.3 - 10.2.5 are performed by the autosampler.

10.2.3 Remove the plunger from a 25 mL syringe and attach a closed syringe valve. Open the sample or standard container that has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Invert the syringe, open the syringe valve, and vent any residual air while adjusting the sample volume to 25 mL.

10.2.4 This process of taking an aliquot destroys the validity of the sample for future analysis, unless the excess sample is immediately transferred to a smaller vial with zero headspace and stored at ≤6°C, but not frozen. Therefore, if only one sample vial is provided, the analyst must fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly. Filling one 25 mL syringe would allow only one analysis of that sample. If an analysis is needed from the second 25 mL syringe, it must be performed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.

10.2.5 Add a sufficient amount of the DMC spiking solution (Section 7.2.2.3.1) and a sufficient amount of internal standard spiking solution (Section 7.2.2.5) through the valve bore of the syringe, then close the valve. Invert the syringe 3 times. The DMCs and internal standards may be mixed and added as a single spiking solution.

10.2.6 Once the sample aliquots have been taken from the VOA vial, the pH of the water sample must be determined. The purpose of the pH determination is to ensure that all VOA samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper (do **not** add pH paper to the vials). Record the pH of each sample and report these data in the SDG Narrative, following the instructions in Exhibit B – Reporting and Deliverables Requirements. No pH adjustment is to be performed by the Contractor.

10.2.7 Attach the valve assembly on the syringe to the valve on the sample sparger. Open the valves and inject the sample into the purging chamber.

10.2.8 Close both valves and purge the sample under the same conditions as the initial calibration.

10.2.9 Sample Desorption - After the purge is complete, attach the trap to the GC, adjust the P/T system to the desorb mode, initiate the temperature program sequence of the GC, and start data acquisition. Introduce the trapped material to the GC column by rapidly heating the trap to the appropriate desorb temperature while backflushing the trap with inert gas. While the trapped material is being introduced into the GC, empty the sample sparger and rinse it with reagent water. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to wash out the sample sparger with a detergent solution, rinse it with reagent water, and then dry it in an oven at 105°C.

10.2.10 Trap Reconditioning - After desorbing the sample, recondition the trap in accordance with manufacturers' instructions with the recommended trap recondition for a minimum of 7.0 (±0.1) minutes at 180°C. The same conditions must be used for all analyses.

10.2.11 Termination of Data Acquisition - 3 minutes after all the purgeable target analytes have eluted from the GC, terminate the MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and appropriate EICPs.

10.2.12 Sample Dilutions

10.2.12.1 The Contractor shall analyze samples undiluted, or at minimal dilution. Samples may be diluted because of target analyte concentration exceeding the concentration of the same target analyte in the high standard, or because of excessive matrix interference that hinders accurate quantitation. It is highly recommended that screening analysis be performed prior to sample analysis to determine estimated compound concentration and matrix problems.

10.2.12.2 In the event that interference precludes accurate quantitation using the primary quantitation ion, but a secondary ion with less interference could be used instead, then secondary ion quantitation should be considered (see Section 11.2.1.4).

10.2.12.3 Use the results of the original sample analysis to determine the approximate Dilution Factor (DF) required to get the highest concentration of the analyte within the calibration range.

10.2.12.4 The DF chosen must keep the concentrations of the trace volatile target analytes that required dilution within the upper half of the initial calibration range.

10.2.12.5 If a sample requires a DF of twenty or greater to meet the criteria in Section 10.2.12.3, then the Contractor shall contact SMO. SMO will in turn contact the EPA Region to determine whether the sample should be analyzed at low level. The results of all original trace level analyses shall also be reported.

10.2.12.6 All dilutions must be made just prior to GC/MS analysis of the sample. Until the diluted sample is in a gas-tight syringe, all steps in the dilution procedure must be performed without delay.

10.2.12.7 Samples may be diluted in a volumetric flask or in a 25 mL Luer-Lok syringe.

10.2.12.8 To dilute the sample in a volumetric flask, use the following procedure:

10.2.12.8.1 Select the volumetric flask that will allow for necessary dilution (25-100 mL).

10.2.12.8.2 Calculate the approximate volume of reagent water that will be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

10.2.12.8.3 Inject the proper sample aliquot from a syringe into the volumetric flask. Only aliquots of 1 mL increments are permitted. Dilute the aliquot to the mark on the flask with reagent water. Cap the flask and invert it 3 times.

10.2.12.8.4 Fill a 25 mL syringe with the diluted sample and analyze according to Section 10.2.

10.2.12.9 To dilute the sample in a 25 mL syringe, use the following procedure:

10.2.12.9.1 Calculate the volume of the reagent water necessary for the dilution. The final volume of the diluted sample should be 25 mL.

10.2.12.9.2 Close the syringe valve, remove the plunger from the syringe barrel, and pour reagent water into the syringe barrel to just short of overflowing.

10.2.12.9.3 Replace the syringe plunger and compress the water.

10.2.12.9.4 Invert the syringe, open the syringe valve, and vent any residual air. Adjust the water volume to the desired amount.

10.2.12.9.5 Adjust the plunger to the 25 mL mark to accommodate the sample aliquot. Inject the proper aliquot of sample from another syringe through the valve bore of the 25 mL syringe. Close the valve and invert the syringe 3 times. Analyze according to Section 10.2.

10.2.12.10 All sample quality control criteria must be met for all diluted and undiluted sample analyses. Sample analyses that fail to meet the sample quality control criteria must be reanalyzed at no additional cost to the EPA.

10.2.12.11 If more than two analyses (i.e., from the original sample and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get concentrations of all target analytes within the calibration range, contact SMO.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Analytes

11.1.1.1 The analytes listed in the TAL in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte List and Contract Required Quantitation Limits, shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component within the Gas Chromatographic Relative Retention Time (RRT) unit window established from the 12-hour calibration standard; and
- Correspondence of the sample component and standard calibration analyte mass spectra.

11.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must be within ±0.06 RRT units of the RRT of the corresponding continuing calibration standard component. For reference, the standard must be analyzed in the same 12-hour period as the sample. If samples are analyzed during the same 12-hour period as the initial calibration standards, use the RRT values from the 5 µg/L standard. Otherwise, use the corresponding opening CCV standard. If coelution of interfering compounds prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned using the EICP for ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/MS (as opposed to library spectra) are required. Once obtained, these standard spectra may be used for identification purposes, only if the Contractor's GC/MS meets the daily instrument performance requirements for BFB. These standard spectra may be obtained from the standard analysis that was also used to obtain the RRTs.

11.1.1.4 The guidelines for qualitative verification by comparison of mass spectra are as follows:

11.1.1.4.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.1.1.4.2 The relative intensities of ions specified in the paragraph above must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30-70%).

11.1.1.4.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra.

11.1.1.4.4 If an analyte cannot be verified by all of the spectral identification criteria listed in Section 11.1.1.4, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantitation and document in the SDG Narrative.

11.1.2 Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target compounds for the purpose of tentative identification. The NIST (2011 release or later), Wiley (2011 release or later), or equivalent mass spectral library, shall be used as the reference library.

11.1.2.2 All organic compounds that have not been positively identified as volatile target analytes using the procedures detailed in Section 11.1, or that are not DMCs, internal standards, or semivolatile target compounds listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, shall be tentatively identified via a forward search of NIST, Wiley, or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form 1B-OR. Peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be reported as "total alkanes". An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds. The concentrations of each of the alkanes is to be summed and reported as a single result for the "total alkanes". The alkanes are not to be counted as part of the 30 compounds individually reported as TICs on Form 1B-OR. Carbon dioxide and compounds with responses less than 10% of the internal standard with which they are to be quantified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.1.2.4 Rules for Making Tentative Identification

11.1.2.4.1 For compounds to be reported, as per the instructions in Section 11.1.2.3, identification (as generated by the library search program) of those receiving a library search match of 85% or higher should be considered a "probable match". The compound should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program.

11.1.2.4.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match. Do not report DMCs, internal standards, or analytes that are on the volatile or semivolatile TAL, unless the semivolatile analysis is not being done.

11.1.2.4.3 If the library search produces a series of obvious isomer compounds with library search matches greater than 85% (e.g., tetramethylnaphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same).

11.1.2.4.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the SDG Narrative the justification for not reporting a compound as listed by the search program. This narrative shall detail explicitly why a library search generated identification for a compound was rejected. If a TIC has obvious isomer analogs, the laboratory shall include in the SDG Narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

11.1.2.4.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialists are encouraged to make a valid tentative identification of the compound. If no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral interpretation specialist should give additional classification of the unknown, if possible (e.g., "unknown aromatic compound", "unknown chlorinated compound", etc.).

11.1.2.4.6 The Chemical Abstracts Service (CAS) registry number is the unique identifier for each chemical compound. As the rules of chemical nomenclature have changed over time, each chemical substance is liable to have several names or synonyms: i.e., trade or brand name(s); generic or common name(s); trivial or systematic; or International Union of Pure and Applied Chemistry (IUPAC) name(s). Whether synonyms or other names are created for this compound, the CAS registry number will generally remain unchanged. The CAS registry number is simply an identifier which has no structural significance. Regardless of retention times (RTs), if the library search produces two or more compounds at or above 85% with the same Chemical Abstract Number, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds) unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match.

11.1.2.4.7 If the library search produces only one and the same compound [i.e., the same CAS registry number] with the match at or above 85% at two different RTs, the compound having the highest percent match should be reported as TIC and the other one could be reported as unknown. If both TICs have the same percent match for the same compound, one of the TICs could be reported as unknown. Such justifications should be included in the SDG Narrative.

11.2 Quantitative Analysis

11.2.1 Data Processing Procedure

11.2.1.1 Target analytes identified shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (Table 9 – Trace Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation. The EICP area of primary characteristic ions of analytes listed in Table 8 – Characteristic Ions for Trace Volatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards, are to be used for quantitation.

11.2.1.2 Xylenes are to be reported as "m,p-xylene" and "o-xylene". Because m- and p-xylene isomers co-elute, special attention must be given to the quantitation of the xylenes. In quantitating sample concentrations, be sure to use the correct corresponding RRF values.

NOTE: The area of each peak (i.e., the peaks for o-xylene and m,p-xylene) must appear on the quantitation report.

11.2.1.3 The stereoisomers, trans-1,2-dichloroethene, and cis-1,2-dichloroethene are to be reported separately.

11.2.1.4 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary quantitation ion, not when saturation occurs. If secondary ion quantitation is used, calculate a RRF using the area response (EICP) from the most intense secondary ion which is free of sample interferences, and document the reasons in the SDG Narrative. A secondary ion cannot be used as the quantitation ion unless the RRF is calculated using the secondary ion.

11.2.1.5 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitation. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific target compound, DMC, or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall also not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instances of manual integration must be documented in the SDG Narrative.

11.2.1.6 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "M" on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all target analytes listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte Lists and Contract Required Quantitation Limits, internal standards, and DMCs.

11.2.2 Target Analyte Calculations

11.2.2.1 Identified target analytes shall be quantified by the internal standard method using Equation 6. The internal standard used shall be that which is assigned in Table 9 - Trace Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation. The $\overline{RRF}$ from the initial calibration standard is used to calculate the concentration in the sample.

11.2.2.2 EQ. 6 Water Concentration

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(I_{is})(DF)}{(A_{is})(\overline{RRF})(V_o)}$$

WHERE,

A_x = Area of the characteristic ion (EICP) for the compound to be measured. The primary quantitation ions for the target analytes, internal standards, and DMCs are listed in Table 8 – Characteristic Ions for Trace Volatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards.

A_{is} = Area of the characteristic ion (EICP) for the internal standard. The target analytes are listed with their associated internal standards in Table 9 – Trace Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation.

I_{is} = Amount of internal standard added, in ng

$\overline{RRF}$ = Mean Relative Response Factor from the initial calibration standard

V_o = Total volume of water purged, in mL

DF = Dilution Factor. The DF for analysis of water samples for volatiles by this method is defined as the ratio of the number of mL of water purged (i.e., V_o above) to the number of mL of the original water sample used for purging. For example, if 5.0 mL of sample is diluted to 25 mL with reagent water and purged, DF = 25 mL/5.0 mL = 5.0. If no dilution is performed, DF = 1.0.

11.2.2.3 Non-Target Compounds

11.2.2.4 An estimated concentration for TICs shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.2.2.5 Equation 6 is also used for calculating TIC concentrations. Total area counts (or peak heights) from the total RICs are to be used for both the TIC to be measured (A_x) and the internal standard (A_{is}). An $\overline{RRF}$ of 1.0 is to be assumed.

11.2.3 Contract Required Quantitation Limit

EQ. 7 Water Adjusted CRQL

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{V_c}{V_o} \times DF$$

WHERE,

Contract CRQL = CRQL value reported in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte List and Required Contract Required Quantitation Limits

V_o, DF = As given in EQ. 6

V_c = Method required purge volume

11.2.4 Deuterated Monitoring Compound Recoveries

11.2.4.1 Calculate the concentration of each DMC using the same equation as used for target analytes (Equation 6).

11.2.4.2 Calculate the recovery of each DMC in all samples and blanks using Equation 8. Report the recoveries on the appropriate forms.

EQ. 8 DMC Percent Recovery

$$\%R = \frac{Q_d}{Q_a} \times 100$$

WHERE,

Q_d = Quantity determined by analysis

Q_a = Quantity added to sample/blank

11.3 Technical Acceptance Criteria for Sample Analysis

11.3.1 The sample must be analyzed on a GC/MS system meeting the BFB, initial calibration, CCV, and blank technical acceptance criteria.

11.3.2 The sample and any required dilution must be analyzed within the contract required holding time.

11.3.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

11.3.4 The Percent Recovery (%R) of each of the DMCs in the sample must be within the recovery limits in Table 10 – Deuterated Monitoring Compound Recovery Limits. Up to three DMCs per sample may fail to meet the recovery limits listed in Table 10 – Deuterated Monitoring Compound Recovery Limits.

11.3.5 The EICP area for each of the internal standards in the sample must be within the range of 50–200% of its response in the most recent opening CCV standard analysis.

11.3.6 The RT shift for each of the internal standards in the sample must be within ±10 seconds of its RT in the most recent opening CCV standard analysis.

11.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. No target analyte concentration may exceed the upper limit of the initial calibration range, unless a more diluted aliquot of the sample is also analyzed according to the procedures in Section 10.2.12.

11.3.8 The Contractor must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target analyte at a level exceeding the initial calibration range, or a non-target compound at a concentration greater than 100 µg/L, or saturated ions from a compound (excluding the compound peaks in the solvent front), the Contractor must either:

- Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (Section 12.1.3.5); or
- Monitor the sample analyzed immediately after the contaminated sample for all the analytes that were in the contaminated sample and that exceeded the calibration range. The maximum carryover criteria are as follows: the sample must not contain a concentration above the CRQL for the target analytes, or above 2 µg/L for the non-target compounds that exceeded the limits in the contaminated sample. If an autosampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample must also meet the maximum contamination criteria.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or any samples not meeting the sample technical acceptance criteria will require reanalysis at no additional cost to the EPA.

11.4.2 Corrective actions for failure to meet technical acceptance criteria for instrument performance checks, initial calibration, CCV, and method blanks must be completed before the analysis of samples.

11.4.3 If the technical acceptance criteria for any of the internal standards and DMCs are not met, check calculations, internal standard and DMC spiking solutions, and instrument performance. It may be necessary to bake out the system to remove the water from the P/T transfer lines, to recalibrate the instrument, or take other corrective action procedures to meet the technical acceptance criteria.

11.4.4 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If DMC recoveries or internal standard compound responses in a sample used for an MS/MSD were outside the acceptance criteria, then it should be reanalyzed only if DMC recoveries and internal standard compound responses met acceptance criteria in both the MS/MSD analyses.

- If the DMC recoveries and the internal standard responses meet the acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. Therefore, submit data only from the reanalysis.
- If the DMC recoveries and/or the internal standard responses fail to meet the acceptance windows in the reanalyzed sample, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes in Exhibit B – Reporting and Deliverables Requirements, Table 5 – Codes for Labeling Data.

11.4.5 If the contractor needs to analyze more than one sample dilution other than the original analysis to have all concentrations of the target analytes within the initial calibration range, contact SMO. SMO will contact the EPA Region for instruction.

11.4.6 All samples to be reported to the EPA must meet the maximum carryover criteria in Section 11.3.8. If any sample fails to meet these criteria, each subsequent analysis must be checked for cross-contamination. The analytical system is considered contaminated until a sample has been analyzed that meets the maximum carryover criteria or an instrument blank has been analyzed that meets the technical acceptance criteria for blanks. If an instrument blank is not analyzed between consecutive samples that have the same analyte with a concentration exceeding the calibration range, then the second sample must be appropriately diluted as indicated in Section 10.2.12 and analyzed. If this analyte in the diluted analysis is detected at or below the adjusted CRQL, then all samples analyzed after the second sample that fail to meet maximum carryover criteria must be reanalyzed. If this analyte in the diluted analysis is detected within the calibration range, then no further corrective action is needed.

11.4.7 Corrective Action for Internal Standard Compound Retention Times Outside Acceptance Criteria

11.4.7.1 If the internal standard compound RTs are not within their acceptance criteria, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the samples.

11.4.7.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If the internal standard compound RTs in a sample used for an MS or MSD were outside the acceptance criteria, then it should be reanalyzed only if the internal standard compound RTs were within the acceptance criteria in both the MS/MSD analyses.
- If the internal standard RTs are within the acceptance criteria, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis when the internal standard compound RTs are within the acceptance limits.

- If the internal standard RTs are outside the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B – Reporting and Deliverables Requirements, Table 5 – Codes for Labeling Data.

12.0 QUALITY CONTROL

12.1 Blank Analyses

12.1.1 Summary

There are three different types of blanks required by this method: the method blank, the instrument blank, and the storage blank.

12.1.2 Method Blank

12.1.2.1 Summary of Method Blank

A method blank is a 25 mL aliquot of reagent water spiked with internal standard spiking solution (Section 7.2.2.5) and DMC solution (Section 7.2.2.3.1), and carried through the entire analytical procedure. The volume of the reference matrix must be approximately equal to the volume of samples associated with the blank. The purpose of the method blank is to determine the levels of contamination associated with processing and analysis of samples.

12.1.2.2 Frequency of Method Blank

12.1.2.2.1 The method blank must be analyzed at least once during every 12-hour period on each GC/MS system used for trace volatile analysis (See Section 9.2.2 for the definition of the 12-hour period).

12.1.2.2.2 The method blank must be analyzed after the initial calibration sequence (Section 9.3.1) if samples are analyzed before the 12-hour period expires. The method blank must be analyzed after the CCV and before any samples, including MS/MSDs, dilutions, or storage blanks are analyzed. A method blank must be analyzed in each 12-hour period in which samples, including dilutions, MS/MSDs, and storage blanks from an SDG are analyzed.

12.1.2.3 Procedure for Method Blank

12.1.2.3.1 Method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.2.

12.1.2.3.2 Under no circumstances should method blanks be analyzed at a dilution.

12.1.2.4 Calculations for Method Blank

Perform data analysis and calculations according to Section 11.0.

12.1.2.5 Technical Acceptance Criteria for Method Blank

12.1.2.5.1 All blanks must be analyzed on a GC/MS system meeting the BFB, initial calibration, and CCV technical acceptance criteria and at the frequency described in Section 12.1.2.2.

12.1.2.5.2 The %R of each of the DMCs in the blank must be within the acceptance windows in Table 10 – Deuterated Monitoring Compound Recovery Limits.

12.1.2.5.3 The blank must meet the sample acceptance criteria listed in Sections 11.3.4 - 11.3.7.

12.1.2.5.4 The concentration of each target analyte found in the method blank must be less than the CRQL listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte List and Contract Required Quantitation Limits, except for methylene chloride, acetone, and 2-butanone, which must be less than 2 times the respective CRQL.

12.1.2.5.5 The concentration of each TIC found in the method blank must be less than 0.5 µg/L.

12.1.2.6 Corrective Action for Method Blank

12.1.2.6.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.

12.1.2.6.2 If contamination is the problem, then the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. It is the Contractor's responsibility to ensure that method interferences caused by the contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in GCs be eliminated.

12.1.2.6.3 Any method blank that fails to meet the technical acceptance criteria must be reanalyzed. Further, all samples processed within the 12-hour period with a method blank that does not meet the blank technical acceptance criteria will require reanalysis at no additional cost to the EPA.

12.1.3 Instrument Blank

12.1.3.1 Summary of Instrument Blank

An instrument blank is a 25 mL aliquot of reagent water spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.5) and DMC solution (Section 7.2.2.3.1) carried through the entire analytical procedure. Instrument blanks are analyzed after a sample/dilution that contains a target analyte exceeding the calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample.

12.1.3.2 Frequency of Instrument Blank

Samples may contain target analytes at levels exceeding the calibration. An instrument blank must be analyzed after the sample that exceeds the calibration range (also in the same purge inlet if an autosampler is used) or a sample that exceeds the maximum contamination criteria in Section 11.3.8 must be analyzed. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system must be decontaminated until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum carryover criteria.

NOTE: Only the instrument blank that demonstrates that there was no carryover from the previous sample or the instrument blank that demonstrates that the system is clean (Section 12.1.3.5.3) must be reported. Instrument blanks analyzed during the instrument decontamination process that exceed the requirements listed in Section 11.3.8 do not need to be reported.

12.1.3.3 Procedure for Instrument Blank

12.1.3.3.1 Instrument blanks shall be analyzed in the same manner as the associated samples following the procedures outlined in Section 10.0 and in accordance with the protocol of Section 11.3.8.

12.1.3.3.2 Under no circumstances should instrument blanks be analyzed at a dilution.

12.1.3.4 Calculations for Instrument Blank

Perform data analysis and calculations according to Section 11.0.

12.1.3.5 Technical Acceptance Criteria for Instrument Blank

12.1.3.5.1 All instrument blanks must be analyzed on a GC/MS system meeting the BFB, initial calibration, and CCV technical acceptance criteria and at the frequency described in Section 12.1.3.2.

12.1.3.5.2 The RT shift for each of the internal standards in the blank must be within 10 seconds of its RT in the most recent opening CCV standard analysis.

12.1.3.5.3 The concentration of each target analyte in the instrument blank must be less than its CRQL listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte Lists and Contract Required Quantitation Limits. The concentration of non-target compounds in blanks must be less than 2.0 ug/L.

12.1.3.5.4 It is the Contractor’s responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms, be eliminated.

12.1.3.6 Corrective Action for Instrument Blank

12.1.3.6.1 If a Contractor’s blanks exceed the criteria in Section 12.1.3.5, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds.

12.1.3.6.2 Any instrument blank that fails to meet the technical acceptance criteria described in Section 12.1.3.5 requires reanalysis of the samples analyzed after the instrument blank having any target analytes detected at levels above the CRQLs at no additional cost to the EPA.

12.1.4 Storage Blank

12.1.4.1 Summary of Storage Blank

A storage blank is a volume of reagent water. The vials are stored with the samples in the SDG under the same conditions. A 25 mL aliquot of this reagent water is spiked with internal standard spiking solution and DMC solution, and analyzed after

all samples in the SDG have been analyzed. The storage blank indicates whether contamination may have occurred during storage of samples.

12.1.4.2 Frequency of Storage Blank

A minimum of one storage blank must be analyzed per SDG, after all samples for the SDG have been analyzed, unless the SDG contains only ampulated PE samples. Analysis of a storage blank is not required for SDGs that contain only ampulated PE samples.

12.1.4.3 Procedure for Storage Blank

12.1.4.3.1 Upon receipt of the first samples in an SDG, two 40 mL screw-cap VOA vials with a PTFE-faced silicone septum and are filled with reagent water are stored with the samples in the SDG under the same conditions.

12.1.4.3.2 Storage blank shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.0.

12.1.4.3.3 Under no circumstances should storage blanks be analyzed at a dilution.

12.1.4.4 Calculations for Storage Blank

Perform data analysis and calculations according to Section 11.0.

12.1.4.5 Technical Acceptance Criteria for Storage Blank

12.1.4.5.1 All storage blanks must be analyzed on a GC/MS system meeting the BFB, initial calibration, and CCV technical acceptance criteria and at the frequency described in Section 12.1.4.2.

12.1.4.5.2 The storage blank must be analyzed on a GC/MS system that also meets the technical acceptance criteria for the method blank.

12.1.4.5.3 The %R of each of the DMCs in the blank must be within the acceptance windows in Table 10 – Deuterated Monitoring Compound Recovery Limits.

12.1.4.5.4 The EICP area for each of the internal standards in the blank must be within the range of 50%-200% of its response in the most recent opening CCV standard analysis.

12.1.4.5.5 The RT shift for each of the internal standards in the blank must be within 10 seconds of its RT in the most recent opening CCV standard analysis.

12.1.4.5.6 The concentration of each target analyte found in the storage blank must be less than the CRQL listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte Lists and Contract Required Quantitation Limits, except for methylene chloride, acetone, and 2-butanone, which must be less than 2 times the respective CRQL.

12.1.4.5.7 It is the Contractor’s responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.4.6 Corrective Action for Storage Blank

12.1.4.6.1 If a Contractor’s storage blanks exceed the criteria in Section 12.1.4.5.6, the Contractor must consider the analytical system to be out of control. The source of the

contamination must be investigated and appropriate corrective measures must be taken and documented before further analysis proceeds.

12.1.4.6.2 If the storage blank does not meet the technical acceptance criteria for blank analyses in Section 12.1.4.5, correct system problems and reanalyze the storage blank.

12.1.4.6.3 If, upon reanalysis, the storage blank meets the criteria, the problem occurred during the analysis and the reanalyzed storage blank results must be reported. If upon reanalysis, the storage blank still does not meet the criteria, the problem occurred during storage. The Laboratory Manager or their designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences.

NOTE: A copy of the storage blank data must also be retained by the Contractor and be made available for inspection during on-site laboratory evaluations.

12.2 Matrix Spike and Matrix Spike Duplicate

12.2.1 Summary of Matrix Spike and Matrix Spike Duplicate

To evaluate the effects of the sample matrix on the method used for trace volatile analysis, the EPA has prescribed a mixture of volatile target analytes to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method. An MS/MSD shall only be analyzed if requested by the EPA Region (through SMO) or specified on the TR/COC Record.

12.2.2 Frequency of Matrix Spike and Matrix Spike Duplicate

12.2.2.1 If requested, an MS/MSD must be performed for each group of 20 field samples in an SDG, or each SDG, whichever is most frequent.

12.2.2.2 The Contractor shall not perform MS/MSD analysis on any of the field QC or PE samples.

12.2.2.3 If an insufficient number of sample vials were received to perform an MS/MSD, and MS/MSD are required, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the EPA Region for instructions. The EPA Region has the option to cancel the MS/MSD analysis. SMO will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.4 If it appears that the EPA Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, the Contractor shall contact SMO. SMO will contact the EPA Region to determine which samples should have an MS/MSD performed on them. SMO will notify the Contractor of the EPA Region’s decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 When a Contractor receives only PE sample(s), no MS/MSD shall be performed within that SDG.

12.2.3 Procedure for Preparing Matrix Spike and Matrix Spike Duplicate

12.2.3.1 Add 10 µL of the matrix spiking solution (Section 7.2.2.4) to each of the 25 mL aliquots of the sample chosen for spiking. Process the samples according to Section 10. Disregarding any dilutions, this is equivalent to a concentration of 5 µg/L of each Matrix Spike analyte.

12.2.3.2 MS/MSD samples must be analyzed at the same dilution as the least diluted aliquot for which the original sample results will be reported to the EPA. Sample dilutions must be performed in accordance with Section 10.2.12. Do not further dilute MS/MSD samples to get either spiked or non-spiked analytes within calibration range.

12.2.4 Calculations for Matrix Spike and Matrix Spike Duplicate

12.2.4.1 Calculate the concentrations of the Matrix Spike analytes using the same equation as used for target analytes (Equation 6). Calculate the recovery of each Matrix Spike analyte using the following equation:

EQ. 9 Matrix Spike Recovery

$$\%R = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD using the following equation:

EQ. 10 Relative Percent Difference

$$RPD = \frac{\left|MSR - MSDR\right|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

WHERE,

MSR = Matrix Spike Recovery

MSDR = Matrix Spike Duplicate Recovery

NOTE: The vertical bars in the equation above indicate the absolute value of the difference.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Matrix Spike Duplicate

12.2.5.1 All MS/MSDs must be analyzed on a GC/MS system meeting the BFB, initial calibration, CCV and blank technical acceptance criteria, and at the frequency described in Section 12.2.2.

12.2.5.2 The MS/MSD must be analyzed within the contract holding time.

12.2.5.3 The RT shift for each of the internal standards in the MS/MSD must be within 10 seconds of its RT in the most recent opening CCV standard analysis.

12.2.5.4 The limits for MS analyte recovery and RPD are given in Table 11 - Matrix Spike Recovery and Relative Percent Difference Limits. As these limits are only advisory, no further action by the Contractor is required.

12.2.6 Corrective Action for Matrix Spike/Matrix Spike Duplicate

Any MS/MSD that does not meet the technical acceptance criteria in Sections 12.2.5.1 through 12.2.5.3 must be reanalyzed at no additional cost to the EPA.

12.3 Laboratory Control Sample

Not applicable to this method.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed, the Method Detection Limit (MDL) for each trace volatile target analyte shall be determined on each instrument used for analysis. The MDLs must be determined annually thereafter or after major instrument maintenance. Major instrument maintenance includes, but is not limited to: cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device); and replacement or overhaul of the P/T device. A new MDL study will not be required after changing the GC column, as long as the replacement has the same length, inner diameter, and stationary phase.

12.4.2 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in the Code of Federal Regulations, Chapter 40, Part 136, Appendix B (40 CFR 136, Appendix B).

12.4.3 The determined concentration of the MDL must be less than the CRQL listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte Lists and Contract Required Quantitation Limits.

12.4.4 All documentation for the MDL studies shall be maintained at the laboratory and submitted to the EPA within seven (7) days of study completion. This schedule and the designated recipients are specified in Exhibit B, Table 1 – Reporting and Deliverables Requirements.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 13.0 of Exhibit D – Introduction to Organic Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 14.0 of Exhibit D – Introduction to Organic Analytical Methods.

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Method 524.2, Revision 4, August 1992.

16.2 U.S. Environmental Protection Agency, Purge-and-Trap for Aqueous Samples, Method 5030C, Revision 3, May 2003.

16.3 U.S. Environmental Protection Agency, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Method 8260C, Revision 3, August 2006.

16.4 U.S. Government Printing Office, 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS

Systematic Name	**EPA Registry Name**	**Synonym**	**CAS #**
Methane, dichlorodifluoro-	CFC-12	Dichlorodifluoromethane	75-71-8
Methane, chloro-	Chloromethane	Methyl chloride	74-87-3
Ethene, chloro-	Vinyl Chloride	Vinyl chloride	75-01-4
Methane, bromo-	Methyl Bromide	Methyl bromide	74-83-9
Ethane, chloro-	Chloroethane	Ethyl chloride	75-00-3
Methane, trichlorofluoro-	CFC-11	Fluorotrichloromethane	75-69-4
Ethene, 1,1-dichloro-	1,1-Dichloroethylene	Vinylidene chloride	75-35-4
Ethane, 1,1,2-trichloro-1,2,2-trifluoro-	CFC-113	Freon 113	76-13-1
2-Propanone	Acetone	Dimethyl ketone	67-64-1
Carbon disulfide	Carbon disulfide	Dithiocarbonic anhydride	75-15-0
Acetic acid, methyl ester	Methyl acetate	Methyl acetate	79-20-9
Methane, dichloro	Methylene chloride	Dichloromethane	75-09-2
Ethene, 1,2-dichloro-, (1E)-	trans-1,2-Dichloroethylene	Ethylene, 1,2-dichloro-, (E)-	156-60-5
Propane, 2-methoxy-2-methyl-	Methyl tert-butyl ether	t-Butyl methyl ether	1634-04-4
Ethane, 1,1-dichloro-	1,1-Dichloroethane	Ethylidene dichloride	75-34-3
Ethene, 1,2-dichloro-, (1Z)-	cis-1,2-Dichloroethylene	Ethylene, 1,2-dichloro-, (Z)-	156-59-2
2-Butanone	Methyl ethyl ketone	Butan-2-one	78-93-3
Methane, bromochloro-	Halon 1011	Chlorobromomethane	74-97-5
Methane, trichloro-	Chloroform	Trichloromethane	67-66-3
Ethane, 1,1,1-trichloro-	1,1,1-Trichloroethane	1,1,1-TCE	71-55-6
Cyclohexane	Cyclohexane	Hexahydrobenzene	110-82-7
Methane, tetrachloro-	Carbon tetrachloride	Tetrachlorocarbon	56-23-5
Benzene	Benzene	Benzol	71-43-2
Ethane, 1,2-dichloro-	1,2-Dichloroethane	Ethylene dichloride	107-06-2
Ethene, 1,1,2-trichloro-	Trichloroethylene	Ethylene, trichloro-	79-01-6
Cyclohexane, methyl-	Methylcyclohexane	Hexahydrotoluene	108-87-2
Propane, 1,2-dichloro-	1,2-Dichloropropane	Propylene dichloride	78-87-5

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS (CON'T)

Systematic Name	**EPA Registry Name**	**Synonym**	**CAS #**
Methane, bromodichloro-	Dichlorobromomethane	Bromodichloromethane	75-27-4
1-Propene, 1,3-dichloro-, (Z)-	cis-1,3-Dichloropropene	cis-1,3-Dichloropropylene	10061-01-5
2-Pentanone, 4-methyl-	Methyl isobutyl ketone	2-Methylpropyl methyl ketone	108-10-1
Benzene, methyl-	Toluene	Methylbenzol	108-88-3
1-Propene, 1,3-dichloro-, (1E)-	trans-1,3-Dichloropropene	trans-1,3-Dichloropropylene	10061-02-6
Ethane, 1,1,2-trichloro-	1,1,2-Trichloroethane	1,1,2-TCA	79-00-5
Ethene, 1,1,2,2-tetrachloro-	Tetrachloroethylene	Tetrachlorethene	127-18-4
2-Hexanone	2-Hexanone	Methyl n-butyl ketone	591-78-6
Methane, dibromochloro-	Chlorodibromomethane	Dibromochloromethane	124-48-1
Ethane, 1,2-dibromo-	Ethylene Dibromide	1,2-Dibromoethane	106-93-4
Benzene, chloro-	Chlorobenzene	Phenyl chloride	108-90-7
Benzene, ethyl-	Ethylbenzene	Phenylethane	100-41-4
Benzene, 1,2-dimethyl-	o-Xylene	1,2-Dimethylbenzene	95-47-6
Benzene, (1,3 and 1,4)-dimethyl-	m,p-Xylene	(1,3 and 1,4)-Dimethyl benzene	179601-23-1
Benzene, ethenyl-	Styrene	Vinyl Benzene	100-42-5
Methane, tribromo-	Tribromomethane	Bromoform	75-25-2
Benzene, (1-methylethyl)-	Cumene	Isopropylbenzene	98-82-8
Ethane, 1,1,2,2-tetrachloro-	1,1,2,2-Tetrachloroethane	Acetylene tetrachloride	79-34-5
Benzene, 1,3-dichloro-	m-Dichlorobenzene	m-Phenylene dichloride	541-73-1
Benzene, 1,4-dichloro-	p-Dichlorobenzene	p-Chlorophenyl chloride	106-46-7
Benzene, 1,2-dichloro-	o-Dichlorobenzene	ortho-Dichlorobenzene	95-50-1
Propane, 1,2-dibromo-3-chloro-	1,2-Dibromo-3-chloropropane	Dibromochloropropane	96-12-8
Benzene, 1,2,4-trichloro-	1,2,4-Trichlorobenzene	1,2,4-Trichlorobenzol	120-82-1
Benzene, 1,2,3-trichloro-	1,2,3-Trichlorobenzene	Vic-Trichlorobenzene	87-61-6
Internal Standards			
Benzene-d5, chloro-	Chlorobenzene-d5	Chlorobenzene-d5	3114-55-4
Benzene, 1,4-difluoro	1,4-Difluorobenzene	p-Difluorobenzene	540-36-3
Benzene-1,2,4,5-d4, 3,6-dichloro	1,4-Dichlorobenzene-d4	1,4-Dichloro-2,3,5,6-tetradeuterobenzene	3855-82-1

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS (CON'T)

Systematic Name	EPA Registry Name	Synonym	CAS #
DMCs			
Ethene-d3, chloro-	Vinyl chloride-d3	Vinyl chloride-d3	6745-35-3
Ethane-d5, chloro-	Chloroethane-d5	Chloroethane-d5	19199-91-8
Ethene-1,1-d2, dichloro-	1,1-Dichloroethene-d2	1,1-Dichloroethene-d2	22280-73-5
2-Butanone-1,1,1,3,3-d5	2-Butanone-d5	2-Butanone-d5	24313-50-6
Methane-d, trichloro-	Chloroform-d	Chloroform-d	865-49-6
Ethane-1,1,2,2-d4, 1,2-dichloro-	1,2-Dichloroethane-d4	1,2-Dichloroethane-d4	17060-07-0
Benzene-1,2,3,4,5,6-d6	Benzene-d6	Benzene-d6	1076-43-3
Propane-1,1,1,2,3,3-d6, 2,3-dichloro-	1,2-Dichloropropane-d6	1,2-Dichloropropane-d6	93952-08-0
Benzene-d5, methyl-d3-	Toluene-d8	Perdeuterotoluene	2037-26-5
1-Propene-1,2,3,3-d4, 1,3-dichloro-(E)-	Trans-1,3-Dichloropropene-d4	Trans-1,3-Dichloropropene-d4	93951-86-1
2-Hexanone-1,1,1,3,3-d5		2-Hexanone-d5	4840-82-8
Ethane-1,2-d2, 1,1,2,2-tetrachloro-	1,1,2,2-Tetrachloroethane-d2	1,1,2,2-Tetrachloroethane-d2	33685-54-0
Benzene-1,2,3,4-d4, 5,6-dichloro-	1,2-Dichlorobenzene-d4	1,2-Dichloro-3,4,5,6-tetradeuterobenzene	2199-69-1

TABLE 2. 4-BROMOFLUOROBENZENE KEY IONS AND ABUNDANCE CRITERIA

Mass	**Ion Abundance Criteria**
50	15.0 - 40.0% of mass 95
75	30.0 - 80.0% of mass 95
95	base peak, 100% Relative Abundance
96	5.0 - 9.0% of mass 95 (see NOTE)
173	less than 2.0% of mass 174
174	50.0 - 120% of mass 95
175	5.0 - 9.0% of mass 174
176	95.0 - 101% of mass 174
177	5.0 - 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% that of m/z 95.

TABLE 3. TRACE VOLATILE DEUTERATED MONITORING COMPOUNDS
AND THE ASSOCIATED TARGET ANALYTES

Vinyl chloride-d_3 (DMC-1)	**Chloroethane-d_5 (DMC-2)**	**1,1-Dichloroethene-d_2 (DMC-3)**
Vinyl chloride	Dichlorodifluoromethane Chloromethane Bromomethane Chloroethane Carbon disulfide	trans-1,2-Dichloroethene cis-1,2-Dichloroethene 1,1-Dichloroethene
2-Butanone-d_5 (DMC-4)	**Chloroform-d (DMC-5)**	**1,2-Dichloroethane-d_4 (DMC-6)**
Acetone 2-Butanone	1,1-Dichloroethane Bromochloromethane Chloroform Dibromochloromethane Bromoform	Trichlorofluoromethane 1,1,2-Trichloro-1,2,2-trifluoroethane Methyl acetate Methylene chloride Methyl tert-butyl ether 1,1,1-Trichloroethane Carbon tetrachloride 1,2-Dibromoethane 1,2-Dichloroethane
Benzene-d_6 (DMC-7)	**1,2-Dichloropropane-d_6 (DMC-8)**	**Toluene-d_8 (DMC-9)**
Benzene	Cyclohexane Methylcyclohexane 1,2-Dichloropropane Bromodichloromethane	Trichloroethene Toluene Tetrachloroethene Ethylbenzene o-Xylene m,p-Xylene Styrene Isopropylbenzene
trans-1,3-Dichloropropene-d_4 (DMC-10)	**2-Hexanone-d_5 (DMC-11)**	**1,1,2,2-Tetrachloroethane-d_2 (DMC-12)**
cis-1,3-Dichloropropene trans-1,3-Dichloropropene 1,1,2-Trichloroethane	4-Methyl-2-pentanone 2-Hexanone	1,1,2,2-Tetrachloroethane 1,2-Dibromo-3-chloropropane
1,2-Dichlorobenzene-d_4 (DMC-13)		
Chlorobenzene 1,3-Dichlorobenzene 1,4-Dichlorobenzene 1,2-Dichlorobenzene 1,2,4-Trichlorobenzene 1,2,3-Trichlorobenzene		

TABLE 4. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION FOR TRACE VOLATILE ORGANIC COMPOUNDS

Analyte	**Opening Minimum RRF**	**Closing Minimum RRF**	**Maximum %RSD**	**Opening Maximum %D[1]**	**Closing Maximum %D**
Dichlorodifluoromethane	0.010	0.010	30.0	±40.0	±50.0
Chloromethane	0.010	0.010	30.0	±30.0	±50.0
Vinyl chloride	0.010	0.010	30.0	±30.0	±50.0
Bromomethane	0.010	0.010	40.0	±30.0	±50.0
Chloroethane	0.010	0.010	30.0	±30.0	±50.0
Trichlorofluoromethane	0.010	0.010	30.0	±30.0	±50.0
1,1-Dichloroethene	0.020	0.020	30.0	±20.0	±25.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	0.010	30.0	±30.0	±50.0
Acetone	0.010	0.010	40.0	±40.0	±50.0
Carbon disulfide	0.010	0.010	20.0	±25.0	±25.0
Methyl acetate	0.010	0.010	40.0	±40.0	±50.0
Methylene chloride	0.010	0.010	40.0	±30.0	±50.0
trans-1,2-Dichloroethene	0.070	0.070	20.0	±20.0	±25.0
Methyl tert-butyl ether	0.010	0.010	30.0	±30.0	±50.0
1,1-Dichloroethane	0.100	0.100	20.0	±20.0	±25.0
cis-1,2-Dichloroethene	0.100	0.100	20.0	±20.0	±25.0
2-Butanone	0.010	0.010	40.0	±40.0	±50.0
Bromochloromethane	0.020	0.020	20.0	±20.0	±25.0
Chloroform	0.040	0.040	20.0	±20.0	±25.0
1,1,1-Trichloroethane	0.050	0.050	30.0	±20.0	±25.0
Cyclohexane	0.100	0.100	30.0	±25.0	±50.0
Carbon tetrachloride	0.020	0.020	20.0	±25.0	±50.0
Benzene	0.300	0.300	20.0	±20.0	±25.0
1,2-Dichloroethane	0.010	0.010	20.0	±25.0	±50.0
Trichloroethene	0.100	0.100	20.0	±20.0	±25.0
Methylcyclohexane	0.200	0.200	30.0	±25.0	±50.0
1,2-Dichloropropane	0.100	0.100	20.0	±20.0	±25.0
Bromodichloromethane	0.090	0.090	20.0	±20.0	±25.0
cis-1,3-Dichloropropene	0.100	0.100	20.0	±20.0	±25.0
4-Methyl-2-pentanone	0.010	0.010	30.0	±30.0	±50.0
Toluene	0.400	0.400	20.0	±20.0	±25.0
trans-1,3-Dichloropropene	0.010	0.010	30.0	±20.0	±25.0
1,1,2-Trichloroethane	0.040	0.040	20.0	±20.0	±25.0
Tetrachloroethene	0.100	0.100	20.0	±20.0	±25.0
2-Hexanone	0.010	0.010	40.0	±40.0	±50.0
Dibromochloromethane	0.050	0.050	20.0	±20.0	±25.0
1,2-Dibromoethane	0.010	0.010	20.0	±20.0	±25.0

TABLE 4. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION FOR TRACE VOLATILE ORGANIC COMPOUNDS (CON'T)

Analyte	**Opening Minimum RRF**	**Closing Minimum RRF**	**Maximum %RSD**	**Opening Maximum %D[1]**	**Closing Maximum %D**
Chlorobenzene	0.400	0.400	20.0	±20.0	±25.0
Ethylbenzene	0.500	0.500	20.0	±20.0	±25.0
m,p-Xylene	0.200	0.200	20.0	±20.0	±25.0
o-Xylene	0.300	0.300	30.0	±20.0	±25.0
Styrene	0.200	0.200	30.0	±20.0	±25.0
Bromoform	0.010	0.010	30.0	±30.0	±50.0
Isopropylbenzene	0.700	0.700	30.0	±25.0	±25.0
1,1,2,2-Tetrachloroethane	0.050	0.050	20.0	±25.0	±25.0
1,3-Dichlorobenzene	0.500	0.500	20.0	±20.0	±25.0
1,4-Dichlorobenzene	0.700	0.700	20.0	±20.0	±25.0
1,2-Dichlorobenzene	0.400	0.400	20.0	±20.0	±25.0
1,2-Dibromo-3-chloropropane	0.010	0.010	40.0	±40.0	±50.0
1,2,4-Trichlorobenzene	0.300	0.300	30.0	±30.0	±50.0
1,2,3-Trichlorobenzene	0.200	0.200	30.0	±40.0	±50.0
Deuterated Monitoring Compounds					
Vinyl chloride-d_3	0.010	0.010	30.0	±30.0	±50.0
Chloroethane-d_5	0.010	0.010	30.0	±30.0	±50.0
1,1-Dichloroethene-d_2	0.010	0.010	30.0	±25.0	±25.0
2-Butanone-d_5	0.010	0.010	40.0	±40.0	±50.0
Chloroform-d	0.010	0.010	20.0	±20.0	±25.0
1,2-Dichloroethane-d_4	0.010	0.010	20.0	±25.0	±25.0
Benzene-d_6	0.030	0.030	20.0	±20.0	±25.0
1,2-Dichloropropane-d_6	0.100	0.100	20.0	±20.0	±25.0
Toluene-d_8	0.200	0.200	20.0	±20.0	±25.0
trans-1,3-Dichloropropene-d_4	0.010	0.010	30.0	±25.0	±25.0
2-Hexanone-d_5	0.010	0.010	40.0	±40.0	±50.0
1,1,2,2-Tetrachloroethane-d_2	0.010	0.010	20.0	±25.0	±25.0
1,2-Dichlorobenzene-d_4	0.060	0.060	20.0	±20.0	±25.0

[1] If a closing CCV is acting as an opening CCV, all target analytes must meet the requirements for an opening CCV.

TABLE 5. PURGE-AND-TRAP ANALYTICAL CONDITIONS

Purge Conditions	
Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ±0.1 min.
Purge Flow Rate:	25-40 mL/min.
Purge Temperature:	Ambient temperature
Desorb Conditions	
Desorb Temperature:	180°C
Desorb Flow Rate:	15 mL/min.
Desorb Time:	4.0 ±0.1 min.
Trap Reconditioning Conditions	
Reconditioning Temperature:	180°C
Reconditioning Time:	7.0 ±0.1 min. (minimum). A longer time may be required to bake contamination or water from the system.

NOTE: Higher purge temperatures may be used provided that manufacturer's instructions are followed and technical acceptance criteria are met for all standards, samples, and blanks. Certain target analytes, such as methyl tert-butyl ether (MTBE), may decompose at high purge temperatures in samples that have been acid preserved.

TABLE 6. GAS CHROMATOGRAPH ANALYTICAL CONDITIONS

Capillary Columns	
Carrier Gas:	Helium
Flow Rate:	15 mL/min.
Initial Temperature:	10°C
Initial Hold Time:	1.0 – 5.0 (±0.1) min.
Ramp Rate:	6°C/min.
Final Temperature:	160°C
Final Hold Time:	Until 3 min. after all analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 1 – Trace Volatiles Target Analyte Lists and Contract Required Quantitation Limits, elute (required)

TABLE 7. MASS SPECTROMETER ANALYTICAL CONDITIONS

Electron Energy	70 volts (nominal)
Mass Range	35-300 u
Ionization Mode	Electron ionization (EI)
Scan Time	To give at least 5 scans per peak, not to exceed 2 sec. per scan.

TABLE 8. CHARACTERISTIC IONS FOR TRACE VOLATILE TARGET ANALYTES, DEUTERATED MONITORING COMPOUNDS, AND INTERNAL STANDARDS

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61,63
1,1,2-Trichloro-1,2,2-trifluoroethane	101	85,151
Acetone	43	58
Carbon disulfide	76	78
Methyl acetate	43	74
Methylene chloride	84	49,86
trans-1,2-Dichloroethene	96	61,98
Methyl tert-butyl ether	73	43,57
1,1-Dichloroethane	63	65,83
cis-1,2-Dichloroethene	96	61,98
2-Butanone	43*	72
Chloroform	83	85
Bromochloromethane	128	49,130,51
1,1,1-Trichloroethane	97	99,61
Cyclohexane	56	69,84
Carbon tetrachloride	117	119
Benzene	78	-
1,2-Dichloroethane	62	98
Trichloroethene	95	97,132,130
Methylcyclohexane	83	55,98
1,2-Dichloropropane	63	112
Bromodichloromethane	83	85,127
cis-1,3-Dichloropropene	75	77
4-Methyl-2-pentanone	43	58,100
Toluene	91	92
trans-1,3-Dichloropropene	75	77
1,1,2-Trichloroethane	97	83,85,99,132,134
Tetrachloroethene	164	129,131,166
2-Hexanone	43	58,57,100
Dibromochloromethane	129	127
1,2-Dibromoethane*	107	109,188
Chlorobenzene	112	77,114
Ethylbenzene	91	106
m,p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78

*m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

TABLE 8. CHARACTERISTIC IONS FOR TRACE VOLATILE TARGET ANALYTES, DEUTERATED MONITORING COMPOUNDS, AND INTERNAL STANDARDS (CON'T)

Analyte	**Primary Quantitation Ion**	**Secondary Ion(s)**
Bromoform	173	175,254
Isopropylbenzene	105	120,77
1,1,2,2-Tetrachloroethane	83	85,131
1,3-Dichlorobenzene	146	111,148
1,4-Dichlorobenzene	146	111,148
1,2-Dichlorobenzene	146	111,148
1,2-Dibromo-3-chloropropane*	75	157,155
1,2,4-Trichlorobenzene	180	182,145
1,2,3-Trichlorobenzene	180	182,145
Deuterated Monitoring Compounds		
Vinyl chloride-d_3	65	67
Chloroethane-d_5	69	71,51
1,1-Dichloroethene-d_2	63	98,65
2-Butanone-d_5	46	77
Chloroform-d	84	86,47,49
1,2-Dichloroethane-d_4	65	67,51
Benzene-d_6	84	82,54,52
1,2-Dichloropropane-d_6	67	65,46,42
Toluene-d_8	98	100,42
trans-1,3-Dichloropropene-d_4	79	81,42
2-Hexanone-d_5	63	46
1,1,2,2-Tetrachloroethane-d_2	84	86
1,2-Dichlorobenzene-d_4	152	150
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115,150
1,4-Difluorobenzene	114	63,88
Chlorobenzene-d_5	117	82,119

*m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

TABLE 9. TRACE VOLATILE TARGET ANALYTES AND DEUTERATED MONITORING COMPOUNDS WITH ASSOCIATED INTERNAL STANDARDS FOR QUANTITATION

1,4-Difluorobenzene (IS)	**Chlorobenzene-d_5 (IS)**	**1,4-Dichlorobenzene-d_4 (IS)**
Dichlorodifluoromethane	1,1,1-Trichloroethane	Bromoform
Chloromethane	Cyclohexane	1,3-Dichlorobenzene
Vinyl chloride	Carbon tetrachloride	1,4-Dichlorobenzene
Bromomethane	Benzene	1,2-Dichlorobenzene
Chloroethane	Trichloroethene	1,2-Dibromo-3-chloropropane
Trichlorofluoromethane	Methylcyclohexane	1,2,4-richlorobenzene
1,1-Dichloroethene	1,2-Dichloropropane	1,2,3-richlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	Bromodichloromethane	1,2-Dichlorobenzene-d_4 (DMC)
Acetone	cis-1,3-Dichloropropene	
Carbon disulfide	4-Methyl-2-pentanone	
Methyl acetate	Toluene	
Bromochloromethane	trans-1,3-Dichloropropene	
Methylene chloride	1,1,2-Trichloroethane	
trans-1,2-Dichloroethene	Tetrachloroethene	
Methyl tert-butyl ether	2-Hexanone	
1,1-Dichloroethane	Dibromochloromethane	
cis-1,2-Dichloroethene	1,2-Dibromoethane	
2-Butanone	Chlorobenzene	
Chloroform	Ethylbenzene	
1,2-Dichloroethane	m,p-Xylene	
Vinyl chloride-d_3 (DMC)	o-Xylene	
Chloroethane-d_5 (DMC)	Styrene	
1,1-Dichloroethene-d_2 (DMC)	Isopropylbenzene	
2-Butanone-d_5 (DMC)	1,1,2,2-Tetrachloroethane	
Chloroform-d (DMC)	Benzene-d_6 (DMC)	
1,2-Dichloroethane-d_4 (DMC)	1,2-Dichloropropane-d_6 (DMC)	
	trans-1,3-Dichloropropene-d_4 (DMC)	
	Toluene-d_8 (DMC)	
	2-Hexanone-d_5 (DMC)	
	1,1,2,2-Tetrachloroethane-d_2 (DMC)	

TABLE 10. DEUTERATED MONITORING COMPOUND RECOVERY LIMITS

Compound	Percent Recovery Limits
Vinyl chloride-d_3	40-130
Chloroethane-d_5	65-130
1,1-Dichloroethene-d_2	60-125
2-Butanone-d_5	40-130
Chloroform-d	70-125
1,2-Dichloroethane-d_4	70-130
Benzene-d_6	70-125
1,2-Dichloropropane-d_6	60-140
Toluene-d_8	70-130
trans-1,3-Dichloropropene-d_4	55-130
2-Hexanone-d_5	45-130
1,1,2,2-Tetrachloroethane-d_2	65-120
1,2-Dichlorobenzene-d_4	80-120

NOTE: The recovery limits for any of the compounds listed above may be expanded at any time during the period of performance if the EPA determines that the limits are too restrictive.

TABLE 11. MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS

Analyte	Percent Recovery	RPD
1,1-Dichloroethene	61-145	0-14
Benzene	76-127	0-11
Trichloroethene	71-120	0-14
Toluene	76-125	0-13
Chlorobenzene	75-130	0-13

THIS PAGE INTENTIONALLY LEFT BLANK

EXHIBIT D
LOW/MEDIUM CONCENTRATIONS OF
VOLATILE ORGANIC COMPOUNDS ANALYSIS

THIS PAGE INTENTIONALLY LEFT BLANK

Exhibit D – Low/Medium Concentrations of
Volatile Organic Compounds Analysis

Table of Contents

Exhibit D – Low/Medium Concentrations of
Volatile Organic Compounds Analysis

Table of Contents

1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze water, leachate derived from the Toxicity Characteristics Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP) and soil/sediment samples from hazardous waste sites for the volatile organic compounds in the Target Analyte List (TAL) for low/medium volatiles in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits. The method, based on U.S. Environmental Protection Agency (EPA) Method 8260C, includes sample preparation and analysis to determine the approximate concentration of volatile organic constituents in the sample. The actual analysis is based on a purge-and-trap (P/T) Gas Chromatograph/Mass Spectrometer (GC/MS) method for aqueous and medium-level soil samples and closed-system purge-and-trap for low-level soil samples.

1.2 Problems that have been associated with the following analytes analyzed using this method include:

- Chloromethane, vinyl chloride, bromomethane, and chloroethane may display peak broadening if the analytes are not delivered to the GC column in a tight band.
- Acetone, hexanone, 2-butanone, and 4-methyl-2-pentanone have poor purge efficiencies and may be lost if purge flow is too slow.
- 1,1,1-trichloroethene and all of the dichloroethenes may dehydrohalogenate during storage or analysis.
- Tetrachloroethane and 1,1-dichloroethane may be degraded by contaminated transfer lines in P/T systems and/or active sites in trapping materials.
- Chloromethane and other gases may be lost if the purge flow is too fast.
- Bromoform is one of the analytes most likely to be adversely affected by cold spots and/or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by tuning of 4-bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio within the specified Quality Control (QC) limits may improve bromoform response.

2.0 SUMMARY OF METHOD

2.1 Water/TCLP or SPLP Leachate

An inert gas is bubbled through a 5 milliliter (mL) sample contained in a specially designed purging chamber at ambient temperature. Higher purge temperatures may be used, provided that all technical acceptance criteria are met for all standards, samples, and blanks. The same purge conditions must be used for all associated standards, samples, and blanks. The purgeable compounds are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeable compounds are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a GC wide-bore capillary column. The GC is temperature-programmed to separate the purgeable compounds, which are then detected with an MS.

2.2 Soil/Sediment

2.2.1 Low-Level Soil/Sediment

Low-level volatile organic compounds are generally determined by analyzing approximately 5 grams (g) of sample in a pre-weighed vial with a septum-sealed screw-cap (Section 6.1.10) that already contains a stirring bar.

NOTE: The sodium bisulfate preservative may be used under limited circumstances. 5 mL of sodium bisulfate solution (Section 7.1.3) is added to each sample when preservation by sodium bisulfate is requested by the U.S. Environmental Protection Agency (EPA) Region.

The entire vial is placed into the instrument carousel. Immediately before analysis, organic-free reagent water, Deuterated Monitoring Compounds (DMCs), and internal standards are automatically added without opening the sample vial. The vial containing the sample is heated to the suggested temperature of 40°C and the volatiles are purged through a sorbent trap using an inert gas combined with agitation of the sample. Higher purge temperatures may be required for the analysis of certain target analytes. When purging is complete, the sorbent column is heated and backflushed with helium to desorb the purgeable compounds onto a capillary GC column. The GC is temperature-programmed to separate the purgeable compounds, which are then detected with an MS.

2.2.2 Medium-Level Soil/Sediment

A soil sample of 5 g is collected, preserved in methanol, and/or extracted with methanol. An aliquot of the methanol extract is added to 5 mL of reagent water. An inert gas is bubbled through this solution in a specially designed purging chamber at ambient temperature. The purgeable compounds are effectively transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeable compounds onto a capillary GC column. The GC is temperature-programmed to separate the purgeable compounds, which are then detected with an MS.

2.3 Wipes

Not applicable to this method.

2.4 Waste

Not applicable to this method.

2.5 Non-Target Compounds

Non-target compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the NIST (2011 release or later), Wiley (2011 release or later), or equivalent mass spectral library. Non-target compounds are quantitated by comparing the area response from the total Reconstructed Ion Chromatogram (RIC) for the non-target compound peaks to the area response provided by the nearest internal standard compound. A Relative Response Factor (RRF) of 1 is assumed.

3.0 DEFINITIONS

See Exhibit G – Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

4.1.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing laboratory method and instrument blanks as described in Section 12.1. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.1.2 Samples can be contaminated by diffusion of purgeable organics (particularly methylene chloride, fluorocarbons, and other common laboratory solvents) through the septum seal into the sample during storage and handling. Therefore, these samples must be stored separately from other laboratory samples and standards, and must be analyzed in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis.

4.1.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it must either be followed by analysis of an instrument blank, or the next sample must be closely monitored to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required.

4.1.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine the presence of methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all Gas Chromatography (GC) carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken. At the time of sample receipt, the Contractor must prepare two 40 mL VOA vials containing reagent water and/or inert sand to be stored as storage blanks with each group of samples (Section 12.1.4).

4.2 Matrix Interferences

Matrix interferences may be caused by compounds that are purged or co-extracted from the sample. The extent of matrix interferences will vary considerably depending on the nature of the site being sampled.

5.0 SAFETY

See Section 12.0 of Exhibit D – Introduction to Organic Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternative equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 General Laboratory Equipment

6.1.1 Balances

6.1.1.1 Top loading, capable of weighing accurately to ±0.01 g.

6.1.1.2 Analytical, capable of weighing accurately to ±0.0001 g.

6.1.1.3 A balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±50% of the expected measured mass) for each type of balance and be accurate to ±0.01 g and ±0.0001 g, respectively. The masses that are used to check the balances daily must be checked on a monthly basis using NIST-traceable known reference masses (Class '0' or Class '1') as defined by ASTM E617-97(2008) or equivalent (e.g., earlier Class 'S' defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must be recertified at least every five years, or sooner if there is reason to believe damage (corrosion, nicks) has occurred. The Contractor shall maintain documentation that demonstrates these criteria have been met.

6.1.2 Bottle - 15 mL, screw-cap, with PTFE cap liner.

6.1.3 Magnetic Stirring Bars - PTFE or glass-coated, of the appropriate size to fit the sample vials. Consult the manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturer of the purging device and the stirring bars for suggested cleaning procedures.

6.1.4 Micro Syringes - 25 microliters (µL) with a 2 inch x 0.006 inch ID, 22 gauge beveled needle. 10 µL and 100 µL. All micro syringes shall be visually inspected and documented monthly.

6.1.5 Pasteur Pipettes, Disposable.

6.1.6 pH Paper - Wide range.

6.1.7 Spatula – Stainless steel or PTFE

6.1.8 Syringes - 25 mL glass hypodermic syringes with a Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used). 5.0, 1.0, and 0.5 mL syringes, gas-tight with shut-off valve.

6.1.9 Syringe Valve - Two-way, with Luer-Lok ends (three each), if applicable to the purging device.

6.1.10 Vials

6.1.10.1 40 mL, screw-cap, PTFE-lined, septum-sealed glass vials. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

6.1.10.2 60 mL, septum-sealed glass vials to collect samples for screening, percent moisture determination.

6.1.10.3 Vials and Caps - Assorted sizes.

6.1.11 Volumetric Flasks - Class A, 10 mL and 100 mL, with ground-glass stoppers.

6.2 Glassware/Extraction/Cleanup Equipment

Not applicable to this method.

6.3 Analytical Instrumentation

6.3.1 Gas Chromatograph

The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout desorption and temperature program operations. The system must include or be interfaced to a P/T system as specified in Section 6.3.4 and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants, or flow controllers with rubber components, are not to be used.

6.3.2 Gas Chromatography Columns

Recommended Column: Minimum length 30 meter (m) x 0.53 mm ID fused silica wide-bore capillary column with a 6% Cyanopropylphenyl 94% Dimethyl Polysiloxane phase having a 3 micrometer (µm) film thickness (i.e., VOCOL, Rtx®-502.2, DB-624, Rtx®-624, CP-Select 624CB, or equivalent fused silica wide-bore capillary column). A description of the column used for analysis shall be provided in the SDG Narrative. Packed GC columns cannot be used. The column shall accept up to 1000 nanograms (ng) of each analyte listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, without becoming overloaded.

6.3.2.1 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the analytes listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits.
- The analytical results generated using the column meet the initial calibration and continuing calibration verification (CCV) technical acceptance criteria (Sections 9.3.5 and 9.4.5) and the CRQLs listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits. Sufficient chromatographic resolution is achieved when the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights.
- The column provides equal or better resolution of the analytes listed in Exhibit C than the columns listed in Section 6.3.2.

6.3.2.1.1 As applicable, follow the manufacturer's instructions for use of its product.

6.3.2.1.2 The Contractor must maintain documentation that the column met the criteria in Section 6.3.2.1. The minimum documentation is as follows:

6.3.2.1.2.1 Manufacturer provided information concerning the performance characteristics of the column.

6.3.2.1.2.2 RICs and data system reports generated on the GC/MS used for Contract Laboratory Program (CLP) analyses:

- From instrument blanks that demonstrate that there are no contaminants that interfere with the volatile analysis when using the alternate column; and
- From initial calibrations and CCV standards analyzed using the alternate column.

6.3.2.1.3 Based on the Contractor-generated data described above, the Contractor shall complete a written comparison/review, signed by the Laboratory Manager, certifying that:

- The alternate column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the volatile CRQLs;
- The high-point initial calibration standard analysis was not overloaded; and
- The column does not introduce contaminants that interfere with the identification and/or quantitation of analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits.

6.3.2.1.4 The documentation must be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional Laboratory Contracting Officer Representative (COR).

6.3.3 Mass Spectrometer

The MS must be capable of scanning from 35-300 atomic mass units (u) every 2 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the BFB GC/MS performance check technical acceptance criteria in Table 2 – 4-Bromofluorobenzene Key Ions and Ion Abundance Criteria when 50 ng of BFB is injected through the GC inlet. The instrument conditions required for the acquisition of the BFB mass spectrum are given in Section 9.2.4.

NOTE: To ensure sufficient precision of mass spectral data, the MS scan rate should allow acquisition of at least five spectra while a sample compound elutes from the GC. The P/T GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis. The instrument must be vented to the outside of the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.3.3.1 Gas Chromatograph/Mass Spectrometer Interface

Any GC/MS interface that gives acceptable calibration points at 25 ng or less per injection for each of the purgeable non-ketone

target analytes and DMCs, and achieves all acceptable performance criteria. GC/MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.3.4 Purge-and-Trap Device

The P/T device consists of three separate pieces of equipment: the sample purge chamber, the trap, and the desorber. The analyst either manually or automatically (through an automated P/T device separate or integral with the GC) samples an appropriate volume (e.g., 5.0 mL) from the vial; adds DMCs, matrix spikes, and internal standards to the sample; and transfers the sample to the purge device. The device also purges volatile organic compounds (VOCs) using an inert gas stream and traps the released VOCs for subsequent desorption into the GC. For low-level soil samples, the P/T device consists of a unit that automatically adds water, DMC spiking solution, and internal standard spiking solution to a hermetically-sealed vial containing the sample; purges the volatile target analytes using an inert gas stream while agitating the contents of the vial; and traps the released volatile target analytes for subsequent desorption into the GC. Such systems shall meet the following specifications:

6.3.4.1 The P/T device must be capable of accepting 40 mL closed-system P/T sample vials from the field, which are not to be opened during the analytical process.

6.3.4.2 The specific required sample containers will depend on the P/T system to be employed. The Contractor shall consult the P/T system manufacturer’s instructions regarding suitable specific vials, septa, caps, and mechanical agitation devices.

6.3.4.3 The sample purge chamber must be designed to accept 5.0 mL samples with a water column at least 3 centimeters (cm) deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column.

6.3.4.4 For soil samples, the purging device should be capable of accepting a vial large enough to contain a 5 g soil/sediment sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging (e.g., using a magnetic stirring bar, sonication, or other means). The analytes being purged must be quantitatively transferred to an adsorber trap. The trap must be capable of transferring the adsorbed volatile compounds to the GC.

6.3.4.5 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inches (2.667 mm). The trap must be packed to contain (starting from the inlet) 0.5 cm silanized glass wool, and the following minimum lengths of adsorbent:

- 8 cm of 2,6-diphenylene oxide polymer (60/80 mesh chromatographic grade Tenax GC or equivalent).

- 1 cm methyl silicone packing, 3.0% OV-1 on Chromasorb W, 60/80 mesh (or equivalent).
- 8 cm of silica gel, 35/60 mesh (or equivalent).
- 7 cm of coconut charcoal.

6.3.4.6 Alternate sorbent traps may be used if:

- The trap packing materials do not introduce contaminants that interfere with identification and quantitation of the analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits.
- The analytical results generated using the trap meet the initial calibration and CCV technical acceptance criteria listed in the analytical method and the CRQLs listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 - Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits.
- The trap must be capable of accepting up to 1000 ng of each analyte listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 - Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits without becoming overloaded.

6.3.4.6.1 Before use of any trap other than the one specified in Section 6.3.4.5, the Contractor must first meet the criteria listed in Section 6.3.4.6. Once this has been demonstrated, the Contractor must document its use in each SDG Narrative by specifying the trap composition (packing material/brand name, amount of packing material). Other sorbent traps include, but are not limited to: Tenax/Silica Gel/Carbon Trap from EPA Method 524.2 and Vocarb 4000 Trap (Supelco) or equivalent.

6.3.4.6.2 The Contractor must maintain documentation that the alternate trap meets the criteria listed in Section 6.3.4.6. The minimum documentation requirements are as follows:

6.3.4.6.2.1 Manufacturer provided information concerning the performance characteristics of the trap.

6.3.4.6.2.2 RICs and data system reports generated on the Contractor's GC/MS used for CLP analyses:

- From instrument blank analyses that demonstrate there are no contaminants that interfere with the volatile analysis when using the alternate trap; and
- From initial calibration and CCV standards analyzed using the trap specified in Section 6.3.4.

6.3.4.6.2.3 Based on Contractor-generated data described above, the Contractor must complete a written comparison/review that has been signed by the Laboratory Manager certifying that:

- The alternate trap performance meets the technical acceptance criteria listed in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the low/medium volatile CRQLs;

- The high-point initial calibration standard analysis was not overloaded; and
- The alternate trap materials do not introduce contaminants that interfere with the identification and/or quantitation of the analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits.

6.3.4.6.2.4 The documentation must be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request of the EPA Regional Laboratory COR.

6.3.4.6.2.5 A description of the trap used for analysis shall be provided in the SDG narrative.

6.3.4.7 The P/T apparatus may be assembled as a separate unit or be an integral unit coupled with a GC.

6.3.4.8 The desorber shall be capable of rapidly heating the trap to the desorb temperature recommended for the trap in use. The polymer section of the recommended trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bake-out mode.

6.4 Data Systems/Data Storage

A computer system must be interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching of any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows comparing sample spectra against reference library spectra. The NIST (2011 release or later), Wiley (2011 release or later), or equivalent mass spectral library shall be used as the reference library. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

7.0 REAGENTS AND STANDARDS

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit D – Introduction to Organic Analytical Methods, Section 4.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1 Reagents

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the CRQL for each analyte of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g [1 pound (lb)] of activated carbon.

7.1.1.2 Reagent water may also be generated using a water purification system.

7.1.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle, seal with a PTFE-lined septum, and cap.

7.1.2 Methanol - High Performance Liquid Chromatography (HPLC) quality or equivalent - Each lot of methanol used for analysis under the contract must be purged with nitrogen and must be demonstrated to be free of contaminants that interfere with the measurement of purgeable analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits.

7.1.3 Sodium Bisulfate Solution - 2 g of ACS reagent grade or equivalent sodium bisulfate is dissolved for every 5 g of water.

7.2 Standards

7.2.1 Stock Standard Solutions

Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be in methanol from pure standard materials or purchased as pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated.

7.2.2 Working Standards

7.2.2.1 Initial and Continuing Calibration Solutions

Prepare working calibration standard solution(s) containing all of the purgeable target analytes (Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits) in methanol. Prepare fresh calibration

standard solution(s) every month, or sooner if the solution has degraded or evaporated.

NOTE: The Contractor may prepare a calibration standard containing all of the non-ketones and a separate standard containing ketones.

7.2.2.1.1 Add a sufficient amount of each working standard to a 5.0 mL aliquot of reagent water to produce the desired calibration standard concentrations listed in Sections 7.2.2.1.2 or 7.2.2.1.4.

7.2.2.1.2 Prepare five aqueous initial calibration standard solutions containing all of the purgeable target analytes and the DMCs at the following levels: all non-ketone target analytes and their associated DMCs (see Table 3 – Volatile Deuterated Monitoring Compounds and the Associated Target Analytes) at 5.0, 10, 50, 100, and 200 µg/L; all ketones and their associated DMCs (see Table 3 - Volatile Deuterated Monitoring Compounds and the Associated Target Analytes) at 10, 20, 100, 200, and 400 µg/L. All three xylene isomers (o-, m-, and p-xylene) must be present in the calibration standards. The o-xylene calibration standard concentrations must be at 5.0, 10, 50, 100, and 200 µg/L, while the concentration of the m- plus p-xylene isomers must total 5.0, 10, 50, 100, and 200 µg/L.

NOTE: The concentrations listed above are based on a 5 mL volume. If 10 mL volumes are to be used (i.e., low-level soil samples), then the concentrations of the standards must be reduced in half to ensure the same on-column amount of each analyte.

7.2.2.1.3 Calibration standards must be prepared in a volumetric flask or in the syringe used to inject the standard into the purging device.

7.2.2.1.4 For CCV (opening and closing CCVs), the standard shall be at the concentration equivalent to the mid-level calibration standards: 50 µg/L for non-ketones and 100 µg/L for ketones.

NOTE: The concentrations listed above are based on a 5.0 mL volume. If 10 mL volumes are to be used (i.e., low-level soil samples) then the concentrations of the standards must be reduced in half to ensure the same on-column amount of each analyte.

7.2.2.1.5 The methanol contained in each of the aqueous calibration standards must not exceed 1% by volume.

7.2.2.2 Instrument Performance Check Solution

Prepare the instrument performance check solution containing BFB in methanol. If the BFB solution is added to the mid-level calibration standard (50 µg/L for non-ketones and 100 µg/L for ketones), add a sufficient amount of BFB to result in a 10 µg/L concentration of BFB (50 ng on-column). The BFB must be analyzed using the same GC and MS analytical conditions as are used for the calibration analysis.

7.2.2.3 Deuterated Monitoring Compound Spiking Solution

7.2.2.3.1 Prepare a DMC spiking solution in methanol (or in deuterated methanol) containing the compounds listed in Table 3 - Volatile Deuterated Monitoring Compounds and the Associated Target Analytes.

7.2.2.3.2 DMCs are to be added to each sample and blank, as well as initial calibration standards and CCV standards.

7.2.2.3.3 For samples and blanks, add sufficient amount of the DMC spiking solution to each sample to result in the addition of 0.25 µg of each non-ketone DMC and 0.50 µg for each ketone DMC.

7.2.2.3.4 For calibration standards, add sufficient amounts of the DMC spiking solution to each 5.0 mL aliquot of calibration standard to result in the concentrations listed in Section 7.2.2.1.2 (initial calibration) and Section 7.2.2.1.4 (CCV).

7.2.2.3.5 Prepare a fresh DMC spiking solution every month, or sooner if the standard has degraded or concentrated.

7.2.2.4 Matrix Spiking Solution

If Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis is requested at the time of scheduling, prepare a spiking solution in methanol that contains the following analytes at a concentration of 12.5 µg/mL: 1,1-dichloroethene; trichloroethene; chlorobenzene; toluene; and benzene. Prepare fresh spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.2.5 Internal Standard Spiking Solution

Prepare an internal standard spiking solution containing 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 in methanol. Add a sufficient amount of the internal standard solution to samples, including MS/MSDs, blanks, and calibration standards to result in a 50 µg/L concentration or the addition of 0.25 µg of each internal standard. Prepare a fresh internal standard spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.3 Storage of Standard Solutions

7.2.3.1 Store the stock standards in PTFE-sealed screw-cap bottles with zero headspace at -10°C to -20°C.

Aqueous standards may be stored for up to 24 hours if held in PTFE-sealed screw-cap vials with zero headspace at ≤6°C, but not frozen. If not stored as such, the standards must be discarded after 1 hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept up to 12 hours in purge tubes connected via the autosampler to the P/T device.

7.2.3.2 Standard solutions purchased from a chemical supply company as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from the preparation date. The expiration date of the ampulated standards, upon the breaking of the glass seal, is 6 months (or sooner if the standard has degraded or evaporated).

7.2.3.3 Protect all standards from light.

7.2.3.4 Purgeable standards must be stored separately from other standards, samples, and blanks.

7.2.3.5 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. Storage of standard solutions in the freezer may cause some compounds to precipitate. This means that standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in the solution.

7.2.3.5.1 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases may need to be replaced after 1 month for working standards and 6 months for opened stocks, or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

7.2.4 Temperature Records for Storage of Standards

7.2.4.1 The temperature of all standards storage refrigerators/freezers shall be recorded daily.

7.2.4.2 Temperature excursion shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.2.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water Samples

8.1.1.1 Water samples may be collected in glass containers having a total volume of at least 40 mL with a PTFE-lined septum and an open top screw-cap.

8.1.1.2 The containers should have been filled in such a manner that no air bubbles were entrained to create a head space in the vial.

8.1.1.3 The samples are preserved to a pH ≤2 at the time of collection.

8.1.1.4 A total of three vials per field sample is the recommended amount the Contractor should receive.

NOTE: If MS/MSD analysis is required for a particular sample, two additional vials should be sent by the field samplers. Contact the Sample Management Office (SMO) if insufficient sample for MS/MSD analysis has been provided.

8.1.2 Soil/Sediment Samples

8.1.2.1 Soil/Sediment samples may be received from the field either in pre-prepared closed-system P/T sample vials, pre-weighed glass vials, or in field core sampling/storage containers (e.g., EnCore™ or equivalent). Samples received in pre-prepared closed-system vials may arrive with no added preservatives, in 5 mL of water (low level only), or preserved with sodium bisulfate (low level only). Samples in pre-weighed glass vials may be preserved with 5 mL of methanol (medium-level samples only). Only vials that are thoroughly sealed may be used for medium-level soil analysis.

8.1.2.2 For soil samples received in pre-prepared, closed-system P/T sample vials (Section 10.2.2), or pre-weighed glass vials that are to be stored at -7°C, ensure that the samples are placed on their side prior to being frozen.

8.1.2.3 For samples received in pre-prepared closed-system P/T vials or pre-weighed glass vials, the Contractor should receive at least three such vials per field sample, plus at least one additional 60 mL sealed glass vial containing sample with minimum headspace. For samples received in field core sampling containers, the Contractor should receive at least three such containers per field sample, plus at least one additional 60 mL sealed glass vial containing sample with minimum headspace. If the minimum number of containers has not been sent by the field samplers, the Contractor is to immediately contact SMO for instructions. A total of four vials per field sample is the recommended amount of vials the Contractor should receive.

NOTE: If MS/MSD analysis is required for a particular sample, eight additional field core containers or glass vials should be sent by the field samplers. Contact SMO if insufficient sample for MS/MSD analysis has been provided.

8.1.2.3.1 For each methanol-preserved sample, samplers should send approximately 5 g (weight excluding preservative) of sample containing preservative in a pre-weighed glass vial. The Contractor shall weigh this vial immediately upon receipt and then store at ≤6°C, but not frozen. If a medium-level analysis of the sample is necessary, use this vial.

8.1.2.4 Samples received in pre-prepared closed-system P/T vials without preservative are to be stored at ≤6°C and analyzed within 24 hours of sample receipt, or they must be stored at less than -7°C until time of analysis if they do not contain visible moisture. If the sample appears to be moist and there is insufficient space above the soil portion in the sample vial, the Contractor shall contact SMO immediately for directions to avoid possible damage of the sample vial during sample storage in the freezer. Ensure that the samples are clean of external dirt and moisture prior to weighing.

8.1.2.5 In limited cases, preservation with sodium bisulfate may be required. Samples received in pre-prepared closed-system purge-and-trap vials preserved with sodium bisulfate shall be stored at ≤6°C, but not frozen, until time of analysis. Samples preserved with sodium bisulfate should be accompanied by field documentation recording the initial weight of the vial with preservative.

8.1.2.6 Medium-level samples may be received in pre-weighed vials preserved with methanol. Samples preserved with methanol should be accompanied by field documentation recording the initial weight of the vial with methanol. If the volume of methanol in the vial does not appear to be equal to 5 mL, or if the vial appears to be dry, or if field documentation of vial tare weight does not accompany the vials, the Contractor shall immediately contact SMO, who will contact the EPA Region.

8.1.2.7 For samples received in field core sampling/storage containers, the Contractor shall transfer the contents of the three containers for each sample, immediately upon receipt, to a pre-prepared closed-system P/T vial, and record the date and time of transfer. The transferred samples are to be analyzed within 24 hours of sample receipt, or they must be stored at less than -7°C. If the samples contain visible moisture, the Contractor shall immediately contact SMO.

8.2 Procedure for Sample and Sample Extract Storage

8.2.1 Sample Storage

8.2.1.1 Unpreserved low/medium soil samples must be protected from light and stored at less than -7°C from the time of receipt until time of analysis. Store unused sample aliquots at less than -7°C until 60 days after delivery of a complete, reconciled, data package to the EPA. Samples received preserved with methanol shall be stored at ≤6°C, but not frozen, until time of analysis. Samples received without preservative are to be analyzed within 24 hours of sample receipt, or they must be stored at less than -7°C until time of preparation and analysis.

8.2.1.2 Sodium bisulfate preserved low soil samples and water samples must be protected from light and stored at ≤6°C, but not frozen, in a refrigerator used only for storage of volatile samples, in an atmosphere demonstrated to be free of all potential contaminants, until 60 days after delivery of a complete, reconciled, data package to the EPA.

8.2.1.3 After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.1.4 Aqueous storage blanks shall be stored at ≤6°C, but not frozen, with preserved low/medium soil samples and water samples within an SDG until all such samples are analyzed. Inert sand storage blanks shall be stored at less than -7°C with unpreserved low/medium soil samples until all such samples are analyzed.

8.2.2 Sample Extract Storage

8.2.2.1 Medium level sample extracts must be protected from light and stored at -7°C until 365 days after delivery of a complete, reconciled data package to the EPA.

8.2.2.2 Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.3 Contract Required Holding Times

Analysis of water and soil/sediment samples must be completed within 10 days of Validated Time of Sample Receipt (VTSR). Analysis of unpreserved, unfrozen soil/sediment samples must be completed within 24 hours of VTSR. The holding time for TCLP/SPLP leachate samples is 7 days from the completion of the TCLP/SPLP extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Initial Instrument Set-up

9.1.1 Purge-and-Trap

9.1.1.1 The recommended P/T analytical conditions are provided in Table 5 – Purge and Trap Analytical Conditions. The conditions are suggested, but other conditions may be used, provided that all technical acceptance criteria are met for all standards, samples, and blanks.

9.1.1.2 Assemble a P/T device that meets the specifications in Section 6.3.4 and that is connected to a GC/MS system.

9.1.1.3 P/T instrumentation that allows internal standards and DMCs to be automatically added to each sample is widely available. Some of this instrumentation may be set up by the manufacturer to add only 1.0 µL of internal standard or DMCs. The 1.0 µL addition of standards will be allowed if the addition is done solely in an automated manner, and if the final concentration of the following standards in the 5 mL water samples and blanks can be met: 50 µg/L full scan for internal standards; the concentrations listed in Section 7.2.2.1.2 for DMCs in the initial calibration; and the concentrations listed in Section 7.2.2.1.4 for DMCs in the CCV.

9.1.1.4 Before initial use, condition the trap overnight at 180°C by backflushing with at least 20 mL/minute flow of inert gas according to the manufacturer's recommendations. Do not vent the trap effluent onto the analytical column. Prior to daily use, condition the trap by heating at 180°C for 10 minutes while backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be conditioned through the temperature program prior to the analysis of samples and blanks.

9.1.1.5 For low-level soil samples, establish the P/T instrument operating conditions. Adjust the instrument to inject 10 mL of reagent water, to heat the sample to 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer. Once established, the same P/T conditions must be used for the analysis of all standards, samples, and blanks.

9.1.1.6 Optimize P/T conditions for sensitivity and to minimize cross-contamination between samples. Once optimized, the same purge-and-trap conditions must be used for the analysis of all standards, samples, and blanks.

NOTE: In certain situations, a heated purge may be used for water samples provided that all standards, samples, and blanks are analyzed under the same conditions and all technical acceptance criteria can be met.

9.1.1.7 A moisture reduction/water management system may be used to improve the chromatographic performance by controlling moisture if:

- The system does not introduce contaminants that interfere with identification and quantitation of target analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits;

- The analytical results generated when using the moisture reduction/water management system meet the initial and continuing calibration verification technical acceptance criteria listed in the analytical method and the CRQLs listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits;
- All calibration standards, samples, and blanks are analyzed under the same conditions; and
- The Contractor performs acceptably on the Performance Evaluation (PE) samples using this system.

9.1.2 Gas Chromatograph

9.1.2.1 The recommended GC analytical conditions are provided in Table 6 – Gas Chromatograph Analytical Conditions. The conditions are recommended unless otherwise noted. GC conditions must achieve all performance criteria required for initial and continuing calibration.

9.1.2.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and MS/MSDs.

9.1.2.3 Target analytes that are isomers (e.g., dichlorobenzenes) must be at least 50% resolved from each other. For xylene isomers, the two peaks representing o-xylene, m- and p-xylene, respectively, must be at least 50% resolved.

9.1.2.4 If the gaseous analytes chloromethane, bromomethane, vinyl chloride, and chloroethane fail to exhibit narrow, symmetrical peak shape, are not separated from the solvent front, or are not resolved greater than 90.0% from each other, then a subambient oven controller must be used, and the initial temperature must be less than or equal to 10°C.

9.1.3 Mass Spectrometer

The recommended MS analytical conditions are provided in Table 7 – Mass Spectrometer Analytical Conditions.

9.2 Instrument Performance Check

9.2.1 Summary of GC/MS Instrument Performance Check

9.2.1.1 The GC/MS system must be tuned to meet the manufacturer’s specifications using a suitable calibrant such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.2.2).

9.2.1.2 Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing 4-BFB.

9.2.2 Frequency of GC/MS Instrument Performance Check

The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples, blanks or standards are to be analyzed. The 12-hour period for the GC/MS instrument performance check, calibration standards (initial calibration or CCV), blank, and sample analysis begins at the moment

of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. However, in cases where a closing CCV can be used as an opening CCV for the next 12-hour period, then an additional BFB tune is not required, and the 12-hour period begins with the injection of the CCV. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for GC/MS Instrument Performance Check

The analysis of the instrument performance check solution shall be performed as follows:

- As an injection of up to 50 ng of BFB into the GC/MS.
- By adding sufficient amount of BFB solution (Section 7.2.2.2) to 5.0 mL of reagent water to result in a 10 µg/L concentration of BFB.
- By adding sufficient amount of BFB solution to the mid-level calibration standard to result in a 10 µg/L concentration of BFB.

9.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

9.2.4.1 The GC/MS system must be tuned at the frequency described in Section 9.2.2.

9.2.4.2 The abundance criteria listed in Table 2 – 4-Bromofluorobenzene Key Ions and Ion Abundance Criteria, must be met for a 50 ng injection of BFB. The mass spectrum of BFB must be acquired in the following manner:

9.2.4.2.1 Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.

9.2.4.2.2 Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must be analyzed under identical GC/MS instrument analytical conditions.

9.2.5 Corrective Action for GC/MS Instrument Performance Check

9.2.5.1 If the BFB technical acceptance criteria are not met, retune the GC/MS system. It may also be necessary to clean the ion source or take other corrective actions to achieve the technical acceptance criteria.

9.2.5.2 Any samples or required blanks analyzed when tuning technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples and required blanks, and after the instrument performance check (including MS/MSDs) technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations (Section 9.3.3.3) to determine instrument sensitivity and the linearity of GC/MS response for the purgeable target analytes and DMCs.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be calibrated prior to analyzing samples whenever the Contractor takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.), or if the CCV acceptance criteria have not been met.

9.3.2.2 If time remains in the 12-hour period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed (Section 9.3.1). It is not necessary to analyze another CCV standard. A method blank is required.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Set up the GC/MS system as described in Section 9.1.

9.3.3.2 All standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.3.3.3 Add sufficient amount of the internal standard solution (Section 7.2.2.5) to each of the five aqueous calibration standard solutions (Section 7.2.2.1.2) containing the DMC solution (Section 7.2.2.3.4) at the time of purge. Analyze each calibration standard according to Section 10.0. The initial calibration sequence is listed below.

INITIAL CALIBRATION SEQUENCE

1. GC/MS Instrument Performance Check
2. CS1 Initial Calibration Standard
3. CS2 Initial Calibration Standard
4. CS3 Initial Calibration Standard
5. CS4 Initial Calibration Standard
6. CS5 Initial Calibration Standard

9.3.3.4 Separate initial calibrations must be performed for water samples and low-level soil/sediment samples if different purge conditions are used (unheated purge vs. heated purge). Extracts of medium-level soil/sediment samples may be analyzed using the calibrations of water samples if the same purge conditions are used.

The Contractor may analyze different matrices in the same 12-hour period under the same tune, as long as separate calibration verifications are performed for each matrix within that 12-hour period.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the RRF for each volatile target analyte and DMC using Equation 1. The primary characteristic ions used for quantitation are listed in Table 8 – Characteristic Ions for Volatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards. If an interference prevents the use of a primary ion for a given internal standard, use a secondary ion listed in the same table. Assign the target analytes and DMCs to an internal standard according to Table 9 – Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation.

NOTE: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 1 Relative Response Factor

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

WHERE,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (Table 8 - Characteristic Ions for Volatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards)

A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (Table 8 - Characteristic Ions for Volatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards). The target analytes are listed with their associated internal standards in Table 9 – Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation.

C_{is} = Concentration or amount of the internal standard

C_x = Concentration or amount of the analyte to be measured

9.3.4.2 Calculating the RRFs of the xylenes requires special attention. Report an RRF for m,p-xylene and one for o-xylene. On the available capillary columns, the m,p-xylene isomers coelute. Therefore, when calculating the RRF in the equation above, use the area response (A_X) and concentration (C_X) of the peak from o-xylene, and A_X and C_X of the peak from m,p-xylene isomers respectively.

9.3.4.3 The Mean RRF ($\overline{RRF}$) must be calculated for all compounds according to Equation 2.

9.3.4.4 Calculate the Percent Relative Standard Deviation (%RSD) of the RRF values for each purgeable target analyte and DMC over the initial calibration range using Equation 3 in conjunction with Equations 2 and 4.

9.3.4.4.1 Equation 2 is the general formula for the mean of a set of values.

EQ. 2 Mean Value

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

WHERE,

X_i = Value

$\overline{X}$ = Mean value

n = Number of values

9.3.4.4.2 Equation 3 is the general formula for the relative standard deviation.

EQ. 3 Percent Relative Standard Deviation

$$\%RSD = \frac{SD_{RRF}}{\overline{X}} \times 100$$

WHERE,

SD_{RRF} = Standard deviation of initial calibration RRFs (per compound) from EQ. 4

$\overline{X}$ = Mean value of the initial calibration RRFs (per compound)

9.3.4.4.3 Equation 4 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 4 Standard Deviation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{(n-1)}}$$

WHERE,

X_i = Each individual value used to calculate the mean

$\overline{X}$ = The mean of n values

n = Total number of values

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentrations described in Section 7.2.2.1.2, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the BFB technical acceptance criteria (Section 9.2.4).

9.3.5.2 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.3.5.3 The RRF at each calibration concentration for each purgeable target analyte and DMC that has a required minimum RRF value must be greater than or equal to the compound's minimum acceptable RRF listed in Table 4 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Volatile Organic Compounds.

9.3.5.4 The %RSD for each target analyte or DMC listed in Table 4 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Volatile Organic Compounds must be less than or equal to that value listed.

9.3.5.5 Up to two target analytes and DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Table 4 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Volatile Organic Compounds. Up to two target analytes and DMCs (excluding those with maximum %RSD requirements of 40.0%) may fail to meet the criteria listed in Table 4 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Volatile Organic Compounds, but these compounds must still meet the maximum %RSD requirements of 40.0%.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, service the P/T device, or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 It may be necessary to adjust the purge gas (helium) flow rate (normally in the range of 25-40 mL/minute). Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Continuing Calibration Verification

Prior to the analysis of samples and required blanks, and after instrument performance check and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing an opening CCV (containing all the purgeable target analytes, DMCs, and internal standards) to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method. A closing CCV using the same standard conditions as for the opening CCV is required after all samples and blanks have been analyzed, and before the end of the 12-hour period (refer to the analytical sequence in Section 9.4.2.3).

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 The calibration for each GC/MS system used for analysis must be verified at the beginning and end of every 12-hour period of operation. The 12-hour period begins with the injection of BFB, followed by the injection of the opening CCV solution. BFB may be added to the CCV solution, in which case only one injection is necessary. If a closing CCV meets the technical acceptance criteria for an opening CCV (Section 9.4.5) and samples are analyzed within that subsequent 12-hour period, then an additional BFB tune is not required and the 12-hour period begins with that calibration verification. If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then a BFB tune, followed by an opening CCV, is required and the next 12-hour period begins with the BFB tune (Section 9.2.2).

9.4.2.2 If time remains in the 12-hour period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. A method blank is required.

9.4.2.3 After the injection of all samples and required blanks, and before the end of the 12-hour period, another injection of the CCV solution is required (closing CCV). The closing CCV used to bracket the end of a 12-hour analytical sequence may be used as the opening CCV for a new 12-hour analytical sequence, provided that all technical acceptance criteria are met for an opening CCV in Section 9.4.5.

Time	Injection #	Material Injected
0 hr	1st - 6th - GC/MS Instrument Performance Check followed by CS1 – CS5 calibration standards	BFB then CS1–CS5 First 6 steps of the initial calibration
	7th - blanks, samples, MS/MSD	Blanks, samples, and MS/MSD
	8th - Subsequent Samples	
End 12 hr	Closing CCV (meeting Closing CCV criteria but not Opening CCV)	CS3 – Closing CCV
New 12 hr	1st GC/MS Instrument Performance Check	BFB Instrument Performance Check
	2nd - Analysis past 12 Opening CCV	CS3 - Opening CCV
		Blank, MS/MSD, subsequent samples
		Subsequent Samples
		Last Sample
End 12 hr	Closing CCV (meeting Closing CCV criteria but not Opening CCV)	CS3 – Closing CCV
New 12 hr	1st Analysis Instrument Performance Check	BFB Instrument Performance Check
	2nd Analysis Opening CCV	CS3 – Opening CCV
		Blank, MS/MSD, subsequent samples
		Subsequent Samples
		Last Sample
		Storage Blank if previous sample is the last sample in SDG
End of 12hr beginning of next 12 hr	Closing CCV (meeting Opening CCV criteria) Instrument Performance Check not required	CS3 – Closing CCV meeting Opening CCV
		Blank, MS/MSD, subsequent samples
		Subsequent Samples
		Last Sample
		Storage Blank (after last sample in SDG)
End of 12 hr	Closing CCV meeting criteria	CS3 – Closing CCV meeting Opening CCV

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 All standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.4.3.2 Add a sufficient amount of the internal standard solution (Section 7.2.2.5) to the CCV (Section 7.2.2.1.4) and the DMC solution (Section 7.2.2.3). Analyze the CCV standard according to Section 10.0.

9.4.3.3 For low-level soil samples, the CCV standard shall be prepared in the same manner as the initial calibration standard of the same concentration as specified in Section 7.2.2.1.

9.4.4 Calculations for Continuing Calibration Verification

9.4.4.1 Calculate an RRF for each target analyte and DMC according to Section 9.3.4.1.

9.4.4.2 Calculate the Percent Difference (%D) between the CCV RRF_C and the most recent initial calibration $\overline{RRF_i}$ for each purgeable target analyte and DMC using the following equation.

EQ. 5 Internal Standard Calibration Percent Difference Calculation

$$\%D = \frac{RRF_C - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

WHERE,

RRF_C = Relative Response Factor from current CCV standard

$\overline{RRF_i}$ = Mean Relative Response Factor from the most recent initial calibration

9.4.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.4.5.1 The concentration of the low/medium volatile organic target analytes and DMCs in the opening and closing CCV must be at or near the mid-point concentration of the calibration standards (50 µg/L for non-ketones and 100 µg/L for ketones). The opening and closing CCV must be analyzed at the frequency described in Section 9.4.2, on a GC/MS system meeting the BFB (Section 9.2.4) and initial calibration (Section 9.3.5) technical acceptance criteria.

9.4.5.2 For an opening/closing CCV, except as noted in Section 9.4.5.4, the RRF for each purgeable target analyte and DMC must be greater than, or equal to, the compound's opening/closing minimum RRF listed in Table 4 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Volatile Organic Compounds.

9.4.5.3 For an opening CCV, the %D for each purgeable target analyte and DMC listed in Table 4 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Volatile Organic Compounds must be in the inclusive range of the compound's %D values listed. For a closing CCV, the %D for each target analyte and DMC must be in the inclusive range of the compound's %D values listed. Up to two target analytes and/or DMCs in the closing CCV are allowed to exceed the %D values listed.

9.4.5.4 For an opening CCV, up to two target analytes and/or DMCs (excluding those compounds with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.4.5.2, but these compounds must still meet the minimum RRF requirements of 0.010. For a closing CCV, all target analytes and DMCs must meet the requirements listed in Sections 9.4.5.2 and 9.4.5.3.

9.4.5.5 No quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Continuing Calibration Verification

9.4.6.1 If the opening CCV technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3. If the closing CCV technical acceptance criteria are not met, then all samples and blanks analyzed within that 12-hour period must be reanalyzed at no additional cost to the EPA.

9.4.6.2 The Contractor shall follow the procedure in Section 10.2.4.1 if they cannot meet the control criteria after the analysis of an original undiluted or minimally diluted sample due to matrix interference. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the CCV technical acceptance criteria.

9.4.6.3 Any samples or required blanks analyzed when opening CCV technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

10.0 PROCEDURE

10.1 Introduction to Sample Analysis

Samples shall be analyzed only after the GC/MS system has met the technical requirements. The same instrument conditions must be employed for the analysis of samples as were used for calibration. All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

NOTE: Contact SMO if sample vials have bubbles entrained resulting in headspace.

10.2 Procedure for Sample Analysis

10.2.1 Water Samples

10.2.1.1 If time remains in the 12-hour period (as described in Section 9.2.2), samples may be analyzed without analysis of a CCV standard.

10.2.1.2 If the autosampler can automatically sample the appropriate volume, then the following Sections 10.2.1.4 - 10.2.1.6 are performed by the autosampler.

10.2.1.3 Remove the plunger from a 5.0 mL syringe and attach a closed syringe valve. Open the sample or standard bottle that has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Invert the syringe, open the syringe valve, and vent any residual air while adjusting the sample volume to 5.0 mL.

10.2.1.4 This process of taking an aliquot destroys the validity of the sample for future analysis, unless the excess sample is immediately transferred to a smaller vial with zero headspace and stored at ≤6°C but not frozen. Therefore, if only one sample vial is provided, the analyst must fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly. Filling one 5.0 mL syringe would allow only one analysis of that

sample. If an analysis is needed from the second 5.0 mL syringe, it must be performed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.

10.2.1.5 Add a sufficient amount of DMC spiking solution (Section 7.2.2.3) and a sufficient amount of internal standard spiking solution (Section 7.2.2.5) through the valve bore of the syringe, then close the valve. Invert the syringe 3 times. The DMCs and internal standards may be mixed and added as a single spiking solution.

10.2.1.6 Once the sample aliquots have been taken from the VOA vial, the pH of the water sample must be determined. The purpose of the pH determination is to ensure that all VOA samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper (do **not** add pH paper to the vial). Record the pH of each sample and report these data in the SDG Narrative, following the instructions in Exhibit B – Reporting and Deliverables Requirements. No pH adjustment is to be performed by the Contractor.

10.2.1.7 Attach the valve assembly on the syringe to the valve on the sample sparger. Open the valves and inject the sample into the purging chamber.

10.2.1.8 Close both valves and purge the sample under the same conditions as the initial calibration.

10.2.1.9 Sample Desorption - After the purge is complete, attach the trap to the GC, adjust the P/T system to desorb mode, initiate the temperature program sequence of the GC, and start data acquisition. Introduce the trapped material into the GC column by rapidly heating the trap to the appropriate desorb temperature while backflushing the trap with inert gas. While the trapped material is being introduced into the GC, empty the sample sparger and rinse it with reagent water. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable levels, it may be necessary to wash out the sample sparger with a detergent solution, rinse it with reagent water, and then dry it in an oven at 105°C.

10.2.1.10 Trap Reconditioning - After desorbing the sample, recondition the trap in accordance with manufacturer's instructions with the recommended trap recondition for a minimum of 7.0 (±0.1) minutes at 180°C. The same conditions must be used for all analyses.

10.2.1.11 Termination of Data Acquisition - 3 minutes after all the purgeable target analytes have eluted from the GC, terminate the MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and appropriate EICPs.

10.2.2 Low-Level Soil/Sediment Samples

10.2.2.1 If samples are received as sealed VOA vials or containers, they are to be analyzed according to Section 10.2.2.9, unless screening analysis indicates samples should be analyzed as medium-level samples. If the results of medium-level analysis indicate that all target analyte concentrations are below the medium-level CRQL in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits, then the samples must be analyzed as low-level samples. If samples are originally analyzed by the low-level method, and any target analyte in the sample exceeds the concentration of the

same target analyte in the high standard, then the sample may be analyzed at a dilution per Section 10.2.4, or by the medium-level method (Section 10.2.3). If the laboratory suspects that any target analyte is at a concentration that may result in instrument performance problems when analyzed even using the medium-level method, SMO should be contacted for further guidance.

If the EPA specifically requests the laboratory to analyze a sample only by the medium-level protocol (i.e., methanol extraction technique), the laboratory is not obligated to perform the low-level analysis. The request to the laboratory is to be made on the Traffic Report/Chain of Custody (TR/COC) Record. After receiving a TR/COC Record with this specific request, the laboratory is to confirm the request through SMO.

10.2.2.2 The following steps apply to the preparation of vials used for the analysis of low-level soil/sediment samples by the closed-system P/T equipment described in this method. If samples are not received in closed-system purge vials, proceed to Section 10.2.2.7.

NOTE: There should be three field core sampling/storage containers for each field sample. The contents of two of the field core containers are to be transferred immediately upon sample receipt and processed using the steps outlined in Sections 10.2.2.9 - 10.2.2.10. One of these prepared samples is then to be used as the primary sample, while the other is to be used as a back-up sample, if necessary. The contents of the third field core container shall be transferred immediately upon sample receipt to a tared dry closed-system P/T container (i.e., no preservative solution or stirring bar is to be added), weighed according to Section 10.2.2.8, and then stored at less than -7°C. This sample shall be used for the medium concentration level methanol extraction procedure as described in Section 10.2.3, if results of the original analysis indicate that medium-level extraction is warranted.

10.2.2.3 Add a clean magnetic stirring bar to each clean vial. If the P/T device stirs the sample with a means other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

10.2.2.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted vials are used, seal both ends as recommended by the manufacturer.

10.2.2.5 Affix a label to each vial and weigh the prepared vial to the nearest 0.01 g. Record the tare weight and final weight.

10.2.2.6 Because volatile organics will partition into the headspace of the vial and will be lost when the vial is opened, DMCs, MS/MSD, and internal standard spiking solutions should only be added to vials after the sample has been added to the vial. The spiking solutions should be introduced either manually by puncturing the septum with a small-gauge needle or automatically by the P/T system just prior to analysis.

10.2.2.7 Using the sample collection device, transfer the contents (approximately 5 g) into the sample vial. This sample transfer must be performed rapidly to minimize loss of volatile analytes. Quickly brush any soil off the vial and immediately seal the vial

with the septum and screw-cap. The soil vial is hermetically sealed and must remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. Record the date and time of sample transfer to pre-prepared vials and also submit this information with the data package.

10.2.2.8 Weigh the vial and contents to the nearest 0.01 g and record this weight. Sample weight is determined by subtracting the sample vial tared weight (Section 10.2.2.5) from this final weight. For samples received in closed-system purge vials, the tared weights should have been provided by the field sampler. If tared weights are not provided, contact SMO for further guidance.

10.2.2.9 Prior to sample purge, all soil/sediment samples must be allowed to warm to ambient temperature. All low-level soil samples should have a total sample volume (reagent water and preservative) of 10 mL. For those samples that have been stored in freezing compartments and will be analyzed by the low concentration level protocol, 10 mL of reagent water must be added to the vials without disturbing the hermetic seal of the sample vial.

For preserved samples, add additional 5.0 mL of reagent water to the vial.

Shake all vials containing aqueous solutions gently to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer’s instructions.

10.2.2.10 Without disturbing the hermetic seal on the sample vial, add 5.0 mL reagent water, sufficient amount of the internal standard spiking solution (Section 7.2.2.5), and the DMC spiking solution (Section 7.2.2.3). All samples, including MS/MSDs, standards, and blanks, within an SDG must have the same amount of reagent water added. Do not increase/change the amount of DMC and internal standard solution added.

10.2.2.11 Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

10.2.2.12 Purge the sample under the same conditions as the initial calibration, while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

10.2.2.13 If a non-cryogenic interface is to be utilized, place the P/T system in the desorb mode after the purge interval, and preheat the trap to the desorb temperature without a flow of desorption gas. Start the flow of desorption gas. Begin the temperature program of the GC and start data acquisition.

10.2.2.14 If a cryogenic interface is to be utilized, place the P/T system in the desorb mode after the purge interval, making sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to desorb the sample. At the end of the desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the GC and start the data acquisition.

10.2.2.15 After desorbing the sample, recondition the trap and adjust the P/T system to prepare for the next sample.

10.2.3 Medium-Level Soil/Sediment Samples

10.2.3.1 The medium-level soil/sediment method is based on extracting the soil/sediment sample with methanol. An aliquot of the methanol extract is added to reagent water containing the DMCs and the internal standards. The reagent water containing the methanol extract is purged at ambient temperature.

10.2.3.2 Prior to the analysis of samples, establish the appropriate P/T GC/MS operating conditions, as outlined in Section 9.1.1. Because the methanol extract and reagent water mixture is purged at ambient temperature, the instrument performance check, initial calibration, and CCV for water samples shall be used for analyses of medium-level soil/sediment sample extracts.

10.2.3.3 Weigh the vial and contents to the nearest 0.01 g and record this weight. Sample weight is determined by subtracting the sample vial tared weight determined in Section 10.2.2.5. For samples received in closed-system purge vials, the tared weights should have been provided by the field sampler. If tared weights are not provided, contact SMO for further guidance.

NOTE: If a methanol preserved sample is to be analyzed, weigh the sample vial and contents to the nearest 0.01 g and record the weight. Record any discrepancies between laboratory-determined weight and sampler-determined weight in the SDG Narrative and utilize the sampler-determined weight in any calculations. Proceed to Section 10.2.3.5.

10.2.3.4 Quickly add 5.0 mL of methanol to the vial. Cap and shake for 2 minutes.

NOTE: The steps in Sections 10.2.3.3 and 10.2.3.4 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

10.2.3.5 Let the solution settle. Then, using a disposable pipette, transfer approximately 1 mL of extract into a GC vial for storage. The remainder may be discarded. The 1 mL extract may be stored in the dark at ≤6°C, but not frozen, prior to the analysis.

10.2.3.6 Add 100 µL of the methanol extract to the 4.9 mL of reagent water for analysis. Otherwise, estimate the concentration range of the sample from the low-level analysis or from the in-house screening procedure to determine the appropriate volume. A 100 µL of methanol extract is the maximum volume that can be added to the 4.9 mL of reagent water for medium-level analysis. If less than 100 µL of methanol extract is used, a volume of clean methanol must be used so that the volumes of methanol extract and clean methanol total 100 µL.

10.2.3.7 Remove the plunger from a 5.0 mL Luer-Lok type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5 mL to allow volume for the addition of sample and standards, and add sufficient amount of DMC spiking solution (Section 7.2.2.3) and sufficient amount of internal standard spiking solution (Section 7.2.2.5). Also add the volume of methanol extract determined in Section 10.2.3.6 and a volume of clean methanol (if necessary) to total 100 µL (excluding methanol in the DMC/internal standard spiking solutions).

10.2.3.8 Attach the syringe-syringe valve assembly to the syringe valve on the purge device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

10.2.3.9 Proceed with the analysis as outlined in Sections 10.2.2.12 - 10.2.2.15.

10.2.4 Sample Dilutions

10.2.4.1 The Contractor shall analyze samples undiluted, or at minimal dilution. Samples may be diluted because of target analyte concentration exceeding the concentration of the same target analyte in the high standard, or because of excessive matrix interference that hinders accurate quantitation. It is highly recommended that screening analysis be performed prior to sample analysis to determine estimated analyte concentration and matrix problems.

NOTE 1: If the laboratory has evidence or highly suspects, because of sample color or other physical properties, that a sample may contain high concentrations of either target or non-target analytes, then the Contractor shall contact SMO to obtain guidance from the EPA as to whether a smaller aliquot or the medium-level method (Section 10.2.3) would be most appropriate.

NOTE 2: In the event that interference precludes accurate quantitation using the primary quantitation ion, but a secondary ion with less interference could be used instead, then secondary ion quantitation should be considered (see Section 11.2.1.4).

10.2.4.2 For water samples, samples may be diluted to keep target analyte concentrations within the calibrated range and/or to keep baseline height from the earliest eluting peak from exceeding one-half the relative height of the highest peak in the chromatogram. If dilution is required due to baseline drift, the laboratory must submit chromatograms in which the highest peak is set to full scale. If the baseline rises less than 10% in the diluted analysis, the sample has been overdiluted.

10.2.4.3 For soil samples analyzed by the low-level method, if the concentration of any target analyte in the sample exceeds the concentration of the same target analyte in the high standard, then the Contractor shall proceed with the medium level sample analysis.

10.2.4.4 Samples may be diluted in a volumetric flask or in a 25 mL Luer-Lok syringe.

10.2.4.5 The Dilution Factor (DF) chosen must keep the concentrations of the volatile target analytes that required dilution in the upper half of the calibration range.

10.2.4.6 All dilutions must be made just prior to GC/MS analysis of the sample. Until the diluted sample is in a gas-tight syringe, all steps in the dilution procedure must be performed without delay.

10.2.4.7 To dilute the sample in a volumetric flask, use the following procedure:

10.2.4.7.1 Select the volumetric flask that will allow for the necessary dilution (10-100 ml). Intermediate dilution may be necessary for extremely large dilutions.

10.2.4.7.2 Calculate the approximate volume of appropriately acidified reagent water that will be added to the selected volumetric flask and add slightly less than this quantity of the reagent water to the flask.

10.2.4.7.3 For water samples, inject the proper aliquot from the syringe into the volumetric flask. Only aliquots of 1.0 mL increments are permitted. Dilute the aliquot to the mark on the flask with reagent water. Cap the flask and invert it 3 times.

10.2.4.7.4 Fill a 5.0 mL syringe with the diluted sample as in Section 10.2.1.3. If this is an intermediate dilution, use it and repeat the above procedure to achieve larger dilutions.

10.2.4.8 If more than two analyses (i.e., from the original sample and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get concentrations of all target analytes within the calibration range, contact SMO.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Analytes

11.1.1.1 The analytes listed in the TAL in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits, shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component within the Gas Chromatographic Relative Retention Time (RRT) unit window established from the 12-hour calibration standard; and
- Correspondence of the sample component and calibration analyte mass spectra.

11.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within ±0.06 RRT units of the RRT of the corresponding continuing calibration standard component. For reference, the standard must be analyzed in the same 12-hour period as the sample. If samples are analyzed during the same 12-hour period as the initial calibration standards, use the RRT values from the 50 µg/L standard. Otherwise, use the corresponding opening CCV standard. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned by using EICP for ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor’s GC/MS (as opposed to library spectra) are required. Once obtained, these standard spectra may be used for identification purposes, only if the Contractor’s GC/MS meets the daily instrument performance requirements for BFB. These standard spectra may be obtained from the standard analysis that was also used to obtain the RRTs.

11.1.1.4 The guidelines for qualitative verification by comparison of mass spectra are as follows:

11.1.1.4.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.1.1.4.2 The relative intensities of ions specified in the paragraph above must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30-70%).

11.1.1.4.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra.

11.1.1.4.4 If an analyte cannot be verified by all of the spectral identification criteria listed in Section 11.1.1.4, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the Contractor shall report that identification and proceed with quantitation and document in the SDG Narrative.

11.1.2 Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target compounds for the purpose of tentative identification. The NIST (2011 release or later), Wiley (2011 release or later), or equivalent mass spectral library, shall be used as the reference library.

11.1.2.2 All organic compounds that have not been positively identified as volatile target analytes using the procedures detailed in Section 11.1, or that are not DMCs, internal standards, or semivolatile target compounds listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, shall be tentatively identified via a forward search of NIST, Wiley, or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form 1B-OR. Peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be reported as "total alkanes". An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds. The concentrations of each of the alkanes are to be summed and reported as a single result for the "total alkanes". The alkanes are not to be counted as part of the 30 compounds individually reported as TICs on Form 1B-OR. Carbon dioxide and compounds with responses less than 10% of the internal standard with which they are to be quantified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.1.2.4 Rules for Making Tentative Identification

11.1.2.4.1 For compounds to be reported, as per the instructions in Section 11.1.2.3, identification (as generated by the library search program) of those receiving a library search match of 85% or higher should be considered a "probable match". The compound should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program.

11.1.2.4.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match. Do not report DMCs, internal standards, or analytes that are on the volatile or semivolatile TAL, unless semivolatile analysis is not being done.

11.1.2.4.3 If the library search produces a series of obvious isomer compounds with library search matches greater than 85% (e.g., tetramethylnaphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same).

11.1.2.4.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the SDG Narrative the justification for not reporting a compound as listed by the search program. This narrative shall detail explicitly why a library search generated identification for a compound was rejected. If a TIC has obvious isomer analogs, the laboratory shall include in the SDG Narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

11.1.2.4.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialists are encouraged to make a valid tentative identification of the compound. If no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral interpretation specialist should give additional classification of the unknown, if possible (e.g., "unknown aromatic compound", "unknown chlorinated compound", etc.).

11.1.2.4.6 The Chemical Abstract Service (CAS) registry number is the unique identifier for each chemical compound. As the rules of chemical nomenclature have changed over time, each chemical is liable to have several names or synonyms: i.e., trade or brand name(s); generic or common name(s); trivial or systematic; or International Union of Pure and Applied Chemistry (IUPAC) name(s). Whether synonyms or other names are created for this compound, the CAS registry number will generally remain unchanged. The CAS registry number is simply an identifier which has no structural significance. Regardless of retention times (RTs), if the library search produces two or more compounds at or above 85% with the same Chemical Abstract Number, report the compound with the highest percent match (report first compound if the percent match is the same for

two or more compounds) unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match.

11.1.2.4.7 If the library search produces only one and the same compound (i.e., the same CAS registry number) with percent match at or above 85% at two different RTs, the compound having the highest percent match should be reported as TIC and the other one should be reported as unknown. If both TICs have the same percent match for the same compound, one of the TICs could be reported as unknown. Such justifications should be included in the SDG Narrative.

11.2 Quantitative Analysis

11.2.1 Data Processing Procedure

11.2.1.1 Target analytes identified shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (Table 9 – Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation). The EICP area of primary characteristic ions of analytes listed in table 8 – Characteristic Ions for Volatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards, are used for quantitation.

11.2.1.2 For water, low-level soil/sediment samples, and medium-level soil/sediment samples, xylenes are to be reported as "m,p-xylenes" and "o-xylene". Because m- and p-xylene isomers coelute, special attention must be given to the quantitation of the xylenes. In quantitating sample concentrations, be sure to use the correct corresponding RRF values.

NOTE: The area of each peak (i.e., the peaks for o-xylene and m,p-xylene) must appear on the complete quantitation report.

11.2.1.3 The stereoisomers, trans-1,2-dichloroethene, and cis-1,2-dichloroethene are to be reported separately.

11.2.1.4 Secondary ion quantitation is only allowed when there are sample interferences with the primary quantitation ion, not when saturation occurs. If secondary ion quantitation is used, calculate an RRF using the area response (EICP) from the most intense secondary ion which is free of sample interferences, and document the reasons in the SDG Narrative. A secondary ion cannot be used unless an RRF is calculated using the secondary ion.

11.2.1.5 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitation. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific target analyte, DMC, or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall also not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the

chromatographic system. Any instances of manual integration must be documented in the SDG Narrative.

11.2.1.6 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS Operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "M" on the quantitation report. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all: target analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits; internal standards; and DMCs.

11.2.2 Target Analyte Calculations

11.2.2.1 Identified target analytes shall be quantitated by the internal standard method using Equation 6, 7 or 8. The internal standard used shall be that which is assigned in Table 9 - Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation. The Mean RRF ($\overline{RRF}$) from the initial calibration standard is used to calculate the concentration in the sample.

11.2.2.2 Water

EQ. 6 Water and TCLP/SPLP Leachate Sample Concentration

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(I_{is})(DF)}{(A_{is})(\overline{RRF})(V_o)}$$

WHERE,

A_x = Area of the characteristic ion (EICP) for the compound to be measured. The primary quantitation ions for the target analytes, internal standards, and DMCs are listed in Table 8 – Characteristic Ions for Volatile Target Analytes, Deuterated Monitoring Compounds and Internal Standards.

A_{is} = Area of the characteristic ion (EICP) for the internal standard. The primary quantitation ions for the internal standards are in Table 8 – Characteristic Ions for Volatile Target Analytes, Deuterated Monitoring Compounds and Internal Standards. The target analytes are listed with their associated internal standards in Table 9 - Volatile Target Analytes and Deuterated Monitoring Compounds with Associated Internal Standards for Quantitation.

I_{is} = Amount of internal standard added, in ng

$\overline{RRF}$ = Mean Relative Response Factor from the initial calibration standard

V_o = Total volume of water purged, in mL

DF = Dilution Factor. The DF for analysis of water samples for volatiles by this method is defined as the ratio of the number of mL of water purged (i.e., V_o above) to the number of mL of the original water sample used for purging. For example, if 2.0 mL of sample is diluted to 5.0 mL with reagent water and purged, DF = 5.0 mL/2.0 mL = 2.5. If no dilution is performed, DF = 1.0.

NOTE: Convert units to mg/L for TCLP leachates by dividing the final calculated concentration by 1000.

11.2.2.3 Low-Level Soil/Sediment

EQ. 7 Low-Level Soil/Sediment Concentration

$$\text{Concentration } (\mu g/Kg) = \frac{(A_x)(I_{is})(DF)}{(A_{is})(\overline{RRF})(W_s)(S)}$$

WHERE,

A_x, I_{is}, A_{is}, DF = As given for water, EQ. 6

$\overline{RRF}$ = Mean Relative Response Factor from the heated purge of the initial calibration standard

S = % Solids/100 (Exhibit D – General Organic Analysis, Section 10.1)

W_s = Weight of sample added to the purge tube, in g

11.2.2.4 Medium-Level Soil/Sediment

EQ. 8 Medium-Level Soil/Sediment Concentration

$$\text{Concentration}(\mu g/Kg) = \frac{(A_x)(I_{is})(AV_t)(1000)(DF)}{(A_{is})(\overline{RRF})(V_a)(W_s)(S)}$$

WHERE,

A_x, I_{is}, A_{is} = As given for water, EQ. 6.

S = As given in EQ. 7

$\overline{RRF}$ = Mean Relative Response Factor from the ambient temperature purge of the initial calibration standard

AV_t = Adjusted total volume of the methanol extract plus soil water in mL determined by:

$$AV_t = V_t + \{W_s - [W_s(S)]\}$$

Where V_t = total volume of methanol extract in mL. This volume is typically 5.0 mL, even though only 0.1 mL is transferred to the vial in Section 10.2.3.6. The quantity derived from $\{W_s - [W_s(S)]\}$ is the soil water volume and is expressed in mL.

V_a = Volume of the aliquot of the sample methanol extract (i.e., sample extract not including the methanol added to equal 100 µL), in µL added to reagent water for purging

W_s = Weight of soil/sediment extracted, in g

DF = Dilution Factor. The DF for analysis of soil/sediment sample extracts for volatiles by the medium-level method is defined as the ratio of the volume (µL) taken from the extract used to make the dilution plus the clean solvent added for the dilution (µL), to the volume taken from the extract used to make the dilution. For example, if 10 µL of the extract was taken and added to 90 µL of clean solvent, then ration would be (10 µL + 90 µL/10 µL)= a DF of 10.

11.2.3 Non-Target Compounds

11.2.3.1 An estimated concentration for TICs shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.2.3.2 Equations 6, 7, and 8 are also used for calculating TIC concentrations. Total area counts (or peak heights) from the total RICs are to be used for both the TIC to be measured (A_x) and the internal standard (A_{is}). An RRF of 1.0 is to be assumed.

11.2.4 Contract Required Quantitation Limit Calculations

11.2.4.1 Water

EQ. 9 Water and TCLP/SPLP Leachate Sample Adjusted CRQL

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{V_c}{V_o} \times DF$$

WHERE,

Contract CRQL = CRQL value reported in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits

V_o, DF = As given in EQ. 6

V_C = Method required purge volume

NOTE: Convert units to mg/L for TCLP leachates by dividing the final calculated CRQL by 1000.

11.2.4.2 Low-Level Soil/Sediment

EQ. 10 Low-Level Soil Adjusted CRQL

$$\text{Adjusted CRQL} = \text{Contract CRQL} \times \frac{(W_c)}{(W_s)\ (S)}$$

WHERE,

W_s, S = As given in EQ. 7

W_C = Method required sample weight (5.0 g)

11.2.4.3 Medium-Level Soil/Sediment

EQ. 11 Medium-Level Soil/Sediment Adjusted CRQL

$$\text{Adjusted CRQL} = \text{Contract CRQL X} \frac{(W_x)\,(AV_t)\,(V_y)\,(1000)\,(DF)}{(W_s)\,(V_c)\,(V_a)\,(S)}$$

WHERE,

AV_t, DF, W_s, V_a, S = As given in EQ. 8

W_x = Method required sample weight (5.0 g)

V_y = Method required soil aliquot volume from soil methanol extract (100 µL).

V_c = Method required soil methanol extract volume (5,000 µL)

11.2.5 Deuterated Monitoring Compound Recoveries

11.2.5.1 Calculate the concentration of each DMC using the same equation as used for target analytes.

11.2.5.2 Calculate the recovery of each DMC in all samples and blanks using Equation 12. Report the recoveries on the appropriate forms.

EQ. 12 DMC Percent Recovery

$$\%R = \frac{Q_d}{Q_a} \times 100$$

WHERE,

Q_d = Quantity determined by analysis

Q_a = Quantity added to sample/blank

11.3 Technical Acceptance Criteria for Sample Analysis

11.3.1 The samples must be analyzed on a GC/MS system meeting the BFB, initial calibration, CCV, and blank technical acceptance criteria.

11.3.2 The sample and any required dilution must be analyzed within the contract holding time.

11.3.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

11.3.4 The Percent Recovery (%R) of each of the DMCs in the sample must be within the recovery limits in Table 10 - Deuterated Monitoring Compound Recovery Limits. Up to three DMCs per sample may fail to meet the recovery limits listed in Table 10 - Deuterated Monitoring Compound Recovery Limits.

11.3.5 The EICP area for each of the internal standards in the sample must be within the range of 50%-200% of its response in the most recent opening CCV standard analysis.

11.3.6 The RT shift for each of the internal standards in the sample must be within ±10 seconds of its RT in the most recent opening CCV standard analysis.

11.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. No target analyte concentration may exceed the upper limit of the initial calibration range, unless a more diluted aliquot of the sample is also analyzed according to the procedures in Section 10.2.4.

11.3.8 The Contractor must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target analyte at a level exceeding the initial calibration range, the Contractor must either:

- Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (Section 12.1.3); or

- Monitor the sample analyzed immediately after the contaminated sample for all analytes that were in the contaminated sample and that exceeded the calibration range. The maximum carryover criteria are as follows: the sample must not contain a concentration above the adjusted CRQL for the target analytes that exceeded the limits in the contaminated sample. If an auto sampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample must also meet the maximum contamination criteria.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or any samples not meeting the sample technical acceptance criteria will require reanalysis at no additional cost to the EPA.

11.4.2 Corrective actions for failure to meet technical acceptance criteria for instrument performance checks, initial calibration, CCV, and method blanks must be completed before the analysis of samples.

11.4.3 If the technical acceptance criteria for any of the internal standards and DMCs are not met, check calculations, internal standard and DMC spiking solutions, and instrument performance. It may be necessary to bake out the system to remove the water from the P/T transfer lines, to recalibrate the instrument, or take other corrective action procedures to meet the technical acceptance criteria.

11.4.4 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If DMC recoveries or internal standard compound responses in a sample used for an MS/MSD were outside the acceptance criteria, then it should be reanalyzed only if DMC recoveries and internal standard compound responses met acceptance criteria in both the MS/MSD analyses.
- If the DMC recoveries and the internal standard responses meet the acceptance criteria in the reanalyzed sample, then the problem was within the Contractor's control. Therefore, submit data only from the reanalysis.
- If the DMC recoveries and/or the internal standard responses fail to meet the acceptance windows in the reanalyzed sample, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables using the suffixes in Exhibit B – Reporting and Deliverables Requirements, Table 5 – Codes for Labeling Data.

11.4.5 If the Contractor needs to analyze more than one sample dilution other than the original analysis to have all concentrations of the target compounds within the initial calibration range, contact SMO. SMO will contact the EPA Region for instruction.

11.4.6 All samples to be reported to the EPA must meet the maximum carryover criteria in Section 11.3.8. If any sample fails to meet these criteria, each subsequent analysis must be checked for cross-contamination. The analytical system is considered contaminated until a sample has been analyzed that meets the maximum carryover criteria or an instrument blank has been analyzed that meets the technical acceptance criteria for blanks. If an instrument blank is not analyzed between consecutive samples that have the same analyte with a concentration exceeding the calibration range, then the second sample must be appropriately diluted as indicated in Section 10.2.4 and analyzed. If this analyte in the diluted analysis is detected at or below the adjusted CRQL, then all samples analyzed after the second sample that fail to meet maximum carryover criteria must be reanalyzed. If in the diluted analysis this analyte in the diluted analysis is detected within the calibration range, then no further corrective action is required.

11.4.7 Corrective Action for Internal Standard Compound Retention Times Outside Acceptance Criteria

11.4.7.1 If the internal standard compound RTs are not within their acceptance criteria, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the samples.

11.4.7.2 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was a matrix effect, take the following corrective action steps:

- Reanalyze the sample. EXCEPTION: If the internal standard compound RTs in a sample used for an MS or MSD were outside the acceptance criteria, then it should be reanalyzed only if the internal standard RTs were within the acceptance criteria in both the MS/MSD analyses.
- If the internal standard RTs are within the acceptance criteria, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis when the internal standard compound RTs are within the acceptance limits.
- If the internal standard RTs are outside the acceptance criteria in the reanalysis, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B – Reporting and Deliverables Requirements, Table 5 – Codes for Labeling Data.

12.0 QUALITY CONTROL

12.1 Blank Analyses

12.1.1 Summary

There are three different types of blanks required by this method: the method blank, the instrument blank, and the storage blank.

12.1.2 Method Blank

12.1.2.1 Summary of Method Blank

A method blank is a volume of a clean reference matrix (reagent water for water samples or a purified solid matrix for soil/sediment samples) spiked with internal standard spiking solution (Section 7.2.2.5) and DMC solution (Section 7.2.2.3), and carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of the method blank is to determine the levels of contamination associated with processing and analysis of samples.

NOTE 1: For soil/sediment samples, if any samples are prepared without the sodium bisulfate preservative, a method blank shall be prepared in the same manner and analyzed in the same 12-hour sequence as the unpreserved samples.

NOTE 2: A leachate blank carried through the TCLP process shall be analyzed with all associated samples.

12.1.2.2 Frequency of Method Blank

12.1.2.2.1 The method blank must be analyzed at least once during every 12-hour period on each GC/MS system used for volatile analysis (Section 9.2.2 for the definition of the 12-hour period).

12.1.2.2.2 The method blank must be analyzed after the initial calibration (Sections 9.3.1) if samples are analyzed before the 12-hour period expires. The method blank must be analyzed after the opening CCV and before any samples, including MS/MSDs or dilutions, are analyzed. A method blank must be analyzed in each 12-hour period in which samples, including dilutions, MS/MSDs, and storage blanks from an SDG are analyzed.

12.1.2.3 Procedure for Method Blank

12.1.2.3.1 For water samples, method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.2.1.

12.1.2.3.2 For low-level soil samples, method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.2.2.

12.1.2.3.3 For medium-level soil samples, method blanks shall be analyzed in the same manner as the associated samples, following the procedure described in Section 10.2.3.

12.1.2.3.4 For TCLP leachates, the leachate blank shall be analyzed in the same manner as the associated leachate samples, following the procedure described in Section 10.2.1.

12.1.2.3.5 Under no circumstances should method blanks be analyzed at a dilution.

12.1.2.4 Calculations for Method Blank

Perform data analysis and calculations according to Section 11.0.

12.1.2.5 Technical Acceptance Criteria for Method Blank

12.1.2.5.1 All blanks must be analyzed on a GC/MS system meeting the BFB, initial calibration, and CCV technical acceptance criteria and at the frequency described in Section 12.1.2.2.

12.1.2.5.2 The %R of each of the DMCs in a blank must be within the acceptance windows in Table 10 – Deuterated Monitoring Compound Recovery Limits.

12.1.2.5.3 The blank must meet the sample acceptance criteria listed in Sections 11.3.4 - 11.3.7.

12.1.2.5.4 The concentration of each target analyte found in the method blank must be less than the CRQL listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits, except for methylene chloride, acetone, and 2-butanone, which must be less than 2 times the respective CRQL.

12.1.2.5.5 The concentration of each TIC found in the method blank must be less than the CRQL.

12.1.2.6 Corrective Action for Method Blank

12.1.2.6.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.

12.1.2.6.2 If contamination is the problem, then the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further analysis proceeds. It is the Contractor’s responsibility to ensure that method interferences caused by the contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in GCs be eliminated.

12.1.2.6.3 Any method blank that fails to meet the technical acceptance criteria must be reanalyzed. Further, all samples processed within the 12-hour period with a method blank that does not meet the blank technical acceptance criteria will require reanalysis at no additional cost to the EPA.

12.1.3 Instrument Blank

12.1.3.1 Summary of Instrument Blank

An instrument blank is a 5.0 mL aliquot of reagent water spiked with internal standard spiking solution (Section 7.2.2.5) and DMC solution (Section 7.2.2.3), and carried through the entire analytical procedure. Instrument blanks are analyzed after a sample/dilution that contains a target analyte exceeding the calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample.

12.1.3.2 Frequency of Instrument Blank

Samples may contain target analytes at levels exceeding the calibration. An instrument blank must be analyzed after the sample that exceeds the calibration range (also in the same purge inlet if an autosampler is used) or a sample that exceeds the

maximum contamination criteria in Section 11.3.8 must be analyzed. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system must be decontaminated until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum carryover criteria.

NOTE: Only the instrument blank that demonstrates that there was no carryover from the previous sample or the instrument blank that demonstrates that the system is clean (Section 12.1.2.5.4) must be reported. Instrument blanks analyzed during the instrument decontamination process that exceed the requirements listed in Section 11.3.8 do not need to be reported.

12.1.3.3 Procedure for Instrument Blank

12.1.3.3.1 Instrument blanks shall be analyzed in the same manner as the associated samples following the procedures outlined in Section 10.0, and in accordance with the protocol of Section 11.3.8.

12.1.3.3.2 Under no circumstances should instrument blanks be analyzed at a dilution.

12.1.3.4 Calculations for Instrument Blank

Perform data analysis and calculations according to Section 11.0.

12.1.3.5 Technical Acceptance Criteria for Instrument Blank

12.1.3.5.1 All instrument blanks must be analyzed on a GC/MS system meeting the BFB, initial calibration, and CCV technical acceptance criteria and at the frequency described in Section 12.1.3.2.

12.1.3.5.2 The RT shift for each of the internal standards in a blank must be within 10 seconds of its RT in the most recent opening CCV standard analysis.

12.1.3.5.3 The concentration of each target analyte in the instrument blank must be less than its CRQL listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits.

12.1.3.5.4 It is the Contractor’s responsibility to ensure that method interferences caused by the contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in Gas Chromatograms, be eliminated.

12.1.3.6 Corrective Action for Instrument Blank

12.1.3.6.1 If a Contractor’s instrument blanks exceed the criteria in Section 12.1.3.5.3, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further analysis proceeds.

12.1.3.6.2 Any instrument blank that fails to meet any technical acceptance criteria described in Sections 12.1.3.5 requires reanalysis of the sample analyzed immediately after the instrument blank having any target analytes detected at levels above the CRQLs at no additional cost to the EPA.

12.1.4 Storage Blank

12.1.4.1 Summary of Storage Blank

A storage blank is a volume of a clean reference matrix (reagent water for water samples and preserved soil samples stored at ≤6°, or inert sand for unpreserved soil samples stored at <-7°C). The storage blanks are stored with the samples in the SDG under the same conditions. The storage blank indicates whether contamination may have occurred during storage of samples.

12.1.4.2 Frequency of Storage Blank

A minimum of one storage blank must be analyzed per matrix type (1 for soils and 1 for water samples) after all samples for the SDG stored in the same manner have been analyzed, unless the SDG contains only ampulated PE samples. Analysis of a storage blank is not required for SDGs that contain only ampulated PE samples.

12.1.4.3 Procedure for Storage Blank

12.1.4.3.1 Upon receipt of the first samples in an SDG, two vials with a clean reference matrix are stored with the samples in the SDG under the same conditions.

NOTE: If the SDG contains samples stored at ≤6°, but not frozen, and samples stored at <-7°C, two storage blanks will be prepared, one for each condition.

12.1.4.3.2 Storage blanks shall be analyzed in the same manner as the associated samples following the procedures outlined in Section 10.0.

12.1.4.3.3 Under no circumstances should storage blanks be analyzed at a dilution.

12.1.4.4 Calculations for Storage Blank

Perform data analysis and calculations according to Section 11.0.

12.1.4.5 Technical Acceptance Criteria for Storage Blank

12.1.4.5.1 All storage blanks must be analyzed on a GC/MS system meeting the BFB, initial calibration, and CCV technical acceptance criteria and at the frequency described in Section 12.1.4.2.

12.1.4.5.2 The storage blank must be analyzed on a GC/MS system that also meets the technical acceptance criteria for the method blank.

12.1.4.5.3 The %R of each of the DMCs in the blank must be within the acceptance windows in Table 10 – Deuterated Monitoring Compound Recovery Limits.

12.1.4.5.4 The EICP area for each of the internal standards in a blank must be within the range of 50%-200% of its response in the most recent opening CCV standard analysis.

12.1.4.5.5 The RT shift for each of the internal standards in a blank must be within 10 seconds of its RT in the most recent opening CCV standard analysis.

12.1.4.5.6 The concentration of each target analyte found in the storage blank must be less than the CRQL listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits, except for methylene chloride, acetone, and 2-butanone, which must be less than 2 times the respective CRQL.

12.1.4.5.7 It is the Contractor's responsibility to ensure that method interferences caused by the contaminants in solvents, reagents, glassware, laboratory air, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.4.6 Corrective Action for Storage Blank

12.1.4.6.1 If a Contractor's storage blanks exceed the criteria in Section 12.1.4.5, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further analysis proceeds.

12.1.4.6.2 If the storage blank does not meet the technical acceptance criteria for blank analyses in Section 12.1.4.5, correct system problems and reanalyze the storage blank.

12.1.4.6.3 If, upon reanalysis, the storage blank meets the criteria, the problem occurred during the analysis and the reanalyzed storage blank results must be reported. If upon reanalysis, the storage blank still does not meet the criteria, the problem occurred during storage. The Laboratory Manager or their designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences.

NOTE: A copy of the storage blank data must also be retained by the Contractor and be made available for inspection during on-site laboratory evaluations.

12.2 Matrix Spike and Matrix Spike Duplicate

12.2.1 Summary of Matrix Spike and Matrix Spike Duplicate

To evaluate the effects of the sample matrix on the methods used for volatile analyses, the EPA has prescribed a mixture of volatile target analytes to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method. An MS/MSD shall only be analyzed if requested by the EPA Region (through SMO) or specified on the TR/COC Record.

12.2.2 Frequency of Matrix Spike and Matrix Spike Duplicate

12.2.2.1 If requested, an MS/MSD must be performed for each group of 20 field samples of a similar matrix in an SDG. An MS/MSD should be analyzed for each sample matrix (water/soil) and each level (low/med).

12.2.2.2 The Contractor shall not perform MS/MSD analysis on any of the field QC or PE samples.

12.2.2.3 If an insufficient number of sample vials were received to perform an MS/MSD, and MS/MSD are required, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the EPA Region for instructions. The EPA Region has the option to cancel the MS/MSD analysis. SMO will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.4 If it appears that the EPA Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, the Contractor shall contact SMO. SMO will contact the EPA Region to determine which samples should have an MS/MSD analysis performed on them. SMO will notify the Contractor of the EPA Region's

decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 When a Contractor receives only PE sample(s), no MS/MSD shall be performed within that SDG.

12.2.3 Procedure for Preparing Matrix Spike and Matrix Spike Duplicate

12.2.3.1 To prepare an MS/MSD for water samples, add 20 µL of the matrix spiking solution (Section 7.2.2.4) to each of the 5.0 mL aliquots of the sample chosen for spiking. Process the samples according to Section 10.2.1. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each Matrix Spike analyte.

12.2.3.2 To prepare an MS/MSD for low-level soil/sediment samples, add 20 µL of the matrix spiking solution (Section 7.2.2.4) either manually by puncturing the septum with a small-gauge needle or automatically by the P/T system just prior to analysis. Analyze the MS/MSD samples by the procedure described in Section 10.2.2. Do not further dilute MS/MSD samples to get either spiked or non-spiked analytes within calibration range.

12.2.3.3 To prepare an MS/MSD for medium-level soil/sediment samples, add 4.0 mL of methanol and 1.0 mL of the matrix spiking solution (Section 7.2.2.4) to each of the two aliquots of the soil/sediment sample chosen for spiking. Analyze the MS/MSD sample according to Section 10.2.3.

12.2.3.3.1 In the cases where methanol has been added as a preservative, do not add additional methanol. Add only 1.0 mL of the matrix spiking solution to each of the two aliquots of the soil/sediment sample chosen for spiking.

12.2.3.3.2 Process samples according to Section 10.2.3. This results in a 2,500 µg/kg concentration of each Matrix Spike analyte when added to a 5 g sample. Add a 100 µL aliquot of this extract to 4.9 mL of water for purging (per Sections 10.2.3.5 and 10.2.3.6).

12.2.3.4 MS/MSD samples shall be analyzed at the same dilution as the least diluted aliquot for which the sample results will be reported to the EPA. Sample dilutions must be performed in accordance with Section 10.2.4. Do not further dilute MS/MSD samples to get either spiked or non-spiked analytes within calibration range.

12.2.4 Calculations for Matrix Spike and Matrix Spike Duplicate

12.2.4.1 Calculate the concentrations of the Matrix Spike analytes using the same equations as used for target analytes (Equations 6, 7, and 8). Calculate the recovery of each Matrix Spike analyte using the following equation:

EQ. 13 Matrix Spike Recovery

$$\% R = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD using the following equation:

EQ. 14 Relative Percent Difference

$$RPD = \frac{\left|MSR - MSDR\right|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

WHERE,

MSR = Matrix Spike Recovery

MSDR = Matrix Spike Duplicate Recovery

NOTE: The vertical bars in the equation above indicate the absolute value of the difference.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Matrix Spike Duplicate

12.2.5.1 All MS/MSDs must be analyzed on a GC/MS system meeting the BFB, initial calibration, CCV, and blank technical acceptance criteria, and at the frequency described in Section 12.2.2.

12.2.5.2 The MS/MSD must be analyzed within the contract holding time.

12.2.5.3 The RT shift for each of the internal standards in the MS/MSD must be within 10 seconds of its RT in the most recent opening CCV standard analysis.

12.2.5.4 The limits for MS analyte recovery and RPD are given in Table 11 – Matrix Spike Recovery and Relative Percent Difference Limits. As these limits are only advisory, no further action by the Contractor is required.

12.2.6 Corrective Action for Matrix Spike and Matrix Spike Duplicate

Any MS/MSD that does not meet the technical acceptance criteria in Sections 12.2.5.1 and 12.2.5.3 must be reanalyzed at no additional cost to the EPA.

12.3 Laboratory Control Sample

Not applicable to this method.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed, the Method Detection Limit (MDL) for each volatile target analyte shall be determined on each instrument used for analysis. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for water,

low-level soil/sediment, and medium-level soil/sediment samples). The MDLs must be determined annually thereafter or after major instrument maintenance. Major instrument maintenance includes, but is not limited to, cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device); and replacement or overhaul of the P/T device. A new MDL study will not be required after changing the GC column, as long as the replacement has the same length, inner diameter, and stationary phase.

12.4.2 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in the Code of Federal Regulations, Chapter 40, Part 136, Appendix B (40 CFR 136, Appendix B).

12.4.3 The determined concentration of the MDL must be less than the CRQL listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits.

12.4.4 All documentation for the MDL studies shall be maintained at the laboratory and submitted to the EPA with seven (7) days of study completion. This schedule and the designated recipients are specified in Exhibit B, Table 1 – Reporting and Deliverables Requirements.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

Refer to Section 13.0 of Exhibit D – Introduction to Organic Analytical Methods.

15.0 WASTE MANAGEMENT

Refer to Section 14.0 of Exhibit D – Introduction to Organic Analytical Methods.

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Method 5035A, July 2002.

16.2 U.S. Environmental Protection Agency, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Method 524.2, Revision 4, August 1992.

16.3 U.S. Environmental Protection Agency, Purge-and-Trap for Aqueous Samples, Method 5030C, Revision 3, May 2003.

16.4 U.S. Environmental Protection Agency, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Method 8260C, Revision 3, August 2006.

16.5 U.S. Government Printing Office, 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE REGISTRY NUMBERS

Systematic Name	EPA Registry Name	Synonym	CAS #
Methane, dichlorodifluoro-	CFC-12	Dichlorodifluoromethane	75-71-8
Methane, chloro-	Chloromethane	Methyl chloride	74-87-3
Ethene, chloro-	Vinyl Chloride	Vinyl chloride	75-01-4
Methane, bromo-	Methyl Bromide	Methyl bromide	74-83-9
Ethane, chloro-	Chloroethane	Ethyl chloride	75-00-3
Methane, trichlorofluoro-	CFC-11	Fluorotrichloromethane	75-69-4
Ethene, 1,1-dichloro-	1,1-Dichloroethylene	Vinylidene chloride	75-35-4
Ethane, 1,1,2-trichloro-1,2,2-trifluoro-	CFC-113	Freon 113	76-13-1
2-Propanone	Acetone	Dimethyl ketone	67-64-1
Carbon disulfide	Carbon disulfide	Dithiocarbonic anhydride	75-15-0
Acetic acid, methyl ester	Methyl acetate	Methyl acetate	79-20-9
Methane, dichloro	Methylene chloride	Dichloromethane	75-09-2
Ethene, 1,2-dichloro-, (1E)-	trans-1,2-Dichloroethylene	Ethylene, 1,2-dichloro-, (E)-	156-60-5
Propane, 2-methoxy-2-methyl-	Methyl tert-butyl ether	t-Butyl methyl ether	1634-04-4
Ethane, 1,1-dichloro-	1,1-Dichloroethane	Ethylidene dichloride	75-34-3
Ethene, 1,2-dichloro-, (1Z)-	cis-1,2-Dichloroethylene	Ethylene, 1,2-dichloro-, (Z)-	156-59-2
2-Butanone	Methyl ethyl ketone	Butan-2-one	78-93-3
Methane, bromochloro-	Halon 1011	Chlorobromomethane	74-97-5
Methane, trichloro-	Chloroform	Trichloromethane	67-66-3
Ethane, 1,1,1-trichloro-	1,1,1-Trichloroethane	1,1,1-TCE	71-55-6
Cyclohexane	Cyclohexane	Hexahydrobenzene	110-82-7
Methane, tetrachloro-	Carbon tetrachloride	Tetrachlorocarbon	56-23-5
Benzene	Benzene	Benzol	71-43-2
Ethane, 1,2-dichloro-	1,2-Dichloroethane	Ethylene dichloride	107-06-2
Ethene, 1,1,2-trichloro-	Trichloroethylene	Ethylene, trichloro-	79-01-6
Cyclohexane, methyl-	Methylcyclohexane	Hexahydrotoluene	108-87-2
Propane, 1,2-dichloro-	1,2-Dichloropropane	Propylene dichloride	78-87-5
Methane, bromodichloro-	Dichlorobromomethane	Bromodichloromethane	75-27-4
1-Propene, 1,3-dichloro-, (Z)-	cis-1,3-Dichloropropene	cis-1,3-Dichloropropylene	10061-01-5

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE REGISTRY NUMBERS (CON'T)

Systematic Name	EPA Registry Name	Synonym	CAS #
2-Pentanone, 4-methyl-	Methyl isobutyl ketone	2-Methylpropyl methyl ketone	108-10-1
Benzene, methyl-	Toluene	Methylbenzol	108-88-3
1-Propene, 1,3-dichloro-, (1E)-	trans-1,3-Dichloropropene	trans-1,3-Dichloropropylene	10061-02-6
Ethane, 1,1,2-trichloro-	1,1,2-Trichloroethane	1,1,2-TCA	79-00-5
Ethene, 1,1,2,2-tetrachloro-	Tetrachloroethylene	Tetrachlorethene	127-18-4
2-Hexanone	2-Hexanone	Methyl n-butyl ketone	591-78-6
Methane, dibromochloro-	Chlorodibromomethane	Dibromochloromethane	124-48-1
Ethane, 1,2-dibromo-	Ethylene Dibromide	1,2-Dibromoethane	106-93-4
Benzene, chloro-	Chlorobenzene	Phenyl chloride	108-90-7
Benzene, ethyl-	Ethylbenzene	Phenylethane	100-41-4
Benzene, 1,2-dimethyl-	o-Xylene	1,2-Dimethylbenzene	95-47-6
Benzene, (1,3 and 1,4)-dimethyl-	m,p-Xylene	(1,3 and 1,4)-Dimethyl benzene	179601-23-1
Benzene, ethenyl-	Styrene	Vinyl Benzene	100-42-5
Methane, tribromo-	Tribromomethane	Bromoform	75-25-2
Benzene, (1-methylethyl)-	Cumene	Isopropylbenzene	98-82-8
Ethane, 1,1,2,2-tetrachloro-	1,1,2,2-Tetrachloroethane	Acetylene tetrachloride	79-34-5
Benzene, 1,3-dichloro-	m-Dichlorobenzene	m-Phenylene dichloride	541-73-1
Benzene, 1,4-dichloro-	p-Dichlorobenzene	p-Chlorophenyl chloride	106-46-7
Benzene, 1,2-dichloro-	o-Dichlorobenzene	ortho-Dichlorobenzene	95-50-1
Propane, 1,2-dibromo-3-chloro-	1,2-Dibromo-3-chloropropane	Dibromochloropropane	96-12-8
Benzene, 1,2,4-trichloro-	1,2,4-Trichlorobenzene	1,2,4-Trichlorobenzol	120-82-1
Benzene, 1,2,3-trichloro-	1,2,3-Trichlorobenzene	Vic-Trichlorobenzene	87-61-6
Internal Standards			
Benzene-d5, chloro-	Chlorobenzene-d5	Chlorobenzene-d5	3114-55-4
Benzene, 1,4-difluoro	1,4-Difluorobenzene	p-Difluorobenzene	540-36-3
Benzene-1,2,4,5-d4, 3,6-dichloro	1,4-Dichlorobenzene-d4	1,4-Dichloro-2,3,5,6-tetradeuterobenzene	3855-82-1

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS (CON'T)

Systematic Name	EPA Registry Name	Synonym	CAS #
DMCs			
Ethene-d3, chloro-	Vinyl chloride-d3	Vinyl chloride-d3	6745-35-3
Ethane-d5, chloro-	Chloroethane-d5	Chloroethane-d5	19199-91-8
Ethene-1,1-d2, dichloro-	1,1-Dichloroethene-d2	1,1-Dichloroethene-d2	22280-73-5
2-Butanone-1,1,1,3,3-d5	2-Butanone-d5	2-Butanone-d5	24313-50-6
Methane-d, trichloro-	Chloroform-d	Chloroform-d	865-49-6
Ethane-1,1,2,2-d4, 1,2-dichloro-	1,2-Dichloroethane-d4	1,2-Dichloroethane-d4	17060-07-0
Benzene-1,2,3,4,5,6-d6	Benzene-d6	Benzene-d6	1076-43-3
Propane-1,1,1,2,3,3-d6, 2,3-dichloro-	1,2-Dichloropropane-d6	1,2-Dichloropropane-d6	93952-08-0
Benzene-d5, methyl-d3-	Toluene-d8	Perdeuterotoluene	2037-26-5
1-Propene-1,2,3,3-d4, 1,3-dichloro-(E)-	Trans-1,3-Dichloropropene-d4	Trans-1,3-Dichloropropene-d4	93951-86-1
2-Hexanone-1,1,1,3,3-d5		2-Hexanone-d5	4840-82-8
Ethane-1,2-d2, 1,1,2,2-tetrachloro-	1,1,2,2-Tetrachloroethane-d2	1,1,2,2-Tetrachloroethane-d2	33685-54-0
Benzene-1,2,3,4-d4, 5,6-dichloro-	1,2-Dichlorobenzene-d4	1,2-Dichloro-3,4,5,6-tetradeuterobenzene	2199-69-1

TABLE 2. 4-BROMOFLUOROBENZENE KEY IONS AND ION ABUNDANCE CRITERIA

Mass	**Ion Abundance Criteria**
50	15.0 - 40.0% of mass 95
75	30.0 - 80.0% of mass 95
95	base peak, 100% Relative Abundance
96	5.0 - 9.0% of mass 95 (see NOTE)
173	less than 2.0% of mass 174
174	50.0 - 120% of mass 95
175	5.0 - 9.0% of mass 174
176	95.0 - 101% of mass 174
177	5.0 - 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% that of m/z 95.

TABLE 3. VOLATILE DEUTERATED MONITORING COMPOUNDS AND THE ASSOCIATED TARGET ANALYTES

Vinyl chloride-d_3 (DMC-1)	**Chloroethane-d_5 (DMC-2)**	**1,1-Dichloroethene-d_2 (DMC-3)**
Vinyl chloride	Dichlorodifluoromethane	trans-1,2-Dichloroethene
	Chloromethane	cis-1,2-Dichloroethene
	Bromomethane	1,1-Dichloroethene
	Chloroethane	
	Carbon disulfide	
2-Butanone-d_5 (DMC-4)	**Chloroform-d (DMC-5)**	**1,2-Dichloroethane-d_4 (DMC-6)**
Acetone	1,1-Dichloroethane	Trichlorofluoromethane
2-Butanone	Bromochloromethane	1,1,2-Trichloro-1,2,2-trifluoroethane
	Chloroform	Methyl acetate
	Dibromochloromethane	Methylene chloride
	Bromoform	Methyl tert-butyl ether
		1,1,1-Trichloroethane
		Carbon tetrachloride
		1,2-Dibromoethane
		1,2-Dichloroethane
Benzene-d_6 (DMC-7)	**1,2-Dichloropropane-d_6 (DMC-8)**	**Toluene-d_8 (DMC-9)**
Benzene	Cyclohexane	Trichloroethene
	Methylcyclohexane	Toluene
	1,2-Dichloropropane	Tetrachloroethene
	Bromodichloromethane	Ethylbenzene
		o-Xylene
		m,p-Xylene
		Styrene
		Isopropylbenzene
trans-1,3-Dichloropropene-d_4 (DMC-10)	**2-Hexanone-d_5 (DMC-11)**	**1,1,2,2-Tetrachloroethane-d_2 (DMC-12)**
cis-1,3-Dichloropropene	4-Methyl-2-pentanone	1,1,2,2-Tetrachloroethane
trans-1,3-Dichloropropene	2-Hexanone	1,2-Dibromo-3-chloropropane
1,1,2-Trichloroethane		
1,2-Dichlorobenzene-d_4 (DMC-13)		
Chlorobenzene		
1,3-Dichlorobenzene		
1,4-Dichlorobenzene		
1,2-Dichlorobenzene		
1,2,4-Trichlorobenzene		
1,2,3-Trichlorobenzene		

TABLE 4. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION FOR VOLATILE ORGANIC COMPOUNDS

Analyte	Opening Minimum RRF	Closing Minimum RRF	Maximum %RSD	Opening Maximum %D[1]	Closing Maximum %D
Dichlorodifluoromethane	0.010	0.010	25.0	±40.0	±50.0
Chloromethane	0.010	0.010	20.0	±30.0	±50.0
Vinyl chloride	0.010	0.010	20.0	±25.0	±50.0
Bromomethane	0.010	0.010	40.0	±30.0	±50.0
Chloroethane	0.010	0.010	40.0	±25.0	±50.0
Trichlorofluoromethane	0.010	0.010	40.0	±30.0	±50.0
1,1-Dichloroethene	0.060	0.060	20.0	±20.0	±25.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.050	0.050	25.0	±25.0	±50.0
Acetone	0.010	0.010	40.0	±40.0	±50.0
Carbon disulfide	0.100	0.100	20.0	±25.0	±25.0
Methyl acetate	0.010	0.010	40.0	±40.0	±50.0
Methylene chloride	0.010	0.010	40.0	±30.0	±50.0
trans-1,2-Dichloroethene	0.100	0.100	20.0	±20.0	±25.0
Methyl tert-butyl ether	0.100	0.100	40.0	±25.0	±50.0
1,1-Dichloroethane	0.300	0.300	20.0	±20.0	±25.0
cis-1,2-Dichloroethene	0.200	0.200	20.0	±20.0	±25.0
2-Butanone	0.010	0.010	40.0	±40.0	±50.0
Bromochloromethane	0.100	0.100	20.0	±20.0	±25.0
Chloroform	0.300	0.300	20.0	±20.0	±25.0
1,1,1-Trichloroethane	0.050	0.050	20.0	±25.0	±25.0
Cyclohexane	0.010	0.010	40.0	±25.0	±50.0
Carbon tetrachloride	0.100	0.100	20.0	±25.0	±25.0
Benzene	0.200	0.200	20.0	±20.0	±25.0
1,2-Dichloroethane	0.070	0.070	20.0	±20.0	±25.0
Trichloroethene	0.200	0.200	20.0	±20.0	±25.0
Methylcyclohexane	0.050	0.050	40.0	±25.0	±50.0
1,2-Dichloropropane	0.200	0.200	20.0	±20.0	±25.0
Bromodichloromethane	0.300	0.300	20.0	±20.0	±25.0
cis-1,3-Dichloropropene	0.300	0.300	20.0	±20.0	±25.0
4-Methyl-2-pentanone	0.030	0.030	25.0	±30.0	±50.0
Toluene	0.300	0.300	20.0	±20.0	±25.0
trans-1,3-Dichloropropene	0.200	0.200	20.0	±20.0	±25.0
1,1,2-Trichloroethane	0.200	0.200	20.0	±20.0	±25.0
Tetrachloroethene	0.100	0.100	20.0	±20.0	±25.0
2-Hexanone	0.010	0.010	40.0	±40.0	±50.0
Dibromochloromethane	0.200	0.200	20.0	±20.0	±25.0
1,2-Dibromoethane	0.200	0.200	20.0	±20.0	±25.0
Chlorobenzene	0.400	0.400	20.0	±20.0	±25.0

TABLE 4. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION FOR VOLATILE ORGANIC COMPOUNDS (CON'T)

Analyte	**Opening Minimum RRF**	**Closing Minimum RRF**	**Maximum %RSD**	**Opening Maximum %D[1]**	**Closing Maximum %D**
Ethylbenzene	0.400	0.400	20.0	±20.0	±25.0
m,p-Xylene	0.200	0.200	20.0	±20.0	±25.0
o-Xylene	0.200	0.200	20.0	±20.0	±25.0
Styrene	0.200	0.200	20.0	±20.0	±25.0
Bromoform	0.100	0.100	20.0	±25.0	±50.0
Isopropylbenzene	0.400	0.400	20.0	±25.0	±25.0
1,1,2,2-Tetrachloroethane	0.200	0.200	20.0	±25.0	±25.0
1,3-Dichlorobenzene	0.500	0.500	20.0	±20.0	±25.0
1,4-Dichlorobenzene	0.600	0.600	20.0	±20.0	±25.0
1,2-Dichlorobenzene	0.600	0.600	20.0	±20.0	±25.0
1,2-Dibromo-3-chloropropane	0.010	0.010	25.0	±30.0	±50.0
1,2,4-Trichlorobenzene	0.400	0.400	20.0	±30.0	±50.0
1,2,3-Trichlorobenzene	0.400	0.400	25.0	±30.0	±50.0
Deuterated Monitoring Compounds					
Vinyl chloride-d_3	0.010	0.010	20.0	±30.0	±50.0
Chloroethane-d_5	0.010	0.010	40.0	±30.0	±50.0
1,1-Dichloroethene-d_2	0.050	0.050	20.0	±25.0	±25.0
2-Butanone-d_5	0.010	0.010	40.0	±40.0	±50.0
Chloroform-d	0.300	0.300	20.0	±20.0	±25.0
1,2-Dichloroethane-d_4	0.060	0.060	20.0	±25.0	±25.0
Benzene-d_6	0.300	0.300	20.0	±20.0	±25.0
1,2-Dichloropropane-d_6	0.200	0.200	20.0	±20.0	±25.0
Toluene-d_8	0.300	0.300	20.0	±20.0	±25.0
trans-1,3-Dichloropropene-d_4	0.200	0.200	20.0	±20.0	±25.0
2-Hexanone-d_5	0.010	0.010	40.0	±40.0	±50.0
1,1,2,2-Tetrachloroethane-d_2	0.200	0.200	20.0	±25.0	±25.0
1,2-Dichlorobenzene-d_4	0.400	0.400	20.0	±20.0	±25.0

[1] If a closing CCV is acting as an opening CCV, all target analytes and DMCs must meet the requirements for an opening CCV.

TABLE 5. PURGE-AND-TRAP ANALYTICAL CONDITIONS

Purge Conditions	
Purge Gas:	Helium or Nitrogen
Purge Time:	11.0 ±0.1 min.
Purge Flow Rate:	25-40 mL/min.
Purge Temperature:	Ambient temperature for water or medium-level soil/sediment samples (required for medium-level soil/sediment samples, suggested for water samples), and 40°C low-level soil/sediment samples.
Desorb Conditions	
Desorb Temperature:	180°C
Desorb Flow Rate:	15 mL/min.
Desorb Time:	4.0 ±0.1 min.
Trap Reconditioning Conditions	
Reconditioning Temperature:	180°C
Reconditioning Time:	7.0 ±0.1 min. (minimum). A longer time may be required to bake contamination or water from the system.

NOTE: Higher purge temperatures may be used provided that manufacturer's instructions are followed and technical acceptance criteria are met for all standards, samples, and blanks. Certain target analytes, such as methyl tert-butyl ether (MTBE), may decompose at high purge temperatures in samples that have been acid preserved.

TABLE 6. GAS CHROMATOGRAPH ANALYTICAL CONDITIONS

Capillary Columns	
Carrier Gas:	Helium
Flow Rate:	15 mL/min.
Initial Temperature:	10°C
Initial Hold Time:	1.0–5.0 (±0.1) min.
Ramp Rate:	6°C/min.
Final Temperature:	160°C
Final Hold Time:	Until 3 min. after all analytes listed in Exhibit C – Organic Target Analyte List and Contract Requires Quantitation Limits, Table 2 – Low/Medium Volatiles Target Analyte List and Contract Required Quantitation Limits, elute (required)

TABLE 7. MASS SPECTROMETER ANALYTICAL CONDITIONS

Electron Energy	70 volts (nominal)
Mass Range	35-300 u
Ionization Mode	Electron ionization (EI)
Scan Time	To give at least 5 scans per peak, not to exceed 2 sec. per scan.

TABLE 8. CHARACTERISTIC IONS FOR VOLATILE TARGET ANALYTES, DEUTERATED MONITORING COMPOUNDS, AND INTERNAL STANDARDS

Analyte	**Primary Quantitation Ion**	**Secondary Ion(s)**
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61,63
1,1,2-Trichloro-1,2,2-trifluoroethane	101	85,151
Acetone	43	58
Carbon disulfide	76	78
Methyl acetate	43	74
Methylene chloride	84	49,86
trans-1,2-Dichloroethene	96	61,98
Methyl tert-butyl ether	73	43,57
1,1-Dichloroethane	63	65,83
cis-1,2-Dichloroethene	96	61,98
2-Butanone	43*	72
Chloroform	83	85
Bromochloromethane	128	49,130,51
1,1,1-Trichloroethane	97	99,61
Cyclohexane	56	69,84
Carbon tetrachloride	117	119
Benzene	78	-
1,2-Dichloroethane	62	98
Trichloroethene	95	97,132,130
Methylcyclohexane	83	55,98
1,2-Dichloropropane	63	112
Bromodichloromethane	83	85,127
cis-1,3-Dichloropropene	75	77
4-Methyl-2-pentanone	43	58,100
Toluene	91	92
trans-1,3-Dichloropropene	75	77
1,1,2-Trichloroethane	97	83,85,99,132,134
Tetrachloroethene	164	129,131,166
2-Hexanone	43	58,57,100
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109,188
Chlorobenzene	112	77,114
Ethylbenzene	91	106
m,p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78

*m/z 43 is used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

TABLE 8. CHARACTERISTIC IONS FOR VOLATILE TARGET ANALYTES, DEUTERATED MONITORING COMPOUNDS, AND INTERNAL STANDARDS (CON'T)

Analyte	**Primary Quantitation Ion**	**Secondary Ion(s)**
Bromoform	173	175,254
Isopropylbenzene	105	120,77
1,1,2,2-Tetrachloroethane	83	85,131
1,3-Dichlorobenzene	146	111,148
1,4-Dichlorobenzene	146	111,148
1,2-Dichlorobenzene	146	111,148
1,2-Dibromo-3-chloropropane	75	157,155
1,2,4-Trichlorobenzene	180	182,145
1,2,3-Trichlorobenzene	180	182,145
Deuterated Monitoring Compounds		
Vinyl chloride-d_3	65	67
Chloroethane-d_5	69	71,51
1,1-Dichloroethene-d_2	63	98,65
2-Butanone-d_5	46	77
Chloroform-d	84	86,47,49
1,2-Dichloroethane-d_4	65	67,51
Benzene-d_6	84	82,54,52
1,2-Dichloropropane-d_6	67	65,46,42
Toluene-d_8	98	100,42
trans-1,3-Dichloropropene-d_4	79	81,42
2-Hexanone-d_5	63	46
1,1,2,2-Tetrachloroethane-d_2	84	86
1,2-Dichlorobenzene-d_4	152	150
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115,150
1,4-Difluorobenzene	114	63,88
Chlorobenzene-d_5	117	82,119

TABLE 9. VOLATILE TARGET ANALYTES, DEUTERATED MONITORING COMPOUNDS WITH ASSOCIATED INTERNAL STANDARDS FOR QUANTITATION

1,4-Difluorobenzene (IS)	**Chlorobenzene-d_5 (IS)**	**1,4-Dichlorobenzene-d_4 (IS)**
Dichlorodifluoromethane	1,1,1-Trichloroethane	Bromoform
Chloromethane	Cyclohexane	1,3-Dichlorobenzene
Vinyl chloride	Carbon tetrachloride	1,4-Dichlorobenzene
Bromomethane	Benzene	1,2-Dichlorobenzene
Chloroethane	Trichloroethene	1,2-Dibromo-3-chloropropane
Trichlorofluoromethane	Methylcyclohexane	1,2,4-Trichlorobenzene
1,1-Dichloroethene	1,2-Dichloropropane	1,2,3-Trichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	Bromodichloromethane	1,2-Dichlorobenzene-d_4 (DMC)
Acetone	cis-1,3-Dichloropropene	
Carbon disulfide	4-Methyl-2-pentanone	
Methyl acetate	Toluene	
Bromochloromethane	trans-1,3-Dichloropropene	
Methylene chloride	1,1,2-Trichloroethane	
trans-1,2-Dichloroethene	Tetrachloroethene	
Methyl tert-butyl ether	2-Hexanone	
1,1-Dichloroethane	Dibromochloromethane	
cis-1,2-Dichloroethene	1,2-Dibromoethane	
2-Butanone	Chlorobenzene	
Chloroform	Ethylbenzene	
1,2-Dichloroethane	m,p-Xylene	
	o-Xylene	
Vinyl chloride-d_3 (DMC)	Styrene	
Chloroethane-d_5 (DMC)	Isopropylbenzene	
1,1-Dichloroethene-d_2 (DMC)	1,1,2,2-Tetrachloroethane	
2-Butanone-d_5 (DMC)	Benzene-d_6 (DMC)	
Chloroform-d (DMC)	1,2-Dichloropropane-d_6 (DMC)	
1,2-Dichloroethane-d_4 (DMC)	trans-1,3-Dichloropropene-d_4 (DMC)	
	Toluene-d_8 (DMC)	
	2-Hexanone-d_5 (DMC)	
	1,1,2,2-Tetrachloroethane-d_2 (DMC)	

TABLE 10. DEUTERATED MONITORING COMPOUND RECOVERY LIMITS

Compound	Percent Recovery for Water Samples	Percent Recovery for Soil Samples
Vinyl chloride-d_3	60-135	30-150
Chloroethane-d_5	70-130	30-150
1,1-Dichloroethene-d_2	60-125	45-110
2-Butanone-d_5	40-130	20-135
Chloroform-d	70-125	40-150
1,2-Dichloroethane-d_4	70-125	70-130
Benzene-d_6	70-125	20-135
1,2-Dichloropropane-d_6	70-120	70-120
Toluene-d_8	80-120	30-130
trans-1,3-Dichloropropene-d_4	60-125	30-135
2-Hexanone-d_5	45-130	20-135
1,1,2,2-Tetrachloroethane-d_2	65-120	45-120
1,2-Dichlorobenzene-d_4	80-120	75-120

NOTE: The recovery limits for any of the analytes listed above may be expanded at any time during the period of performance if the EPA determines that the limits are too restrictive.

TABLE 11. MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS

Analyte	Percent Recovery Water	RPD Water	Percent Recovery Soil	RPD Soil
1,1-Dichloroethene	61-145	0-14	59-172	0-22
Trichloroethene	71-120	0-14	62-137	0-24
Benzene	76-127	0-11	66-142	0-21
Toluene	76-125	0-13	59-139	0-21
Chlorobenzene	75-130	0-13	60-133	0-21

THIS PAGE INTENTIONALLY LEFT BLANK

EXHIBIT D

SEMIVOLATILE ORGANIC COMPOUNDS ANALYSIS

THIS PAGE INTENTIONALLY LEFT BLANK

Exhibit D – Semivolatile Organic Compounds Analysis

Table of Contents

Table of Contents

1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze water, leachates derived from the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP), and soil/sediment samples from hazardous waste sites to determine the presence and concentration of the semivolatile organic analytes (SVOA) contained in the Target Analyte List (TAL) for semivolatiles in Exhibit C – Organic Target Analyte List (and Contract Required Quantitation Limits). The method, based on the U.S. Environmental Protection Agency (EPA) SW-846 Method 8270D, covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to Gas Chromatography (GC). The method involves solvent extraction of the matrix sample, characterization to determine the appropriate analytical protocol to be used, followed by appropriate cleanup procedure and GC/Mass Spectrometry (MS) analysis to determine the semivolatile organic analytes present in the sample.

1.2 If requested, sample extracts will be analyzed for the specific group of Polynuclear Aromatic Hydrocarbon (PAH) analytes and pentachlorophenol (PCP) by GC/MS, using the full scan method and/or the Selected Ion Monitoring (SIM) technique. If a SIM analysis is requested, a full scan analysis using the low-level method must be performed first. If all PAHs and PCP are detected at or above the Contract Required Quantitation Limits (CRQLs) during the full scan analysis using the low-level method, then a SIM analysis is not to be performed and this should be documented in the Sample Delivery Group (SDG) Narrative. If only PAHs and PCP are requested by the full scan method, quantitate and report only these target analytes along with the associated Deuterated Monitoring Compounds (DMCs) and internal standards for calibration standards, method blanks, and samples. The SIM analysis is not required for a specific PAH target analyte or PCP which is detected at or above the sample-adjusted CRQL in the full scan analysis. However, if any single PAH analyte or PCP exceeds the calibration range, do not proceed with the SIM method for any of the target analytes scheduled for SIM analysis.

1.3 Problems that have been associated with the following analytes using this method include:

- Dichlorobenzidine and 4-Chloroaniline can be subject to oxidative losses during solvent concentration.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the GC inlet, chemical reactions in acetone solution, and photochemical decomposition.
- N-nitrosodiphenylamine decomposes in the GC inlet forming diphenylamine and consequently, may be detected as diphenylamine.
- PCP, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

2.0 SUMMARY OF METHOD

2.1 Water/TCLP or SPLP Leachate

A 1 liter (L) aliquot of sample is mixed with DMCs, acidified to pH 2.0, and extracted with methylene chloride using a continuous liquid-liquid extractor. Separatory funnel extraction is NOT permitted. The methylene chloride extract is dried with sodium sulfate (or an equivalent drying agent such as Hydromatrix™), concentrated, and subjected to Gel Permeation Chromatography (GPC) cleanup. GPC is required when higher molecular weight compounds are present that interfere with the analyses of target analytes; GPC is optional for all other circumstances. The extract is then analyzed by GC/MS for extractable organics.

2.2 Soil/Sediment

2.2.1 Low-Level Soil/Sediment

A 30 gram (g) aliquot of soil/sediment is spiked with DMCs, mixed with anhydrous powdered sodium sulfate (or Hydromatrix™) and extracted with 1:1 (v/v) methylene chloride/acetone solution using an ultrasonic probe, a Soxhlet extractor, or a pressurized fluid extractor. The extract is concentrated, subjected to GPC cleanup, and analyzed by GC/MS for extractable organics.

The Contractor must determine whether a soil/sediment sample should be analyzed by the low-level or medium-level method, using an EPA-approved screening procedure or an in-house laboratory screening procedure.

2.2.2 Medium-Level Soil/Sediment

Approximately 1 g aliquot of sample is mixed with anhydrous powdered sodium sulfate (or Hydromatrix™) and DMCs in a vial and extracted with methylene chloride. The methylene chloride extract is subjected to GPC cleanup and optional silica gel cleanup (SW-846 Method 3630C), prior to analysis by GC/MS for extractable organics.

2.3 Wipes

Not applicable to this method.

2.4 Waste

Not applicable to this method.

2.5 Non-Target Compounds

Non-target compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the NIST (2011 release or later), Wiley (2011 release or later), or equivalent mass spectral library. Non-target compounds are quantitated by comparing the mass spectra response from the total Reconstructed Ion Chromatogram (RIC) for the non-target compound peaks to the mass spectra response produced by the nearest internal standard. A Relative Response Factor (RRF) of 1 is assumed.

3.0 DEFINITIONS

See Exhibit G – Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These contaminants lead to discrete artifacts and/or elevated baselines in the Extracted Ion Current Profiles (EICPs). These materials must be routinely demonstrated to be free from interferences under the sample preparation and analysis conditions by analyzing laboratory method blanks.

4.2 Matrix Interferences

Matrix interferences may be caused by compounds that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled.

5.0 SAFETY

See Section 12.0 of Exhibit D – Introduction to Organic Analytical Methods.

5.1 Reagents

Concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to skin and mucous membranes. Use this reagent in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with this reagent.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the SDG Narrative.

6.1 General Laboratory Equipment

6.1.1 Balances

6.1.1.1 Top loading, capable of weighing accurately to ±0.01 g.

6.1.1.2 Analytical, capable of weighing accurately to ±0.0001 g.

A balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±50% of the expected measured mass) for each type of balance and be accurate to ±0.01 g and ±0.0001 g, respectively. The masses that are used to check the balances daily must be checked on a monthly basis using NIST-traceable known reference masses (Class ‘0’ or Class ‘1’) as defined by ASTM E617-97(2008) or equivalent (e.g., earlier Class ‘S’ defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must be recertified at least every five years, or sooner if there is reason to believe damage

(corrosion, nicks)has occurred. The Contractor shall maintain documentation that demonstrates these criteria have been met.

6.1.2 Beakers - 100 milliliters (mL), 125 mL, 250 mL, and 400 mL.

6.1.3 Centrifuge, Table top (optional).

6.1.3.1 Centrifuge Tube - 12-15 mL with 19 mm ground-glass joint (optional).

6.1.4 Graduated Cylinder Class A - 1 L and 100 mL capacity.

6.1.5 Desiccator.

6.1.6 Erlenmeyer Flasks - 250 mL.

6.1.7 Volumetric Flask, Class A – 5.0, 10, 20, 50, 100, 250, and 500 mL.

6.1.8 Magnetic Stirring Bar - polytetrafluoroethylene (PTFE) coated, at least 4 centimeters (cm) long.

6.1.9 Ovens – drying, capable of maintaining 105°C (±5°C).

6.1.10 pH Meter - With a combination glass electrode. Calibrate according to manufacturer's instructions. The pH meter shall be calibrated prior to each use, using reference standards bracketing the range expected in samples. The pH reference standards shall be replaced when their expiration dates have passed.

6.1.11 pH Paper – Wide range.

6.1.12 Pipettes - Glass volumetric, 1.0 mL or 2.0 mL.

6.1.13 Spatula - Stainless steel or PTFE.

6.1.14 Syringes – 10 microliters (µL), 25 µL, 100 µL, and 1000 µL.

6.1.15 Vials and Caps - 10 mL (optional), with screw-cap and PTFE or aluminum foil liner; autosampler vial with 2 mL capacity for GC autosampler.

6.1.16 Weigh Dish – Porcelain crucibles or disposable aluminum weighing pans.

6.2 Glassware/Extraction/Cleanup Equipment

6.2.1 Automated Soxhlet Extraction System - With temperature-controlled oil bath. Silicone oil must not be used because it destroys the rubber parts. The apparatus must be used in a hood.

6.2.1.1 Cellulose or Glass Extraction Thimble - 26 millimeters (mm) ID x 60 mm.

6.2.1.2 Glass Extraction Cups.

6.2.1.3 Thimble Adapters.

6.2.1.4 Viton Seals.

6.2.2 Soxhlet Extraction, Manual

6.2.2.1 Allihn Condenser.

6.2.2.2 Soxhlet Extractor body, 40 mm ID.

6.2.2.3 Round bottom flask, 500 mL.

6.2.3 Borosilicate Glass Wool - Rinsed with methylene chloride.

6.2.4 Continuous Liquid-Liquid Extractors - Equipped with PTFE or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.2.5 Drying Column - 400 mm long x 19 mm ID chromatographic column with coarse frit (substitution of a small pad of borosilicate glass wool for the frit will help prevent cross contamination of sample extracts).

6.2.6 Gel Permeation Chromatography Cleanup System

6.2.6.1 Gel Permeation Cleanup System - Systems that perform satisfactorily have been assembled from the following components - a High Performance Liquid Chromatography (HPLC) pump, an autosampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Section 10.3.3.

NOTE: GPC cleanup is required for all soil/sediment extracts, and for water extracts containing higher molecular weight contaminants that interfere with the analyses of the target analytes.

6.2.6.2 Chromatographic Column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the ultraviolet (UV) detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve may be attached so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

6.2.6.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect the inlet side of the analytical column.

6.2.6.4 Bio Beads (SX-3) - 200-400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, or equivalent). An additional 5 g of Bio Beads are required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.2.6.5 Ultraviolet Detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

6.2.6.6 Strip Chart Recorder, recording integrator, or laboratory data system.

6.2.6.7 Syringe Filter Assembly, - disposable 5 micron filter discs.

NOTE: Consult the instrument operation manual to determine the proper filter disc to use in the system. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

6.2.6.8 Viscometer

6.2.7 Kuderna-Danish Apparatus

6.2.7.1 Concentrator Tubes - 15 mL and 10 mL, graduated. Ground-glass stoppers are used to prevent evaporation of extracts.

6.2.7.2 Evaporative Flasks - 500 mL.

6.2.7.3 Silicon Carbide Boiling Chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride. PTFE boiling chips solvent rinsed prior to use are acceptable.

6.2.7.4 Snyder Column - Three-ball macro.

6.2.7.5 Snyder Column - Two-ball micro.

6.2.8 Nitrogen Evaporation Device - Equipped with a water bath that can be maintained at 35-40°C. To prevent the release of solvent fumes into the laboratory, the nitrogen evaporator device must be used in a hood.

6.2.9 Pressurized Fluid Extraction Device

6.2.9.1 Dionex Accelerated Solvent Extractor (ASE-300) or equivalent with appropriately sized extraction cells. Currently, 100 mL cells are available that will accommodate greater than 30 g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure environments [2000+ pounds per square inch (psi)] necessary for this procedure.

6.2.9.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.2.10 Sonabox Acoustic Enclosure (or equivalent) - For use with disrupter to decrease noise level.

6.2.11 Ultrasonic Cell Disruptors - QSonica LLC, (53 Church Hill Road, Newtown, CT 06470) model S-4000 or equivalent ultrasonic liquid disruptor – equipped with a 3/4-inch horn and a 1/2-inch tapered horn, and a 1/8 inch standard tapered microtip probe with a minimum output capacity of 300 watts.

NOTE 1: To ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. A rough tip surface is an indication of erosion.

NOTE 2: Follow manufacturer’s instructions for set-up.

6.2.12 Vacuum Filtration Apparatus

6.2.12.1 Buchner Funnel.

6.2.12.2 Filter Paper - Whatman No. 42 or equivalent.

6.2.13 Water Bath - Heated, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

6.3 Analytical Instrumentation

6.3.1 Gas Chromatograph

The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout temperature program operations. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants, or flow controllers with rubber components, are not to be used.

6.3.2 Gas Chromatography Columns

Recommended Columns: Minimum length 30 meter (m) x 0.25 mm ID (or 0.32 mm) bonded-phase fused silica capillary column DB-5 (J&W Scientific); Rtx®-5, Rtx®-5 Sil Ms (Restek); Zebron ZB-5 (Phenomenex); SPB-5 (Supelco); AT-5 (Alltech); HP-5 (Agilent); CP-Sil 8CB (Chrompack); 007-2 (Quadrex); BP-5 (SGE); or equivalent. A description of the GC column used for analysis shall be provided in the SDG Narrative. Packed columns cannot be used.

6.3.2.1 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the analytes listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contract Required Quantitation Limits;
- The analytical results generated using the column meet the initial and continuing calibration verification (CCV) technical acceptance criteria (Sections 9.3.5 and 9.4.5) and the CRQLs listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contract Required Quantitation Limits ;
- The column must be capable of accepting up to 160 ng of each analyte listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contract Required Quantitation Limits, without becoming overloaded; and
- The column provides equal or better resolution of the analytes listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contract Required Quantitation Limits, than columns listed in Section 6.3.2.

6.3.2.1.1 As applicable, follow the manufacturer's instructions for use of its product.

6.3.2.1.2 The Contractor must maintain documentation that the column meets the criteria in Section 6.3.2.1. The minimum documentation is as follows:

6.3.2.1.2.1 Manufacturer provided information concerning the performance characteristics of the column.

6.3.2.1.2.2 RICs and data system reports generated on the GC/MS used for Contract Laboratory Program (CLP) analyses:

- From method blanks that demonstrate that there are no contaminants that interfere with the semivolatile analysis when using the alternate column; and
- From initial calibration and CCV standards analyzed using the alternate column.

6.3.2.1.3 Based on the Contractor-generated data, the Contractor must complete a written review, signed by the Laboratory Manager, certifying that:

- The alternate column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the semivolatile CRQLs;
- The high-point initial calibration standard analysis was not overloaded; and

- The column does not introduce contaminants that interfere with the identification and/or quantitation of analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contract Required Quantitation Limits.

6.3.2.1.4 The documentation must be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional Laboratory Contracting Officer (COR).

6.3.3 Mass Spectrometer

The MS must be capable of scanning from 35-500 atomic mass units (u) every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the decafluorotriphenylphosphine (DFTPP) GC/MS performance check technical acceptance criteria in Table 2 – Decafluorotriphenylphosphine Key Ions and Ion Abundance Criteria, when 50 ng of DFTPP is injected through the GC inlet. The system must be capable of SIM. The Contractor is to use professional judgment and the instrument manufacturer's instructions and guidelines in choosing an appropriate single ion scan or dwell time (usually 50-500 msec per ion).

The instrument must be vented to the outside of the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.3.4 Gas Chromatograph/Mass Spectrometer Interface

Any GC/MS interface that gives acceptable sensitivity at the CRQLs. However, direct insertion of the GC column into the MS ion source is the recommended interface. GC/MS interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.4 Data Systems/Data Storage

A computer system must be interfaced to the MS that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching of any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an EICP. Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows comparing sample spectra against reference library spectra. The NIST (2011 release or later), Wiley (2011 release or later), or equivalent mass spectral library shall be used as the reference library. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

7.0 REAGENTS AND STANDARDS

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit D – Introduction to Organic Analytical Methods, Section 11.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1 Reagents

7.1.1 Reagent Water - Reagent water is defined as water in which an interferent is not observed at or above the CRQL for each analyte of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g [1 pound (lb)] of activated carbon.

7.1.1.2 Reagent water may also be generated using a water purification system.

7.1.2 Acetone/methylene chloride (1:1 v/v).

7.1.3 Hydromatrix™ - Diatomaceous earth-based material rinsed with methylene chloride and dried at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle.

7.1.4 Sodium sulfate - Granular anhydrous reagent grade, heated at 400°C for 4 hours, cooled in a desiccator, and stored in a glass bottle. Each lot must be extracted with hexane and analyzed by a GC/Electron Capture Detector (ECD) to demonstrate that it is free of interference before use or must be purchased with certification that it is free of interference.

CAUTION: AN OPEN CONTAINER OF SODIUM SULFATE MAY BECOME CONTAMINATED DURING STORAGE IN THE LABORATORY.

7.1.5 Solvents: Acetone, methanol, methylene chloride, iso-octane, 2-propanol, and toluene - pesticide residue analysis grade or equivalent.

7.1.6 Sulfuric acid, concentrated, 95-98% (sp. gr. 1.84).

7.1.7 Glycerol

7.2 Standards

7.2.1 Stock Standard Solutions

7.2.1.1 Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be prepared in methylene chloride from pure standard materials, or purchased as pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated.

7.2.2 Working Standards

7.2.2.1 Initial and Continuing Calibration Solutions

7.2.2.1.1 Prepare the calibration standards at a minimum of five concentrations in methylene chloride that are applicable to the sensitivity of the instrument. For most operations, the calibration standards are to be prepared at 5.0, 10, 20, 40, and 80 ng/µL for each target analyte and associated DMCs, except 1,4-Dioxane and target analytes in Section 7.2.2.1.2 and DMCs 1,4-Dioxane-d8 and DMCs,(see Table 3 – Semivolatile Deuterated Monitoring Compounds and the Associated Target Analytes and Table 4 – Semivolatile Deuterated Monitoring Compounds and the Associated Target Analytes for Optional Analysis by Selected Ion Monitoring). For 1,4-Dioxane and 1,4-Dioxane-d8, the calibration standard concentrations shall be at 2.0, 4.0, 8.0, 16 and 32 ng/uL. These levels are based upon 1.0 mL final volume extracts for samples not undergoing GPC cleanup, and 0.5 mL final volume extracts for those samples undergoing GPC cleanup. Other concentrations may be used for more sensitive instrumentation and final extract volumes. For example, a laboratory may use a final extract volume of 1.0 mL for samples undergoing GPC cleanup, and a low calibration standard of 2.5 ng/µL. The alternate calibration standards and final volumes may be used as long as the following requirements are met:

7.2.2.1.1.1 The laboratory can demonstrate that the CRQL for each analyte listed in Exhibit C –Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contract Required Quantitation Limits can be reached using the calibration and final volume scheme. This demonstration is made when there is formal documentation of laboratory Method Detection Limit (MDL) studies indicating that the calculated MDL for each target analyte is below the required CRQL for that analyte when using the laboratory's specific final volume and calibration level scheme.

7.2.2.1.1.2 All five calibration levels are in the same ratio as that shown above (e.g., if a laboratory were using a 1.0 ng/µL low standard, then the other calibration levels must be 2.0, 4.0, 8.0, and 16 ng/µL).

7.2.2.1.2 Each calibration standard should contain each target analyte. Each DMC may be added to the other calibration standards, or may be contained in a separate mixture and combined with the calibration standard in the autosampler vials just prior to analysis. Twenty-one target analytes and seven DMCs (Benzaldehyde, Phenol, Bis(2-chloroethyl) ether, 2-Methylphenol, 2,2'-Oxybis(1—chloropropane), Acetophenone, 4-Chloroaniline, Caprolactam, Hexachlorocyclopentadiene, Atrazine, Carbazole, Fluoranthene, 3,3'-Dichlorobenzidine, Di-n-octylphthalate, 2,4-Dinitrophenol, PCP, 4-Methylphenol, 4,6-Dinitro-2-methylphenol, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, Phenol-d_5, Bis(2-chloroethyl) ether-d_8, 4-Methylphenol-d_8, 4-Chloroaniline-d_4, 2,4-Dinitrophenol-d_3, 4-Nitrophenol-d_4, and 4,6-Dinitro-2-methylphenol-d_2) have shown to be less sensitive. These analytes will require a five-point initial calibration at 10, 20, 40, 80, and 160 ng/µL.

NOTE: 1.0 or 2.0 µL injections of all calibration standards may be used. All samples analyzed must have been injected at the same volume (1.0 or 2.0 µL) as the calibration standard.

7.2.2.1.2.1 For PAHs and PCP only full scan analyses, the initial calibration containing all target analytes and DMCs can be used to substitute the five point initial calibration containing only these target analytes and associated DMCs at the concentrations in Sections 7.2.2.1 and 7.2.2.2.

7.2.2.1.2.2 If the optional analysis of PAHs and PCP using the SIM technique is to be performed, prepare calibration standards at a minimum of five concentration levels that are applicable to the sensitivity of the instrument. For most operations, the calibration standards are to be prepared at 0.10, 0.20, 0.40, 0.80, and 1.6 ng/µL for each target analyte of interest and the associated DMCs (see Table 10 – Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation of Polynuclear Aromatic Hydrocarbon and Pentachlorophenol). PCP will require a five-point initial calibration at 0.20, 0.40, 0.80, 1.6 and 3.2 ng/µL.

NOTE: 1.0 or 2.0 µL injections of all calibration standards may be used. All samples analyzed must have been injected at the same volume (1.0 or 2.0 µL) as the calibration standard.

7.2.2.1.3 The CCV standard should be at or near the mid-point concentration level of the calibration standards. If the optional analysis of PAHs and PCP by SIM is to be performed, the CCV standard should be at or near the mid-point calibration level, normally 0.40 ng/µL (0.80 ng/µL for PCP).

7.2.2.1.4 To facilitate the confirmation of single component pesticides from the semivolatile library search data (see Exhibit D – Pesticides Analysis, Section 11.1.2), the laboratory may include the single component pesticide target analytes listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits in the semivolatile CCV standard. The laboratory may add any or all of these analytes to the semivolatile CCV standard, but at a concentration of 10 ng/µL or less. Do not include the Aroclor or Toxaphene mixtures in the semivolatile initial and CCV standards. If added to this standard, these additional analytes must be included in the quantitation report for the CCV standard. As only a single point calibration would be performed, no Percent Relative Standard Deviation (%RSD) or Percent Difference (%D) criteria would apply to these additional analytes.

7.2.2.2 Instrument Performance Check Solution

Prepare a solution containing DFTPP in methylene chloride. The solution may be incorporated into the calibration standard used as the mid-level initial calibration standard and the CCV standard, or may be prepared as a single compound solution. If DFTPP is incorporated into the calibration standard, then an aliquot of the DFTPP solution is to be added to the autosampler vial containing either the initial calibration mid-level standard

or the CCV standard before calibration analysis. The DFTPP must be analyzed using the same GC and MS analytical conditions as is used for the calibration analysis. The DFTPP solutions are to be prepared such that 50 ng of DFTPP is injected onto the column.

7.2.2.3 Gel Permeation Chromatography Calibration Solution

Prepare a GPC calibration solution in methylene chloride containing the following analytes at the minimum concentration listed (in elution order). The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Compound	Concentration (mg/mL)
Corn oil (CAS #8001-30-7)	25.0
Bis(2-ethylhexyl)phthalate (CAS #117-81-7)	0.5
Methoxychlor (CAS #72-43-5)	0.1
Perylene (CAS #198-55-0)	0.02
Sulfur (CAS #7704-34-9)	0.08

NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.2.2.4 Deuterated Monitoring Compound Spiking Solution

7.2.2.4.1 Prepare a DMC spiking solution containing the following DMC analytes in methanol at the concentration given:

DMC	Concentration µg/mL
1,4-Dioxane-d_8	16
Phenol-d_5	80
Bis(2-chloroethyl)ether-d_8	80
2-Chlorophenol-d_4	80
4-Methylphenol-d_8	80
4-Chloroaniline-d_4	80
Nitrobenzene-d_5	80
2-Nitrophenol-d_4	80
2,4-Dichlorophenol-d_3	80
Dimethylphthalate-d_6	80
Acenaphthylene-d_8	80
4-Nitrophenol-d_4	80
Fluorene-d_{10}	80
4,6-Dinitro-methylphenol-d_2	80
Anthracene-d_{10}	80
Pyrene-d_{10}	80
Benzo(a)pyrene-d_{12}	80
Fluoranthene-d_{10} (SIM analysis)	0.8
2-Methylnapthalene-d_{10} (SIM analysis)	0.8

7.2.2.4.2 DMC spiking solution is added (500 µL) prior to sample processing to all samples, blanks, requested Matrix Spike and Matrix Spike Duplicates (MS/MSDs), and calibration solutions.

7.2.2.4.3 The SIM DMC compounds (Table 4 – Semivolatile Deuterated Monitoring Compounds and the Associated Target Analytes for Optional Analysis by Selected Ion Monitoring) can be added as part of the DMC spiking solution or added separately to all standards, samples, and blanks that require SIM analysis.

7.2.2.4.4 The DMC spiking solution must be prepared every 12 months, or sooner if the solution has degraded or concentrated.

7.2.2.5 Matrix Spiking Solution

7.2.2.5.1 If MS/MSD analysis is requested at the time of scheduling, prepare a spiking solution in methanol that contains the following analytes and concentrations:

Bases/Neutrals	µg/mL	Acids	µg/mL
Acenaphthene	80	Pentachlorophenol	80
2,4-Dinitrotoluene	80	Phenol	80
Pyrene	80	2-Chlorophenol	80
N-Nitroso-di-n-propylamine	80	4-Chloro-3-methylphenol	80
		4-Nitrophenol	80

7.2.2.5.2 For the analysis of PAH and PCP-only, the laboratory has the option of using the matrix spiking solution in Section 7.2.2.5.1 or preparing a matrix spiking solution containing only acenaphthene, pyrene, and PCP at the concentration of 80 µg/mL in methanol for full scan or 0.80 µg/mL for SIM analysis.

7.2.2.6 Internal Standard Spiking Solution

7.2.2.6.1 Prepare an internal standard spiking solution containing each of the following compounds in methylene chloride: 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. It may be necessary to use 5-10% toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. Just prior to full scan analysis by GC/MS, add sufficient amount of the internal standard spiking solution to an aliquot of the water, low-level, or medium-level soil sample extracts to result in a 20 ng/µL concentration of each internal standard. Prepare a fresh internal standard spiking solution monthly, or sooner if the solution has degraded or concentrated.

7.2.2.6.2 If the optional analysis of PAHs and PCP using the SIM analysis is to be performed, the Contractor shall add sufficient amount of the internal standard spiking solution to an aliquot of the water or low-level sample extracts just prior to SIM analysis to result in a 0.40 ng/µL concentration of each internal standard. 1,4-dichlorobenzene-d_4 is not required to be evaluated as internal standard when performing SIM analysis.

7.2.3 Storage of Standard Solutions

7.2.3.1 Store the working standards at ≤6°C, but not frozen, in PTFE-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 6 months, or sooner if comparison with quality control (QC) check samples indicates a problem.

7.2.3.2 Store the stock standard solutions at ≤6°C, but not frozen, in PTFE-lined screw-cap amber bottles.

7.2.3.3 Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from the preparation date. The expiration date of the ampulated standards, upon the breaking of the glass seal, is 6 months (or sooner if the standard has degraded or evaporated).

7.2.3.4 Refrigeration of the GPC calibration solution may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves. Replace this calibration solution every 6 months, or more frequently if necessary.

7.2.3.5 Protect all standards from light.

7.2.3.6 Samples, sample extracts, and standards must be stored separately.

7.2.3.7 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. This means, at a minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution.

7.2.4 Temperature Records for Storage of Standards

7.2.4.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.

7.2.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.2.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water Samples

Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with PTFE-lined screw-caps. If amber containers are not available, the samples should be protected from light.

8.1.2 Soil/Sediment Samples

Soil/sediment samples may be collected in glass containers.

8.2 Procedure for Sample and Sample Extract Storage

8.2.1 Sample Storage

The samples must be protected from light and refrigerated at ≤6°C, but not frozen, from the time of receipt until 60 days after delivery of a complete, reconciled data package to the EPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 Sample Extract Storage

Sample extracts must be protected from light and stored at ≤6°C, but not frozen, until 365 days after delivery of a complete, reconciled data package to the EPA.

8.3 Contract Required Holding Times

8.3.1 Extraction of water samples shall be started within 5 days of Validated Time of Sample Receipt (VTSR). Extraction of Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) leachates shall begin within 7 days from the completion of the leaching procedure. Extraction of soil/sediment samples shall be completed within 10 days of VTSR.

8.3.2 Analysis of sample extracts must be analyzed within 40 days following the start of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Initial Instrument Set-Up

9.1.1 Gas Chromatograph

9.1.1.1 The recommended GC analytical conditions are provided in Table 6 – Gas Chromatograph Analytical Conditions. Other conditions may be used, provided that all technical acceptance criteria in Sections 9.3.5, 9.4.5, and 11.3 are met. For example, newer columns that are stable at temperatures of up to 370°C may be used. The use of these columns would decrease analysis time while still providing adequate resolution.

9.1.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and MS/MSD.

9.1.1.3 The same injection volume, 1.0 or 2.0 µL, must be used for all standards, samples (including MS/MSD, and required method blanks).

9.1.2 Mass Spectrometer

The recommended MS analytical conditions are provided in Table 7 – Mass Spectrometer Analytical Conditions.

9.2 Instrument Performance Check

9.2.1 Summary of Gas Chromatograph/Mass Spectrometer Instrument Performance Check

9.2.1.1 The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.2.2).

9.2.1.2 Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing DFTPP.

9.2.1.3 The requirement to analyze the instrument performance check solution is optional when SIM analysis of PAHs and PCP is to be performed.

9.2.2 Frequency of Gas Chromatograph/Mass Spectrometer Instrument Performance Check

The instrument performance check solution must be injected once at the beginning of each 12-hour period during which samples, blanks, or standards are analyzed. The 12-hour period for the GC/MS instrument performance check, calibration standards (initial or calibration CCV), blank, and sample analysis begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant instrument performance check. However, in cases where a closing CCV can be used as an opening CCV for the next 12-hour period, then an additional DFTPP tune is not required, and the 12-hour period begins with the injection of the CCV. The period ends after 12 hours have elapsed according to the system clock.

NOTE: For the optional analysis of PAHs and PCP by the SIM technique, the 12-hour period begins at the moment of injection of the first initial calibration standard or at the moment of injection of the CCV standard, if initial calibration is not to be performed. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for Gas Chromatograph/Mass Spectrometer Instrument Performance Check

The analysis of the instrument performance check solution shall be performed as follows:

- As an injection of 50 ng of DFTPP into the GC/MS.
- By adding a sufficient amount of DFTPP to the mid-level calibration standard to result in an on-column amount of 50 ng of DFTPP (Section 7.2.2.2).

9.2.4 Technical Acceptance Criteria for Gas Chromatograph/Mass Spectrometer Instrument Performance Check

9.2.4.1 The GC/MS system must be tuned at the frequency described in Section 9.2.2.

9.2.4.2 The abundance criteria listed in Table 2 – Decafluorotriphenylphosphine Key Ions and Ion Abundance Criteria, must be met for a 50 ng injection of DFTPP. The mass spectrum of DFTPP must be acquired in the following manner:

9.2.4.2.1 Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.

9.2.4.2.2 Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. Do not background subtract part of the DFTPP peak.

NOTE: All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must be analyzed under the identical GC/MS instrument analytical conditions.

9.2.4.3 The chromatographic resolution of the GC system must be capable of resolving the structural isomers Benzo[b] and Benzo[k]fluoranthene. The chromatographic resolution of the GC system must show a minimum 50% valley between Benzo[b] and Benzo[k]fluoranthene (i.e., the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights).

9.2.5 Corrective Action for Gas Chromatograph/Mass Spectrometer Instrument Performance Check

9.2.5.1 If the DFTPP technical acceptance criteria are not met, retune the GC/MS system. It may also be necessary to clean the ion source or take other actions to achieve the technical acceptance criteria.

9.2.5.2 Any samples or required blanks analyzed when the instrument performance check technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to the analysis of samples (including MS/MSDs) and required blanks, and after the instrument performance check technical acceptance criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.2.1.1) to determine instrument sensitivity and the linearity of GC/MS response for the semivolatile target analytes and DMCs. For PAHs and PCP only full scan analysis, initial calibration shall be performed for these target analytes and their associated DMCs at the required concentration levels (see Section 7.2.2.1.2.2).

NOTE: For optional analysis of PAHs and PCP only using the SIM technique, the GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.2.1.2.2), prior to the analysis of samples and required blanks, to determine instrument sensitivity and linearity.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be calibrated prior to analyzing samples, whenever the Contractor takes corrective action that may change or affect the initial calibration criteria (e.g., ion source cleaning or repairs, column replacement, etc.), or if the CCV technical acceptance criteria have not been met.

9.3.2.2 If time still remains in the 12-hour period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed (Section 9.2.2). It is not necessary to analyze another CCV standard. A method blank is required.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Set up the GC/MS system as described in Section 9.1.

9.3.3.2 All standards must be allowed to warm to ambient temperature before analysis.

9.3.3.3 Add internal standard spiking solution (Section 7.2.2.6) to aliquots of each of the five calibration standards to result in a 20 ng/µL concentration of each internal standard. The internal standards specified in Section 7.2.2.6 should permit most of the semivolatile target analytes to have Relative Retention Times (RRTs) of 0.80 to 1.20, using the assignments of internal standards to target analytes given in Table 9 – Semivolatile Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation.

9.3.3.4 Analyze each calibration standard by injecting 1.0 or 2.0 µL of standard. The initial calibration sequence is listed below.

INITIAL CALIBRATION SEQUENCE

1. GC/MS Instrument Performance Check
2. CS1 Initial Calibration Standard
3. CS2 Initial Calibration Standard
4. CS3 Initial Calibration Standard
5. CS4 Initial Calibration Standard
6. CS5 Initial Calibration Standard

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the RRF for each semivolatile target analyte and DMC using Equation 1. The primary characteristic ions used for quantitation are listed in Table 8 – Characteristic Ions for Semivolatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards. Assign the target analytes and DMCs to an internal standard according to Table 9 - Semivolatile Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation and Table 10 – Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation of Polynuclear Aromatic Hydrocarbon and Pentachlorophenol. For internal standards, use the primary ion listed in Table 8 – Characteristic Ions for Semivolatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards unless interferences are present. If interferences prevent the use of the primary ion for a given internal standards, use the secondary ion(s) listed in Table 8 – Characteristic Ions for Semivolatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards.

NOTE: Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion.

EQ. 1 Relative Response Factor

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

WHERE,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (Table 8 – Characteristic Ions for Semivolatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards)

A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (Table 8 – Characteristic Ions for Semivolatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards). The target analytes are listed with their associated internal standards in Table 9 - Semivolatile Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation

C_{is} = Amount of the internal standard injected (ng)

C_x = Amount of the target analyte or DMC injected (ng)

9.3.4.2 The Mean RRF ($\overline{RRF}$) must be calculated for all compounds according to Equation 2.

9.3.4.3 Calculate the %RSD of the RRF values for each target analyte and DMC over the initial calibration using Equation 3 in conjunction with Equations 2 and 4.

9.3.4.3.1 Equation 2 is the general formula for the mean of a set of values.

EQ. 2 Mean Value

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

WHERE,

X_i = Value

$\overline{X}$ = Mean value

n = Number of values

9.3.4.3.2 Equation 3 is the general formula for the relative standard deviation.

EQ. 3 Percent Relative Standard Deviation

$$\%RSD = \frac{SD_{RRF}}{\overline{X}} \times 100$$

WHERE,

SD_{RRF} = Standard deviation of initial calibration RRFs (per compound) from EQ. 4

$\overline{X}$ = Mean value of the initial calibration RRFs (per compound)

9.3.4.3.3 Equation 4 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 4 Standard Deviation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{(n-1)}}$$

WHERE,

X_i = Each individual value used to calculate the mean

$\overline{X}$ = The mean of n values

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.2.1.1 and at the frequency described in Section 9.3.2 on a GC/MS system meeting the DFTPP technical acceptance criteria (Section 9.2.4).

9.3.5.2 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument manual to determine how saturation is indicated for your instrument.

NOTE: The EPA Regional customer may specify, at the time of scheduling, that certain analytes of interest (i.e., PCP) may not fail the performance criteria.

9.3.5.3 The RRF at each calibration concentration for each semivolatile target analyte and DMC must be greater than or equal to the compound's minimum RRF listed in Table 5 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds.

9.3.5.4 The %RSD for target analyte or DMC listed in Table 5 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds must be less than or equal to the value listed.

9.3.5.5 Up to four target analytes or DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Table 5 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds. Up to four target analytes or DMCs (excluding those with maximum %RSD requirements of 40.0%) may fail to meet the criteria listed in Table 5 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds, but these compounds must still meet the maximum %RSD requirements of 40.0%.

9.3.5.6 For the optional analysis of PAHs and PCP either by full scan or using the SIM technique, two target analytes or DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Table 5 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds. Up to two target analytes and/or DMCs (excluding those with maximum %RSD requirements of 40.0%) may fail to meet the criteria listed in Table 5 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds, but these compounds must still meet the maximum %RSD requirements of 40.0%.

9.3.5.7 The chromatographic resolution should be verified with the mid-point concentration of the initial calibration as well as the CCV standards if closely eluting isomers are to be reported. Sufficient chromatographic resolution is achieved when the height of the valley between the two isomer peaks is less than 50% of the average of the two peak heights.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the acceptance criteria.

9.3.6.2 Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Continuing Calibration Verification

Prior to the analysis of samples and required blanks, and after instrument performance check and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing an opening CCV (containing all the semivolatile target analytes, DMCs, and internal standards) to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method. A closing CCV using the same standard as for the opening CCV is required after all samples and blanks have been analyzed, and before the end of the 12-hour period (refer to the analytical sequence in Section 9.4.2.3). If the closing CCV meets opening CCV criteria, an additional DFTPP time is not required and the next 12-hour period begins with this CCV.

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 The calibration for each GC/MS system used for analysis must be verified at the beginning and end of every 12-hour period of

operation. The 12-hour period begins with the injection of DFTPP for full scan analysis, followed by the injection of the opening CCV. If a closing CCV meets the technical acceptance criteria for an opening CCV (Section 9.4.5) and samples are analyzed within the next 12-hour period, then an additional DFTPP tune is not required and the 12-hour period begins with that calibration verification. If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then a DFTPP tune, followed by an opening CCV, is required and the next 12-hour period begins with the DFTPP tune (Section 9.2.2).

9.4.2.2 If time still remains in the 12-hour period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed.

9.4.2.3 After the injection of all samples and required blanks, and before the end of the 12-hour period, another injection of the CCV solution is required (closing CCV). The closing CCV used to bracket the end of a 12-hour analytical sequence may be used as the opening CCV for a new 12-hour analytical sequence, provided that all technical acceptance criteria are met for an opening CCV in Section 9.4.5.

Time	**Injection #**	**Material Injected**
0 hr	1st - 6th - GC/MS Instrument Performance Check followed by CS1 – CS5 calibration standards	DFTPP then CS1–CS5 First 6 steps of the initial calibration
	7th - blanks, samples, MS/MSD	Blanks, samples, MS/MSD
	8th - Subsequent Samples	
End 12 hr	Closing CCV (meeting Closing CCV criteria, but not opening CCV)	CS3 – Closing CCV
New 12 hr	1st GC/MS Instrument Performance Check	DFTPP Instrument Performance Check
	2nd - injection past 12 Opening CCV	CS3 - Opening CCV
		Blank, MS/MSD, subsequent samples Subsequent Samples Last Sample
End 12 hr	Closing CCV (meeting Closing CCV criteria but not Opening CCV)	CS3 – Closing CCV
New 12 hr	1st injection Instrument Performance Check	DFTPP Instrument Performance Check
	2nd Injection Opening CCV	CS3 – Opening CCV
		Blank, MS/MSD, subsequent samples Subsequent Samples Last Sample
End of 12 hr begins next 12 hr	Closing CCV (meeting Opening CCV criteria) Instrument Performance Check not required	CS3 – Closing CCV meeting Opening CCV
		Blank, MS/MSD, subsequent samples Subsequent Samples Last Sample

Time	Injection #	Material Injected
End of 12 hr	Closing CCV meeting criteria	CS3 – Closing CCV meeting Opening CCV

NOTE: For analysis using the SIM technique, prior to the analysis of samples and required blanks, and after initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a CCV standard.

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 All standards must be allowed to warm to ambient temperature before analysis.

9.4.3.2 Add internal standard spiking solution (Section 7.2.2.6) to an aliquot of CCV standard to result in 20 ng/µL concentration of each internal standard. The internal standards specified in Section 7.2.2.6 should permit most of the semivolatile target analytes to have RRTs of 0.80-1.20, using the assignments of internal standards to target analytes given in Table 9 – Semivolatile Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation.

9.4.3.3 Analyze the CCV standard according to Section 10.4 using the same injection volume as in the initial calibration.

9.4.4 Calculations for Continuing Calibration Verification

9.4.4.1 Calculate an RRF for each semivolatile target analyte and DMC according to Section 9.3.4.1.

9.4.4.2 Calculate the %D between the CCV RRF_c and the most recent initial calibration for each semivolatile target analyte and DMC using the following equation:

EQ. 5 Internal Standard Calibration Percent Difference

$$\%D = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

WHERE,

RRF_c = Relative Response Factor from current CCV standard

$\overline{RRF_i}$ = Mean Relative Response Factor from the most recent initial calibration

9.4.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.4.5.1 The concentration of the semivolatile target analytes and DMCs in the opening and closing CCV must be at or near the mid-point concentration of the calibration standards. The opening and closing CCV standard must be analyzed at the frequency described in Section 9.4.2, on a GC/MS system meeting the DFTPP (Section 9.2.4.2) and the initial calibration (Section 9.3.5) technical acceptance criteria.

NOTE: For the optional analysis of PAHs and PCP using only SIM, the opening and closing CCV must be analyzed at or near the mid-point concentration level of the calibration range, 0.40 ng/µL (0.80 ng/µL for PCP), at the frequency described in Section 9.4.2, and on a GC/MS system meeting the initial calibration technical acceptance criteria.

9.4.5.2 For an opening or closing CCV, except as noted in Section 9.4.5.5, the RRF for each semivolatile target analyte and DMC must be greater than, or equal to, the compound's minimum RRF listed in Table 5 – Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds.

9.4.5.3 For a closing CCV, the %D for each semivolatile target analyte and DMC must be in the inclusive range of the compound's %D value in Table 5 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds, with the exception of the following eleven target analytes: 4-Chloroaniline, Pentachlorophenol, 2,4-Dinitrophenol, Benzo(a)pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[g,h,i]perylene, Di-n-octylphthalate, Dibenzo[a,h]anthracene, Hexachlorocyclopentadiene, and Indeno(1,2,3-cd)pyrene. The closing CCV RRF %D requirement is advisory for these eleven target analytes.

9.4.5.4 For the opening CCV of the optional analysis of PAHs, PCP, and DMC using SIM, the %D must be within the inclusive range of the compound's %D value listed in Table 5 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds. For a closing CCV, the %D must be within the inclusive range of the compound's %D value listed, with the exception of the following seven target analytes: Benzo(a)pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[g,h,i]perylene, Dibenzo[a,h]anthracene, Indeno(1,2,3-cd)pyrene, and PCP. The closing CCV RRF %D requirement for analysis by SIM is advisory for these seven target analytes.

9.4.5.5 For an opening CCV, up to four target analytes and/or DMCs (excluding those compounds with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Table 5 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds. Up to four target analytes and/or DMCs (excluding those with maximum %D requirements of ±40.0%) may fail to meet the requirements listed.

9.4.5.6 For the opening CCV of the optional analysis of PAHs and PCP using the full scan method or the SIM technique, up to two target analytes and/or DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Table 5 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds. Up to two target analytes and/or DMCs (excluding those with maximum %D requirements of ±40.0%) may fail to meet the criteria listed. For a closing CCV, all PAHs and PCP must meet the criteria listed in Table 5 - Technical Acceptance Criteria for Initial and Continuing Calibration Verification for Semivolatile Organic Compounds.

9.4.5.7 Excluding those ions in the solvent front, no quantitation ion may saturate the detector. Consult the manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.4.6 Corrective Action for Continuing Calibration Verification

9.4.6.1 If the opening CCV technical acceptance criteria in Section 9.4.5 are not met, recalibrate the GC/MS instrument according to Section 9.3. Any samples or required blanks analyzed when opening CCV technical acceptance (including MS/MSDs) criteria have not been met will require reanalysis at no additional cost to the EPA. Refer to sample dilution procedure in Section 10.4.3 for target analytes that exceed the calibration range of the method.

9.4.6.2 If the closing CCV technical acceptance criteria in Section 9.4.5 are not met, then all associated samples and blanks analyzed within that 12-hour period must be reanalyzed at no additional cost to the EPA. The laboratory must carefully document the situations in the SDG Narrative.

It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the CCV technical acceptance criteria.

9.4.6.3 If this re-analysis is unsuccessful and the laboratory has evidence or suspects, because of preliminary results, sample color, or physical properties, that a sample or samples (including requested SIM analysis) may contain high concentrations of either target or non-target compounds that may be impacting the stability of the analytical system (i.e., causing closing CCV failures), then the Contractor shall proceed with the sample dilution/reanalysis procedure in Section 10.4.4.

10.0 PROCEDURE

The Contractor must have the capability to perform all the sample cleanup procedures presented in this Exhibit. The Contractor may use any of the procedures or combinations of procedures to clean up the samples prior to analysis, unless the Contractor is specifically directed by the EPA Region to use a particular cleanup procedure or combination of cleanup procedures.

The Contractor must demonstrate that each cleanup procedure is capable of producing data that meets the technical acceptance criteria for the method, including MDLs (Section 12.4) and any precision and recovery limits.

NOTE: If SIM analysis of PAHs and PCP is requested for a sample, a full scan analysis at the regular concentration levels must be performed on that sample prior to the SIM analysis. For all SIM target analytes detected at or above CRQLs during the full scan analysis, a SIM analysis is not to be performed for those target analytes. Any SIM analyses not performed for this reason must be noted in the SDG Narrative.

10.1 Sample Preparation

10.1.1 Water and Leachate Samples

Continuous liquid-liquid extraction is used to extract the samples. Separatory funnel extraction or other manual extraction techniques cannot be used. Allow the sample to warm to ambient temperature before extraction.

10.1.1.1 Continuous Liquid-Liquid Extraction without Hydrophobic Membrane

10.1.1.1.1 Follow the manufacturer’s instructions for set-up.

10.1.1.1.2 Add 300-500 mL of methylene chloride to the bottom of the extractor and fill it to a depth of at least 1 inch above the bottom sidearm.

10.1.1.1.3 If the samples have been received in 1 L bottles, the Contractor shall mark the meniscus and transfer the entire sample into the continuous liquid-liquid extraction apparatus. If the sample was not received in a 1 L bottle, measure out a 1 L sample aliquot in a separate, clean graduated cylinder and transfer the aliquot to the continuous extractor.

10.1.1.1.4 Using a syringe or volumetric pipette, add 500 µL of the DMC spiking solution to result in the addition of 40 µg of each DMC and (if SIM is requested) 0.4 µg of the SIM DMCs (fluoranthene-d_{10} and 2-methylnapthalene-d_{10})(Section 7.2.2.4) into the sample and mix well. Perform spiking prior to pH adjustment or any other processing steps.

10.1.1.1.5 Measure the pH of the sample with narrow range pH paper or a pH meter and record the pH. Adjust the pH to 2.0 with 1:1 sulfuric acid if required. Samples requiring pH adjustment must be noted in the SDG Narrative.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.1.1.6 Rinse the one-liter sample bottle and/or graduated cylinder with a small amount of methylene chloride and transfer the rinsate to the continuous extractor. Measure and record the volume of sample contained in the 1 L sample bottle with water, using a graduated cylinder.

10.1.1.1.7 Add sufficient methylene chloride to the continuous extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5-15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mL/minute is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool and then detach the distillation flask. Proceed to Section 10.2.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.1.2 Continuous Liquid-Liquid Extraction with Hydrophobic Membrane

10.1.1.2.1 Follow the procedure in Sections 10.1.1.1 - 10.1.1.5, but reduce the amount of methylene chloride used to 50 mL and extract for a minimum of 6 hours.

10.1.1.2.2 Add sufficient methylene chloride to the continuous liquid-liquid extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 6 hours.

10.1.1.2.3 Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion that will consume the solvent volume, preventing the efficient extraction of the sample. When this occurs, add additional solvent to ensure efficient extraction of the sample and extend the extraction time by a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

10.1.1.2.4 Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor. Using the hydrophobic membrane, it may not be necessary to dry the extract with sodium sulfate.

If low DMC recoveries occur, ensure that: 1) the apparatus was properly assembled to prevent leaks, 2) the drip rate/solvent cycling was optimized, and 3) there was proper cooling for condensation of solvent. Document the problem and the corrective action.

10.1.1.2.5 Alternate continuous liquid-liquid extractor types that meet the requirements of the analytical method may also be used. If using alternate extractors or design types, follow the

manufacturer's instruction for set-up. Optimize the extraction procedure.

10.1.2 Soil/Sediment Samples

Mix samples thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase.

10.1.2.1 Mandatory Determination of Concentration Level

10.1.2.1.1 The Contractor must determine whether a soil/sediment sample should be analyzed by the low-level or medium-level soil/sediment method. It is the responsibility of the Contractor to analyze the sample at the correct level.

10.1.2.1.2 When there is doubt as to the best approach, the Contractor should begin by processing the sample as low level. However, any subsequent unnecessary reanalysis at the medium level shall not be billable to the EPA.

10.1.2.1.3 Use of an EPA screening procedure or an in-house laboratory screening procedure is strongly encouraged. The procedure must be documented and available for review during on-site laboratory evaluation.

10.1.2.2 Low-Level Extraction of Soil/Sediment Samples

10.1.2.2.1 Three procedures are provided for the extraction of semivolatile analytes from low-level soil/sediment samples:

- ultrasonic extraction;
- Soxhlet extraction (automated or manual); and
- pressurized fluid extraction (PFE).

NOTE: All low-level soil/sediment samples in a Case must be extracted by the same procedure.

10.1.2.2.2 For soil/sediment sample extractions, perform the following steps rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample to the nearest 0.1 g, into a 400 mL beaker. If the system cannot accommodate 30 g of a sample, a smaller sample size may be used. The specified CRQLs must be met. Adjust the amount of solvents and standards added as necessary. Document the smaller sample size in the SDG Narrative along with all steps taken to ensure sample homogeneity.

10.1.2.2.3 Add 60 g of anhydrous powdered or granulated sodium sulfate, or 30 g of Hydromatrix™, and mix well to produce a sandy texture. Add additional drying agent as needed.

NOTE: For samples extracted by the PFE procedure (Section 10.1.2.2.7), the use of sodium sulfate is not recommended. As applicable, follow the manufacturer's instructions for use of all extraction equipment.

10.1.2.2.4 Add 500 µL of the DMC spiking solution to result in the addition of 40 µg of each DMC and if SIM is requested, 0.40 µg of the SIM DMCs (fluoranthene-d_{10} and 2-methylnapthalene-d_{10})(Section 7.2.2.4.2) to the sample. Proceed to Section 10.1.2.2.5 for ultrasonic extraction, Section 10.1.2.2.6 for automated Soxhlet extraction, or Section 10.2.2.7 for pressurized fluid extraction.

10.1.2.2.5 Ultrasonic Extraction

10.1.2.2.5.1 Add 100 mL of 1:1 (v/v) acetone/methylene chloride.

10.1.2.2.5.2 Place the bottom of the tip of the 3/4 inch tapered disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer. Do not use a microtip probe.

10.1.2.2.5.3 Sonicate for 3 minutes with output set at full power with pulse on (pulse energy as opposed to continuous) and percent duty cycle knob set at 50%.

NOTE: Refer to the manufacturer's instructions for appropriate output settings.

10.1.2.2.5.4 Transfer and filter extracts through Whatman No. 42 (or equivalent) filter paper using vacuum filtration or centrifuge and decant extraction solvent.

10.1.2.2.5.5 Repeat the extraction two more times with two additional 100 mL portions of 1:1 (v/v) acetone/methylene chloride. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula. Transfer the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 (v/v) acetone/methylene chloride.

10.1.2.2.5.6 If the sample is to be screened following the low-level preparation method prior to GPC, proceed to the appropriate screening procedure. Otherwise, proceed to Section 10.2.

10.1.2.2.6 [Automated] Soxhlet Extraction

The Contractor may use either automated or non-automated Soxhlet extraction. The following procedure is based on the use of a Soxtec HT-6 automated Soxhlet extraction system. When using a different system, refer to the instructions provided by the manufacturer for the appropriate procedure.

10.1.2.2.6.1 Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit. Press the "MAINS" button and observe that the switch lamp is now "ON". Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/minute to prevent solvent loss through the condensers.

10.1.2.2.6.2 Transfer the entire sample from the beaker (Sections 10.1.2.2.2 - 10.1.2.2.4) to the thimble.

10.1.2.2.6.3 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

10.1.2.2.6.4 Insert the extraction cups containing boiling chips, and load each with appropriate volume of extraction solvent 1:1 (v/v) acetone/methylene chloride. Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position.

NOTE: The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

10.1.2.2.6.5 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.

10.1.2.2.6.6 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set the timer for 60 minutes. Condenser valves are still open. Extract for the preset time. After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

10.1.2.2.6.7 When all but 2-5 mL of the solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the cups with methylene chloride and add the rinsates to the glass tubes.

10.1.2.2.6.8 If the sample is to be screened following the low-level preparation method prior to GPC, proceed to the appropriate screening procedure. Otherwise, proceed to Section 10.2.

10.1.2.2.7 Pressurized Fluid Extraction

10.1.2.2.7.1 Transfer the entire sample from the beaker (Sections 10.1.2.2.2 - 10.1.2.2.4) to an extraction cell of the appropriate size for the aliquot.

10.1.2.2.7.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.2.2.7.3 Place a pre-cleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5-1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

10.1.2.2.7.4 The following are recommended extraction conditions:

Oven temperature	100°C
Pressure	1500-2000 psi
Static time	5 min. (after 5 min. pre-heat equilibration)
Flush volume	60% of the cell volume
Nitrogen purge	60 sec. at 150 psi (purge time may be extended for larger cells)
Static cycles	1

10.1.2.2.7.5 Optimize the extraction conditions as needed, according to the manufacturer’s instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice. An

appropriate amount of 1:1 (v/v) acetone/methylene chloride should be used to achieve the conditions in Section 10.1.2.2.7.4.

10.1.2.2.7.6 Once established, the same pressure should be used for all samples in the same SDG.

10.1.2.2.7.7 Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete.

10.1.2.2.7.8 If the sample is to be screened following the low-level preparation method prior to GPC, proceed to the appropriate screening procedure. Otherwise, proceed to Section 10.2.

10.1.2.3 Medium-Level Extraction of Soil/Sediment Samples

The procedure described below is for the extraction of soil/sediment samples by the ultrasonic method (Section 10.1.2.2.5). The Contractor may also use the [automated or manual] Soxhlet extraction or PFE procedures described in Sections 10.1.2.2.6 and 10.1.2.2.7, respectively. The requirements of this analytical method must be met at all times (i.e., sample weight used for medium-level soil/sediment extraction and original CRQLs for medium-level soils). As applicable, follow the manufacturer's instructions for the use of all extraction equipment.

NOTE: All medium-level soil/sediment samples in a Case must be extracted by the same procedure.

10.1.2.3.1 Transfer approximately 1 g (record weight to the nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

10.1.2.3.2 Add 500 µL of DMC spiking solution to result in the addition of 40 µg of each DMC excluding the two SIM DMCs (fluoranthene-d_{10} and 2-methylnapthylene-d_{10}) (Section 7.2.2.4.2) to the sample mixture.

10.1.2.3.3 Add 2.0 g or sufficient quantity of anhydrous powdered or granulated sodium sulfate or Hydromatrix™ to the sample in the 20 mL vial and mix well to produce a sandy texture.

10.1.2.3.4 Immediately add sufficient methylene chloride to the sample so that the total volume is approximately 10 mL and disrupt the sample with the 1/8 inch tapered microtip ultrasonic probe for 2 minutes at output control setting 5, in continuous mode. Before extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. Decant and filter extract through Whatman No. 42 (or equivalent) filter paper using vacuum filtration or centrifuge and decant extraction solvent.

NOTE: Concentration of the extracts of soil/sediment samples prepared by the medium-level procedure described above may not be necessary. Proceed to Section 10.2.1.7 if no extract concentration is to be performed.

10.2 Extract Concentration

10.2.1 Concentration by Kuderna-Danish

10.2.1.1 Assemble a Kuderna-Danish (K-D) apparatus by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D, if equivalency is demonstrated for all the semivolatile target analytes listed in Exhibit C –Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contract Required Quantitation Limits.

10.2.1.2 For water samples, transfer the extract to a K-D concentrator by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate.

10.2.1.3 For soil/sediment samples, directly transfer the extract to the K-D concentrator, if the extract is known to be dry.

10.2.1.4 Rinse the original container collecting the extract (for both water and soil/sediment samples) and the column (for water samples) with at least two 20-30 mL portions of methylene chloride to complete the quantitative transfer.

10.2.1.5 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-15 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 or 2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

10.2.1.6 For water extracts that do not require GPC cleanup, proceed to final concentration of extract (Section 10.2.2). Oily water samples extracts require GPC cleanup.

10.2.1.7 For water extracts that require GPC cleanup, adjust the volume of the extract to 10.0 mL with methylene chloride and proceed with GPC cleanup (Section 10.3).

10.2.1.8 For soil/sediment extracts, adjust the volume of the extract to 10.0 mL with methylene chloride and proceed with GPC cleanup (Section 10.3).

10.2.1.9 For water or soil/sediment extracts that have undergone GPC cleanup, proceed to final concentration of extract (Section 10.2.2).

10.2.2 Final Concentration of Extract

Two different techniques are permitted to concentrate the extract to volume before instrument analysis. They are the Micro Snyder Column and the Nitrogen Evaporation Technique.

10.2.2.1 Micro Snyder Column Technique

10.2.2.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two-ball Micro Snyder Column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and lower joint into the concentrator tube with 0.20 mL (0.10 mL for low-level soil/sediment samples and water samples that have undergone GPC cleanup) of methylene chloride.

10.2.2.1.2 Adjust the final volume to 1.0 mL (0.50 mL for low-level soil/sediment samples and water samples that have undergone GPC cleanup) with methylene chloride. Transfer the extract to the PTFE-sealed screw-cap bottle, label the bottle, and store at ≤6°C. If no further cleanup is needed, proceed to Section 10.4 for GC/MS analysis.

10.2.2.2 Nitrogen Evaporation Technique

Place the concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to just below 1 mL (below 0.50 mL for low-level soil/sediment samples and water samples that have undergone GPC cleanup) using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). DO NOT ALLOW THE EXTRACT TO GO DRY.

10.2.2.2.1 Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or PTFE tubing. Plastic tubing must not be used between the carbon trap and the sample as it may introduce interferences. The internal wall of the concentrator tube must be rinsed down several times with methylene chloride during the operation.

10.2.3 Final Extract Volumes

The final extract volumes in Sections 10.2.3.1 and 10.2.3.2 are recommended volumes. If more sensitive GC/MS systems are employed, then the larger extract volumes (less concentrated extracts) may be used, provided that the CRQLs for all target analytes can be achieved, and that all DMCs and internal standards have an expected extract concentration that is at the mid-point of the calibration curve.

10.2.3.1 Water

For water samples that did not undergo GPC cleanup, the extract must be brought to a final volume of 1.0 mL with methylene chloride. Remove boiling chips before adjusting final volume. For water samples that underwent GPC cleanup, the extract must be brought to a final volume equal to V_{out} (volume of extract collected from GPC cleanup) with methylene chloride [concentrating the extract to 0.50 mL will result in no loss of sensitivity despite the volume of extract (5.0 mL) not recovered after GPC cleanup].

10.2.3.2 Soil/Sediment

Adjust the final volume for low-level and medium-level soil/sediment samples to equal V_{out} with methylene chloride. For example, if V_{out} equals 0.50 mL, then the final volume must be adjusted to 0.50 mL. Concentrating the extract to 0.50 mL will result in no loss of sensitivity despite the volume of extract not recovered after GPC cleanup. Remove boiling chips before adjusting final volume.

10.2.3.3 Transfer the extract to a PTFE-sealed screw-cap bottle, label the bottle, and store at ≤6°C, but not frozen.

10.3 Cleanup by Gel Permeation Chromatography

10.3.1 Introduction

10.3.1.1 GPC is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the size of the molecules to be separated.

10.3.1.2 GPC must be performed for all soil/sediment extracts. GPC may be performed for water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. In addition, GPC must be performed for all associated blanks and MS/MSDs. If the cleanup procedure is inadequate, contact SMO.

10.3.2 GPC Column Preparation

Prepare the GPC column using Bio Beads. Alternative column packings may be used if: 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration and GPC CCV, and 2) the column packings do not introduce contaminants/artifacts into the sample that interfere with the analysis of the semivolatile analytes. Follow the manufacturer’s instructions for preparation of the GPC column.

10.3.3 Calibration of GPC

10.3.3.1 Summary of GPC Calibration

The GPC calibration procedure is based on monitoring the elution of standards with a UV detector connected to the GPC column.

10.3.3.2 Frequency of GPC Calibration

Each GPC system must be calibrated prior to processing samples under the contract, when the GPC CCV solution fails to meet criteria (Section 10.3.3.4), when the column is changed, when channeling occurs, and once every 7 days when in use. Also, the RT shift must be less than 5% when compared to RTs in the last calibration UV traces.

10.3.3.3 Procedure for GPC Calibration

Follow the manufacturer’s instructions for operating the GPC system. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte RTs and must be monitored.

10.3.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.2.3) onto the GPC. Establish appropriate "COLLECT" and "DUMP" time periods to ensure collection of all target analytes. Initiate column eluate collection just before

elution of bis(2-ethylhexyl)phthalate and after the elution of corn oil. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "WASH" time of 10 minutes after the elution of sulfur. Each laboratory is required to establish its specific time sequences.

10.3.3.3.2 Reinject the calibration solution after appropriate "COLLECT" and "DUMP" cycles have been set, and the solvent flow and column pressure have been established.

10.3.3.3.3 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

10.3.3.3.4 Analyze a GPC blank of methylene chloride after each GPC calibration or each GPC CCV. Concentrate the methylene chloride that passes through the system during the "COLLECT" cycle using a K-D evaporator. Add internal standards at the appropriate concentration and analyze the concentrate by GC/MS.

10.3.3.4 Technical Acceptance Criteria for GPC Calibration

10.3.3.4.1 The GPC system must be calibrated at the frequency described in Section 10.3.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution;
- Corn oil and the phthalate peaks should exhibit greater than 85% resolution;
- Phthalate and methoxychlor peaks should exhibit greater than 85% resolution;
- Methoxychlor and perylene peaks should exhibit greater than 85% resolution; and
- Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.

10.3.3.4.2 The solvent flow rate and column pressure must be within the manufacturer’s specified ranges.

10.3.3.4.3 The RTs for bis(2-ethylhexyl)phthalate and perylene must not vary more than 5% between calibrations. Excessive RT shifts are caused by the following:

- Poor laboratory temperature control or system leaks;
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight; and/or
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.3.3.4.4 The analyte concentrations in the GPC blank must be less than the CRQL for all target analytes in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contract Required Quantitation Limits, except bis(2-ethylhexyl)phthalate, which must be less than 5 times the CRQL.

10.3.3.4.5 A copy of the two most recent UV traces of the calibration solution must be submitted with the data for the associated samples.

10.3.3.5 Corrective Action for GPC Calibration

10.3.3.5.1 If the requirements in Section 10.3.3.4 cannot be met, the column may be cleaned by processing several 5 mL volumes of butylchloride through the system. Butylchloride removes the discoloration and particles that may have precipitated out of the methylene chloride extracts. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore the performance of the column, the column must be repacked with new packing and recalibrated. It may be necessary to obtain a new lot of Bio Beads if the column fails all criteria.

10.3.3.5.2 If the flow rate and/or column pressure do not fall within the manufacturer's specified ranges, a new column should be prepared.

10.3.3.5.3 A UV trace that does not meet the criteria in Section 10.3.3.4.1 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

10.3.3.5.4 If the GPC blank exceeds the requirements in Section 10.3.3.4.4, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.3.4 GPC Calibration Verification

10.3.4.1 Summary of GPC Calibration Verification

The GPC calibration must be routinely verified with the calibration verification check mixture according to Exhibit D – Pesticides Analysis (Section 10.3.1.4).

10.3.4.2 Frequency of GPC Calibration Verification

10.3.4.2.1 The calibration verification must be performed at least once every 7 days (immediately following the GPC Calibration) whenever samples (including MS/MSDs and blanks) are cleaned up using the GPC.

10.3.4.2.2 Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore, system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration must be checked not less than once every 7 days.

10.3.4.3 Procedure for GPC Calibration Verification

The GPC calibration verification solution contains six pesticide target analytes that are not included in the calibration standards (Section 7.2.2.1); therefore, the Contractor must follow the GPC calibration verification procedure according to Exhibit D – Pesticides Analysis instructions (Section 10.3.1.4) prior to the analysis of semivolatile target analytes in samples, blanks, and MS/MSDs. The Contractor shall establish pesticide initial calibration prior to GPC calibration verification even if the samples are not scheduled for pesticide analysis.

10.3.4.3.1 The pesticide GPC calibration verification solution contains gamma-BHC (Lindane), Heptachlor, Aldrin, 4,4'-DDT, Endrin, and Dieldrin.

10.3.4.3.2 Load the 5 mL sample loop by using a 10 mL syringe containing 8 mL of the pesticide GPC calibration verification solution. Fractions are collected in an autosequence by using the GPC program established by the UV detector calibration procedure (Section 10.3.3.3).

10.3.4.3.3 The collected GPC calibration verification fraction is transferred to a K-D apparatus, and the collection vessel is rinsed with two additional 10 mL portions of methylene chloride to complete the transfer. The volume of methylene chloride is reduced according to Section 10.2.1. After cooling, the solvent is exchanged to hexane according to the instructions in Exhibit D - Pesticide Analysis (Section 10.2.2). The final volume is adjusted to 10 mL, and the sample is analyzed by GC/Electron Capture Detector (ECD) according to the procedure in Exhibit D - Pesticides Analysis (Section 10.4). The analysis must be performed on only one of the GC/ECD columns used for pesticides analysis.

10.3.4.3.4 The recovery of each analyte must be determined for evaluation and reporting purposes. Calculate the Percent Recovery (%R) of each analyte using Equation 13 in Exhibit D - Pesticides Analysis (Section 10.3.2).

10.3.4.4 Technical Acceptance Criteria for GPC Calibration Verification

The technical criteria specified in Exhibit D – Pesticides Analysis must be met prior to the GPC cleanup on samples, blanks, and MS/MSD.

10.3.4.5 Corrective Action for GPC Calibration Verification

The Contractor may continue to use the GPC column if the technical acceptance criteria for the GPC calibration verification are met. If the recoveries are outside of the acceptance criteria, the columns must be replaced and the GPC recalibrated according to the instructions in Section 10.3.3 and Section 10.3.4 before proceeding with any GPC cleanup on samples (including LCSs and MS/MSDs) and required method blanks.

10.3.5 Daily Ultraviolet Calibration Check (Optional)

The calibration of the GPC may be monitored daily by use of the UV-GPC calibration solution (Section 7.2.2.3) and the UV detector calibration procedure (Section 10.3.3). The UV detector should be used to monitor the elution times for the phthalate, methoxychlor, and perylene, in that order. The precalibrated GPC program should "DUMP" greater than 85% of the phthalate and should "COLLECT" greater than 95% of the methoxychlor and perylene. Significant changes in elution times of the analytes (e.g., greater than 30 seconds) indicate that the column is out of calibration and must be recalibrated or replaced.

10.3.6 Sample Extract Cleanup by GPC

10.3.6.1 Summary of GPC Cleanup

10.3.6.1.1 It is very important to have constant laboratory temperatures during an entire GPC analysis, which could be 24 hours or more. If temperatures are not constant, RTs will shift, and the "DUMP" and "COLLECT" times determined by the calibration standard will no longer be appropriate. The ideal laboratory

temperature to prevent outgassing of the methylene chloride is 22°C.

10.3.6.1.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 (v/v) glycerol/water solution must be diluted and loaded into several loops. Similarly, extracts containing more than the manufacturer recommended non-volatile residue must be diluted and loaded into several loops. The non-volatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or other suitable container.

10.3.6.1.3 Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is being injected on the column. Viscous extracts or extracts containing a large amount of non-volatile residue will cause problems with injecting the proper amount of sample extract onto the column using automated injection systems. After the sample extract has been processed, the remaining sample extract in the injection vial must be checked to ensure the proper amount was injected on the column. If the proper amount of extract was not injected, the sample must be reprepared at no additional cost to the EPA, and the sample extract must either be diluted and loaded into several loops, or the sample extract must be injected manually.

10.3.6.2 Frequency of Sample Extract Cleanup by GPC

GPC cleanup must be performed once for each soil/sediment and all associated QC samples (blanks, LCSs, and MS/MSDs) must be subjected to this procedure. GPC cleanup on the method blank must be performed after all associated samples have been cleaned up (GPC sequence: calibration, sample 1, sample 2, etc., method blank, calibration verification).

10.3.6.3 Procedure for Sample Extract Cleanup by GPC

10.3.6.3.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 mL culture tube with a PTFE-lined screw-cap).

10.3.6.3.2 Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

NOTE 1: Some GPC instrument manufacturers recommend using a smaller micron size filter. Follow the manufacturer's recommended operating instructions.

NOTE 2: INTRODUCTION OF PARTICULATES OR GLASS WOOL INTO THE GPC SWITCHING VALVES MAY REQUIRE FACTORY REPAIR OF THE APPARATUS.

10.3.6.3.3 Follow the manufacturer's instructions for operation of the GPC system being utilized. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL injection loop is used, concentrate the sample extract to 4 mL instead of 10 mL and inject 4 mL instead of 10 mL.

10.3.6.3.4 If the sample is difficult to load, part of the system may be blocked. Take appropriate corrective action, following the manufacturer's recommendations. The problem must be resolved prior to loading sample extracts.

10.3.6.3.5 After loading each sample loop, wash the loading port with methylene chloride to minimize cross-contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

10.3.6.3.6 After loading the samples, process each sample using the "COLLECT" and "DUMP" cycle times established in Section 10.3.3.3.1.

10.3.6.3.7 Collect each sample in a 250 mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a K-D evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure;
- Increase in column operating pressure due to the accumulation of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used; or
- Leaks in the system or significant variances in room temperature.

NOTE: Any samples that were loaded into multiple loops must be recombined before proceeding with concentration.

10.3.6.4 Final Concentration

Concentrate the extract as per Section 10.2.2. After removing boiling chips, final volumes should be brought to the volumes stated in Section 10.2.3.

10.4 Gas Chromatography/Mass Spectrometry Analysis

10.4.1 Introduction

Sample extracts shall be analyzed only after the GC/MS system has met the instrument performance check, initial calibration, and CCV requirements. The same instrument conditions must be employed for the analysis of samples as were used for calibration. The same injection volume must be used for all standards, samples, and blanks.

10.4.2 Procedure for Sample Analysis by GC/MS

10.4.2.1 The internal standard spiking solution is added to an aliquot of each sample extract. Add sufficient amount of the internal standard spiking solution (Section 7.2.2.6) to each accurately measured aliquot of water, low-level, or medium-level soil/sediment sample extract to result in 20 ng/µL concentration of each internal standard.

NOTE: The internal standard spiking solution must be added to aliquots of sample extracts, not the entire extract in order to make provision for sample dilutions and optional analysis of PAHs and PCP by the SIM technique, if requested.

10.4.2.2 If SIM is to be performed, the Contractor shall add sufficient amount of the internal standard spiking solution to each accurately measured aliquot of water and low-level soil/sediment sample extract to result in a 0.40 ng/µL concentration of each internal standard.

10.4.2.3 If sample extracts are to be diluted, add internal standards after dilution. Internal standards must be added to maintain the required 20 ng/µL (0.40 ng/µL for SIM) of each internal standard in the extract volume.

10.4.2.4 Inject 1.0 or 2.0 µL of the sample extract into the GC/MS.

10.4.3 Sample Dilutions

10.4.3.1 All samples must be analyzed undiluted.

10.4.3.2 If the concentration of any target analyte in any sample exceeds the concentration of the same target analyte in the high standard of the initial calibration, that sample extract must be diluted. Add the internal standard spiking solution to the diluted extract for a concentration of 20 ng/µL (0.40 ng/µL for optional analysis of PAHs and PCP by SIM) of each internal standard, and analyze the diluted extract. Guidance in performing dilution and exceptions to this requirement are given below.

10.4.3.3 Use the results of the original analysis to determine the approximate DF required for the analyte with the highest concentration to be within the initial calibration range.

10.4.3.4 The DF chosen must keep the concentration of the largest peak for a target analyte in the upper half of the calibration range of the instrument.

10.4.3.5 The maximum DF permitted for low-level soils is 30.0. If a low-level soil sample requires a DF greater than 30.0 to bring target analyte concentrations within the calibration range, then the medium-level method shall be utilized.

10.4.4 Procedure for Continually Failing Closing CCV

10.4.4.1 If the Contractor has followed the procedures in Sections 9.4.6 and 10.4.3, but the closing CCV is still not compliant with the criteria in Table 5, then the Contractor shall follow the procedures below.

10.4.4.1.1 Examine the sample data from the non-compliant sample sequence, including screening data if available, and segregate the samples that showed high levels of potential interference from those that appear normal.

10.4.4.1.2 The samples that appear not to contain significant interference (if any) shall be reanalyzed with appropriate dilutions in a new sequence or sequences that the closing CCV shall meet all technical acceptance criteria in Table 5.

10.4.4.1.3 Those samples in this segregated group that show high levels of interference but none of the detected target analytes would not require any further dilution per Section 10.4.3 above, shall be treated as follows: the steps in 10.4.4.1.3.1 –

10.4.4.1.3.3 shall be carried out only once for the affected samples.

10.4.4.1.3.1 Samples with a clearly defined baseline rise exceeding four times the peak height of the associated internal standards must be reanalyzed at a nominal 1:4 dilution (or further dilution), sufficient to reduce the baseline to within this factor of four criterion, including adjustment of the concentration of internal standard to that of a normal extract.

10.4.4.1.3.2 Samples that do not fit this description but still are suspected of containing significant interference shall be diluted 1:4, as described above.

10.4.4.1.3.3 These extracts shall be analyzed in a separate analytical sequence. The use of interstitial instrument blanks is required. If the closing CCV criteria are not met for this sequence, the Contractor shall document the procedure followed and any non-compliance in the SDG Narrative. All analyses of these samples shall be reported.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Analytes

11.1.1.1 The analytes listed in the TAL in Exhibit C –Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs), shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of the standard of the suspected analyte. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component within the GC RRT unit window established from the 12-hour calibration standard; and
- Correspondence of the sample component and calibration analyte mass spectra.

11.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within ±0.06 RRT units of the RRT of the corresponding continuing calibration standard component. For reference, the standard must be analyzed on the same 12-hour period as the sample. If samples are analyzed during the same 12-hour period as the initial calibration standards, use the RT values from the 20 ng/µL standard (0.40 ng/µL for the calibration standard by SIM). Otherwise, use the corresponding opening CCV standard. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned by using EICPs for ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained from the Contractor’s GC/MS (as opposed to library obtained spectra) are required. Once obtained, these standard spectra may be used for identification purposes, only if the Contractor’s GC/MS meets the daily instrument performance requirements for DFTPP. These standard spectra may be obtained from the standard analysis that was also used to obtain the RRTs.

11.1.1.4 The guidelines for qualitative verification by comparison of mass spectra are as follows:

11.1.1.4.1 All ions present in the standard mass spectrum at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.1.1.4.2 The relative intensities of ions specified in the paragraph above must agree within ±20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30-70%).

11.1.1.4.3 Ions greater than 10% in the sample spectrum, but not present in the standard spectrum, must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra.

11.1.1.4.4 If an analyte cannot be verified by all of the spectral identification criteria in Section 11.1.1.4, but in the technical judgment of the mass spectra interpretation specialist the identification is correct, then the Contractor shall report the identification and proceed with quantitation and document in the SDG Narrative.

11.1.2 Identification of Non-Target Compounds

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST (2011 release or later), Wiley (2011 release or later), or equivalent mass spectral library shall be used as the reference library.

11.1.2.2 All organic compounds that have not been positively identified as semivolatile target analytes using the procedures detailed in Section 11.1.1, or that are not DMCs, internal standards, or volatile target analytes listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, unless the volatile analysis was not requested, shall be tentatively identified via a forward search of the NIST, Wiley, or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.1.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form 1B-OR. Peaks that are tentatively identified as straight-chain, branched, or cyclic alkanes, and are alone or part of an alkane series, shall be reported as "total alkanes". An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds. The concentrations of each of the alkanes are to be summed and reported as a single result for the "total alkanes". The alkanes are not to be counted as part of the 30 compounds individually reported as TICs on Form 1B-OR. Carbon dioxide and compounds with responses less than 10% of the internal standard in which they are to be quantified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.1.2.4 Peaks that are suspected to be aldol-condensation reaction products (i.e., 4-methyl-4-hydroxy-2-pentanone and 4-methyl-3-pentene-2-one) shall be searched, reported, and counted as part of the 30 most intense non-target semivolatile compounds, and qualified with an "A" flag on Form 1B-OR.

11.1.2.5 Rules for Making Tentative Identification

11.1.2.5.1 For compounds to be reported, as per the instructions in Section 11.1.2, identification (as generated by the library search program) of those receiving a library search match of 85% or higher should be considered a "probable match". The compound should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program.

11.1.2.5.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds), unless the mass spectra interpretation specialist feels there is just evidence not to report the compound with the highest match. Do not report DMCs, internal standards, or analytes that are on the volatile or semivolatile TAL, unless the volatile analysis was not requested.

11.1.2.5.3 If the library search produces a series of obvious isomer compounds with library search matches greater than 85% (e.g., tetramethylnaphthalenes), the compound with the highest library search percent match should be reported (or first compound if library search matches are the same).

11.1.2.5.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the SDG Narrative the justification for not reporting a compound as listed by the search program. This narrative shall detail explicitly why a library search generated identification for a compound was rejected. If a TIC has obvious isomer analogs, the laboratory shall include in the SDG Narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

11.1.2.5.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialists are encouraged to make a valid tentative identification of the compound. If no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral interpretation specialist should give additional classification of the unknown, if possible (e.g., "unknown aromatic compound", "unknown chlorinated compound", etc.).

11.1.2.5.6 The Chemical Abstracts Service (CAS) registry number is the unique identifier for each chemical compound. As the rules of chemical nomenclature have changed over time, each chemical is liable to have several names or synonyms: i.e., trade or brand name(s); generic or common name(s); trivial or systematic; or International Union of Pure and Applied Chemistry (IUPAC) name(s). Whether synonyms or other names are created for this compound, the CAS registry number will generally remain

unchanged. The CAS registry number is simply an identifier which has no structural significance. Regardless of retention times (RTs), if the library search produces two or more compounds at or above 85% with the same Chemical Abstract Number, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds) unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match.

11.1.2.5.7 If the library search produces only one and the same compound (i.e., the same CAS registry number) with percent match at or above 85% at two different RTs, the compound having the highest percent match should be reported as TIC and the other one could be reported as unknown. If both TICs have the same percent match for the same compound, one of the TICs could be reported as unknown. Such justifications should be included in the SDG Narrative.

11.1.2.6 Qualitative identification of non-target compounds is not required when performing SIM analyses.

11.2 Quantitative Analysis

11.2.1 Data Processing Procedure

11.2.1.1 Target analytes identified shall be quantitated by the internal standard method. The internal standard used shall be the one assigned to that analyte for quantitation (Table 9 – Semivolatile Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation and Table 10 – Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation of Polynuclear Aromatic Hydrocarbon and Pentachlorophenol). The EICP area of primary characteristic ions of analytes listed in Table 8 – Characteristic Ions for Semivolatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards are used for quantitation.

11.2.1.2 It is expected that situations will arise where the automated quantitation procedures in the GC/MS software provide inappropriate quantitations. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the Contractor must perform a manual quantitation. Manual quantitations are performed by integrating the area of the quantitation ion of the compound. This integration shall only include the area attributable to the specific target analyte, DMC, or internal standard compound. The area integrated shall not include baseline background noise. The area integrated shall also not extend past the point where the sides of the peak intersect with the baseline noise. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system. Any instance of manual integration must be documented in the SDG Narrative.

11.2.1.3 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS Operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. The GC/MS Operator shall also mark each integrated area with the letter "M" on the quantitation report. In addition, a hardcopy printout of the

11.2.1.4 EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all: target analytes listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatile Target Analyte List and Contract Required Quantitation Limits; internal standards; and DMCs.

11.2.1.5 Secondary ion quantitation is only allowed when there are sample interferences with the primary quantitation ion, not when saturation occurs. If secondary ion quantitation is used, calculate an RRF using the area response (EICP) from the most intense secondary ion which is free of sample interferences, and document the reasons in the SDG Narrative. A secondary ion cannot be used unless an RRF is calculated using the secondary ion.

11.2.1.6 The factor (CV_{out}/CV_{in}) *E) used in Equations 6 to 9, will only apply when GPC is performed for semivolatile analysis. It is applied when GPC is performed (always for soil) to account for the factor of loss in the GPC, i.e., 50% efficiency, expressed as 0.50.

11.2.1.7 Target Analyte Calculations

Identified target analytes shall be quantitated by the internal standard method using Equation 6 or 7. The internal standard used shall be that which is assigned in Table 9 – Semivolatile Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation. The Mean RRF ($\overline{RRF}$) from the initial calibration standard is used to calculate the concentration in the sample.

11.2.1.8 Water

EQ. 6 Water and TCLP/SPLP Leachate Sample Concentration

$$\text{Concentration } (\mu g/L) = \left(\frac{A_x \times I_{is}}{A_{is} \times \overline{RRF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{V_o}\right)\left(\frac{CV_{out}}{CV_{in} \times E}\right)_1\left(\frac{CV_{out}}{CV_{in} \times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in} \times E}\right)_n$$

WHERE,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (Table 8 – Characteristic Ions for Semivolatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards)

A_{is} = Area of the characteristic ion (EICP) for the internal standard (Table 8 – Characteristic Ions for Semivolatile Target Analytes, Deuterated Monitoring Compounds, and Internal Standards). The target analytes are listed with their associated internal standards in Table 9 – Semivolatile Internal Standards with Associated Target and Deuterated Monitoring Compounds Assigned for Quantitation

I_{is} = Amount of internal standard added, in ng

$\overline{RRF}$ = Mean Relative Response Factor determined from the initial calibration standard

V_i = Volume of extract injected, in µL

V_O = Volume of the water sample extracted, in mL

V_t = Volume of the concentrated extract, in µL

CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in µL

CV_{in} = Volume of extract subjected to a cleanup process, in µL

E = The efficiency of the cleanup process expressed as a fraction of material that passes through or is not mechanically lost during the cleanup step (e.g., 50% efficiency must be expressed as 0.50)

DF = Dilution Factor. The DF for analysis of water samples for semivolatiles by this method is defined as follows:

$$DF = \frac{\text{µL most conc. extract used to make dilution + µL clean solvent}}{\text{µL most conc. extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

NOTE: Convert units to mg/L for TCLP leachates by dividing the final calculated concentration by 1000.

11.2.1.9 Soil/Sediment

EQ. 7 Soil/Sediment Concentration

$$\text{Concentration µ/kg} = \left(\frac{A_x \times I_{is}}{A_{is} \times \overline{RRF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{W_t \times S}\right)\left(\frac{CV_{out}}{CV_{in} \times E}\right)_1 \left(\frac{CV_{out}}{CV_{in} \times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in} \times E}\right)_n$$

WHERE,

A_x, A_{is}, I_{is}, $\overline{RRF}$, DF, V_i, V_t, CV_{out}, CV_{in}, E = As given for water, as EQ. 6

W_t = Weight of the soil sample extracted, in g

S = % Solids/100 (Exhibit D – General Organic Analysis, Section 10.1)

11.2.2 Non-Target Compounds

11.2.2.1 An estimated concentration for TICs shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.2.2.2 Equations 6 and 7 are also used for calculating TIC concentrations. Total area counts (or peak heights) from the total RICs are to be used for both the TICs to be measured (A_x) and the internal standard (A_{is}). An $\overline{RRF}$ of 1.0 is to be assumed.

11.2.3 Contract Required Quantitation Limit Calculations

11.2.3.1 Water

EQ. 8 Water and TCLP/SPLP Leachate Sample Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{V_x}{V_o}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in} \times E}\right)_1 \left(\frac{CV_{out}}{CV_{in} \times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in} \times E}\right)_n$$

WHERE,

V_o, V_t, DF, CV_{out}, CV_{in}, E = As given in EQ. 6

Contract CRQL = The CRQL value reported in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contact Required Quantitation Limits

V_x = Method required sample volume (1000 mL)

V_y = Method required concentrated extract volume (1000 µL)

NOTE: Convert units to mg/L for TCLP leachates by dividing the final calculated CRQL by 1000.

11.2.3.2 Soil/Sediment

EQ. 9 Soil/Sediment Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL}) \left(\frac{W_x}{W_t \times S}\right) \left(\frac{V_t}{V_y}\right) (DF) \left(\frac{CV_{out}}{CV_{in} \times E}\right)_1 \left(\frac{CV_{out}}{CV_{in} \times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in} \times E}\right)_n$$

WHERE,

W_t, V_t, DF, CV_{out}, CV_{in}, E = As given in EQ. 7

Contract CRQL = The CRQL value reported in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contact Required Quantitation Limits

W_x = Method required sample weight (30 g for low-level soil/sediment samples and 1.0 g for medium-level soil/sediment samples)

S = % Solids/100 (Exhibit D – Analytical Methods for General Organic Analysis, Section 10.1)

V_y = Method required concentrated extract volume (1000 µL)

11.2.4 Deuterated Monitoring Compound Recoveries

11.2.4.1 Calculate the concentration of each DMC using the same equation as used for the target analytes.

11.2.4.2 Calculate the recovery of each DMC in all samples and blanks using Equation 10. Report the recoveries on the appropriate forms.

EQ. 10 DMC Percent Recovery

$$\%\ R = \frac{Q_d \times DF}{Q_a} \times 100$$

WHERE,

Q_d = Quantity determined by analysis

Q_a = Quantity added to sample/blank

DF = Dilution Factor

11.3 Technical Acceptance Criteria for Sample Analysis

11.3.1 The samples must be analyzed on a GC/MS system meeting the DFTPP, initial calibration, CCV, and blank technical acceptance criteria. The sample must undergo cleanup procedures, when required, on a GPC meeting the technical acceptance criteria for GPC calibration.

11.3.2 The sample must be extracted and analyzed within the contract holding times.

11.3.3 The sample must have an associated method blank meeting the blank technical acceptance criteria.

11.3.4 The %R of each of the DMCs in a sample must be within the recovery limits listed in Table 11 – Deuterated Monitoring Compounds Recovery Limits. Up to four DMCs per sample may fail to meet the recovery limits listed, but all %Rs must be greater than zero. The %R for 4-Chloroaniline-d_4 is advisory only. If the optional analysis of PAHs and PCP only by the full scan method is to be performed, no more than two DMCs per sample may fail to meet the recovery limits listed in Table 11 – Deuterated Monitoring Compounds Recovery Limits, but all %Rs must be greater than zero. If the optional analysis of PAHs and PCP using the SIM technique is to be performed, both SIM DMCs must meet the recovery limits in Table 11 – Deuterated Monitoring Compounds Recovery Limits.

NOTE: The DMC recovery requirements do not apply to samples that have been diluted.

11.3.5 The EICP area for each of the internal standards in the sample must be within the range of 50.0%-200% of its response in the most recent opening CCV standard analysis.

11.3.6 The RT shift for each of the internal standards in the sample must be within ±30 seconds of its RT in the most recent opening CCV standard analysis.

11.3.7 Excluding those ions in the solvent front, no ion may saturate the detector. No target analyte concentration may exceed the upper limit of the initial calibration range unless a more dilute aliquot of the sample extract is also analyzed according to the procedures in Section 10.4.3.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or any samples not meeting the sample technical acceptance criteria will require re-extraction and/or reanalysis at no additional cost to the EPA.

11.4.2 Corrective actions for failure to meet technical acceptance criteria for instrument performance checks, initial calibration, and CCV must be completed before the analysis of samples.

11.4.3 If the technical acceptance criteria for any of the internal standards and DMCs are not met, check calculations, internal standard and DMC spiking solutions, and instrument performance. It may be necessary to bake out the system, to recalibrate the instrument, or take other corrective action procedures to meet the technical acceptance criteria.

11.4.4 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

- Re-extract and reanalyze the sample. EXCEPTION: If DMC recoveries or internal standard compound responses in a sample used for an MS/MSD were outside the acceptance criteria, then it should be re-extracted/reanalyzed only if DMC recoveries and internal standard compound responses met the acceptance criteria in both the MS/MSD analyses.

- If the DMC recoveries and the internal standard responses meet the acceptance criteria in the re-extracted/reanalyzed sample, then the problem was within the Contractor’s control. Therefore, submit only data from the re-extraction/reanalysis.

- If the DMC recoveries and/or internal standard responses fail to meet the acceptance windows in the re-extracted/reanalyzed sample, then submit data from both analyses. Distinguish between the initial analysis and the re-extraction/reanalysis on all deliverables, using the suffixes in Exhibit B, Table 5 - Codes for Labeling Data.

11.4.5 Corrective Action for Internal Standard Compound Retention Times Outside Acceptance Criteria

If the internal standard compound RTs are not within their acceptance criteria, check the instrument for malfunctions. If the instrument malfunctioned, correct the instrument problem and reanalyze the sample extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

11.4.5.1 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the corrective action steps:

- Reanalyze the sample extract. EXCEPTION: If the internal standard compound RTs in a sample used for an MS or MSD were outside the acceptance criteria, then it should be reanalyzed only if the internal standard compound RTs were within the acceptance criteria in both of the MS/MSD analyses.
- If the internal standard compound RTs are within the acceptance criteria in the reanalyzed sample extract, then the problem was within the Contractor's control. Therefore, submit only data from the reanalysis when the internal standard compound RTs within the acceptance limits.
- If the internal standard compound RTs are outside the acceptance criteria in the reanalyzed sample extract, then submit data from both analyses. Distinguish between the initial analysis and the reanalysis on all deliverables, using the suffixes in Exhibit B – Reporting and Deliverables Requirements, Table 5 – Codes for Labeling Data.

12.0 QUALITY CONTROL

12.1 Blank Analyses

12.1.1 Summary

There is one type of blank required by this method: the method blank.

12.1.2 Method Blank

12.1.2.1 Summary of Method Blank

A method blank is a volume of a clean reference matrix (reagent water for water samples, or purified sodium sulfate or Hydromatrix™ for soil/sediment samples), carried through the entire analytical procedure. The volume or weight or the reference matrix must be approximately equal to the volume of weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples. The leachate extraction blank shall be extracted and reported as SLEB## on Form 1A-OR and Form 1B-OR.

12.1.2.2 Frequency of Method Blank

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding MS/MSDs and Performance Evaluation (PE) samples]. In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples; and
- Be analyzed on each GC/MS system under the same conditions used to analyze associated;

12.1.2.3 Procedure for Method Blank

12.1.2.3.1 For water samples, measure 1.0 L volume of reagent water and spike with 40 µg of each DMC and, if SIM is requested, 0.40 µg of each SIM DMC (Section 7.2.2.4). For soil/sediment samples, measure 1 g (medium-level) or 30 g (low-level) of sodium sulfate or Hydromatrix™ and spike with 40 µg of each DMC and 0.40 µg (low-level) of each SIM DMC. Extract, concentrate, cleanup, and analyze the blank following the procedures for water and soil samples (Section 10.0).

12.1.2.3.2 Under no circumstances should method blanks be analyzed at a dilution.

12.1.2.4 Calculations for Method Blank

Perform data analysis and calculations according to Section 11.0.

12.1.2.5 Technical Acceptance Criteria for Method Blank

12.1.2.5.1 All blanks must be prepared and analyzed on a GC/MS system meeting the DFTPP, initial calibration, and CCV technical acceptance criteria and at the frequency described in Section 12.1.2.2.

12.1.2.5.2 The %R of each of the DMCs in the blank must be within the acceptance limits listed in Table 11 – Deuterated Monitoring Compounds Recovery Limits. These limits are not advisory except for 4-Chloroaniline-d_4.

12.1.2.5.3 The blank must meet the sample acceptance criteria listed in Sections 11.3.4 - 11.3.7.

12.1.2.5.4 A method blank for semivolatile analysis for low-level soil and water samples must contain less than five times the CRQL of the bis(2-ethylhexyl) phthalate listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs). For all other target analytes, the method blank must contain less than the CRQL of any single target analyte [Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs)]. For medium-level soils, the method blank must contain less than the CRQL of any single target analyte.

12.1.2.5.5 All method blanks must be analyzed undiluted.

12.1.2.6 Corrective Action for Method Blank

12.1.2.6.1 If a method blank does not meet the technical acceptance criteria, the Contractor shall consider the analytical system to be out of control.

12.1.2.6.2 If contamination is the problem, then the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. All samples associated with a method blank that does not meet the method blank technical acceptance criteria will require re-extraction and reanalysis at no additional cost to the EPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvent, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in the GC/MS be eliminated.

12.1.2.6.3 If DMC recoveries in the method blank do not meet the acceptance criteria listed in Section 12.1.2.5.2 and Table 11 - Deuterated Monitoring Compounds Recovery Limits, first reanalyze the method blank. If the DMC recoveries do not meet the acceptance criteria after reanalysis, the method blank and all samples associated with that method blank must be re-extracted and reanalyzed at no additional cost to the EPA.

12.1.2.6.4 If the method blank does not meet internal standard response requirements listed in Section 11.3.5, follow the corrective action procedure outlined in Section 11.4.5.1. The Contractor shall resolve and document the resolution of the problem before proceeding with sample analysis.

12.1.2.6.5 If the method blank does not meet the RT requirements for internal standards (Section 11.3.6), check the instrument for malfunction and recalibrate. Reanalyze the method blank.

12.2 Matrix Spike and Matrix Spike Duplicate

12.2.1 Summary of Matrix Spike and Matrix Spike Duplicate

To evaluate the effects of the sample matrix on the methods used for semivolatile analyses, the EPA has prescribed a mixture of semivolatile target analytes to be spiked into two aliquots of a sample and analyzed in accordance with the appropriate method. An MS/MSD shall be extracted and analyzed only if requested by the EPA Region (through SMO) or specified on the Traffic Report/Chain of Custody Record (TR/COC).

12.2.2 Frequency of Matrix Spike and Matrix Spike Duplicate Analyses

12.2.2.1 If requested, an MS/MSD must be performed for each group of 20 field samples of a similar matrix in an SDG. An MS/MSD should be analyzed for each sample matrix (water/soil) and each level (low/med). For the optional analysis by the SIM method, MS/MSD will not be required unless specifically requested by the EPA Region.

12.2.2.2 The Contractor shall not perform MS/MSD analysis on any of the field QC or PE samples.

12.2.2.3 If the EPA Region designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample remaining to perform an MS/MSD, then the Contractor shall choose another sample on which to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the EPA sample selected for the MS/MSD analysis. SMO shall contact the EPA Region for confirmation immediately after notification. The

rationale for the choice of another sample other than the one designated by the EPA shall be documented in the SDG Narrative.

12.2.2.4 If there is insufficient sample remaining in any of the samples in an SDG to perform the requested MS/MSD, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the EPA Region for instructions. The EPA Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the EPA Region's decision. The Contractor shall document the decision in the SDG Narrative.

If it appears that the EPA Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, the Contractor shall contact SMO. SMO will contact the EPA Region to determine which samples should have an MS/MSD analysis performed on them. SMO will notify the Contractor of the EPA Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.

12.2.2.6 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the MS/MSD analysis when the EPA Region did not designate samples to be used for this purpose. If the PE sample is an ampulated standard, the ampulated PE sample is not considered to be another matrix type.

12.2.3 Procedure for Preparing Matrix Spike and Matrix Spike Duplicate

12.2.3.1 For water samples, prepare two additional 1 L aliquots of the sample chosen for spiking in two continuous extractors. Add 500 µL MS/MSD spiking solution corresponding to 40 µg of each DMC (0.40 µg of each SIM DMC if SIM is requested) and 500 µL MS/MSD spiking solution corresponding to 40 µg each of the Matrix Spike compound (0.40 µg of each Matrix Spike compound for SIM analysis). These additions shall be made to the samples prior to transferring to the continuous liquid-liquid extraction apparatus. Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for water samples (Section 10.1.1).

NOTE: For analysis of PAHs and PCP only, add 500 µL of each DMC standard corresponding to 40 µg of each PAH and PCP (0.40 µg of each SIM DMC) and 500 µL MS/MSD standard to the corresponding to 40 µg each of acenaphthene, pyrene, and PCP Matrix Spike analytes (0.40 µg each of acenaphthene, pyrene, and PCP Matrix Spike compound for SIM analysis).

12.2.3.2 For low-level soil/sediment samples, prepare two additional 30 g aliquots (record weight to nearest 0.1 g) of the sample chosen for spiking in the two 400 mL beakers. Add 500 µL of the DMC spiking solution and 500 µL of the matrix spiking solution to each aliquot, to result in the addition of 40 µg of each DMC (0.40 µg of each SIM DMC) and 500 µL MS/MSD spiking solution corresponding to 40 µg of each Matrix Spike analyte (0.40 µg of each Matrix Spike analyte for SIM analysis). Add 60 g of anhydrous powdered sodium sulfate or 30 g of Hydromatrix™ to each aliquot. Mix well. Follow the appropriate extraction procedure in Section 10.1.2, extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for low-level soil samples.

NOTE: For analysis of PAHs and pentachlorophenol only, add 500 µL each DMC standard corresponding to 40 µg of each PAH and

PCP (0.40 µg of each SIM DMC) and 500 µL MS/MSD spiking solution corresponding to 40 µg each of acenaphthene, pyrene, and PCP Matrix Spike compounds (0.40 µg each of acenaphthene, pyrene, and PCP Matrix Spike compound for SIM analysis).

12.2.3.3 For medium-level soil/sediment samples, prepare two additional 1.0 g aliquots (record weight to nearest 0.1 g) of the sample chosen for spiking in two 20 mL vials. Add a sufficient amount of DMC spiking solution and the matrix spiking solution to result in the addition of 40 µg of each DMC and 40 µg of each Matrix Spike analyte. Add 2.0 g of anhydrous powdered sodium sulfate or 1.0 g of Hydromatrix™ to each aliquot. Mix well. Proceed with the appropriate extraction procedure (Section 10.1.2.3). Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for medium-level samples.

12.2.3.4 Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported. For example, if the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do not further dilute the MS/MSD samples to get either spiked or non-spiked analytes within calibration range. Sample dilutions must be performed in accordance with Section 10.4.3.

NOTE: In cases where PAHs and PCP-only SIM MS/MSD is requested, and the sample designated for MS/MSD analysis has PAH target analytes and PCP detected at or above the sample adjusted CRQL or any target exceeding the calibration range, during the full scan analysis, then the laboratory must contact SMO to determine if another sample should be chosen for PAH and PCP only SIM MS/MSD analysis.

12.2.4 Calculations for Matrix Spike and Matrix Spike Duplicate

12.2.4.1 Calculate the concentrations of the Matrix Spike analytes using the same equations as used for target analytes (Equations 6 and 7). Calculate the recovery of each Matrix Spike analyte using the following equation:

EQ. 11 Matrix Spike Recovery

$$\%R = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spike Sample Result

SR = Original Sample Result

SA = Spike Added

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD using the following equation:

EQ. 12 Relative Percent Difference

$$RPD = \frac{\left|MSR - MSDR\right|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

WHERE,

MSR = Matrix Spike Recovery

MSDR = Matrix Spike Duplicate Recovery

NOTE: The vertical bars in the equation above indicate the absolute value of the difference.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Matrix Spike Duplicate

12.2.5.1 All MS/MSDs must be analyzed on a GC/MS system meeting DFTPP, initial calibration, CCV, and method blank technical acceptance criteria and at the frequency described in Section 12.2.2. The MS/MSD must undergo cleanup procedures when required on a GPC meeting the technical acceptance criteria for GPC calibration.

12.2.5.2 The MS/MSD must be extracted and analyzed within the contract holding time.

12.2.5.3 The RT shift for each of the internal standards must be within 30 seconds of its RT and the most recent opening CCV standard analysis.

12.2.5.4 The limits for MS analyte recovery and RPD are given in Table 12 - Matrix Spike Recovery and Relative Percent Difference Limits. As these limits are only advisory, no further action by the Contractor is required. However, frequent failure to meet the limits for recovery or RPD warrant investigation by the Contractor, and may result in questions from the EPA.

12.2.6 Corrective Action for Matrix Spike and Matrix Spike Duplicate

Any MS/MSD that fails to meet the technical acceptance criteria in Sections 12.2.5.1 through 12.2.5.3 must be reanalyzed at no additional cost to the EPA.

12.3 Laboratory Control Sample

Not applicable to this method.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed under the contract, the Method Detection Limit (MDL) for each semivolatile target analyte shall be determined on each instrument used for analysis. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for water, low-level soil/sediment, and medium-level soil/sediment samples). The MDLs must be determined annually thereafter and after major instrument maintenance. Major instrument maintenance includes, but is not limited to: cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device). A new MDL study will not be required after changing the GC column, as long as the replacement has the same length, inner diameter, and stationary phase.

12.4.2 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in 40 Code of Federal Regulations (CFR) Part 136.

12.4.3 The determined concentration of the MDL must be less than the CRQL listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List (TAL) and Contract Required Quantitation Limits (CRQLs).

12.4.4 All documentation for the MDL studies shall be maintained at the laboratory and submitted to the EPA within seven (7) days of study completion. This schedule and the designated recipients are specified in Exhibit B, Table 1 – Reporting and Deliverables Requirements.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 13.0 of Exhibit D – Introduction to Organic Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 14.0 of Exhibit D – Introduction to Organic Analytical Methods.

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Automated Soxhlet Extraction, SW-846 Method 3541, Revision 0, September 1994.

16.2 U.S. Environmental Protection Agency, Continuous Liquid-Liquid Extraction, SW-846 Method 3520C, Revision 3, December 1996.

16.3 U.S. Environmental Protection Agency, Pressurized Fluid Extraction (PFE), SW-846 Method 3545A, Revision 1, January 1998.

16.4 U.S. Environmental Protection Agency, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), SW-846 Method 8270D, Revision 4, February 2007.

16.5 U.S. Environmental Protection Agency, Silica Gel Cleanup, SW-846 Method 3630C, Revision 3, December 1996.

16.6 U.S. Environmental Protection Agency, Ultrasonic Extraction, SW-846 Method 3550C, Revision 3, November 2000.

16.7 U.S. Government Printing Office, 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS

Systematic Name	EPA Registry Name	Synonym	CAS #
1,4-Dioxane	1,4-Diethyleneoxide	Diethylene dioxide	123-91-1
Benzaldehyde	Benzaldehyde	Benzoic aldehyde	100-52-7
Phenol	Phenol	Hydroxybenzene	108-95-2
Ethane, 1,1'-oxybis[2-chloro-	Bis(2-chloroethyl)ether	Dichloroethyl ether	111-44-4
Phenol, 2-chloro-	o-Chlorophenol	2-Hydroxychlorobenzene	95-57-8
Phenol, 2-methyl-	o-Cresol	1-Hydroxy-2-methylbenzene	95-48-7
Phenol, 3-methyl-	m-Cresol	1-Methyl-3-hydroxybenzene	108-39-4
Propane, 2,2'-oxybis[1-chloro-	Bis(2-chloro-1-methylethyl)ether	1,1'-Dichlorodiisopropyl ether	108-60-1
Ethanone, 1-phenyl-	Acetophenone	Acetylbenzene	98-86-2
Phenol, 4-methyl-	p-Cresol	1-methyl-4-hydroxybenzene	106-44-5
1-Propanamine, N-nitroso-N-propyl-	N-Nitrosodi-n-propylamine	Di-n-propylnitrosamine	621-64-7
Ethane, 1,1,1,2,2,2-hexachloro-	Hexachloroethane	Carbon hexachloride	67-72-1
Benzene, nitro-	Nitrobenzene	Nitrobenzol	98-95-3
2-Cyclohexen-1-one, 3,5,5-trimethyl-	Isophorone	Isoacetophorone	78-59-1
Phenol, 2-nitro-	o-Nitrophenol	o-Hydroxynitrobenzene	88-75-5
Phenol, 2,4-dimethyl-	2,4-Dimethylphenol	1-Hydroxy-2,4-dimethylbenzene	105-67-9
Ethane, 1,1'-[methylenebis(oxy)]bis[2-chloro-	Bis(2-chloroethoxy)methane	Formaldehyde bis(2-chloroethyl) acetal	111-91-1
Phenol, 2,4-dichloro-	2,4-Dichlorophenol	1-Hydroxy-2,4-dichlorobenzene	120-83-2
Naphthalene	Naphthalene	Naphthalin	91-20-3
Benzenamine, 4-chloro-	4-Chloroaniline	4-Chloroaniline	106-47-8
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	Hexachlorobutadiene	Hexachloro-1,3-Butadiene	87-68-3
2H-Azepin-2-one, hexahydro-	Caprolactam	2-oxohexamethyleneimine	105-60-2
Phenol, 4-chloro-3-methyl-	p-Chloro-m-cresol	2-Chloro-5-hydroxytoluene	59-50-7
Naphthalene, 2-methyl-	2-Methylnaphthalene	β-Methylnaphthalene	91-57-6

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS (CON'T)

Systematic Name	EPA Registry Name	Synonym	CAS #
1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-	Hexachlorocyclopentadiene	Hexachloro-1,3-cyclopentadiene	77-47-4
Phenol, 2,4,6-trichloro-	2,4,6-Trichlorophenol	Trichloro-2-hydroxybenzene	88-06-2
Phenol, 2,4,5-trichloro-	2,4,5-Trichlorophenol	Collunosol	95-95-4
1,1'-Biphenyl	Biphenyl	Phenylbenzene	92-52-4
Naphthalene, 2-chloro-	2-Chloronaphthalene	beta-Chloronaphthalene	91-58-7
Benzenamine, 2-nitro-	o-Nitroaniline	2-Nitroaniline	88-74-4
1,2-Benzenedicarboxylic acid, 1,2-dimethyl ester	Dimethyl phthalate	Phthalic acid, dimethyl ester	131-11-3
Benzene, 2-methyl-1,3-dinitro-	2,6-Dinitrotoluene	1-Methyl-2,6-dinitrobenzene	606-20-2
Acenaphthylene	Acenaphthylene	Cyclopenta[de]naphthalene	208-96-8
Benzenamine, 3-nitro-	m-Nitroaniline	3-Nitroaniline	99-09-2
Acenaphthylene, 1,2-dihydro-	Acenaphthene	1,8-Ethylenenaphthalene	83-32-9
Phenol, 2,4-dinitro-	2,4-Dinitrophenol	1-Hydroxy-2,4-dinitrobenzene	51-28-5
Phenol, 4-nitro-	p-Nitrophenol	p-Hydroxynitrobenzene	100-02-7
Dibenzofuran	Dibenzofuran	2,2'-Biphenylene Oxide	132-64-9
Benzene, 1-methyl-2,4-dinitro-	2,4-Dinitrotoluene	4-Methyl-1,3-Dinitrobenzene	121-14-2
1,2-Benzenedicarboxylic acid,1,2-diethyl ester	Diethyl phthalate	Phthalic acid, diethyl ester	84-66-2
9H-Fluorene	Fluorene	o-Biphenylenemethane	86-73-7
Benzene, 1-chloro-4-phenoxy-	p-Chlorophenylphenyl ether	4-Chlorophenylphenyl ether	7005-72-3
Benzenamine, 4-nitro-	p-Nitroaniline	4-Nitroaniline	100-01-6
Phenol, 2-methyl-4,6-dinitro-	4,6-Dinitro-o-cresol	4,6-Dinitro-2-methylphenol	534-52-1
Benzenamine, N-nitroso-N-phenyl-	N-Nitrosodiphenylamine	Diphenylnitrosamine	86-30-6
Benzene, 1,2,4,5-tetrachloro-	1,2,4,5-Tetrachlorobenzene	s-Tetrachlorobenzene	95-94-3
Benzene, 1-bromo-4-phenoxy-	p-Bromophenyl phenyl ether	4-Bromophenyl phenyl ether	101-55-3
Benzene, hexachloro-	Hexachlorobenzene	Hexachlorobenzol	118-74-1

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS (CON'T)

Systematic Name	EPA Registry Name	Synonym	CAS #
1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-N'-(1-methylethyl)-	Atrazine	Fenatrol	1912-24-9
Phenol, 2,3,4,5,6-pentachloro-	Pentachlorophenol	Phenol, pentachloro	87-86-5
Phenanthrene	Phenanthrene	Phenanthrin	85-01-8
Anthracene	Anthracene	Paranaphthalene	120-12-7
9H-Carbazole	Carbazole	Diphenylenimine	86-74-8
1,2-Benzenedicarboxylic acid, dibutyl ester	Dibutyl phthalate	Di-n-butylphthalate	84-74-2
Fluoranthene	Fluoranthene	Benzo[j,k]fluorene	206-44-0
Pyrene	Pyrene	Benzo[d,e,f]phenanthrene	129-00-0
1,2-Benzenedicarboxylic acid, 1-butyl 2-(phenylmethyl) ester	Butyl benzyl phthalate	Phthalic acid, benzyl butyl ester	85-68-7
[1,1'-Biphenyl]-4,4'-diamine, 3,3'-dichloro-	3,3'-Dichlorobenzidine	o,o'-Dichlorobenzidine	91-94-1
Benz[a]anthracene	Benz[a]anthracene	1,2-Benzanthracene	56-55-3
Chrysene	Chrysene	1,2-Benzphenanthrene	218-01-9
1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	Di(2-ethylhexyl) phthalate	phthalic acid, (2-ethyl hexyl)ester	117-81-7
1,2-Benzenedicarboxylic acid, 1,2-dioctyl ester	Di-n-octyl phthalate	n-Octyl phthalate	117-84-0
Benz[e]acephenanthrylene	Benzo(b)fluoranthene	2,3-Benzofluoranthene	205-99-2
Benzo[k]fluoranthene	Benzo[k]fluoranthene	11,12-Benzofluoranthene	207-08-9
Benzo[a]pyrene	Benzo[a]pyrene	3,4-Benzopyrene	50-32-8
Indeno[1,2,3-cd]pyrene	Indeno[1,2,3-cd]pyrene	1,10-(1,2-Phenylene)pyrene	193-39-5
Dibenzo[a,h]-anthracene	Dibenzo[a,h]-anthracene	1,2,5,6-Dibenzanthracene	53-70-3
Benzo[ghi]perylene	Benzo[ghi]perylene	1,12-Benzoperylene	191-24-2
Phenol,2,3,4,6-tetrachloro	2,3,4,6-Tetrachlorophenol	1-Hydroxy-2,3,4,6-tetrachlorobenzene	58-90-2

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS (CON'T)

Systematic Name	EPA Registry Name	Synonym	CAS #
Internal Standards			
Benzene-d4, 1,4-dichloro-	1,4-Dichlorobenzene-d4	1,4-Dichloro-2,3,5,6-	3855-82-1
Naphthalene-d8	Naphthalene-d8	Tetradeuterobenzene	1146-65-2
Acenaphthylene-d8, 1,2-dihydro-d2-	Acenaphthene-d10	Perdeuteronaphthalene	15067-26-2
Phenanthrene-d10	Phenanthrene-d10	Phenanthrene, perdeutero-	1517-22-2
Chrysene-d12	Chrysene-d12	Chrysene, perdeutero-	1719-03-5
Perylene-d12	Perylene-d12	Perylene- perdeutero-	1520-96-3
DMCs			
1,4-Dioxane-2,2,3,3,5,5,6,6-d8	1,4-Dioxane-d8	1,4-Diethyleneoxide-d8	17647-74-4
Phen-d5-ol	Phenol-d5	Phenol-d5	4165-62-2
Ethane-1,1,2,2-d4, 1,1'-oxybis[2-chloro-	Bis(2-chloroethyl)ether-d8	Bis(2-chloroethyl)ether-d8	93952-02-4
Phen-2,3,4,5-d4-ol, 6-chloro-		2-chlorophenol-d4	93951-73-6
Phen-2,3,5,6-d4-ol-d, 4-(methyl-d3)-	4-methylphenol-d8	4-methylphenol-d8	190780-66-6
Benzen-2,3,5,6-d4-amine, 4-chloro	4-Chloroaniline-d4	4-Chloroaniline-d4	191656-33-4
Benzene-d5, Nitro-	Nitrobenzene-d5	Nitro(2H5)benzene	4165-60-0
Phen-2,3,4,5-d4-ol, 6-nitro-		2-Nitrophenol-d4	93951-78-1
Phen-2,3,5-d3-ol, 4,6-dichloro-		2,4-Dichlorophenol-d3	93951-74-7
1,2-Benzenedicarboxylic acid, di(methyl-d3)ester		Dimethylphthalate-d6	85448-30-2
Acenaphthylene-d8	Acenaphthylene-d8	Acenaphthylene-d8	93951-97-4
Phen-2,3,5,6-d4-ol, 4-nitro-		4-Nitrophenol-d4	93951-79-2
9H-Fluorene-1,2,3,4,5,6,7,8,9,9-d10	Fluorene-d10	Fluorene-d10	81103-79-9
Phen-3,5-d2-ol, 2-methyl-4,6-dinitro-		4,6-Dinitro-methylphenol-d2	93951-76-9
Anthracene-d10	Anthracene-d10	Anthracene, perdeutero-	1719-06-8
Pyrene-d10	Pyrene-d10	Pyrene-d10	1718-52-1
Benzo[a]pyrene-d12	Benzo[a]pyrene-d12	Benzo[a]pyrene-d12	63466-71-7
Fluoranthene-1,2,3,4,5,6,7,8,9,10-d10		Fluoranthene-d10 (SIM DMC)	93951-69-0
Naphthalene-1,2,3,4,5,6,8-d7, 7(methyl-d3)		2-Methylphthalene-d10 (SIM DMC)	7297-45-2

TABLE 2. DECAFLUOROTRIPHENYLPHOSPHINE KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	10.0 - 80.0% of mass 198
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	10.0 - 80.0% of mass 198
197	Less than 2.0% of mass 198
198	Base peak 100% relative abundance (see Note)
199	5.0 - 9.0% of mass 198
275	10.0 - 60.0% of mass 198
365	Greater than 1.0% of mass 198
441	Present but less than mass 443
442	Greater than 50.0% of mass 198
443	15.0 - 24.0% of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may exceed that of m/z 198.

TABLE 3. SEMIVOLATILE DEUTERATED MONITORING COMPOUNDS AND THE ASSOCIATED TARGET ANALYTES

1,4-Dioxane-d_8 (DMC-1)	**Phenol-d_5 (DMC-2)**	**Bis(2-Chloroethyl) ether-d_8 (DMC-3)**
1,4-Dioxane	Benzaldehyde	Bis(2-chloroethyl)ether
	Phenol	2,2'-Oxybis(1-chloropropane)
		Bis(2-chloroethoxy)methane
2-Chlorophenol-d_4 (DMC-4)	**4-Methylphenol-d_8 (DMC-5)**	**4-Chloroaniline-d_4 (DMC-6)**
2-Chlorophenol	2-Methylphenol	4-Chloroaniline
	3-Methylphenol	Hexachlorocyclopentadiene
	4-Methylphenol	Dichlorobenzidine
	2,4-Dimethylphenol	
Nitrobenzene-d_5 (DMC-7)	**2-Nitrophenol-d_4 (DMC-8)**	**2,4-Dichlorophenol-d_3 (DMC-9)**
Acetophenone	Isophorone	2,4-Dichlorophenol
N-Nitroso-di-n-propylamine	2-Nitrophenol	Hexachlorocyclopentadiene
Hexachloroethane		Hexachlorobutadiene
Nitrobenzene		4-Chloro-3-methylphenol
2,6-Dinitrotoluene		2,4,6-Trichlorophenol
2,4-Dinitrotoluene		2,4,5-Trichlorophenol
N-Nitrosodiphenylamine		1,2,4,5-Tetrachlorobenzene
		*Pentachlorophenol
		2,3,4,6-Tetrachlorophenol
Dimethylphthalate-d_6 (DMC-10)	**Acenaphthylene-d_8 (DMC-11)**	**4-Nitrophenol-d_4 (DMC-12)**
Caprolactam	*Naphthalene	2-Nitroaniline
1,1'-Biphenyl	*2-Methylnaphthalene	3-Nitroaniline
Dimethylphthalate	2-Chloronaphthalene	2,4-Dinitrophenol
Diethylphthalate	*Acenaphthylene	4-Nitrophenol
Di-n-butylphthalate	*Acenaphthene	4-Nitroaniline
Butylbenzylphthalate		
Bis(2-ethylhexyl)phthalate		
Di-n-octylphthalate		

TABLE 3. SEMIVOLATILE DEUTERATED MONITORING COMPOUNDS AND THE ASSOCIATED TARGET ANALYTES (CON'T)

Fluorene-d_{10} (DMC-13)	**4,6-Dinitro-2-methylphenol-d_2 (DMC-14)**	**Anthracene-d_{10} (DMC-15)**
Dibenzofuran	4,6-Dinitro-2-methylphenol	Hexachlorobenzene
*Fluorene		Atrazine
4-Chlorophenyl-phenylether		*Phenanthrene
4-Bromophenyl-phenylether		*Anthracene
Carbazole		
Pyrene-d_{10} (DMC-16)	**Benzo(a)pyrene-d_{12} (DMC-17)**	
*Fluoranthene	3,3'-Dichlorobenzidine	
*Pyrene	*Benzo(b)fluoranthene	
*Benzo(a)anthracene	*Benzo(k)fluoranthene	
*Chrysene	*Benzo(a)pyrene	
	*Indeno(1,2,3-cd)pyrene	
	*Dibenzo(a,h)anthracene	
	*Benzo(g,h,i)perylene	

*Included in optional TAL of PAHs and PCP only.

TABLE 4. SEMIVOLATILE DEUTERATED MONITORING COMPOUNDS AND THE ASSOCIATED TARGET ANALYTES FOR OPTIONAL ANALYSIS BY SELECTED ION MONITORING

Fluoranthene-d_{10}	**2-Methylnaphthalene-d_{10}**
Fluoranthene	Napthalene
Pyrene	2-Methylnaphthalene
Benzo(a)anthracene	Acenapthylene
Chrysene	Acenaphthene
Benzo(b)fluoranthene	Fluorene
Benzo(k)fluoranthene	Pentachlorophenol
Benzo(a)pyrene	Phenanthrene
Indeno(1,2,3-cd)pyrene	Anthracene
Dibenzo(a,h)anthracene	
Benzo(g,h,i)perylene	

TABLE 5. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION FOR SEMIVOLATILE ORGANIC COMPOUNDS

Analyte	Opening Minimum RRF	Closing Minimum RRF	Maximum %RSD	Opening Maximum %D[1]	Closing Maximum %D
1,4-Dioxane	0.010	0.010	40.0	±40.0	±50.0
Benzaldehyde	0.100	0.100	40.0	±40.0	±50.0
Phenol	0.080	0.080	20.0	±20.0	±25.0
Bis(2-chloroethyl)ether	0.100	0.100	20.0	±20.0	±25.0
2-Chlorophenol	0.200	0.200	20.0	±20.0	±25.0
2-Methylphenol	0.010	0.010	20.0	±20.0	±25.0
3-Methylphenol	0.010	0.010	20.0	±20.0	±25.0
2,2'-Oxybis-(1-chloropropane)	0.010	0.010	20.0	±25.0	±50.0
Acetophenone	0.060	0.060	20.0	±20.0	±25.0
4-Methylphenol	0.010	0.010	20.0	±20.0	±25.0
N-Nitroso-di-n-propylamine	0.080	0.080	20.0	±25.0	±25.0
Hexachloroethane	0.100	0.100	20.0	±20.0	±25.0
Nitrobenzene	0.090	0.090	20.0	±20.0	±25.0
Isophorone	0.100	0.100	20.0	±20.0	±25.0
2-Nitrophenol	0.060	0.060	20.0	±20.0	±25.0
2,4-Dimethylphenol	0.050	0.050	20.0	±25.0	±50.0
Bis(2-chloroethoxy)methane	0.080	0.080	20.0	±20.0	±25.0
2,4-Dichlorophenol	0.060	0.060	20.0	±20.0	±25.0
Naphthalene	0.200	0.200	20.0	±20.0	±25.0
4-Chloroaniline	0.010	0.010	40.0	±40.0	±50.0
Hexachlorobutadiene	0.040	0.040	20.0	±20.0	±25.0
Caprolactam	0.010	0.010	40.0	±30.0	±50.0
4-Chloro-3-methylphenol	0.040	0.040	20.0	±20.0	±25.0
2-Methylnaphthalene	0.100	0.100	20.0	±20.0	±25.0
Hexachlorocyclopentadiene*	0.010	0.010	40.0	±40.0	±50.0
2,4,6-Trichlorophenol	0.090	0.090	20.0	±20.0	±25.0
2,4,5-Trichlorophenol	0.100	0.100	20.0	±20.0	±25.0
1,1'-Biphenyl	0.200	0.200	20.0	±20.0	±25.0
2-Chloronaphthalene	0.300	0.300	20.0	±20.0	±25.0
2-Nitroaniline	0.060	0.060	20.0	±25.0	±25.0
Dimethylphthalate	0.300	0.300	20.0	±20.0	±25.0
2,6-Dinitrotoluene	0.080	0.080	20.0	±20.0	±25.0
Acenaphthylene	0.400	0.400	20.0	±20.0	±25.0
3-Nitroaniline	0.010	0.010	20.0	±25.0	±50.0
Acenaphthene	0.200	0.200	20.0	±20.0	±25.0
2,4-Dinitrophenol*	0.010	0.010	40.0	±50.0	±50.0
4-Nitrophenol*	0.010	0.010	40.0	±40.0	±50.0
Dibenzofuran	0.300	0.300	20.0	±20.0	±25.0
2,4-Dinitrotoluene	0.070	0.070	20.0	±20.0	±25.0
Diethylphthalate	0.300	0.300	20.0	±20.0	±25.0
1,2,4,5-Tetrachlorobenzene	0.100	0.100	20.0	±20.0	±25.0
4-Chlorophenyl-phenylether	0.100	0.100	20.0	±20.0	±25.0
Fluorene	0.200	0.200	20.0	±20.0	±25.0
4-Nitroaniline	0.010	0.010	40.0	±40.0	±50.0

TABLE 5. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION FOR SEMIVOLATILE ORGANIC COMPOUNDS (CON'T)

Analyte	**Opening Minimum RRF**	**Closing Minimum RRF**	**Maximum %RSD**	**Opening Maximum %D[1]**	**Closing Maximum %D**
4,6-Dinitro-2-methylphenol	0.010	0.010	40.0	±30.0	±50.0
4-Bromophenyl-phenyl ether	0.070	0.070	20.0	±20.0	±25.0
N-Nitrosodiphenylamine	0.100	0.100	20.0	±20.0	±25.0
Hexachlorobenzene	0.050	0.050	20.0	±20.0	±25.0
Atrazine	0.010	0.010	40.0	±25.0	±50.0
Pentachlorophenol	0.010	0.010	40.0	±40.0	±50.0
Phenanthrene	0.200	0.200	20.0	±20.0	±25.0
Anthracene	0.200	0.200	20.0	±20.0	±25.0
Carbazole	0.050	0.050	20.0	±20.0	±25.0
Di-n-butylphthalate	0.500	0.500	20.0	±20.0	±25.0
Fluoranthene	0.100	0.100	20.0	±20.0	±25.0
Pyrene	0.400	0.400	20.0	±25.0	±50.0
Butylbenzylphthalate	0.100	0.100	20.0	±25.0	±50.0
3,3'-Dichlorobenzidine	0.010	0.010	40.0	±40.0	±50.0
Benzo(a)anthracene	0.300	0.300	20.0	±20.0	±25.0
Chrysene	0.200	0.200	20.0	±20.0	±50.0
Bis(2-ethylhexyl)phthalate	0.200	0.200	20.0	±25.0	±50.0
Di-n-octylphthalate	0.010	0.010	40.0	±40.0	±50.0
Benzo(b)fluoranthene	0.010	0.010	20.0	±25.0	±50.0
Benzo(k)fluoranthene	0.010	0.010	20.0	±25.0	±50.0
Benzo(a)pyrene	0.010	0.010	20.0	±20.0	±50.0
Indeno(1,2,3-cd)pyrene	0.010	0.010	20.0	±25.0	±50.0
Dibenzo(a,h)anthracene	0.010	0.010	20.0	±25.0	±50.0
Benzo(g,h,i)perylene	0.010	0.010	20.0	±30.0	±50.0
2,3,4,6-Tetrachlorophenol	0.040	0.040	20.0	±20.0	±50.0
Selective Ion Monitoring					
Naphthalene	0.600	0.600	20.0	±25.0	±25.0
2-Metylnapthalene	0.300	0.300	20.0	±20.0	±25.0
Acenaphthylene	0.900	0.900	20.0	±20.0	±25.0
Acenaphthene	0.500	0.500	20.0	±20.0	±25.0
Fluorene	0.700	0.700	20.0	±25.0	±50.0
Phenanthrene	0.300	0.300	20.0	±25.0	±50.0
Anthracene	0.400	0.400	20.0	±25.0	±50.0
Fluoranthene	0.400	0.400	20.0	±25.0	±50.0
Pyrene	0.500	0.500	20.0	±30.0	±50.0
Benzo(a)anthracene	0.400	0.400	20.0	±25.0	±50.0
Chyrsene	0.400	0.400	20.0	±25.0	±50.0
Benzo(b)fluoranthene	0.100	0.100	20.0	±30.0	±50.0
Benzo(k)fluoranthene	0.100	0.100	20.0	±30.0	±50.0
Benzo(a)pyrene	0.100	0.100	20.0	±25.0	±50.0
Indeno(1,2,3-cd)pyrene	0.100	0.100	20.0	±40.0	±50.0
Dibenzo(a,h)anthracene	0.010	0.010	25.0	±40.0	±50.0
Benzo(g,h,i)perylene	0.020	0.020	25.0	±40.0	±50.0
Pentachlorophenol	0.010	0.010	40.0	±50.0	±50.0

TABLE 5. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION FOR SEMIVOLATILE ORGANIC COMPOUNDS (CON'T)

Analyte	Opening Minimum RRF	Closing Minimum RRF	Maximum %RSD	Opening Maximum %D[1]	Closing Maximum %D
Deuterated Monitoring Compounds					
1,4-Dioxane-d_8	0.010	0.010	20.0	±25.0	±50.0
Phenol-d_5	0.010	0.010	20.0	±25.0	±25.0
Bis-(2-chloroethyl)ether-d_8	0.100	0.100	20.0	±20.0	±25.0
2-Chlorophenol-d_4	0.200	0.200	20.0	±20.0	±25.0
4-Methylphenol-d_8	0.010	0.010	20.0	±20.0	±25.0
4-Chloroaniline-d_4	0.010	0.010	40.0	±40.0	±50.0
Nitrobenzene-d_5	0.050	0.050	20.0	±20.0	±25.0
2-Nitrophenol-d_4	0.050	0.050	20.0	±20.0	±25.0
2,4-Dichlorophenol-d_3	0.060	0.060	20.0	±20.0	±25.0
Dimethylphthalate-d_6	0.300	0.300	20.0	±20.0	±25.0
Acenaphthylene-d_8	0.400	0.400	20.0	±20.0	±25.0
4-Nitrophenol-d_4	0.010	0.010	40.0	±40.0	±50.0
Fluorene-d_{10}	0.100	0.100	20.0	±20.0	±25.0
4,6-Dinitro-2-methylphenol-d_2	0.010	0.010	40.0	±30.0	±50.0
Anthracene-d_{10}	0.300	0.300	20.0	±20.0	±25.0
Pyrene-d_{10}	0.300	0.300	20.0	±25.0	±50.0
Benzo(a)pyrene-d_{12}	0.010	0.010	20.0	±20.0	±50.0
Fluoranthene-d_{10} (SIM)	0.400	0.400	20.0	±25.0	±50.0
2-Methylnapthalene-d_{10} (SIM)	0.300	0.300	20.0	±20.0	±25.0

[1] If a closing CCV is acting as an opening CCV, all target analytes must meet the requirements for an opening CCV.

TABLE 6. GAS CHROMATOGRAPH ANALYTICAL CONDITIONS

Carrier Gas:	Helium or Hydrogen 99.999% purity
Column Flow:	30 cm/sec or 1-2 mL/min.
Injector Temperature:	250-300°C
Transfer Line Temperature	250-300°C
Source Temperature	According to manufacturer's specifications
Injection Technique:	On-column
Injection Volume:	1 or 2 µl
Initial Column Temperature Hold	40°C for 4 min.
Column Temperature Program	40-270°C at 10°C/min.
Final Column Temperature Hold	270°C; Hold Required: 3 min. after all analytes listed in Exhibit C - Semivolatiles, have eluted

TABLE 7. MASS SPECTROMETER ANALYTICAL CONDITIONS

Electron Energy	70 Volts (nominal)
Mass Range	35-500 u
Ionization Mode	Electron Ionization (EI)
Scan Time	Not to exceed 1 sec. per scan

NOTE: For SIM analyses, the Contractor is to use professional judgment and the instrument manufacturer's instructions and guidelines in choosing an appropriate single ion scan or dwell time (usually 50-500 msec per ion).

TABLE 8. CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET ANALYTES, DEUTERATED MONITORING COMPOUNDS, AND INTERNAL STANDARDS

Analyte	Primary Quantitation Ion	Secondary Ion(s)
1,4-Dioxane	88	43,58
Benzaldehyde	77	105,106
Phenol	94	65,66
Bis(2-chloroethyl)ether	93	63,95
2-Chlorophenol	128	64,130
2-Methylphenol	108	107
3-Methylphenol	108	107
2,2'-Oxybis(1-chloropropane)	45	77,79
Acetophenone	105	77,51
4-Methylphenol	108	107
N-Nitroso-di-n-propylamine	70	42,101,130
Hexachloroethane	117	201,199
Nitrobenzene	77	123,65
Isophorone	82	95,138
2-Nitrophenol	139	65,109
2,4-Dimethylphenol	107	121,122
Bis(2-chloroethoxy)methane	93	95,123
2,4-Dichlorophenol	162	164,98
Naphthalene	128	129,127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223,227
Caprolactam	113	55,56
4-Chloro-3-methylphenol	107	144,142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235,272
2,4,6-Trichlorophenol	196	198,200
2,4,5-Trichlorophenol	196	198,200
1,1'-Biphenyl	154	153,76
2-Chloronaphthalene	162	164,127
2-Nitroaniline	65	92,138
Dimethylphthalate	163	194,164
Acenaphthylene	152	151,153
3-Nitroaniline	138	108,92
Acenaphthene	153	152,154
2,4-Dinitrophenol	184	63,154
4-Nitrophenol	109	139,65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63,182
2,6-Dinitrotoluene	165	89,121
Diethylphthalate	149	177,150
1,2,4,5-Tetrachlorobenzene	216	214,179,108,143,218
4-Chlorophenyl-phenylether	204	206,141
Fluorene	166	165,167
4-Nitroaniline	138	92,108
4,6-Dinitro-2-methylphenol	198	182,77
N-Nitrosodiphenylamine	169	168,167
4-Bromophenyl-phenylether	248	250,141
Hexachlorobenzene	284	142,249
Atrazine	200	173,215

TABLE 8. CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET ANALYTES, DEUTERATED MONITORING COMPOUNDS, AND INTERNAL STANDARDS (CON'T)

Analyte	**Primary Quantitation Ion**	**Secondary Ion(s)**
Pentachlorophenol	266	264,268
Phenanthrene	178	179,176
Anthracene	178	179,176
Carbazole	167	166,139
Di-n-butylphthalate	149	150,104
Fluoranthene	202	101,100
Pyrene	202	101,100
Butylbenzylphthalate	149	91,206
3,3'-Dichlorobenzidine	252	254,126
Benzo(a)anthracene	228	229,226
Bis(2-ethylhexyl)phthalate	149	167,279
Chrysene	228	226,229
Di-n-octyl phthalate	149	none
Benzo(b)fluoranthene	252	253,125
Benzo(k)fluoranthene	252	253,125
Benzo(a)pyrene	252	253,125
Indeno(1,2,3-cd)pyrene	276	138,227
Dibenzo(a,h)anthracene	278	139,279
Benzo(g,h,i)perylene	276	138,277
2,3,4,6-Tetrachlorophenol	232	131,230,166,234,168
Deuterated Monitoring Compounds		
1,4-Dioxane-d_8	96	64,34
Phenol-d_5	99	71,42
Bis(2-chloroethyl)ether-d_8	67	99,69
2-Chlorophenol-d_4	132	134,68,66
4-Methylphenol-d_8	113	115,54
4-Chloroaniline-d_4	131	133,69
Nitrobenzene-d_5	128	82,54
2-Nitrophenol-d_4	143	69,41,42
2,4-Dichlorophenol-d_3	165	167,101
Dimethylphthalate-d_6	166	78
Acenaphthylene-d_8	160	80,158
4-Nitrophenol-d_4	143	113,41,42
Fluorene-d_{10}	176	174,87,86
4,6-Dinitro-2-methylphenol-d_2	200	170,52
Anthracene-d_{10}	188	94,80
Pyrene-d_{10}	212	106,104
Benzo(a)pyrene-d_{12}	264	132,118
Fluoranthene-d_{10}(SIM)	212	106,104
2-Methylnapthalene-d_{10} (SIM)	152	151
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162,160
Phenanthrene-d_{10}	188	94,80
Chrysene-d_{12}	240	120,236
Perylene-d_{12}	264	260,265

TABLE 9. SEMIVOLATILE INTERNAL STANDARDS WITH ASSOCIATED TARGET AND DEUTERATED MONITORING COMPOUNDS ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	**Naphthalene-d_8**	**Acenaphthene-d_{10}**
1,4-Dioxane Benzaldehyde Phenol Bis(2-chloroethyl) ether 2-Chlorophenol 2-Methylphenol 3-Methylphenol 2,2'-Oxybis(1-chloro-propane) Acetophenone 4-Methylphenol N-Nitroso-di-n-propylamine Hexachloroethane 1,4-Dioxane-d_8 (DMC) Phenol-d_5 (DMC) Bis(2-chloroethyl)ether-d_8 (DMC) 2-Chlorophenol-d_4 (DMC) 4-Methylphenol-d_8 (DMC)	Nitrobenzene Isophorone 2-Nitrophenol 2,4-Dimethylphenol Bis(2-chloroethoxy)methane 2,4-Dichlorophenol Hexachlorobutadiene Caprolactam 4-Chloro-3-methylphenol *2-Methylnaphthalene *Naphthalene 4-Chloroaniline Nitrobenzene-d_5 (DMC) 2-Nitrophenol-d_4 (DMC) 2,4-Dichlorophenol-d_3 (DMC) 4-Chloroaniline-d_4 (DMC) 2-Methylnapthalene-d_{10} (SIM-DMC)	Hexachlorocyclopentadiene 2,4,6-Trichlorophenol 2,4,5-Trichlorophenol 2,3,4,6-Tetrachlorophenol 1,1'-Biphenyl 2-Chloronaphthalene 2-Nitroaniline Dimethylphthalate *Acenaphthylene 3-Nitroaniline *Acenaphthene 2,4-Dinitrophenol 4-Nitrophenol Dibenzofuran 2,4-Dinitrotoluene 2,6-Dinitrotoluene 1,2,4,5-Tetrachlorobenzene Diethylphthalate 4-Chlorophenyl-phenylether *Fluorene 4-Nitroaniline Acenaphthylene-d_8 (DMC) 4-Nitrophenol-d_4 (DMC) Dimethylphthalate-d_6 (DMC) Fluorene-d_{10} (DMC)
Phenanthrene-d_{10}	**Chrysene-d_{12}**	**Perylene-d_{12}**
4,6-Dinitro-2-methylphenol N-Nitrosodiphenylamine 4-Bromophenyl-phenylether Hexachlorobenzene Atrazine *Pentachlorophenol *Phenanthrene *Anthracene Carbazole Di-n-butylphthalate *Fluoranthene 4,6-Dinitro-2-methylphenol-d_2 (DMC) Anthracene-d_{10} (DMC) Fluoranthene-d_{10} (SIM-DMC)	*Pyrene Butylbenzylphthalate 3,3'-Dichlorobenzidine *Benzo(a)anthracene Bis(2-ethylhexyl)phthalate *Chrysene Pyrene-d_{10} (DMC)	Di-n-octylphthalate *Benzo(b)fluoranthene *Benzo(k)fluoranthene *Benzo(a)pyrene *Indeno(1,2,3-cd)pyrene *Dibenzo(a,h)anthracene *Benzo(g,h,i)perylene Benzo(a)pyrene-d_{12} (DMC)

* Included in optional TAL of PAHs and PCP only.

TABLE 10. INTERNAL STANDARDS WITH ASSOCIATED TARGET AND DEUTERATED MONITORING COMPOUNDS ASSIGNED FOR QUANTITATION OF POLYNUCLEAR AROMATIC HYDROCARBON AND PENTACHLOROPHENOL

Naphthalene-d_8	**Acenaphthene-d_{10}**	**Phenanthrene-d_{10}**
2-Methylnaphthalene Naphthalene *2-Methylnapthalene-d_{10} (DMC)	Acenaphthylene Acenaphthene Fluorene Acenaphthylene-d_8 (DMC) Fluorene-d_{10} (DMC)	Phenanthrene Anthracene Fluoranthene Pentachlorophenol 4,6-Dinitro-2-methylphenol-d_2 (DMC) Anthracene-d_{10} (DMC) *Fluoranthene-d_{10} (DMC)
Chrysene-d_{12}	**Perylene-d_{12}**	
Pyrene Benzo(a)anthracene Chrysene Pyrene-d_{10} (DMC)	Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene Benzo(a)pyrene-d_{12} (DMC)	

* DMC assigned only for PAH and PCP by SIM analysis.

TABLE 11. DEUTERATED MONITORING COMPOUND RECOVERY LIMITS

Compound	Percent Recovery For Water Samples	Percent Recovery For Soil Samples
1,4-Dioxane-d_8	40-110	40-110
Phenol-d_5	10-130	10-130
Bis(2-chloroethyl)ether-d_8	25-120	10-150
2-Chlorophenol-d_4	20-130	15-120
4-Methylphenol-d_8	25-125	10-140
4-Chloroaniline-d_4	1-146*	1-145*
Nitrobenzene-d_5	20-125	10-135
2-Nitrophenol-d_4	20-130	10-120
2,4-Dichlorophenol-d_3	20-120	10-140
Dimethylphthalate-d_6	25-130	10-145
Acenaphthylene-d_8	10-130	15-120
4-Nitrophenol-d_4	10-150	10-150
Fluorene-d_{10}	25-125	20-140
4,6-Dinitro-2-methylphenol-d_2	10-130	10-130
Anthracene-d_{10}	25-130	10-150
Pyrene-d_{10}	15-130	10-130
Benzo(a)pyrene-d_{12}	20-130	10-140
Fluoranthene-d_{10} (SIM)	30-130	30-130
2-Methylnapthalene-d_{10} (SIM)	30-130	20-140

* Limits are advisory.

TABLE 12. MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS

Analyte	Percent Recovery Water	RPD Water	Percent Recovery Soil	RPD Soil
Phenol	12-110	0-42	26-90	0-35
2-Chlorophenol	27-123	0-40	25-102	0-50
N-Nitroso-di-n-propylamine	41-116	0-38	41-126	0-38
4-Chloro-3-methylphenol	23-97	0-42	26-103	0-33
Acenaphthene	46-118	0-31	31-137	0-19
4-Nitrophenol	10-80	0-50	11-114	0-50
2,4-Dinitrotoluene	24-96	0-38	28-89	0-47
Pentachlorophenol	9-103	0-50	17-109	0-47
Pyrene	26-127	0-31	35-142	0-36

EXHIBIT D

PESTICIDES ANALYSIS

THIS PAGE INTENTIONALLY LEFT BLANK

EXHIBIT D - Pesticides Analysis

Table of Contents

EXHIBIT D - Pesticides Analysis

Table of Contents

1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze water, leachate derived from the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP), and soil/sediment samples from hazardous waste sites to determine the presence and concentration of the chlorinated pesticides contained in the Target Analyte List (TAL) for pesticides in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits. The method, based on U.S. Environmental Protection Agency (EPA) SW-846 Method 8081C, can be used for determining analyte concentrations in the range from the Contract Required Quantitation Limits (CRQLs) to one million times the CRQL in these matrices, when appropriate dilutions are made. The method includes sample extraction, extract cleanup techniques, and Gas Chromatograph/Electron Capture Detector (GC/ECD) analytical methods for chlorinated pesticides.

1.2 Co-elution problems have been associated with the following pairs of analytes using this method include:

- On a DB-608 or equivalent column, DDE and Dieldrin; Methoxychlor and Endrin ketone; and Endosulfan I and trans-Chlordane; and
- On a DB-1701 or equivalent column, Endosulfan I and trans-Chlordane, and Methoxychlor and Endosulfan sulfate.

1.3 There are two isomers of heptachlor epoxide, the endo epoxy isomer (Isomer A) and the exo epoxy isomer (Isomer B). The two isomers are separable using current GC capillary columns. Only the exo epoxy isomer (Isomer B) is of environmental significance. This is the isomer that must be used as an analytical standard, identified and quantitated in sample analysis, and reported on appropriate forms as heptachlor epoxide.

2.0 SUMMARY OF METHOD

2.1 Water/TCLP or SPLP Leachate

Continuous liquid-liquid or separatory funnel extraction procedures are employed for aqueous samples. A 1.0 liter (L) aliquot of sample is spiked with the surrogate solution and extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried with anhydrous sodium sulfate (or Hydromatrix™), concentrated, and subjected to Gel Permeation Chromatography (GPC) cleanup. GPC is required when higher molecular weight compounds are present that interfere with the analyses of target analytes; GPC is optional for all other circumstances. The extract is then solvent exchanged into hexane, cleaned up by Florisil cartridges or other methods as applicable, and analyzed using a dual column wide-bore capillary GC/ECD.

2.2 Soil/Sediment

A 30 gram (g) aliquot of sample is spiked with the surrogates, mixed with anhydrous sodium sulfate (or Hydromatrix™), and extracted with a 1:1 (v/v) acetone/methylene chloride solvent mixture by ultrasonic extraction, Soxhlet extraction, or pressurized fluid extraction. The extract is filtered (for ultrasonic extraction), concentrated, and solvent-exchanged into methylene chloride. The methylene chloride extract is then subjected to GPC (mandatory), solvent-exchanged into hexane, cleaned up by a Florisil cartridge or other methods as

applicable, and analyzed using a dual column wide-bore capillary GC/ECD.

2.3 Wipes

Not applicable to this method.

2.4 Waste

Not applicable to this method.

3.0 DEFINITIONS

See Exhibit G – Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method interferences may be caused by compounds in solvents, reagents, glassware, and other sample processing hardware. These contaminants lead to discrete artifacts and/or to elevated baselines in Gas Chromatograms. These materials must be routinely demonstrated to be free from interferences under the sample preparation and analysis conditions by analyzing instrument and method blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Because common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

4.2 Matrix Interferences

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures in this method must be used to remove such interferences in order to achieve the CRQLs.

5.0 SAFETY

See Section 12.0 of Exhibit D – Introduction to Organic Analytical Methods.

5.1 Reagents

Concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to skin and mucous membranes. Use this reagent in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with this reagent.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternative equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 General Laboratory Equipment

6.1.1 Balances

6.1.1.1 Top loading, capable of weighing accurately to ±0.01 g.

6.1.1.2 Analytical, capable of weighing accurately to ±0.0001 g.

6.1.1.3 A balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±50% of the expected measured mass) for each type of balance and be accurate to ±0.01 g and ±0.0001 g, respectively. The masses that are used to check the balances daily must be checked on a monthly basis using NIST-traceable known reference masses (Class '0' or Class '1') as defined by ASTM E617-97(2008) or equivalent (e.g., earlier Class 'S' defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must be recertified at least every five years or sooner if there is reason to believe damage (corrosion, nicks) has occurred. The Contractor shall maintain documentation that demonstrates these criteria have been met.

6.1.2 Beakers - 100 milliliter (mL), 125 mL, 250 mL, and 400 mL.

6.1.3 Centrifuge, Table top (optional).

6.1.3.1 Centrifuge Tube - 12-15 mL with 19 mm ground-glass joint (optional).

6.1.4 Graduated Cylinder Class A – 1.0 L and 100 mL capacity.

6.1.5 Desiccator.

6.1.6 Erlenmeyer Flasks - 250 mL.

6.1.7 Volumetric Flask, Class A – 5.0, 10, 20, 50, 100, 250, and 500 mL.

6.1.8 Magnetic Stirring Bar - polytetrafluoroethylene (PTFE) coated, at least 4 centimeters (cm) long.

6.1.9 Ovens – drying, capable of maintaining 105°C (+/- 5°C).

6.1.10 pH Meter - With a combination glass electrode. Calibrate according to manufacturer's instructions. The pH meter shall be calibrated prior to each use, using reference standards bracketing the range expected in samples. The pH reference standards shall be replaced when their expiration dates have passed.

6.1.11 pH Paper – Wide range.

6.1.12 Pipettes - Glass volumetric, l mL or 2 mL.

6.1.13 Spatula - Stainless steel or PTFE.

6.1.14 Syringes – 10 microliters (µL), 25 µL, 100 µL, and 1000 µL.

6.1.15 Vials and Caps - 10 mL (optional), with screw-cap and PTFE or aluminum foil liner; autosampler vial with 2 mL capacity for GC auto sampler.

6.1.16 Weigh Dish – Porcelain crucibles or disposable aluminum weighing pans.

6.2 Glassware/Extraction/Cleanup Equipment

6.2.1 Automated Soxhlet Extraction System - With temperature-controlled oil bath. Silicone oil must not be used because it destroys the rubber parts. The apparatus must be used in a hood.

6.2.1.1 Cellulose or Glass Extraction Thimble (26 mm x 60 mm).

6.2.1.2 Glass Extraction Cups.

6.2.1.3 Thimble Adapters.

6.2.1.4 Viton Seals.

6.2.2 Soxhlet Extraction Manual

6.2.2.1 Allihn Condenser.

6.2.2.2 Soxhlet Extractor body, 40 mm ID.

6.2.2.3 Round bottom flask, 500 mL.

6.2.3 Borosilicate Glass Wool - Rinsed with methylene chloride.

6.2.4 Continuous Liquid-Liquid Extractors - Equipped with PTFE or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.2.5 Drying Column – 400 millimeter (mm) ID x 19 ID mm Chromatographic column, with coarse frit (substitution of a small pad of disposable borosilicate glass wool for the frit will help prevent cross-contamination of sample extracts).

6.2.6 Florisil Cleanup Equipment

6.2.6.1 Florisil - 500 milligram (mg) or 1 g cartridges with stainless steel or PTFE frits.

6.2.6.2 Vacuum System for Eluting Multiple Cleanup Cartridges.

6.2.6.3 Vacuum Trap - Made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.

6.2.6.4 Vacuum Pressure Gauge.

6.2.7 Gel Permeation Chromatography Equipment

6.2.7.1 GPC System - Systems that perform satisfactorily have been assembled from the following components: a High Performance Liquid Chromatography (HPLC) pump; an auto sampler or a valving system with sample loops; and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements in Section 10.3.1.3.

NOTE: GPC cleanup is required for all soils/sediments extracts, and for water extracts containing higher molecular weight contaminants that interfere with the analyses of the target analytes.

6.2.7.2 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the ultraviolet (UV) detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve may be attached so that

the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

6.2.7.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column.

Bio Beads (SX-3) - 200 to 400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, or equivalent). An additional 5 g of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.2.7.4 UV Detector - Fixed wavelength [254 nanometers (nm)] with a semi-prep flow-through cell.

6.2.7.5 Strip Chart Recorder - Recording integrator or laboratory data system.

6.2.7.6 Syringe Filter Assembly, disposable - 5 micron filter discs.

NOTE: Consult your instrument operation manual to determine the proper filter disc to use in your system. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

6.2.7.7 Viscometer

6.2.8 Kuderna-Danish (K-D) Apparatus

6.2.8.1 Concentrator Tubes - 10 mL and 15 mL, graduated.

6.2.8.2 Evaporative Flasks - 500 mL.

6.2.8.3 Silicon Carbide Boiling Chips – Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride. PTFE boiling chips solvent rinsed prior to use are acceptable.

6.2.8.4 Snyder Column - Three-ball macro.

6.2.8.5 Snyder Column - Two-ball micro.

6.2.9 Nitrogen Evaporation Device - Equipped with a water bath that can be maintained at 35-40°C. To prevent the release of solvent fumes into the laboratory, the nitrogen evaporator device must be used in a hood.

6.2.10 Pressurized Fluid Extraction Device

6.2.10.1 Dionex Accelerated Solvent Extractor (ASE-300) or equivalent with appropriately-sized extraction cells. Currently, 100 mL cells are available that will accommodate greater than 30 g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure requirements [2000+ pounds per square inch (psi)] necessary for this procedure.

6.2.10.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.2.11 Separatory Funnels - 2 L with PTFE stopcock.

6.2.12 Sonabox Acoustic Enclosure (or equivalent) - For use with disruptor to decrease noise level.

6.2.13 Ultrasonic Cell Disruptor - QSonica LLC, (53 Church Hill Road, Newtown, CT 06470) model S-4000 or equivalent ultrasonic liquid disruptor – equipped with a 3/4-inch horn and a 1/2-inch horn with a minimum output capacity of 300 watts.

NOTE 1: To ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. A rough tip surface is an indication of erosion.

NOTE 2: Follow manufacturer's instructions for set-up.

6.2.13.1 Vacuum or Pressure Filtration Apparatus.

6.2.13.2 Buchner Funnel.

6.2.13.3 Filter Paper – Whatman No. 42, or equivalent.

6.2.14 Water Bath - Heated, with concentric ring cover, capable of temperature control. The bath should be used in the hood.

6.3 Analytical Instrumentation

6.3.1 Gas Chromatograph

The GC must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout the temperature program operations. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases. The instrument must be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.3.1.1 GCs may have difficulty in meeting certain method Quality Control (QC) requirements of Endrin and DDT breakdown in the injector. This problem can be minimized by operating the injector at 200-205°C, using a borosilicate glass (not quartz) methyl silicone deactivated injector liner, and deactivating the metal parts in the injector with dichlorodimethylsilane. In some cases, using a 0.25 inch packed column injector converted for use with 0.53 mm capillary columns works better than a Grob-type injector. If a Grob-type injector is used, a 4 mm liner may be required to meet breakdown criteria.

6.3.2 Gas Chromatography Columns

Recommended Columns: Wide-bore (0.53mm ID) fused silica GC columns may be used provided that the resolution requirements are met (Section 9.3.5.2); if two wide-bore (0.53 mm ID) fused silica GC columns are used, then a separate detector is required for each column. The specified analytical columns are a 30 m x 0.53 mm ID, 1.0 µm film thickness DB-1701 (J&W Scientific); SPB 1701 (Supelco); AT 1701 (Alltech); Rtx®-1701, Rtx® CLP I (Restek); CP-Sil 19CB (Chrompack); 007-1701 (Quadrex); BP-10 (SGE); or equivalent, and a 30 m x 0.53 mm ID, 0.5 to 1.0 µm film thickness DB-608 (J&W Scientific); HP-608 (Agilent); SPB-608 (Supelco); 007-608 (Quadrex); BP-608 (SGE); Rtx® CLP II, CP-Sil 8CB (Chrompack); or equivalent. A description of the GC columns used for analysis shall be provided in the SDG Narrative. Packed columns may not be used.

6.3.2.1 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits;
- The analytical results generated using the column meet the initial calibration and continuing calibration verification (CCV) technical acceptance criteria listed in the analytical method in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits;
- The column can accept at least 16 times the low-point initial calibration concentration level in Table 2 – Concentration Levels of Initial Calibration and Continuing Calibration Verification and Technical Acceptance Criteria for Pesticides, without becoming overloaded; and
- The column pair chosen must have dissimilar phases/chemical properties in order to separate the analytes of interest in different Retention Time (RT) order.

6.3.2.1.1 The column provides equal or better resolution of the analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits, than the columns listed in Section 6.3.2. Although the instructions included in the analytical method are for wide-bore capillary columns, narrower bore capillary columns may be evaluated for use. Follow manufacturer's instructions for use of its product. Document in the SDG Narrative if other columns are used by specifying the column used.

6.3.2.1.2 The Contractor must maintain documentation verifying that the alternate column met the criteria in Sections 9.3.5 and 9.4.5. The minimum documentation is indicated below.

6.3.2.1.2.1 Manufacturer provided information concerning the performance characteristics of the column.

6.3.2.1.2.2 Chromatograms and data system reports generated on the GC/ECD and used for the EPA Contract Laboratory Program (CLP), including those from:

- Instrument blanks demonstrating there are no contaminants that interfere with the Pesticides analysis when using the alternate column; and
- The analysis of initial calibration and CCV standards using the alternate column.

6.3.2.1.3 Based on the Contractor-generated data described above, the Contractor shall complete a written review, signed by the Laboratory Manager, certifying that:

- The alternate column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analyses have adequate sensitivity to meet the pesticide CRQLs;

- The high-point initial calibration standard analyses were not overloaded; and
- The alternate column does not introduce contaminants which interfere with the identification and quantitation of analytes listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits.

6.3.2.1.4 The documentation must be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional Laboratory Contracting Officer Representative (COR).

6.3.2.1.5 Columns may be mounted in a press-fit Y-shaped glass 3-way union splitter or a Y-shaped fused-silica connector from a variety of commercial sources. The two columns may be mounted in an 8-inch deactivated glass injection tee. The Contractor should follow the manufacturer's recommendations for mounting 0.53 mm capillary columns in injector ports. Optionally, the dual column GC with separate autosamplers can be used for sample extract injection.

6.3.2.1.6 The carrier gas for routine applications is helium. The Contractor may choose to use hydrogen as a carrier gas, but they must clearly identify its use in the SDG Narrative in submissions to the EPA. Laboratories that choose to use hydrogen are advised to exercise caution in its use. Use of a hydrogen leak detector is highly recommended when hydrogen is used as the carrier gas. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.3.2.2 Gel Permeation Chromatography Column Preparation

Prepare the GPC column using BioBeads. Alternate column packings may be use if: 1)the column packings have equivalent or better performance than the BioBeads and meet the technical acceptance criteria for GPC calibration and GPC calibration checks, and 2) the column packings do not introduce contaminants/artifacts into the sample that interfere with the analysis of the pesticide analytes. Follow the manufacturer's instructions for preparation of the GPC column.

6.3.3 Electron Capture Detector

6.3.3.1 The linearity of the response of the ECD may be greatly dependent on the flow rate of the make-up gas. The make-up gas must be P-5, P-10 (argon/methane), or nitrogen according to the instrument specification. Care must be taken to maintain stable and an appropriate flow of make-up gas to the detector. The GC/ECD system must be in a room in which the atmosphere has been demonstrated to be free of all contaminants that may interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.3.3.2 At least annually, each ECD should be checked for radiation leakage from their Ni-63 source. Wipe tests should be conducted by wiping the inlet, outlet, and body of the ECD cell with swabs and sending the swabs for radiation tests.

6.4 Data Systems/Data Storage

A data system must be interfaced to the GC/ECD that allows the continuous acquisition and storage of data from each column throughout the duration of the chromatographic program and must permit, at a minimum, the output of time vs. intensity (peak height or peak area) data. The data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method.

7.0 REAGENTS AND STANDARDS

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit D – Introduction to Organic Analytical Methods, Section 11.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1 Reagents

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the CRQL for each analyte of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g [1 pound (lb)] of activated carbon.

7.1.1.2 Reagent water may also be generated using a water purification system.

7.1.2 10% acetone in hexane (v/v) - Prepare by adding 10.0 mL of acetone to 90.0 mL of hexane.

7.1.3 Acetone/methylene chloride (1:1 v/v).

7.1.4 Copper powder (optional) - Fine, granular. Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.

7.1.5 Hydromatrix™ - Diatomaceous earth-based material rinsed with methylene chloride and dried at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle.

7.1.6 Nitric Acid - Dilute, for sulfur removal with copper.

7.1.7 Sodium Hydroxide Solution (10 N) - Carefully dissolve 40 g of NaOH in reagent water and dilute the solution to 100 mL.

7.1.8 Sodium sulfate - Granular anhydrous reagent grade, heated at 400°C for 4 hours, cooled in a desiccator, and stored in a glass bottle. Each lot must be extracted with hexane and analyzed by a GC/ECD to demonstrate that it is free of interference before use or must be purchased with certification that it is free of interference.

CAUTION: AN OPEN CONTAINER OF SODIUM SULFATE MAY BECOME CONTAMINATED DURING STORAGE IN THE LABORATORY.

7.1.9 Sodium sulfite.

7.1.10 Solvents: Methylene chloride, hexane, acetone, toluene, iso-octane, petroleum ether, and methanol (optional) - pesticide quality or equivalent. It is recommended that each lot of solvent be analyzed to demonstrate that it is free of interference before use or must be purchased with certified that it is free of interference. Methylene chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.1.11 Sulfuric acid, concentrated, 95-98% (sp. gr. 1.84).

7.1.12 Tetrabutylammonium sulfite.

7.1.13 Glycerol

7.2 Standards

7.2.1 Stock Standard Solutions

7.2.1.1 Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be prepared in methylene chloride from pure standard materials, or purchased as pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated.

7.2.2 Working Standards

7.2.2.1 Individual Standard Mixtures

7.2.2.1.1 The Calibration Standard Mixture solutions must be prepared in either hexane or iso-octane. The analysis of the Resolution Check Mixture will determine whether one or two sets of Individual Standard Mixture solutions will be needed.

7.2.2.1.2 The suggested compositions of Individual Standard Mixture A and Mixture B are listed in Table 2 – Concentration Levels of Initial Calibration and Continuing Calibration Verification and Technical Acceptance Criteria for Pesticides, with the concentrations of each target compound and surrogate given for the low-point standard mixtures (CS1 Standard A and CS1 Standard B) in Table 4 – Low Concentration Calibration Standard (CS1) for Individual Standard Mixtures A and B. The CS1 Standard C for Individual Standard Mixture C will contain all target analytes and surrogates for both Mixture A and Mixture B at the same concentrations as the CS1 Standard for Mixture A and Mixture B.

7.2.2.1.3 Prepare calibration standards at a minimum of five concentration levels. The concentrations of the pesticides in the low-point standard mixtures (CS1) correspond to the low-point concentration (refer to Table 2 – Concentration Levels of Initial Calibration and Continuing Calibration Verification and Technical Acceptance Criteria for Pesticides) or lower for each analyte. The concentration for each analyte in the high-point standard must be at least 16 times the concentration of the low-point standard, but a higher concentration may be chosen by the Contractor provided that the higher concentration standards meet the technical acceptance criteria in Sections 9.3.5 and 9.4.5.

7.2.2.1.4 The concentration of each target analyte for each calibration standard are listed in Table 2 – Concentration Levels of Initial Calibration and Continuing Calibration Verification and Technical Acceptance Criteria for Pesticides. These levels are based upon 10 mL final volume extracts for samples not undergoing GPC cleanup, and 5.0 mL final volume extracts for those samples undergoing GPC cleanup.

7.2.2.1.5 Other concentration levels may be used for more sensitive instrumentation and final extract volumes. For example, in the case of alpha-BHC, a laboratory may use a final extract volume of 10 mL for samples undergoing GPC cleanup, and a low calibration standard of 2.5 nanograms (ng)/mL. The alternate calibration standards and final volumes may be used as long as the following requirements are met:

- The Contractor can demonstrate by Method Detection Limits (MDL) studies that the MDL study calculated MDL for each target analyte is below the required CRQL for that analyte when using the laboratory's specific final volume and calibration level scheme.
- All five calibration levels are in the same ratio as that shown in Table 2 – Concentration Levels of Initial Calibration and Continuing Calibration Verification and Technical Acceptance Criteria for Pesticides (e.g., if a laboratory were using a 2.5 ng/mL low standard, then the other calibration levels must be 5, 10, 20, and 40 ng/mL).

7.2.2.2 Toxaphene Standards

Prepare Toxaphene standard solutions at a minimum of five concentration levels. The Toxaphene standards must be prepared in hexane or iso-octane and contain the surrogates at the appropriate concentrations.

7.2.2.2.1 For CS1, the concentrations of tetrachloro-m-xylene and decachlorobiphenyl should be 5 and 10 ng/mL respectively.

7.2.2.2.2 The concentration of Toxaphene in the low-point standard (CS1) should be 500 ng/mL or lower. The concentration in the high-point standard (CS5) must be at least 16 times the low-point standard for Toxaphene, but a higher concentration may be chosen by the Contractor. For most operations, the calibration standards are to be prepared at 500, 1000, 2000, 4000, and 8000 ng/mL (for calibration standards and final volumes, see Section 7.2.2.1.2).

7.2.2.2.3 The low-point Toxaphene standard (CS1) in Section 7.2.2.2.2 shall be used as the single-point initial calibration standard. When Toxaphene is detected in a sample, a five-point toxaphene initial calibration must be initiated on the GC/ECD and the sample containing the Toxaphene must be reanalyzed.

7.2.2.3 Continuing Calibration Standard

7.2.2.3.1 The CCV Standards INDA and INDB or INDC should contain the target analytes and surrogates at or near the mid-point CS3 concentration of the Initial Calibration Standard (ICAL) (Table 2 - Concentration Levels of Initial Calibration and Continuing Calibration Verification and Technical Acceptance Criteria for Pesticides).

7.2.2.4 Instrument Performance Check Standards

7.2.2.4.1 Resolution Check Mixture

Prepare the Resolution Check Mixture containing the pesticides and surrogates listed in Table 3 – Instrument Performance Check Standards, in hexane or iso-octane at the concentrations specified. The mixture must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.5 Performance Evaluation Mixture

Prepare the Performance Evaluation Mixture (PEM) solution containing the pesticides and surrogates listed in Table 3 – Instrument Performance Check Standards, in hexane or iso-octane at the concentration specified. The PEM must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.6 Gel Permeation Chromatography Calibration and Calibration Verification Solutions

7.2.2.6.1 GPC Calibration Solution

Prepare a GPC calibration solution in methylene chloride that contains the following analytes at the minimum concentrations listed below. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Analyte	Concentration (mg/mL)
Corn oil (CAS # 8001-30-7)	25.0
Bis(2-ethylhexyl)phthalate (CAS # 117-81-7)	0.50
Methoxyclor (CAS # 72-43-5)	0.10
Perylene (CAS # 198-55-0)	0.020
Sulfur (CAS # 7704-34-9)	0.080

NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.2.2.6.2 GPC Calibration Verification Solution

Prepare the GPC calibration verification solution containing the pesticides listed in Table 7 – Concentration of Matrix Spike/Matrix Spike Duplicate Spiking, Laboratory Control Sample Spiking, and Gel Permeation Chromatography Verification Standard Solutions in methylene chloride at the concentrations specified for a 5 mL GPC injection loop. See Section 10.3.1.4.3 for analyte concentrations if a smaller size loop is being used. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.7 Florisil Cartridge Check Solution

Prepare a solution containing 2,4,5-trichlorophenol at 0.10 µg/mL in acetone. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.8 Surrogate Standard Spiking Solution

The surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added prior to sample processing to all standards, samples [including Laboratory Control Samples (LCSs)], Matrix Spike/Matrix Spike Duplicates (MS/MSD), Performance Evaluation (PE) samples (if required), and required blanks (method/sulfur cleanup/instrument). Prepare a surrogate spiking solution of 0.20 µg/mL for tetrachloro-m-xylene and 0.40 µg/mL for decachlorobiphenyl in acetone. The solution should be checked frequently for stability. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

NOTE: Other concentrations for surrogate standard spiking solutions may be used, provided that the appropriate amount of each surrogate is added to all standards, samples (including LCSs), MS/MSDs, PE samples, and blanks.

7.2.2.9 Matrix Spiking Solution

Prepare a matrix spiking solution containing the pesticides in Table 7 – Concentration of Matrix Spike/Matrix Spike Duplicate Spiking, Laboratory Control Sample Spiking, and Gel Permeation Chromatography Calibration Verification Standard Solutions in methanol at the concentrations specified. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.10 Laboratory Control Sample Spiking Solution

Prepare a LCS spiking solution containing the analytes as specified in Table 7 – Concentration of Matrix Spike/Matrix Spike Duplicate Spiking, Laboratory Control Sample Spiking, and Gel Permeation Chromatography Calibration Verification Standard Solutions in methanol. The LCS solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.3 Storage of Standards

7.2.3.1 Store the stock standard solutions at ≤ 6°C, but not frozen, in PTFE-lined, screw-cap, amber bottles/vials.

7.2.3.2 The working standards must be prepared every 6 months, or sooner if the solutions have degraded or concentrated. The working standards must be checked frequently for signs of degradation or evaporation. Store the working standard solutions at ≤ 6°C in PTFE-lined screw-cap, amber bottles/vials.

NOTE: Refrigeration of GPC calibration solutions may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves. Replace this calibration solution every 6 months, or more frequently if necessary.

7.2.3.3 Standard solutions purchased from a chemical supply company as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer’s expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from the preparation date. The expiration date of the ampulated standards, upon the breaking of the glass seal, is 6 months, or sooner if the standard has degraded or evaporated.

7.2.3.4 Protect all standards from light.

7.2.3.5 Samples, sample extracts, and standards must be stored separately.

7.2.3.6 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. Storage of standard solutions in the freezer may cause some compounds to precipitate. This means at a minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

7.2.4 Temperature Records for Storage of Standards

7.2.4.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.

7.2.4.2 Temperature excursions shall be noted and appropriate corrective actions shall be taken to correct problems, when required.

7.2.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples

Water samples may be collected in 1 L (or 1 quart) amber glass containers, fitted with PTFE-lined screw-caps. If amber containers are not available, the samples should be protected from light.

8.1.2 Soil/Sediment Samples

Soil/sediment samples may be collected in glass containers.

8.2 Procedure for Sample and Sample Extract Storage

8.2.1 Sample Storage

The samples must be protected from light and refrigerated at ≤ 6°C, but not frozen from the time of receipt until 60 days after delivery of a complete, reconciled data package to the EPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 Sample Extract Storage

Sample extracts must be protected from light and stored at ≤6 °C, but not frozen until 365 days after delivery of a complete, reconciled data package to the EPA.

8.3 Contract Required Holding Times

8.3.1 Extraction of water samples by separatory funnel procedures must be completed within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of water samples by continuous liquid-liquid extraction must be started within 5 days of VTSR. Extraction of the Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP)/leachate shall begin within 7 days of completion of leaching procedure (see Exhibit D – General Organic Analysis). Extraction of soil/sediment samples shall be completed within 10 days of VTSR.

8.3.2 Analysis of sample extracts must be completed within 40 days following the start of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Initial Instrument Set-up

9.1.1 Gas Chromatograph

9.1.1.1 The GC analytical conditions are provided in Table 6 – Gas Chromatograph Analytical Conditions. Other conditions may be used, provided that all technical acceptance criteria in Sections 9.3.5, 9.4.5, and 11.3 are met.

9.1.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples (including LCS and MS/MSD), and required blanks (method/sulfur cleanup/instrument).

9.1.1.3 The same injection volume, 1.0 or 2.0 µL, must be used for all standards, samples (including LCS and MS/MSD), and required blanks (method/sulfur cleanup/instrument).

9.1.1.4 The linearity of the ECD may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

9.1.1.5 Cold (ambient temperature) on-column injectors that allow injection directly onto a 0.53 mm ID column may be used as long as the initial calibration and calibration verification technical acceptance criteria are met.

9.2 Instrument Performance Check

The instrument performance checks include the Resolution Check Standard (RESC), and the PEM, which are incorporated into the calibration procedures below. Target analyte resolution and stability are verified by the analysis of these instrument performance checks.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to analysis of samples (including LCS and MS/MSD) and required blanks (method/sulfur cleanup/instrument), each GC/ECD system must be calibrated at a minimum of five concentrations for single component analytes and surrogates, in order to determine instrument sensitivity and the linearity of GC response. For Toxaphene detected using a single-point calibration, a reanalysis of the sample is required after a five-point calibration.

9.3.2 Frequency of Initial Calibration

Each GC/ECD system must be calibrated prior to analyzing samples, after major instrument maintenance or modification is performed (e.g., column replacement or repair, cleaning or replacement of ECD, etc.), or if the CCV technical acceptance criteria have not been met.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Set up the GC/ECD system as described in Section 9.1. Optimize the instrumental conditions for resolution of the target analytes and sensitivity.

NOTE: Once the GC conditions have been established, the same operating conditions must be used for both calibrations and sample analyses.

9.3.3.2 Prepare the initial calibration standards using the procedures, analytes, and concentrations specified in Section 7.2.2.

9.3.3.3 All standards and instrument blanks must be allowed to warm to ambient temperature before analysis.

9.3.3.4 The initial calibration sequence shall begin with a Resolution Check Mixture, followed by a PEM. The sequence shall end with analysis of an Instrument Blank, followed immediately with a PEM. The appropriate calibration sequence is determined by the results of the Resolution Check Mixture (Section 9.3.4 and 9.3.5.2). All steps pertaining to the initial calibration sequence shall be performed uninterrupted with no more than the length of one chromatographic run separating any step. When mis-injection occurs during the initial calibration procedures, the laboratory is allowed to perform re-injection as long as it is within the 12-hour period.

NOTE: The steps pertaining to Instrument Blank and PEM are used as part of the continuing calibration verification as well (Section 9.4).

9.3.3.5 Choose the appropriate initial calibration sequence below (Sequence 1 or 2). If two Individual Standard Mixtures are used, choose Initial Calibration Sequence 2. The appropriate calibration sequence is determined by the results of the Resolution Check Mixture (Section 9.3.4). A single-point Toxaphene calibration at low standard shall be included in the initial calibration at a minimum. Optionally, all five-point initial calibration standards may be included in the initial calibration as in Sequence 1 or 2.

INITIAL CALIBRATION SEQUENCE 1

1. Resolution Check
2. PEM
3. Toxaphene CS1
4. Toxaphene CS2
5. Toxaphene CS3
6. Toxaphene CS4
7. Toxaphene CS5
8. CS1 Individual Standard Mixture C
9. CS2 Individual Standard Mixture C
10. CS3 Individual Standard Mixture C
11. CS4 Individual Standard Mixture C
12. CS5 Individual Standard Mixture C
13. Instrument Blank
14. PEM

INITIAL CALIBRATION SEQUENCE 2

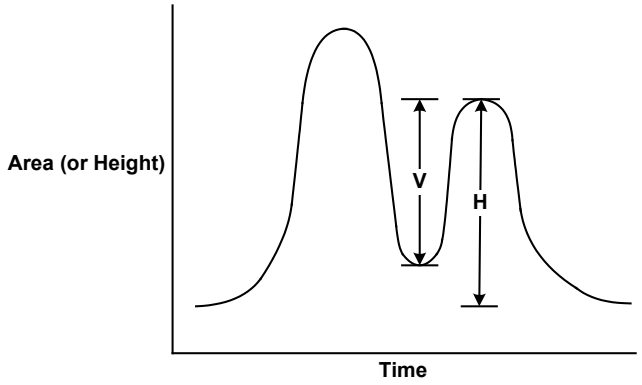
1. Resolution Check
2. PEM
3. Toxaphene CS1
4. Toxaphene CS2

5. Toxaphene CS3
6. Toxaphene CS4
7. Toxaphene CS5
8. CS1 Individual Standard Mixture A
9. CS1 Individual Standard Mixture B
10. CS2 Individual Standard Mixture A
11. CS2 Individual Standard Mixture B
12. CS3 Individual Standard Mixture A
13. CS3 Individual Standard Mixture B
14. CS4 Individual Standard Mixture A
15. CS4 Individual Standard Mixture B
16. CS5 Individual Standard Mixture A
17. CS5 Individual Standard Mixture B
18. Instrument Blank
19. PEM

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the resolution between the analytes in the Resolution Check Mixture, PEM, and CS3 Standard concentrations of the Individual Standard Mixtures using Equation 1.

Figure 1. Peak Height and Valley



EQ. 1 Percent Resolution

$$\%\text{Resolution} = \frac{V}{H} \times 100$$

WHERE,

V = Depth of the valley between the two peaks. The depth of the valley is measured along a vertical line from the level of the apex of the shorter peak to the floor of the valley between the two peaks.

H = Height of the shorter of the adjacent peaks

9.3.4.2 During the initial calibration sequence, absolute $\overline{RT}$s are determined for all single component pesticides, surrogates, and five major peaks of Toxaphene for both columns.

9.3.4.3 For each single component pesticide, an RT is measured in each of the five calibration standards for all Individual Standard Mixtures A and B and Individual Standard Mixture C. If Toxaphene is performed using a single-point calibration, use the RT for each peak from this standard. For Toxaphene five-point calibrations, an RT is measured in each of the five calibration standards for the major peaks. The mean absolute $\overline{RT}$ is calculated for each single component pesticide, surrogate, and Toxaphene as the average of the five values. Calculate $\overline{RT}$ for each single component pesticide, surrogate, and Toxaphene using the following equation:

EQ. 2 Mean Absolute Retention Time

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

WHERE,
RT_i = Retention Time of analyte
n = Total number of measurements (n=5)

9.3.4.4 An RT window is calculated for each single component analyte and surrogate and for the five major peaks of Toxaphene using Table 5 – Retention Time Windows for Single Component Analytes, Toxaphene, and Surrogates. The $\overline{RT}$s for surrogates are calculated from the five analyses of the Individual Standard Mixtures. If two Individual Standard Mixtures are used, calculate the $\overline{RT}$s for the surrogates from the Individual Standard Mixture A only. Windows are centered around the $\overline{RT}$ for the analyte established during the initial calibration. Compounds are identified when peaks are observed in the RT window for the compound on both GC columns.

9.3.4.5 Calculate the Calibration Factors (CFs) for each single component pesticide and surrogates over the initial calibration range using Equation 3. The CFs for surrogates are calculated from the five analyses of the Individual Standard Mixtures. If two Individual Standard Mixtures are used, calculate the CFs for surrogates from Individual Standard Mixture A only. Either peak area or peak height may be used to calculate the CFs using Equation 6.

9.3.4.5.1 For example, it is permitted to calculate the CF for Endrin based on peak area and to calculate CF for Aldrin based on peak height. It is not permitted to calculate CFs for an analyte from both peak area and peak height. For example, it is not permitted to calculate the CFs for the CS1 Standard for Endrin using peak height and calculate the CS3 and CS5 Standard CFs for Endrin using peak area.

EQ. 3 Calibration Factor

$$CF = \frac{\text{Peak area (or Peak height) of the standard}}{\text{Mass Injected (ng)}}$$

9.3.4.6 Calculate the Mean CF ($\overline{CF}$) and the %RSD of the CF for each single component pesticide and surrogate over the initial calibration range using Equations 4 and 6.

EQ. 4 Mean Calibration Factor

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

WHERE,

CF_i = Calibration Factor

n = Total number of values (n=5)

9.3.4.7 The linearity of the instrument is determined by calculating a %RSD of the CFs from a five-point calibration curve for each of the single component pesticides and surrogates using Equations 5 and 6.

EQ 5. Standard Deviation of Calibration Factors

$$SD_{CF} = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{(n-1)}}$$

WHERE,

CF_i, $\overline{CF}$, n = As given in EQ. 4

EQ. 6 Percent Relative Standard Deviation of the Calibration Factors

$$\%RSD = \frac{SD_{CF}}{\overline{CF}} \times 100$$

WHERE,

SD_{CF} = Standard Deviation of Calibration Factors

CF_i, $\overline{CF}$, n = As given in EQ. 4

9.3.4.8 Toxaphene shall be calibrated at a single low-point CS1 for pattern recognition. The Toxaphene standard may be analyzed before or after the analysis of the five levels of the single component pesticides standards during the initial calibration. A CF is calculated for each peak in a selected set of five major peaks for Toxaphene using Equation 3.

9.3.4.9 If Toxaphene is detected in a sample analysis following a single-point initial calibration, a separate five-point Toxaphene calibration must be prepared (Section 7.2.2.2) and analyzed, followed by a reanalysis of the sample. A CF is calculated for each peak in a selected set of five major peaks for Toxaphene using Equation 3. The $\overline{CF}$ and the %RSD of the CFs for each selected Toxaphene peak are calculated using Equations 4 and 6. When Toxaphene is detected in any sample without a valid five-point calibration during initial calibration, Toxaphene results are calculated by the single-point CFs. Subsequently, the sample must be reanalyzed following a valid five-point calibration of Toxaphene.

9.3.4.10 Calculate the Percent Breakdown (%Breakdown) of DDT, the Percent Breakdown of Endrin, and the combined breakdown of DDT and Endrin in the PEM using Equations 7, 8, 9, and 10.

EQ. 7 Amount Found

$$\text{Amount found (ng)} = \frac{\text{Peak area (or peak height) of compound in PEM}}{\overline{CF}}$$

WHERE,

$\overline{CF}$ = Mean Calibration Factor from the initial calibration (area/ng)

EQ. 8 Percent Breakdown of DDT

$$\%\text{Breakdown DDT} = \frac{\text{Amount found (ng) (DDD + DDE)}}{\text{Amount (ng) of DDT injected}} \times 100$$

EQ. 9 Percent Breakdown of Endrin

$$\%\text{Breakdown Endrin} = \frac{\text{Amount found (ng) (Endrin Aldehyde + Endrin Ketone)}}{\text{Amount (ng) of Endrin injected}} \times 100$$

EQ. 10 Combined Percent Breakdown of DDT and Endrin

Combined %Breakdown = %Breakdown DDT + %Breakdown Endrin

9.3.4.11 Calculate the Percent Difference (%D) between the calculated and nominal concentrations of each pesticide and surrogate in the PEM using Equations 7 and 11.

EQ. 11 Percent Difference Between the Calculated and Nominal Amount

$$\%D = \frac{C_{calc} - C_{nom}}{C_{nom}} \times 100$$

WHERE,

C_{calc} = Calculated amount of each analyte from the analysis of the standard [Amount found (ng) in EQ. 7]

C_{nom} = Nominal amount of each analyte

9.3.5 Technical Acceptance Criteria for Initial Calibration

All initial calibration technical acceptance criteria apply independently to each GC column.

9.3.5.1 The initial calibration sequence must be analyzed according to the procedure and in the order listed in Section 9.3.3, at the concentrations listed in Section 7.2.2, and at the frequency listed in Section 9.3.2. The GC/ECD operating conditions optimized in Section 9.1 must be followed.

9.3.5.2 The identification of single component pesticides by GC methods is based primarily on RT data. The RT of the apex of a peak can only be verified from an on-scale chromatogram. The identification of Toxaphene by GC methods is based primarily on recognition of patterns of RTs displayed on a chromatogram.

Therefore, the following requirements apply to all data presented for single component and Toxaphene.

9.3.5.2.1 The chromatograms of the Resolution Check Mixture, the PEM, and the Individual Standard Mixtures analyzed during the initial calibration sequence must display the single component analytes present in each standard at greater than 10% of full scale, but less than 100% of full scale.

9.3.5.2.2 The chromatograms for at least one of the five analyses of each Individual Standard Mixture from the initial calibration sequence must display the single component analytes at greater than 50% of full scale, but less than 100% of full scale.

9.3.5.2.3 For all Resolution Check Mixtures, PEMs, Individual Standard Mixtures, and blanks, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

9.3.5.2.4 If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

9.3.5.3 The resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 80% for all analytes for the primary column and greater than or equal to 50% for the confirmation column in order to use one Individual Standard Mixture (C). If two Individual Standard Mixtures (A and B) are to be used, then the resolution between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60% for both GC columns.

9.3.5.4 All single component pesticides and surrogates in both analyses of the PEM must be greater than or equal to 90% resolved on each column.

9.3.5.5 The absolute RTs of each of the single component pesticides and surrogates in both analyses of the PEM must be within the RT window determined from the five-point initial calibration in Sections 9.3.4.2 and 9.3.4.3.

9.3.5.6 If Individual Standard Mixture (C) is used, then the resolution between any two adjacent peaks in the CS3 Individual Standard Mixture C must be at least 80% for the primary column and 50% for the confirmation column. If two Individual Standard Mixtures (A and B) are used, then the resolution between any two adjacent peaks in the CS3 Individual Standard Mixtures (A and B) must be greater than or equal to 90% on both columns.

9.3.5.7 The %D between the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in both of the PEM analyses on each GC column must be in the inclusive range of ±25.0% when calculated using Equation 11.

9.3.5.8 The %Breakdown of DDT and Endrin in each of the PEM analyses must be ≤ 20.0% calculated using Equations 8 and 9. The combined %Breakdown of DDT and Endrin must be ≤ 30.0% calculated using Equation 10.

9.3.5.9 The %RSD of the CFs for each single component target analyte must be ≤ 20.0%, except alpha-BHC and delta-BHC. The %RSD of the CFs for alpha-BHC and delta-BHC must be ≤ 25.0%. The %RSD of the CFs

for the two surrogates must be ≤20.0%. Up to two single component target analytes (not surrogates) per column may exceed the maximum %RSD of 20.0% (25.0% for alpha-BHC and delta-BHC), but those analytes must have a %RSD of less than or equal to 30.0%. The %RSD of the CFs for Toxaphene five-point calibration must be less than or equal to 30.0%.

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, reinject the initial calibration standards in sequence. If the technical acceptance criteria for the initial calibration are still not met, inspect the system for problems. It may be necessary to change the column, bake-out the detector, clean the injection port, or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 Contamination should be suspected as a cause if the detector cannot achieve acceptable linearity using this method. It is recommended to refer to manufacturer's guidelines for performing detector maintenance. In the case of severe contamination, the detector may require servicing by the ECD manufacturer.

CAUTION: DO NOT OPEN THE DETECTOR. THE ECD CONTAINS RADIOCHEMICAL SOURCES.

9.3.6.3 After major maintenance is completed, the detector must be recalibrated using the initial calibration sequence.

9.3.6.4 Any samples or required blanks analyzed when the initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Continuing Calibration Verification

Three types of analyses are used to verify the calibration and evaluate instrument performance: instrument blanks, PEMs, and the CS3 Standards. A calibration verification consists of an instrument blank and PEM, or an instrument blank and the CS3 Individual Standard Mixture(s), and a CS3 Toxaphene Standard (if necessary). Sample (including LCS and MS/MSD) and required blank (method/sulfur cleanup) data are not acceptable unless bracketed by acceptable analyses of instrument blanks, PEMs, and CS3 Standards. When Toxaphene is detected in sample analyses during the analytical sequence that includes a five-point Toxaphene calibration, the closing CCV must include the CS3 Toxaphene Standard.

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 An instrument blank and the PEM must bracket one end of a 12-hour period during which sample and required blank data are collected, and a second instrument blank and the CS3 Individual Standard Mixture(s) must bracket the other end of the 12-hour period. If Individual Standard Mixtures A and B were used in the associated initial calibration sequence, then CS3 Individual Standard Mixtures A and B must be used for the calibration verification. If Individual Standard Mixture C was used in the associated initial calibration sequence, then CS3 Individual Standard Mixture C must be used in the calibration verification.

9.4.2.2 For the 12-hour period immediately following the initial calibration sequence, the instrument blank and the PEM that are the last two steps in the initial calibration sequence that bracket the front end of that 12-hour period. The injection of the instrument blank starts the beginning of the 12-hour period (Section 9.3.3.4). Samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup) may be injected during the 12 hours from the injection of the instrument blank. The first injections immediately after that 12-hour period must be an instrument blank and the CS3 Individual Standard Mixture(s). The instrument blank must be analyzed first, before the standard(s). If two Individual Standard Mixtures are used, they may be analyzed in either order (A, B or B, A).

9.4.2.3 The analyses of the instrument blank and CS3 Individual Standard Mixture(s) immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided that they meet the technical acceptance criteria in Section 9.4.5. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a PEM, in that order. Those two analyses may in turn be used to bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks, PEMs, or Individual Standard Mixture(s) fails to meet the technical acceptance criteria in Section 9.4.5. The 12-hour period begins with the injection of the instrument blank.

9.4.2.4 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an acceptable instrument blank and PEM must be analyzed to start a new sequence. This requirement applies even if no analyses were performed since that standard was injected.

9.4.2.5 If the entire 12-hour period is not required for the analyses of all samples and blanks to be reported and all data collection is to be stopped, the sequence must be ended with either the instrument blank/PEM combination or the instrument blank/CS3 Individual Standard Mixture(s) combination, whichever was due to be performed at the end of the 12-hour period. For Toxaphene analyses under a five-point calibration, the sequence must end with an instrument blank and a CS3 Toxaphene Standard.

9.4.2.6 No more than 14 hours may elapse from the injection beginning the opening CCV and the injection ending the closing CCV (PEM or CS3 Standard Mixture).

All acceptable samples must be analyzed within a valid analysis sequence as given below:

Time	Injection #	Material Injected
0 hr		Instrument Blank at end of initial calibration
		PEM at end of initial calibration
		First sample if using initial calibration
		Subsequent samples
		Last Sample

Time	Injection #	Material Injected
12 hrs	1st injection past 12 hours	Instrument blank
	Next injections past 12 hours	Individual Standard Mixtures A and B or **Individual Standard Mixture C**
		Sample
		Subsequent samples
		Last Sample
Another 12 hrs	1st injection past 12 hours	Instrument blank
	Next injection past 12 hours	PEM
		Sample
		Samples with Toxaphene detected
		Subsequent samples
		Last Sample
Another 12 hrs	1st injection past 12 hours	Instrument blank
	Next injections past 12 hours	Individual Standard Mixtures A and B or **Individual Standard Mixture C**
	Next injection past 12 hours	Toxaphene CS3

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 All standards and instrument blanks must be allowed to warm to ambient temperature before analysis.

9.4.3.2 Analyze the instrument blank, PEM, and the CS3 Individual Standard Mixture(s) according to Section 10.4.2 using the same injection volumes as in the initial calibration.

9.4.4 Calculations for Continuing Calibration Verification

9.4.4.1 For each analysis of the PEM used to demonstrate calibration verification, calculate the %D between the amount of each analyte (including the surrogates) found in the PEM and the nominal amount, using Equation 11.

9.4.4.2 For each analysis of the PEM used to demonstrate calibration verification, calculate the % Breakdown of Endrin and DDT, and the combined %Breakdown, using Equations 7, 8, 9, and 10.

9.4.4.3 For each analysis of the CS3 Individual Standard Mixture(s) or CS3 Toxaphene used to demonstrate calibration verification, calculate the %D between the CF of each analyte (including the surrogates) in the standard mixture and the corresponding $\overline{CF}$ from the initial calibration, using Equation 12. Do not calculate the breakdown of Endrin and DDT in the Individual Standard Mixtures, as these standards contain the breakdown products as well as the parent compounds.

EQ. 12 External Standard Calibration Percent Difference

$$\%D = \frac{CF-\overline{CF}}{\overline{CF}} \times 100$$

WHERE,

CF = Calibration Factor for CS3 Standard used for Calibration Verification

$\overline{CF}$ = Mean Calibration Factor

9.4.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.4.5.1 All CCV technical acceptance criteria apply independently to each GC column, and must meet the chromatographic criteria specified in Section 9.3.5.2.

9.4.5.2 The PEMs, CS3 Standards, and instrument blanks must be analyzed at the required frequency on a GC/ECD system that has met the initial calibration technical acceptance criteria.

9.4.5.3 All single component pesticides and surrogates in the PEMs used to demonstrate calibration verification must be greater than or equal to 90.0% resolved. If one Individual Standard Mixture is used, the resolution between any two adjacent peaks in the CS3 Individual Standard Mixture C must be at least 80% for the primary column and 50% for the confirmation column. If two Individual Standard Mixtures are used, the resolution between any two adjacent peaks in the CS3 Individual Standard Mixture A and B used to demonstrate calibration verification must be greater than or equal to 90.0% for both columns.

9.4.5.4 The absolute RT for each of the single component pesticides and surrogates in the PEMs and CS3 Standards used to demonstrate calibration verification must be within the RT windows determined from the five-point initial calibration in Sections 9.3.4.2 and 9.3.4.3.

9.4.5.5 The %D between the calculated amount (amount found) and the nominal amount (amount added) for each of the single component pesticides and surrogates in the PEM used to demonstrate calibration verification must not exceed ±25.0%.

9.4.5.6 The % Breakdown of 4,4'-DDT in the PEM must be less than or equal to 20.0% on each column. The % Breakdown of Endrin in the PEM must be less than or equal to 20.0% on each column. The combined %Breakdown of DDT and Endrin must be less than or equal to 30.0% on each column.

9.4.5.7 The %D between the CF of each of the single component pesticides and surrogates in the mid-point concentration of the Individual Standard Mixtures CS3 and the $\overline{CF}$ from the initial calibration must be in the inclusive range of ±25.0% and ±30.0%, respectively.

9.4.5.8 All instrument blanks must meet the technical acceptance criteria in Section 12.1.4.5.

9.4.5.9 A Toxaphene closing calibration verification standard (CS3) must be analyzed within a valid 12-hour analytical sequence including the reanalysis of samples in which Toxaphene was detected. The %D between the CF of each peak used to identify Toxaphene in the calibration verification standard and the $\overline{CF}$ from the initial calibration must not exceed ±25.0%.

9.4.6 Corrective Action for Continuing Calibration Verification

9.4.6.1 If the technical acceptance criteria for the CCV are not met, inspect the system for problems and take corrective action to achieve the technical acceptance criteria.

9.4.6.2 Major corrective actions, such as replacing the GC column or baking out the detector, will require that a new initial calibration be performed that meets the technical acceptance criteria in Section 9.3.5.

9.4.6.3 Minor corrective actions may not require performing a new initial calibration, provided that a new analysis of the standard (PEM or CS3 Standard) that originally failed the criteria and an associated instrument blank immediately after the corrective action do meet all the technical acceptance criteria.

9.4.6.4 If a PEM or CS3 Standard does not meet the technical acceptance criteria listed in Section 9.4.5, it must be re-injected immediately. If the second injection of the PEM or CS3 Standard meets the criteria, sample analysis may continue. If the second injection does not meet the criteria, all data collection must be stopped. Appropriate corrective action must be taken, and a new initial calibration sequence must be established before more sample data are collected.

9.4.6.5 If an instrument blank does not meet the technical acceptance criteria listed in Section 12.1.4.5, all data collection must be stopped. Appropriate corrective action must be taken to clean out the system, and an acceptable instrument blank must be analyzed before more sample data are collected.

9.4.6.6 The Contractor is reminded that analyzing an instrument blank and a PEM or CS3 Standard once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to analyze instrument blanks and standards more often to avoid discarding data.

9.4.6.7 If a successful instrument blank and PEM cannot be analyzed after an interruption in analysis (Section 9.4.2.6), an acceptable initial calibration must be established before sample data may be collected. All acceptable sample analyses (including LCSs and MS/MSDs) and required blank (method/sulfur cleanup) analyses must be preceded and followed by acceptable instrument blanks and standards as described in Section 9.4.2.

9.4.6.8 Any samples and required blanks associated with a CCV that do not meet the technical acceptance criteria will require reanalysis at no additional cost to the EPA.

10.0 PROCEDURE

The Contractor must have the capability to perform all sample cleanup procedures presented in this Exhibit. The Contractor may use any of the procedures or combinations of procedures to clean up the samples prior to analysis, unless the Contractor is specifically directed by the EPA Region to use a particular cleanup procedure or combination of cleanup procedures.

The Contractor must demonstrate that each cleanup procedure is capable of producing data that meets the technical acceptance criteria for the method, including MDLs (Section 12.4) and any precision and recovery limits.

10.1 Sample Preparation

10.1.1 Water and Leachate Samples

Water and leachate samples may be extracted by either a separatory funnel procedure or a continuous liquid-liquid extraction procedure. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, continuous liquid-liquid extraction must be employed. Allow the samples to warm to ambient temperature before extraction.

10.1.1.1 Separatory Funnel Extraction

10.1.1.1.1 For samples received in 1 L bottles, the Contractor shall mark the meniscus and transfer the entire sample into the separatory funnel. If the sample was not received in a 1 L bottle, measure out each 1.0 L sample aliquot in a separate graduated cylinder.

10.1.1.1.2 Measure and record the volume of sample contained in the 1 L sample bottle with water using a graduated cylinder.

10.1.1.1.3 Using a syringe or a volumetric pipette, add 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.8) to all water samples.

10.1.1.1.4 Measure and record the pH of the sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the SDG Narrative. Place the sample aliquot into a 2 L separatory funnel.

10.1.1.1.5 Rinse the 1 L sample bottle and/or graduated cylinder with 30 mL of methylene chloride and transfer the rinsate to the separatory funnel.

10.1.1.1.6 Add another 30 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure.

NOTE: The total volume of solvent used for extraction is 60 mL. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than 1/3 the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration through glass wool, centrifugation, or other physical means. Drain the methylene chloride into a 250 mL Erlenmeyer flask.

10.1.1.1.7 Add a second 60 mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Proceed to Section 10.2.

10.1.1.2 Continuous Liquid-Liquid Extraction

10.1.1.2.1 Continuous Liquid-Liquid Extraction without Hydrophobic Membrane

10.1.1.2.1.1 Follow the manufacturer's instructions for set-up.

10.1.1.2.1.2 Add 300-500 mL of methylene chloride to the bottom of the extractor and fill it to a depth of at least 1 inch above the bottom sidearm.

10.1.1.2.1.3 If the samples have been received in 1 L bottles, the Contractor shall mark the meniscus and transfer the entire sample into the continuous extractor. If the sample was not received in a 1 L bottle, measure out each 1.0 L sample aliquot in a separate, clean graduated cylinder and transfer the aliquot to the continuous extractor.

10.1.1.2.1.4 Using a syringe or volumetric pipette, add 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.8) into the sample and mix well. Perform spiking prior to pH adjustment or any other processing steps.

10.1.1.2.1.5 Measure the pH of the sample with wide range pH paper or a pH meter and record the pH. Adjust the pH to between 5 and with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring the pH adjustment must be noted in the SDG Narrative.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.1.2.1.6 Rinse the graduated cylinder with a small amount of methylene chloride and transfer the rinsate to the continuous extractor. If the sample container is empty, rinse the container with a small amount of methylene chloride and add the rinsate to the continuous extractor.

10.1.1.2.1.7 Add sufficient methylene chloride to the continuous liquid-liquid extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5-15 mL/minute (recommended); optimize the extraction drip rate. Extract for a <u>minimum</u> of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mL/minute is maintained throughout the extraction, the extraction time may be reduced to a <u>minimum</u> of 12 hours. Allow to cool, and then detach the distillation flask. Proceed to Section 10.2.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.1.2.2 Continuous Liquid-Liquid Extraction with Hydrophobic Membrane

10.1.1.2.2.1 Follow the procedure in Sections 10.1.1.2.1.1 - 10.1.1.2.1.5, but reduce the amount of methylene chloride used to 50 mL and extract for a minimum of 6 hours.

10.1.1.2.2.2 Add sufficient methylene chloride to the continuous liquid-liquid extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 6 hours.

10.1.1.2.2.3 Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion that will consume the solvent volume, preventing efficient extraction of the sample. When this occurs, add additional solvent to ensure efficient extraction of the sample, and extend the extraction time for a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

10.1.1.2.2.4 Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor. Using the hydrophobic membrane, it may not be necessary to dry the extract with sodium sulfate.

10.1.1.2.2.5 If low surrogate recoveries occur, ensure that: 1) the apparatus was properly assembled to prevent leaks, 2) the drip rate/solvent cycling was optimized, and 3) there was proper cooling for condensation of solvent. Document the problem and the corrective action.

10.1.1.2.2.6 Alternate continuous liquid-liquid extractor types that meet the requirements of the analytical method may also be used. If using alternate extractors or design types, follow the manufacturer's instructions for set-up. Optimize the extraction procedure.

10.1.2 Soil/Sediment Samples

Mix samples thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase.

10.1.2.1 Extraction of Soil/Sediment Samples

10.1.2.1.1 Three procedures are provided for the extraction of pesticide analytes from soil/sediment samples:

- ultrasonic extraction;
- Soxhlet extraction (automated and manual); and
- pressurized fluid extraction (PFE).

NOTE: All soil/sediment samples in a Case must be extracted by the same procedure.

10.1.2.1.2 For soil/sediment sample extractions, weigh 30-50 g of sample, to the nearest 0.1 g, into a 400 mL beaker. 30 g is ideal, as more sample may be used to compensate for high moisture content. If the system cannot accommodate 30 g of a sample, a smaller sample size may be used. The specified CRQLs must be met. Adjust the amount of solvents and standards added as necessary. Document the smaller sample size in the SDG Narrative along with all steps taken to ensure sample homogeneity.

10.1.2.1.3 Add 60 g of anhydrous powdered or granulated sodium sulfate, or add 30 g of Hydromatrix™, and mix well to produce a sandy texture. Additional drying agent may be added as needed.

NOTE: For samples extracted by the PFE procedure (Section 10.1.2.1.7) the use of sodium sulfate is not recommended.

10.1.2.1.4 Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.8) to the sample, then immediately add 100 mL of 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.1.2.1.5 for ultrasonic extraction, Section 10.1.2.1.6 for automated Soxhlet extraction, or Section 10.1.2.1.7 for pressurized fluid extraction. As applicable, follow the manufacturer's instructions for use of all extraction equipment.

10.1.2.1.5 Ultrasonic Extraction

10.1.2.1.5.1 Place the bottom surface of the tip of the 3/4-inch tapered disruptor horn about 1/2 inch below the surface of the solvent, but above the sediment layer. Do <u>not</u> use a microtip probe.

10.1.2.1.5.2 Sonicate for 3 minutes with output at full power with pulse on (pulsing energy as opposed to continuous), and percent duty cycle knob set at 50%.

NOTE: Refer to the manufacturer's instructions for appropriate output settings.

10.1.2.1.5.3 Transfer and filter extracts through Whatman No. 42 (or equivalent) filter paper using vacuum filtration or centrifuge and decant extraction solvent.

10.1.2.1.5.4 Repeat the extraction two more times with two additional 100 mL portions of 1:1 (v/v) acetone/methylene chloride. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula. Transfer the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.2.

10.1.2.1.6 [Automated] Soxhlet Extraction

The Contractor may use either automated or non-automated Soxhlet extraction. The following procedure is based on the use of a Soxtec HT-6 automated Soxhlet extraction system. When using a different system, refer to the instructions provided by the manufacturer for the appropriate procedure.

10.1.2.1.6.1 Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit. Press the "MAINS" button and observe that the switch lamp is now "ON". Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/minute to prevent solvent loss through the condensers.

10.1.2.1.6.2 Transfer the entire sample from the beaker (Section 10.1.2.1.2) to the thimble.

10.1.2.1.6.3 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

10.1.2.1.6.4 Insert the extraction cups containing boiling chips, and load each with an appropriate volume of 1:1 (v/v) acetone/methylene chloride. Using the cup holder, lower the locking handle and ensure that the safety catch engages. The cups are now clamped into position.

NOTE: The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

10.1.2.1.6.5 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.

10.1.2.1.6.6 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set timer for 60 minutes. Condenser valves are still open. Extract for the preset time. After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

10.1.2.1.6.7 When all but 2-5 mL of solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the cups with methylene chloride and add the rinsates to the glass tubes. Proceed to Section 10.2.

10.1.2.1.7 Pressurized Fluid Extraction

10.1.2.1.7.1 Transfer the entire sample from the beaker (Section 10.1.2.1.2) to an extraction cell of the appropriate size for the aliquot.

10.1.2.1.7.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.2.1.7.3 Place a pre-cleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 - 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

10.1.2.1.7.4 The following are recommended extraction conditions:

Oven temperature:	100°C
Pressure:	1500-2000 psi
Static time:	5 min. (after 5 min. pre-heat equilibration)
Flush volume:	60% of the cell volume
Nitrogen purge:	60 sec. at 150 psi (purge time may be extended for larger cells)
Static cycles:	1

10.1.2.1.7.5 Optimize the extraction conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice. An appropriate amount of 1:1 (v/v) acetone/methylene chloride should be used to achieve the conditions in Section 10.1.2.1.7.4.

10.1.2.1.7.6 Once established, the same pressure should be used for all samples in the same SDG.

10.1.2.1.7.7 Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete. Proceed to Section 10.2.

10.2 Extract Concentration

10.2.1 Concentration by Kuderna-Danish

10.2.1.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all target analytes listed in Exhibit C –Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits.

10.2.1.2 For water samples, transfer the extract to a K-D concentrator by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate.

10.2.1.3 For soil/sediment samples, directly transfer the extract to the K-D concentrator, if the extract is known to be dry.

10.2.1.4 Rinse the original container collecting the extract (for both water and soil/sediment samples) and the column (for water samples) with at least two 20-30 mL portions of methylene chloride to complete the quantitative transfer.

10.2.1.5 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the

concentration in 15-30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-5 mL for water samples (and less than 10 mL for soil/sediment samples), remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.2.1.6 For water extracts that do not require GPC cleanup, and for water and soil/sediment extracts that have been through the GPC cleanup step, proceed with the hexane exchange described in Section 10.2.2.

10.2.1.7 For water extracts that require GPC cleanup, remove the Snyder column, rinse the flask and its lower joint, collect the rinsate in the concentrator tube, and adjust the volume to 10 mL with methylene chloride. Proceed to Section 10.3.1.

10.2.1.8 For soil/sediment extracts that have not been cleaned-up using GPC, it is absolutely necessary to further reduce the volume of all soil/sediment extracts to 1 mL in order to remove most of the acetone. This is best accomplished using the nitrogen evaporation technique (Section 10.2.3.2). The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause loss of surrogates and analytes during GPC cleanups. Adjust the soil/sediment extract volume to 10 mL with methylene chloride. Proceed to Section 10.3.1 for mandatory GPC.

10.2.2 Solvent Exchange into Hexane

This procedure applies to both extracts of water samples and extracts of soil/sediment samples.

10.2.2.1 With the extract in a K-D apparatus, remove the Snyder column, add 50 mL of hexane and a new boiling chip, and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as described previously (Section 10.2.1), but increase the temperature of the water bath (80-90°C is recommended) to maintain proper distillation. When the apparent volume of liquid reaches 3-5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.2.2.2 Remove the Snyder column. Using 1-2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Complete quantitative transfer of the extract to a 10 mL vial by using hexane.

10.2.2.3 For samples that have <u>not</u> been subjected to GPC cleanup, adjust the volume of the hexane extract to 10 mL. For samples that <u>have</u> been subjected to GPC cleanup, concentrate the hexane extract to 5.0 mL using a Micro Snyder Column or nitrogen evaporation, as described in Section 10.2.3.1 or 10.2.3.2, then proceed to Section 10.3.2 for Florisil cartridge cleanup.

10.2.3 Final Concentration of Extract

Two different techniques are permitted to concentrate the extract to volume before Florisil cleanup or instrumental analysis. They are the Micro Snyder Column and the Nitrogen Evaporation Technique.

10.2.3.1 Micro Snyder Column Concentration

10.2.3.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two-ball Micro Snyder Column. Pre-wet the Snyder column by adding about 0.5 mL of hexane to the top of

the column. Place the K-D apparatus in a hot water bath (80-90°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and lower joint into the concentrator tube with 0.2 mL of hexane.

10.2.3.1.2 If GPC cleanup is needed and not yet performed, adjust the volume to 10 mL with methylene chloride and proceed to Section 10.3.1 for GPC cleanup. For water samples that do not require GPC cleanup, adjust the volume to 10 mL with hexane and proceed to Section 10.3.2 for Florisil cleanup. For soil/sediment samples that have already undergone GPC cleanup, adjust the volume with hexane to 5.0 mL and proceed to Section 10.3.2 for Florisil cleanup. If no further cleanup is needed, adjust the volume with hexane to the same volume of the aliquot used for Florisil and/or sulfur cleanup (1 or 2 mL) and proceed to Section 10.4 for GC/ECD analysis. Extracts may be stored at ≤6°C, but not frozen, prior to analysis.

10.2.3.2 Nitrogen Evaporation Technique

10.2.3.2.1 Place the concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to the final volume using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). DO NOT ALLOW THE EXTRACT TO GO DRY.

10.2.3.2.2 If GPC cleanup is needed and not yet performed, adjust the volume to 10 mL with methylene chloride and proceed to Section 10.3.1 for GPC cleanup. For water samples that do not require GPC cleanup, adjust the volume to 10 mL with hexane and proceed to Section 10.3.2 for Florisil cleanup. For soil/sediment samples that have already undergone GPC cleanup, adjust the volume with hexane to 5.0 mL and proceed to Section 10.3.2 for Florisil cleanup. If no further clean-up is needed, adjust the volume with hexane to the same volume of the aliquot used for Florisil and/or sulfur clean-up (1.0 or 2.0 mL) and proceed to Section 10.4 for GC/ECD analysis. Extracts may be stored at ≤6°C, but not frozen, prior to analysis.

10.2.3.2.3 Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or PTFE tubing. Plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane and then dried prior to use.

10.3 Cleanup Procedures

There are three cleanup procedures specified in this method: GPC, Florisil cartridge cleanup, and sulfur cleanup. GPC must be performed for all soil/sediment extracts. GPC may be performed for water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. Florisil cartridge

clean-up is mandatory for all extracts. Sulfur clean-up must be performed for all sample extracts contaminated with sulfur. Method blanks must be subjected to the same cleanup procedures as the samples (including LCSs and MS/MSDs).

10.3.1 Gel Permeation Chromatography

10.3.1.1 Introduction

GPC is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the size of the molecules to be separated.

10.3.1.2 GPC Column Preparation

Prepare the GPC column using Bio Beads. Alternate column packings may be used if: 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration and GPC calibration checks, and 2) the column packings do not introduce contaminants/artifacts into the sample that interfere with the analysis of the pesticide analytes. Follow the manufacturer's instructions for preparation of the GPC column.

10.3.1.3 Calibration of GPC

10.3.1.3.1 Summary of GPC Calibration

The GPC calibration procedure is based on monitoring the elution of standards with an UV detector connected to the GPC column.

10.3.1.3.2 Frequency of GPC Calibration

Each GPC system must be calibrated prior to processing samples under the contract; when the GPC CCV solution fails to meet criteria (Section 10.3.1.3.4), when the column is changed, when channeling occurs, and once every 7 days when in use. Also, the RT shift must be less than 5% when compared to RTs in the last calibration UV traces.

10.3.1.3.3 Procedure for GPC Calibration

Follow the manufacturer's instructions for operating the GPC system. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte RTs and must be monitored.

10.3.1.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.2.6) onto the GPC. Determine the elution times for bis(2-ethylhexyl)phthalate, methoxychlor, and perylene. Bis(2-ethylhexyl)phthalate will elute first; perylene will elute last.

10.3.1.3.3.2 Choose a "DUMP" time that removes greater than 85% of the phthalate. Choose a "COLLECT" time so that greater than 95% of the methoxychlor is collected, and continue to collect until just prior to the elution time of sulfur. Use a "WASH" time of 10 minutes.

NOTE: The "DUMP" and "COLLECT" times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask.

10.3.1.3.3.3 Reinject the calibration solution after appropriate "COLLECT" and "DUMP" cycles have been set, and the solvent flow and column pressure have been established.

10.3.1.3.3.4 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

10.3.1.3.3.5 Analyze a GPC blank of methylene chloride. Concentrate the methylene chloride that passed through the system during the "COLLECT" cycle using a K-D evaporator. Exchange the solvent to hexane and analyze the concentrate by GC/ECD according to the usual protocol. Assuming that the blank represents the extract from a 1 L water sample, calculate the analyte concentrations using Equation 14.

10.3.1.3.4 Technical Acceptance Criteria for GPC Calibration

10.3.1.3.4.1 The GPC system must be calibrated at the frequency described in Section 10.3.1.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution;
- Corn oil and phthalate peaks should exhibit greater than 85% resolution;
- Phthalate and methoxychlor peaks should exhibit greater than 85% resolution;
- Methoxychlor and perylene peaks should exhibit greater than 85% resolution; and
- Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.

10.3.1.3.4.2 The solvent flow rate and column pressure must be within the manufacturer's specified ranges.

10.3.1.3.4.3 The RTs for Bis(2-ethylhexyl) phthalate and perylene must not vary more than ±5% between calibrations. Excessive RT shifts are caused by the following:

- Poor laboratory temperature control or system leaks;
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight; and/or
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.3.1.3.4.4 The analyte concentrations in a GPC blank must be less than the CRQL for all target analytes in Exhibit C –Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits.

10.3.1.3.4.5 A copy of the two most recent UV traces of the calibration solution must be submitted with the data for the associated samples.

10.3.1.3.5 Corrective Action for GPC Calibration

10.3.1.3.5.1 If the flow rate and/or column pressure do not fall within the manufacturer's specified ranges, a new column should be prepared.

10.3.1.3.5.2 A UV trace that does not meet the criteria in Section 10.3.1.3.4 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

10.3.1.3.5.3 If the GPC blank exceeds the requirements in Section 10.3.1.3.4.4, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.3.1.4 GPC Calibration Verification

10.3.1.4.1 Summary of GPC Calibration Verification

The GPC calibration must be routinely verified with the calibration verification check mixture (Section 7.2.2.6.2).

10.3.1.4.2 Frequency of GPC Calibration Verification

10.3.1.4.2.1 The calibration verification must be performed at least once every 7 days (immediately following the GPC Calibration) whenever samples (including MS/MSDs and blanks) are cleaned up using the GPC.

10.3.1.4.2.2 Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore, system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration must be checked not less than once every 7 days.

10.3.1.4.3 Procedure for GPC Calibration Verification

The instructions below are for a GPC injection loop of 5 mL. If a 2 mL injection loop is used, the Contractor should adjust the volume to 4 mL instead of 10 mL before the injection of the extract on the GPC.

10.3.1.4.3.1 The GPC calibration verification solution contains gamma-BHC (Lindane), Heptachlor, Aldrin, and 4,4'-DDT, Endrin, and Dieldrin in methylene chloride at the concentrations in Table 7 – Concentration of Matrix Spike/Matrix Spike Duplicate Spiking, Laboratory Control Sample Spiking, and Gel Permeation Chromatography Calibration Verification Standard Solutions.

10.3.1.4.3.2 Load the 5 mL sample loop by using a 10 mL syringe containing at least 8 mL of the GPC calibration verification solution. Fractions are collected in an auto-sequence by using the GPC program established by the UV detector calibration procedure (Section 10.3.1.3).

10.3.1.4.3.3 The collected GPC calibration verification fraction is transferred to a K-D apparatus, and the collection vessel is rinsed with two additional 10 mL portions of methylene chloride to complete the transfer. The volume of methylene chloride is reduced according to Section 10.2.1. After cooling, the solvent is exchanged to hexane according to the instructions in Section 10.2.2. The final volume is

adjusted to 10 mL, and the sample is analyzed by GC according to the procedure in Section 10.4. The analysis must be performed on only one of the GC columns used for sample analysis.

10.3.1.4.3.4 The recovery of each analyte must be determined for evaluation and reporting purposes. Calculate the Percent Recovery (%R) of each analyte using Equation 13 in Section 10.3.2.2.3.

10.3.1.4.4 Technical Acceptance Criteria for GPC Calibration Verification

The recovery of each of the analytes must be between 80-120%.

10.3.1.4.5 Corrective Action for GPC Calibration Verification

The Contractor may continue to use the GPC column if the technical acceptance criteria for the GPC calibration verification are met. If the recoveries are out of the acceptance criteria, the columns must be replaced and the GPC recalibrated according to the instructions in Section 10.3.1.3 before proceeding with any GPC cleanup on samples (including LCSs and MS/MSDs) and required method blanks.

10.3.1.5 Daily Ultraviolet Calibration Check (Optional)

The calibration of the GPC may be monitored daily by use of the UV-GPC calibration solution (Section 7.2.2.6) and the UV detector calibration procedure (Section 10.3.1.3). The UV detector should be used to monitor the elution times for the phthalate, methoxychlor, and perylene, in that order. The precalibrated GPC program should "DUMP" greater than 85% of the phthalate and should "COLLECT" greater than 95% of the methoxychlor and perylene. Significant changes in elution times of the analytes (e.g., greater than 30 seconds) indicate that the column is out of calibration and must be recalibrated or replaced.

10.3.1.6 Sample Extract Cleanup by GPC

10.3.1.6.1 Summary of GPC Cleanup

10.3.1.6.1.1 It is very important to have consistent laboratory temperatures during an entire GPC analysis, which could be 24 hours or more. If temperatures are not consistent, RTs will shift, and the "DUMP" and "COLLECT" times determined by the calibration standard will no longer will be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C.

10.3.1.6.1.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of 1:1 (v/v) glycerol/water solution must be diluted and loaded into several loops. Similarly, extracts containing more than the manufacturer recommended non-volatile residue must be diluted and loaded into several loops. The non-volatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or another suitable container.

10.3.1.6.1.3 Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is injected onto the column. Viscous extracts or extracts containing large amounts of non-volatile residue will cause problems with injecting the

proper amount of sample extract onto the column using automated injection systems. After the sample extract has been processed, the remaining sample extract in an injection vial must be checked to assure that the proper amount of extract was injected on the column before proceeding with the extract cleanup. If the proper amount of extract was not injected, the sample must be reprepared at no additional cost to the EPA, and the sample extract must be either diluted and loaded into several loops, or the sample extract must be injected manually.

10.3.1.6.2 Frequency of Sample Extract Cleanup by GPC

GPC cleanup must be performed at least once for each soil/sediment extract that contains high molecular weight contaminants that interfere with the analysis of the target analytes. All associated QC samples (blanks, LCSs, and MS/MSDs) must be subjected to this procedure. GPC cleanup on the method blank must be performed after all associated samples have been cleaned up (GPC sequence: calibration, sample 1, sample 2, etc., method blank, calibration verification).

10.3.1.6.3 Procedure for Sample Extract Cleanup by GPC

10.3.1.6.3.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 mL culture tube with a PTFE-lined screw-cap).

10.3.1.6.3.2 Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

NOTE 1: Some GPC instrument manufacturers recommend using a smaller micron size filter disc. Follow the manufacturer’s recommended operating instructions.

NOTE 2: INTRODUCTION OF PARTICULATES OR GLASS WOOL INTO THE GPC SWITCHING VALVES MAY REQUIRE FACTORY REPAIR OF THE APPARATUS.

10.3.1.6.3.3 Follow the manufacturer’s instructions for operation of the GPC system being utilized. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL injection loop is used, concentrate the extract to 4 mL instead of 10 mL, and then inject 4 mL instead of 10 mL.

10.3.1.6.3.4 If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action, following the manufacturer’s recommendations. The problem must be resolved prior to loading sample extracts.

10.3.1.6.3.5 After loading each sample loop, wash the loading port with methylene chloride to minimize cross contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

10.3.1.6.3.6 After loading the samples, process each sample using the "COLLECT" and "DUMP" cycle times established in Section 10.3.1.3.3.1.

10.3.1.6.3.7 Collect each sample in a 250 mL Erlenmeyer flask covered with aluminum foil to reduce solvent evaporation, or directly into a K-D evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure;
- Increase in column operating pressure due to the accumulation of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used; and/or
- Leaks in the system or significant variances in room temperature.

10.3.1.6.3.8 After the appropriate GPC fraction has been collected for each sample, concentrate the extract as per Section 10.2.1 and proceed to solvent exchange into hexane as described in Section 10.2.2 and Florisil cleanup in Section 10.3.2.

NOTE: Any samples that were loaded into multiple loops must be recombined before proceeding with concentration.

10.3.2 Florisil Cartridge

10.3.2.1 Summary of Florisil Cartridge Cleanup

Florisil cartridge cleanup significantly reduces matrix interference caused by polar compounds and is required for all extracts. The same volume of the concentrated extract taken for Florisil cleanup must be maintained after Florisil cleanup (1.0 or 2.0 mL).

10.3.2.2 Florisil Cartridge Performance Check

10.3.2.2.1 Summary of Florisil Cartridge Performance Check

Every lot number of Florisil cartridges must be tested before it is used for sample cleanup.

10.3.2.2.2 Frequency of Florisil Cartridge Performance Check

The Florisil cartridge performance check must be conducted at least once on each lot of cartridges used for sample cleanup or every 6 months, whichever is most frequent.

10.3.2.2.3 Procedure for Florisil Cartridge Performance Check

Add 0.5 mL of 2,4,5-trichlorophenol solution (0.10 µg/mL in acetone; Section 7.2.2.7) and 0.5 mL of Individual Standard Mixture A or C (mid-point concentration; Section 7.2.2.3) to 4 mL of hexane. Reduce the volume to 0.5 mL using nitrogen (Section 10.2.3.2). Place the mixture onto the top of a washed Florisil cartridge, and elute it with 9 mL of hexane/acetone [(90:10) (V/V)]. Use two additional 1 mL hexane rinses to ensure quantitative transfer of the standard from the cartridge. Concentrate to a final volume of 1 mL and analyze the solution by GC/ECD using at least one of the GC columns specified for sample analysis. Determine the recovery of each analyte for evaluation and reporting purposes. Calculate the %R using Equation 13.

EQ. 13 Percent Recovery

$$\%R = \frac{(Q_d \times DF)}{Q_a} \times 100$$

WHERE,

Q_d = Quantity determined by analysis

Q_a = Quantity added

DF = Dilution Factor

NOTE: For the Florisil cartridge performance check, use DF = 1.0 in calculations.

10.3.2.2.4 Technical Acceptance Criteria for Florisil Cartridge Performance Check

10.3.2.2.4.1 The Florisil cartridge performance check solution must be analyzed on a GC/ECD meeting the initial calibration and CCV technical acceptance criteria.

10.3.2.2.4.2 The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80-120% (Table 8 – Florisil Cartridge Performance Check), if the recovery of 2,4,5-trichlorophenol is less than 5%, and if no peaks interfering with the target analytes are detected.

10.3.2.2.5 Corrective Action for Florisil Cartridge Performance Check

Any lot of Florisil cartridges that does not meet the criteria above must be discarded and a new lot, meeting criteria, must be used for sample cleanup.

10.3.2.3 Sample Extract Cleanup by Florisil Cartridge

10.3.2.3.1 Summary of Florisil Cartridge Cleanup

The required Florisil cartridge size and the final volume of the extract after Florisil cleanup are a function of the GC autosampler that a laboratory uses. If the autosampler operates reliably with 1.0 mL of sample extract, then a 500 mg cartridge is used and the required final volume is 1 mL. If the autosampler requires more sample, prepare 2 mL of sample extract using a 1 g cartridge. Manual injection requires only a 1 mL final extract and a 500 mg cartridge.

10.3.2.3.2 Frequency of Sample Extract Cleanup by Florisil Cartridge

All sample extracts (including LCSs and MS/MSDs) and method blank extracts are required to be cleaned up by the Florisil cartridge technique.

10.3.2.3.3 Procedure for Sample Extract Cleanup by Florisil Cartridge

10.3.2.3.3.1 Attach the vacuum manifold to a water aspirator or to a vacuum pump with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 5-10 lbs of vacuum.

10.3.2.3.3.2 Place one Florisil cartridge into the vacuum manifold for each sample extract.

10.3.2.3.3.3 Prior to cleanup of samples, the cartridges must be washed with hexane/acetone (90:10). This is accomplished by placing the cartridge on the vacuum manifold, by pulling a vacuum, and by passing at least 5 mL of the hexane/acetone

solution through the cartridge. While the cartridges are being washed, adjust the vacuum applied to each cartridge so that the flow rate through each cartridge is approximately equal. DO NOT ALLOW THE CARTRIDGES TO GO DRY AFTER THEY HAVE BEEN WASHED.

10.3.2.3.3.4 After the cartridges on the manifold are washed, the vacuum is released, and a rack containing labeled 10 mL volumetric flasks is placed inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is placed inside of the appropriate volumetric flask as the manifold top is replaced.

10.3.2.3.3.5 After the volumetric flasks are in place, the vacuum to the manifold is restored, and a volume of extract equal to the required final volume (1.0 or 2.0 mL) from each sample, blank, or Matrix Spike extract is transferred to the top frit of the appropriate Florisil cartridge. This must equal the final volume after Florisil cleanup.

10.3.2.3.3.6 Because the volumes marked on concentrator tubes are not necessarily accurate at the 1 mL level, the use of a syringe or a volumetric pipette is required to transfer the extract to the cleanup cartridge.

10.3.2.3.3.7 The pesticides in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL volumetric flasks held in the rack inside the vacuum manifold.

10.3.2.3.3.8 Transfer the eluate in each volumetric flask to a clean centrifuge tube or 10 mL vial. Use two additional 1 mL hexane rinses to ensure quantitative transfer of the cartridge eluate.

10.3.2.3.3.9 Adjust the extract to the same 1.0 or 2.0 mL aliquot volume as was taken for cleanup using either of the blowdown techniques (Section 10.2.3.1 or 10.2.3.2). Measure the final volume with a syringe or by transferring the extract to a volumetric flask.

10.3.2.3.3.10 If sulfur cleanup is to be performed, proceed to Section 10.3.3. Otherwise, transfer the sample to a GC vial and label the vial. The extract is ready for GC/ECD analysis.

10.3.3 Sulfur Cleanup

10.3.3.1 Summary of Sulfur Cleanup

Sulfur contamination will cause a rise in the baseline of a chromatogram and may interfere with the analyses of the later eluting pesticides. If crystals of sulfur are evident or if the presence of sulfur is suspected, sulfur removal must be performed. Interference which is due to sulfur is not acceptable. Sulfur can be removed by one of two methods, according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract, and withdraw the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean centrifuge tube or clean concentrator tube before proceeding with further sulfur cleanup.

10.3.3.2 Frequency of Sulfur Cleanup

Sulfur removal is required for all sample extracts that contain sulfur.

10.3.3.3 Procedure for Sulfur Cleanup

10.3.3.3.1 Removal of Sulfur using Tetrabutylammonium (TBA) Sulfite

The TBA Sulfite procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water-soluble. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

Add 2 mL TBA Sulfite Reagent, 1 mL 2-propanol, and approximately 0.65 g of sodium sulfite crystals to the extract and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed, add one or two more aliquots (approximately 0.65 g) to the extract and observe. Place the samples on the wrist shaker for 45 minutes, observing at 15-minute intervals to make sure that the sodium sulfite is not consumed. Add 5 mL organic free water and shake for 10-15 minutes. Place the samples into the centrifuge and spin at a setting and duration appropriate to spin down the solids. Transfer the hexane layer to a clean 10 mL vial and cap. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume.

10.3.3.3.2 Removal of Sulfur using Copper

Add approximately 2 g of cleaned copper powder to the extract in the centrifuge or concentrator tube (2 g will fill the tube to about the 0.5 mL mark). Mix the copper and extract for at least 1 minute on a mechanical shaker. Separate the extract from the copper powder by drawing off the extract with a disposable pipette, and transfer the extract to a clean vial. The extract transferred to the vial still represents the 1 or 2 mL of extract. The separation of the extract from the copper powder is necessary to prevent degradation of the pesticides. If the copper appears bright, proceed to Section 10.4 and analyze the extract. If the copper changes color, repeat the sulfur removal procedure as necessary.

10.4 Gas Chromatography/Electron Capture Detector Analysis

10.4.1 Introduction

Before samples (including LCSs and MS/MSDs) and required blanks (method, sulfur cleanup, and/or instrument) can be analyzed, the instrument must meet the initial calibration and calibration CCV technical acceptance criteria. All sample extracts, required blanks, and calibration standards must be analyzed under the same instrumental conditions. All sample extracts, required blank extracts, and standard/spiking solutions must be allowed to warm to ambient temperature before preparation/analysis. Sample analysis on two different non-equivalent GC columns (Section 6.3.2) is required for all samples and blanks.

10.4.1.1 Set up the GC/ECD system per the requirements in Section 9.1. Unless ambient temperature on-column injection is used, the injector must be heated to at least 200°C. The optimized GC conditions must be used.

10.4.2 Procedure for Sample Analysis by GC/ECD

The injection must be made on-column by using either automatic or manual injection. 1.0 or 2.0 µL injector volumes may be used

provided that all associated standards, samples, and blanks use the same injection volume. The same injection volume must be used for all standards, samples (including LCSs and MS/MSDs), and blanks associated with the same initial calibration. If a single injection is used for two GC columns attached to a single injection port, it may be necessary to use an injection volume greater than 2.0 µL. However, the same injection volume must be used for all analyses.

10.4.2.1 Analytical Sequence

All acceptable samples must be analyzed within a valid analysis sequence as given below.

NOTE: The injection # will depend on whether initial calibration sequence 1 or 2 is used.

Time	**Injection #**	**Material Injected**
	12 steps (sequence 1) or 17 steps (sequence 2)	First steps of the initial calibration sequence 1 or 2
0 hr	1st injection past the Initial Calibration sequence	Instrument Blank at end of initial calibration sequence
	2nd injection past the Initial Calibration sequence	PEM at end of initial calibration sequence
		First sample following initial calibration sequence
		Subsequent samples
		Last Sample
12 hrs	1st injection past 12 hours	Instrument Blank
	2nd and 3rd injections past 12 hours	Individual Standard Mixtures A and B
	2nd injection past 12 hours	Individual Standard Mixture C
		Sample
		Subsequent samples
		Last Sample
Another 12 hrs	1st injection past 12 hours	Instrument Blank
	2nd injection past 12 hours	PEM
		Sample
	2nd last injection of 12 hours	Instrument Blank
	Last injection of 12 hours	CCV

10.4.2.1.1 For initial calibration sequence 2, the first 12 hours are counted from injection #18 (the Instrument Blank at the end of the initial calibration sequence), not from injection #1. Samples and required blanks may be injected until 12 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. If more than 12 hours elapse between the injection of two instrument blanks that bracket a 12-hour period in which samples or required blanks are analyzed, then the time between the injection of the second instrument blank and the preceding sample may not exceed the length of one chromatographic run. While the 12-hour period may not be exceeded, the laboratory may analyze instrument blanks and standards more frequently, for instance, to accommodate staff working on 8-hour shifts. No more than 14 hours may elapse from the injection beginning the opening CCV (instrument blank) and the injection ending the closing CCV (PEM or Individual Standard Mixture).

10.4.2.1.2 After the initial calibration, the analysis sequence may continue as long as acceptable instrument blanks, PEMs, and Individual Standard Mixtures (A and B) or C are analyzed at the required frequency. This analysis sequence shows only the minimum required blanks and standards. More blanks and standards may be analyzed at the discretion of the Contractor; however, the blanks and standards must also satisfy the criteria presented in Sections 12.0 and 9.0 in order to continue the analytical sequence.

10.4.2.1.3 An analysis sequence must also include all samples and required blank analyses, but the Contractor may decide at what point in the sequence they are to be analyzed.

10.4.2.1.4 The requirements for the analysis sequence apply to both GC columns and for all instruments used for these analyses.

10.4.3 Sample Dilutions

10.4.3.1 All samples must be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography as defined in Section 11.3.

10.4.3.2 Use the results of the original analysis to determine the approximate DF required to get the largest analyte peak (for the lower of the two column concentrations) within the initial calibration range.

10.4.3.3 If more than two analyses (i.e., from the original sample extract and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get all target analytes within the calibration range, contact SMO.

10.4.3.4 If the concentration of any single component pesticide is greater than the concentration of the high standard (CS5) of the initial calibration range on both GC columns, then the extract must be diluted. The concentration of the pesticide analyte(s) in the diluted extract must be between the initial calibration low-point (CS1) and high-point (CS5) standards for the lower column concentration of the two analyses.

10.4.3.5 If the concentration of any Toxaphene peak used for quantitation is greater than the concentration of the corresponding Toxaphene peak in the high standard (CS5) on both columns, then the sample must be diluted to have the concentration of the same peak be between the mid-point (CS3) and high-point (CS5) standards of Toxaphene.

10.4.3.6 If dilution is employed solely to bring a peak within the calibration range or to get the Toxaphene pattern on scale, the results for both the greater and the less concentrated extracts must be reported. The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.

10.4.3.7 If the DF is greater than 10, an additional extract 10 times more concentrated than the diluted sample extract must be analyzed and reported with the sample data. If the DF is less than or equal to 10, but greater than 1, the results of the original undiluted analysis must also be reported.

10.4.3.8 When diluted, the chromatographic data for the single component pesticide must be able to be reported at greater than 10% of full scale but less than 100% of full scale.

10.4.3.9 When diluted, Toxaphene must be able to be reported at greater than 25% of full scale but less than 100% of full scale.

10.4.3.10 Samples with analytes detected at a level greater than the high calibration point must be diluted until the concentration is within the linear range established during calibration, or to a maximum of 1:100,000.

10.4.3.11 If the concentration is still above the high calibration standard concentration after the dilution of 1:100,000, the Contractor shall contact SMO immediately.

10.4.3.12 Sample dilutions must be made quantitatively. Dilute the sample extract with hexane.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Analytes

11.1.1.1 The laboratory will identify single component analyte peaks based on the RT windows established during the initial calibration sequence. Single component analytes are identified when peaks are observed in the RT window for the analyte on both GC columns.

11.1.1.2 A set of five major peaks is selected for Toxaphene. RT windows for each peak are determined from the initial calibration analysis. Identification of Toxaphene in the sample is based on pattern recognition in conjunction with the elution of five sample peaks within the RT windows of the corresponding peaks of the standard on both GC columns.

11.1.1.3 If Toxaphene is identified in a sample using a single-point calibration of a Toxaphene CS1 standard from initial calibration, then the sample must be reanalyzed with a five-point calibration and CS3 Toxaphene standard is required as the CCV.

11.1.1.4 The choice of the peaks used for Toxaphene identification and the recognition of those peaks may be complicated by the environmental alteration of Toxaphene, and by the presence of coeluting analytes, matrix interferences, or both. Because of the alteration of Toxaphene in the environment, it may give patterns in samples similar to, but not identical with, those of the standards.

11.1.2 Gas Chromatography/Mass Spectrometry Confirmation

11.1.2.1 Any pesticide listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits for which a concentration is reported from analysis must have the identification confirmed by GC/Mass Spectrometry (GC/MS) if the concentration is sufficient for that purpose. The following paragraphs are to be used as guidance in performing GC/MS confirmation. If the Contractor fails to perform GC/MS confirmation as appropriate, the EPA may require reanalysis of any affected samples at no additional cost to the EPA.

11.1.2.2 GC/MS confirmation may be accomplished by one of three general means:

- Examination of the semivolatile GC/MS library search results [i.e., Tentatively Identified Compound (TIC) data]; or
- A second analysis of the semivolatile extract; or
- Analysis of the pesticide extract, following any solvent exchange and concentration steps that may be necessary.

11.1.2.3 The semivolatile GC/MS analysis procedures outlined in Exhibit D – Semivolatile Organic Compounds Analysis are based on the injection into the instrument of approximately 10 ng of a target analyte in a 2 µL volume. The semivolatile CRQL values in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 3 – Semivolatiles Target Analyte List and Contract Required Quantitation Limits are based on the sample concentration that corresponds to an on-column concentration (extract concentration) of 5 ng/µL of target analyte. Although these are quantitation limits, and the detection of analytes and generation of reproducible mass spectra will routinely be possible at levels 3-10 times lower, the sample matrix may prevent detection of target analytes at less than 5 ng/µL. If any single component pesticide has an on-column concentration of greater than or equal to 5 ng/µL for both columns, then GC/MS confirmation is required. Similarly, for Toxaphene, if an individual peak concentration is greater than or equal to 125 ng/µL for both columns, then GC/MS confirmation is required.

11.1.2.3.1 For water samples prepared according to the method described in Section 10.1.1, 10 ng/2 µL corresponds to a sample concentration of 50 µg/L for single component pesticides, and a sample concentration of 1250 µg/L for Toxaphene.

11.1.2.3.2 For soil/sediment samples prepared according to the method described in Section 10.1.2, the corresponding sample concentration is 1,700 µg/kg for single component pesticides and 42,000 µg/kg for Toxaphene.

11.1.2.4 In order to confirm the identification of Toxaphene, the laboratory must also analyze a reference standard for Toxaphene. In order to demonstrate the ability of the GC/MS system to identify Toxaphene, the concentration of the standard should be 125 ng/µL.

11.1.2.5 To facilitate the confirmation of the single component pesticide analytes from the semivolatile library search data, the Contractor may wish to include these analytes in the semivolatile continuing calibration standard at a concentration of 5.0 ng/µL or less. Do not include Toxaphene in the semivolatile initial and continuing calibration standard. If added to this GC/MS standard, the response factors, RTs, etc., for these analytes would be reported on the GC/MS quantitation report, but not on the GC/MS calibration data reporting forms. As only a single concentration of each analyte would be analyzed, no linearity (%RSD) or %D criteria would be applied to the response factors for these additional analytes.

11.1.2.6 The Contractor is advised that library search results from the NIST (2011 release or later) mass spectral library will not likely list the name of the pesticide analyte as it appears in this analytical method; hence, the mass spectral interpretation specialist is advised to compare the Chemical Abstracts Service (CAS) Registry Numbers for the pesticides to those from the library search routine.

11.1.2.7 If the analyte cannot be confirmed from the semivolatile library search data for the original semivolatile GC/MS analysis, the Contractor may analyze another aliquot of the semivolatile sample extract after further concentration of the aliquot. This second aliquot must either be analyzed as part of a routine semivolatile GC/MS analysis, including instrument performance checks (DFTPP)

and calibration standards containing the pesticides as described in Section 11.1.2.5, or it must be analyzed along with separate reference standards for the analytes to be confirmed.

11.1.2.8 If the analyte cannot be confirmed by either the procedures in Sections 11.1.2.5 or 11.1.2.7, then an aliquot of the extract prepared for the GC/ECD analysis must be analyzed by GC/MS, following any necessary solvent exchange and concentration steps. As in Section 11.1.2.4, analysis of a reference standard is required if the GC/MS continuing calibration standard does not contain the analyte to be confirmed.

11.1.2.9 Regardless of which of the three approaches above is used for GC/MS confirmation, the appropriate blank must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination. If the confirmation is based on the analysis of the semivolatile extract, then the semivolatile method blank extracted with the sample must also be analyzed. If the confirmation is based on the analysis of the extract prepared for the GC/ECD analysis, then the pesticide method blank extracted with the sample must be analyzed.

11.1.2.10 If the identification of the analyte cannot be confirmed by any of the GC/MS procedures above, and the concentration calculated from the GC/ECD analysis is greater than or equal to the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit (the value associated with the "U" qualifier) to a sample concentration equivalent to the concentration of the GC/MS reference standard, and qualify the results on Form 1-OR with one of the laboratory-defined qualifiers ("X", "Y", or "Z"). In this instance, define the qualifier explicitly in the SDG Narrative, and describe the steps taken to confirm the analyte in the SDG Narrative.

11.1.2.11 For GC/MS confirmation of single component analytes, the required deliverables are copies of the library search results (best TIC matches) or analyte spectrum and the spectrum of the reference standard. For Toxaphene, spectra of five characteristic peaks are required for both the sample component and the reference standard.

11.1.2.12 The purpose of the GC/MS analysis for the single component pesticides is for identification. The purpose of the GC/MS analysis for Toxaphene is to confirm the presence of chlorinated camphenes. The GC/MS analytical results for the pesticides shall not be used for quantitation and the GC/MS results shall not be reported on Form 1-OR and Form 10-OR. The exception noted in Section 11.1.2.10 applies only to analytes that cannot be confirmed above the reference standard concentration.

11.2 Quantitative Analysis

11.2.1 Data Processing Procedure

11.2.1.1 Target analytes identified shall be quantitated by the external standard method.

11.2.1.2 Quantitation for all analytes and surrogates must be performed and reported for each GC column.

11.2.1.3 Manual integration of peaks (e.g., measuring peak height with a ruler) is only permitted when accurate electronic integration of

peaks cannot be done. If manual integration of peaks is required, it must be documented in the SDG Narrative.

11.2.1.4 The Contractor must quantitate each single component analyte and CF from the most recent initial calibration. Do not use the analyses of the Individual Standard Mixtures used to demonstrate calibration verification for quantitation of samples.

11.2.1.5 If Toxaphene is identified and the peak concentrations are calculated using a single-point calibration standard CS3 from the initial calibration, the Contractor must reanalyze the sample and quantitate with a valid five-point calibration.

NOTE: An estimated concentration (reported with an "S" flag) of the initial detection for a Toxaphene using a single-point calibration standard will be quantitated using the CF, of five major peaks, from the specific single-point calibration standard.

11.2.1.6 The chromatograms of all samples (including LCSs and MS/MSDs), standards, and required blanks must be reviewed by a qualified pesticide analyst before they are reported.

11.2.2 Target Analyte Calculations

11.2.2.1 Calculate the sample concentration and on-column concentration of the pesticides and surrogates by using the following equations:

11.2.2.2 Water

EQ. 14 Water and TCLP/SPLP Leachate Sample Concentration

$$\text{Concentration } (\mu g/L) = \left(\frac{A_X}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{V_o}\right)\left(\frac{CV_{out}}{CV_{in}\times E}\right)_1\left(\frac{CV_{out}}{CV_{in}\times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in}\times E}\right)_n$$

WHERE,

A_x = Peak area or peak height of the compound or Toxaphene peak to be measured

$\overline{CF}$ = Mean Calibration Factor determined from the initial calibration for the peak to be measured, in area/ng

V_i = Volume of extract injected in µL

V_t = Volume of extract produced by the preparation process (extraction and concentration), and before cleanup, in µL

V_o = Volume of the water sample extracted in mL

NOTE: For instrument and sulfur blanks, assume a volume of 1,000 mL.

CV_{out} = Volume of extract produced by a cleanup process (cleanup and concentration), in µL

CV_{in} = Volume of extract subjected to a cleanup process, in µL

E = The efficiency of the cleanup process expressed as a fraction of the material that passes through or is not mechanically lost during the cleanup step (e.g., 50% efficiency must be expressed as 0.50)

DF = Dilution Factor, which is defined as follows:

$$DF = \frac{\text{most concentrated extract used to make dilution + µL clean solvent}}{\text{µL most concentrated extract used to make dilution}}$$

If no dilution is performed, DF = 1.0.

The $\overline{CF}$s used in Equations 14-16 are those from the most recent initial calibration. If the $\overline{CF}$s used to determine the linearity of the initial calibration were based on peak area, then the concentration of the analyte in the sample must be based on peak area. Similarly, if peak height was used to determine linearity, use peak height to determine the concentration in the sample.

NOTE: Convert units to mg/L for TCLP leachates by dividing the final calculated concentration by 1000.

EQ. 15 On-Column Concentration

$$\text{On-Column Concentration (ng/µL)} = \frac{(A_x)}{(\overline{CF})(V_i)}$$

WHERE,

A_x, $\overline{CF}$ = As given in EQ. 14

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use ½ the volume in the syringe as the volume injected onto each column.)

11.2.2.3 Soil/Sediment

EQ. 16 Soil/Sediment Concentration

$$\text{Concentration (µg/kg)} = \left(\frac{A_X}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{W_t \times S}\right)\left(\frac{CV_{out}}{CV_{in} \times E}\right)_1\left(\frac{CV_{out}}{CV_{in} \times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in} \times E}\right)_n$$

WHERE,

A_x, $\overline{CF}$, V_i, V_t, CV_{out}, CV_{in}, E = As given in EQ. 14

W_t = Weight of the original soil sample extracted, in g

S = % Solids/100 (Exhibit D – General Organic Analysis, Section 10.1)

11.2.2.4 The lower of the two concentrations calculated for each single component pesticide is reported on Form 1-OR. In addition, the concentrations calculated for both the GC columns are reported on Form 10-OR, along with a %D comparing the two concentrations. The %Difference is calculated using the following equation:

EQ. 17 Percent Difference Between Concentrations on both GC Columns

$$\%D = \frac{Conc_H - Conc_L}{Conc_L} \times 100$$

WHERE,

$Conc_H$ = The higher of the two concentrations for the target compound in question

$Conc_L$ = The lower of the two concentrations for the target compound in question

NOTE: Using this equation will result in %D values that are always positive.

11.2.3 Toxaphene

11.2.3.1 The quantitation of Toxaphene must be accomplished by comparing the heights or the areas of each of the five major peaks of the sample with the CF for the same peaks established during the initial calibration sequence. The concentration of Toxaphene is calculated by using Equations 14 or 16, where A_x is the area for each of the major peaks. The concentration of each peak is determined and then a mean concentration for the five major peaks is determined on each column.

11.2.3.2 The reporting requirement for Toxaphene is similar to that for the single component analytes, except that the lower mean concentration (from five peaks) is reported on Form 1-OR, and the two mean concentrations reported on Form 10-OR. The two mean concentrations are compared by calculating the %D using Equation 17.

11.2.4 Contract Required Quantitation Limit Calculations

11.2.4.1 Water

EQ. 18 Water and TCLP/SPLP Leachate Sample Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{V_x}{V_o}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in}\times E}\right)_1\left(\frac{CV_{out}}{CV_{in}\times E}\right)_2\cdots\left(\frac{CV_{out}}{CV_{in}\times E}\right)_n$$

WHERE,

V_o, V_t, DF, CV_{out}, CV_{in}, E = As given in EQ. 14

V_x = Method required sample volume (1,000 mL)

V_y = Method required concentrated extract volume (10,000 µL)

NOTE: Convert units to mg/L for TCLP leachates by dividing the final calculated CRQL by 1000.

11.2.4.2 Soil/Sediment

EQ. 19 Soil/Sediment Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{W_x}{W_t\times S}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in}\times E}\right)_1\left(\frac{CV_{out}}{CV_{in}\times E}\right)_2\cdots\left(\frac{CV_{out}}{CV_{in}\times E}\right)_n$$

WHERE,

V_t, DF, CV_{out}, CV_{in}, E = As given in EQ. 16

W_x = Method required sample weight (30 g)

W_t = Weight of sample extracted in g

S = % Solids/100 (Exhibit D – General Organic Analysis, Section 10.1.1)

V_y = Method required concentrated extract volume (10,000 µL)

11.2.5 Deuterated Monitoring Compound Recoveries

Not applicable to this method.

11.2.6 Surrogate Recoveries

11.2.6.1 The concentrations for surrogate compounds are calculated by using Equations 14 or 16. Use the $\overline{CF}$s (Equation 4)from the initial calibration. If two Individual Standard Mixtures are used, $\overline{CF}$s from Individual Standard Mixture A are to be used.

11.2.6.2 The recoveries of the surrogates are calculated for each GC column according to Equation 13.

11.2.6.3 The recovery limits for the surrogates are 30-150% for both surrogate compounds.

11.2.6.4 Surrogate recovery data from both GC columns are reported (see Exhibit B – Reporting and Deliverables Requirements).

11.3 Technical Acceptance Criteria for Sample Analysis

The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

11.3.1 Samples must be analyzed under the GC/ECD operating conditions in Section 9.1.1. The instrument must have met all initial calibration, CCV, and blank technical acceptance criteria. Samples must be cleaned up, when required, with GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration verification. Samples must be cleaned-up using Florisil that meets the technical acceptance criteria for Florisil Cartridge Performance Check. Sample data must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and Individual Standard Mixture(s), as described in Section 9.4.2.

11.3.2 Samples must be extracted and analyzed within the contract holding times.

11.3.3 The LCS associated with the samples must meet the LCS technical acceptance criteria.

11.3.4 The samples must have an associated method blank meeting the technical acceptance criteria for method blanks. If a sulfur cleanup blank is associated with the samples, that blank must meet the sulfur cleanup blank technical acceptance criteria.

11.3.5 The RT for each of the surrogates must be within the RT window (Section 9.3.4.4) for both GC columns.

11.3.6 The %R for the surrogates must be between 30-150%, inclusive. Up to one surrogate per sample may fail this criteria per column.

NOTE: The surrogate recovery requirements do not apply to a sample that has been diluted.

11.3.7 No target analyte concentration may exceed the upper limit concentration of the initial calibration or else extracts must be diluted and reanalyzed.

11.3.8 The identification of single component pesticides by GC methods is based primarily on RT data. The RT of the apex of a peak can only be verified from an on-scale chromatogram. The identification of Toxaphene by GC methods is based primarily on recognition of the pattern of RTs displayed on a chromatogram. Therefore, the

following requirements apply to all data presented for single component analytes and Toxaphene.

11.3.8.1 When no analytes are identified in a sample, the chromatograms from the analyses of the sample extract must use the same scaling factor as was used for the low-point standard of the initial calibration associated with those analyses.

11.3.8.2 Chromatograms must display single component pesticides detected in the sample at less than full scale.

11.3.8.3 Chromatograms must display the largest peak of Toxaphene detected in the sample at less than full scale.

11.3.8.4 If an extract must be diluted, chromatograms must display single component pesticides between 10-100% of full scale.

11.3.8.5 If an extract must be diluted, chromatograms must display Toxaphene between 25-100% of full scale.

11.3.8.6 For any sample or blank, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

11.3.8.7 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample analysis technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or associated with a contaminated method blank or sulfur cleanup blank will require re-extraction and reanalysis at no additional cost to the EPA. Any samples analyzed that do not meet the technical acceptance criteria will require re-extraction and/or reanalysis at no additional cost to the EPA.

11.4.2 If the sample analysis technical acceptance criteria are not met, check calculations, surrogate solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the technical acceptance criteria, in which case, the affected samples must be reanalyzed at no additional cost to the EPA after the corrective action.

11.4.3 The extracts from samples that were cleaned up by GPC using an automated injection system, and have both surrogate recoveries outside the lower surrogate acceptance limits, must be checked to assure that the proper amount was injected on the GPC column. If insufficient volume was injected, the sample must be reprepared and reanalyzed at no additional cost to the EPA.

11.4.4 If sample chromatograms have a high baseline or interfering peaks, inspect the system to determine the cause of the problem (e.g., carryover, column bleed, dirty ECD, contaminated gases, leaking septum, etc.). After correcting the problem, analyze an instrument blank to demonstrate that the system is functioning properly. Reanalyze the sample extracts. If the problem with the samples still exists, then those samples must be re-extracted and reanalyzed. Samples that cannot be made to meet the given specifications after one re-extraction and minimum three-step cleanup (GPC, Florisil, and sulfur cleanups) are reported in the SDG Narrative and do not require further analysis.

11.4.5 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

- Re-extract and reanalyze the sample. EXCEPTION: If surrogate recoveries in a sample used for an MS/MSD were outside the acceptable criteria, then it should be re-extracted/reanalyzed only if surrogate recoveries met the acceptance criteria in both the MS/MSD analyses.
- If the surrogate recoveries meet the acceptance criteria in the re-extracted/reanalyzed sample, then the problem was within the Contractor's control. Therefore, submit only data from the re-extraction/reanalysis.
- If the surrogate recoveries fail to meet the acceptance windows in the re-extracted/reanalyzed sample, then submit data from both analyses. Distinguish between the initial analysis and the re-extraction/reanalysis on all deliverables, using the suffixes in Exhibit B – Reporting and Deliverables Requirements, Table 5 – Codes for Labeling Data.

12.0 QUALITY CONTROL

12.1 Blank Analyses

12.1.1 Summary

There are two types of blanks required by this method: the method blank and the instrument blank. A separate sulfur cleanup blank may also be required if some, but not all of the samples are subjected to sulfur cleanup. Samples that are associated with a sulfur cleanup blank are also associated with the method blank with which they were extracted. Both the method and sulfur cleanup blanks must meet the respective technical acceptance criteria for the sample analysis technical acceptance criteria to be met.

NOTE: Under no circumstances should blanks (method/instrument/ sulfur cleanup) be analyzed at a dilution.

12.1.2 Method Blank

12.1.2.1 Summary of Method Blank

A method blank is a volume of a clean reference matrix (reagent water for aqueous samples, or purified sodium sulfate or Hydromatrix™ for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples. The leachate extraction blank shall be extracted and reported as PLEB## on Form 1A-OR.

12.1.2.2 Frequency of Method Blank

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples [excluding MS/MSDs, Performance Evaluation (PE) samples, and LCSs]. In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples;

- Be analyzed on each GC/ECD system under the same conditions used to analyze associated samples; and

12.1.2.3 Procedure for Method Blank

For water samples, measure 1.0 L volume of reagent water and spike with 1 mL of the surrogate spiking solution (Section 7.2.2.8). For soil/sediment samples, measure 30 g of sodium sulfate or Hydromatrix™ and spike with 1 mL of the surrogate spiking solution. Extract, concentrate, clean up, and analyze the method blank following the procedures for water and soil samples (Section 10.0).

12.1.2.4 Calculations for Method Blank

Perform data analysis and calculations according to Section 11.0.

12.1.2.5 Technical Acceptance Criteria for Method Blank

12.1.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.1.2.5.2 All method blanks must be prepared and analyzed at the frequency described in Section 12.1.2.2, using the procedure above and in Section 10.0 on a GC/ECD system meeting the initial calibration and CCV technical acceptance criteria. Method blanks must undergo GPC cleanup, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks. Method blanks must be cleaned up using Florisil meeting the technical acceptance criteria for Florisil.

12.1.2.5.3 Method blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and CS3 Standards, as described in Section 9.4.2.

12.1.2.5.4 The concentration of the target analytes (Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits) in the method blank must be less than the CRQL for each target analyte.

12.1.2.5.5 The method blank must meet sample technical acceptance criteria in Sections 11.3.5 and 11.3.8.

12.1.2.5.6 Surrogate recoveries must fall within the acceptance window in Table 10 – Surrogate Recovery Limits. These limits are not advisory.

12.1.2.6 Corrective Action for Method Blank

12.1.2.6.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.

12.1.2.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. All samples associated with a method blank that does not meet the method blank technical acceptance criteria will require re-extraction and reanalysis at no additional cost to the EPA. It is the Contractor’s responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and

processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.2.6.3 If surrogate recoveries in the method blank do not meet the acceptance criteria listed in Section 12.1.2.5.6, first reanalyze the method blank. If the surrogate recoveries do not meet the acceptance criteria after reanalysis, then the method blank and all samples associated with that method blank must be re-extracted and reanalyzed at no additional cost to the EPA.

12.1.2.6.4 If the method blank fails to meet a technical acceptance criteria other than Sections 12.1.2.5.4 and 12.1.2.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary), and reanalyze the method blank.

12.1.3 Sulfur Cleanup Blank

12.1.3.1 Summary of Sulfur Cleanup Blank

The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup and analysis procedures. The purpose of the sulfur cleanup blank is to determine the levels of contamination associated with the separate sulfur cleanup steps.

12.1.3.2 Frequency of Sulfur Cleanup Blank

The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur cleanup blank is associated with the part of the set that required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then no separate sulfur cleanup blank is required.

12.1.3.3 Procedure for Sulfur Cleanup Blank

12.1.3.3.1 The concentrated volume of the blank must be the same as the final volume of the samples associated with the blank. The sulfur blank must also contain the surrogates at the same concentrations as the sample extracts (assuming 100.0% recovery). Therefore, add 0.60 mL of the surrogate spiking solution (Section 7.2.2.8) to 1.4 mL of hexane in a clean vial.

12.1.3.3.2 Proceed with the sulfur removal (Section 10.3.3) using the same technique (TBA sulfite or copper) as the samples associated with the blank.

12.1.3.3.3 Analyze the sulfur blank according to Section 10.4.2.

12.1.3.4 Calculations for Sulfur Cleanup Blank

12.1.3.4.1 Assuming that the material in the sulfur blank resulted from the extraction of a 1.0 L water sample, calculate the concentration of each analyte using Equation 14. Compare the results to the CRQL values in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits.

12.1.3.4.2 See Section 11.2 for the equations for the other calculations.

12.1.3.5 Technical Acceptance Criteria for Sulfur Cleanup Blanks

12.1.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each column.

12.1.3.5.2 All sulfur cleanup blanks must be prepared and analyzed at the frequency described in Section 12.1.3.2 using the procedure in Section 12.1.3.3 on a GC/ECD system meeting the initial calibration and CCV technical acceptance criteria.

12.1.3.5.3 Sulfur cleanup blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and Individual Standard Mixtures, as described in Section 9.4.2.

12.1.3.5.4 The concentration of the target analytes [Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits] in the sulfur cleanup blank must be less than the CRQL for each target analyte.

12.1.3.5.5 The sulfur cleanup blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.8.

12.1.3.5.6 Surrogate recoveries must fall within the acceptance windows in Table 10 – Surrogate Recovery Limits. These limits are not advisory.

12.1.3.6 Corrective Action for Sulfur Cleanup Blank

12.1.3.6.1 If a sulfur cleanup blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.

12.1.3.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples processed with a sulfur cleanup blank that does not meet the sulfur cleanup blank technical acceptance criteria (i.e., contaminated) will require re-extraction and reanalysis at no additional cost to the EPA. It is the Contractor’s responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.3.6.3 If surrogate recoveries in the sulfur cleanup blank do not meet the technical acceptance criteria in Section 12.1.3.5.6, first reanalyze the sulfur cleanup blank. If the surrogate recoveries do not meet the technical acceptance criteria after reanalysis, then the sulfur cleanup blank and all samples associated with that sulfur cleanup blank must be reprepared/re-extracted and reanalyzed at no additional cost to the EPA.

12.1.3.6.4 If the sulfur cleanup blank fails to meet a technical acceptance criterion other than what is listed in Sections 12.1.3.5.4 and 12.1.3.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary), and reanalyze the sulfur cleanup blank.

12.1.4 Instrument Blank

12.1.4.1 Summary of Instrument Blank

An instrument blank is a volume of clean solvent spiked with the surrogates and analyzed on each GC column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis, particularly with regard to carryover of analytes from standards or highly contaminated samples into other analyses.

12.1.4.2 Frequency of Instrument Blank

The first analysis in a 12-hour analysis sequence (Section 9.4.2) must be an instrument blank. All groups of acceptable sample analyses are to be preceded and followed by acceptable instrument blanks (Section 10.4.2.1). If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an instrument blank must be analyzed to initiate a new 12-hour sequence (Section 9.4.2).

12.1.4.3 Procedure for Instrument Blank

12.1.4.3.1 Prepare the instrument blank by spiking the surrogates into hexane or iso-octane for a concentration of 20.0 ng/mL of tetrachloro-m-xylene and 40.0 ng/mL of decachlorobiphenyl.

12.1.4.3.2 Analyze the instrument blank according to Section 10.4, at the frequency listed in Section 12.1.4.2.

12.1.4.4 Calculations for Instrument Blank

12.1.4.4.1 Assuming that the material in the instrument blank resulted from the extraction of a 1.0 L water sample, calculate the concentration of each analyte using Equation 14. Compare the results to the CRQL values for water samples in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits.

12.1.4.4.2 See Section 11.2 for the equations for the other calculations.

12.1.4.5 Technical Acceptance Criteria for Instrument Blanks

12.1.4.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed and reported independently on Form 1-OR for each GC column.

12.1.4.5.2 All instrument blanks must be prepared and analyzed at the frequency described in Section 12.1.4.2, using the procedure in Section 10.4 on a GC/ECD system meeting the initial calibration and CCV technical acceptance criteria.

12.1.4.5.3 The concentration of each target analyte [Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits] in the instrument blank must be less than the CRQL for that analyte.

12.1.4.5.4 The instrument blank must meet all sample technical acceptance criteria in Sections 11.3.5 and 11.3.8.

12.1.4.5.5 Instrument blanks must be analyzed undiluted.

12.1.4.6 Corrective Action for Instrument Blank

If target analytes are detected at concentrations greater than the CRQL, or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples that were analyzed between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be analyzed before additional data are collected. All samples (including LCSs, MS/MSDs, and PE samples) and required blanks that were analyzed after the last acceptable instrument blank must be reinjected during a valid analytical sequence and must be reported at no additional cost to the EPA.

12.2 Matrix Spike and Matrix Spike Duplicate

12.2.1 Summary of Matrix Spike and Matrix Spike Duplicate

To evaluate the effects of the sample matrix on the methods used for pesticide analyses, the EPA has prescribed a mixture of pesticide target analytes to be spiked into two aliquots of a sample and analyzed in accordance with the appropriate method.

12.2.2 Frequency of Matrix Spike and Matrix Spike Duplicate Analysis

12.2.2.1 An MS/MSD must be extracted and analyzed for every 20 field samples of a similar matrix in an SDG. MS/MSD samples must be analyzed unless otherwise specified on the Traffic Report/Chain of Custody (TR/COC) Record. If no MS/MSD samples are specified on the TR/COC Record, the Contactor shall contact SMO to confirm that MS/MSD analyses are not required.

12.2.2.2 The Contractor shall not perform MS/MSD analysis on any of the field QC or PE samples.

12.2.2.3 If the EPA Region designates a sample to be used, then that sample must be used. If there is insufficient sample volume remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the EPA sample selected for the MS/MSD analysis. SMO shall contact the EPA Region for confirmation immediately after notification. The rationale for the choice of another sample other than the one designated by the EPA shall be documented in the SDG Narrative.

12.2.2.4 If there is insufficient sample volume remaining in any of the samples in an SDG to perform the requested MS/MSD, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the EPA Region for instructions. The EPA Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the EPA Region’s decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the EPA Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2, the Contractor shall contact SMO. SMO will contact the EPA Region to determine which samples should have MS/MSD performed on them. SMO will notify the Contractor of the EPA Region’s decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.6 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the MS/MSD analysis when the EPA Region did not designate a sample to be used for this purpose. SMO will notify the Contractor of the chosen sample. The Contractor must document the decision in the SDG Narrative.

12.2.3 Procedure for Preparing Matrix Spike and Matrix Spike Duplicate

12.2.3.1 For water samples, measure out two additional 1 L aliquots of the sample chosen for spiking. Fortify each with 1.0 mL of the matrix spiking solution (Section 7.2.2.9). Using a syringe or volumetric pipette, add 1 mL of surrogate spiking solution to each sample (Section 7.2.2.8). Adjust the pH of the samples (if required). Extract, concentrate, cleanup, and analyze the MS/MSD according to Section 10.0.

12.2.3.2 For soil/sediment samples, weigh out two additional 30 g (to the nearest 0.1 g) aliquots of the sample chosen for spiking. Add 1.0 mL of the matrix spiking solution (Section 7.2.2.9) and 1 mL of the surrogate spiking solution (Section 7.2.2.8). Extract, concentrate, cleanup, and analyze the MS/MSD according to Section 10.0.

12.2.3.3 Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do not dilute MS/MSD samples further to get either spiked or nonspiked analytes within calibration range. Sample dilutions must be performed in accordance with Section 10.4.3.

12.2.4 Calculations for Matrix Spike and Matrix Spike Duplicate

12.2.4.1 Calculate the concentrations of the Matrix Spike analytes using the same equations as used for target analytes (Equations 14 and 16). Calculate the recovery of each Matrix Spike analyte using the following equation:

EQ. 20 Matrix Spike Recovery

$$\%R = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spike Sample Result

SR = Original Sample Result

SA = Spike Added

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD using the following equation:

EQ. 21 Relative Percent Difference

$$RPD = \frac{\left|MSR - MSDR\right|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

WHERE,

MSR = Matrix Spike Recovery

MSDR = Matrix Spike Duplicate Recovery

NOTE: The vertical bars in the equation above indicate the absolute value of the difference.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Matrix Spike Duplicate

12.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.2.5.2 All MS/MSDs must be prepared and analyzed at the frequency described in Section 12.2.2, using the procedure above and in Section 10.0, on a GC/ECD system meeting the initial calibration, CCV, and blank technical acceptance criteria. MS/MSDs must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and Individual Standard Mixture(s) (A, B, or C) as described in Section 9.4.2.

12.2.5.3 The MS/MSD must be extracted and analyzed within the contract required holding times.

12.2.5.4 The RT for each of the surrogates must be within the RT window as calculated in Section 9.3.4.4 for both GC columns.

12.2.5.5 The limits for spike analyte recovery and RPD are given in Table 11 – Matrix Spike Recovery and Relative Percent Difference Limits. As these limits are only advisory, no further action by the Contractor is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the Contractor, and may result in questions from the EPA.

12.2.6 Corrective Action for Matrix Spike and Matrix Spike Duplicate

Any MS/MSD which fails to meet the technical acceptance criteria in Sections 12.2.5.1, 12.2.5.2, and 12.2.5.4 must be reanalyzed at no additional cost to the EPA.

12.3 Laboratory Control Sample

12.3.1 Summary of Laboratory Control Sample

The LCS is an internal laboratory QC sample designed to assess (on an SDG—by-SDG basis) the capability of the Contractor to perform the analytical method listed in this Exhibit.

12.3.2 Frequency of Laboratory Control Sample

The LCS must be prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix, per preparation batch. The LCS must be extracted and analyzed concurrently with the samples in the SDG using the same extraction protocol, cleanup procedure, and instrumentation as the samples in the SDG.

NOTE: An LCS requires sulfur cleanup only if all samples in the specific preparation batch required this procedure.

12.3.3 Procedure for Laboratory Control Sample

12.3.3.1 For water samples, measure out 1.0 L of reagent water and spike with 1.0 mL of the LCS spiking solution (Section 7.2.2.10) and 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.8). Extract, concentrate, and analyze the sample according to Section 10.0.

12.3.3.2 For soil/sediment samples, measure out 30 g of a clean reference matrix (e.g., sodium sulfate, Hydromatrix™) and spike with 1.0 mL of the LCS spiking solution (Section 7.2.2.10) and 1.0 mL of surrogate standard spiking solution (Section 7.2.2.8). Extract, concentrate, and analyze the LCS according to Section 10.0.

12.3.4 Calculations for Laboratory Control Sample

12.3.4.1 Calculate the results according to Section 11.0.

12.3.4.2 Calculate individual compound recoveries of the LCS using Equation 13.

12.3.5 Technical Acceptance Criteria for Laboratory Control Sample

12.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.3.5.2 The LCS must be analyzed at the frequency described in Section 12.3.2 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.3.5.3 The LCS must be prepared as described in Section 12.3.3.

12.3.5.4 The LCS must meet all sample technical acceptance criteria in Section 12.3.5.

12.3.5.5 The %R for each of the analytes in the LCS must be within the recovery limits listed in Table 12 – Laboratory Control Sample Recovery Limits.

12.3.5.6 Surrogate recoveries must fall within the acceptance windows in Table 10 – Surrogate Recovery Limits. These limits are <u>not</u> advisory.

12.3.6 Corrective Action for Laboratory Control Sample

12.3.6.1 If the LCS technical acceptance criteria for the surrogates or the LCS compound recoveries are not met, check calculations, the surrogate and LCS solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the surrogate and LCS recovery criteria.

12.3.6.2 LCS technical acceptance criteria MUST be met before data are reported. LCS contamination from laboratory sources or any LCS analyzed not meeting the technical acceptance criteria will

require re-extraction and reanalysis of the LCS at no additional cost to the EPA.

12.3.6.3 All samples (including MS/MSD and PE samples) and required blanks, prepared and analyzed in an SDG with an LCS that does not meet the technical acceptance criteria, will also require re-extraction and reanalysis at no additional cost to the EPA.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed, the Method Detection Limit (MDL) for each single compound pesticide target analyte and Toxaphene shall be determined on each instrument used for analysis. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for water and soil/sediment samples). The MDLs must be determined annually thereafter or after major instrument maintenance. Major instrument maintenance includes, but is not limited to: cleaning or replacement of the detector. A new MDL study will not be required after changing the GC column, as long as the replacement has the same length, inner diameter, and stationary phase.

12.4.2 To determine the MDLs, the Contractor shall perform MDL studies following the procedures specified in 40 Code of Federal Regulations (CFR) Part 136.

12.4.3 The determined concentration of the MDL must be less than the CRQL listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 4 – Pesticides Target Analyte List and Contract Required Quantitation Limits.

12.4.4 All documentation for the MDL studies shall be maintained at the laboratory and submitted to the EPA within seven (7) days of study completion. This schedule and the designated recipients are specified in Exhibit B, Table 1 – Reporting and Deliverables Requirements.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

See Section 13.0 of Exhibit D – Introduction to Organic Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 14.0 of Exhibit D – Introduction to Organic Analytical Methods.

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Acid-Base Partition Cleanup, SW-846 Method 3650B, Revision 2, December 1996.

16.2 U.S. Environmental Protection Agency, Alumina Cleanup, SW-846 Method 3610B, Revision 2, December 1996.

16.3 U.S. Environmental Protection Agency, Automated Soxhlet Extraction, SW-846 Method 3541, Revision 0, September 1994.

16.4 U.S. Environmental Protection Agency, Continuous Liquid-Liquid Extraction, SW-846 Method 3520C, Revision 3, December 1996.

16.5 U.S., Environmental Protection Agency, Gel-Permeation Cleanup, SW-846 Method 3640A, Revision 1, September 1994.

16.6 U.S. Environmental Protection Agency, Organochlorine Pesticides by Gas Chromatography, SW-846 Method 8081B Revision 2, January 1998.

16.7 U.S. Environmental Protection Agency, Pressurized Fluid Extraction (PFE), SW-846 Method 3545A, Revision 1, January 1998.

16.8 U.S. Environmental Protection Agency, Separatory Funnel Liquid-Liquid Extraction, SW-846 Method 3510C Revision 3, December 1996.

16.9 U.S. Environmental Protection Agency, Florisil Cleanup, SW-846 Method 3620C, Revision 3, February 2007.

16.10 U.S. Environmental Protection Agency, Silica Gel Cleanup, SW-846 Method 3630C, Revision 3, December 1996.

16.11 U.S. Environmental Protection Agency, Ultrasonic Extraction, SW-846 Method 3550C, Revision 3, November 2000.

16.12 U.S. Government Printing Office, 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS

Systematic Name	EPA Registry Name	Synonym	CAS #
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1.alpha.,2.alpha.,3.beta.,4.alpha.,5.beta.,6.beta.)-	.alpha.-Hexacyclo hexane	.alpha.-BHC	319-84-6
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1.alpha.,2.beta.,3.alpha.,4.beta.,5.alpha.,6.beta.)-	.beta.-Hexacyclo hexane	.beta.-BHC	319-85-7
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1.alpha.,2.alpha.,3.alpha.,4.beta.,5.alpha.,6.beta.)-	.delta.-Hexacyclo hexane	.delta.-BHC	319-86-8
Cyclohexane, 1,2,3,4,5,6-hexachloro-, (1.alpha.,2.alpha.,3.beta.,4.alpha.,5.alpha.,6.beta.)-	Lindane	.gamma.-BHC (Lindane)	58-89-9
4,7-Methano-1H-indene, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-	Heptachlor	Heptachlor	76-44-8
1,4:5,8-Dimethanonaphthalene, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-, (1.alpha.,4.alpha.,4a.beta.,5.alpha.,8.alpha.,8a.beta.)-	Aldrin	Aldrin	309-00-2
2,5-Methano-2H-indeno[1,2-b]oxirene, 2,3,4,5,6,7,7-heptachloro-1a,1b,5,5a,6,6a-hexahydro-, (1aR,1bS,2R,5S,5aR,6S,6aR)-rel-	Heptachlor epoxide	Heptachlor epoxide	1024-57-3
6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide, (3.alpha.,5a.beta.,6.alpha.,9.alpha.,9a.beta.)-	.alpha.Endosulfan	Endosulfan I	959-98-8
2,7:3,6-Dimethanonaphth[2,3-b]oxirene, 3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-, (1aR,2R,2aS,3S,6R,6aR,7S,7aS)-rel-	Dieldrin	Dieldrin	60-57-1
Benzene, 1,1'-(dichloroethenylidene)bis[4-chloro-	p,p'-DDE	4,4'-DDE	72-55-9
2,7:3,6-Dimethanonaphth[2,3-b]oxirene, 3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-, (1aR,2R,2aR,3R,6S,6aS,7S,7aS)-rel, and metabolites	Endrin	Endrin	72-20-8
6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide, (3.alpha.,5a.alpha.,6.beta.,9.beta.,9a.alpha.)-	.beta.-Endosulfan	Endosulfan II	33213-65-9

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS (CON'T)

Systematic Name	EPA Registry Name	Synonym	CAS #
Benzene, 1,1'-(2,2-dichloroethylidene)bis[4-chloro-	p,p'-DDD	4,4'-DDD	72-54-8
6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3,3-dioxide	Endosulfan sulfate	Endosulfan sulfate	1031-07-8
Benzene, 1,1'-(2,2,2-trichloroethylidene)bis[4-chloro-	p,p'-DDT	4,4'-DDT	50-29-3
Benzene, 1,1'-(2,2,2-trichloroethylidene)bis[4-methoxy-	Methoxychlor	Methoxychlor	72-43-5
2,5,7-Metheno-3H-cyclopenta[a]pentalen-3-one, 3b,4,5,6,6,6a-hexachlorodecahydro-, (2R,3aR,3bS,4R,5R,6aS,7S,7aR,8R)-	Endrin ketone	Endrin ketone	53494-70-5
1,2,4-Methenocyclopenta[cd]pentalene-5-carboxaldehyde, 2,2a,3,3,4,7-hexachlorodecahydro-, (1.alpha.,2.beta.,2a.beta.,4.beta.,4a.beta.,5.beta.,6a.beta.,6b.beta.,7R*)-	Endrin aldehyde	Endrinaldehyde	7421-93-4
4,7-Methano-1H-indene, 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-, (1R,2S,3aS,4S,7R,7aS)-rel-	Chlorodane(cis)	cis-Chlordane	5103-71-9
4,7-Methano-1H-indene, 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-, (1R,2R,3aS,4S,7R,7aS)-rel-	Chlorodane(trans)	trans-Chlordane	5103-74-2
Toxaphene	Toxaphene	Chlorinated camphene	8001-35-2
Benzene, 1,2,3,5-tetrachloro-4,6-dimethyl	Tetrachloro-m-xylene	2,4,5,6-Tetrachloroxylene	877-09-8
1,1'-Biphenyl, 2,2',3,3',4,4',5,5',6,6'-decachloro-	Decachlorobiphenyl	Decachloro-1,1'-biphenyl	2051-24-3

TABLE 2. CONCENTRATION LEVELS OF INITIAL CALIBRATION AND CONTINUING CALIBRATION VERIFICATION AND TECHNICAL ACCEPTANCE CRITERIA FOR PESTICIDES

Analyte	Concentration (ng/mL)					Maximum %RSD	Opening Maximum %D	Closing Maximum %D
	CS1	CS2	CS3	CS4	CS5			
alpha-BHC	5.0	10.	20.	40.	80.	25.0	±25.0	±25.0
gamma-BHC	5.0	10.	20.	40.	80.	20.0	±25.0	±25.0
Heptachlor	5.0	10.	20.	40.	80.	20.0	±25.0	±25.0
Endosulfan I	5.0	10.	20.	40.	80.	20.0	±25.0	±25.0
Dieldrin	10.	20.	40.	80.	160	20.0	±25.0	±25.0
Endrin	10.	20.	40.	80.	160	20.0	±25.0	±25.0
4,4'-DDD	10.	20.	40.	80.	160	20.0	±25.0	±25.0
4,4'-DDT	10.	20.	40.	80.	160	20.0	±25.0	±25.0
Methoxychlor	50.	100	200	400	800	20.0	±25.0	±25.0
beta-BHC	5.0	10.	20.	40.	80.	20.0	±25.0	±25.0
delta-BHC	5.0	10.	20.	40.	80.	25.0	±25.0	±25.0
Aldrin	5.0	10.	20.	40.	80.	20.0	±25.0	±25.0
Heptachlor-epoxide	5.0	10.	20.	40.	80.	20.0	±25.0	±25.0
4,4'-DDE	10.	20.	40.	80.	160	20.0	±25.0	±25.0
Endosulfan II	10.	20.	40.	80.	160	20.0	±25.0	±25.0
Endosulfan sulfate	10.	20.	40.	80.	160	20.0	±25.0	±25.0
Endrin ketone	10.	20.	40.	80.	160	20.0	±25.0	±25.0
Endrin aldehyde	10.	20.	40.	80.	160	20.0	±25.0	±25.0
cis-Chlordane	5.0	10.	20.	40.	80.	20.0	±25.0	±25.0
trans-Chlordane	5.0	10.	20.	40.	80.	20.0	±25.0	±25.0
Toxaphene	500	1000	2000	4000	8000	30.0	±25.0	±25.0
Tetrachloro-m-xylene (surrogate)	5.0	10.	20.	40.	80.	20.0	±30.0	±30.0
Decachlorobiphenyl (surrogate)	10.	20.	40.	80.	160	20.0	±30.0	±30.0

NOTE: Only the exo-epoxy isomer (Isomer B) of heptachlor epoxide is used as an analytical standard.

TABLE 3. INSTRUMENT PERFORMANCE CHECK STANDARDS

	Resolution Check Mixture (RESC)	**Performance Evaluation Mixture (PEM)**
Analyte	**Concentration (ng/mL)**	
alpha-BHC	10.0	10.0
beta-BHC	10.0	10.0
delta-BHC	10.0	-
gamma-BHC	10.0	10.0
Aldrin	10.0	-
Heptachlor	10.0	-
Heptachlor-epoxide	10.0	-
cis-Chlordane	10.0	-
trans-Chlordane	10.0	-
Endosulfan I	10.0	-
Endosulfan II	20.0	-
4,4'-DDD	20.0	-
4,4'-DDE	20.0	-
4,4'-DDT	20.0	100.0
Dieldrin	20.0	-
Endrin	20.0	50.0
Endosulfan sulfate	20.0	-
Endrin ketone	20.0	-
Endrin aldehyde	20.0	-
Methoxychlor	100.0	250.0
Tetrachloro-m-xylene	10.0	20.0
Decachlorobiphenyl	20.0	20.0

TABLE 4. LOW CONCENTRATION CALIBRATION STANDARD (CS1) FOR INDIVIDUAL STANDARD MIXTURES A AND B

Individual Standard Mixture A	**Low-Point (CS1) Concentration (ng/mL)**	**Individual Standard Mixture B**	**Low-Point (CS1) Concentration (ng/mL)**
alpha-BHC	5.0	beta-BHC	5.0
gamma-BHC	5.0	delta-BHC	5.0
Heptachlor	5.0	Aldrin	5.0
Endosulfan I	5.0	Heptachlor-epoxide (exo-epoxy isomer)	5.0
Dieldrin	10.	4,4'-DDE	10.
Endrin	10.	Endosulfan II	10.
4,4'-DDD	10.	Endosulfan sulfate	10.
4,4'-DDT	10.	Endrin ketone	10.
Methoxychlor	50.	Endrin aldehyde	10.
Tetrachloro-m-xylene	5.0	cis-Chlordane	5.0
Decachlorobiphenyl	10.	trans-Chlordane	5.0
		Tetrachloro-m-xylene	5.0
		Decachloro-biphenyl	10.

TABLE 5. RETENTION TIME WINDOWS FOR
SINGLE COMPONENT ANALYTES, TOXAPHENE, AND SURROGATES

Compound	**Retention Time Window (minutes)**
alpha-BHC	± 0.05
beta-BHC	± 0.05
gamma-BHC (Lindane)	± 0.05
delta-BHC	± 0.05
Heptachlor	± 0.05
Aldrin	± 0.05
cis-Chlordane	± 0.07
trans-Chlordane	± 0.07
Heptachlor epoxide	± 0.07
Dieldrin	± 0.07
Endrin	± 0.07
Endrin aldehyde	± 0.07
Endrin ketone	± 0.07
4,4'-DDD	± 0.07
4,4'-DDE	± 0.07
4,4'-DDT	± 0.07
Endosulfan I	± 0.07
Endosulfan II	± 0.07
Endosulfan sulfate	± 0.07
Methoxychlor	± 0.07
Toxaphene	± 0.07
Tetrachloro-m-xylene	± 0.05
Decachlorobiphenyl	± 0.10

TABLE 6. GAS CHROMATOGRAPH ANALYTICAL CONDITIONS

Carrier Gas:	Helium or Hydrogen 99.999% purity
Column Flow:	5 mL/min.
Make-up Gas:	Argon/Methane (P-5 or P-10) or N_2 (required)
Injector Temperature:	> 200°C
Injection Technique:	On-column
Injection Volume:	1 or 2 µl
Injector:	Grob-type, splitless
Initial Temperature:	150°C
Initial Hold Time:	0.5 min.
Temperature Ramp:	5°C to 6°C/min.
Final Temperature:	275°C
Final Hold Time:	After decachlorobiphenyl has eluted

TABLE 7. CONCENTRATION OF MATRIX SPIKE/MATRIX SPIKE DUPLICATE SPIKING, LABORATORY CONTROL SAMPLE SPIKING, AND GEL PERMEATION CHROMATOGRAPHY CALIBRATION VERIFICATION STANDARD SOLUTIONS

Analyte	**MS/MSD Spiking Solution** (µg/mL)	**LCS Spiking Solution** (µg/mL)	**GPC Calibration Verification Solution** (µg/mL)
gamma-BHC (Lindane)	0.50	0.050	0.020
Heptachlor	0.50		0.020
Aldrin	0.50		0.020
Dieldrin	1.0	0.10	0.040
Endrin	1.0	0.10	0.040
4,4'-DDT	1.0		0.040
trans-Chlordane		0.050	
Heptachlor epoxide		0.050	
4,4'-DDE		0.10	
Endosulfan sulfate		0.10	

TABLE 8. FLORISIL CARTRIDGE PERFORMANCE CHECK

COMPOUND	**QC LIMITS**
alpha-BHC	80-120
gamma-BHC (Lindane)	80-120
Heptachlor	80-120
Endosulfan I	80-120
Dieldrin	80-120
Endrin	80-120
4,4'-DDD	80-120
4,4'-DDT	80-120
Methoxychlor	80-120
TCX	80-120
DCB	80-120
2,4,5 -Trichlorophenol	<5

TABLE 9. GEL PERMEATION CHROMATOGRAPHY CALIBRATION VERIFICATION

ANALYTE	QC LIMITS
gamma-BHC (Lindane)	80-110
Heptachlor	80-110
Aldrin	80-110
Dieldrin	80-110
Endrin	80-110
4,4'-DDT	80-110

TABLE 10. SURROGATE RECOVERY LIMITS

Compound	Percent Recovery
Tetrachloro-m-xylene	30-150
Decachlorobiphenyl	30-150

TABLE 11. MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS

Analyte	Percent Recovery Water	RPD Water	Percent Recovery Soil	RPD Soil
gamma-BHC (Lindane)	56-123	0-15	46-127	0-50
Heptachlor	40-131	0-20	35-130	0-31
Aldrin	40-120	0-22	34-132	0-43
Dieldrin	52-126	0-18	31-134	0-38
Endrin	56-121	0-21	42-139	0-45
4,4'-DDT	38-127	0-27	23-134	0-50

TABLE 12. LABORATORY CONTROL SAMPLE RECOVERY LIMITS

Analyte	Percent Recovery Water/Soil
gamma-BHC	50-120
Heptachlor epoxide	50-150
Dieldrin	30-130
4,4'-DDE	50-150
Endrin	50-120
Endosulfan sulfate	50-120
trans-Chlordane	30-130

THIS PAGE INTENTIONALLY LEFT BLANK

EXHIBIT D

AROCLORS ANALYSIS

THIS PAGE INTENTIONALLY LEFT BLANK

Exhibit D – Aroclors Analysis

Table of Contents

Exhibit D – Aroclors Analysis

Table of Contents

1.0 SCOPE AND APPLICATION

The analytical method that follows is designed to analyze water and soil/sediment samples from hazardous waste sites to determine the presence and concentration of the Aroclors contained in the Target Analyte List (TAL) for Aroclors in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits. The method, based on the U.S. Environmental Protection Agency (EPA) SW-846 Method 8082A, can be used for determining compound concentrations in the range from the Contract Required Quantitation Limits (CRQLs) to one million times the CRQL in these matrices when appropriate dilutions are made. The method includes sample extraction, extract cleanup techniques, and Gas Chromatograph/Electron Capture Detector (GC/ECD) analytical methods for Aroclors.

2.0 SUMMARY OF METHOD

2.1 Water

Continuous liquid-liquid extraction or separatory funnel extraction procedures are employed for aqueous samples. A 1.0 liter (L) aliquot of sample is spiked with the surrogate solution and extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried with anhydrous sodium sulfate (or Hydromatrix™), concentrated, and subjected to Gel Permeation Chromatography (GPC) (GPC cleanup is optional). The extract is then solvent exchanged into hexane, a 1 or 2 milliliter (mL) aliquot of the extract is subjected to a sulfuric acid cleanup, and the final volume adjusted to the same volume as the aliquot (1 mL or 2 mL). The extract is analyzed using a dual column wide-bore capillary GC/ECD.

2.2 Soil/Sediment

A 30 gram (g) aliquot of sample is spiked with the surrogates, mixed with anhydrous sodium sulfate (or Hydromatrix™), and extracted with a 1:1 (v/v) acetone/methylene chloride solvent mixture by ultrasonic extraction, Soxhlet extraction, or pressurized fluid extraction. The extract is filtered, concentrated, and subjected to GPC (GPC cleanup is optional). The extract is then solvent-exchanged into hexane, a 1 or 2 mL aliquot of the extract is subjected to a sulfuric acid cleanup, and the final volume adjusted to the same volume as the aliquot (1 mL or 2 mL). The extract is analyzed using a dual column wide-bore capillary GC/ECD.

2.3 Wipes

Not applicable to this method.

2.4 Waste

Not applicable to this method.

3.0 DEFINITIONS

See Exhibit G – Glossary of Terms for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These contaminants lead to discrete artifacts or to elevated baselines in Gas Chromatograms. These materials must be routinely demonstrated to be free from interferences under the sample preparation and analysis conditions by analyzing instrument and method blanks. Interferences caused by phthalate esters can pose a major problem in Aroclor analysis. Because common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

4.2 Matrix Interferences

Matrix interferences may be caused by compounds that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. The cleanup procedures must be used to remove such interferences in order to achieve the CRQLs.

5.0 SAFETY

See Section 12.0 of Exhibit D – Introduction to Organic Analytical Methods.

5.1 Reagents

Concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to skin and mucous membranes. Use this reagent in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with this reagent.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here; however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternative equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 General Laboratory Equipment

6.1.1 Balances

6.1.1.1 Top loading, capable of weighing accurately to ±0.01 g.

6.1.1.2 Analytical, capable of weighing accurately to ±0.0001 g.

6.1.1.3 A balance calibration must be checked with known masses once per each day of use. This verification consists of a check with two weights covering the range expected (approximately ±50% of the expected measured mass) for each type of balance and be accurate to ±0.01 g and ±0.0001 g, respectively. The masses that are used to check the balances daily must be checked on a monthly basis

using NIST-traceable known reference masses (Class '0' or Class '1') as defined by ASTM E617-97(2008) or equivalent (e.g., earlier Class 'S' defined masses). All balances must be checked at least once annually by a certified technician. The reference masses used by the Contractor must be recertified at least every five years, or sooner if there is reason to believe damage (corrosion, nicks) has occurred. The Contractor shall maintain documentation that demonstrates these criteria have been met.

6.1.2 Beakers - 100 mL, 125 mL, 250 mL, and 400 mL.

6.1.3 Centrifuge, Table Top (optional).

6.1.3.1 Centrifuge Tube - 12-15 mL with 19 mm ground-glass joint (optional).

6.1.4 Graduated Cylinder Class A – 1.0 L and 100 mL capacity.

6.1.5 Desiccator.

6.1.6 Erlenmeyer Flasks - 250 mL.

6.1.7 Volumetric Flask, Class A – 5.0, 10, 20, 50, 100, 250 and 500 mL

6.1.8 Magnetic Stirring Bar – Polytetrafluoroethylene (PTFE) coated, at least 4 centimeters (cm) long.

6.1.9 Ovens – drying, capable of maintaining 105°C (±5°C).

6.1.10 pH Meter - With a combination glass electrode. Calibrate according to manufacturer's instructions. The pH meter shall be calibrated prior to each use, using reference standards bracketing the range expected in samples. The pH reference standards shall be replaced when their expiration dates have passed.

6.1.11 pH Paper – Wide range.

6.1.12 Pipettes - Glass volumetric, 1 mL or 2 mL.

6.1.13 Spatula - Stainless steel or PTFE.

6.1.14 Syringes – 10 microliters (µL), 25 µL, 100 µL, and 1000 µL.

6.1.15 Vials and Caps - 10 mL (optional), with screw-cap and PTFE or aluminum foil liner; autosampler vial with 2 mL capacity for GC auto sampler.

6.1.16 Weigh Dish – Porcelain crucibles or disposable aluminum weighing pans.

6.2 Glassware/Extraction/Cleanup Equipment

6.2.1 Automated Soxhlet Extraction System - With temperature-controlled oil bath. Silicone oil must not be used because it destroys the rubber parts. The apparatus must be used in a hood.

6.2.1.1 Cellulose or Glass Extraction Thimble (26 mm x 60 mm).

6.2.1.2 Glass Extraction Cups.

6.2.1.3 Thimble Adapters.

6.2.1.4 Viton Seals.

6.2.2 Soxhlet Extraction, Manual.

6.2.2.1 Allihn Condenser.

6.2.2.2 Soxhlet Extractor body, 40 mm ID.

6.2.2.3 Round bottom flask, 500 mL.

6.2.3 Borosilicate Glass Wool - Rinsed with methylene chloride.

6.2.4 Continuous Liquid-Liquid Extractors - Equipped with PTFE or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.2.5 Drying Column – 400 millimeter (mm) x 19 mm ID Chromatographic column, with coarse frit (substitution of a small pad of disposable borosilicate glass wool for the frit will help prevent cross-contamination of sample extracts).

6.2.6 Gel Permeation Chromatography Equipment

6.2.6.1 GPC System - Systems that perform satisfactorily have been assembled from the following components: a High Performance Liquid Chromatography (HPLC) pump; an auto sampler or a valving system with sample loops; and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements in Section 10.2.1.3.4.

NOTE: Optional GPC cleanup is for all soils/sediments, extracts, and for water extracts containing higher molecular weight contaminants that interfere with the analyses of the target analytes.

6.2.6.2 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. To simplify switching from the ultraviolet (UV) detector during calibration to the GPC collection device during extract cleanup, an optional double 3-way valve may be attached so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

6.2.6.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column.

6.2.6.4 Bio Beads (SX-3) - 200 to 400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, or equivalent). An additional 5 g of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

6.2.6.5 UV Detector - Fixed wavelength [254 nanometers (nm)] with a semi-prep flow-through cell.

6.2.6.6 Strip Chart Recorder - Recording integrator or laboratory data system.

6.2.6.7 Syringe Filter Assembly, disposable – 5 micron filter discs.

NOTE: Consult your instrument operation manual to determine the proper filter disc to use in your system. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

6.2.6.8 Viscometer

6.2.7 Kuderna-Danish Apparatus

6.2.7.1 Concentrator Tubes - 10 mL and 15 mL, graduated.

6.2.7.2 Evaporative Flasks - 500 mL.

6.2.7.3 Silicon Carbide Boiling Chips – Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride. PTFE boiling chips solvent rinsed prior to use are acceptable.

6.2.7.4 Snyder Column - Three-ball macro.

6.2.7.5 Snyder Column - Two-ball micro.

6.2.8 Nitrogen Evaporation Device - Equipped with a water bath that can be maintained at 35-40°C. To prevent the release of solvent fumes into the laboratory, the nitrogen evaporator device must be used in a hood.

6.2.9 Pressurized Fluid Extraction Device

6.2.9.1 Dionex Accelerated Solvent Extractor (ASE-300) or equivalent with appropriately-sized extraction cells. Currently, 100 mL cells are available that will accommodate greater than 30 g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure requirements [2000+ pounds per square inch (psi)] necessary for this procedure.

6.2.9.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.2.10 Separatory Funnels - 2 L with PTFE stopcock.

6.2.11 Sonabox Acoustic Enclosure (or equivalent) - For use with disruptor to decrease noise level.

6.2.12 Sulfuric Acid Cleanup

6.2.12.1 Syringe or Class A volumetric glass pipette; 1.0, 2.0, and 5.0 mL.

6.2.12.2 Vials – 1.0, 2.0, and 10 mL, glass with PTFE-lined screw-caps or crimp tops.

6.2.12.3 Vortex Mixer.

6.2.13 Ultrasonic Cell Disruptor - QSonica LLC, (53 Church Hill Road, Newtown, CT 06470) model S-4000 or equivalent ultrasonic liquid disruptor – equipped with a 3/4-inch horn and a 1/2-inch horn with a minimum output capacity of 300 watts.

NOTE 1: To ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. A rough tip surface is an indication of erosion.

NOTE 2: Follow manufacturer’s instructions for set-up.

6.2.13.1 Vacuum or Pressure Filtration Apparatus.

6.2.13.2 Buchner Funnel.

6.2.13.3 Filter Paper – Whatman No. 42, or equivalent.

6.2.14 Water Bath - Heated, with concentric ring cover, capable of temperature control. The bath should be used in the hood.

6.3 Analytical Instrumentation

6.3.1 Gas Chromatograph

The GC must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout the temperature program operations. The system must be suitable for splitless injection and have all required accessories including syringes, analytical columns, and gases. The instrument must be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room. All GC

carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.3.1.1 GCs may have difficulty in meeting certain method Quality Control (QC) requirements. This problem can be minimized by operating the injector at 200-205°C, using a borosilicate glass (not quartz) methyl silicone deactivated injector liner, and deactivating the metal parts in the injector with dichlorodimethylsilane. In some cases, using a 0.25 inch packed column injector converted for use with 0.53 mm capillary columns works better than a Grob-type injector. If a Grob-type injector is used, a 4 mm liner may be required to meet breakdown criteria.

6.3.2 Gas Chromatography Columns

Recommended Columns: Wide-bore (0.53mm ID) fused silica GC columns may be used provided that the resolution requirements are met (Section 9.3.5); if two wide-bore (0.53 mm ID) fused silica GC columns are used, then a separate detector is required for each column. The specified analytical columns are a 30 m x 0.53 mm ID, 1.0 µm film thickness DB-1701 (J&W Scientific); SPB 1701 (Supelco); AT 1701 (Alltech); Rtx®-1701, Rtx® CLP I, Rtx® (Restek); CP-Sil 19CB (Chrompack); 007-1701 (Quadrex); BP-10 (SGE); or equivalent, and a 30 m x 0.53 mm ID, 0.5 to 1.0 µm film thickness DB-608 (J&W Scientific); HP-608 (Agilent); SPB-608 (Supelco); 007-608 (Quadrex); BP-608 (SGE); Rtx® CLP II; CP-Sil 8CB (Chrompack); or equivalent. A description of the GC columns used for analysis shall be provided in the SDG Narrative. Packed columns may not be used.

6.3.2.1 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits;
- The analytical results generated using the column meet the initial calibration and continuing calibration verification (CCV) technical acceptance criteria listed in the analytical method in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits;
- The column can accept at least 16 times the low-point initial calibration concentration level in Table 2 – Concentration Levels of Initial Calibration and Continuing Calibration Verification Standards and Technical Acceptance Criteria for Aroclors, without becoming overloaded; and
- The column pair chosen must have dissimilar phases and should produce different patterns to aid in Aroclor confirmation despite chromatographic interferences.

6.3.2.1.1 The column provides equal or better resolution of the analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits, than the columns listed in Section 6.3.2. Although the instructions included in the analytical method are for wide-bore capillary columns, narrower bore capillary columns may be evaluated for use. Follow manufacturer’s instructions for use

of its product. Document in the SDG Narrative if other columns are used by specifying the column used.

6.3.2.1.2 The Contractor must maintain documentation verifying that the alternate column met the criteria in Sections 9.3.5 and 9.4.5. The minimum documentation is indicated below.

6.3.2.1.2.1 Manufacturer provided information concerning the performance characteristics of the column.

6.3.2.1.2.2 Chromatograms and data system reports generated on the GC/ECD and used for EPA Contract Laboratory Program (CLP) analyses, including those from:

- Instrument blanks demonstrating there are no contaminants that interfere with the Aroclors analysis when using the alternate column; and
- The analysis of initial calibration and CCV standards using the alternate column.

6.3.2.1.3 Based on the Contractor-generated data described above, the Contractor shall complete a written review, signed by the Laboratory Manager, certifying that:

- The column performance meets the technical acceptance criteria in Section 6.3.2;
- The low-point initial calibration standard analyses have adequate sensitivity to meet the Aroclor CRQLs;
- The high-point initial calibration standard analyses were not overloaded; and
- The alternate column does not introduce contaminants which interfere with the identification and quantitation of analytes listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits.

6.3.2.1.4 The documentation must be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request of the EPA Regional Laboratory Contracting Officer Representative(COR).

6.3.2.1.5 Columns may be mounted in a press-fit Y-shaped glass 3-way union splitter or a Y-shaped fused-silica connector from a variety of commercial sources. The two columns may be mounted in an 8-inch deactivated glass injection tee. The Contractor should follow the manufacturer’s recommendations for mounting 0.53 mm capillary columns in injector ports. Dual column GC with separate autosamplers may be used for sample extractor injection.

6.3.2.1.6 The carrier gas for routine applications is helium. The Contractor may choose to use hydrogen as a carrier gas, but they must clearly identify its use in the SDG Narrative in submissions to the EPA. Laboratories that choose to use hydrogen are advised to exercise caution in its use. Use of a hydrogen leak detector is highly recommended when hydrogen is used as the carrier gas. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-PTFE thread sealants or flow controllers with rubber components are not to be used.

6.3.2.2 Gel Permeation Chromatography Column Preparation

Prepare the GPC column using Bio Beads. Alternate column packings may be used if: 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration and GPC calibration checks, and 2) the column packings do not introduce contaminants/artifacts into the sample that interfere with the analysis of the aroclor analytes. Follow the manufacturer's instructions for preparation of the GPC column.

6.3.3 Electron Capture Detector

6.3.3.1 The linearity of the response of the ECD may be greatly dependent on the flow rate of the make-up gas. The make-up gas must be P-5, P-10 (argon/methane), or nitrogen according to the instrument specification. Care must be taken to maintain stable and an appropriate flow of make-up gas to the detector. The GC/ECD system must be in a room in which the atmosphere has been demonstrated to be free of all contaminants that may interfere with the analysis. The instrument must be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.3.3.2 At least annually, each ECD should be checked for radiation leakage from their Ni-63 source. Wipe tests should be conducted by wiping the inlet, outlet, and body of the ECD cell with swabs and sending the swabs for radiation tests.

6.4 Data Systems/Data Storage

A data system must be interfaced to the GC/ECD that allows the continuous acquisition and storage of data from each column throughout the duration of the chromatographic program and must permit, at a minimum, the output of time vs. Intensity (peak height or peak area) data. The data system must be able to rescale chromatographic data in order to report chromatograms meeting the requirements listed within this method.

7.0 REAGENTS AND STANDARDS

The Contractor must provide all standards to be used with the contract. These standards may be used only after they have been certified according to the procedure in Exhibit D – Introduction to Organic Analytical Methods, Section 11.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

Reagents shall be dated with the receipt date and used on a first-in, first-out basis. The purity of the reagents shall be verified before use.

7.1 Reagents

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the CRQL for each analyte of interest.

7.1.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g [1 pound (lb)] of activated carbon.

7.1.1.2 Reagent water may also be generated using a water purification system.

7.1.2 10% acetone in hexane (v/v) - Prepare by adding 10.0 mL of acetone to 90.0 mL of hexane.

7.1.3 Acetone/methylene chloride (1:1 v/v).

7.1.4 Acid Solutions: Sulfuric Acid Solution (50% v/v) - Prepare a 1:1 (v/v) solution by slowly adding 50 mL of concentrated sulfuric acid to 50 mL of reagent water.

7.1.5 Copper powder (optional) - Fine, granular. Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.

7.1.6 Hydromatrix™ - Diatomaceous earth-based material rinsed with methylene chloride and dried at 400°C for 4 hours in a shallow tray, cooled in a desiccator, and stored in a glass bottle.

7.1.7 Nitric Acid - Dilute, for sulfur removal with copper.

7.1.8 Sodium Hydroxide Solution (10 N) - Carefully dissolve 40 g of NaOH in reagent water and dilute the solution to 100 mL.

7.1.9 Sodium sulfate - Granular anhydrous reagent grade, heated at 400°C for 4 hours, cooled in a desiccator, and stored in a glass bottle. Each lot must be extracted with hexane and analyzed by a GC/ECD to demonstrate that it is free of interference before use or must be purchased with a certification that it is free of interference.

CAUTION: AN OPEN CONTAINER OF SODIUM SULFATE MAY BECOME CONTAMINATED DURING STORAGE IN THE LABORATORY.

7.1.10 Sodium sulfite.

7.1.11 Solvents: Methylene chloride, hexane, acetone, toluene, iso-octane, methanol (optional), - Aroclor quality or equivalent, and petroleum ether. It is recommended that each lot of solvent be analyzed to demonstrate that it is free of interference before use or must be purchased with certified that it is free of interference. Methylene

chloride must be certified as acid free or must be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride must be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.1.12 Sulfuric acid, concentrated, 95-98% (sp. gr. 1.84).

7.1.13 Tetrabutylammonium sulfite.

7.1.14 Glycerol.

7.2 Standards

7.2.1 Stock Standard Solutions

7.2.1.1 Stock standard solutions are defined as standards that are to be used to produce working standards. They may be in the form of single compounds or mixtures. They may be prepared in methylene chloride from pure standard materials, or purchased as pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated.

7.2.2 Working Standards

7.2.2.1 Aroclor Standard Mixtures

Prepare Aroclor and surrogates tetrachloro-m-xylene and decachlorobiphenyl standard solutions at a minimum of five concentration levels listed in Table 2 – Concentration Levels of Initial Calibration and Continuing Calibration Verification Standards and Technical Acceptance Criteria for Aroclors. The standard solutions of each target analyte plus surrogates must be prepared individually for each Aroclor, except for Aroclor 1260 and Aroclor 1016 which may be combined in one standard mixture.

7.2.2.1.1 Prepare a single-point calibration for Aroclor 1221, 1232, 1242, 1248, 1254, 1262, and 1268 including surrogates at the lowest standard concentration in Table 2– Concentration Levels of Initial Calibration and Continuing Calibration Verification Standards and Technical Acceptance Criteria for Aroclors.

7.2.2.1.2 If Aroclor 1221, 1232, 1242, 1248, 1254, 1262, or 1268 are detected in a sample, then the five-point initial calibration solution for the detected Aroclor must be used for the initial calibration of the GC/ECD.

7.2.2.1.3 The Calibration Standard Mixture solutions must be prepared in either hexane or iso-octane. The solutions must be prepared every 6 months, or sooner if the solutions have degraded or concentrated.

7.2.2.1.4 The concentration of each target analyte for each calibration standard are listed in Table 2– Concentration Levels of Initial Calibration and Continuing Calibration Verification Standards and Technical Acceptance Criteria for Aroclors. These levels are based upon 10 mL final volume extracts for samples not undergoing GPC cleanup, and 5.0 mL final volume extracts for those samples undergoing GPC cleanup.

7.2.2.1.5 Other concentration levels may be used for more sensitive instrumentation and final extract volume levels. For example, in the case of Aroclor 1016, a laboratory may use a final extract volume of 10 mL for samples undergoing GPC cleanup, and a low calibration standard of 50 nanograms (ng)/mL. The alternative calibration standards and final extract volumes may be used as long as the following requirements are met:

- The Contractor can demonstrate by Method Detection Limits (MDL) studies that the MDL study calculated MDL for each target analyte is below the required CRQL for that analyte when using the laboratory's specific final volume and calibration level scheme.
- All five calibration levels are in the same ratio as that shown in Table 2– Concentration Levels of Initial Calibration and Continuing Calibration Verification Standards and Technical Acceptance Criteria for Aroclors (e.g., if a laboratory were using a 2.5 ng/mL low standard, then the other calibration levels must be 100, 200, 400, and 800 ng/mL).

7.2.2.2 Continuing Calibration Standard

The CCV Aroclor Standards must be prepared individually, except for Aroclor 1260 and Aroclor 1016 which may be combined in one standard solution with surrogates at or near the mid-point concentration of the initial calibration standard (Table 2– Concentration Levels of Initial Calibration and Continuing Calibration Verification Standards and Technical Acceptance Criteria for Aroclors).

7.2.2.3 Gel Permeation Chromatography Calibration and Calibration Verification Solutions

7.2.2.3.1 GPC Calibration Solution

Prepare a GPC calibration solution in methylene chloride that contains the following analytes at the minimum concentrations listed below. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

Analyte	Concentration (mg/mL)
Corn oil (CAS# 8001-30-7)	25.0
Bis(2-ethylhexyl)phthalate (CAS# 117-81-7)	0.50
Methoxychlor (CAS# 72-43-5)	0.10
Perylene (CAS# 198-55-0)	0.020
Sulfur (CAS# 7704-34-9)	0.080

NOTE: Sulfur is not very soluble in methylene chloride, but it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

7.2.2.3.2 GPC Calibration Verification Solution

Prepare the GPC calibration verification solution containing the Aroclors listed in Table 5 – Concentration of Matrix Spike/Matrix Spike Duplicate Spiking, Laboratory Control Sample Spiking, and Gel Permeation Chromatography Calibration Verification Standard Solutions, in methylene chloride at the concentrations specified for a 5 mL GPC injection loop. See Section 10.3.1.4.3 for compound concentrations if a smaller size loop is being used. The solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.4 Surrogate Standard Spiking Solution

The surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added prior to extraction to all standards, samples [including Laboratory Control Samples (LCSs)], Matrix Spike/Matrix Spike Duplicates (MS/MSD), Performance Evaluation (PE) samples (if required), and required blanks (method/sulfur cleanup/instrument). Prepare a surrogate standard spiking solution of 0.20 µg/mL for tetrachloro-m-xylene and 0.40 µg/mL for decachlorobiphenyl in acetone. The solution should be checked frequently for stability. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

NOTE: Other concentrations for surrogate standard spiking solutions may be used, provided that the appropriate amount of each surrogate is added to all standards, samples (including LCSs), MS/MSDs, PE samples, and blanks.

7.2.2.5 Matrix Spiking Solution

Prepare a matrix spiking solution containing the Aroclors in Table 5 - Concentration of Matrix Spike/Matrix Spike Duplicate Spiking, Laboratory Control Sample Spiking, and Gel Permeation Chromatography Calibration Verification Standard Solutions, in acetone or methanol at the concentrations specified. The solution must be replaced every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.6 Laboratory Control Sample Spiking Solution

Prepare a laboratory control spiking solution containing the Aroclors in Table 5 - Concentration of Matrix Spike/Matrix Spike Duplicate Spiking, Laboratory Control Sample Spiking, and Gel Permeation Chromatography Calibration Verification Standard Solutions, in acetone or methanol at the concentration specified. The LCS solution must be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.3 Storage of Standards

7.2.3.1 Store the stock standard solutions at ≤6°C, but not frozen in PTFE-lined, screw-cap, amber bottles/vials.

7.2.3.2 The working standards must be prepared every 6 months, or sooner if the solutions have degraded or concentrated. The working standards must be checked frequently for signs of degradation or evaporation. Store the working standard solutions at ≤6°C in PTFE-lined screw-cap, amber bottles/vials.

NOTE: Refrigeration of GPC calibration solution may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves. Replace this calibration solution every 6 months, or more frequently if necessary.

7.2.3.3 Standard solutions purchased from a chemical supply company as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no Manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from the preparation date. The expiration date of the ampulated standards, upon the breaking of

the glass seal, is 6 months, or sooner if the standard has degraded or evaporated.

7.2.3.4 Protect all standards from light.

7.2.3.5 Samples, sample extracts, and standards must be stored separately.

7.2.3.6 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. Storage of standard solutions in the freezer may cause some compounds to precipitate. This means at a minimum, the standards must be brought to room temperature prior to use, checked for losses, and checked that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

7.2.4 Temperature Records for Storage of Standards

7.2.4.1 The temperature of all standard storage refrigerators/freezers shall be recorded daily.

7.2.4.2 Temperature excursions shall be taken noted and appropriate corrective actions shall be taken to correct problems, when required.

7.2.4.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators/freezers.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples

Water samples may be collected in 1.0 L (or 1.0 quart) amber glass containers, fitted with PTFE-lined screw-caps. If amber containers are not available, the samples should be protected from light.

8.1.2 Soil/Sediment Samples

Soil/sediment samples may be collected in glass containers.

8.2 Procedure for Sample and Sample Extract Storage

8.2.1 Sample Storage

The samples must be protected from light and refrigerated at ≤ 6°C but not frozen from the time of receipt until 60 days after delivery of a complete, reconciled data package to the EPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 Sample Extract Storage

Sample extracts must be protected from light and stored at ≤6 °C until 365 days after delivery of a complete, reconciled data package to the EPA.

8.3 Contract Required Holding Times

8.3.1 Extraction of water samples by separatory funnel procedures must be completed within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of water samples by continuous liquid-liquid extraction must be started within 5 days of VTSR. Extraction of soil/sediment samples shall be completed within 10 days of VTSR.

8.3.2 Analysis of sample extracts must be completed within 40 days following the start of extraction.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Initial Instrument Set-up

9.1.1 Gas Chromatograph

9.1.1.1 The GC analytical conditions are provided in Table 4 – Gas Chromatograph Analytical Conditions. Other conditions may be used, provided that all technical acceptance criteria in Sections 9.3.5, 9.4.5, and 11.3 are met.

9.1.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples (including LCS and MS/MSD), and required blanks (method/sulfur cleanup/instrument).

9.1.1.3 The same injection volume, 1.0 or 2.0 µL, must be used for all standards, samples (including LCS and MS/MSD), and required blanks (method/sulfur cleanup/instrument).

9.1.1.4 The linearity of the ECD may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

9.1.1.5 Cold (ambient temperature) on-column injectors that allow injection directly onto a 0.53 mm ID column may be used as long as the initial calibration and calibration verification technical acceptance criteria are met.

9.2 Instrument Performance Check

Not applicable to this method.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

Prior to analysis of samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup/instrument), each GC/ECD system must be calibrated to determine instrument sensitivity and the linearity of GC response. An initial five-point calibration is performed using Aroclors 1016 and 1260 to demonstrate the linearity of the detector response. The other seven Aroclors can be calibrated at a single low-point at a minimum, for pattern recognition. The standards for these seven Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five levels of the Aroclor 1016/1260 standards.

NOTE: All Aroclor target analytes may have five-point calibrations performed initially, prior to sample analyses. Alternately, as long as a valid five-point calibration of Aroclor 1016/1260 is present, five-point calibrations for any of the remaining Aroclor target analytes must be performed prior to reanalysis of samples known to contain the Aroclor.

9.3.2 Frequency of Initial Calibration

Each GC/ECD system must be calibrated prior to analyzing samples, after major instrument maintenance or modification is performed (e.g., column replacement or repair, cleaning or replacement of the ECD, etc.), or if the CCV technical acceptance criteria have not

been met. Also, for any sample in which an Aroclor (other than Aroclor 1016 or Aroclor 1260) is detected for which a valid five-point calibration curve is not available, the sample shall be reanalyzed following a valid five-point calibration of the specific Aroclor.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Set up the GC/ECD system as described in Section 9.1. Optimize the instrumental conditions for resolution of the target analytes and sensitivity.

NOTE: Once the GC conditions have been established, the same operating conditions must be used for both calibrations and sample analyses.

9.3.3.2 All standards and instrument blanks must be allowed to warm to ambient temperature before analysis.

9.3.3.3 Prepare the initial calibration standards using the procedures, analytes, and the concentrations specified in Section 7.2.2.1.

9.3.3.4 If Aroclors other than Aroclor 1016/1260 are detected in a sample analysis, following a single-point calibration for that particular Aroclor, a separate five-point calibration must be prepared (Section 7.2.2.1) and analyzed for that particular Aroclor, followed by a re-analysis of the sample.

9.3.3.5 Analyze the initial calibration sequence which includes a five-point calibration for the Aroclor 1016/1260, and either single or five-point calibration standards for the other Aroclor analytes. All steps pertaining to the initial calibration sequence shall be performed uninterrupted with no more than the length of one chromatographic analysis separating any step. When mis-injection occurs during the initial calibration, the laboratory is allowed to perform re-injection as long as it is within the 12-hour period.

9.3.3.6 The single point calibration of Aroclors shall be at the lowest concentration (CS1) for pattern recognition at the CRQL. Each Aroclor standard shall be analyzed before the analysis of any sample. Single point Aroclor calibration may be made before or after the analysis of the five-point Aroclor calibration.

9.3.4 Calculations for Initial Calibration

9.3.4.1 During the initial calibration sequence, absolute RTs are determined for each surrogate and five major peaks of each Aroclor (three major peaks for Aroclor 1221) on both columns.

NOTE: It is the Contractor’s responsibility to ensure that DDT, DDD, and DDE do not co-elute at the same retention times as the target Aroclor analyte peaks.

9.3.4.2 For Aroclors 1016 and 1260, an RT is measured for a minimum of five peaks in each of the five calibration standards and the $\overline{RT}$ is calculated for each of the peaks as the average of the five values obtained from the five calibration standards. For Aroclor 1221, an RT is measured for three peaks for a single-point calibration standard. For Aroclors 1232, 1242, 1248, 1254, 1262, and 1268, an RT is measured for five peaks for a single-point calibration standard. For Aroclor 1262 and Aroclor 1268, the peak for DCB shall not be used as one of the five peaks for calibration. If a valid five-point calibration is present for a specific Aroclor, then an RT is measured for five peaks (three for Aroclor 1221) in each of the five calibration standards and

the $\overline{RT}$ is calculated as the average of the five values for each of the peaks obtained from the five calibration standards. An RT is measured for the surrogates in each of the five calibration standards of Aroclor 1016/1260, or from Aroclor 1016 if analyzed as a separate mixture. The surrogate $\overline{RT}$ is calculated as the average of the five values. Calculate the mean absolute $\overline{RT}$ using the following equation:

EQ. 1 Mean Absolute Retention Time

$$\overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

WHERE,

RT_i = Retention Time of analyte peak

n = Total number of measurements (n=5)

9.3.4.3 An RT window is calculated for five major peaks of each Aroclor (three major peaks for Aroclor 1221) and for each surrogate using the RT window listed in Table 3 – Retention Time Windows for Analytes and Surrogates. The $\overline{RT}$s for surrogates are calculated from the five analyses of Aroclor 1016. If Aroclor 1016 and 1260 calibration standards are combined, calculate the $\overline{RT}$s for the surrogates from the combined calibration standard. Compounds are identified when peaks are observed in the RT window for the compound on both GC columns.

9.3.4.4 Five sets of CFs, one for each of the five selected peaks (three for Aroclor 1221), will be generated for the five-point initial calibration of Aroclor 1016/1260 mixture using Equation 2. Calculate the $\overline{CF}$s for each set of Aroclor peaks and surrogates over the initial calibration range using Equation 3. The $\overline{CF}$s for surrogates are calculated from the five analyses of the Aroclor 1016. If Aroclor 1016 and 1260 calibration standards are combined, calculate the CFs for surrogates from the combined calibration standard.

9.3.4.5 For single-point Aroclor calibrations, calculate the CF for each selected peak.

9.3.4.6 Five sets of CFs, one for each selected peak, shall be calculated for all Aroclors that required a five-point initial calibration using Equation 2. Either peak area or peak height may be used to calculate the CFs used in the %RSD equation.

9.3.4.7 Calculate CFs, the mean CF ($\overline{CF}$), and the %RSD of the CFs for each peak in a selected set of five major peaks for each Aroclor (three major peaks for Aroclor 1221) using Equations 2, 3, 4, and 5. Either peak area or peak height may be used to calculate the CFs. For example, it is permitted to calculate the CF for Aroclor 1016 based on peak area and to calculate CF for Aroclor 1260 based on peak height. It is not permitted to calculate CFs for an Aroclor from both peak area and peak height. For example, it is not permitted to calculate the CFs for the CS1 Standard for Aroclor 1260 using peak height and calculate the CS3 and CS5 Standard CFs for Aroclor 1260 using peak area.

EQ. 2 Calibration Factor

$$CF = \frac{\text{Peak area (or peak height) of the standard}}{\text{Mass Injected (ng)}}$$

9.3.4.8 Calculate the $\overline{CF}$ and the %RSD of the CF for each Aroclor analyte peak and surrogate over the initial calibration range using Equations 3 and 5.

EQ. 3 Mean Calibration Factor

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

WHERE,
CF_i = Calibration Factor
n = Total number of values (n=5)

9.3.4.9 The linearity of the instrument is determined by calculating a %RSD of the CFs from a five-point calibration curve for each of the Aroclors requiring a five-point calibration and surrogates using Equations 5 and 6.

EQ. 4 Standard Deviation of Calibration Factors

$$SD_{CF} = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{(n-1)}}$$

WHERE,
CF_i, $\overline{CF}$, n = As given in EQ. 3

EQ. 5 Percent Relative Standard Deviation of the Calibration Factors

$$\%RSD = \frac{SD_{CF}}{\overline{CF}} \times 100$$

WHERE,

SD_{CF} = Standard Deviation of Calibration Factors

CF_i, $\overline{CF}$, n = As given in EQ.3

9.3.5 Technical Acceptance Criteria for Initial Calibration

All initial calibration technical acceptance criteria apply independently to each GC column.

9.3.5.1 The initial calibration sequence must be analyzed according to the procedure listed in Section 9.3.3, at the concentration listed in Section 7.2.2.1, and at the frequency listed in Section 9.3.2. The GC/ECD operating conditions optimized in Section 9.1 must be followed.

9.3.5.2 The identification of Aroclors by GC methods is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for Aroclors.

9.3.5.2.1 The chromatograms of the standards for the Aroclors analyzed during the initial calibration sequence must display the peaks chosen for identification of each analyte at greater than 25% of full scale, but less than 100% of full scale.

9.3.5.2.2 If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

9.3.5.3 The %RSD of the CFs for each Aroclor peak and surrogates must be less than or equal to 20% (Table 2 - Concentration Levels of Initial Calibration and Continuing Calibration Verification Standards and Technical Acceptance Criteria for Aroclors). The %RSD requirement applies to any other Aroclor analyzed at the five-point calibration (if required in Section 9.3.3).

9.3.6 Corrective Action for Initial Calibration

9.3.6.1 If the initial calibration technical acceptance criteria are not met, reinject the initial calibration standards in sequence. If the technical acceptance criteria for the initial calibration are not met again, inspect the system for problems. It may be necessary to change the column, bake-out the detector, clean the injection port, or take other corrective actions to achieve the acceptance criteria.

NOTE: If any of the DDT analogs elute at the same retention time as an Aroclor peak that was chosen for use in quantitation, then the analyst should either adjust the GC conditions to achieve better resolution, or choose another peak that is characteristic of that Aroclor and does not correspond to a peak from a DDT analog.

9.3.6.2 Contamination should be suspected as a cause if the detector cannot achieve acceptable linearity using this method. It is recommended to refer to manufacturer's guidelines for performing detector maintenance. In the case of severe contamination, the detector may require servicing by the ECD manufacturer.

CAUTION: DO NOT OPEN THE DETECTOR. THE ECD CONTAINS RADIOCHEMICAL SOURCES.

9.3.6.3 After major maintenance is completed, the detector must be recalibrated using the initial calibration sequence.

9.3.6.4 Any samples or required blanks analyzed when the initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to the EPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Continuing Calibration Verification

The analyses of instrument blanks and the required Aroclor CS3 standard (Section 9.4.2) constitute the calibration verification. Sample data (including LCS and MS/MSD) and required blank (method/sulfur cleanup/instrument) are not acceptable unless bracketed by acceptable analyses of instrument blanks and the Aroclor CS3 standard (refer to Section 10.4.2.1 for the Analytical Sequence).

9.4.2 Frequency of Continuing Calibration Verification

An instrument blank and Aroclor 1016/1260 CS3 Standard Mixture must bracket one end of a 12-hour period during which sample and required blank data are collected and a second instrument blank, Aroclor 1016/1260 CS3 standard, and Aroclor CS3 standard of every other detected Aroclor(s) must bracket the other end of a 12-hour period. Each CCV must include an instrument blank and Aroclor 1016/1260 CS3 standard; additional Aroclor CS3 standards may be performed at the

laboratory's discretion. If a valid five-point calibration is available for Aroclor(s) in addition to 1016/1260, an opening CCV with an instrument blank and Aroclor 1016/1260 CS3 standard is sufficient; however, the closing CCV must include the Aroclor (CS3) matching each Aroclor detected in the sample(s) and meet opening Aroclor CCV technical acceptance criteria in Section 9.4.5.3.

9.4.2.1 Injection of an instrument blank and Aroclor 1016/1260 CS3 standard bracket the front end of the 12-hour period immediately following the initial calibration sequence (Section 9.3.3.5). The injection of any additional CS3 Aroclor standard(s) as determined by the laboratory should follow the opening instrument blank and Aroclor 1016/1260 CS3 standard. Samples (including LCSs and MS/MSDs) and required blanks (method/sulfur cleanup) may be injected for 12 hours from the injection of the instrument blank. The first injections immediately after the 12-hour period must be an instrument blank, Aroclor 1016/1260 CS3 standard (closing CCV), and CS3 standard (s) of every other detected Aroclor. A closing CCV must bracket the end of a 12-hour sequence.

9.4.2.2 The analyses of the instrument blank and CS3 Aroclor standard(s) (closing CCV) immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided that they meet the technical acceptance criteria in Section 9.4.5. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a CS3 Aroclor standard(s) (closing CCV), in that order. Those two analyses may in turn be used to bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks or the required CS3 Aroclor standard (s) fails to meet the technical acceptance criteria in Section 9.4.5. The 12-hour period begins with the injection of the instrument blank.

9.4.2.3 If more than 12 hours elapse between the injections of the two instrument blanks (opening and closing CCV) that bracket a 12-hour period in which samples or required blanks are analyzed, then the time between the injection of the instrument blank (closing CCV) and the preceding sample may not exceed the length of one chromatographic analysis.

NOTE: Additional Aroclor CCV standards may be analyzed at the laboratory's discretion. The closing CCV must include Aroclor 1016/1260 CS3 and all detected Aroclors in the sample(s). When an Aroclor, other than Aroclor 1016/1260, is detected in a sample, the closing CCV CS3 standard of this detected Aroclor standard must meet opening CCV technical acceptance criteria in Section 9.4.5, if the sample was not preceded by the Aroclor included as a CS3 standard in the opening CCV. If the entire 12-hour period is not required for the analyses of all samples and blanks to be reported and all data collection is to be stopped, the sequence must end with an appropriate closing CCV combination, that is, an instrument blank, Aroclor 1016/1260 CS3 standard, and CS3 Aroclor standard(s) for every Aroclor detected in samples.

9.4.2.4 No more than 14 hours may elapse from the injection beginning the opening CCV (instrument blank) and the injection ending the closing CCV (Aroclor Standard).

All acceptable samples must be analyzed within a valid analysis sequence as given below:

Time	Injection #	Material Injected
0 hr		Instrument Blank at end of initial calibration
		First sample if using initial calibration
		Subsequent samples
		Last Sample
12 hrs	1st injection past 12 hours	Instrument Blank
	Next injections past 12 hours	Aroclor 1016/1260 CS3 Standard
		Any other CS3 Standard (as required)
		Sample
		Subsequent samples
		Last Sample
Another 12 hrs	1st injection past 12 hours	Instrument Blank
	Next injection past 12 hours	Aroclor 1016/1260 CS3 Standard
		Any other CS3 Standard (as required)
		Sample
		Samples with Toxaphene detected
		Subsequent samples
		Last Sample
Another 12 hrs	1st injection past 12 hours	Instrument Blank
	Next injections past 12 hours	Aroclor 1016/1260 CS3 Standard
		Any other CS3 Standard (as required)
	Next injection past 12 hours	Toxaphene CS3

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 All standards and instrument blanks must be allowed to warm to ambient temperature before analysis.

9.4.3.2 Analyze the instrument blank and the CS3 Aroclor Standard Mixture(s) according to Section 10.4 using the same injection volumes as in the initial calibration.

9.4.4 Calculations for Continuing Calibration Verification

For each analysis of the CS3 Aroclor standard(s) used to demonstrate calibration verification, calculate the %D between the CF of each Aroclor peak (and surrogate) in the standard and the corresponding $\overline{CF}$ from the Aroclor initial calibration, using the following equation:

EQ. 6 External Standard Calibration Percent Difference

$$\%D = \frac{CF - \overline{CF}}{\overline{CF}} \times 100$$

WHERE,

CF = Calibration Factor for CS3 Standard used for Calibration Verification

$\overline{CF}$ = Mean Calibration Factor

9.4.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.4.5.1 All CCV technical acceptance criteria apply independently to each column, and must meet the chromatogram criteria specified in Section 9.3.5.2.

9.4.5.2 The Aroclor 1016/1260 standards and Aroclor standards of other detected Aroclors must be analyzed at the required frequency on a GC/ECD system that has met the initial calibration technical acceptance criteria.

9.4.5.3 The absolute RT of each of the Aroclor peaks and surrogates in the calibration verification standard must be within the RT window determined from the initial calibration standard in Section 9.3.4.3.

9.4.5.4 For the opening CCV, the %D for each Aroclor peak and surrogates calculated from the CCV standard must not exceed ±25% and ±30.0%, respectively. For the closing CCV, the %D for each Aroclor peak and surrogates calculated from the CCV must not exceed ±50%. If the %D for the closing CCV meets the criteria for an opening CCV, then it can be used for the opening CCV of the next 12-hour period.

NOTE: When a required closing CCV of an Aroclor other than Aroclor 1016/1260 is preceded by an opening CCV of Aroclor 1016/1260 CS3 only, the %D of each Aroclor peak must not exceed ±25%. The %D requirement is waived for a closing Aroclor 1262 or Aroclor 1268 CCV standard since the DCB surrogate makes it impossible to meet the requirement.

9.4.5.5 All instrument blanks must meet the technical acceptance criteria in Section 12.1.4.5.

9.4.6 Corrective Action for Continuing Calibration Verification

9.4.6.1 If the technical acceptance criteria for the CCV are not met, inspect the system for problems and take corrective action to achieve the acceptance criteria.

9.4.6.2 Major corrective actions, such as replacing the GC column or baking out the detector, will require that a new initial calibration be performed that meets the technical acceptance criteria in Section 9.3.5.

9.4.6.3 Minor corrective actions may not require performing a new initial calibration, provided that a new analysis of the standard that originally failed the criteria and an associated instrument blank immediately after the corrective action does meet all the acceptance criteria.

9.4.6.4 If the Aroclor 1016/1260 standard does not meet technical acceptance criteria listed in Sections 9.4.5.2 and 9.4.5.3, it must be re-injected immediately. If the second injection of the Aroclor 1016/1260 standard meets the criteria, sample analysis may continue. If the second injection does not meet the criteria, all data collection must be stopped. Appropriate corrective action must be taken, and a new initial calibration

sequence must be established before more sample data are collected.

9.4.6.5 If an instrument blank does not meet the technical acceptance criteria listed in Section 12.1.4.5, all data collection must be stopped. Appropriate corrective action must be taken to clean out the system, and an acceptable instrument blank must be analyzed before more sample data are collected.

9.4.6.6 The Contractor is reminded that analyzing an instrument blank and an Aroclor 1016/1260 standard once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to analyze instrument blanks and standards more often to avoid discarding data.

9.4.6.7 If a successful instrument blank and Aroclor 1016/1260 standard cannot be analyzed after an interruption in analysis (Section 9.4.2), an acceptable initial calibration must be analyzed before sample data may be collected. All acceptable sample analyses (including LCSs and MS/MSDs) and required blank (method/sulfur cleanup) analyses must be preceded and followed by acceptable instrument blanks and standards (opening and closing CCV) as described in Section 9.4.2.

9.4.6.8 Any samples and required blanks associated with a CCV that do not meet the technical acceptance criteria will require reanalysis at no additional cost to the EPA.

10.0 PROCEDURE

The Contractor must have the capability to perform all sample cleanup procedures presented in this Exhibit. The Contractor may use any of the procedures or combinations of procedures to clean up the samples prior to analysis, unless the Contractor is specifically directed by the EPA Region to use a particular cleanup procedure or combination of cleanup procedures.

The Contractor must demonstrate that each cleanup procedure is capable of producing data that meets the technical acceptance criteria for the method, including MDLs (Section 12.4) and any precision and recovery limits.

10.1 Sample Preparation

10.1.1 Water Samples

Water samples may be extracted by either a separatory funnel procedure or a continuous liquid-liquid extraction procedure. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, continuous liquid-liquid extraction must be employed. Allow the samples to warm to ambient temperature before extraction.

10.1.1.1 Separatory Funnel Extraction

10.1.1.1.1 For samples received in 1 L bottles, the Contractor shall mark the meniscus and transfer the entire sample into the separatory funnel. If the sample was not received in a 1 L bottle, measure out each 1 L sample aliquot in a separate graduated cylinder.

10.1.1.1.2 Measure and record the volume of sample contained in the 1 L sample bottle with water using a graduated cylinder.

10.1.1.1.3 Using a syringe or a volumetric pipette, add 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.4) to all water samples.

10.1.1.1.4 Measure and record the pH of the sample with wide range pH paper and adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring pH adjustment must be noted in the SDG Narrative. Place the sample aliquot into a 2 L separatory funnel.

10.1.1.1.5 Rinse the 1 L sample bottle and/or graduated cylinder with 30 mL of methylene chloride and transfer the rinsate to the separatory funnel.

10.1.1.1.6 Add another 30 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 minutes, with periodic venting to release excess pressure.

NOTE: The total volume of solvent used for extraction is 60 mL. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than 1/3 the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration through glass wool, centrifugation, or other physical means. Drain the methylene chloride into a 250 mL Erlenmeyer flask.

10.1.1.1.7 Add a second 60 mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Proceed to Section 10.2.

10.1.1.2 Continuous Liquid-Liquid Extraction

10.1.1.2.1 Continuous Liquid-Liquid Extraction without Hydrophobic Membrane

10.1.1.2.1.1 Follow the manufacturer's instructions for set-up.

10.1.1.2.1.2 Add 300-500 mL of methylene chloride to the bottom of the extractor and fill it to a depth of at least 1 inch above the bottom sidearm.

10.1.1.2.1.3 If the samples have been received in 1 L bottles, the Contractor shall mark the meniscus and transfer the entire sample into the continuous extractor. If the sample was not received in a 1 L bottle, measure out each 1.0 L sample aliquot in a separate, clean graduated cylinder and transfer the aliquot to the continuous extractor.

10.1.1.2.1.4 Using a syringe or volumetric pipette, add 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.4) into the water samples and mix well. Perform spiking prior to pH adjustment or any other processing steps.

10.1.1.2.1.5 Rinse the graduated cylinder with a small amount of methylene chloride and transfer the rinsate to the continuous extractor. If the sample container is empty, rinse the container with 50 mL of methylene chloride and add the rinsate to the continuous extractor.

10.1.1.2.1.6 Measure the pH of the sample with wide range pH paper or a pH meter and record the pH. Adjust the pH to between 5 and 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring the pH adjustment must be noted in the SDG Narrative.

NOTE: With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and the water layer in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction.

10.1.1.2.1.7 Add sufficient methylene chloride to the continuous liquid-liquid extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 5-15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 18 hours.

NOTE 1: When a minimum drip rate of 10-15 mL/minute is maintained throughout the extraction, the extraction time may be reduced to a minimum of 12 hours. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

NOTE 2: Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor.

10.1.1.2.2 Continuous Liquid-Liquid Extraction with Hydrophobic Membrane

10.1.1.2.2.1 Follow the procedure in Sections 10.1.1.2.1.1 - 10.1.1.2.1.5, but reduce the amount of methylene chloride used to 50 mL and extract for a minimum of 6 hours.

10.1.1.2.2.2 Add sufficient methylene chloride to the continuous liquid-liquid extractor to ensure proper solvent cycling during operation. Adjust the drip rate to 15 mL/minute (recommended); optimize the extraction drip rate. Extract for a minimum of 6 hours.

10.1.1.2.2.3 Due to the smaller volume of solvent used during the extraction process, some sample matrices (e.g., oily samples, samples containing a high concentration of surfactants) may create an emulsion that will consume the solvent volume, preventing efficient extraction of the sample. When this occurs, add additional solvent to ensure efficient extraction of the sample, and extend the extraction time for a minimum of 6 hours. If the sample matrix prevents the free flow of solvent through the membrane, then the non-hydrophobic membrane continuous liquid-liquid type extractor must be used. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

10.1.1.2.2.4 Some continuous liquid-liquid extractors are also capable of concentrating the extract within the extraction set-up. Follow the manufacturer's instructions for concentration when using this type of extractor. Using the hydrophobic membrane, it may not be necessary to dry the extract with sodium sulfate.

10.1.1.2.2.5 If low surrogate recoveries occur, ensure that: 1) the apparatus was properly assembled to prevent leaks, 2) the drip rate/solvent cycling was optimized, and 3) there was proper cooling for condensation of solvent. Document the problem and the corrective action.

10.1.1.2.2.6 Alternate continuous liquid-liquid extractor types that meet the requirements of the analytical method may also be used. If using alternate extractors or design types, follow the manufacturer's instructions for set-up. Optimize the extraction procedure.

10.1.2 Soil/Sediment Samples

Mix samples thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves and rocks. Also, decant and discard any standing aqueous phase.

10.1.2.1 Extraction of Soil/Sediment Samples

10.1.2.1.1 Three procedures are provided for the extraction of aroclor analytes from soil/sediment samples:

- ultrasonic extraction;
- Soxhlet extraction[automated and manual]; and
- pressurized fluid extraction (PFE).

NOTE: All soil/sediment samples in a Case must be extracted by the same procedure.

10.1.2.1.2 For soil/sediment sample extractions, weigh 30-50 g of sample, to the nearest 0.1 g, into a 400 mL beaker. 30 g is ideal, as more sample may be used to compensate for high moisture content. If the system cannot accommodate 30 g of sample, a smaller sample size may be used. The specified CRQLs must be met. Adjust the amount of solvents and standards added as necessary. Document the smaller sample size in the SDG Narrative along with all steps taken to ensure sample homogeneity.

10.1.2.1.3 Add 60 g of anhydrous powdered or granulated sodium sulfate, or add 30 g of Hydromatrix™, and mix well to produce a sandy texture. Additional drying agent may be added as needed.

NOTE: For samples extracted by the PFE procedure (Section 10.1.2.1.7) the use of sodium sulfate is not recommended.

10.1.2.1.4 Add 1.0 mL of surrogate standard spiking solution to the sample, then immediately add 100 mL of 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.1.2.1.5 for ultrasonic extraction, Section 10.1.2.1.6 for automated Soxhlet extraction, or Section 10.1.2.1.7 for pressurized fluid extraction. As applicable, follow the manufacturer's instructions for use of all extraction equipment.

10.1.2.1.5 Ultrasonic Extraction

10.1.2.1.5.1 Place the bottom surface of the tip of the 3/4-inch tapered disruptor horn about 1/2 inch below the surface of the solvent, but above the sediment layer. Do <u>not</u> use a microtip probe.

10.1.2.1.5.2 Sonicate for 3 minutes with output at full power with pulse on (pulsing energy as opposed to continuous), and percent duty cycle knob set at 50%.

NOTE: Refer to the manufacturer's instructions for appropriate output settings.

10.1.2.1.5.3 Transfer and filter extracts through Whatman No. 42 (or equivalent) filter paper using vacuum filtration or centrifuge and decant extraction solvent.

10.1.2.1.5.4 Repeat the extraction two more times with two additional 100 mL portions of 1:1 (v/v) acetone/methylene chloride. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with a clean spatula. Transfer the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.2.

10.1.2.1.6 [Automated] Soxhlet Extraction

The Contractor may use either automated or non-automated Soxhlet extraction. The following procedure is based on the use of a Soxtec HT-6 automated Soxhlet extraction system. When using a different system, refer to the instructions provided by the manufacturer for the appropriate procedure.

10.1.2.1.6.1 Check the heating oil level in the automated Soxhlet unit and add oil if needed. Follow the manufacturer's instructions to set the temperature on the service unit.

10.1.2.1.6.2 Press the "MAINS" button and observe that the switch lamp is now "ON". Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/minute to prevent solvent loss through the condensers.

10.1.2.1.6.3 Transfer the entire sample from the beaker (Sections 10.1.2.1.2 - 10.1.2.1.4) to the thimble.

10.1.2.1.6.4 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

10.1.2.1.6.5 Insert the extraction cups containing boiling chips, and load each with an appropriate volume of 1:1 (v/v) acetone/methylene chloride. Using the cup holder, lower the locking handle and ensure that the safety catch engages. The cups are now clamped into position.

NOTE: The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

10.1.2.1.6.6 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.

10.1.2.1.6.7 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set timer for 60 minutes. Condenser valves are still open. Extract for the preset time. After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

10.1.2.1.6.8 When all but 2-5 mL of solvent have been collected, open the system and remove the cups. Transfer the contents of the cups to graduated, conical-bottom glass tubes. Rinse the cups with methylene chloride and add the rinsates to the glass tubes. Proceed to Section 10.2.

10.1.2.1.7 Pressurized Fluid Extraction

10.1.2.1.7.1 Transfer the entire sample from the beaker (Sections 10.1.2.1.2 - 10.1.2.1.4) to an extraction cell of the appropriate size for the aliquot.

10.1.2.1.7.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.2.1.7.3 Place a pre-cleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 - 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

10.1.2.1.7.4 The following are recommended extraction conditions:

Oven temperature:	100°C
Pressure:	1500-2000 psi
Static time:	5 min. (after 5 min. pre-heat equilibration)
Flush volume:	60% of the cell volume
Nitrogen purge:	60 sec. at 150 psi (purge time may be extended for larger cells)
Static cycles:	1

10.1.2.1.7.5 Optimize the extraction conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500-2000 psi should suffice. An appropriate amount of 1:1 (v/v) acetone/methylene chloride should be used to achieve the conditions in Section 10.1.2.1.7.4.

10.1.2.1.7.6 Once established, the same pressure should be used for all samples in the same SDG.

10.1.2.1.7.7 Begin the extraction according to the manufacturer's instructions. Collect each extract in a clean vial. Allow the extracts to cool after the extractions are complete. Proceed to Section 10.2.

10.2 Extract Concentration

10.2.1 Concentration by Kuderna-Danish

10.2.1.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if equivalency is demonstrated for all target analytes listed in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits.

10.2.1.2 For water samples, transfer the extract to a K-D concentrator by pouring the extract through a drying column containing about 10 cm of anhydrous granular sodium sulfate.

10.2.1.3 For soil/sediment samples, directly transfer the extract to the K-D concentrator, if the extract is known to be dry.

10.2.1.4 Rinse the original container collecting the extract (for both water and soil/sediment samples) and the column (for water samples) with at least two 20-30 mL portions of methylene chloride to complete the quantitative transfer.

10.2.1.5 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60-70°C recommended) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the

concentration in 15-30 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-5 mL for water samples (and less than 10 mL for soil/sediment samples), remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.2.1.6 For both water and soil/sediment extracts that do not require GPC cleanup, proceed with the hexane exchange described in Section 10.2.2.

10.2.1.7 For water extracts that may require GPC cleanup, remove the Snyder column, rinse the flask and its lower joint, collect the rinsate in the concentrator tube, and adjust the volume to 10 mL with methylene chloride. Proceed to Section 10.3.1.

10.2.1.8 For soil/sediment extracts that may require GPC cleanup, it is absolutely necessary to further reduce the volume of all soil/sediment extracts to 1 mL in order to remove most of the acetone. This is best accomplished using the nitrogen evaporation technique (Section 10.2.3.2). The presence of acetone will cause a dead volume to develop in the GPC column and thus will cause a loss of surrogates and analytes during the GPC cleanups. Adjust the soil/sediment extract volume to 10 mL with methylene chloride. Proceed to Section 10.3.1.

10.2.2 Solvent Exchange into Hexane

This procedure applies to both extracts of water samples and extracts of soil/sediment samples.

10.2.2.1 With the extract in a K-D apparatus, remove the Snyder column, add 50 mL of hexane and a new boiling chip, and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as described previously (Section 10.2.1), but increase the temperature of the water bath (80-90°C recommended) to maintain proper distillation. When the apparent volume of liquid reaches 3-5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

10.2.2.2 Remove the Snyder column; using 1-2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Complete quantitative transfer of the extract to a 10 mL vial by using hexane.

10.2.2.3 For samples that have <u>not</u> been subjected to GPC cleanup, adjust the volume of the hexane extract to 10 mL. For samples that <u>have</u> been subjected to GPC cleanup, concentrate the hexane extract to 5 mL using a Micro Snyder Column or nitrogen evaporation, as described in Section 10.2.3.1 or 10.2.3.2, then proceed to Section 10.3.2 for sulfuric acid cleanup.

10.2.3 Final Concentration of Extract

Two different techniques are permitted to concentrate the extract to volume before cleanup or instrumental analysis. They are the Micro Snyder Column and Nitrogen Evaporation Technique.

10.2.3.1 Micro Snyder Column Concentration

10.2.3.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two-ball Micro Snyder Column. Pre-wet the Snyder column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath

(80-90°C recommended) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse its flask and lower joint into the concentrator tube with 0.2 mL of hexane.

10.2.3.1.2 If GPC cleanup is needed and not yet performed, adjust the volume to 10 mL with methylene chloride and proceed to Section 10.3.1 for GPC cleanup. For samples that do not require GPC cleanup, adjust the volume to 10 mL with hexane and proceed to Section 10.3.2 for sulfuric acid cleanup. For samples that have already undergone GPC cleanup, adjust the volume with hexane to 5 mL and proceed to Section 10.3.2 for sulfuric acid cleanup. If no further cleanup is needed, adjust the volume with hexane to the same volume of the aliquot used for sulfuric acid and/or sulfur cleanup (1 or 2 mL) and proceed to Section 10.4 for GC/ECD analysis. Extracts may be stored at ≤6°C, but not frozen, prior to analysis.

10.2.3.2 Nitrogen Evaporation Technique

10.2.3.2.1 Place the concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to the final volume using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). DO NOT ALLOW THE EXTRACT TO GO DRY.

10.2.3.2.2 If GPC cleanup is needed and not yet performed, adjust the volume to 10 mL with methylene chloride and proceed to Section 10.3.6 for GPC cleanup. For samples that do not require GPC cleanup, adjust the volume to 10 mL with hexane and proceed to Section 10.3.2 for sulfuric acid cleanup. For samples that have already undergone GPC cleanup, adjust the volume with hexane to 5 mL and proceed to Section 10.3.2 for sulfuric acid cleanup. If no further cleanup is needed, adjust the volume with hexane to the same volume of the aliquot used for sulfuric acid and/or sulfur cleanup (1 or 2 mL) and proceed to Section 10.4 for GC/ECD analysis. Extracts may be stored at ≤6°C, but not frozen, prior to analysis

10.2.3.2.3 Gas lines from the gas source to the evaporation apparatus must be stainless steel, copper, or PTFE tubing. Plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane and then dried prior to use.

10.3 Cleanup Procedures

There are three cleanup procedures specified in this method: GPC cleanup, sulfuric acid cleanup, and sulfur cleanup. Sulfur cleanup must be performed for all sample extracts contaminated with sulfur. GPC clean-up is optional for water and soil sediment extracts.

Sulfuric acid clean-up is mandatory for all extracts. Method blanks must be subjected to the same cleanup procedures as the samples (including LCSs and MS/MSDs).

10.3.1 Gel Permeation Chromatography

10.3.1.1 Introduction

GPC is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the size of the molecules to be separated.

10.3.1.2 GPC Column Preparation

Prepare the GPC column using Bio Beads. Alternate column packings may be used if: 1) the column packings have equivalent or better performance than the Bio Beads and meet the technical acceptance criteria for GPC calibration and GPC calibration checks, and 2) the column packings do not introduce contaminants/artifacts into the sample that interfere with the analysis of the aroclor analytes. Follow the manufacturer's instructions for preparation of the GPC column.

10.3.1.3 Calibration of GPC

10.3.1.3.1 Summary of GPC Calibration

The GPC calibration procedure is based on monitoring the elution of standards with a UV detector connected to the GPC column.

10.3.1.3.2 Frequency of GPC Calibration

Each GPC system must be calibrated prior to processing samples under the contract; when the GPC CCV solution fails to meet criteria (Section 10.3.1.3.4); when the column is changed; when channeling occurs; and once every 7 days, when in use. Also, the RT shift must be less than 5% when compared to RTs in the last calibration UV traces.

10.3.1.3.3 Procedure for GPC Calibration

Follow the manufacturer's instructions for operating the GPC system. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte RTs and must be monitored.

10.3.1.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.2.3.1) onto the GPC. Determine the elution times for bis(2-ethylhexyl)phthalate, methoxychlor, and perylene. Bis(2-ethylhexyl)phthalate will elute first; perylene will elute last.

10.3.1.3.3.2 Choose a "DUMP" time that removes greater than 85% of the phthalate. Choose a "COLLECT" time so that greater than 95% of the methoxychlor is collected, and continue to collect until just prior to the elution time of sulfur. Use a "WASH" time of 10 minutes.

NOTE: The "DUMP" and "COLLECT" times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask.

10.3.1.3.3.3 Reinject the calibration solution after appropriate "COLLECT" and "DUMP" cycles have been set, and the solvent flow and column pressure have been established.

10.3.1.3.3.4 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

10.3.1.3.3.5 Analyze a GPC blank of methylene chloride. Concentrate the methylene chloride that passed through the system during the "COLLECT" cycle using a K-D evaporator. Exchange the solvent to hexane and analyze the concentrate by GC/ECD according to the usual protocol. Assuming that the blank represents the extract from a 1 L water sample, calculate the analyte concentrations using Equation 7.

10.3.1.3.4 Technical Acceptance Criteria for GPC Calibration

10.3.1.3.4.1 The GPC system must be calibrated at the frequency described in Section 10.3.1.3.2. The UV trace must meet the following requirements:

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution;
- Corn oil and phthalate peaks should exhibit greater than 85% resolution;
- Phthalate and methoxychlor peaks should exhibit greater than 85% resolution;
- Methoxychlor and perylene peaks should exhibit greater than 85% resolution; and
- Perylene and sulfur peaks must not be saturated and should exhibit greater than 90% baseline resolution.

10.3.1.3.4.2 The solvent flow rate and column pressure must be within the manufacturer’s specified ranges.

10.3.1.3.4.3 The RTs for Bis(2-ethylhexyl) phthalate and perylene must not vary more than ±5% between calibrations. Excessive RT shifts are caused by the following:

- Poor laboratory temperature control or system leaks;
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight; and/or
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

10.3.1.3.4.4 The analyte concentrations in a GPC blank must be less than the CRQL for all target analytes in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits.

10.3.1.3.4.5 A copy of the two most recent UV traces of the calibration solution must be submitted with the data for the associated samples.

10.3.1.3.5 Corrective Action for GPC Calibration

10.3.1.3.5.1 If the flow rate and/or column pressure do not fall within the manufacturer's specified ranges, a new column should be prepared.

10.3.1.3.5.2 A UV trace that does not meet the criteria in Section 10.3.1.3.4 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

10.3.1.3.5.3 If the GPC blank exceeds the requirements in Section 10.3.1.3.4.4, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

10.3.1.4 GPC Calibration Verification

10.3.1.4.1 Summary of GPC Calibration Verification

The GPC calibration must be routinely verified with the calibration verification solution specified in Section 7.2.2.3.2.

10.3.1.4.2 Frequency of GPC Calibration Verification

10.3.1.4.2.1 The calibration verification must be performed at least once every 7 days (immediately following the GPC Calibration) whenever samples (including MS/MSDs and blanks) are cleaned up using the GPC.

10.3.1.4.2.2 Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore, system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration must be checked not less than once every 7 days.

10.3.1.4.3 Procedure for GPC Calibration Verification

The instructions below are for a GPC injection loop of 5 mL. If a 2 mL injection loop is used, the Contractor should adjust the volume to 4 mL instead of 10 mL before injection of the extract on the GPC.

10.3.1.4.3.1 The GPC calibration verification solution contains the Aroclor 1016 and Aroclor 1260 in methylene chloride at the concentrations in Table 5 – Concentration of Matrix Spike/Matrix Spike Duplicate Spiking, Laboratory Control Sample Spiking, and Gel Permeation Chromatography Calibration Verification Standard Solutions.

10.3.1.4.3.2 Load the 5 mL sample loop by using a 10 mL syringe containing at least 8 mL of the GPC calibration verification solution. Fractions are collected in an auto sequence by using the GPC program established by the UV detector calibration procedure (Section 10.3.1.3).

10.3.1.4.3.3 The collected GPC calibration verification fraction is transferred to a K-D apparatus, and the collection vessel is rinsed with two additional 10 mL portions of methylene chloride to complete the transfer. The volume of methylene chloride is reduced according to Section 10.2.1. After cooling, the solvent is exchanged to hexane according to the instructions in Section 10.2.2. The final volume is adjusted to 10 mL, and the sample is analyzed by GC

according to the procedure in Section 10.4. The analysis must be performed on only one of the GC columns used for sample analysis.

10.3.1.4.3.4 The recovery of each analyte must be determined for evaluation and reporting purposes. Calculate the Percent Recovery (%R) of each analyte using Equation 13.

10.3.1.4.4 Technical Acceptance Criteria for GPC Calibration Verification

The recovery of each analyte must be between 80-120%.

10.3.1.4.5 Corrective Action for GPC Calibration Verification

The Contractor may continue to use the GPC column if the technical acceptance criteria for the GPC calibration verification are met. If the recoveries are out of the acceptance criteria, the columns must be replaced and the GPC recalibrated according to the instructions in Section 10.3.1.3.3 before proceeding with any GPC cleanup on samples (including LCSs and MS/MSDs) and required method blanks.

10.3.1.5 Daily Ultraviolet Calibration Check (Optional)

The calibration of the GPC may be monitored daily by use of the UV-GPC calibration solution (Section 7.2.2.3.1) and the UV detector calibration procedure (Section 10.3.1.3.3). The UV detector should be used to monitor the elution times for the phthalate, methoxychlor, and perylene, in that order. The precalibrated GPC program should "DUMP" greater than 85% of the phthalate and should "COLLECT" greater than 95% of the methoxychlor and perylene. Significant changes in elution times of the analytes (e.g., greater than 0.5 minutes) indicate that the column is out of calibration and must be recalibrated or replaced.

10.3.1.6 Sample Extract Cleanup by GPC

10.3.1.6.1 Summary of GPC Cleanup

10.3.1.6.1.1 It is very important to have consistent laboratory temperatures during an entire GPC analysis, which could be 24 hours or more. If temperatures are not consistent, RTs will shift, and the "DUMP" and "COLLECT" times determined by the calibration standard will no longer will be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C.

10.3.1.6.1.2 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of 1:1 (v/v) glycerol/water solution must be diluted and loaded into several loops. Similarly, extracts containing more than manufacturer recommended non-volatile residue must be diluted and loaded into several loops. The non-volatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or another suitable container.

10.3.1.6.1.3 Systems using automated injection devices to load the sample on the column must be carefully monitored to assure that the required amount is injected onto the column. Viscous extracts or extracts containing large amounts of non-volatile residue will cause problems with injecting the proper amount of sample extract onto the column using automated injection systems. After the sample extract has

been processed, the remaining sample extract in an injection vial must be checked to assure that the proper amount of extract was injected on the column before proceeding with the extract cleanup. If the proper amount of extract was not injected, the sample must be reprepared at no additional cost to the EPA, and the sample extract must be either diluted and loaded into several loops, or the sample extract must be injected manually.

10.3.1.6.2 Frequency of Sample Extract Cleanup by GPC

GPC cleanup may be performed at least once for each soil/sediment or water extract that contains high molecular weight contaminants that interfere with the analysis of the target analytes and all associated QC samples (blanks, LCSs, and MS/MSDs) must be subjected to this procedure. GPC cleanup on the method blank must be performed after all associated samples have been cleaned up (GPC sequence: calibration, sample 1, sample 2, etc., method blank, calibration verification).

10.3.1.6.3 Procedure for Sample Extract Cleanup by GPC

10.3.1.6.3.1 Particles greater than 5 microns may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container (e.g., a 15 mL culture tube with a PTFE-lined screw-cap).

10.3.1.6.3.2 Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe.

NOTE 1: Some GPC instrument manufacturers recommend using a smaller micron size filter disc. In this instance, follow the manufacturer’s recommended operating instructions.

NOTE 2: INTRODUCTION OF PARTICULATES OR GLASS WOOL INTO THE GPC SWITCHING VALVES MAY REQUIRE FACTORY REPAIR OF THE APPARATUS.

10.3.1.6.3.3 Follow the manufacturer’s instructions for operation of the GPC system being utilized. A 2 mL injection loop may be used in place of a 5 mL injection loop. If a 2 mL injection loop is used, concentrate the extract to 4 mL instead of 10 mL, and then inject 4 mL instead of 10 mL.

10.3.1.6.3.4 If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action, following the manufacturer’s recommendations. The problem must be resolved prior to loading sample extracts.

10.3.1.6.3.5 After loading each sample loop, wash the loading port with methylene chloride to minimize cross contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

10.3.1.6.3.6 After loading the samples, process each sample using the "COLLECT" and "DUMP" cycle times established in Section 10.3.1.

10.3.1.6.3.7 Collect each sample in a 250 mL Erlenmeyer flask covered with aluminum foil to reduce solvent evaporation, or directly into a K-D evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure;
- Increase in column operating pressure due to the accumulation of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used; and/or
- Leaks in the system or significant variances in room temperature.

10.3.1.6.3.8 After the appropriate GPC fraction has been collected for each sample, concentrate the extract as per Section 10.2.1 and proceed to solvent exchange into hexane as described in Section 10.2.2 and Sulfuric Acid cleanup in Section 10.3.2.

NOTE: Any samples that were loaded into multiple loops must be recombined before proceeding with concentration.

10.3.2 Sulfuric Acid Cleanup

10.3.2.1 Summary of Sulfuric Acid Cleanup

Sulfuric acid cleanup uses hexane solvent that will be treated with concentrated sulfuric acid. This method is used for rigorous cleanup of sample extracts prior to analysis of Aroclors. This method is used to provide accuracy in quantitation of Aroclors by eliminating elevated baselines or overly complex chromatograms.

10.3.2.2 Frequency of Sample Extract Cleanup by Sulfuric Acid

Sulfuric acid cleanup is required for all water and soil/sediment extracts.

10.3.2.3 Procedure for Sample Extract Cleanup by Sulfuric Acid

10.3.2.3.1 The volume of hexane extract used depends on the requirements of the GC autosampler used by the laboratory. If the autosampler functions reliably with 1.0 mL of sample volume, 1.0 mL of extract should be used. If the autosampler requires more than 1.0 mL of sample volume, 2.0 mL of extract should be used.

NOTE: Make sure that there is no exothermic reaction or evolution of gas prior to proceeding.

10.3.2.3.2 Using a syringe or a volumetric pipette, transfer an aliquot (1.0 or 2.0 mL) of the hexane extract to a 10 mL vial and, in a fume hood, carefully add 5.0 mL of the 1:1 (v/v) sulfuric acid/water solution.

10.3.2.3.3 Cap the vial tightly and vortex for 1 minute. A vortex must be visible in the vial.

NOTE: Stop the vortexing immediately if the vial leaks. AVOID SKIN CONTACT, AS SULFURIC ACID BURNS.

10.3.2.3.4 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer; it should not be highly colored, nor should it have a visible emulsion or cloudiness.

10.3.2.3.5 If a clean phase separation is achieved, proceed to Section 10.3.2.3.8.

10.3.2.3.6 If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial and dispose of it properly. Add another 5 mL portion of the clean 1:1 (v/v) sulfuric acid/water solution and perform another acid cleanup, beginning at Section 10.3.2.3.7.

NOTE: Do not remove any hexane from the vial at this stage of the procedure.

If the extract is no longer colored, the analyst may proceed to Section 10.3.2.3.9.

10.3.2.3.7 Vortex the sample for 1 minute and allow the phases to separate.

10.3.2.3.8 Transfer the hexane layer to a clean 10 mL vial. Take care not to include any of the acid layer in this clean vial, as it can cause damage to the analytical instrumentation.

10.3.2.3.9 Once the hexane layer is removed, perform a second "extraction" of the acid layer, as follows. Add an additional 1.0 mL of hexane to the sulfuric acid layer, cap, and vortex. This second extraction is done to ensure quantitative transfer of the Aroclors. Remove the second hexane layer and combine with the hexane from Section 10.3.2.3.8.

Reduce the volume of the combined hexane layers to the original volume (1.0 mL or 2.0 mL) using an appropriate concentration technique. Analyze the extract immediately. If analysis of the extract is not performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract is stored longer than 2 days, it should be transferred to a vial with a PTFE-lined screw-cap top, and labeled appropriately.

10.3.3 Sulfur Cleanup

10.3.3.1 Summary of Sulfur Cleanup

Sulfur contamination will cause a rise in the baseline of a chromatogram and may interfere with the analyses of the later eluting Aroclors. If crystals of sulfur are evident or if the presence of sulfur is suspected, sulfur removal must be performed. Interference which is due to sulfur is not acceptable. Sulfur can be removed by one of two methods, according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract, and withdraw the solvent with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean centrifuge tube or clean concentrator tube before proceeding with further sulfur cleanup.

10.3.3.2 Frequency of Sulfur Cleanup

Sulfur removal is required for all sample extracts that contain sulfur.

10.3.3.3 Procedure for Sulfur Cleanup

10.3.3.3.1 Removal of Sulfur using Tetrabutylammonium (TBA) Sulfite

The TBA sulfite procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water-soluble. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

Add 2 mL TBA Sulfite Reagent, 1 mL 2-propanol, and approximately 0.65 g of sodium sulfite crystals to extract and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed, add one or two more aliquots (approximately 0.65 g) to the extract and observe. Place the samples on the wrist shaker for 45 minutes, observing at 15-minute intervals to make sure that the sodium sulfite is not consumed. Add 5.0 mL organic free water and shake for 10-15 minutes. Place the samples into the centrifuge and spin at a setting and duration appropriate to spin down the solids. Transfer the hexane layer to a clean 10 mL vial and cap. The extract transferred to the vial still represents the 1.0 or 2.0 mL final volume.

10.3.3.3.2 Removal of Sulfur Using Copper

Add approximately 2 g of cleaned copper powder to the extract in a centrifuge or concentrator tube (2 g will fill the tube to about the 0.5 mL mark). Mix the copper and extract for at least 1 minute on a mechanical shaker. Separate the extract from the copper powder by drawing off the extract with a disposable pipette, and transfer the extract to a clean vial. The extract transferred to the vial still represents the 1.0 or 2.0 mL of extract. If upon separation of the extract, the copper appears bright, proceed to Section 10.4 and analyze the extract. If the copper changes color, repeat the sulfur removal procedure as necessary.

10.4 Gas Chromatography/Electron Capture Detector Analysis

10.4.1 Introduction

10.4.1.1 Before samples (including LCSs and MS/MSDs) and required blanks (method, sulfur, and/or instrument) can be analyzed, the instrument must meet the initial calibration and CCV technical acceptance criteria. All sample extracts, required blanks, and calibration standards must be analyzed under the same instrumental conditions. All sample extracts, required blank extracts, and standard/spiking solutions must be allowed to warm to ambient temperature before preparation/analysis. Sample analysis on two different non-equivalent GC columns (Section 6.3.2) is required for <u>all</u> samples and blanks.

10.4.1.2 Set up the GC/ECD system per the requirements in Section 9.1. Unless ambient temperature on-column injection is used, the injector must be heated to at least 200°C. The optimized GC conditions must be used.

10.4.2 Procedure for Sample Analysis by GC/ECD

The injection must be made on-column by using either automatic or manual injection. 1 or 2 µL injection volumes may be used provided that all associated standards, samples, and blanks use the same injection volume. The same injection volume must be used for all standards, samples (including LCSs and MS/MSDs), and blanks

associated with the same initial calibration. If a single injection is used for two GC columns attached to a single injection port, it may be necessary to use an injection volume greater than 2 µL. However, the same injection volume must be used for all analyses.

10.4.2.1 Analytical Sequence

All acceptable samples must be analyzed within a valid analysis sequence as given below:

Time	**Injection #**	**Material Injected**
	1-12 (or 5-points of all Aroclors)	First 12 steps of the initial calibration (or 5-points of all Aroclors)
0 hr	13	Instrument Blank
	14	Aroclor 1016/1260 CS3 Standard
	15	Additional Aroclor CS3 Standard (optional)
	16	Subsequent Blank or Samples Last Sample
12 hr		
	1st injection past 12 hours	Instrument Blank
	2nd injection past 12 hours	Aroclor 1016/1260 CS3 Standard Any other Aroclor CS3
	Subsequent injection past 12 hours	Standard (as required)
14 hr	Last injection past 12 hours	Any other Aroclor CS3 Standard
Another 12 hr	1st injection past 12 hours	Instrument Blank
	2nd injection past 12 hours	Aroclor 1016/1260 CS3 Standard
	Subsequent injection past 12 hours	Any other Aroclor CS3 Standard (as required)
	Injection past 12 hours	Last Sample
End of 12 hr beginning of the next 12 hr	2nd last injection of 12 hours	Instrument Blank
	Last injection of 12 hours	Aroclor 1016/1260 CS3 Standard and any other required Aroclor CS3

10.4.2.1.1 Injections #1 through #12 in Section 10.4.2.1 may be expanded to include all injections of initial calibration standards. The first 12 hours are counted from injection #13, not from injection #1, in the initial calibration sequence Option 1 detailed in Section 10.4.2.1. Alternately, the first 12 hours are counted from the injection of the instrument blank of an opening CCV when performed immediately after completion of the initial calibration. Samples and required blanks may be injected until 12 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. If more than 12 hours elapse between the injections of two instrument blanks that bracket a 12-hour period in which samples or required

blanks are analyzed, then the time between the injection of the second instrument blank and the preceding sample may not exceed the length of one chromatographic analysis. While the 12-hour period may not be exceeded, the laboratory may analyze instrument blanks and standards more frequently, for instance, to accommodate staff working on 8-hour shifts. No more than 14 hours may elapse from the injection beginning the opening CCV (instrument blank) and the injection ending the closing CCV (Aroclor Standard).

10.4.2.1.2 After the initial calibration, the analysis sequence may continue as long as acceptable calibration verification(s) are analyzed at the required frequency. This analysis sequence shows only the minimum required blanks and standards. More blanks and standards may be analyzed at the discretion of the Contractor; however, the blanks and standards must also satisfy the criteria presented in Sections 12.0 and 9.0 in order to continue the analytical sequence.

10.4.2.1.3 An analysis sequence must also include all samples and required blank analyses, but the Contractor may decide at what point in the sequence they are to be analyzed.

10.4.2.1.4 The requirements for the analysis sequence apply to both GC columns and for all instruments used for these analyses.

10.4.3 Sample Dilutions

10.4.3.1 All samples must be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography as defined in Section 11.3.

10.4.3.2 Use the results of the original analysis to determine the approximate DF required to get the largest analyte peak (for the lower of the two column concentrations) within the initial calibration range.

10.4.3.3 If more than two analyses (i.e., from the original sample extract and more than one dilution, or from the most concentrated dilution analyzed and further dilutions) are required to get all target compounds within the calibration range, contact SMO.

10.4.3.4 If the concentration of any Aroclor peak used for quantitation is greater than the concentration of the corresponding Aroclor peak in the high standard (CS5) on both columns, then the sample must be diluted. The concentration of the target Aroclor in the diluted extract must be between the initial calibration low-point (CS1) and high-point (CS5) standards for the lower column concentration of the two analyses.

10.4.3.5 If dilution is employed solely to bring a peak within the calibration range or to get an Aroclor pattern on scale, the results for both the more and the less concentrated extracts must be reported. The resulting changes in quantitation limits and surrogate recovery must be reported also for the diluted samples.

10.4.3.6 If the DF is greater than 10, an additional extract 10 times more concentrated than the diluted sample extract must be injected and reported with the sample data. If the DF is less than or equal to 10 but greater than 1, then the results of the original undiluted sample extract must also be reported.

10.4.3.7 When diluted, Aroclors must be able to be reported at greater than 25% of full scale but less than 100% of full scale.

10.4.3.8 Samples with analytes detected at a level greater than the high calibration point must be diluted until the concentration is within the linear range established during calibration, or to a maximum of 1:100,000.

10.4.3.9 If the concentration is still above the high calibration standard calibration after the dilution of 1:100,000, the Contractor shall contact SMO immediately.

10.4.3.10 Sample dilutions must be made quantitatively. Dilute the sample extract with hexane.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Analytes

11.1.1.1 The laboratory will identify analyte peaks based on the RT windows established during the initial calibration sequence.

11.1.1.2 Analytes are identified when peaks are observed in the RT window for the analyte on both GC columns.

11.1.1.3 A set of a minimum of five major peaks is selected for each Aroclor (three major peaks for Aroclor 1221). RT windows for each peak are determined from the initial calibration analysis. Identification of an Aroclor in the sample is based on pattern recognition in conjunction with the elution of a minimum of five sample peaks (three for Aroclor 1221) within the RT windows of the corresponding peaks of the standard on both GC columns.

11.1.1.4 The choice of the peaks used for Aroclor identification and the recognition of those peaks may be complicated by the environmental alteration of the Aroclors, and by the presence of coeluting analytes, matrix interferences, or both. Because of the alteration of Aroclors in the environment, Aroclors in samples may give patterns similar to, but not identical with, those of the standards.

11.1.2 Gas Chromatography/Mass Spectrometry Confirmation

11.1.2.1 Any Aroclor analyte listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits, for which a concentration is reported from a GC/ECD analysis may have the identification confirmed by GC/Mass Spectrometry (GC/MS) if the concentration is sufficient for that purpose. The following paragraphs are to be used as guidance in performing GC/MS confirmation. If the Contractor fails to perform GC/MS confirmation as appropriate, the EPA may require reanalysis of any affected samples at no additional cost to the EPA.

11.1.2.2 GC/MS confirmation may be accomplished by one of three general means:

- Examination of the semivolatile GC/MS library search results [i.e., Tentatively Identified Compound (TIC) data]; or
- A second analysis of the semivolatile extract; or
- Analysis of the Aroclor extract, following any solvent exchange and concentration steps that may be necessary.

11.1.2.3 If an individual peak concentration (on-column concentration) for an Aroclor is greater than or equal to 10 ng/µL for both columns, the Contractor shall contact SMO to determine whether GC/MS confirmation is required. The on-column concentration is calculated using Equation 8.

11.1.2.3.1 For water samples prepared according to the method in Section 10.1.1, the corresponding sample concentration is 100 µg/L.

11.1.2.3.2 For soil/sediment samples prepared according to the method described in Section 10.1.2, the corresponding sample concentration is 3,300 µg/kg.

11.1.2.4 In order to confirm the identification of the target Aroclor, the Contractor must also analyze a reference standard for the analyte. In order to demonstrate the ability of the GC/MS system to identify the analyte in question, the concentration of the standard should be 50 ng/µL for Aroclors.

11.1.2.5 The Contractor is advised that library search results from the NIST (2011 release or later) mass spectral library will not likely list the name of the Aroclor analyte as it appears in this analytical method; hence, the mass spectral interpretation specialist is advised to compare the Chemical Abstracts Service (CAS) Registry numbers for the Aroclors to those from the library search routine.

11.1.2.6 If the analyte cannot be confirmed from the semivolatile library search data for the original semivolatile GC/MS analysis, the Contractor may analyze another aliquot of the semivolatile sample extract after further concentration of the aliquot. This second aliquot must either be analyzed as part of a routine semivolatile GC/MS analysis, including instrument performance checks (DFTPP) and calibration standards containing the Aroclors as described in Section 11.1.2.4, or it must be analyzed along with separate reference standards for the analyte to be confirmed.

11.1.2.7 If the analyte cannot be confirmed by the procedure in Section 11.1.2.6, then an aliquot of the extract prepared for the GC/ECD analysis must be analyzed by GC/MS, following any necessary solvent exchange and concentration steps. As in Section 11.1.2.4, analysis of a reference standard is required if the GC/MS continuing calibration standard does not contain the analyte to be confirmed.

11.1.2.8 Regardless of which of the three approaches above is used for GC/MS confirmation, the appropriate blank must also be analyzed by GC/MS to demonstrate that the presence of the analyte was not the result of laboratory contamination. If the confirmation is based on the analysis of the semivolatile extract, then the semivolatile method blank extracted with the sample must also be analyzed. If the confirmation is based on the analysis of the extract prepared for the GC/ECD analysis, then the method blank extracted with the sample must also be analyzed.

11.1.2.9 If the identification of the analyte cannot be confirmed by any of the GC/MS procedures above, and the concentration calculated from the GC/ECD analysis is greater than or equal to the concentration of the reference standard analyzed by GC/MS, then report the analyte as undetected, adjust the sample quantitation limit (the value associated with the "U" qualifier) to a sample concentration equivalent to the concentration of the GC/MS reference standard, and qualify the results on Form 1-OR with one of the laboratory-defined qualifiers ("X", "Y", or "Z"). In this

instance, define the qualifier explicitly in the SDG Narrative, and describe the steps taken to confirm the analyte in the SDG Narrative.

11.1.2.10 For GC/MS confirmation of Aroclors, spectra of three characteristic peaks are required for both the sample component and the reference standard.

11.1.2.11 The purpose of the GC/MS analysis for the Aroclors is to confirm the presence of chlorinated biphenyls in the samples. The GC/MS analytical results for the Aroclors shall not be used for quantitation and the GC/MS results shall not be reported on Form 1-OR or Form 10-OR. The exception noted in Section 11.1.2.9 applies only to analytes that cannot be confirmed above the reference standard concentration.

11.2 Quantitative Analysis

11.2.1 Data Processing Procedure

11.2.1.1 Target analytes identified shall be quantitated by the external standard method.

11.2.1.2 Except for an estimated value reported for an Aroclor other than 1016 or 1260, the quantitation of Aroclors must be accomplished by comparing the heights or the areas of each of five major peaks of the Aroclor (three major peaks for Aroclor 1221) in the sample with the $\overline{CF}$ for the same peaks established during the specific five-point calibration. The concentration of the target aroclor analytes is calculated by using Equations 7 and 9, where A_x is the area for each of the major peaks of the Aroclor. The concentration of each peak is determined and then a mean concentration for five major peaks (three major peaks for Aroclor 1221) is determined on each column.

11.2.1.3 To quantitate and report the estimated concentration of an Aroclor other than 1016 or 1260, use the CF for five major peaks (three major peaks for Aroclor 1221), from the single point Aroclor calibration standard used for the Aroclor pattern recognition. It will be necessary to substitute the single CF for the $\overline{CF}$ in Equations 7, 8, and 9.

NOTE: The $\overline{CF}$s used for the quantitation of target Aroclors are the $\overline{CF}$s from the concentration of the specific five-point calibration.

11.2.1.4 When an Aroclor other than 1016 or 1260 is detected in a sample, using a single point calibration, a valid five-point calibration of the specific Aroclor must be performed, followed by reanalysis of the sample or appropriately diluted sample (if the sample concentration of Aroclor exceeded calibration) with the Aroclor detected initially. If a valid five-point calibration curve is available for an Aroclor other than 1016 or 1260, the $\overline{CF}$ will be used for quantitation of the Aroclor in the sample; however, quantitation of the surrogate compounds shall use surrogate $\overline{CF}$ from the initial five-point Aroclor 1016/1260 or from Aroclor 1016 if analyzed as a separate mixture.

NOTE: An estimated concentration (reported with an "S" flag) of the initial detection for an Aroclor other than 1016 or 1260, using a single-point calibration standard will be quantitated using the CF, of five major peaks (three major peaks for Aroclor 1221), from the specific single-point calibration standard. The surrogates will be quantitated

using the initial five-point Aroclor 1016/1260, or from Aroclor 1016 if analyzed as a separate mixture.

11.2.1.5 If more than one Aroclor is observed in a sample, the Contractor must choose different peaks to quantitate each Aroclor. A peak common to both analytes present in the sample must not be used to quantitate either analyte.

11.2.2 Target Analyte Calculations

11.2.2.1 Calculate the sample concentration and on-column concentration of target analytes and surrogates by using the following equations:

11.2.2.2 Water

EQ. 7 Water Concentration

$$\text{Concentration } (\mu g/L) = \left(\frac{A_x}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{V_o}\right)\left(\frac{CV_{out}}{CV_{in} \times E}\right)_1\left(\frac{CV_{out}}{CV_{in} \times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in} \times E}\right)_n$$

WHERE,

A_x	=	Peak area or peak height of the peak to be measured
$\overline{CF}$	=	Mean Calibration Factor determined from the initial calibration for the peak to be measured, in area/ng
V_i	=	Volume of extract injected, in µL
V_t	=	Volume of extract produced by the preparation process (extraction and concentration), and before cleanup, in µL
V_o	=	Volume of the water sample extracted, in mL NOTE: For instrument and sulfur blanks, assume a volume of 1,000 mL.
CV_{out}	=	Volume of extract produced by a cleanup process (cleanup and concentration), in µL
CV_{in}	=	Volume of extract subjected to a cleanup process, in µL
E	=	The efficiency of the cleanup process expressed as a fraction of the material that passes through or is not mechanically lost during the cleanup step (e.g., 50% efficiency must be expressed as 0.50)
DF	=	Dilution Factor, which is defined as follows:

$$DF = \frac{\text{µL most concentrated extract used to make dilution + µL clean solvent}}{\text{µL most concentrated extract used to make dilution}}$$

If no dilution is performed, DF=1.0.

The CFs used in Equations 7-9 are those from the most recent calibration. If the CFs used to determine the linearity of the initial calibration were based on peak area, then the concentration of the analyte in the sample must be based on peak area. Similarly, if peak height was used to determine linearity, use peak height to determine the concentration in the sample.

EQ. 8 On-Column Concentration

$$\text{On} - \text{Column Concentration } (ng/\mu L) = \frac{(A_X)}{(\overline{CF})\,(V_i)}$$

WHERE,

A_x and $\overline{CF}$ = As given in EQ. 7

V_i = Volume of extract injected (µL). (If a single injection is made onto two columns, use 1/2 the volume in the syringe as the volume injected onto each column.)

11.2.2.3 Soil/Sediment

EQ. 9 Soil/Sediment Concentration

$$\text{Concentration (µg/kg)} = \left(\frac{A_x}{\overline{CF}}\right)\left(\frac{DF}{V_i}\right)\left(\frac{V_t}{W_t \times S}\right)\left(\frac{CV_{out}}{CV_{in} \times E}\right)_1 \left(\frac{CV_{out}}{CV_{in} \times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in} \times E}\right)_n$$

WHERE,

A_x, $\overline{CF}$, DF, V_i, V_t, CV_{out}, CV_{in}, E = As given in EQ. 7

W_t = Weight of the soil sample extracted in g

S = % Solids/100 (Exhibit D –General Organic Analysis, Section 10.1)

11.2.2.4 The lower mean concentration (from a minimum of three peaks for Aroclor 1221 and a minimum of five peaks for the remaining Aroclors) is reported on Form 1-OR, and the two mean concentrations reported on Form 10. The two mean concentrations are compared by calculating the %D using the following equation:

EQ. 10 Percent Difference

$$\%D = \frac{Conc_H - Conc_L}{Conc_L} \times 100$$

WHERE,

$Conc_H$ = The higher of the two concentrations for the target compound in question

$Conc_L$ = The lower of the two concentrations for the target compound in question

NOTE: Using this equation will result in %D values that are always positive.

11.2.3 Contract Required Quantitation Limit

11.2.3.1 Water

EQ. 11 Water Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{V_x}{V_o}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in} \times E}\right)_1 \left(\frac{CV_{out}}{CV_{in} \times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in} \times E}\right)_n$$

WHERE,

V_o, V_t, DF, CV_{out}, CV_{in}, E = As given in EQ. 7

V_x = Method required sample volume (1,000 mL)

V_y = Method required concentrated extract volume (10,000 µL)

11.2.3.2 Soil/Sediment

EQ. 12 Soil/Sediment Adjusted CRQL

$$\text{Adjusted CRQL} = (\text{Contract CRQL})\left(\frac{W_x}{W_t \times S}\right)\left(\frac{V_t}{V_y}\right)(DF)\left(\frac{CV_{out}}{CV_{in} \times E}\right)_1\left(\frac{CV_{out}}{CV_{in} \times E}\right)_2 \cdots \left(\frac{CV_{out}}{CV_{in} \times E}\right)_n$$

WHERE,

DF, V_t, CV_{out}, CV_{in}, E	=	As given in EQ. 7
Contract CRQL	=	The CRQL value reported in Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits
W_x	=	Method required sample weight (30 g)
W_t	=	Weight of sample extracted, in g
S	=	% Solids/100 (Exhibit D – General Organic Analysis, Section 10.1)
V_y	=	Method required concentrated extract volume (10,000 µL)

11.2.4 Deuterated Monitoring Compound Recoveries

Not applicable to this method.

11.2.5 Surrogate Recoveries

11.2.5.1 The concentrations for surrogate compounds on each column are calculated by using Equations 7 and 9. Use the $\overline{CF}$s from a valid initial five-point calibration of Aroclor 1016/1260, or from Aroclor 1016 if analyzed as a separate mixture.

11.2.5.2 Calculate surrogate recoveries for each GC column using the following equation:

EQ. 13 Surrogate Recovery

$$\%R = \frac{(Q_d \times DF)}{Q_a} \times 100$$

WHERE,

Q_d = Quantity determined by analysis

Q_a = Quantity added

DF = Dilution Factor

11.2.5.3 The recovery limits for the surrogates are 30-150% for both surrogate compounds.

11.2.5.4 Surrogate recovery data from both GC columns are reported (see Exhibit B – Reporting and Deliverables Requirements).

11.3 Technical Acceptance Criteria for Sample Analysis

The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

11.3.1 Samples must be analyzed under the GC/ECD operating conditions in Section 9.1. The instrument must have met all initial calibration, CCV, and blank technical acceptance criteria. Sample data must be

bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks and CCV standards described in Section 9.4.2.

11.3.2 Samples must be extracted and analyzed within the contract required holding times.

11.3.3 The LCS associated with the samples must meet the LCS technical acceptance criteria.

11.3.4 The samples must have an associated method blank meeting the technical acceptance criteria for method blanks. If a sulfur cleanup blank is associated with the samples, that blank must meet the sulfur cleanup blank technical acceptance criteria.

11.3.5 Surrogate compounds RT must be compared to the window established during a valid initial five-point calibration of Aroclor 1016/1260 or from Aroclor 1016 if analyzed as a separate mixture. The RT for each of the surrogates must be within the RT window (Section 9.3.4.3) for both GC columns.

11.3.6 The %R for the surrogates must be between 30-150% inclusive. Up to one surrogate per sample may fail this criteria per column. Exception: If Aroclor 1262 or 1268 is detected in a sample, the %R of the DCB surrogate is advisory for both column analyses of the specific sample. However, %R for TCX must meet the acceptance criteria.

NOTE: The surrogate recovery requirements do not apply to a sample that has been diluted.

11.3.7 No target analyte concentration may exceed the upper limit of the initial calibration or else the extract must be diluted and reanalyzed.

11.3.8 If a valid initial calibration is not available, then a five-point calibration curve specific for any identified Aroclor must be analyzed during a valid analytical sequence on the same instrument and column upon its detection in a sample.

11.3.9 The identification of Aroclors is based primarily on recognition of patterns of RTs displayed on a chromatogram. Therefore, the following requirements apply to all data presented for Aroclors.

11.3.9.1 Five peaks must be chosen for each Aroclor with the exception of Aroclor 1221, where three peaks must be chosen. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of five peaks (three for Aroclor 1221) should include at least one peak that is unique to that Aroclor.

11.3.9.2 Chromatograms must display the largest peak of any Aroclor detected in the sample at less than full scale.

11.3.9.3 If an extract must be diluted, chromatograms must display the peaks chosen for quantitation of Aroclors between 25-100% of full scale.

11.3.9.4 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

11.4 Corrective Action for Sample Analysis

11.4.1 Sample analysis technical acceptance criteria must be met before data are reported. Samples contaminated from laboratory sources or associated with a contaminated method blank or sulfur cleanup blank

will require re-extraction and reanalysis at no additional cost to the EPA. Any samples analyzed that do not meet the technical acceptance criteria will require re-extraction and/or reanalysis at no additional cost to the EPA.

11.4.2 If the sample analysis technical acceptance criteria are not met, check calculations, surrogate solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the technical acceptance criteria, in which case, the affected samples must be reanalyzed at no additional cost to the EPA after the corrective action. Reanalyses of the MS and MSD samples are not required for any target Aroclor qualified with an "S" flag, if this same Aroclor target is detected and reported with a five-point calibration in the original sample.

11.4.3 The extracts from samples that were cleaned up by GPC using an automated injection system, and have both surrogate recoveries outside the lower surrogate acceptance limits, must be checked to assure that the proper amount was injected on the GPC column. If insufficient volume was injected, the sample must be reprepared and reanalyzed at no additional cost to the EPA.

11.4.4 If sample chromatograms have a high baseline or interfering peaks, inspect the system to determine the cause of the problem (e.g., carryover, column bleed, dirty ECD, contaminated gases, leaking septum, etc.). After correcting the problem, analyze an instrument blank to demonstrate that the system is functioning properly. Reanalyze the sample extracts. If the problem with the samples still exists, then those samples must be re-extracted and reanalyzed. Samples that cannot be made to meet the given specifications after one re-extraction and cleanup procedures (sulfuric acid and GPC cleanups) are reported in the SDG Narrative and do not require further analysis.

11.4.5 If the above actions do not correct the problem, then the problem may be due to a sample matrix effect. To determine if there was matrix effect, take the following corrective action steps:

- Re-extract and reanalyze the sample. EXCEPTION: If surrogate recoveries in a sample used for an MS/MSD were outside the acceptance criteria, then it should be re-extracted/reanalyzed only if surrogate recoveries met the acceptance criteria in both the MS/MSD analyses.

- If the surrogate recoveries meet the acceptance windows in the re-extracted/reanalyzed sample, then the problem was within the Contractor’s control. Therefore, submit only data from the re-extraction/reanalysis.

  If the surrogate recoveries fail to meet the acceptance windows in the re-extracted/reanalyzed sample, then submit data from both analyses. Distinguish between the initial analysis and the re-extraction/reanalysis on all deliverables using the suffixes in Exhibit B – Reporting and Deliverables Requirements, Table 5 – Codes for Labeling Data.

12.0 QUALITY CONTROL

12.1 Blank Analyses

12.1.1 Summary

There are two types of blanks required by this method: the method blank and the instrument blank. A separate sulfur cleanup blank may also be required if some, but not all of the samples are subjected to sulfur cleanup. Samples that are associated with a sulfur cleanup blank are also associated with the method blank with which they were extracted. Both the method and sulfur cleanup blanks must meet the respective technical acceptance criteria for the sample analysis technical acceptance criteria to be met.

NOTE: Under no circumstances should blanks (method/instrument/ sulfur cleanup) be analyzed at a dilution.

12.1.2 Method Blank

12.1.2.1 Summary of Method Blank

A method blank is a volume of a clean reference matrix (reagent water for aqueous samples, or purified sodium sulfate or Hydromatrix™ for soil/sediment samples) carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

12.1.2.2 Frequency of Method Blank

A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples (excluding MS/MSDs, PE samples, and LCSs). In addition, a method blank shall:

- Be extracted by the same procedure used to extract samples;
- Be analyzed on each GC/ECD system under the same conditions used to analyze associated samples; and

12.1.2.3 Procedure for Method Blank

For water samples, measure a 1.0 L volume of reagent water and spike with 1.0 mL of the surrogate spiking solution (Section 7.2.2.4). For soil/sediment samples, measure 30 g of sodium sulfate or Hydromatrix™ and spike with 1.0 mL of the surrogate spiking solution. Extract, concentrate, clean up, and analyze the method blank according to Section 10.0.

12.1.2.4 Calculations for Method Blank

Perform data analysis and calculations according to Section 11.0.

12.1.2.5 Technical Acceptance Criteria for Method Blank

12.1.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.1.2.5.2 All method blanks must be prepared and analyzed at the frequency described in Section 12.1.2.2, using the procedure above and in Section 10.0 on a GC/ECD system meeting the initial calibration and CCV technical acceptance criteria. Method blanks must undergo GPC cleanup, when required, on a

GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration checks.

12.1.2.5.3 Method blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, and required Aroclor standards, as described in Section 10.4.2.1.

12.1.2.5.4 The concentration of the target analytes, (Exhibit C – Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits) in the method blank must be less than the CRQL for each target analyte.

12.1.2.5.5 The method blank must meet all sample technical acceptance criteria in Sections 11.3.5.

12.1.2.5.6 Surrogate recoveries must fall within the acceptance window in Table 6 – Surrogate Recovery Limits. These limits are not advisory.

12.1.2.6 Corrective Action for Method Blank

12.1.2.6.1 If a method blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.

12.1.2.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. All samples associated with a method blank that does not meet the method blank technical acceptance criteria will require re-extraction and reanalysis at no additional cost to the EPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.2.6.3 If surrogate recoveries in the method blank do not meet the acceptance criteria listed in Section 12.1.2.5.6, first reanalyze the method blank. If the surrogate recoveries do not meet the acceptance criteria after reanalysis, then the method blank and all samples associated with that method blank must be re-extracted and reanalyzed at no additional cost to the EPA.

12.1.2.6.4 If the method blank fails to meet a technical acceptance criterion other than what is listed in Sections 12.1.2.5.4 and 12.1.2.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary), and reanalyze the method blank.

12.1.3 Sulfur Cleanup Blank

12.1.3.1 Summary of Sulfur Cleanup Blank

The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup and analysis procedures. The purpose of the sulfur cleanup is to determine the levels of contamination associated with the separate sulfur cleanup steps.

12.1.3.2 Frequency of Sulfur Cleanup Blank

The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur

cleanup blank is associated with the part of the set that required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then no separate sulfur cleanup blank is required.

12.1.3.3 Procedure for Sulfur Cleanup Blank

12.1.3.3.1 The concentrated volume of the blank must be the same as the final volume of the samples associated with the blank. The sulfur blank must also contain the surrogates at the same concentrations as the sample extracts (assuming 100.0% recovery).

12.1.3.3.2 Proceed with the sulfur removal (Section 10.3.3) using the same technique (TBA sulfite or copper) as the samples associated with the blank.

12.1.3.3.3 Analyze the sulfur blank according to Section 10.4.

12.1.3.4 Calculations for Sulfur Cleanup Blank

12.1.3.4.1 Assuming that the material in the sulfur blank resulted from the extraction of a 1.0 L water sample, calculate the concentration of each analyte using Equation 7. Compare the results to the CRQL values in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits.

12.1.3.4.2 See Section 11.2 for the equations for the other calculations.

12.1.3.5 Technical Acceptance Criteria for Sulfur Cleanup Blank

12.1.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each column.

12.1.3.5.2 All sulfur cleanup blanks must be prepared and analyzed at the frequency described in Section 12.1.3.2 using the procedure in Section 12.1.3.3 on a GC/ECD system meeting the initial calibration and CCV technical acceptance criteria.

12.1.3.5.3 Sulfur cleanup blanks must be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks and required Aroclor Standards, as described in Section 10.4.2.1.

12.1.3.5.4 The concentration of the target analytes [Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits] in the sulfur cleanup blank must be less than the CRQL for each target analyte.

12.1.3.5.5 The sulfur cleanup blank must meet all sample technical acceptance criteria in Sections 11.3.5.

12.1.3.5.6 Surrogate recoveries must fall within the acceptance criteria in Table 6 – Surrogate Recovery Limits. These limits are not advisory.

12.1.3.6 Corrective Action for Sulfur Cleanup Blank

12.1.3.6.1 If a sulfur cleanup blank does not meet the technical acceptance criteria, the Contractor must consider the analytical system to be out of control.

12.1.3.6.2 If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. Further, all samples processed with a sulfur

cleanup blank that does not meet the sulfur cleanup blank technical acceptance criteria (i.e., contaminated) will require re-extraction and reanalysis at no additional cost to the EPA. It is the Contractor's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated.

12.1.3.6.3 If surrogate recoveries in the sulfur cleanup blank do not meet the technical acceptance criteria in Section 12.1.3.5.6, first reanalyze the sulfur cleanup blank. If the surrogate recoveries do not meet the technical acceptance criteria after reanalysis, then the sulfur cleanup blank and all samples associated with that sulfur cleanup blank must be re-prepared/re-extracted and reanalyzed at no additional cost to the EPA.

12.1.3.6.4 If the sulfur cleanup blank fails to meet a technical acceptance criterion other than what is listed in Sections 12.1.3.5.4 and 12.1.3.5.6, then the problem is an instrument problem. Correct the instrument problem, recalibrate the instrument (if necessary), and reanalyze the sulfur cleanup blank.

12.1.4 Instrument Blank

12.1.4.1 Summary of Instrument Blank

An instrument blank is a volume of clean solvent spiked with the surrogates and analyzed on each GC column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis, particularly with regard to carryover of analytes from standards or highly contaminated samples into other analysis.

12.1.4.2 Frequency of Instrument Blank

The first analysis in a 12-hour analysis sequence (Section 9.4) must be an instrument blank. All groups of acceptable sample analyses are to be preceded and followed by acceptable instrument blanks (Section 10.4.2.1). If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an instrument blank must be analyzed to initiate a new 12-hour sequence (Section 9.4.2).

12.1.4.3 Procedure for Instrument Blank

12.1.4.3.1 Prepare the instrument blank by spiking the surrogates into hexane or iso-octane for a concentration of 20.0 ng/mL of tetrachloro-m-xylene and 40.0 ng/mL of decachlorobiphenyl.

12.1.4.3.2 Analyze the instrument blank according to Section 10.4.2, at the frequency listed in Section 12.1.4.2.

12.1.4.4 Calculations for Instrument Blank

12.1.4.4.1 Assuming that the material in the instrument blank resulted from the extraction of a 1 L water sample, calculate the concentration of each analyte using Equation 7. Compare the results to the CRQL values for water samples in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits.

12.1.4.4.2 See Section 11.2 for the equations for the other calculations.

12.1.4.5 Technical Acceptance Criteria for Instrument Blanks

12.1.4.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed and reported independently on Form 1-OR for each GC column.

12.1.4.5.2 All instrument blanks must be prepared and analyzed at the frequency described in Section 12.1.4.2, using the procedure in Section 10.4.2 on a GC/ECD system meeting the initial calibration and CCV technical acceptance criteria.

12.1.4.5.3 The concentration of each target analyte [Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits] in the instrument blank must be less than the CRQL for that analyte.

12.1.4.5.4 The instrument blank must meet all sample technical acceptance criteria in Sections 11.3.5.

12.1.4.5.5 Instrument blanks must be analyzed undiluted.

12.1.4.6 Corrective Action for Instrument Blank

If target analytes are detected at concentrations greater than the CRQL, or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples that were analyzed between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be analyzed before additional data are collected. All samples (including LCSs, MS/MSDs, and PE samples) and required blanks that were analyzed after the last acceptable instrument blank must be re-injected during a valid analytical sequence and must be reported at no additional cost to the EPA.

12.2 Matrix Spike and Matrix Spike Duplicate

12.2.1 Summary of Matrix Spike and Matrix Spike Duplicate

To evaluate the effects of the sample matrix on the methods used for Aroclor analyses, the EPA has prescribed a multi-component mixture of Aroclor 1016 and Aroclor 1260 to be spiked into two aliquots of a sample and analyzed in accordance with the appropriate method.

An MS/MSD shall only be extracted and analyzed if requested by the EPA Region (through SMO) or specified on the Traffic Report/Chain of Custody (TR/COC) Record.

12.2.2 Frequency of Matrix Spike and Matrix Spike Duplicate Analysis

12.2.2.1 An MS/MSD must be extracted and analyzed for every 20 field samples of a similar matrix in an SDG. MS/MSD samples must be analyzed unless otherwise specified on the TR/COC Record. If no MS/MSD samples are specified on the TR/COC Record, the Contractor shall contact SMO to confirm that MS/MSD analyses are not required.

12.2.2.2 The Contractor shall not perform MS/MSD analysis on any of the field QC or PE samples.

12.2.2.3 If the EPA Region designates a sample to be used, then that sample must be used. If there is insufficient sample volume remaining to perform an MS/MSD, then the Contractor shall choose

another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the EPA sample selected for the MS/MSD analysis. SMO shall contact the EPA Region for confirmation immediately after notification. The rationale for the choice of another sample other than the one designated by the EPA shall be documented in the SDG Narrative.

12.2.2.4 If there is insufficient sample volume remaining in any of the samples in an SDG to perform the requested MS/MSD, the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the EPA Region for instructions. The EPA Region will either approve that no MS/MSD be performed, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the EPA Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the EPA Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, the Contractor shall contact SMO. SMO will contact the EPA Region to determine which samples should have an MS/MSD performed on them. SMO will notify the Contractor of the EPA Region's decision. The Contractor shall document the decision in the SDG Narrative.

12.2.2.6 When a Contractor receives only PE samples, no MS/MSD shall be performed within that SDG.

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the MS/MSD analysis when the EPA Region did not designate samples to be used for this purpose. If the PE sample is received as an ampulated standard extract, the ampulated PE sample is not considered to be another matrix type. SMO will notify the Contractor of the chosen sample. The Contractor must document the decision in the SDG Narrative.

12.2.3 Procedure for Preparing Matrix Spike and Matrix Spike Duplicate

12.2.3.1 For water samples, measure out two additional 1.0 L aliquots of the sample chosen for spiking. Fortify each with 1.0 mL of matrix spiking solution (Section 7.2.2.5). Using a syringe or volumetric pipette, add 1.0 mL of surrogate spiking solution to each sample (Section 7.2.2.4). Adjust the pH of the samples (if required). Extract, concentrate, cleanup, and analyze the MS/MSD according to Section 10.0.

12.2.3.2 For soil/sediment samples, weigh out two additional 30 g (to the nearest 0.1 g) aliquots of the sample chosen for spiking. Add 1 mL of the matrix spiking solution (Section 7.2.2.5) and 1 mL of the surrogate standard spiking solution (Section 7.2.2.4). Extract, concentrate, cleanup, and analyze the MS/MSDs according to Section 10.0.

12.2.3.3 Before any MS/MSD analysis, analyze the original sample, then analyze the MS/MSD at the same concentration as the most concentrated extract for which the original sample results will be reported. For example, if the original sample is to be reported at a 1:1 dilution and a 1:10 dilution, then analyze and report the MS/MSD at a 1:1 dilution only. However, if the original sample is to be reported at a 1:10 dilution and a 1:100 dilution, then the MS/MSD must be analyzed and reported at a 1:10 dilution only. Do not dilute MS/MSD samples further to get either spiked or nonspiked analytes within calibration range.

Sample dilutions must be performed in accordance with Section 10.4.3.

12.2.4 Calculations for Matrix Spike and Matrix Spike Duplicate

12.2.4.1 Calculate the concentrations of the Matrix Spike analytes using the same equation as used for target analytes (Equations 7 and 9). Calculate the recovery of each Matrix Spike analyte using the following equation:

EQ. 14 Matrix Spike Recovery

$$\%R = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spike Sample Result

SR = Original Sample Result

SA = Spike Added

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD using the following equation:

EQ. 15 Relative Percent Difference

$$RPD = \frac{\left|MSR - MSDR\right|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

WHERE,

MSR = Matrix Spike Recovery

MSDR = Matrix Spike Duplicate Recovery

NOTE: The vertical bars in the equation above indicate the absolute value of the difference.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Matrix Spike Duplicate

12.2.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on both GC columns.

12.2.5.2 All MS/MSDs must be prepared and analyzed at the frequency described in Section 12.2.2.1 using the procedure above, and in Section 10.0, on a GC/ECD system meeting the initial calibration, CCV, and blank technical acceptance criteria. MS/MSDs must be bracketed at 12-hour intervals (or less) by acceptable calibration verification described in Section 10.4.2.1.

12.2.5.3 The MS/MSD must be extracted and analyzed within the contract required holding times.

12.2.5.4 The RT for each of the surrogates must be within the RT window as calculated in Section 9.3.4.3 for both GC columns.

12.2.5.5 The limits for MS analyte recovery and RPD are given in Table 7 – Matrix Spike Recovery and Relative Percent Difference Limits. As these limits are only advisory, no further action by the Contractor is required. However, frequent failure to meet the limits for recovery or RPD warrants investigation by the Contractor, and may result in questions from the EPA.

12.2.6 Corrective Action for Matrix Spike and Matrix Spike Duplicate

Any MS/MSD that fails to meet the technical acceptance criteria in Sections 12.2.5.1, 12.2.5.2, and 12.2.5.4 must be reanalyzed at no additional cost to the EPA.

12.3 Laboratory Control Sample

12.3.1 Summary of Laboratory Control Sample

The LCS is an internal laboratory QC sample designed to assess (on an SDG-by-SDG basis) the capability of the Contractor to perform the analytical method listed in this Exhibit.

12.3.2 Frequency of Laboratory Control Sample

The LCS must be prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix per preparation batch. The LCS must be extracted and analyzed concurrently with the samples in the SDG using the same extraction protocol, cleanup procedures, and instrumentation as the samples in the SDG.

NOTE: An LCS requires sulfur cleanup only if all samples in the specific preparation batch required this procedure.

12.3.3 Procedure for Preparing Laboratory Control Sample

12.3.3.1 For water samples, measure out 1.0 L of reagent water and spike with 1 mL of the LCS spiking solution (Section 7.2.2.6) and 1 mL of the surrogate standard spiking solution (Section 7.2.2.4). Extract, concentrate, and analyze the sample according to Section 10.0.

12.3.3.2 For soil/sediment samples, measure out 30 g of a clean reference matrix (e.g., sodium sulfate, Hydromatrix™) and spike with 1 mL of the LCS spiking solution (Section 7.2.2.6) and 1 mL of surrogate standard spiking solution (Section 7.2.2.4). Extract, concentrate, and analyze the LCS according to Section 10.0.

12.3.4 Calculations for Laboratory Control Sample

12.3.4.1 Calculate the results according to Section 11.0.

12.3.4.2 Calculate individual analyte recoveries of the LCS using Equation 13.

12.3.5 Technical Acceptance Criteria for Laboratory Control Sample

12.3.5.1 The requirements below apply independently to each GC column and to all instruments used for these analyses. Quantitation must be performed on each GC column.

12.3.5.2 The LCS must be analyzed at the frequency described in Section 12.3.2 on a GC/ECD system meeting the initial calibration and calibration verification technical acceptance criteria.

12.3.5.3 The LCS must be prepared as described in Section 12.3.3.

12.3.5.4 The LCS must meet all sample technical acceptance criteria in Sections 11.3.5 - 11.3.6.

12.3.5.5 The %R for each of the compounds in the LCS must be within the recovery limits listed in Table 8 – Laboratory Control Sample Recovery Limits.

12.3.5.6 Surrogate recoveries must fall within the acceptable criteria in Table 6 – Surrogate Recovery Limits. These limits are <u>not</u> advisory.

12.3.6 Corrective Action for Laboratory Control Sample

12.3.6.1 If the LCS technical acceptance criteria for the surrogates or the LCS compound recovery are not met, check calculations, the surrogate and LCS solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the surrogate and LCS recovery criteria.

12.3.6.2 LCS technical acceptance criteria MUST be met before data are reported. LCS contamination from laboratory sources or any LCS analyzed not meeting the technical acceptance criteria will require re-extraction and reanalysis of the LCS at no additional cost to the EPA.

12.3.6.3 All samples (including MS/MSDs and PE samples) and required blanks, prepared and analyzed in an SDG with an LCS that does not meet the technical acceptance criteria, will also require re-extraction and reanalysis at no additional cost to the EPA.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed, the Method Detection Limit (MDL) for each Aroclor target analyte shall be determined on each instrument used for analysis. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for water and soil/sediment samples). The MDLs must be determined annually thereafter or after major instrument maintenance. Major instrument maintenance includes, but is not limited to: cleaning or replacement of the detector. A new MDL study will not be required after changing the GC column, as long as the replacement has the same length, inner diameter, and stationary phase.

12.4.2 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in 40 Code of Federal Regulations (CFR) Part 136.

12.4.3 The determined concentration of the MDL must be less than the CRQL listed in Exhibit C - Organic Target Analyte List and Contract Required Quantitation Limits, Table 5 – Aroclors Target Analyte List and Contract Required Quantitation Limits.

12.4.4 All documentation for the MDL studies shall be maintained at the laboratory and submitted to the EPA within seven (7) days of study completion. This schedule and the designated recipients are specified in Exhibit B, Table 1 – Reporting and Deliverables Requirements.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 13.0 of Exhibit D – Introduction to Organic Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 14.0 of Exhibit D – Introduction to Organic Analytical Methods.

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Automated Soxhlet Extraction, SW-846 Method 3541, Revision 0, September 1994.

16.2 U.S. Environmental Protection Agency, Continuous Liquid-Liquid Extraction, SW-846 Method 3520C, Revision 3, December 1996.

16.3 U.S. Environmental Protection Agency, Gel-Permeation Cleanup, SW-846 Method 3640A, Revision 1, September 1994.

16.4 U.S. Environmental Protection Agency, Polychlorinated Biphenyls (PCBs) by Gas Chromatography, SW-846 Method 8082A, Revision 1, November 2000.

16.5 U.S. Environmental Protection Agency, Pressurized Fluid Extraction (PFE), SW-846 Method 3545A, Revision 1, January 1998.

16.6 U.S. Environmental Protection Agency, Separatory Funnel Liquid-Liquid Extraction, SW-846 Method 3510C, Revision 3, December 1996.

16.7 U.S. Environmental Protection Agency, Silica Gel Cleanup, SW-846 Method 3630C, Revision 3, December 1996.

16.8 U.S. Environmental Protection Agency, Sulfuric Acid/Permanganate Cleanup, SW-846 Method 3665A, Revision 1, December 1996.

16.9 U.S. Environmental Protection Agency, Ultrasonic Extraction, SW-846 Method 3550C, Revision 3, November 2000.

16.10 U.S. Government Printing Office, 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. EPA REGISTRY NAMES, SYNONYMS, AND CHEMISTRY ABSTRACT SERVICE (CAS) REGISTRY NUMBERS

Systematic Name	EPA Registry Name	Synonym	CAS #
Aroclor 1016	Aroclor 1016	PCB-1016	12674-11-2
Aroclor 1221	Aroclor 1221	PCB-1221	11104-28-2
Aroclor 1232	Aroclor 1232	PCB-1232	11141-16-5
PCB 1242	Aroclor 1242	PCB-1242	53469-21-9
PCB 1248	Aroclor 1248	PCB-1248	12672-29-6
PCB 1254	Aroclor 1254	PCB-1254	11097-69-1
PCB 1260	Aroclor 1260	PCB-1260	11096-82-5
Aroclor 1262	Aroclor 1262	PCB-1262	37324-23-5
Aroclor 1268	Aroclor 1268	PCB-1268	11100-14-4
Benzene 1,2,3,5-tetrachloro-4,6-dimethyl	Tetrachloro-m-xylene	2,4,5,6-Tetrachloroxylene	877-09-8
1,1'-Biphenyl, 2,2',3,3',4,4',5,5',6,6'-decachloro	Decachlorobiphenyl	Decachloro-1,1'-biphenyl	2051-24-3

TABLE 2. CONCENTRATION LEVELS OF INITIAL CALIBRATION AND CONTINUING CALIBRATION VERIFICATION STANDARDS AND TECHNICAL ACCEPTANCE CRITERIA FOR AROCLORS

Analyte	Concentration (ng/mL)					Maximum %RSD	Opening Maximum %D	Closing Maximum %D
	CS1	CS2	CS3	CS4	CS5			
Aroclor 1016	100	200	400	800	1600	20.0	±25.0	±50.0
Aroclor 1260	100	200	400	800	1600	20.0	±25.0	±50.0
Aroclor 1221	100	200	400	800	1600	20.0	±25.0	±50.0
Aroclor 1232	100	200	400	800	1600	20.0	±25.0	±50.0
Aroclor 1242	100	200	400	800	1600	20.0	±25.0	±50.0
Arolcor 1248	100	200	400	800	1600	20.0	±25.0	±50.0
Aroclor 1262	100	200	400	800	1600	20.0	±25.0	±50.0
Aroclor 1268	100	200	400	800	1600	20.0	±25.0	±50.0
*Tetracholor-m-xylene	5.0	10.	20.	40.	80.	20.0	±30.0	±50.0
*Decachlorobiphenyl	10.	20.	40.	80.	160	20.0	±30.0	±50.0

*Surrogates are present in all calibration standards at the above concentrations.

NOTE: Aroclor 1016 and 1260 standards may be prepared together but the other Aroclor standards (1221 - 1268) must be prepared individually. For example, Aroclor 1016/1260 CS3 standard will contain both Aroclor 1016 and Aroclor 1260 at a concentration of 400 ng/mL, and the surrogates tetrachloro-m-xylene and decachlorobiphenyl, at concentrations of 20 and 40 ng/mL respectively. Aroclor 1242 CS1 Standard will contain only Aroclor 1242, tetrachloro-m-xylene, and decachlorobiphenyl at 100, 20, and 40 ng/mL respectively.

TABLE 3. RETENTION TIME WINDOWS FOR ANALYTES AND SURROGATES

Compound	**Retention Time Windows (minutes)**
Aroclors	±0.07
Tetrachloro-m-xylene	±0.05
Decachlorobiphenyl	±0.10

TABLE 4. GAS CHROMATOGRAPH ANALYTICAL CONDITIONS

Carrier Gas:	Helium or Hydrogen 99.999% purity
Column Flow:	5 mL/min.
Make-up Gas:	Argon/Methane (P-5 or P-10) or N_2 (required)
Injector Temperature:	> 200°C
Injection Technique:	On-column
Injection Volume:	1 or 2 µl
Injector:	Grob-type, splitless
Initial Temperature:	150°C
Initial Hold Time:	0.5 min.
Temperature Ramp:	5°C to 6°C/min.
Final Temperature:	275°C
Final Hold Time:	After decachlorobiphenyl has eluted

TABLE 5. CONCENTRATION OF MATRIX SPIKE/MATRIX SPIKE DUPLICATE SPIKING, LABORATORY CONTROL SAMPLE SPIKING, AND GEL PERMEATION CHROMATOGRAPHY CALIBRATION VERIFICATION STANDARD SOLUTIONS

Analyte	**MS/MSD Spiking Solution** (µg/mL)	**LCS Spiking Solution** (µg/mL)	**GPC Calibration Verification Solution** (µg/mL)
Aroclor 1016	4.0	1.0	0.40
Aroclor 1260	4.0	1.0	0.40

TABLE 6. SURROGATE RECOVERY LIMITS

Compound	Percent Recovery QC Limits
Tetrachloro-m-xylene	30-150
Decachlorobiphenyl	30-150

TABLE 7. MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS

Analyte	Percent Recovery Water/Soil	RPD Water/Soil
Aroclor 1016	29-135	0-15
Aroclor 1260	29-135	0-20

TABLE 8. LABORATORY CONTROL SAMPLE RECOVERY LIMITS

Analyte	Percent Recovery Water/Soil
Aroclor 1016	50-150
Aroclor 1260	50-150

THIS PAGE INTENTIONALLY LEFT BLANK