EXHIBIT D

TRACE CONCENTRATIONS OF
VOLATILE ORGANIC COMPOUNDS ANALYSIS

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Exhibit D – Trace Concentrations of
Volatile Organic Compounds Analysis

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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze aqueous/water samples containing trace concentrations of the volatile organic analytes (VOA) listed in the Target Analyte List (TAL) for trace volatiles in Exhibit C – 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 If requested, samples shall be analyzed for a select group of analytes (vinyl chloride, trichloroethene, 1,2-dibromoethane, 1,2,3-trichloropropane, and 1,2-dibromo-3-chloropropane) by GC/MS using the Selected Ion Monitoring (SIM) technique. A full scan analysis by the trace method shall be performed prior to the trace SIM analysis. The SIM analysis is not required for a sample when the full scan analysis meets the requirements in Section 10.1.

1.3 Problems that have been associated with the following analytes 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.
- 1,1,2,2-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 shall be exercised when identifying analytes.

2.0 SUMMARY OF METHOD

2.1 Aqueous/Water

An inert gas is bubbled through a 25 milliliter (mL) aliquot of sample, that has been spiked with Deuterated Monitoring Compound (DMC) and internal standard spiking solutions, 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 shall 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

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 National Institute of Standards and Technology (NIST) (2017 release or later), Wiley (2014 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 - List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 shall 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 shall 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 shall be stored separately from other laboratory samples and standards, and shall be analyzed in a room where the atmosphere is demonstrated to be free of all potential contaminants that would 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 shall 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 reagent 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 shall be completely free of solvents. Special precautions shall be taken to determine the presence of methylene chloride. The analytical and sample storage area shall be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing shall 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 shall be taken. At the time of sample receipt, the Contractor shall 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).

4.1.5 The desorb and trap reconditioning conditions specified in Exhibit D – Trace VOA, Table 5, shall be followed when using the trap recommended in Section 6.3.4.2 and a gas chromatograph (GC) with a direct capillary interface. Certain target analytes, such as methyl tert-butyl ether (MTBE), may decompose at high purge temperatures in samples that have been acid preserved.

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 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, demonstration of equivalent performance that meets 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.

All instruments, balances, heating, and measuring equipment and devices shall be uniquely identified and labeled to allow traceability to any corresponding records of use.

6.1 General Laboratory Equipment

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

6.1.2 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.

6.1.3 Pasteur Pipettes - Disposable.

6.1.4 pH Paper - Wide range.

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

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

6.1.7 Vials

6.1.7.1 Glass Vials and PTFE-lined Caps - Assorted sizes.

6.1.7.2 Optional vials with PTFE Mininert® caps and septa, Certan® vials, or equivalent, for standard solutions.

6.1.8 Volumetric Flasks - Class A, 5, 10, 50, 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. The instrument shall be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.3.2 Gas Chromatography Columns

Recommended Column: A fused silica high resolution capillary GC column with an intermediate polarity column phase (e.g., 6% Cyanopropylphenyl/94% polydimethylsiloxane or equivalent), with 20-75 meter (m) column length, 0.18-0.53 mm inner diameter, and 1-3 micrometer (µm) film thickness, is generally recommended for this procedure. Examples include but are not limited to: VOCOL®, Rtx-502.2®, Optima-624®, BP624®, ZB-624®, DB-624®, Rtx-624®, CP-Select 624CB®, or equivalent. A typical column, DB-624, with a column specification of 30 m length x 0.25 mm ID, 1.4 µm film thickness, has been found to provide satisfactory separation for the analysis. Alternative GC column phases or dimensions may also be acceptable for use provided that all specified performance criteria in the SOW can be met on a routine basis. Regardless of the column used, the operating conditions of the system must be demonstrated by the laboratory to meet the performance criteria described in Section 6.3.2.1, and this demonstration must be made available for review upon request by the EPA. A description of the GC column used for analysis shall be provided in the SDG Narrative. Packed GC columns cannot be used.

The analytical system must be able to accept up to 1,000 nanograms (ng) of each analyte listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, without becoming overloaded. The gas flow from the concentrator may be split at an appropriate ratio prior to introduction to the GC to prevent overloading of the column as needed, provided the sensitivity is acceptable and the same conditions are used for the demonstration of performance described in Section 6.3.2.1 as are used for analysis of standards and samples.

6.3.2.1 A capillary column is considered acceptable if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1.
- The analytical results generated using the column meet the initial calibration, initial calibration verification (ICV), and continuing calibration verification (CCV) technical acceptance criteria (Sections 9.3.5, 9.4.5, and 9.5.5), and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1.
- The column provides acceptable peak shapes and resolution of the analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1 (refer to Section 9.1).
- 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 laboratory generates acceptable method detection limits (MDLs) with the integrated system including the same GC column and operation conditions as will be used for sample analysis.

6.3.2.1.1 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 shall maintain documentation verifying 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 EPA 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, ICV, 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, 9.4.5, and 9.5.5;
- 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 - Target Analyte List and Contract Required Quantitation Limits, Table 1.

6.3.2.1.4 The documentation shall be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional CLP Contracting Officer's 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 Exhibit D – Trace VOA, Table 2, when 50 ng of BFB is injected through the GC inlet. The system must be capable of performing SIM analysis. 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 shall 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 that prevents the release of contaminants into the instrument room. Adsorbents used in

the trapping system must be replaced according to the product replacement periods recommended by the manufacturer, and at a minimum annually, or more frequently as needed when such product information is not provided.

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 DMCs and achieves all acceptable performance criteria.

6.3.4 Purge-and-Trap Device

The Purge-and-Trap (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, 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. The adsorbent must be replaced according to the product replacement periods recommended by the manufacturer, and at a minimum annually, or more frequently if such product information is not provided and/or the laboratory routinely has difficulty meeting the QC criteria identified in Section 6.3.4.3. The systems must 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 headspace 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 the identification and quantitation of the analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1;
- The analytical results generated using the trap meet the initial calibration, ICV, and CCV technical acceptance criteria listed in the analytical method and the CRQLs listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1; and

- The trap must be capable of accepting up to 1000 ng of each analyte listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, 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 shall demonstrate that the trap meets the criteria listed in Section 6.3.4.3 and document its use in the 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.

6.3.4.3.2 The Contractor shall 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, ICV, and CCV standards analyzed using the trap specified in Section 6.3.4.2.

6.3.4.3.2.3 Based on the Contractor-generated data described above, the Contractor shall 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, 9.4.5, and 9.5.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the Trace volatiles 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 - Target Analyte List and Contract Required Quantitation Limits, Table 1.

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

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

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

6.3.4.6 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 specified in Section 6.3.4.2 shall not be heated higher than 180°C and the remaining sections shall not exceed 220°C during bake-out mode. Manufacturer recommendations shall be followed regarding maximum temperatures for other types of sorbent traps.

6.4 Data Systems/Data Storage

A computer system must be interfaced to the MS to allow 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 (2017 release or later), Wiley (2014 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 shall provide all standards to be used with the contract. These standards shall be used only after they have been certified according to the procedure in Exhibit D – Introduction to Analytical Methods, Section 11.0. The Contractor shall be able to verify that the standards are certified. Manufacturer’s certificates of analysis shall 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 a contaminant or 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.

7.1.1.3 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 shall be demonstrated to be free of contaminants that interfere with the measurement of the purgeable analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1.

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 prepared in methanol from pure standard materials or purchased as certified pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated, unless acceptability of the standard can be documented (Section 7.2.3.6).

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 - Target Analyte List and Contract Required Quantitation Limits, Table 1) in methanol. Prepare fresh calibration standard solution(s) once a week for the room-temperature gases (i.e., chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride, bromomethane, and chloroethane), once a month for the room-temperature solids or liquids, or sooner if the solution has degraded or evaporated, unless acceptability of the standard can be documented (Section 7.2.3.6). Standards of reactive analytes such as styrene may need to be prepared more frequently.

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, 7.2.2.1.3, or 7.2.2.1.5.

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 associated DMCs at 0.50, 1.0, 5.0, 10, and 20 micrograms/Liter (µg/L) (in Exhibit D – Trace VOA, Table 3); all ketones and their associated DMCs (see Exhibit D – Trace VOA, Table 3) 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 If SIM analysis of vinyl chloride, trichloroethene, 1,2-dibromoethane, 1,2,3-trichloropropane, and 1,2-dibromo-3-chloropropane is requested, prepare calibration standards containing the analytes and their associated DMCs (see Exhibit D – Trace VOA, Table 3) at concentrations of 0.050, 0.10, 0.50, 1.0, and 2.0 µg/L.

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

7.2.2.1.5 For CCV (opening and closing CCVs), the standard shall be at a concentration equivalent to the mid-level calibration standards listed in Section 7.2.2.1.2 (i.e., 5.0 µg/L for non-ketones, 50 µg/L for ketones, and 0.50 µg/L for analytes listed in Section 7.2.2.1.3 that are analyzed by the SIM technique). Use the same source of target analytes (i.e., same manufacturer lot) for CCVs as were used for preparation of initial calibration standards.

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

7.2.2.2 Initial Calibration Verification Solution

Prepare the working ICV standard solution containing all of the purgeable target analytes (Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1) from an alternate source or a different lot than used for the initial calibration (ICAL) standard analyses in methanol. Prepare a fresh standard solution every month, or sooner if the solution has degraded or evaporated.

7.2.2.2.1 The ICV standard shall be at a concentration equivalent to the mid-level calibration standard listed in Section 7.2.2.1.2 (i.e., 5.0 µg/L for non-ketones, 50 µg/L for ketones, and 0.50 µg/L for analytes listed in Section 7.2.2.1.3 that are analyzed by the SIM technique).

7.2.2.2.2 The ICV standard shall be prepared by the same procedures as the CCVs.

7.2.2.3 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 shall be analyzed using the same GC and MS analytical conditions as are used for the calibration analysis.

7.2.2.4 Deuterated Monitoring Compound Spiking Solution

7.2.2.4.1 Prepare a DMC spiking solution in methanol (or in deuterated methanol) containing the compounds listed in Exhibit D – Trace VOA, Table 3.

7.2.2.4.2 DMCs are to be added to each sample, blank, and matrix spike/matrix spike duplicate (MS/MSD), as well as to the ICAL standards, ICV standard, and CCV standards. Use the same source of DMCs (i.e., same manufacturer lot) for the preparation of calibration standards, initial and continuing calibration verification standards, samples, blanks, and MS/MSDs. Add the same DMC spiking solution to CCVs, samples, blanks, and MS/MSDs.

7.2.2.4.3 For samples, blanks, and MS/MSDs, add a 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.

7.2.2.4.4 For ICAL, ICV, and CCV standards, add a sufficient amount 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), Section 7.2.2.2.1 (ICV), and Section 7.2.2.1.5 (CCV).

7.2.2.4.5 For SIM analysis, add a sufficient amount of the DMC spiking solution to each sample and blank to result in 0.0125 µg for each non-ketone DMC.

7.2.2.4.6 For SIM ICAL, ICV, and CCV standards, add a sufficient amount of the DMC spiking solution to each 25 mL aliquot of calibration standard to result in the concentrations listed in Section 7.2.2.1.3 (initial calibration), Section 7.2.2.2.1 (ICV), and Section 7.2.2.1.5 (CCV).

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

NOTE: The DMC spiking solution may be combined with the internal standard spiking solution (Section 7.2.2.6) and/or BFB solution (Section 7.2.2.3).

7.2.2.5 Matrix Spiking Solution

If MS/MSD analysis is requested at the time of scheduling, prepare a matrix spiking solution containing all target analytes in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, with the same working standard used for the preparation of CCVs (Section 7.2.2.1.5), in methanol, at a concentration of 12.5 µg/mL for each non-ketone analyte and 125 µg/mL for each ketone analyte in methanol. Add a sufficient amount of the matrix spiking solution to 25 mL of the sample assigned to be the MS/MSD to result in the addition of 0.125 µg of each non-ketone and 1.25 µg of each ketone spiked target analyte, resulting in concentrations of 5 µg/L and 50 µg/L respectively. Prepare fresh matrix spiking solution monthly, or sooner if the solution has degraded or evaporated.

NOTE: Analyses of MS/MSD are not required for the SIM analysis.

7.2.2.6 Internal Standard Spiking Solution

Use the same source of internal standard spiking solution as was used to prepare the initial calibration (i.e., same manufacturer and lot) for all calibration check standards, samples, and QC samples. This solution shall contain 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 each 25 mL sample, including samples, MS/MSDs, blanks, and calibration standards, to result in the addition of 0.125 µg of each internal standard. Prepare a fresh internal standard spiking solution monthly, or sooner if the solution has degraded or evaporated.

For SIM analysis, follow the procedure described above using the same source of internal standards for all standards, samples, and QC samples. Add a sufficient amount of internal standard spiking solution to each 25 mL aliquot, to result in the addition of 0.0125 µg of each internal standard.

7.2.3 Storage of Standard Solutions

7.2.3.1 Store the stock standard solutions in PTFE-sealed screw-cap bottles with zero headspace at -10°C to -20°C. Other containers designed to minimize volatile loss may be used, including Certan® vials and/or with Mininert® valves, particularly for maximizing the shelf life of the room-temperature gases.

7.2.3.2 Aqueous standards may be stored for up to 24 hours if held in glass vials with PTFE-lined screw-caps with zero headspace at ≤6°C, but not frozen. When using an autosampler, the standards may be kept up to 12 hours in the autosampler of the P/T device.

7.2.3.3 Store premixed certified solutions according to the manufacturer's documented holding time and storage temperature recommendations. Once the seal is compromised (e.g., ampule is opened), stock solutions for most compounds shall be used to prepare working standards and for the preparation of calibration standards within the shelf life of the working standards (Section 7.2.2.1). Stock solutions must be replaced in the same timeframe as the working standards unless acceptability of the standard can be documented to meet the SOW criteria (Section 7.2.3.6.1).

7.2.3.4 Protect all standards from light.

7.2.3.5 Purgeable standards shall 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 solidify. This means that, at a minimum, the standards shall be brought to room temperature prior to use, checked for losses, and checked to verify that all components have remained in solution.

7.2.3.6.1 Working standards shall be monitored frequently by comparison to the initial calibration. Fresh standards shall be prepared if the opening CCV criteria can no longer be met (Section 9.5.5) and the shelf life of the working standard is exceeded (Section 7.2.2.1). Standards shall be replaced upon expiration of the shelf life unless acceptability of the standard can be documented to meet all applicable SOW criteria, either by comparison to a compliant initial calibration generated from standards prepared within the shelf life of the working standards or by comparison to a freshly prepared standard. Standards of reactive analytes such as 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 Aqueous/water samples should be collected in glass containers that have a total volume of at least 40 mL with a PTFE-lined septum and an open top screw-cap. If SIM analysis is requested, an additional sample aliquot should have been collected.

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

8.1.3 The samples should be preserved to a pH ≤2 at the time of collection. Contact the Sample Management Office (SMO) immediately if aqueous/water samples are received without documentation of preservation.

8.1.4 The Contractor should receive at least three vials per field sample. If SIM analysis is requested, the Contractor should receive at least four vials per field sample.

NOTE: If MS/MSD analysis is required for a given sample, four additional vials per sample should be sent by the field samplers. Contact SMO if insufficient sample has been provided for the requested MS/MSD analysis.

8.2 Sample Storage

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

8.2.2 The samples shall be stored in an upright position 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 shall 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 preserved aqueous/water samples shall be completed within 10 days of the 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 Purge-and-Trap (P/T) analytical conditions are provided in Exhibit D – Trace VOA, Table 5. 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 addition of 1.0 µL of these standard solutions, either in an automated manner or manually, will be allowed only if the final concentration of the following standards in the 25 mL aqueous/water samples and blanks can be met: 5 µg/L for internal standards by the full-scan mode and 0.5 µg/L for the SIM mode; the concentrations listed in Section 7.2.2.1.2 for DMCs in the initial calibration; and the equivalent concentration listed for the mid-level calibration standard in Sections 7.2.2.2.1 and 7.2.2.1.5 for DMCs in the ICV and the CCV.

9.1.1.4 Before initial use, condition the trap overnight at 180°C by backflushing with at least a 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. Follow manufacturer’s recommendations for conditioning alternative traps. The trap may be vented to the analytical column during daily conditioning; however, the column shall be conditioned through the temperature program prior to the analysis of samples and blanks.

9.1.1.5 Optimize the P/T conditions for sensitivity and to minimize cross-contamination between samples. Once optimized, the same P/T conditions shall 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 - Target Analyte List and Contract Required Quantitation Limits, Table 1;
- The analytical results generated when using the moisture reduction/water management system meet the initial calibration, initial calibration verification, and continuing calibration verification technical acceptance criteria listed in the analytical method and the CRQLs listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1;
- 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 Exhibit D – Trace VOA, Table 6. The conditions are recommended unless otherwise noted. GC conditions must achieve all performance criteria required for initial calibration, initial calibration verification, and continuing calibration verification.

9.1.2.2 Optimize the GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions shall 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 and m,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 shall be used, and the initial temperature must be ≤10°C.

9.1.3 Mass Spectrometer

The recommended MS analytical conditions are provided in Exhibit D – Trace VOA, Table 7.

9.2 Instrument Performance Check

9.2.1 Summary of GC/MS Instrument Performance Check

9.2.1.1 The GC/MS system shall 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 7.2.2.3).

9.2.1.2 Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the Contractor shall 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 shall be injected once at the beginning of each initial calibration sequence for the full scan and SIM analyses during which samples, blanks, or standards are to be analyzed.

NOTE: For SIM acquisition, the instrument performance check solution shall be analyzed in full scan mode, but the same optimized mass spectrometer settings (e.g., electron multiplier voltage, lens settings) shall be used for full scan analysis of the instrument performance check as will be used for SIM acquisition.

9.2.3 Procedure for GC/MS Instrument Performance Check

The analysis of the instrument performance check solution shall be performed using one of the following options:

- As an injection of up to 50 ng of BFB into the GC/MS.
- By adding a sufficient amount of BFB solution (Section 7.2.2.3) 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 GC/MS Instrument Performance Check

9.2.4.1 The GC/MS system instrument performance check shall be performed at the frequency described in Section 9.2.2.

9.2.4.2 The abundance criteria listed in Exhibit D – Trace VOA, Table 2, must be met for a ≤50 ng injection of BFB. The mass spectrum of BFB shall 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 within 20 scans 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 shall 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 BFB technical acceptance criteria have not been met will require reanalysis.

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 shall 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.

NOTE: For analysis using the SIM technique, the GC/MS system shall be calibrated at a minimum of five concentrations (Section 7.2.2.1.3), 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 shall 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, 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 (Section 9.3.5), the ICV, method blank, samples, and closing CCV may be analyzed. It is not necessary to analyze another opening 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 shall be allowed to warm to ambient temperature before analysis.

9.3.3.3 Add the specified amount of the internal standards (Section 7.2.2.6) to each of the five aqueous calibration standard solutions containing the DMCs (Sections 7.2.2.1.2 and 7.2.2.1.3) 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 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. The primary characteristic ions used for quantitation are listed in Exhibit D – Trace VOA, Table 8. 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 Exhibit D – Trace VOA, Table 9.

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

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 Equation 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations, 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 the m,p-xylene isomers respectively.

9.3.4.3 The Mean RRF ($\overline{RRF}$) must be calculated for all target analytes and DMCs according to Equation 1 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 1 and 2 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards shall be analyzed at the concentrations described in Sections 7.2.2.1.2 and 7.2.2.1.3, 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 the instrument.

9.3.5.3 The chromatographic resolution shall be verified with the mid-point concentration of the initial calibration 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.

9.3.5.4 The required minimum RRF value for each target analyte and DMC at each calibration concentration for the full scan analysis is listed in Exhibit D – Trace VOA, Table 4. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet this criteria. Up to two different target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D – Trace VOA, Table 4, but these compounds must still meet the minimum RRF requirement of 0.010 for the ICAL to be considered acceptable.

9.3.5.5 The required maximum %RSD value for each target analyte and DMC for the full scan analysis is listed in Exhibit D – Trace VOA, Table 4. Target analytes and DMCs with a maximum %RSD requirement of 40.0% must meet the criteria. Up to two target analytes and DMCs with maximum %RSD requirements of less than 40.0% may fail to meet the %RSD criteria listed in Exhibit D – Trace VOA, Table 4, but these compounds must still meet the maximum %RSD requirement of 40.0% for the ICAL to be considered acceptable.

9.3.5.6 For SIM analysis, all target analytes and DMCs must meet the minimum RRF and maximum %RSD requirements listed in Exhibit D – Trace VOA, Table 4.

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 or nitrogen) 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 analytes, 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.

9.4 Initial Calibration Verification

9.4.1 Summary of Initial 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 shall be routinely checked by analyzing an ICV (containing all the purgeable target analytes from an alternate source or a different lot than used for the ICAL standards, and the DMCs and internal standards from the same source or lot as used for the ICAL standards) to ensure that the instrument is calibrated accurately.

9.4.2 Frequency of Initial Calibration Verification

The calibration for each GC/MS system used for analysis shall be verified with an ICV at the frequency of one per ICAL analytical sequence. The ICV shall be analyzed following the last ICAL standard analysis and prior to any method blank, sample, or applicable CCV analysis.

Injection #	**Material Injected**
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 - ICV	ICV
8th - Blanks, samples, MS/MSDs	Blanks, samples, and MS/MSDs
9th - Subsequent Samples	

9.4.3 Procedure for Initial Calibration Verification

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

9.4.3.2 Add the specified amount of the internal standards (Section 7.2.2.6) and DMCs (Section 7.2.2.4) specified for the full scan or SIM analysis to the appropriate ICV (Section 7.2.2.2) at the time of purge. Analyze the ICV standards according to Section 10.0.

9.4.4 Calculations for Initial Calibration Verification

9.4.4.1 Calculate an RRF for each target analyte and DMC using Equation 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.4.2 Calculate the Percent Difference (%D) between the ICV RRF_c and the preceding initial calibration $\overline{RRF}_i$ for each purgeable target analyte and DMC using Equation 17 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

9.4.5.1 The concentration of the trace volatile target analytes and DMCs in the ICV shall 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 ICV shall 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 ICV for the full scan analysis, the required minimum RRF value for each target analyte and DMC is listed in Exhibit D – Trace VOA, Table 4. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet the criteria. Up to two target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D – Trace VOA, Table 4, but these compounds must still meet the minimum RRF requirement of 0.010 for the CCV to be considered acceptable.

9.4.5.3 For an ICV for the full scan analysis, the required maximum %D value for each target analyte and DMC is listed in Exhibit D – Trace VOA, Table 4. Target analytes and DMCs with a maximum %D requirement of 40.0% must meet the criteria. Up to two target analytes and DMCs with maximum %D requirements of less than 40.0% may fail to meet the maximum %D criteria listed in Exhibit D – Trace VOA, Table 4, but these compounds must still meet the maximum %D requirement of 40.0% for the ICV to be considered acceptable.

9.4.5.4 For SIM analysis, all target analytes and DMCs in the ICV must meet the minimum RRF and maximum %D requirements listed in Exhibit D - Trace VOA, Table 4.

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 the instrument.

9.4.6 Corrective Action for Initial Calibration Verification

9.4.6.1 If the ICV analyzed immediately after the ICAL sequence does not meet the technical acceptance criteria, and a subsequent reanalysis of the ICV meets the technical acceptance criteria, proceed with the blank and sample analyses.

9.4.6.2 If the ICV analyzed immediately after the ICAL sequence does not meet the technical acceptance criteria, and a subsequent reanalysis does not meet the technical acceptance criteria, recalibrate the GC/MS instrument according to Section 9.3. All sample and required blank analyses must be associated to a compliant ICV analysis following the associated ICAL.

9.5 Continuing Calibration Verification

9.5.1 Summary of Continuing Calibration Verification

Prior to the analysis of samples and required blanks, and after instrument performance check, initial calibration, and ICV technical acceptance criteria have been met, each GC/MS system shall 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 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 9.5.2.3).

9.5.2 Frequency of Continuing Calibration Verification

9.5.2.1 The calibration for each GC/MS system used for analysis shall be verified at the beginning and end of every 12-hour period of operation. The 12-hour period begins with the injection of an opening CCV solution that meets the technical acceptance criteria in Section 9.5.5, followed by the injection of the blank and samples. The 12-hour period ends with the injection of a closing CCV. If the closing CCV does not meet the technical acceptance criteria for an opening CCV (Section 9.5.5), an injection of an opening CCV is required to start the next 12-hour period.

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

9.5.2.3 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 in Section 9.5.5 are met for an opening CCV.

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 - ICV	ICV
	8th - Blanks, samples, MS/MSDs	Blanks, samples, and MS/MSDs
	9th – Subsequent Samples	
End 12 hr	Closing CCV (meeting Closing CCV criteria, but not Opening CCV)	CS3 – Closing CCV
New 12 hr	1st Analysis 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 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

Time	Injection #	Material Injected
End of 12 hr beginning of next 12 hr	Closing CCV (meeting Opening CCV criteria)	CS3 – Closing CCV meeting Opening CCV criteria 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 criteria

9.5.3 Procedure for Continuing Calibration Verification

9.5.3.1 All standard/spiking solutions shall be allowed to reach ambient temperature before analysis.

9.5.3.2 Add the internal standards (Section 7.2.2.6) and DMCs (Section 7.2.2.4) for the full scan or SIM analysis to the appropriate CCV (Section 7.2.2.1.5) at the time of purge. Analyze the CCV standard according to Section 10.0.

9.5.4 Calculations for Continuing Calibration Verification

9.5.4.1 Calculate an RRF for each target analyte and DMC using Equation 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.4.2 Calculate the %D between the CCV RRF_c and the most recent initial calibration $\overline{RRF_i}$ for each purgeable target analyte and DMC using Equation 17 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The concentration of the trace volatile organic target analytes and DMCs in the opening and closing CCV shall 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 shall be analyzed at the frequency described in Section 9.5.2, on a GC/MS system meeting the BFB (Section 9.2.4), the initial calibration (Section 9.3.5), and the ICV (Section 9.4.5) technical acceptance criteria.

NOTE: For analysis using the SIM technique, the concentration for the target analytes and DMCs listed in Section 7.2.2.1.3 must be 0.50 µg/L.

9.5.5.2 For an opening or closing CCV for the full scan analysis, the required minimum RRF value for each target analyte and DMC is listed in Exhibit D – Trace VOA, Table 4. Target analytes and DMCs with a minimum RRF requirement of 0.010 must pass this criteria (the minimum RRF for DMC trans-1,3-dichloropropene-d_4 is advisory). Up to two target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D - Trace VOA, Table 4, but these compounds must still meet the minimum RRF requirements of 0.010 for the CCV to be considered acceptable.

9.5.5.3 For an opening CCV for the full scan analysis, the required maximum %D value for each target analyte and DMC is listed in Exhibit D – Trace VOA, Table 4. Target analytes and DMCs with maximum %D requirements of 40.0% must pass this criteria. Up to two target analytes and DMCs with maximum %D requirements of less than 40.0% may fail to meet the maximum %D criteria listed in Exhibit D – Trace VOA, Table 4, but these compounds must still meet the maximum %D requirement of 40.0% for the opening CCV to be considered acceptable.

9.5.5.4 For a closing CCV for the full scan analysis, the required maximum %D value for each target analyte and DMC is listed in Exhibit D – Trace VOA, Table 4. Up to two target analytes and DMCs may fail to meet the maximum %D criteria listed in Exhibit D - Trace VOA, Table 4.

9.5.5.5 For SIM analysis, all target analytes and DMCs in the opening and closing CCVs must meet the minimum RRF requirements listed in Exhibit D - Trace VOA, Table 4.

9.5.5.6 For SIM analysis, all target analytes and DMCs in the opening and closing CCVs must meet the maximum %D requirements listed in Exhibit D - Trace VOA, Table 4.

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

9.5.6 Corrective Action for Continuing Calibration Verification

9.5.6.1 If the opening CCV technical acceptance criteria are not met, reanalyze the opening CCV. If the reanalyzed opening CCV criteria still are not met, recalibrate the GC/MS instrument and take other corrective actions 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 shall be reanalyzed.

9.5.6.2 The Contractor shall follow the procedure in Section 10.2.13.1 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.

9.5.6.3 All samples and required blanks are to be associated with an opening CCV meeting the technical acceptance criteria or reanalyses are required.

9.5.6.4 The corrective action for sample reanalysis is not required when noncompliant analytes or associated DMCs, in the opening or closing CCVs bracketing a dilution or a reanalysis, are not the same analytes or associated DMCs for which the dilution analysis or reanalysis was intended.

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 shall be employed for the analysis of samples as were used for calibration. All samples, required blanks, and standard/spiking solutions shall be allowed to warm to ambient temperature before analysis.

NOTE 1: Contact SMO if sample vials have entrained bubbles ≥6 mm in size resulting in headspace.

NOTE 2: If SIM analysis is requested for a sample, a full scan analysis at trace level shall be performed on that sample prior to the SIM analysis. If all the SIM target analytes are detected at or above the sample adjusted CRQLs in the full scan analysis, a SIM analysis is not to be performed for that sample.

NOTE 3: If any single SIM analyte exceeds the calibration range in the full scan sample analysis, do not proceed with the SIM method for any of the other target analytes scheduled for SIM analysis for that sample.

Any SIM sample analyses not performed for the reasons in the above notes shall be included in the SDG Narrative.

10.2 Procedure for Sample Analysis

10.2.1 If time remains in the 12-hour period (as described in Section 9.3.2.2), samples may be analyzed without analysis of an opening CCV standard.

10.2.2 If the autosampler can automatically sample the appropriate volume, then Sections 10.2.3 - 10.2.6 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 The process of taking an aliquot from the container 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 shall 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 shall be performed within 24 hours. Care shall also be taken to prevent air from leaking into the syringe.

10.2.5 Add a sufficient amount of the DMC spiking solution (Section 7.2.2.4.3) and a sufficient amount of internal standard spiking solution (Section 7.2.2.6) 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 For analysis by the SIM technique, add a sufficient amount of the DMC spiking solution (Section 7.2.2.4.5) and a sufficient amount of the internal standard spiking solution (Section 7.2.2.6) through the valve bore of the syringe, then close the valve. Invert the syringe 3 times.

10.2.7 Once the sample aliquots have been taken from the VOA vial, the pH of the aqueous/water sample shall be determined. The purpose of the pH determination is to ensure that all VOA samples were acidified in the field. Record the pH of each sample and report these data in the Electronic Data Deliverable (EDD). No pH adjustment is to be performed by the Contractor.

10.2.8 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.

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

10.2.10 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 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.

10.2.11 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 shall be used for all analyses.

10.2.12 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.

10.2.13 Sample Dilutions

10.2.13.1 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 a screening analysis be performed prior to sample analysis to determine estimated analyte concentration and matrix problems.

10.2.13.2 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 shall be considered (see Section 11.2.1.4).

10.2.13.3 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.

10.2.13.4 The DF selected shall keep the concentrations of the trace volatile target analytes that required dilution within the upper half of the initial calibration range.

10.2.13.5 All dilutions shall 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 shall be performed without delay.

10.2.13.6 Samples shall be diluted in a volumetric flask or in a 25 mL Luer-Lok syringe.

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

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

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

10.2.13.7.3 Inject the proper sample aliquot from a 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.

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

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

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

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

10.2.13.8.3 Replace the syringe plunger and compress the water.

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

10.2.13.8.5 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.

10.2.13.9 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 shall be reanalyzed.

10.2.13.10 Contact SMO for direction prior to using the last replicate vial.

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 – Target Analyte List and Contract Required Quantitation Limits, Table 1, 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 Relative Retention Time (RRT) unit window established from the 12-hour calibration standard; and
- Correspondence of the sample component and calibration standard analyte mass spectra.

11.1.1.2 Establish correspondence between the RRT of the analyte in the continuing calibration standard and the sample component 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 shall 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 mid-point CS3 ICAL 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 shall 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 on the Contractor’s GC/MS (as opposed to library spectra) are required. Once obtained, these standard spectra shall be used for identification purposes, only if the Contractor’s GC/MS meets the daily instrument performance requirements for BFB. These standard spectra shall 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 the ions specified in the section 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%), barring the influence of interference.

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 shall 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 (2017 release or later), Wiley (2014 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 11.1.1, or that are not DMCs, internal standards, or semivolatile target analytes listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2, 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. 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. 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, identification (as generated by the library search program) of those receiving a library search match of 85% or higher shall be considered a "probable match". The compound shall 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 shall 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 Contractor 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 Contractor 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 shall 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: 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 percent match at or above 85% at two different RTs, the compound having the highest percent match shall be reported as a TIC and the other one shall be reported as unknown. If both TICs have the same percent match for the same compound, one of the TICs shall be reported as unknown. Such justifications shall 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 (Exhibit D – Trace VOA, Table 9). The EICP area of primary characteristic ions of analytes listed in Exhibit D – Trace VOA, Table 8, are 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 coelute on the available capillary columns, special attention shall 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 an RRF from the initial calibration 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 shall perform a manual quantitation or integration. Manual integrations are performed by manually choosing the area of the quantitation ion of the compound to integrate, either by drawing the baseline by hand or by choosing times for setting baselines in the software. 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 shall 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 instrument operator shall 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 instrument operator shall also mark each integrated area with the letter "m" on the quantitation report. All edits and manual integrations shall be verified by a second person, who shall also initial the change(s). In addition, graphical display(s) of the EICPs of the quantitation ion displaying the original integration(s) shall be included in the raw data, in addition to

the graphical display(s) of the EICPs of the quantitation ion displaying the manual integration(s). Chromatographic baselines shall be clearly visible in the original and edited EICPs at the same scaling. This applies to all target analytes listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 1.

11.2.2 Target Analyte Calculations

Identified target analytes shall be quantitated by the internal standard method using Equation 4A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. The internal standard used shall be that which is assigned in Exhibit D – Trace VOA, Table 9. The $\overline{RRF}$ from the initial calibration is used to calculate the concentration in the sample.

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 Equation 4A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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.

11.2.4 Contract Required Quantitation Limit Calculations

Calculate the adjusted CRQL using Equation 6A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.5 Deuterated Monitoring Compound Recoveries

11.2.5.1 Calculate the amount of each DMC in samples and blanks using Equation 22A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations).

11.2.5.2 Calculate the recovery of each DMC in all samples and blanks using Equation 22 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.3 Technical Acceptance Criteria for Sample Analysis

11.3.1 The sample shall be analyzed on a GC/MS system meeting the BFB, initial calibration, ICV, CCV, and blank technical acceptance criteria. Do not apply BFB criteria to SIM analysis.

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

11.3.3 The sample must have an associated method blank.

11.3.4 Up to three DMCs per sample may fail to meet the recovery limits listed in Exhibit D – Trace VOA, Table 10. For SIM analysis, all associated DMCs must meet the recovery limits listed in Exhibit D – Trace VOA, Table 10.

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 or in the ICV standard analysis in the analytical sequence.

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 or in the ICV standard analysis in the analytical sequence.

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 10.2.13.

11.3.8 The Contractor shall 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 shall either:

- Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank shall 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 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 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 analysis 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.

11.4.2 Corrective actions for failure to meet technical acceptance criteria for instrument performance checks, initial calibration, ICV, CCV, and method blanks shall 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 After completing the corrective actions outlined above, the Contractor shall proceed to reanalyzing the sample as appropriate.

11.4.4.1 If the DMC recoveries do not meet the acceptance criteria in the initial (undiluted) sample analysis, reanalyze the sample.

- If the DMC recoveries do not meet the acceptance criteria in the reanalyzed sample, then submit the data from both analyses. Distinguish between the initial analysis and the reanalysis in all deliverables using the suffixes in Appendix B – Codes for Labeling Data.

11.4.4.2 If the internal standard compound responses do not meet the acceptance criteria in the initial (undiluted) sample analysis, reanalyze the sample.

- If the internal standard compound responses are still noncompliant after the reanalysis, the Contractor shall dilute the original sample by an appropriate dilution factor (nominally 2-10) and reanalyze the sample. If the internal standard compound responses are acceptable in the subsequent diluted analysis, submit the data from the reanalysis and the diluted analysis.
- No further corrective action is required if the internal standard compound responses do not meet the acceptance criteria in the reanalysis and in the subsequent diluted analysis. Submit the data from the reanalysis and the diluted analysis. Distinguish between the initial analysis, reanalysis, and the diluted analysis in all deliverables using the suffixes in Appendix B – Codes for Labeling Data.

NOTE: If the internal standard and/or DMC performance issue appears to be caused by the presence of high levels of target analytes (i.e., above the highest calibration standard), the Contractor may analyze the sample at an appropriate dilution factor (nominally 2-10) after the initial analysis that did not meet the criteria (without first reanalyzing the undiluted sample). However, if no target analytes are measured in the upper half of the calibration range in the diluted sample, the Contractor must proceed with reanalysis of the undiluted sample.

11.4.4.3 If the DMC recoveries in Section 11.4.4.1, the internal standard compound responses in Section 11.4.4.2, or both the DMC recoveries and the internal standard compound responses meet the acceptance criteria in the reanalyzed sample, it indicates that the problem was within the Contractor’s control. Therefore, only submit the data from the reanalysis.

11.4.4.4 If the DMC recoveries or internal standard compound responses in a sample used for the MS/MSD analyses are outside the acceptance criteria, the Contractor shall proceed to the following corrective actions:

- If the DMC recoveries in the sample used for the MS/MSD analyses are outside the acceptance criteria, then the sample shall be reanalyzed (Section 11.4.4.1) only if the DMC recoveries meet the acceptance criteria in both the MS and MSD analyses.
- If the internal standard compound responses do not meet the acceptance criteria, the Contractor shall proceed to the reanalysis in Section 11.4.4.2 only if the internal standard compound responses meet the technical acceptance criteria in both the MS and MSD analyses.

11.4.5 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 shall 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 shall be appropriately diluted as indicated in Section 10.2.13 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 do not meet maximum carryover criteria shall be reanalyzed. If this analyte in the diluted analysis is detected within the calibration range, then no further corrective action is required.

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

11.4.6.1 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.

11.4.6.2 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 analysis were outside the acceptance criteria, then it shall be reanalyzed only if the internal standard RTs were within the acceptance criteria in both the MS/MSD analyses.
- If the internal standard compound 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 compound 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 Appendix B – Codes for Labeling Data.

11.4.7 If the required corrective actions for sample reanalysis and/or dilution cannot be performed due to insufficient sample volume, the Contractor shall contact SMO.

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 7.2.2.6) and DMC spiking solution (Section 7.2.2.4), 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 method blank. The purpose of the method blank is to determine the levels of contamination associated with the processing and analysis of the samples.

12.1.2.2 Frequency of Method Blank

12.1.2.2.1 The method blank shall be analyzed at least once during every 12-hour period on each GC/MS system used for trace volatile analysis (see Section 9.3.2.2 for the definition of the 12-hour period).

12.1.2.2.2 The method blank shall be analyzed after the ICV or opening CCV (see sample sequence in Section 9.4.2 or 9.5.2) if samples, including MS/MSDs, dilutions, or storage blanks, are analyzed before the 12-hour period expires. The method blank shall be analyzed after the opening CCV and before any samples, including MS/MSDs, dilutions, or storage blanks are analyzed. A method blank shall be analyzed in each 12-hour period in which samples, including MS/MSDs, dilutions, 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 shall 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 method blanks shall be prepared and analyzed on a GC/MS system meeting the BFB, initial calibration, ICV, 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 method blank must be within the acceptance windows in Exhibit D – Trace VOA, Table 10. If a DMC %D does not meet the acceptance criteria in the associated opening CCV, the same DMC is also permitted to fail to meet the recovery criteria in the method blank, up to the maximum specified in section 9.5.5.3 (e.g., DMC %R limits of 40-130% will become 40-140%).

12.1.2.5.3 The internal standards in the method blank must meet the sample technical acceptance criteria listed in Sections 11.3.5 - 11.3.6.

12.1.2.5.4 The concentration of each target analyte in the method blank must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, 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 in the method blank must be less than 0.5 µg/L.

12.1.2.5.6 All method blanks shall 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 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 shall 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 gas chromatograms be eliminated.

12.1.2.6.3 Any method blank that fails to meet the technical acceptance criteria shall 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.

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 internal standard spiking solution (Section 7.2.2.6) and DMC spiking solution (Section 7.2.2.4), and carried through the entire analytical procedure. Instrument blanks are analyzed after a sample/dilution that contains a target analyte at levels that exceed the calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample analysis.

12.1.3.2 Frequency of Instrument Blank

Samples may contain target analytes at levels exceeding the calibration. An instrument blank shall 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. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system shall 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) shall 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 in Section 11.3.8.

12.1.3.3.2 Under no circumstances shall 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 shall be analyzed on a GC/MS system meeting the BFB, initial calibration, ICV, and CCV technical acceptance criteria and at the frequency described in Section 12.1.3.2.

12.1.3.5.2 The internal standards in the instrument blank must meet the sample acceptance criteria listed in Sections 11.3.5 - 11.3.6.

12.1.3.5.3 The concentration of each target analyte in the instrument blank must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1. The concentration of each non-target compound in the instrument blank must be less than four times the nominal CRQL (2.0 µg/L) of the target analyte.

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 any instrument blank exceeds 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 shall be investigated and appropriate corrective measures shall be taken and documented before further sample analysis proceeds.

12.1.3.6.2 If an instrument blank fails to meet the technical acceptance criteria described in Section 12.1.3.5, the samples analyzed immediately after the instrument blank must be reanalyzed and meet the technical acceptance criteria in Section 11.4.1.

12.1.4 Storage Blank

12.1.4.1 Summary of Storage Blank

A storage blank is a volume of reagent water that is stored with the samples in an SDG under the same conditions. A 25 mL aliquot of this reagent water is spiked with internal standard spiking solution and DMC spiking 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 shall 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 are filled with reagent water and stored with the samples in the SDG under the same conditions.

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 shall 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 shall be analyzed on a GC/MS system meeting the BFB, initial calibration, ICV, and CCV technical acceptance criteria and at the frequency described in Section 12.1.4.2.

12.1.4.5.2 The storage blank shall 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 Exhibit D – Trace VOA, Table 10.

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 or in the ICV standard analysis in the analytical sequence.

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 or in the ICV standard analysis in the analytical sequence.

12.1.4.5.6 The concentration of each target analyte in the storage blank must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, except for methylene chloride, acetone, and 2-butanone, which must be less than 2 times the respective CRQL. The concentration of each TIC in the storage blank must be less than 0.50 µg/L.

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 shall be investigated and appropriate corrective measures shall be taken and documented before further sample 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 shall be reported. If upon reanalysis, the storage blank still does not meet the criteria, the problem occurred during storage. The Contractor shall address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences of contamination.

NOTE: A copy of the storage blank data shall 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 Traffic Report/Chain of Custody (TR/COC) Record.

12.2.2 Frequency of Matrix Spike and Matrix Spike Duplicate

12.2.2.1 If requested, an MS/MSD analysis shall be performed for each group of 20 field samples in an SDG, or each SDG, whichever is most frequent. The Contractor shall not perform MS/MSD analysis when using the SIM technique.

12.2.2.2 Samples identified as field blanks or PE samples shall not be used for MS/MSD analysis.

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

12.2.3 Procedure for Preparing Matrix Spike and Matrix Spike Duplicate

12.2.3.1 Add a sufficient volume (e.g., 10 µL) of the matrix spiking solution (Section 7.2.2.5) to result in addition of 0.125 µg of each non-ketone target analyte and 1.25 µg of each ketone target analyte to 25 mL aliquots of the sample selected for spiking. Process the samples according to Section 10.0.

12.2.3.2 MS/MSD samples shall 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 shall be performed in accordance with Section 10.2.13. 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 4A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations). Calculate the recovery of each Matrix Spike analyte using Equation 23 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD sample using Equation 24A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Matrix Spike Duplicate

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

12.2.5.2 The MS/MSD sample shall be analyzed within the contract required holding time.

12.2.5.3 The internal standards in the MS/MSD samples must meet the sample acceptance criteria listed in Sections 11.3.5 - 11.3.6.

12.2.5.4 The percent recovery and RPD limits for the spiking analytes listed in Exhibit D – Trace VOA, Table 11, are advisory. No further action by the Contractor is required when these criteria are not met. There are no specified limits for the spiking analytes that are not listed in Exhibit D – Trace VOA, Table 11; however, all target analyte concentrations and DMC concentrations and recoveries shall be reported.

12.2.6 Corrective Action for Matrix Spike and Matrix Spike Duplicate

Any MS/MSD sample that does not meet the technical acceptance criteria in Sections 12.2.5.1 and 12.2.5.3 shall be reanalyzed.

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 MDL for each trace volatile target analyte shall be determined for each instrument under the same conditions used for analysis (i.e., analytical system configuration, as well as type and dimension of GC column), prior to the start of contract analyses and verified annually thereafter. MDL determination is level-specific (i.e., the MDL shall be determined for trace and trace SIM levels). An MDL study shall also be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis. Major instrument maintenance includes, but is not limited to: replacement of the mass

spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), or 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.

12.4.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.

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

12.4.1.3 The delivery requirements for the MDL values are specified in Exhibit B – Reporting and Deliverables Requirements, Table 1.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Method 524.4, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 1, May 2013.

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 5030C, Purge-and-Trap for Aqueous Samples, Revision 3, May 2003.

16.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 8260D, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, June 2018.

16.4 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

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-	Trichloroethene	Ethylene, trichloro-	79-01-6
Cyclohexane, methyl-	Methylcyclohexane	Hexahydrotoluene	108-87-2

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

Systematic Name	EPA Registry Name	Synonym	CAS #
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
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
Propane, 1,2,3-trichloro-	1,2,3-Trichloropropane	Glycerol trichlorohydrin	96-18-4
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-trimethyl-	1,2,4-Trimethylbenzene	Asymmetrical trimethylbenzene	95-63-6
Benzene, 1,3,5-trimethyl-	1,3,5-Trimethylbenzene	sym-Trimethylbenzene	108-67-8

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

Systematic Name	EPA Registry Name	Synonym	CAS #
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
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
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% of mass 95
175	5.0 - 9.0% of mass 174
176	95.0 - 105% of mass 174
177	5.0 - 10% of mass 176

NOTE: All ion abundances shall 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. Criteria based on EPA method 524.4.

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 1,2,3-Trichloropropane	Trichloroethene Toluene Tetrachloroethene Ethylbenzene o-Xylene m,p-Xylene Styrene Isopropylbenzene 1,2,4-Trimethylbenzene 1,3,5-Trimethylbenzene
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 CALIBRATION, INITIAL CALIBRATION VERIFICATION, AND CONTINUING CALIBRATION VERIFICATION FOR TRACE VOLATILE ORGANIC COMPOUNDS

Analyte	ICAL/ICV Minimum RRF	Opening/ Closing CCV Minimum RRF	ICAL Maximum %RSD	ICV/Opening CCV Maximum %D[1]	Closing CCV 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	±40.0	±50.0
Chloroethane	0.010	0.010	40.0	±30.0	±50.0
Trichlorofluoromethane	0.010	0.010	40.0	±30.0	±50.0
1,1-Dichloroethene	0.020	0.020	30.0	±25.0	±50.0
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	30.0	±30.0	±50.0
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	30.0	±25.0	±50.0
Methyl tert-butyl ether	0.010	0.010	30.0	±30.0	±50.0
1,1-Dichloroethane	0.100	0.100	30.0	±20.0	±50.0
cis-1,2-Dichloroethene	0.100	0.100	20.0	±25.0	±50.0
2-Butanone	0.010	0.010	40.0	±40.0	±50.0
Bromochloromethane	0.020	0.020	20.0	±20.0	±50.0
Chloroform	0.040	0.040	30.0	±20.0	±50.0
1,1,1-Trichloroethane	0.050	0.050	30.0	±20.0	±50.0
Cyclohexane	0.010	0.010	30.0	±30.0	±50.0
Carbon tetrachloride	0.020	0.020	30.0	±25.0	±50.0
Benzene	0.300	0.300	20.0	±20.0	±50.0
1,2-Dichloroethane	0.010	0.010	20.0	±25.0	±50.0
Trichloroethene	0.100	0.100	30.0	±20.0	±50.0
Methylcyclohexane	0.100	0.100	30.0	±30.0	±50.0
1,2-Dichloropropane	0.100	0.100	20.0	±20.0	±50.0
Bromodichloromethane	0.090	0.090	20.0	±20.0	±50.0
cis-1,3-Dichloropropene	0.100	0.100	30.0	±20.0	±50.0
4-Methyl-2-pentanone	0.010	0.010	30.0	±30.0	±50.0
Toluene	0.400	0.400	20.0	±20.0	±50.0
trans-1,3-Dichloropropene	0.010	0.010	30.0	±20.0	±50.0
1,1,2-Trichloroethane	0.040	0.040	20.0	±20.0	±50.0
Tetrachloroethene	0.100	0.100	20.0	±20.0	±50.0
2-Hexanone	0.010	0.010	40.0	±40.0	±50.0
Dibromochloromethane	0.050	0.050	20.0	±20.0	±50.0

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

Analyte	**ICAL/ICV Minimum RRF**	**Opening/ Closing CCV Minimum RRF**	**ICAL Maximum %RSD**	**ICV/Opening CCV Maximum %D[1]**	**Closing CCV Maximum %D**
1,2-Dibromoethane	0.010	0.010	20.0	±20.0	±50.0
Chlorobenzene	0.400	0.400	20.0	±20.0	±50.0
Ethylbenzene	0.500	0.500	30.0	±25.0	±50.0
m,p-Xylene	0.200	0.200	30.0	±25.0	±50.0
o-Xylene	0.300	0.300	30.0	±25.0	±50.0
Styrene	0.200	0.200	30.0	±25.0	±50.0
Bromoform	0.010	0.010	30.0	±30.0	±50.0
Isopropylbenzene	0.700	0.700	30.0	±30.0	±50.0
1,2,3-Trichloropropane	0.010	0.010	30.0	±30.0	±50.0
1,1,2,2-Tetrachloroethane	0.010	0.010	20.0	±25.0	±50.0
1,3-Dichlorobenzene	0.500	0.500	20.0	±20.0	±50.0
1,4-Dichlorobenzene	0.700	0.700	20.0	±20.0	±50.0
1,2-Dichlorobenzene	0.400	0.400	20.0	±20.0	±50.0
1,2-Dibromo-3-chloropropane	0.010	0.010	40.0	±40.0	±50.0
1,2,4-Trimethylbenzene	0.010	0.010	30.0	±30.0	±50.0
1,3,5-Trimethylbenzene	0.010	0.010	30.0	±30.0	±50.0
1,2,4-Trichlorobenzene	0.200	0.200	30.0	±30.0	±50.0
1,2,3-Trichlorobenzene	0.050	0.050	30.0	±40.0	±50.0
Selective Ion Monitoring					
Vinyl chloride	0.010	0.010	30.0	±30.0	±50.0
Trichloroethene	0.100	0.100	30.0	±20.0	±50.0
1,2-Dibromoethane	0.010	0.010	20.0	±20.0	±50.0
1,2,3-Trichloropropane	0.010	0.010	30.0	±30.0	±50.0
1,2-Dibromo-3-chloropropane	0.010	0.010	40.0	±40.0	±50.0
Deuterated Monitoring Compounds					
Vinyl chloride-d_3	0.010	0.010	40.0	±30.0	±50.0
Chloroethane-d_5	0.010	0.010	40.0	±30.0	±50.0
1,1-Dichloroethene-d_2	0.010	0.010	30.0	±25.0	±50.0
2-Butanone-d_5	0.010	0.010	40.0	±40.0	±50.0
Chloroform-d	0.010	0.010	20.0	±20.0	±50.0
1,2-Dichloroethane-d_4	0.010	0.010	20.0	±25.0	±50.0
Benzene-d_6	0.030	0.030	20.0	±20.0	±50.0

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

Analyte	**ICAL/ICV Minimum RRF**	**Opening/ Closing CCV Minimum RRF**	**ICAL Maximum %RSD**	**ICV/Opening CCV Maximum %D[1]**	**Closing CCV Maximum %D**
1,2-Dichloropropane-d_6	0.100	0.100	20.0	±20.0	±50.0
Toluene-d_8	0.200	0.200	20.0	±20.0	±50.0
trans-1,3-Dichloropropene-d_4*	0.010	0.010	30.0	±25.0	±50.0
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	±50.0
1,2-Dichlorobenzene-d_4	0.060	0.060	20.0	±20.0	±50.0
Vinyl chloride-d_3 (SIM)	0.010	0.010	40.0	±30.0	±50.0
1,2-Dichloroethane-d_4 (SIM)	0.010	0.010	20.0	±25.0	±50.0
1,2-Dichloropropane-d_6 (SIM)	0.100	0.100	20.0	±20.0	±50.0
Toluene-d_8 (SIM)	0.200	0.200	20.0	±20.0	±50.0
1,1,2,2-Tetrachloroethane-d_2 (SIM)	0.010	0.010	20.0	±25.0	±50.0

*NOTE: The minRRF for trans-1,3-dichloropropene-d_4 is advisory for the opening and closing continuing calibration verification standards.

[1] If a closing CCV is acting as an opening CCV, all target analytes and DMCs shall 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: The desorb conditions and trap reconditioning conditions in this table are intended for the trap recommended in Section 6.3.4.2 and a GC with a jet separator. Alternative traps and GCs with split/splitless inlets may require different desorb conditions. For alternative traps and GC setups, use the trap manufacturer's and/or GC instrument manufacturer's recommended conditions. 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.

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 - Target Analyte List and Contract Required Quantitation Limits, Table 1, 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

*m/z 96 is used for quantitation of 1,1-Dichloroethene since the secondary ions at m/z 61 and 63 are also present in the spectrum of the associated DMC 1,1-Dichloroethene-d_2.

**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)**
o-Xylene	106	91
Styrene	104	78
Bromoform	173	175,254
Isopropylbenzene	105	120,77
1,2,3-Trichloropropane	75	110,77
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-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
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	65	100,102
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. 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	Isopropylbenzene
1,1-Dichloroethene	1,2-Dichloropropane	1,2,3-Trichloropropane
1,1,2-Trichloro-1,2,2-trifluoroethane	Bromodichloromethane	1,2,4-Trimethylbenzene
Acetone	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
Carbon disulfide	4-Methyl-2-pentanone	1,2,4-Trichlorobenzene
Methyl acetate	Toluene	1,2,3-Trichlorobenzene
Bromochloromethane	trans-1,3-Dichloropropene	1,2-Dichlorobenzene-d_4 (DMC)
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)	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 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

EXHIBIT D

LOW/MEDIUM CONCENTRATIONS OF
VOLATILE ORGANIC COMPOUNDS ANALYSIS

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

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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze aqueous/water, leachate derived from the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP), soil/sediment, and waste samples from hazardous waste sites for the volatile organic analytes (VOA) in the Target Analyte List (TAL) for low/medium volatiles in Exhibit C – Target Analyte List and Contract Required Quantitation Limits. The method, based on U.S. Environmental Protection Agency (EPA) Method 8260D, 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/water and medium-level soil/sediment and waste samples, and closed-system purge-and-trap for low-level soil/sediment and waste samples.

1.2 Problems that have been associated with the following analytes 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.
- 1,1,2,2-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.

2.0 SUMMARY OF METHOD

2.1 Aqueous/Water, TCLP, or SPLP Leachate

An inert gas is bubbled through a 5.0 milliliter (mL) aliquot of sample, that has been spiked with Deuterated Monitoring Compound (DMC) and internal standard spiking solutions, 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 shall 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 5.0 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: A sodium bisulfate preservative may be used under limited circumstances. 5.0 mL of sodium bisulfate solution (Section 7.1.3) may be added to the samples at the time of collection when preservation by sodium bisulfate is requested by the EPA Region.

The entire vial is placed into the instrument carousel. Immediately before analysis, the device automatically adds organic-free reagent water, DMCs, and internal standards. The vial containing the sample is heated to a 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/sediment sample of 5.0 g is collected, preserved with methanol, and/or extracted with methanol. An aliquot of the methanol extract is added to 5.0 mL of reagent water. An inert gas is bubbled through this solution, that has been spiked with DMC and internal standard spiking solutions, 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

Solid waste samples are analyzed using the soil/sediment methods in Section 2.2. Waste samples that have undergone TCLP/SPLP procedures are analyzed using the aqueous/water methods in Section 2.1.

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 National Institute of Standards and Technology (NIST) (2017 release or later), Wiley (2014 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 – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 shall 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 shall 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 shall be stored separately from other laboratory samples and standards, and shall be analyzed in a room where the atmosphere is demonstrated to be free of all potential contaminants that would 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 shall 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 reagent 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 shall be completely free of solvents. Special precautions shall be taken to determine the presence of methylene chloride. The analytical and sample storage area shall 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 shall 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 shall be taken. At the time of sample receipt, the Contractor shall 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).

4.1.5 The desorb and trap reconditioning conditions specified in Exhibit D – Low/Med VOA, Table 5, shall be followed when using the trap recommended in Section 6.3.4.5 and GC with a direct capillary interface. Certain target analytes, such as methyl tert-butyl ether (MTBE), may decompose at high purge temperatures in samples that have been acid preserved.

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 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, demonstration of equivalent performance that meets 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.

All instruments, balances, heating, and measuring equipment and devices shall be uniquely identified and labeled to allow traceability to any corresponding records of use.

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 The balance calibration shall be checked with known masses once per each day of use. This verification shall consist 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 shall be checked on a monthly basis using NIST-traceable known reference masses (Class ‘0’ or Class ‘1’) as defined by ASTM E617-13 or equivalent (e.g., earlier Class ‘S’ defined masses). All balances shall be checked at least once annually by a certified technician. The reference masses used by the Contractor shall 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 Spatulas – 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 Valves - 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 and percent moisture determination.

6.1.10.3 Glass Vials and PTFE-lined Caps - Assorted sizes.

6.1.10.4 Optional vials with PTFE Mininert® caps and septa, Certan® vials, or equivalent, for standard solutions.

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. The instrument shall be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.3.2 Gas Chromatography Columns

Recommended Column: A fused silica high resolution capillary GC column with an intermediate polarity column phase (e.g., 6% Cyanopropylphenyl/94% polydimethylsiloxane or equivalent), with 20-75 meter (m) column length, 0.18-0.53 millimeter (mm) inner diameter, and 1-3 micrometer (µm) film thickness, is generally recommended for this procedure. Examples include but are not limited to: VOCOL®, Rtx-502.2®, Optima-624®, BP624®, ZB-624®, DB-624®, Rtx-624®, CP-Select 624CB®, or equivalent). A typical column, DB-624, with a column specification of 30 m length x 0.25 mm ID and 1.4 µm film thickness, has been found to provide satisfactory separation for the analysis. Alternative GC column phases or dimensions may also be acceptable for use provided that all specified performance criteria in the SOW can be met on a routine basis. Regardless of the column used, the operating conditions of the system must be demonstrated by the laboratory to meet the performance criteria described in Section 6.3.2.1, and this demonstration must be made available for review upon request by the EPA. A description of the column used for analysis shall be provided in the SDG Narrative. Packed GC columns cannot be used.

The analytical system must be able to accept up to 1,000 nanograms (ng) of each analyte listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, without becoming overloaded. The gas flow from the concentrator may be split at an appropriate ratio prior to introduction to the GC to prevent overloading of the column as needed, provided the sensitivity is

acceptable and the same conditions are used for the demonstration of performance described in Section 6.3.2.1 as are used for analysis of standards and samples.

6.3.2.1 A capillary column is considered acceptable if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the analytes listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 1.
- The analytical results generated using the column meet the initial calibration, initial calibration verification (ICV), and continuing calibration verification (CCV) technical acceptance criteria (Sections 9.3.5, 9.4.5, and 9.5.5), and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1.
- The column provides acceptable peak shapes and resolution of the analytes listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 1 (refer to Section 9.1).
- 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 laboratory generates acceptable method detection limits (MDLs) with the integrated system including the same GC column and operation conditions as will be used for sample analysis.

6.3.2.1.1 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 shall maintain documentation verifying 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 EPA 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, ICV, 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, 9.4.5, and 9.5.5;
- 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 - Target Analyte List and Contract Required Quantitation Limits, Table 1.

6.3.2.1.4 The documentation shall be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional CLP Contracting Officer's 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 Exhibit D – Low/Med VOA, Table 2, 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 shall 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 that prevents the release of contaminants into the instrument room. Adsorbents used in the trapping system must be replaced according to the product replacement periods recommended by the manufacturer, and at a minimum annually, or more frequently as needed when such product information is not provided.

6.3.3.1 Gas Chromatograph/Mass Spectrometer Interface

Any GC/MS interface may be used 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.

6.3.4 Purge-and-Trap Device

The Purge-and-Trap (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 the volatile organic compounds (VOCs) using an inert gas stream and traps the released VOCs for subsequent desorption into the GC. For low-level soil/sediment samples, the P/T device consists of a unit that automatically adds reagent 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. The adsorbent must be replaced according to the product replacement periods recommended by the manufacturer, and at a minimum annually, or more frequently if such product information is not provided

and/or the laboratory routinely has difficulty meeting the QC criteria identified in Section 6.3.4.6. The systems must 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 headspace 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/sediment and waste samples, the purging device shall be capable of accepting a vial large enough to contain a 5.0 g soil/sediment or waste 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 shall also be capable of introducing at least 5.0 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 the identification and quantitation of the analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1;
- The analytical results generated using the trap meet the initial calibration, ICV, and CCV technical acceptance criteria listed in the analytical method and the CRQLs listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1; and

- The trap must be capable of accepting up to 1000 ng of each analyte listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, 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 shall demonstrate that the trap meets the criteria listed in Section 6.3.4.6 and document its use in the 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 shall 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 that there are no contaminants that interfere with the volatile analysis when using the alternate trap; and
- From initial calibration, ICV, and CCV standards analyzed using the trap specified in Section 6.3.4.5.

6.3.4.6.2.3 Based on the Contractor-generated data described above, the Contractor shall 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, 9.4.5, and 9.5.5;
- 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 - Target Analyte List and Contract Required Quantitation Limits, Table 1.

6.3.4.6.2.4 The documentation shall be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional CLP COR.

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

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

6.3.4.9 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 specified in Section 6.3.4.5 shall not be heated higher than 180°C and the remaining sections shall not exceed 220°C during bake-out mode. Manufacturer recommendations shall be followed regarding maximum temperatures for other types of sorbent traps.

6.4 Data Systems/Data Storage

A computer system must be interfaced to the MS to allow 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 (2017 release or later), Wiley (2014 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 shall provide all standards to be used with the contract. These standards shall be used only after they have been certified according to the procedure in Exhibit D – Introduction to Analytical Methods, Section 11.0. The Contractor shall be able to verify that the standards are certified. Manufacturer’s certificates of analysis shall 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 a contaminant or 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.

7.1.1.3 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 shall be demonstrated to be free of contaminants that interfere with the measurement of the purgeable analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1.

7.1.3 Sodium Bisulfate Solution – 2.0 g of ACS reagent grade or equivalent sodium bisulfate is dissolved for every 5.0 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 prepared in methanol from pure standard materials or purchased as certified pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated, unless acceptability of the standard can be documented (Section 7.2.3.6).

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 - Target Analyte List and Contract Required Quantitation Limits, Table 1) in methanol. Prepare fresh calibration standard solution(s) once a week for the room-temperature gases (i.e., chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride, bromomethane, and chloroethane), once a month for the room-temperature solids or liquids, or sooner if the solution has degraded or evaporated, unless acceptability of the standard can be documented (Section 7.2.3.6). Standards of reactive analytes such as styrene may need to be prepared more frequently.

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 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 following levels: all non-ketone target analytes and their associated DMCs (see Exhibit D – Low/Med VOA, Table 3) at 5.0, 10, 50, 100, and 200 micrograms/Liter (µg/L); all ketones and their associated DMCs (see Exhibit D – Low/Med VOA, Table 3) 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/sediment samples), then the concentrations of the standards shall be reduced in half to ensure the same on-column amount of each analyte.

7.2.2.1.3 Calibration standards shall 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: 50 µg/L for non-ketones and 100 µg/L for ketones. Use the same source of target analytes (i.e., same manufacturer lot) for CCVs as were used for the preparation of initial calibration standards.

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/sediment samples), then the concentrations of the standards shall 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 Initial Calibration Verification Solution

Prepare the working ICV standard solution containing all of the purgeable target analytes (Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1) from an alternate source or a different lot than used for the initial calibration (ICAL) standard analyses in methanol. Prepare a fresh standard solution every month, or sooner if the solution has degraded or evaporated.

7.2.2.2.1 The ICV standard shall be at a concentration equivalent to the mid-level calibration standards: 50 µg/L for non-ketones and 100 µg/L for ketones.

7.2.2.2.2 The ICV standard shall be prepared by the same procedures as the CCVs.

7.2.2.3 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 shall be analyzed using the same GC and MS analytical conditions as are used for the calibration analysis.

7.2.2.4 Deuterated Monitoring Compound Spiking Solution

7.2.2.4.1 Prepare a DMC spiking solution in methanol (or in deuterated methanol) containing the compounds listed in Exhibit D – Low/Med VOA, Table 3.

7.2.2.4.2 DMCs are to be added to each sample blank, and matrix spike/matrix spike duplicate (MS/MSD), as well as to the ICAL standards, ICV standard, and CCV standards. Use the same source of DMCs (i.e., same manufacturer and lot) for the preparation of calibration standards, initial and continuing calibration verification standards, samples, blanks, and MS/MSDs.

7.2.2.4.3 For samples, blanks, and MS/MSDs, add a sufficient amount of the DMC spiking solution to each sample to result in 0.25 µg for each non-ketone DMC and 0.50 µg for each ketone DMC.

7.2.2.4.4 For ICAL, ICV, and CCV standards, add a sufficient amount 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), Section 7.2.2.2.1 (ICV), and Section 7.2.2.1.4 (CCV).

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

NOTE: The DMC spiking solution may be combined with the internal standard spiking solution (Section 7.2.2.6) and/or BFB solution (Section 7.2.2.3).

7.2.2.5 Matrix Spiking Solution

If MS/MSD analysis is requested at the time of scheduling, prepare a matrix spiking solution containing all target analytes in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, with the same working standard used for the preparation of CCVs (Section 7.2.2.1.4), in methanol, at a concentration of 12.5 µg/mL for each non-ketone analyte and 25 µg/mL for each ketone analyte in methanol. Add a sufficient amount of the matrix spiking solution to 5 mL of the sample assigned to be the MS/MSD to result in the addition of 0.25 µg of each non-ketone and 0.50 µg of each ketone spiked target analyte, resulting in concentrations of 50 µg/L and 100 µg/L, respectively. Prepare fresh matrix spiking solution monthly, or sooner if the solution has degraded or evaporated.

7.2.2.6 Internal Standard Spiking Solution

Use the same source of internal standard spiking solution as was used to prepare the initial calibration (i.e., same manufacturer and lot) for all calibration check standards, samples, and QC samples. This solution shall contain 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 in methanol. Add a sufficient amount of the internal standard spiking solution to each 5 mL sample, including samples, 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 standard solutions in PTFE-sealed screw-cap bottles with zero headspace at -10°C to -20°C. Other containers designed to minimize volatile loss may be used, including Certan® vials and/or with Mininert® valves, particularly for maximizing the shelf life of the room-temperature gases.

7.2.3.2 Aqueous standards may be stored for up to 24 hours if held in glass vials with PTFE-lined screw-caps with zero headspace at ≤6°C, but not frozen. When using an autosampler, the standards may be kept up to 12 hours in the autosampler of the P/T device.

7.2.3.3 Store premixed certified solutions according to the manufacturer’s documented holding time and storage temperature recommendations. Once the seal is compromised (e.g., ampule is opened), stock solutions for most compounds shall be used to prepare working standards and for the preparation of calibration

standards within the shelf life of the working standards (Section 7.2.2.1). Stock solutions must be replaced in the same timeframe as the working standards unless acceptability of the standard can be documented to meet the SOW criteria (Section 7.2.3.6.1).

7.2.3.4 Protect all standards from light.

7.2.3.5 Purgeable standards shall be stored separately from other standards, samples, sample extracts, 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 compounds to solidify. This means that, at a minimum, the standards shall be brought to room temperature prior to use, checked for losses, and checked to verify that all components have remained in solution.

7.2.3.6.1 Working standards shall be monitored frequently by comparison to the initial calibration. Fresh standards shall be prepared if the opening CCV criteria can no longer be met (Section 9.5.5) and the shelf life of the working standard is exceeded (Section 7.2.2.1). Standards shall be replaced upon expiration of the shelf life unless acceptability of the standard can be documented to meet all applicable SOW criteria, either by comparison to a compliant initial calibration generated from standards prepared within the shelf life of the working standards or by comparison to a freshly prepared standard. Standards of reactive analytes such as 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 Aqueous/Water Samples

8.1.1.1 Aqueous/water samples should be collected in glass containers that have 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 be filled in such a manner that no air bubbles were entrained to create a headspace in the vial.

8.1.1.3 The samples should be preserved to a pH ≤2 at the time of collection. Contact the Sample Management Office (SMO) immediately if aqueous/water samples are received without documentation of preservation.

8.1.1.4 The Contractor should receive at least three vials per field sample.

NOTE: If MS/MSD analysis is required for a given sample, four additional vials per sample should be sent by the field samplers. Contact SMO if insufficient sample has been provided for the MS/MSD analysis.

8.1.2 Soil/Sediment and Waste Samples

8.1.2.1 The Contractor should receive a minimum of three replicates per soil/sediment and waste field sample either in pre-weighed, prepared closed-system P/T glass vials; pre-weighed glass vials; or field core sampling/storage containers (e.g., EnCore™ or equivalent). Two of these replicates shall be used for low-level analysis, and the third for medium-level analysis if required. An additional soil sample in a sealed glass vial with minimum headspace should also be provided to the Contractor for percent solids determination. If the correct number of vials or containers has not been sent by the field samplers, the Contractor shall immediately contact SMO.

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

8.1.2.2 Samples that have been collected for low-level analysis (in pre-weighed, prepared closed-system P/T glass vials or pre-weighed glass vials) may arrive in 5 mL of water with no added preservatives or preserved with sodium bisulfate. Samples that have been collected for medium-level analysis (in pre-weighed, prepared closed-system P/T glass vials or pre-weighed glass vials) may arrive with no added preservatives or preserved nominally with 5.0 mL of methanol. All samples should arrive accompanied by field documentation of the tared weight of the labeled vial. Immediately after samples are received by the laboratory, the sample vials shall be inspected to verify that there was no preservative loss during transport. If the volume of preservative in the vial does not appear to be correct, if the vial appears to be dry, or if field documentation is not provided, the Contractor shall immediately notify SMO, who will contact the EPA Region for direction.

8.1.2.3 The Contractor shall weigh unpreserved and preserved samples received in pre-weighed, prepared closed-system P/T glass vials or pre-weighed glass vials immediately upon receipt, and record the weight. Ensure that the vials are free of external dirt and moisture prior to weighing.

8.1.2.4 All samples collected in field core sampling/storage containers (e.g., EnCore™ or equivalent) will arrive unpreserved. The Contractor shall transfer the content of each container to a pre-weighed, 40 mL, screw-cap, PTFE-lined, septum-sealed glass vial, immediately upon receipt, and record the date and time of the transfer. Proceed to Section 10.2.2.2 for additional processing instructions regarding this sample type.

8.2 Sample and Sample Extract Storage

8.2.1 Sample Storage

8.2.1.1 Unpreserved, unfrozen soil/sediment and waste samples received in pre-weighed, prepared closed-system P/T glass vials or pre-weighed glass vials, and those transferred from field core sampling/storage containers (e.g., EnCore™ or equivalent) to prepared closed-system P/T glass vials, shall be protected from light and either stored at ≤6°C, but not frozen, and analyzed within 24 hours of sample receipt, or placed on their side and stored at <-7°C until time of analysis if they do not contain visible moisture. If the samples appear to be moist and there is insufficient space above the soil portion in the vials, the Contractor shall contact SMO immediately for instructions to avoid possible damage of the vials during storage in the freezer. Inert sand storage blanks shall be stored at <-7°C with the samples until all samples are analyzed. Unused sample aliquots shall be stored at <-7°C until 60 days after the delivery of a complete, reconciled data package to the EPA. After 60 days, the samples shall be disposed of in a manner that complies with all applicable regulations.

8.2.1.2 Sodium bisulfate-preserved soil/sediment and waste samples received in pre-weighed, prepared closed-system P/T glass vials or pre-weighed glass vials and aqueous/water samples shall be protected from light and stored at ≤6°C, but not frozen, until time of analysis in a refrigerator used only for storage of volatile samples, in an atmosphere demonstrated to be free of all potential contaminants. Inert sand and aqueous storage blanks shall be stored at ≤6°C, but not frozen, with the samples until all samples are analyzed. Unused sample aliquots shall be stored at ≤6°C, but not frozen, until 60 days after the delivery of a complete, reconciled data package to the EPA. After 60 days, the samples shall be disposed of in a manner that complies with all applicable regulations.

8.2.1.3 Methanol-preserved soil/sediment and waste samples received in pre-weighed, prepared closed-system P/T glass vials or pre-weighed glass vials shall be protected from light and stored at ≤6°C, but not frozen, until time of analysis in a refrigerator used only for storage of volatile samples, in an atmosphere demonstrated to be free of all potential contaminants. Aqueous storage blanks shall be stored at ≤6°C, but not frozen, with the samples until all samples are analyzed. Unused sample aliquots shall be stored at ≤6°C, but not frozen, until 60 days after the delivery of a complete, reconciled data package to the EPA.

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

8.2.2 Sample Extract Storage

8.2.2.1 Sample extracts for medium-level analysis shall be protected from light and stored at <-7°C until 365 days after the delivery of a complete, reconciled data package to the EPA.

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

8.3 Contract Required Holding Times

Analysis of preserved aqueous/water, soil/sediment, and waste samples shall be completed within 10 days of the Validated Time of Sample Receipt (VTSR). Analysis of unpreserved, unfrozen soil/sediment and waste samples, including those received in field core sampling/storage containers (e.g., EnCore™ or equivalent), shall be completed within 24 hours of the VTSR. Analysis of unpreserved, frozen soil/sediment and waste samples, including those received in field core sampling/storage containers (e.g., EnCore™ or equivalent), shall be completed within 10 days of the VTSR. The holding time for the analysis of TCLP or SPLP filtrates and leachates is 7 days from the completion of the TCLP or SPLP filtration and extraction procedures.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Initial Instrument Set-up

9.1.1 Purge-and-Trap

9.1.1.1 The recommended Purge-and-Trap (P/T) analytical conditions are provided in Exhibit D – Low/Med VOA, Table 5. 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 addition of 1.0 µL of these standard solutions, either in an automated manner or manually, will be allowed only if the final concentration of the following standards in the 5 mL aqueous/water samples and blanks can be met: 50 µg/L for internal standards; the concentrations listed in Section 7.2.2.1.2 for DMCs in the initial calibration; the concentrations listed in Section 7.2.2.2.1 for DMCs in the ICV; 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 a 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. Follow manufacturer’s recommendations for conditioning alternative traps. The trap may be vented to the analytical column during daily conditioning; however, the column shall be conditioned through the temperature program prior to the analysis of samples and blanks.

9.1.1.5 For low-level soil/sediment and waste 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 shall be used for the analysis of all standards, samples, and blanks.

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

NOTE: In certain situations, a heated purge may be used for aqueous/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 - Target Analyte List and Contract Required Quantitation Limits, Table 1;
- The analytical results generated when using the moisture reduction/water management system meet the initial calibration, initial calibration verification, and continuing calibration verification technical acceptance criteria listed in the analytical method and the CRQLs listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1;
- 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 Exhibit D – Low/Med VOA, Table 6. The conditions are recommended unless otherwise noted. GC conditions must achieve all performance criteria required for initial calibration, initial calibration verification, and continuing calibration verification.

9.1.2.2 Optimize the GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions shall 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 and m,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 shall be used, and the initial temperature must be ≤10°C.

9.1.3 Mass Spectrometer

The recommended MS analytical conditions are provided in Exhibit D – Low/Med VOA, Table 7.

9.2 Instrument Performance Check

9.2.1 Summary of GC/MS Instrument Performance Check

9.2.1.1 The GC/MS system shall 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 7.2.2.3).

9.2.1.2 Prior to the analysis of any samples, including MS/MSDs, blanks, or calibration standards, the Contractor shall 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 shall be injected once at the beginning of each initial calibration sequence during which samples, blanks, or standards are to be analyzed.

9.2.3 Procedure for GC/MS Instrument Performance Check

The analysis of the instrument performance check solution shall be performed using one of the following options:

- As an injection of up to 50 ng of BFB into the GC/MS.
- By adding a sufficient amount of BFB solution (Section 7.2.2.3) to 5.0 mL of reagent water to result in a ≤10 µg/L concentration of BFB.
- By adding a 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 instrument performance check shall be performed at the frequency described in Section 9.2.2.

9.2.4.2 The abundance criteria listed in Exhibit D – Low/Med VOA, Table 2, must be met for a ≤50 ng injection of BFB. The mass spectrum of BFB shall 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 within 20 scans 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 shall 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 BFB technical acceptance criteria have not been met will require reanalysis.

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 shall 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 shall 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, 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 (Section 9.3.5), the ICV, method blank, samples, and closing CCV may be analyzed. It is not necessary to analyze another opening 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 shall be allowed to warm to ambient temperature before analysis.

9.3.3.3 Add the specified amount of the internal standards (Section 7.2.2.6) to each of the five aqueous calibration standard solutions (Section 7.2.2.1.2) containing the DMCs (Section 7.2.2.4.1) 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

9.3.3.4 Separate initial calibrations shall be performed for aqueous/water, low-level soil/sediment, and low-level waste samples if different purge conditions are used (unheated purge vs. heated purge, differences in purge flow pathways). Extracts of medium-level soil/sediment and waste samples may be analyzed using the calibrations of aqueous/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 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. The primary characteristic ions used for quantitation are listed in Exhibit D – Low/Med VOA, Table 8. 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 Exhibit D – Low/Med VOA, Table 9.

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

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 Equation 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations, 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 the m,p-xylene isomers respectively.

9.3.4.3 The Mean RRF ($\overline{RRF}$) must be calculated for all target analytes and DMCs according to Equation 1 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 1 and 2 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards shall 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 the instrument.

9.3.5.3 The chromatographic resolution shall be verified with the mid-point concentration of the initial calibration 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.

9.3.5.4 The required minimum RRF value for each target analyte and DMC at each calibration concentration is listed in Exhibit D – Low/Med VOA, Table 4. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet this criteria. Up to two different target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D – Low/Med VOA, Table 4, but these compounds must still meet the minimum RRF requirement of 0.010 for the ICAL to be considered acceptable.

9.3.5.5 The required maximum %RSD value for each target analyte and DMC is listed in Exhibit D – Low/Med VOA, Table 4. Target analytes and DMCs with a maximum %RSD requirement of 40.0% must meet the criteria. Up to two target analytes and DMCs with maximum %RSD requirements of less than 40.0% may fail to meet the %RSD criteria listed in Exhibit D – Low/Med VOA, Table 4, but these compounds must still meet the maximum %RSD requirement of 40.0% for the ICAL to be considered acceptable.

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 or nitrogen) 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 analytes, 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.

9.4 Initial Calibration Verification

9.4.1 Summary of Initial 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 shall be routinely checked by analyzing an ICV (containing all the purgeable target analytes from an alternate source or a different lot than used for the ICAL standards, and the DMCs and internal standards from the same source or lot as used for the ICAL standards) to ensure that the instrument is calibrated accurately.

9.4.2 Frequency of Initial Calibration Verification

The calibration for each GC/MS system used for analysis shall be verified with an ICV at the frequency of one per ICAL analytical sequence. The ICV shall be analyzed following the last ICAL standard analysis and prior to any method blank, sample, or applicable CCV analysis.

Injection #	**Material Injected**
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 - ICV	ICV
8th - Blanks, samples, MS/MSDs	Blanks, samples, and MS/MSDs
9th - Subsequent Samples	

9.4.3 Procedure for Initial Calibration Verification

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

9.4.3.2 Add the specified amount of the internal standards (Section 7.2.2.6) and DMCs (Section 7.2.2.4) to the ICV (Section 7.2.2.2) at the time of purge. Analyze the ICV Standard according to Section 10.0.

9.4.3.3 For low-level soil/sediment and waste samples, the ICV standard shall be analyzed 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 Initial Calibration Verification

9.4.4.1 Calculate an RRF for each target analyte and DMC using Equation 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.4.2 Calculate the Percent Difference (%D) between the ICV RRF_c and the preceding initial calibration $\overline{RRF}_i$ for each purgeable target analyte and DMC using Equation 17 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

9.4.5.1 The concentration of the low/medium volatile organic target analytes and DMCs in the ICV shall 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 ICV shall 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 ICV, the required minimum RRF value for each target analyte and DMC is listed in Exhibit D – Low/Med VOA, Table 4. Target analytes and DMCs with a minimum RRF requirement of 0.010 may not fail the criteria. Up to two target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D – Low/Med VOA, Table 4, but these compounds must still meet the minimum RRF requirement of 0.010 for the ICV to be considered acceptable.

9.4.5.3 For an ICV, the required maximum %D value for each target analyte and DMC is listed in Exhibit D – Low/Med VOA, Table 4. Target analytes and DMCs with a maximum %D requirement of 40.0% must meet the criteria. Up to two target analytes and DMCs with maximum %D requirements of less than 40.0% may fail to meet the maximum %D criteria listed in Exhibit D – Low/Med VOA, Table 4, but these compounds must still meet the maximum %RSD requirement of 40.0% for the ICV to be considered acceptable.

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

9.4.6 Corrective Action for Initial Calibration Verification

9.4.6.1 If the ICV analyzed immediately after the ICAL sequence does not meet the technical acceptance criteria, and a subsequent reanalysis of the ICV meets the technical acceptance criteria, proceed with the blank and sample analyses.

9.4.6.2 If the ICV analyzed immediately after the ICAL sequence does not meet the technical acceptance criteria, and a subsequent reanalysis does not meet the technical acceptance criteria, recalibrate the GC/MS instrument according to Section 9.3. All sample and required blank analyses must be associated to a compliant ICV analysis following the associated ICAL.

9.5 Continuing Calibration Verification

9.5.1 Summary of Continuing Calibration Verification

Prior to the analysis of samples and required blanks, and after instrument performance check, initial calibration, and ICV technical acceptance criteria have been met, each GC/MS system shall 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 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 9.5.2.3).

9.5.2 Frequency of Continuing Calibration Verification

9.5.2.1 The calibration for each GC/MS system used for analysis shall be verified at the beginning and end of every 12-hour period of operation. The 12-hour period begins with the injection of an opening CCV solution that meets the technical acceptance criteria in Section 9.5.5, followed by the injection of the blank and samples, provided that the opening CCV meets the technical acceptance criteria in Section 9.5.5. The 12-hour period ends with the injection of a closing CCV. If the closing CCV does not meet the technical acceptance criteria for an opening CCV (Section 9.5.5), an injection of an opening CCV is required to start the next 12-hour period.

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

9.5.2.3 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 in Section 9.5.5 are met for an opening CCV.

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 - ICV	ICV
	8th - Blanks, samples, MS/MSDs	Blanks, samples, and MS/MSDs
	9th – Subsequent Samples	
End 12 hr	Closing CCV (meeting Closing CCV criteria, but not Opening CCV)	CS3 – Closing CCV
New 12 hr	1st Analysis Opening CCV	CS3 - Opening CCV Blank, MS/MSD, subsequent samples Subsequent Samples Last Sample

Time	Injection #	Material Injected
End 12 hr	Closing CCV (meeting Closing CCV criteria, but not Opening CCV)	CS3 – Closing CCV
New 12 hr	1st 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 beginning of next 12 hr	Closing CCV (meeting Opening CCV criteria)	CS3 – Closing CCV meeting Opening CCV criteria 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 criteria

9.5.3 Procedure for Continuing Calibration Verification

9.5.3.1 All standard/spiking solutions shall be allowed to reach ambient temperature before analysis.

9.5.3.2 Add the internal standards (Section 7.2.2.6) and DMCs (Section 7.2.2.4) to the CCV (Section 7.2.2.1.4) at the time of purge. Analyze the CCV standard according to Section 10.0.

9.5.3.3 For low-level soil/sediment 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.

9.5.4 Calculations for Continuing Calibration Verification

9.5.4.1 Calculate an RRF for each target analyte and DMC using Equation 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.4.2 Calculate the %D between the CCV RRF_C and the most recent initial calibration $\overline{RRF}_i$ for each purgeable target analyte and DMC using Equation 17 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The concentration of the low/medium volatile organic target analytes and DMCs in the opening and closing CCV shall 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 shall be analyzed at the frequency described in Section 9.5.2, on a GC/MS system meeting the BFB (Section 9.2.4), the initial calibration (Section 9.3.5), and the ICV (Section 9.4.5) technical acceptance criteria.

9.5.5.2 For an opening or closing CCV, the required minimum RRF value for each target analyte and DMC is listed in Exhibit D – Low/Med VOA, Table 4. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet this criteria (the minimum RRF for DMC trans-1,3-dichloropropene-d_4 is advisory). Up to two target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D – Low/Med VOA, Table 4, but these compounds must still meet the minimum RRF requirements of 0.010 for the CCV to be considered acceptable.

9.5.5.3 For an opening CCV, the required maximum %D value for each target analyte and DMC is listed in Exhibit D – Low/Med VOA, Table 4. Target analytes and DMCs with a maximum %D requirement of 40.0% must pass this criteria. Up to two target analytes and DMCs with maximum %D requirements of less than 40.0% may fail to meet the maximum %D criteria listed in Exhibit D – Low/Med VOA, Table 4, but these compounds must still meet the maximum %RSD requirement of 40.0% for the opening CCV to be considered acceptable.

9.5.5.4 For a closing CCV, the required maximum %D value for each target analyte and DMC is listed in Exhibit D – Low/Med VOA, Table 4. Up to two target analytes and DMCs may fail to meet the maximum %D criteria listed in Exhibit D – Low/Med VOA, Table 4.

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

9.5.6 Corrective Action for Continuing Calibration Verification

9.5.6.1 If the opening CCV technical acceptance criteria are not met, reanalyze the opening CCV. If the reanalyzed opening CCV criteria still are not met, recalibrate the GC/MS instrument and take other corrective actions 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 shall be reanalyzed.

9.5.6.2 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.

9.5.6.3 All samples and required blanks are to be associated with an opening CCV meeting the technical acceptance criteria or reanalyses are required.

9.5.6.4 The corrective action for sample reanalysis is not required when noncompliant analytes or associated DMCs, in the opening or closing CCVs bracketing a dilution or a reanalysis, are not the same analytes or associated DMCs for which the dilution analysis or reanalysis was intended.

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 shall be employed for the analysis of samples as were used for calibration. All samples, required blanks, and standard/spiking solutions shall be allowed to warm to ambient temperature before analysis. TCLP leachate samples including the requested MS/MSD leachates shall be diluted with reagent water by a dilution factor of 10 prior to analysis.

NOTE: Contact SMO if sample vials have entrained bubbles ≥6 mm in size resulting in headspace.

10.2 Procedure for Sample Analysis

10.2.1 Aqueous/Water Samples

10.2.1.1 If time remains in the 12-hour period (as described in Section 9.3.2.2), samples may be analyzed without analysis of an opening CCV standard.

10.2.1.2 If the autosampler can automatically sample the appropriate volume, then Sections 10.2.1.3 - 10.2.1.5 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 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 5.0 mL.

10.2.1.4 This process of taking an aliquot of the sample from the container 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 shall 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 shall be performed within 24 hours. Care shall also be taken to prevent air from leaking into the syringe.

10.2.1.5 Add a sufficient amount of the DMC spiking solution (Section 7.2.2.4.1) and a sufficient amount of internal standard spiking solution (Section 7.2.2.6) 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 aqueous/water sample shall be determined. The purpose of the pH determination is to ensure that all VOA samples were acidified in the field. Record the pH of each sample and report these data in the Electronic Data Deliverable (EDD). 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 the 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 shall 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 and Waste Samples

10.2.2.1 If samples are received in field core sampling/storage containers (e.g., EnCore™ or equivalent), proceed to Section 10.2.2.2. Samples received in closed-system P/T glass vials or glass vials shall be analyzed according to Section 10.2.2.9, unless screening analysis indicates that the samples are to 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 - Target Analyte List and Contract Required Quantitation Limits, Table 1, then the samples shall 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 shall 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 or through scheduling notification. After receiving this specific request, the laboratory is to confirm the request through SMO.

10.2.2.2 The following steps (Sections 10.2.2.3 - 10.2.2.6) apply to the preparation of vials used for the analysis of low-level soil/sediment and waste samples by the closed-system P/T equipment described in this method.

NOTE: There should be three field core sampling/storage containers (e.g., EnCore™ or equivalent) 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 10.2.2.7 - 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 <-7°C if not analyzed within 24 hours of VTSR. 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 employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stirring bar is omitted.

10.2.2.4 Seal the vial with the screw-cap and septum seal. If 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/MSDs, and internal standard spiking solutions shall only be added to the vial after the sample has been added to the vial. The spiking solutions shall 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 prepared sample vial. This sample transfer shall 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 shall be worn when handling the sample vial since the vial has been tared. Record the date and time of sample transfer to the 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 P/T glass vials or glass 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 samples shall be allowed to reach ambient temperature and should have a total water volume (reagent water and preservative if applicable) of 10 mL:

For samples transferred from field core sampling/storage containers (e.g., EnCore™ or equivalent), add 10 mL of reagent water to the vial.

For samples received in closed-system P/T glass vials or glass vials, add 5.0 mL of reagent water to the vial.

10.2.2.10 Without disturbing the hermetic seal on the sample vial, add sufficient amount of reagent water (Section 10.2.2.9), sufficient amount of the internal standard spiking solution (Section 7.2.2.6), and sufficient amount of the DMC spiking solution (Section 7.2.2.4). All samples, including MS/MSDs, standards, and blanks, within an SDG shall have the same amount of reagent water added. Do not increase/change the amount of DMC and internal standard solution added.

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.

10.2.2.11 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 appropriate desorb temperature without a flow of desorption gas. Start the flow of desorption gas. Begin the temperature program of the GC and start the 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 and Waste Samples

10.2.3.1 The medium-level soil/sediment method requires extracting the soil/sediment or waste sample with methanol. An aliquot of the methanol extract is introduced, either automatically or manually, into a specified amount of reagent water (Section 10.2.3.6) containing the internal standard (Section 7.2.2.6) and DMC (Section 7.2.2.4) spiking solutions. 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. The instrument performance check, initial calibration, ICV, and CCV for aqueous/water samples shall be used for analyses of medium-level soil/sediment and waste 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 P/T glass vials or glass 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. 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 shall be performed rapidly to avoid loss of volatile organics. These steps shall 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 shall 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 aliquot 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 shall be used so that the combined volume of methanol extract and clean methanol totals 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 reagent 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 7.2.2.4) and sufficient amount of internal standard spiking solution (Section 7.2.2.6). 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 the 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 a screening analysis be performed prior to sample analysis to determine estimated analyte concentration and matrix problems.

NOTE 1: If the Contractor has evidence or highly suspects, because of sample color or other physical properties, that a sample may contain high concentrations of target analytes or non-target compounds, 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 shall be considered (see Section 11.2.1.4).

10.2.4.2 Aqueous/water 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 Contractor shall 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/sediment and waste 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 (Section 10.2.3).

10.2.4.4 The Dilution Factor (DF) selected shall keep the concentrations of the volatile target analytes that required dilution within the upper half of the initial calibration range.

10.2.4.5 All dilutions shall 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 shall be performed without delay.

10.2.4.6 Aqueous/water samples may be diluted in a volumetric flask or in a 25 mL Luer-Lok syringe.

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 reagent water to the flask.

10.2.4.7.3 For aqueous/water samples, inject the proper aliquot from a 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 Contact SMO for direction prior to using the last aqueous sample replicate vial.

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 - Target Analyte List and Contract Required Quantitation Limits, Table 1, 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 Relative Retention Time (RRT) unit window established from the 12-hour calibration standard; and
- Correspondence of the sample component and calibration standard analyte mass spectra.

11.1.1.2 Establish correspondence between the RRT of the analyte in the continuing calibration standard and the sample component 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 shall 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 mid-point CS3 ICAL 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 shall 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 on the Contractor’s GC/MS (as opposed to library spectra) are required. Once obtained, these standard spectra shall be used for identification purposes, only if the Contractor’s GC/MS meets the daily instrument performance requirements for BFB. These standard spectra shall 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 the ions specified in the section 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%), barring the influence of interference.

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 shall 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 (2017 release or later), Wiley (2014 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 11.1.1, or that are not DMCs, internal standards, or semivolatile target analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 2, 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. 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. 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, identification (as generated by the library search program) of those receiving a library search match of 85% or higher shall be considered a "probable match". The compound shall 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 shall 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 Contractor 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 Contractor 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 shall 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: 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 percent match at or above 85% at two different RTs, the compound having the highest percent match shall be reported as a TIC and the other one shall be reported as unknown. If both TICs have the same percent match for the same compound, one of the TICs shall be reported as unknown. Such justifications shall 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 (Exhibit D – Low/Med VOA, Table 9). The EICP area of primary characteristic ions of analytes listed in Exhibit D – Low/Med VOA, Table 8, are used for quantitation.

11.2.1.2 For aqueous/water, low-level soil/sediment, and waste samples, and medium-level soil/sediment and waste samples, xylenes are to be reported as "m,p-xylene" and "o-xylene". Because m- and p-xylene isomers coelute on the available capillary columns, special attention shall 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 an RRF from the initial calibration 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 shall perform a manual quantitation or integration. Manual integrations are performed by manually choosing the area of the quantitation ion of the compound to integrate, either by drawing the baseline by hand or by choosing times for setting baselines in the software. 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 shall 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 instrument operator shall 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 instrument operator shall also mark each integrated area with the letter "m" on the quantitation report. All edits and manual integrations shall be verified by a second person, who shall also initial the change(s). In addition, graphical display(s) of the EICPs of the quantitation ion displaying the original

integration(s) shall be included in the raw data, in addition to the graphical display(s) of the EICPs of the quantitation ion displaying the manual integration(s). Chromatographic baselines shall be clearly visible in the original and edited EICPs at the same scaling. This applies to all target analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1.

11.2.2 Target Analyte Calculations

Identified target analytes shall be quantitated by the internal standard method using Equation 4A, 5A, or 5B in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. The internal standard used shall be that which is assigned in Exhibit D – Low/Med VOA, Table 9. The $\overline{RRF}$ from the initial calibration standard is used to calculate the concentration in the sample.

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 4A, 5A, and 5B in Exhibit G - List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 $\overline{RRF}$ of 1.0 is to be assumed.

11.2.4 Contract Required Quantitation Limit Calculations

Calculate the aqueous/water and soil/sediment or waste sample adjusted CRQL using Equation 6A, 7A, or 7B in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.5 Deuterated Monitoring Compound Recoveries

11.2.5.1 Calculate the amount of each DMC in samples and blanks using Equation 22A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.5.2 Calculate the recovery of each DMC in all samples and blanks using Equation 22 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.3 Technical Acceptance Criteria for Sample Analysis

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

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

11.3.3 The sample must have an associated method blank.

11.3.4 Up to three DMCs per sample may fail to meet the recovery limits listed in Exhibit D – Low/Med VOA, Table 10. For TCLP leachate sample analysis, up to two DMCs associated to the TCLP analytes may fail to meet the recovery limits listed in Exhibit D – Low/Med VOA, Table 10.

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 or in the ICV standard analysis in the analytical sequence.

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 or in the ICV standard analysis in the analytical sequence.

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 shall 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 shall either:

- Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank shall 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 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 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 analysis 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.

11.4.2 Corrective actions for failure to meet technical acceptance criteria for instrument performance checks, initial calibration, ICV, CCV, and method blanks shall 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 After completing the corrective actions outlined above, the Contractor shall proceed to reanalyzing the sample as appropriate.

11.4.4.1 If the DMC recoveries do not meet the acceptance criteria in the initial (undiluted) sample analysis, reanalyze the sample.

- If the DMC recoveries do not meet the acceptance criteria in the reanalyzed sample, then submit the data from both analyses. Distinguish between the initial analysis and the reanalysis in all deliverables using the suffixes in Appendix B – Codes for Labeling Data.

11.4.4.2 If the internal standard compound responses do not meet the acceptance criteria in the initial (undiluted) sample analysis, reanalyze the sample.

- If the internal standard compound responses are still noncompliant after the reanalysis, the Contractor shall dilute the original sample by an appropriate dilution factor (nominally 2-10 for aqueous/waters or medium-level analysis for solids) and reanalyze the sample. If the internal standard compound responses are acceptable in the subsequent diluted analysis, submit the data from the reanalysis and the diluted analysis.
- No further corrective action is required if the internal standard compound responses do not meet the acceptance criteria in the reanalysis and in the subsequent diluted analysis. Submit the data from the reanalysis and the diluted analysis. Distinguish between the initial analysis, reanalysis, and the diluted analysis in all deliverables using the suffixes in Appendix B – Codes for Labeling Data.

NOTE: If the internal standard and/or DMC performance issue appears to be caused by the presence of high levels of target analytes (i.e., above the highest calibration standard), the Contractor may analyze the sample at an appropriate dilution factor (nominally 2-10 for aqueous/water or medium-level analysis for solids) after the initial analysis that did not meet the criteria (without first reanalyzing the undiluted sample). However, if no target analytes are measured in the upper half of the calibration range in the diluted aqueous/water sample or the medium-level sample for solids, the Contractor must proceed with reanalysis of the undiluted sample.

11.4.4.3 If the DMC recoveries in Section 11.4.4.1, the internal standard compound responses in Section 11.4.4.2, or both the DMC recoveries and the internal standard compound responses meet the acceptance criteria in the reanalyzed sample, it indicates that the problem was within the Contractor’s control. Therefore, only submit the data from the reanalysis.

11.4.4.4 If the DMC recoveries or internal standard compound responses in a sample used for the MS/MSD analyses are outside the acceptance criteria, the Contractor shall proceed to the following corrective actions:

- If the DMC recoveries in the sample used for the MS/MSD analyses are outside the acceptance criteria, then the sample shall be reanalyzed (Section 11.4.4.1) only if the DMC recoveries meet the acceptance criteria in both the MS and MSD analyses.
- If the internal standard compound responses do not meet the acceptance criteria, the Contractor shall proceed to the reanalysis in Section 11.4.4.2 only if the internal standard compound responses meet the technical acceptance criteria in both the MS and MSD analyses.

11.4.5 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 shall 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 shall 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 do not meet maximum carryover criteria shall be reanalyzed. If this analyte in the diluted analysis is detected within the calibration range, then no further corrective action is required.

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

11.4.6.1 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.

11.4.6.2 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 analysis were outside the acceptance criteria, then it shall be reanalyzed only if the internal standard RTs were within the acceptance criteria in both the MS/MSD analyses.
- If the internal standard compound 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 compound 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 Appendix B – Codes for Labeling Data.

11.4.7 If the required corrective actions for sample reanalysis and/or dilution cannot be performed due to insufficient sample volume, the Contractor shall contact SMO.

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 aqueous/water samples or a purified solid matrix for soil/sediment and waste samples) spiked with internal standard spiking solution (Section 7.2.2.6) and DMC spiking solution (Section 7.2.2.4), 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 method blank. The purpose of the method blank is to determine the levels of contamination associated with the processing and analysis of the samples.

NOTE 1: For soil/sediment and waste 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 shall be analyzed at least once during every 12-hour period on each GC/MS system used for volatile analysis (see Section 9.3.2.2 for the definition of the 12-hour period).

12.1.2.2.2 The method blank shall be analyzed after the ICV or opening CCV (see sample sequence in Section 9.4.2 or 9.5.2) if samples are analyzed before the 12-hour period expires. The method blank shall be analyzed after the opening CCV and before any samples, including MS/MSDs, dilutions, or storage blanks are analyzed. A method blank shall be analyzed in each 12-hour period in which samples, including MS/MSDs, dilutions, and storage blanks from an SDG are analyzed.

12.1.2.3 Procedure for Method Blank

12.1.2.3.1 For aqueous/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/sediment and waste 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/sediment and waste 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 shall 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 method blanks shall be prepared and analyzed on a GC/MS system meeting the BFB, initial calibration, ICV, 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 method blank must be within the acceptance windows in Exhibit D – Low/Med VOA, Table 10. If a DMC %D does not meet the acceptance criteria in the associated opening CCV, the same DMC is also permitted to fail to meet the recovery criteria in the method blank, up to the maximum specified in Section 9.5.5.3 (e.g., DMC %R limits of 40-130% will become 40-140%).

12.1.2.5.3 The internal standards in the method blank must meet the sample technical acceptance criteria listed in Sections 11.3.5 - 11.3.6.

12.1.2.5.4 The concentration of each target analyte in the method blank must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, 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 in the aqueous method blank must be less than 5.0 µg/L or 5.0 µg/kg in the solid method blank.

12.1.2.5.6 All method blanks shall 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 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 shall 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 gas chromatograms be eliminated.

12.1.2.6.3 Any method blank that fails to meet the technical acceptance criteria shall 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.

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 7.2.2.6) and DMC spiking solution (Section 7.2.2.4), and carried through the entire analytical procedure. Instrument blanks are analyzed after a sample/dilution that contains a target analyte at levels

that exceed the calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample analysis.

12.1.3.2 Frequency of Instrument Blank

Samples may contain target analytes at levels exceeding the calibration. An instrument blank shall 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. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system shall 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 12.1.2.5.3) shall 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 in Section 11.3.8.

12.1.3.3.2 Under no circumstances shall 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 shall be analyzed on a GC/MS system meeting the BFB, initial calibration, ICV, and CCV technical acceptance criteria and at the frequency described in Section 12.1.3.2.

12.1.3.5.2 The internal standards in the instrument blank must meet the sample acceptance criteria listed in Sections 11.3.5 - 11.3.6.

12.1.3.5.3 The concentration of each target analyte in the instrument blank must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1. The concentration of each non-target compound in the instrument blank must be less than four times the nominal CRQL (20 µg/L) of the target analyte.

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 any instrument blank exceeds 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 shall be investigated and appropriate corrective measures shall be taken and documented before further sample analysis proceeds.

12.1.3.6.2 If an instrument blank fails to meet the technical acceptance criteria described in Section 12.1.3.5, the samples analyzed immediately after the instrument blank must be reanalyzed and meet the technical acceptance criteria in Section 11.4.1.

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 aqueous/water and inert sand for preserved soil/sediment samples stored at ≤6°C, or inert sand for unpreserved soil/sediment and waste 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 shall be analyzed per sample medium type (one for solid including soil/sediment/waste matrix samples and one for aqueous including aqueous/water matrix samples), storage condition, and SDG 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 1: If the SDG contains samples stored at ≤6°C, but not frozen, and samples stored at <-7°C, two storage blanks will be prepared, one for each condition.

NOTE 2: When aqueous/water and preserved soil/sediment samples are stored together, one aqueous storage blank and one inert sand storage blank shall be prepared.

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 shall 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 shall be analyzed on a GC/MS system meeting the BFB, initial calibration, ICV, and CCV technical acceptance criteria and at the frequency described in Section 12.1.4.2.

12.1.4.5.2 The storage blank shall 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 Exhibit D – Low/Med VOA, Table 10.

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 or in the ICV standard analysis in the analytical sequence.

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 or in the ICV standard analysis in the analytical sequence.

12.1.4.5.6 The concentration of each target analyte in the storage blank must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 1, except for methylene chloride, acetone, and 2-butanone, which must be less than 2 times the respective CRQL. The concentration of each TIC in the storage blank must be less than the nominal value of either 5.0 µg/L or 5.0 µg/kg.

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 shall be investigated and appropriate corrective measures shall be taken and documented before further sample 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 shall be reported. If upon reanalysis, the storage blank still does not meet the criteria, the problem occurred during storage. The Contractor shall address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences of contamination.

NOTE: A copy of the storage blank data shall 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 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 analysis shall be performed for each group of 20 field samples of a similar matrix in an SDG. An MS/MSD shall be analyzed for each sample matrix (water/soil/waste) and each level (low/medium).

12.2.2.2 Samples identified as field blanks or PE samples shall not be used for MS/MSD analysis.

12.2.2.3 When a Contractor receives only PE sample(s), no MS/MSD analysis 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 aqueous/water samples, add a sufficient amount (e.g., 20 µL) of the matrix spiking solution to result in addition of 0.25 µg of each non-ketone target analyte and 0.50 µg of each ketone target analyte (Section 7.2.2.5). 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 or waste samples, add a sufficient amount (e.g., 20 µL) of the matrix spiking solution to result in addition of 0.25 µg of each non-ketone target analyte and 0.5 µg of each ketone target analyte (Section 7.2.2.5). Add 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 or waste samples, add 5.0 mL of methanol to each of the two aliquots of the soil/sediment or waste sample selected for spiking. Prepare and analyze the MS/MSD sample according to Section 10.2.3, adding a sufficient amount of the matrix spiking solution (Section 7.2.2.5) to result in addition of 0.25 µg of the non-ketone target analytes and 0.50 µg of the ketone target analytes to the diluted extract. The matrix spiking solution shall be added at the same point as the DMC spiking solution (See Section 10.2.3.6). 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.

12.2.3.3.2 Process the samples according to Section 10.2.3. This results in a 2,500 µg/kg concentration of each non-ketone matrix spike analyte and a 5,000 µg/kg concentration of each ketone matrix spike analyte when added to a 5 g sample. Add a 100 µL aliquot of this extract to 4.9 mL of reagent water for purging (per Sections 10.2.3.6 and 10.2.3.7).

12.2.3.4 MS/MSD samples shall 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 shall 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 4A, 5A, and 5B in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations). Calculate the recovery of each Matrix Spike analyte using Equation 23 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD sample using Equation 24A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Matrix Spike Duplicate

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

12.2.5.2 The MS/MSD sample shall be analyzed within the contract required holding time.

12.2.5.3 The internal standards in the MS/MSD samples must meet the sample acceptance criteria listed in Sections 11.3.5 - 11.3.6.

12.2.5.4 The percent recovery and RPD limits for the spiking analytes listed in Exhibit D – Low/Med VOA, Table 11, are advisory. No further action by the Contractor is required when these criteria are not met. There are no specified limits for the spiking analytes that are not listed in Exhibit D – Low/Med VOA, Table 11; however, all target analyte concentrations and recoveries shall be reported.

12.2.6 Corrective Action for Matrix Spike and Matrix Spike Duplicate

Any MS/MSD sample that does not meet the technical acceptance criteria in Sections 12.2.5.1 and 12.2.5.3 shall be reanalyzed.

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 MDL for each volatile target analyte shall be determined for each instrument under the same conditions used for analysis (i.e., analytical system configuration, as well as type and dimension of GC column), prior to the start of contract analyses and verified annually thereafter. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for aqueous/water, low-level soil/sediment, and medium-level soil/sediment samples. The MDL determined for soil/sediment samples shall be used for waste samples.). An MDL study shall also be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis. Major instrument maintenance includes, but is not limited to: replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), or 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.

12.4.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.

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

12.4.1.3 The MDLs for TCLP and SPLP are not required to be determined or reported.

12.4.1.4 The delivery requirements for the MDL values are specified in Exhibit B – Reporting and Deliverables Requirements, Table 1.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Method 524.4, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 1, May 2013.

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 5030C, Purge-and-Trap for Aqueous Samples, Revision 3, May 2003.

16.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 5035A, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, July 2002.

16.4 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 8260D, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, June 2018.

16.5 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

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-	Trichloroethene	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
Propane, 1,2,3-trichloro-	1,2,3-Trichloropropane	Glycerol trichlorohydrin	96-18-4
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-trimethyl-	1,2,4-Trimethylbenzene	Asymmetrical trimethylbenzene	95-63-6
Benzene, 1,3,5-trimethyl-	1,3,5-Trimethylbenzene	sym-Trimethylbenzene	108-67-8
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

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-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
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
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% of mass 95
175	5.0 - 9.0% of mass 174
176	95.0 - 105% of mass 174
177	5.0 - 10% of mass 176

NOTE: All ion abundances shall 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. Criteria based on EPA method 524.4.

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 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 1,2,3-Trichloropropane	Trichloroethene Toluene Tetrachloroethene Ethylbenzene o-Xylene m,p-Xylene Styrene Isopropylbenzene 1,2,4-Trimethylbenzene 1,3,5-Trimethylbenzene
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 CALIBRATION, INITIAL CALIBRATION VERIFICATION, AND CONTINUING CALIBRATION VERIFICATION FOR VOLATILE ORGANIC COMPOUNDS

Analyte	ICAL/ICV Minimum RRF	Opening/ Closing CCV Minimum RRF	ICAL Maximum %RSD	ICV/Opening CCV Maximum %D[1]	Closing CCV Maximum %D
Dichlorodifluoromethane	0.010	0.010	30.0	±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	±40.0	±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	±25.0	±50.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	0.010	25.0	±30.0	±50.0
Acetone	0.010	0.010	40.0	±40.0	±50.0
Carbon disulfide	0.010	0.010	30.0	±25.0	±50.0
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	±50.0
Methyl tert-butyl ether	0.100	0.100	30.0	±25.0	±50.0
1,1-Dichloroethane	0.300	0.300	20.0	±20.0	±50.0
cis-1,2-Dichloroethene	0.200	0.200	20.0	±20.0	±50.0
2-Butanone	0.010	0.010	40.0	±40.0	±50.0
Bromochloromethane	0.050	0.050	20.0	±20.0	±50.0
Chloroform	0.300	0.300	20.0	±20.0	±50.0
1,1,1-Trichloroethane	0.050	0.050	20.0	±25.0	±50.0
Cyclohexane	0.010	0.010	30.0	±25.0	±50.0
Carbon tetrachloride	0.100	0.100	20.0	±25.0	±50.0
Benzene	0.200	0.200	20.0	±20.0	±50.0
1,2-Dichloroethane	0.070	0.070	20.0	±20.0	±50.0
Trichloroethene	0.100	0.100	20.0	±20.0	±50.0
Methylcyclohexane	0.050	0.050	40.0	±30.0	±50.0
1,2-Dichloropropane	0.100	0.100	20.0	±20.0	±50.0
Bromodichloromethane	0.010	0.010	20.0	±20.0	±50.0
cis-1,3-Dichloropropene	0.300	0.300	30.0	±20.0	±50.0
4-Methyl-2-pentanone	0.010	0.010	30.0	±30.0	±50.0
Toluene	0.400	0.400	20.0	±20.0	±50.0
trans-1,3-Dichloropropene	0.200	0.200	30.0	±20.0	±50.0
1,1,2-Trichloroethane	0.100	0.100	20.0	±20.0	±50.0
Tetrachloroethene	0.100	0.100	20.0	±25.0	±50.0
2-Hexanone	0.010	0.010	40.0	±40.0	±50.0

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

Analyte	ICAL/ICV Minimum RRF	Opening/ Closing CCV Minimum RRF	ICAL Maximum %RSD	ICV/Opening CCV Maximum %D[1]	Closing CCV Maximum %D
Dibromochloromethane	0.010	0.010	20.0	±20.0	±50.0
1,2-Dibromoethane	0.010	0.010	20.0	±20.0	±50.0
Chlorobenzene	0.400	0.400	20.0	±20.0	±50.0
Ethylbenzene	0.400	0.400	30.0	±25.0	±50.0
m,p-Xylene	0.200	0.200	30.0	±25.0	±50.0
o-Xylene	0.200	0.200	30.0	±25.0	±50.0
Styrene	0.200	0.200	30.0	±25.0	±50.0
Bromoform	0.010	0.010	30.0	±25.0	±50.0
Isopropylbenzene	0.400	0.400	30.0	±25.0	±50.0
1,2,3-Trichloropropane	0.010	0.010	30.0	±30.0	±50.0
1,1,2,2-Tetrachloroethane	0.010	0.010	20.0	±25.0	±50.0
1,3-Dichlorobenzene	0.500	0.500	20.0	±20.0	±50.0
1,4-Dichlorobenzene	0.600	0.600	20.0	±20.0	±50.0
1,2-Dichlorobenzene	0.600	0.600	20.0	±20.0	±50.0
1,2-Dibromo-3-chloropropane	0.010	0.010	30.0	±30.0	±50.0
1,2,4-Trimethylbenzene	0.400	0.400	30.0	±30.0	±50.0
1,3,5-Trimethylbenzene	0.400	0.400	30.0	±30.0	±50.0
1,2,4-Trichlorobenzene	0.400	0.400	30.0	±30.0	±50.0
1,2,3-Trichlorobenzene	0.300	0. 300	30.0	±30.0	±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	40.0	±30.0	±50.0
1,1-Dichloroethene-d_2	0.050	0.050	20.0	±25.0	±50.0
2-Butanone-d_5	0.010	0.010	40.0	±40.0	±50.0
Chloroform-d	0.300	0.300	20.0	±20.0	±50.0
1,2-Dichloroethane-d_4	0.060	0.060	20.0	±25.0	±50.0
Benzene-d_6	0.300	0.300	20.0	±20.0	±50.0
1,2-Dichloropropane-d_6	0.200	0.200	20.0	±20.0	±50.0
Toluene-d_8	0.300	0.300	20.0	±20.0	±50.0
trans-1,3-Dichloropropene-d_4*	0.010	0.010	30.0	±20.0	±50.0
2-Hexanone-d_5	0.010	0.010	40.0	±40.0	±50.0

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

Analyte	ICAL/ICV Minimum RRF	Opening/ Closing CCV Minimum RRF	ICAL Maximum %RSD	ICV/Opening CCV Maximum %D[1]	Closing CCV Maximum %D
1,1,2,2-Tetrachloroethane-d_2	0.200	0.200	20.0	±25.0	±50.0
1,2-Dichlorobenzene-d_4	0.400	0.400	20.0	±20.0	±50.0

*NOTE: The minRRF for trans-1,3-dichloropropene-d_4 is advisory for the opening and closing continuing calibration verification standards.

[1] If a closing CCV is acting as an opening CCV, all target analytes and DMCs shall 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 aqueous/water or medium-level soil/sediment and waste samples (required for medium-level soil/sediment samples; suggested for aqueous/water samples). 40°C for low-level soil/sediment and waste 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: The desorb conditions and trap reconditioning conditions in this table are intended for the trap recommended in Section 6.3.4.5 and a GC with a jet separator. Alternative traps and GCs with split/splitless inlets may require different desorb conditions. For alternative traps and GC setups, use the trap manufacturer’s and/or GC instrument manufacturer’s recommended conditions.

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 – Target Analyte List and Contract Required Quantitation Limits, Table 1, 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

*m/z 96 is used for quantitation of 1,1-Dichloroethene since the secondary ions at m/z 61 and 63 are also present in the spectrum of the associated DMC 1,1-Dichloroethene-d_2.

**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)**
o-Xylene	106	91
Styrene	104	78
Bromoform	173	175,254
Isopropylbenzene	105	120,77
1,2,3-Trichloropropane	75	110,77
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-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
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	65	100,102
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 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	Isopropylbenzene
1,1-Dichloroethene	1,2-Dichloropropane	1,2,4-Trimethylbenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	Bromodichloromethane	1,3,5-Trimethylbenzene
Acetone	cis-1,3-Dichloropropene	1,2,4-Trichlorobenzene
Carbon disulfide	4-Methyl-2-pentanone	1,2,3-Trichlorobenzene
Methyl acetate	Toluene	1,2-Dichlorobenzene-d_4 (DMC)
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)	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 Aqueous/Water Samples	Percent Recovery for Soil/Sediment and Waste 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 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 Aqueous/Water	RPD Aqueous/Water	Percent Recovery Soil/Sediment and Waste	RPD Soil/Sediment and Waste
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

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EXHIBIT D

SEMIVOLATILE ORGANIC COMPOUNDS ANALYSIS

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Exhibit D – Semivolatile Organic Compounds Analysis

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Exhibit D – Semivolatile Organic Compounds Analysis

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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze aqueous/water, leachate derived from the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP), soil/sediment, and waste samples from hazardous waste sites to determine the presence and concentration of the semivolatile organic analytes (SVOA) listed in the Target Analyte List (TAL) for semivolatiles in Exhibit C – Target Analyte List and Contract Required Quantitation Limits. The method, based on the U.S. Environmental Protection Agency (EPA) 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 the appropriate cleanup procedure and GC/Mass Spectrometry (MS) analysis to determine the SVOAs present in the sample.

1.2 If requested, sample extracts are 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 only PAHs and PCP analysis is requested by the full scan method, only these target analytes are quantitated and reported along with the associated Deuterated Monitoring Compounds (DMCs) and internal standards for calibration standards, method blanks, and samples. If a SIM analysis is requested, a full scan analysis using the low-level method is performed first. The SIM analysis is not required for a sample when the full scan analysis meets the requirements in Section 10.1.

1.3 If requested, sample extracts are analyzed for the target analyte 1,4-Dioxane only, by GC/MS, using the full scan method and the SIM technique. The aqueous/water samples without visible solids are extracted by Solid-Phase Extraction (SPE) and the extracts are analyzed for the target analyte 1,4-Dioxane only, for both the full scan analysis and the required SIM analysis. The same soil/sediment sample extracts from the full scan analysis are to be used for the required SIM analysis for the target analyte 1,4-Dioxane only, and the DMC is not required to be re-evaluated for the SIM analysis. The SIM analysis is not required for the target analyte 1,4-Dioxane when it is detected at or above the sample-adjusted Contract Required Quantitation Limit (CRQL) in the full scan analysis. Analysis of the full suite of target analytes, as listed in Exhibit C, includes 1,4-Dioxane.

1.4 A laboratory control sample (LCS) containing all target analytes is required for analyses by the full scan method and SIM technique. The LCS spiking analyte recoveries are used to verify that the laboratory can perform the analysis in a clean matrix. For the requested matrix spike and matrix spike duplicate (MS/MSD) samples, the spiking solution is to include all target analytes for the analyses by the full scan method and SIM technique. The spiking analyte recoveries will be collected and potentially used in the future to improve program performance.

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

- 3,3'-dichlorobenzidine and 4-chloroaniline can be subject to oxidative losses during solvent concentration.

- Depending on matrix characteristics, some organic base target analytes may not recovery well using the aqueous sample preparation procedures described in this exhibit. These basic analytes are pyridine, 4-chloroaniline, 3,3'-dichlorobenzidine, and 3-nitroaniline (to a lesser extent).
- DMCs 4-chloroaniline-d_4 associated to the basic target analytes and pyridine-d_5 associated to the TCLP target analyte pyrindine may not recovery well by the aqueous sample preparation procedures.
- DMC 4-chloroaniline-d_4 is added to all aqueous extractions with basic target analytes in them, and pyridine-d_5 is added for aqueous extractions when pyridine is reported as a target analyte. These DMCs provide sample-specific performance/recovery information that is relevant to the native analogs of these DMCs, and they may also provide an indication of recovery of other basic target analytes.
- 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, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline and the heavier PAHs are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

2.0 SUMMARY OF METHOD

2.1 Aqueous/Water, TCLP, or SPLP Leachate

A suitable sample aliquot volume [minimum 1 Liter (L)] is mixed with DMCs, acidified to pH 2.0 with exception of the TCLP/SPLP leachate samples, and extracted using a continuous liquid-liquid extractor. Separatory funnel extraction is NOT permitted. Aqueous samples without visible solids are extracted by SPE for the requested 1,4-Dioxane only analysis by the full scan method and the required SIM technique. Aqueous samples unsuitable for extraction by SPE are extracted by continuous liquid-liquid extraction. The extract is dried with anhydrous sodium sulfate (or an equivalent drying agent such as Hydromatrix™), concentrated, and subjected to Gel Permeation Chromatography (GPC) cleanup. GPC cleanup is required when higher molecular weight compounds are present that interfere with the analyses of target analytes; GPC cleanup is optional for all other circumstances. The extract is then analyzed by GC/MS for extractable organics. Aqueous or water-miscible TCLP leachate samples are diluted with water by a factor of 10 prior to extraction. If 1,4-Dioxane is requested to be reported in addition to the other SVOA target analytes, laboratories have the option to calibrate and measure 1,4-Dioxane in the same injection as the other semivolatile target analytes with chromatographic conditions optimized appropriately or from separate injections with chromatographic conditions optimized for only 1,4-Dioxane or for the other SVOA target analytes, respectively.

2.2 Soil/Sediment

2.2.1 Low-Level Soil/Sediment

A suitable sample aliquot amount [minimum 30 grams (g)] is spiked with DMCs, 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, pressurized fluid extraction, or microwave extraction. The extract is concentrated, subjected to GPC cleanup, and analyzed by GC/MS for extractable organics. If 1,4-Dioxane is requested to be reported in addition to the other SVOA target analytes, laboratories have the option to calibrate and measure 1,4-Dioxane in the same injection as the other semivolatile target analytes with chromatographic conditions optimized appropriately or from separate injections with chromatographic conditions optimized for only 1,4-Dioxane or for the other SVOA target analytes, respectively.

The Contractor shall determine whether a soil/sediment sample should be analyzed by the low-level or medium-level method, using an EPA-approved screening procedure described in Section 10.1.2.1 or an in-house laboratory screening procedure.

2.2.2 Medium-Level Soil/Sediment

Approximately 1 g aliquot of sample is spiked with DMCs, mixed with anhydrous sodium sulfate (or Hydromatrix™), and extracted with methylene chloride. The methylene chloride extract is subjected to GPC cleanup, prior to analysis by GC/MS for extractable organics.

2.3 Wipes

Not applicable to this method.

2.4 Waste

Solid waste samples are extracted and analyzed using the soil/sediment methods in Section 2.2. Alternatively, oily waste samples are prepared using a waste dilution procedure. A 0.20 g aliquot of the oily waste sample is spiked with a DMC spiking solution, mixed with anhydrous sodium sulfate (or Hydromatrix™), and diluted to a volume of 10 milliliters (mL) with methylene chloride. The extract is then cleaned up by GPC (optional, based on sample characteristics) and analyzed. Waste samples that have undergone TCLP/SPLP procedures and are aqueous or water-miscible are extracted and analyzed using the aqueous/water methods described in Section 2.1.

2.5 Non-Target Compounds

Non-target semivolatile compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the National Institute of Standards and Technology (NIST) (2017 release or later), Wiley (2014 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 – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 shall 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 on the nature of the site being sampled.

5.0 SAFETY

See Section 12.0 of Exhibit D – Introduction to 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. Do not store mineral acids such as sulfuric acid or nitric acid with organic chemicals, including acetic acid.

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, demonstration of equivalent performance that meets 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.

All instruments, balances, heating, and measuring equipment and devices shall be uniquely identified and labeled to allow traceability to any corresponding records of use.

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 The balance calibration shall be checked with known masses once per each day of use. This verification shall consist 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 shall be checked on a monthly basis using NIST-traceable known reference masses (Class

'0' or Class '1') as defined by ASTM E617-13 or equivalent (e.g., earlier Class 'S' defined masses). All balances shall be checked at least once annually by a certified technician. The reference masses used by the Contractor shall 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, Tabletop (optional).

6.1.3.1 Centrifuge Tube - 12-15 mL with 19 millimeter (mm) ground-glass joint (optional).

6.1.4 Desiccator - Containing a desiccant indicator compound.

6.1.5 Erlenmeyer Flasks - 250 mL.

6.1.6 Graduated Cylinders Class A – Glass with 100 mL, 500 mL, and 1 L capacity.

6.1.7 Sieve – No. 18 mesh with nominal pore size of 1 mm with a collection pan and cover.

6.1.8 Magnetic Stirring Bars - 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 Pasteur Pipettes – Regular and packed with glass wool plugs.

6.1.13 Pipettes (Calibrated) - Glass volumetric, l.0 mL or 2.0 mL. Manufacturer's instructions shall be followed for the calibration and maintenance of adjustable pipettes.

6.1.14 Spatulas - Stainless steel or PTFE.

6.1.15 Syringes – 10 microliters (µL), 25 µL, 100 µL, and 1000 µL.

6.1.16 Vials and Caps - 10 mL (optional), with screw-cap and PTFE or aluminum foil liner, or other suitable extract storage vessel; autosampler vial with 2 mL capacity for GC autosampler.

6.1.17 Volumetric Flasks, Class A – 5.0, 10, 20, 50, 100, 250, and 500 mL.

6.1.18 Weigh Dishes – Disposable aluminum weighing pans or porcelain crucibles with factory (glazed) or engraved identification.

6.2 Glassware/Extraction/Cleanup Equipment

6.2.1 Continuous Liquid-Liquid Extractor - Equipped with PTFE or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.2.2 Solid-Phase Extraction System

6.2.2.1 Extraction cartridge for 1,4-Dioxane for use with a sample volume ≤500 mL but >100 mL (Option 1) – 6 mL Polypropylene tubes packed with 2 g coconut charcoal (80-120 mesh, approximately 150 µm).

6.2.2.2 Vacuum Extraction Manifold – Equipped with flow/vacuum control.

6.2.2.3 Sample Delivery System – Equipped with transfer tube system and sample reservoir(s) attached to the cartridge, or 60 mL collection tubes.

6.2.3 Sonication Equipment

6.2.3.1 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 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 shall 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.

6.2.3.2 Sonabox Acoustic Enclosure (or equivalent) - For use with disrupter to decrease noise level.

6.2.3.3 Vacuum Filtration Apparatus

6.2.3.3.1 Buchner Funnel.

6.2.3.3.2 Filter Paper - Whatman No. 42 or equivalent.

6.2.4 Automated Soxhlet Extraction System - With temperature-controlled electric heating mantles or oil bath. Silicone oil shall not be used because it destroys the rubber parts. The apparatus shall be used in a hood.

6.2.4.1 Cellulose or Glass Extraction Thimble, 26 mm ID x 60 mm.

6.2.4.2 Glass Extraction Cups.

6.2.4.3 Thimble Adapters.

6.2.4.4 Viton Seals.

6.2.5 Soxhlet Extraction, Manual

6.2.5.1 Allihn Condenser.

6.2.5.2 Cellulose or Glass Extraction Thimble, 35 mm x 90 mm.

6.2.5.3 Soxhlet Extractor body, 40 mm ID.

6.2.5.4 Round bottom flask, 500 mL.

6.2.6 Pressurized Fluid Extraction Device

6.2.6.1 Dionex Accelerated Solvent Extractor (ASE-350) or equivalent with appropriately sized extraction cells. Currently, 100 mL cells that will accommodate greater than 30 g samples are available. 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.

6.2.6.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.2.7 Microwave Extraction System

6.2.7.1 Laboratory Microwave – Capable of maintaining sample temperature within ±2.5°C and adjusting power within 2 seconds.

6.2.7.2 Microwave Extraction Vessels – Capable of accepting 30 g of sample plus drying agent, transparent to microwave energy, and capable of withstanding temperatures of 200°C minimum and pressures of 200 psi minimum. Vessels with 20 g capacity may be used, with appropriate adjustments in extract volumes to ensure CRQLs are met.

6.2.7.3 The laboratory shall maintain separate vessels for digestion of metals and solvent extraction of organics and follow manufacturer's instructions with regard to monitoring and maintaining sample temperature during microwave extraction.

6.2.8 Kuderna-Danish (K-D) Apparatus

6.2.8.1 Concentrator Tubes - 10 mL and 15 mL, graduated. Ground-glass stoppers are to be used to prevent evaporation of extracts.

6.2.8.2 Drying Column - 400 mm 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).

6.2.8.3 Evaporative Flasks - 500 mL.

6.2.8.4 Silicon Carbide Boiling Chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes solvent-rinsed with methylene chloride.

6.2.8.5 Snyder Column - Three-ball macro.

6.2.8.6 Snyder Column - Two-ball micro.

6.2.8.7 Water Bath - Heated, with concentric ring cover, capable of temperature control. The bath shall be used in a hood.

6.2.9 Nitrogen Evaporation Device - Equipped with a water bath that can be maintained at 30-40°C. To prevent the release of solvent fumes into the laboratory, the nitrogen evaporator device shall be used in a hood.

6.2.10 Gel Permeation Chromatography Cleanup System

6.2.10.1 GPC 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, shall meet the calibration requirements of Section 10.3.3.

NOTE: GPC cleanup is required for all soil/sediment and waste sample extracts, and for aqueous/water sample extracts containing higher molecular weight contaminants that interfere with the analyses of the target analytes.

6.2.10.2 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.

6.2.10.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect the inlet side of the analytical column.

6.2.10.4 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.

6.2.10.5 UV Detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

6.2.10.6 Strip Chart Recorder - Recording integrator or laboratory data system.

6.2.10.7 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.

6.2.10.8 Viscometer.

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. The instrument shall be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room. Adsorbents used in trapping systems must be replaced according to the product replacement periods recommended by the manufacturer, and at a minimum annually. 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: A fused-silica capillary column coated with a slightly polar silicone with 20-60 meter (m) column length, 0.18-0.32 mm inner diameter, and 0.2-0.5 or 1 micrometer (µm) film thickness, is generally recommended for this procedure. Examples include but are not limited to: 30 m DB-5 (J&W Scientific); Rtx®-5, Rtx®-5MS (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. Appropriate columns shall be selected to achieve the optimum chromatographic performance for the separate analyses of 1,4-Dioxane and the rest of the target analytes. Alternative GC column phases or dimensions may also be acceptable for use provided all specified performance criteria can be met on a routine basis. Regardless of the column used, the operating conditions of the system must be demonstrated by the laboratory to meet the performance criteria described in Section 6.3.2.1, and this demonstration must be made available for review upon request by the EPA. A description of the column used for analysis shall be provided in the SDG Narrative. Packed GC 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 – Target Analyte List and Contract Required Quantitation Limits, Table 2.
- The analytical results generated using the column meet the initial calibration, initial calibration verification (ICV), and continuing calibration verification (CCV) technical acceptance criteria (Sections 9.3.5, 9.4.5, and 9.5.5) and the CRQLs listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2.
- The column must be capable of accepting up to at least 16 times the low point standard concentration for each analyte listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2, without becoming overloaded.
- The column provides equal or better resolution of the analytes listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2, than the columns listed in Section 6.3.2.

6.3.2.1.1 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 shall maintain documentation verifying 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 EPA 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, ICV, 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, 9.4.5, and 9.5.5;
- 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 - Target Analyte List and Contract Required Quantitation Limits, Table 2.

6.3.2.1.4 The documentation shall be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional CLP Contracting Officer's Representative (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 Exhibit D – SVOA, Table 2, 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. Adsorbents used in trapping systems must be replaced according to the product replacement periods recommended by the manufacturer, and at a minimum annually.

6.3.4 Gas Chromatograph/Mass Spectrometer Interface

Any GC/MS interface may be used that gives acceptable sensitivity at the CRQLs. However, direct insertion of the GC column into the MS ion source is the recommended interface.

6.4 Data Systems/Data Storage

A computer system must be interfaced to the MS to allow 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 (2017 release or later), Wiley (2014 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 shall provide all standards to be used with the contract. These standards shall be used only after they have been certified according to the procedure in Exhibit D – Introduction to Analytical Methods, Section 11.0. The Contractor shall be able to verify that the standards are certified. Manufacturer's certificates of analysis shall 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 a contaminant or 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 shall be extracted with methylene chloride and analyzed by GC/MS to demonstrate that it is free of interferences before use or shall 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, ethyl acetate, methanol, methylene chloride, cyclohexane, iso-octane, 2-propanol, and toluene - pesticide residue analysis grade or equivalent. Methanol shall be purge-and-trap grade only for SPE.

7.1.6 Sulfuric acid, concentrated, 95-98% (specific gravity 1.84).

7.1.7 Glycerol.

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 prepared in methylene chloride from pure standard materials, or purchased as certified pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated, unless acceptability of the standard can be documented (Section 7.2.3.6).

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 nanograms/microliter (ng/µL) for each target analyte and associated DMCs (see Exhibit D – SVOA, Table 3, and Exhibit D – SVOA, Table 4), except 1,4-Dioxane and the target analytes in Section 7.2.2.1.2. For 1,4-Dioxane and 1,4-Dioxane-d_8, the calibration standard concentrations shall be at 2.0, 4.0, 8.0, 16, and 32 ng/µL. 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 – Target Analyte List and Contract Required Quantitation Limits, Table 2, 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 shall be 2.0, 4.0, 8.0, and 16 ng/µL).

7.2.2.1.2 Each calibration standard shall 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. The following target analytes and DMCs [pyridine (TCLP only), benzaldehyde, phenol, bis(2-chloroethyl) ether, 2-methylphenol, 2,2'-oxybis(1—chloropropane), acetophenone, 4-chloroaniline, caprolactam, hexachlorocyclopentadiene, atrazine, carbazole, 3,3'-dichlorobenzidine, di-n-octylphthalate, 2,4-dinitrophenol, PCP, 4-methylphenol, 4,6-dinitro-2-methylphenol, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, pyridine-d_5 (TCLP only), phenol-d_5, bis(2-chloroethyl) ether-d_8, 4-methylphenol-d_8, 4-chloroaniline-d_4, 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 µL or 2.0 µL injections of all calibration standards may be used. All samples analyzed shall have been injected at the same volume (1.0 µL or 2.0 µL) as the calibration standard.

7.2.2.1.2.1 For the analysis of PAHs and PCP only, by the full scan method, 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 7.2.2.5.

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 (except PCP) and the associated DMCs (see Exhibit D – SVOA, Table 10). For PCP, the five-point initial calibration standards are to be prepared at 0.20, 0.40, 0.80, 1.6, and 3.2 ng/µL.

NOTE: 1.0 µL or 2.0 µL injections of all calibration standards may be used. All samples analyzed shall have been injected at the same volume (1.0 µL or 2.0 µL) as the calibration standard.

7.2.2.1.2.3 If the optional analysis of 1,4-Dioxane using the SIM technique is to be performed, prepare calibration standards in methylene chloride 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 0.20, 0.40, 0.80, 1.6, and 3.2 ng/µL for the target analyte and the associated DMC (see Exhibit D – SVOA, Table 9).

NOTE: 1.0 µL or 2.0 µL injections of all calibration standards may be used. All samples analyzed shall have been injected at the same volume (1.0 µL or 2.0 µL) as the calibration standard.

7.2.2.1.3 The CCV standard shall be at or near the mid-point concentration level of the calibration standards. If the optional analysis of PAHs and PCP or 1,4-Dioxane by SIM is to be performed, the CCV standard shall be at or near the mid-point calibration level, normally 0.40 ng/µL (0.80 ng/µL for PCP and 1,4-Dioxane). Use the same source of target analytes (i.e., same manufacturer lot) for CCVs as were used for the preparation of initial calibration standards.

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 – Target Analyte List and Contract Required Quantitation Limits, Table 3, 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 shall 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 Initial Calibration Verification Solution

Prepare the working ICV standard solution containing all of the target analytes (Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 2) from an alternate source or a different lot than used for the initial calibration (ICAL) standard analyses in methylene chloride. Prepare a fresh standard solution every six months, or sooner if the solution has degraded or evaporated.

7.2.2.2.1 The ICV standard shall be at a concentration equivalent to the mid-level calibration standards. If the optional analysis of PAHs and PCP or 1,4-Dioxane by SIM is to be performed, the ICV standard shall be at or near the mid-point calibration level, normally 0.40 ng/µL (0.80 ng/µL for PCP and 1,4-Dioxane).

7.2.2.2.2 The ICV standard shall be prepared by the same procedures as the CCVs. The ICV solution shall be stored and/or replaced in accordance with Section 7.2.3.

7.2.2.3 Instrument Performance Check Solution

Prepare the instrument performance check 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 shall be analyzed using the same GC and MS analytical conditions as are used for the calibration analysis. The DFTPP solutions are to be prepared such that ≤50 ng of DFTPP is injected into the GC/MS system.

7.2.2.4 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 shall 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)	0.50
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.

7.2.2.5 Deuterated Monitoring Compound Spiking Solution

7.2.2.5.1 Prepare a DMC spiking solution containing the following full scan level DMC analytes in methanol at the concentrations given below. If SVOA SIM analysis is requested, the SVOA SIM DMCs below may be prepared in a separate solution or in the same solution as the full scan DMCs. If analysis of only 1,4-Dioxane is requested, a separate DMC spiking solution containing only 1,4-Dioxane-d_8 may be prepared in methanol at the concentration specified below (except 1,4-Dioxane-d_8 for SIM analysis, which is prepared as a separate spiking solution):

Full Scan DMCs	Concentration µg/mL
1,4-Dioxane-d_8	16
Pyridine-d_5	80
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-2-methylphenol-d_2	80
Anthracene-d_{10}	80
Pyrene-d_{10}	80
Benzo(a)pyrene-d_{12}	80
SIM DMCs	
Fluoranthene-d_{10}	0.80
2-Methylnaphthalene-d_{10}	0.80
1,4-Dioxane-d_8	1.6

NOTE: 1,4-Dioxane-d_8 is added to the SIM calibration standards and separately extracted QC samples.

7.2.2.5.2 The DMC spiking solution is added (500 µL) prior to sample processing to all samples, blanks, requested MS/MSDs, LCSs, and calibration solutions. Use the same source of DMCs (i.e., same manufacturer lot) for all calibration standards, field samples, and QC samples, and add the same DMC spiking solution to samples, blanks, MS/MSDs, and LCSs in the same preparation batch.

7.2.2.5.3 The SIM DMCs for PAH and PCP analysis (Exhibit D – SVOA, Table 4) can be added as part of the DMC spiking solution or added separately to all standards, samples, and blanks that require SIM analysis.

7.2.2.5.4 DMC 1,4-Dioxane-d_8 shall be added at the full scan level to all standards, samples, and blanks that require 1,4-Dioxane only full scan analysis. DMC 1,4-Dioxane-d_8 is not evaluated for the SIM sample analysis if the same extract is used for both the full scan and SIM analyses. Add the DMC at the SIM level to the standards and separately extracted QC samples and blanks for the 1,4-Dioxane only SIM analysis.

7.2.2.5.5 The DMC spiking solution shall be prepared every 12 months, or sooner if the solution has degraded or concentrated.

7.2.2.6 Matrix Spiking Solution

7.2.2.6.1 If MS/MSD analysis is requested at the time of scheduling, prepare a matrix spiking solution containing all the target analytes in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 2, from the same source (i.e., same manufacturer lot) used for the preparation of initial calibration standards and CCVs (Section 7.2.2.1), in methanol, at a concentration of 80 µg/mL for each analyte.

7.2.2.6.2 For the analysis of PAHs and PCP only, the Contractor has the option of using the matrix spiking solution in Section 7.2.2.6.1 or preparing a matrix spiking solution containing all PAH and PCP target analytes in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 2, from the same source used for the preparation of initial calibration standards and CCVs (Section 7.2.2.1), in methanol, at a concentration of 80 µg/mL for each PAH analyte and 160 µg/mL for PCP for full scan analysis, or at a concentration of 0.80 µg/mL for each PAH analyte and 1.6 µg/mL for PCP for SIM analysis.

7.2.2.6.3 If MS/MSD analysis for 1,4-Dioxane only is requested at the time of scheduling, prepare a matrix spiking solution that contains the target analyte, from the same source (i.e., same manufacturer lot) used for the preparation of initial calibration standards and CCVs (Section 7.2.2.1), in methanol, at a concentration of 32 µg/mL for full scan analysis and a concentration of 4.0 µg/mL for SIM analysis.

7.2.2.7 Internal Standard Spiking Solution

7.2.2.7.1 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 aqueous/water, low-level, or medium-level soil/sediment or waste sample extracts for the initial analysis, dilution, and reanalysis, or to the re-extracts if applicable, to result in a 20 ng/µL concentration of each internal standard.

7.2.2.7.2 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 aqueous/water or low-level soil/sediment and waste sample extracts for the initial analysis, dilution, and reanalysis, or to the re-extracts if applicable, 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 an internal standard when performing PAHs and PCP SIM analysis.

7.2.2.7.3 For the SIM analysis of 1,4-Dioxane, add sufficient amount of the internal standard spiking solution containing 1,4-dichlorobenzene-d_4 to an aliquot of the sample extracts to result in a concentration of 0.40 ng/µL.

7.2.2.7.4 The internal standard solution shall be stored and/or replaced in accordance with Section 7.2.3. Add the same internal standard spiking solution, prepared using the same source of internal standards (i.e., same manufacturer lot), to the ICAL standards, ICVs, CCVs, samples, blanks, LCSs, and MS/MSDs.

7.2.2.8 Laboratory Control Sample Spiking Solution

The LCS spiking solution shall contain all the target analytes in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 2. The same matrix spiking solutions specified in Sections 7.2.2.6.1 – 7.2.2.6.3 shall be used as the LCS spiking solutions for the full scan analysis, the optional PAH and PCP analysis by the full scan method and the SIM technique, and the optional 1,4-Dioxane only analysis by the full scan method and the SIM technique, respectively.

7.2.3 Storage of Standard Solutions

7.2.3.1 Store the stock standard solutions at ≤6°C, but not frozen, in PTFE-lined screw-cap amber bottles.

7.2.3.2 The working standards shall be checked frequently for signs of degradation or evaporation. Store the working standards at ≤6°C, but not frozen, in PTFE-sealed glass containers. Working standards shall be replaced after 6 months unless the integrity of the solution is suspected of being compromised prior to that time.

7.2.3.3 Store premixed certified solutions according to the manufacturer’s documented holding time and storage temperature recommendations. Once the seal is compromised (e.g., ampule is opened), stock solutions for most compounds shall be used to prepare working standards and for the preparation of calibration standards within the shelf life of the working standards (Section 7.2.3.2). Stock solutions must be replaced in the same timeframe as the working standards unless acceptability of the standard can be documented to meet the SOW criteria (Section 7.2.3.6.1).

NOTE: Refrigeration of the GPC calibration solutions may cause the corn oil to solidify. Before use, allow the solution to stand at room temperature until the corn oil dissolves.

7.2.3.4 Protect all standards from light.

7.2.3.5 Samples, sample extracts, and standards shall be stored separately.

7.2.3.6 The Contractor is responsible for maintaining and verifying the integrity of standard solutions prior to use. This means that, at a minimum, the standards shall be brought to room temperature prior to use, checked for losses, and checked to verify that all components have remained in solution.

7.2.3.6.1 Working standards shall be monitored frequently by comparison to the initial calibration. Fresh standards shall be prepared if the opening CCV criteria can no longer be met (Section 9.5.5) and the shelf life of the working standard is exceeded (Sections 7.2.2.1 and 7.2.2.2). Standards shall be replaced upon expiration of the shelf life unless acceptability of the standard can be documented to meet all applicable SOW criteria, either by comparison to a compliant initial calibration generated from standards prepared within the shelf life of the working standards or by comparison to a freshly prepared standard.

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 Aqueous/Water Samples

Aqueous/water samples should 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. Smaller sample containers may be used if the Contractor’s analytical system can accommodate small volume sample preparation accompanied by large volume injection capability.

8.1.2 Soil/Sediment and Waste Samples

Soil/sediment and waste samples should be collected in glass containers.

8.2 Sample and Sample Extract Storage

8.2.1 Sample Storage

The samples shall be protected from light and refrigerated at ≤6°C, but not frozen, in an upright position from the time of receipt until 60 days after the delivery of a complete, reconciled data package to the EPA. After 60 days, the samples shall be disposed of in a manner that complies with all applicable regulations.

8.2.2 Sample Extract Storage

Sample extracts shall be protected from light and stored at ≤6°C, but not frozen, until 365 days after the delivery of a complete, reconciled data package to the EPA.

8.3 Contract Required Holding Times

8.3.1 Extraction of aqueous/water samples shall be started within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of TCLP or SPLP leachates shall begin within 7 days from the completion of the leaching procedure. Extraction of soil/sediment/waste samples by the Soxhlet method shall be started within 10 days of the VTSR. Extraction of soil/sediment/waste samples by methods other than Soxhlet shall be completed within 10 days of the VTSR. The waste dilution procedure for oily waste samples shall be completed within 10 days of the VTSR.

8.3.2 Sample extracts shall 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 Exhibit D – SVOA, Table 6. Other conditions may be used, provided that all technical acceptance criteria in Sections 9.3.5, 9.4.5, 9.5.5, 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 the GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions shall be used for the analysis of all standards, samples, blanks, and MS/MSDs.

9.1.1.3 The same injection volume, 1.0 µL or 2.0 µL, must be used for all standards and samples (including MS/MSDs and required method blanks).

9.1.2 Mass Spectrometer

The recommended MS analytical conditions are provided in Exhibit D – SVOA, Table 7.

9.2 Instrument Performance Check

9.2.1 Summary of GC/MS Instrument Performance Check

9.2.1.1 The GC/MS system shall 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 7.2.2.3).

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

9.2.2 Frequency of GC/MS Instrument Performance Check

The instrument performance check solution shall be injected once at the beginning of each initial calibration sequence for the full scan and SIM analyses, followed by the analyses of the ICAL standards, ICVs, samples, blanks, or standards.

NOTE: For SIM acquisition, the instrument performance check solution shall be analyzed in full scan mode, but the same optimized mass spectrometer settings (e.g., electron multiplier voltage, lens settings) shall be used for full scan analysis of the instrument performance check as will be used for SIM acquisition.

9.2.3 Procedure for GC/MS Instrument Performance Check

The analysis of the instrument performance check solution shall be performed using one of the following options:

- 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 7.2.2.3).

9.2.4 Technical Acceptance Criteria for GC/MS Instrument Performance Check

9.2.4.1 The GC/MS system instrument performance check shall be performed at the frequency described in Section 9.2.2.

9.2.4.2 The abundance criteria listed in Exhibit D – SVOA, Table 2, must be met. The mass spectrum of DFTPP shall 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 within 20 scans of 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 shall be analyzed under 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 GC/MS 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 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.

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 shall 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 7.2.2.1.2.1).

NOTE 1: For the optional analysis of PAHs and PCP only, using the SIM technique, the GC/MS system shall 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.

NOTE 2: For the optional analysis of 1,4-Dioxane only, using the SIM technique, the GC/MS system shall be calibrated at a minimum of five concentrations (Section 7.2.2.1.2.3), 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 shall 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 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 (Section 9.3.5), the ICV, method blank, samples, and closing CCV may be analyzed. It is not necessary to analyze another opening 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 shall be allowed to warm to ambient temperature before analysis.

9.3.3.3 Add a sufficient amount of the internal standard spiking solution (Section 7.2.2.7) to aliquots of each of the five calibration standards containing the DMCs (Sections 7.2.2.1.1 and 7.2.2.1.2) to result in a 20 ng/µL concentration of each internal standard. The internal standards specified in Section 7.2.2.7 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 Exhibit D – SVOA, Table 9.

9.3.3.4 Add a sufficient amount of the internal standard spiking solutions (Section 7.2.2.7) to aliquots of each of the five calibration standards containing the DMCs (Sections 7.2.2.1.2.2 and 7.2.2.1.2.3) to result in a 0.40 ng/µL concentration of each internal standard in the initial calibration standards associated with the PAHs and PCP or 1,4-Dioxane SIM analysis.

9.3.3.5 Analyze each calibration standard by injecting 1.0 µL 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 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. The primary characteristic ions used for quantitation are listed in Exhibit D – SVOA, Table 8. Assign the target analytes and DMCs to an internal standard according to Exhibit D – SVOA, Table 9, and Exhibit D – SVOA, Table 10. For internal standards, use the primary ion listed in Exhibit D – SVOA, Table 8, unless interferences are present. If interferences prevent the use of the primary ion for a given internal standard, use the secondary ion(s) listed in Exhibit D – SVOA, Table 8.

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

9.3.4.2 The Mean RRF ($\overline{RRF}$) must be calculated for all compounds according to Equation 1 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.4.3 Calculate the %RSD of the RRF values for each target analyte and DMC over the initial calibration range using Equation 3, in conjunction with Equations 1 and 2 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.4.3.1 Equation 1 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations is the general formula for the mean of a set of values.

9.3.4.3.2 Equation 2 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations is the general formula for Standard Deviation (SD) for a statistically small set of values.

9.3.4.3.3 Equation 3 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations is the general formula for the relative standard deviation.

9.3.5 Technical Acceptance Criteria for Initial Calibration

9.3.5.1 All initial calibration standards shall be analyzed at the concentrations described in Section 7.2.2.1 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 operating manual to determine how saturation is indicated for the instrument.

NOTE: The EPA Regional customer may specify, at the time of scheduling, that certain analytes of interest (e.g., PCP) must meet the performance criteria.

9.3.5.3 The chromatographic resolution shall be verified with the mid-point concentration of the initial calibration if closely eluting isomers are to be reported. Sufficient chromatographic resolution is achieved when the height of the valley between the two isomer peaks or analytes having similar ion peaks is less than 50% of the average of the two peak heights.

9.3.5.4 The required minimum RRF value for each target analyte and DMC at each calibration concentration for the full scan analysis is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet the criteria. Up to four different target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the minimum RRF requirement of 0.010 for the initial calibration to be considered acceptable.

9.3.5.5 The %RSD for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a maximum %RSD requirement of 40.0% must meet the criteria. Up to four target analytes and DMCs with maximum %RSD requirements of less than 40.0% may fail to meet the %RSD criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the maximum %RSD requirement of 40.0% for the initial calibration to be considered acceptable.

9.3.5.6 For the optional analysis of PAHs and PCP using the full scan method or the SIM technique, the required minimum RRF value for each target analyte and DMC at each calibration concentration for the full scan analysis and the SIM analysis is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet the criteria. Up to two different target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D – SVOA, Table 5, for the full scan and the SIM analysis, respectively, but these compounds must still meet the minimum RRF requirement of 0.010 for the initial calibration to be considered acceptable.

9.3.5.7 The %RSD for each target analyte and DMC for the optional PAH and PCP analysis using the full scan method is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a maximum %RSD requirement of 40.0% must meet the criteria. Up to two target analytes and DMCs with maximum %RSD requirements of less than 40.0% may fail to meet the %RSD criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the maximum %RSD requirement of 40.0% for the initial calibration to be considered acceptable.

9.3.5.8 The %RSD for each target analyte and DMC for the optional PAH and PCP analysis using the SIM technique is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with the maximum %RSD requirements of 40.0% (or 50.0% for PCP) must meet the criteria. Up to two target analytes and DMCs with maximum %RSD requirements of less than 40.0% (excluding PCP) may fail to meet the %RSD criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the maximum %RSD requirement of 40.0% for the initial calibration to be considered acceptable.

9.3.5.9 For the optional analysis of 1,4-Dioxane using the full scan method and the SIM technique, the target analyte and associated DMC must meet the minimum RRF and maximum %RSD criteria listed in Exhibit D – SVOA, Table 5, for the initial calibration to be considered acceptable.

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.

9.4 Initial Calibration Verification

9.4.1 Summary of Initial 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 shall be routinely checked by analyzing an ICV (containing all the target analytes from an alternate source or a different lot than used for the ICAL standards, and the DMCs and internal standards from the same source or lot as used for the ICAL standards) to ensure that the instrument is calibrated accurately.

9.4.2 Frequency of Initial Calibration Verification

The calibration for each GC/MS system used for analysis shall be verified with an ICV at the frequency of one per ICAL analytical sequence. The ICV shall be analyzed following that last ICAL standard analysis and prior to any method blank, sample, or applicable CCV analysis.

Injection #	**Material Injected**
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 - ICV	ICV
8th - Blanks, samples, MS/MSDs	Blanks, samples, and MS/MSDs
9th - Subsequent Samples	

9.4.3 Procedure for Initial Calibration Verification

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

9.4.3.2 Add the specified amount of the internal standards (Section 7.2.2.7) and the DMCs (Section 7.2.2.5) specified for the full scan or the SIM analysis to the appropriate ICV standards (Section 7.2.2.2). Analyze the ICV standards according to Section 10.4.

9.4.4 Calculations for Initial Calibration Verification

9.4.4.1 Calculate an RRF for each target analyte and DMC according to Equation 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.4.2 Calculate the %D between the ICV RRF_c and the preceding initial calibration $\overline{RRF}_i$ for each target analyte and DMC using Equation 17 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification

9.4.5.1 The concentration of the semivolatile target analytes and DMCs in the ICV shall be at or near the mid-point concentration of the calibration standards. The ICV shall be analyzed at the frequency described in Section 9.4.2, on a GC/MS system meeting the DFTPP (Section 9.2.4) and the initial calibration (Section 9.3.5) technical acceptance criteria. For the optional analysis of PAHs and PCP or 1,4-Dioxane only, using the SIM technique, the ICV shall be analyzed at or near the mid-point concentration level of the calibration range, 0.40 ng/µL (0.80 ng/µL for PCP and 1,4-Dioxane), 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 ICV for the full scan analysis, the required minimum RRF for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet the criteria. Up to four target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the minimum RRF requirement of 0.010 for the ICV to be considered acceptable.

9.4.5.3 For an ICV for the full scan analysis, the required maximum %D for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a maximum %D requirement of 40.0% must meet the criteria. Up to four target analytes and DMCs with maximum %D requirements of less than 40.0% may fail to meet the maximum %D criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the maximum %D requirement of 40.0% for the ICV to be considered acceptable.

9.4.5.4 For the ICV of the optional analysis of PAHs and PCP using the full scan method or the SIM technique, the required minimum RRF for each target analyte and DMC by the full scan method or the SIM technique is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet the criteria. Up to two target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D – SVOA, Table 5, for the full scan or SIM technique, respectively, but these compounds must still meet the minimum RRF requirement of 0.010 for the ICV to be considered acceptable.

9.4.5.5 For the ICV of the optional analysis of PAHs and PCP using the full scan method, the required maximum %D for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a maximum %D requirement of 40.0% must meet the criteria. Up to two target analytes and DMCs with maximum %D requirements of less than 40.0% may fail to meet the %D criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the maximum %RSD requirement of 40.0% for the ICV to be considered acceptable.

9.4.5.6 For the ICV of the optional analysis of PAHs and PCP using the SIM technique, the required maximum %D for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a maximum %D requirement of 40.0% (50.0% for PCP) must meet the criteria. Up to two target analytes and DMCs with maximum %D requirements of less than 40.0% (excluding PCP) may fail to meet the %D criteria listed in Exhibit D – SVOA, Table 5,

but these compounds must still meet the maximum %RSD requirement of 40.0% for the ICV to be considered acceptable.

9.4.5.7 For the ICV of the optional analysis of 1,4-Dioxane only using the full scan method or the SIM technique, the target analyte and associated DMC must meet the minimum RRF and maximum %D criteria listed in Exhibit D – SVOA, Table 5, for the full scan and the SIM analysis, respectively, for the ICV to be considered acceptable.

9.4.5.8 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 the instrument.

9.4.6 Corrective Action for Initial Calibration Verification

9.4.6.1 If the ICV analyzed immediately after the ICAL sequence does not meet the technical acceptance criteria, and a subsequent reanalysis of the ICV meets the technical acceptance criteria, proceed with the blank and sample analyses.

9.4.6.2 If the ICV analyzed immediately after the ICAL sequence does not meet the technical acceptance criteria, and a subsequent reanalysis does not meet the technical acceptance criteria, recalibrate the GC/MS instrument according to Section 9.3. All sample and required blank analyses must be associated to a compliant ICV analysis following the associated ICAL.

9.5 Continuing Calibration Verification

9.5.1 Summary of Continuing Calibration Verification

Prior to the analysis of samples and required blanks, and after instrument performance check, initial calibration, and ICV technical acceptance criteria have been met, each GC/MS system shall 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 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 9.5.2.3). If the closing CCV meets opening CCV criteria, an additional DFTPP tune is not required and the next 12-hour period begins with this CCV.

9.5.2 Frequency of Continuing Calibration Verification

9.5.2.1 The calibration for each GC/MS system used for analysis shall be verified at the beginning and end of every 12-hour period of operation. The 12-hour period begins with the injection of an opening CCV solution, followed by the injection of the blank and samples, provided that the opening CCV meets the technical acceptance criteria in Section 9.5.5. The 12-hour period ends with the injection of a closing CCV. If the closing CCV does not meet the technical acceptance criteria for an opening CCV (Section 9.5.5), an injection of an opening CCV is required to start the next 12-hour period.

9.5.2.2 If time remains in the 12-hour period after meeting the technical acceptance criteria for the initial calibration and ICV, samples may be analyzed.

9.5.2.3 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 in Section 9.5.5 are met for an opening CCV.

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 - ICV	ICV
	8th - Blanks, samples, MS/MSDs	Blanks, samples, MS/MSDs
	9th - Subsequent Samples	
End 12 hr	Closing CCV (meeting Closing CCV criteria, but not Opening CCV)	CS3 – Closing CCV
New 12 hr	1st Analysis 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 Opening CCV	CS3 - Opening CCV Blank, MS/MSD, subsequent samples Subsequent Samples Last Sample
End of 12 hr beginning of next 12 hr	Closing CCV (meeting Opening CCV criteria)	CS3 – Closing CCV meeting Opening CCV criteria Blank, MS/MSD, subsequent samples Subsequent Samples Last Sample
End of 12 hr	Closing CCV meeting criteria	CS3 – Closing CCV meeting Opening CCV criteria

9.5.3 Procedure for Continuing Calibration Verification

9.5.3.1 All standard/spiking solutions shall be allowed to warm to ambient temperature before analysis.

9.5.3.2 Add a sufficient amount of the internal standard spiking solution (Section 7.2.2.7) and the DMCs (Section 7.2.2.5) to an aliquot of CCV standard (7.2.2.1.3) to result in 20 ng/µL concentration of each internal standard. The internal standards specified in Section 7.2.2.7 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 Exhibit D – SVOA, Table 9.

9.5.3.3 Add the specified amount of the internal standards (Sections 7.2.2.7.2 and 7.2.2.7.3) and the DMCs (Sections 7.2.2.5.3 and 7.2.2.5.4) to the CCV (Section 7.2.2.1.3) for the optional SIM analyses of PAHs and PCP or 1,4-Dioxane only.

9.5.3.4 Analyze the CCV standard according to Section 10.4 using the same injection volume as in the initial calibration.

9.5.4 Calculations for Continuing Calibration Verification

9.5.4.1 Calculate an RRF for each semivolatile target analyte and DMC according to Equation 8 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.4.2 Calculate the %D between the CCV RRF_c and the most recent initial calibration $\overline{RRF}_i$ for each semivolatile target analyte and DMC using Equation 17 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The concentration of the semivolatile target analytes and DMCs in the opening and closing CCV shall be at or near the mid-point concentration of the calibration standards. The opening and closing CCV standard shall be analyzed at the frequency described in Section 9.5.2, on a GC/MS system meeting the DFTPP (Section 9.2.4), the initial calibration (Section 9.3.5), and the ICV (Section 9.4.5) technical acceptance criteria.

9.5.5.2 For an opening or closing CCV for the full scan analysis, the required minimum RRF value for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet the criteria. Up to four target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the RRF criteria listed in Exhibit D - SVOA, Table 5, but these compounds must still meet the minimum RRF requirements of 0.010 for the CCV to be considered acceptable.

9.5.5.3 For an opening CCV for the full scan analysis, the required maximum %D value for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a maximum %D requirement of 40.0% must meet this criteria. Up to four target analytes and DMCs with maximum %D requirements of less than 40.0% may fail to meet the maximum %D criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the maximum %RSD requirement of 40.0% for the CCV to be considered acceptable.

9.5.5.4 For a closing CCV for the full scan analysis, the required maximum %D value for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Up to six target analytes and DMCs may fail to meet the maximum %D criteria listed in Exhibit D - SVOA, Table 5, for the CCV to be considered acceptable. The closing CCV maximum %D requirement for Di-n-octylphthalate is advisory.

9.5.5.5 For an opening or closing CCV of the optional analysis of PAHs and PCP using the full scan method or the SIM technique, the required minimum RRF for each target analyte and DMC by full scan or the SIM technique is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a minimum RRF requirement of 0.010 must meet the criteria. Up to two target analytes and DMCs with minimum RRF requirements greater than 0.010 may fail to meet the

RRF criteria listed in Exhibit D – SVOA, Table 5, for the full scan method or the SIM technique, respectively, but these compounds must still meet the minimum RRF requirement of 0.010 for the CCV to be considered acceptable.

9.5.5.6 For an opening CCV of the optional analysis of PAHs and PCP using the full scan method, the required maximum %D for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a maximum %D requirement of 40.0% must meet the criteria. Up to two target analytes and DMCs with maximum %D requirements of less than 40.0% may fail to meet the %D criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the maximum %RSD requirement of 40.0% for the CCV to be considered acceptable.

9.5.5.7 For an opening CCV of the optional analysis of PAHs and PCP using the SIM technique, the required maximum %D for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Target analytes and DMCs with a maximum %D requirement of 40.0% (50.0% for PCP) must meet the criteria. Up to two target analytes and DMCs with maximum %D requirements of less than 40.0% (excluding PCP) may fail to meet the %D criteria listed in Exhibit D – SVOA, Table 5, but these compounds must still meet the maximum %RSD requirement of 40.0% for the CCV to be considered acceptable.

9.5.5.8 For a closing CCV of the optional analysis of PAHs and PCP using the full scan method and the SIM technique, the required maximum %D value for each target analyte and DMC is listed in Exhibit D – SVOA, Table 5. Up to two target analytes and DMCs may fail to meet the maximum %D criteria listed in Exhibit D - SVOA, Table 5, for the CCV to be considered acceptable. The closing CCV maximum %D criteria for PCP is advisory.

9.5.5.9 For an opening or closing CCV of the optional analysis of 1,4-Dioxane only using the full scan method or the SIM technique, the target analyte and associated DMC must meet the minimum RRF and maximum %D criteria listed in Exhibit D – SVOA, Table 5, for the full scan and the SIM analysis, respectively, for the CCV to be considered acceptable.

9.5.5.10 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 the instrument.

9.5.6 Corrective Action for Continuing Calibration Verification

9.5.6.1 If the opening CCV technical acceptance criteria are not met, reanalyze the opening CCV. If the reanalyzed opening CCV criteria still are not met, recalibrate the GC/MS instrument and take other corrective actions 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 shall be reanalyzed.

9.5.6.2 All samples and required blanks are to be associated with an opening CCV meeting the technical acceptance criteria or reanalyses are required.

9.5.6.3 The corrective action for sample reanalysis is not required when noncompliant analytes or associated DMCs, in the opening or closing CCVs bracketing a dilution, a re-extraction, or a reanalysis, are not the same analytes or associated DMCs for which the dilution, re-extraction, or reanalysis was intended.

10.0 PROCEDURE

The Contractor shall 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 shall 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 Aqueous/Water and TCLP/SPLP Leachate Samples

Continuous liquid-liquid extraction is used to extract the samples. Separatory funnel extraction or other manual extraction techniques cannot be used. Solid-phase extraction is used for aqueous/water samples without visible solids for 1,4-Dioxane analysis only by the full scan method and the SIM technique. Allow the sample to warm to ambient temperature before extraction. Sample aliquot amounts other than the specified 1 L can be used for the extraction procedure, provided that the CRQLs listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits can still be achieved by using proportionally reduced final extract volume, without altering the initial calibration curve.

If a smaller sample aliquot amount is selected, 500 mL for example, add a reduced amount of the DMC spiking solution (e.g., 250 µL) to all laboratory QC samples including the method blank, LCS, and MS/MSD, with the proportionally reduced final extract volume (e.g., from 1.0 mL to 0.50 mL). The same proportionally decreased spiking volume (e.g., 250 µL) shall be used for the LCS and matrix spiking solutions.

10.1.1.1 Continuous Liquid-Liquid Extraction

10.1.1.1.1 Continuous Liquid-Liquid Extraction without Hydrophobic Membrane

10.1.1.1.1.1 Follow the manufacturer’s instructions for set-up.

10.1.1.1.1.2 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.

10.1.1.1.1.3 If the samples were 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 samples were not received in 1 L bottles, measure out each 1 L sample aliquot in a separate, clean graduated cylinder and transfer the aliquot to the continuous extractor.

10.1.1.1.1.4 Using a syringe or volumetric pipette, add 500 µL of the DMC spiking solution (Section 7.2.2.5) 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-methylnaphthalene-d_{10} or 1,4-Dioxane-d_8 (in the separate extract for 1,4-Dioxane only SIM analysis) into the sample and mix well. Perform spiking prior to pH adjustment or any other processing steps.

10.1.1.1.1.5 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 shall 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.

10.1.1.1.1.6 Rinse the 1 L 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.

10.1.1.1.1.7 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 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.

10.1.1.1.2 Continuous Liquid-Liquid Extraction with Hydrophobic Membrane

10.1.1.1.2.1 Follow the procedure in Sections 10.1.1.1.1.1 - 10.1.1.1.1.6, but reduce the amount of methylene chloride used to 50 mL and extract for a minimum of 6 hours.

10.1.1.1.2.2 Add sufficient methylene chloride to the continuous 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.

10.1.1.1.2.3 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 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 shall be used. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

10.1.1.1.2.4 Some continuous 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.

10.1.1.1.2.5 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.

10.1.1.1.2.6 Alternate continuous 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.

10.1.1.2 Solid-Phase Extraction

Solid-phase extraction is primarily used for aqueous/water samples without visible solids prior to analysis of 1,4-Dioxane only, by the full scan method and the SIM technique (EPA Method 522).

10.1.1.2.1 Only the full scan method and the appropriate solid-phase cartridges shall be used for the selected sample aliquot amounts. Cartridges containing 2 g of coconut charcoal shall be used for sample aliquots ≤500 mL (nominally 500 mL) (Option 1). If the samples were received in 1.0 L bottles, the Contractor shall measure out a 500 mL sample aliquot for Option 1 in a separate, clean graduated cylinder. Other volumes may be used provided that method performance criteria and CRQLs are met.

10.1.1.2.2 Follow the manufacturer's instructions for set-up with the solid-phase cartridges used for Option 1.

10.1.1.2.3 Using a syringe or volumetric pipette, add 250 µL of the full scan DMC spiking solution (Section 7.2.2.5), to result in the addition of 4.0 µg for the full scan 1,4-Dioxane-d_8, to the sample and mix well. Add 250 µL of the SIM DMC spiking solution (7.2.2.5) to result in the addition of 0.40 µg for the SIM analysis if separate extractions for full scan and SIM analyses are performed. Perform spiking prior to pH adjustment or any other processing steps.

10.1.1.2.4 Measure the pH of the sample with narrow range pH paper or a pH meter and record the pH. Samples requiring pH adjustment shall be noted in the SDG Narrative.

10.1.1.2.5 Condition the cartridge with the following four steps:

- Fill the cartridge with 3 or 1 mL of methylene chloride), for Option 1 or 2, respectively, turn on the vacuum and pull the solvent through, aspirating completely;
- Fill the cartridge with 3 or 2 mL of methanol, for Option 1 or 2, respectively, turn on the vacuum and pull the solvent through, aspirating completely;

- Fill the cartridge with 3 or 2 mL of methanol, for Option 1 or 2, respectively, and elute with vacuum to just above the top frit, not allowing the cartridge to go dry at the end. From this point forward, the cartridge shall never be dry; and
- Fill the cartridge with 3 mL of reagent water, turn on the vacuum and pull the water through; repeat five times without allowing the cartridge to go dry in between washes or at the end for Option 1.

10.1.1.2.6 Attach a transfer tube from the sample cylinder to the cartridge and turn on the vacuum.

10.1.1.2.7 Adjust the vacuum to a flow rate of approximate 10 mL/min.

10.1.1.2.8 Detach the transfer tube or the reservoir and draw air through the cartridge for 10 minutes at full vacuum after the entire sample has passed through the cartridge. Turn off and release the vacuum. Proceed with cartridge elution immediately.

10.1.1.2.9 Elute the cartridge with the following steps:

- Lift the extraction manifold top and insert a rack with the collection tube into the vacuum manifold tank to collect the extract;
- Fill the cartridge with methylene chloride and soak the sorbent by pulling enough the solvent into the cartridge at low vacuum;
- Turn off the vacuum and vent the system. Allow the sorbent to soak in methylene chloride for approximately 1 minute;
- Apply a low vacuum and pull the methylene chloride through the cartridge in a downward direction into the collection tube; and
- Continue to add methylene chloride to the cartridge as it is drawn through until the volume of extract is about 0.50 mL, determined by the markings on the side of the collection tube.
- Remove collection tubes containing the extract from the vacuum manifold. Collect the extract with a beaker and dry with the addition of 0.50 g anhydrous sodium sulfate. Proceed to Section 10.2.

10.1.2 Soil/Sediment and Waste Samples

Mix samples thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves, and rocks. Given the types of the collected samples, soil/sediment/waste shall not require further grinding. However, the Contractor shall contact the Sample Management Office (SMO) if samples cannot be processed as received. The appropriate extraction methods to be used are to be determined based on the sample characteristics. The microwave extraction method shall be used only for samples with finely divided particle size (≤1 mm) and alternative extraction methods shall be used for samples with particle size of greater than >1 mm.

10.1.2.1 Mandatory Determination of Concentration Level

10.1.2.1.1 The Contractor shall determine whether a soil/sediment or waste 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 shall process the sample as low level.

10.1.2.1.3 Use of an EPA screening procedure or an in-house laboratory screening procedure is strongly encouraged. The procedure shall be documented and available for review during on-site laboratory evaluation.

10.1.2.2 Low-Level Extraction of Soil/Sediment and Waste Samples

Four procedures are provided for the extraction of semivolatile analytes from low-level soil/sediment and waste samples:

- Ultrasonic extraction;
- Soxhlet extraction (automated and manual);
- Pressurized Fluid Extraction (PFE); and
- Microwave extraction.

NOTE: All low-level samples of the same matrix in a Case shall be extracted by the same procedure.

10.1.2.2.1 For soil/sediment and waste sample extractions by the ultrasonic, Soxhlet, or pressurized fluid extraction procedure, proceed to Sections 10.1.2.2.2 - 10.1.2.2.4. For soil/sediment and waste sample extraction by the microwave procedure, proceed to Section 10.1.2.2.8.

10.1.2.2.2 For soil/sediment and waste 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 shall be met. For example, 15 g of sample aliquot can be used along with a final extract volume proportionally reduced from 1.0 mL to 0.50 mL prior to GPC cleanup. 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 After the dried sample is transferred to the extraction device, add 500 µL of the DMC spiking solution (Section 7.2.2.5) to result in the addition of 40 µg of each DMC (8.0 µg for 1,4-Dioxane-d_8) or, if SIM is requested, 0.40 µg of the SIM DMCs fluoranthene-d_{10} and 2-methylnaphthalene-d_{10} to the sample. Proceed to Section 10.1.2.2.5 for ultrasonic extraction, Section 10.1.2.2.6 for automated or manual Soxhlet

extraction, or Section 10.1.2.2.7 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 to the transferred and spiked sample (Section 10.1.2.2.4).

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 Soxhlet Extraction (Automated and Manual)

The Contractor may use either automated or manual Soxhlet extraction.

10.1.2.2.6.1 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.

10.1.2.2.6.1.1 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.

10.1.2.2.6.1.2 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.

10.1.2.2.6.1.3 Transfer the entire sample from the beaker (Sections 10.1.2.2.2 - 10.1.2.2.3) to the thimble and then add the DMC spiking solution (Section 7.2.2.5) as described in Section 10.1.2.2.4.

10.1.2.2.6.1.4 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.

10.1.2.2.6.1.5 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 shall be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

10.1.2.2.6.1.6 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves shall be in the "OPEN" position. Extract for the preset time.

10.1.2.2.6.1.7 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.

10.1.2.2.6.1.8 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.

10.1.2.2.6.2 Manual Soxhlet Extraction

10.1.2.2.6.2.1 Transfer the entire sample (Sections 10.1.2.2.2 - 10.1.2.2.3) to an extraction thimble and then add 500 µL of the DMC spiking solution (Section 7.2.2.5) as described in 10.1.2.2.4. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble.

10.1.2.2.6.2.2 Place approximately 300 mL of the extraction solvent into a 500 mL round bottom flask containing one or two clean boiling chips.

10.1.2.2.6.2.3 Attach the flask to the extractor and extract the sample for 16 - 24 hours at 4 - 6 cycles/hour. Allow the extract to cool after the extraction is complete.

10.1.2.2.6.2.4 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 - 10.1.2.2.3) to an extraction cell of the appropriate size for the aliquot, and add 500 µL of the DMC spiking solution (Section 7.2.2.5) as described in Section 10.1.2.2.4 to the sample.

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 shall 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 shall 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.

10.1.2.2.8 Microwave Extraction

10.1.2.2.8.1 For soil/sediment and non-oily waste samples, weigh out 30 ± 0.1 g of the processed sample (Section 10.1.2) and transfer to a microwave extraction vessel. Add sufficient anhydrous powdered or granulated sodium sulfate, or Hydromatrix™ and mix well to produce a free-flowing mixture.

10.1.2.2.8.2 Add 500 µL of the DMC spiking solution (Section 7.2.2.5) to result in the addition of 40 µg of each DMC (8.0 µg for 1,4-Dioxane-d_8) or, if SIM is requested, 0.40 µg of the SIM DMCs fluoranthene-d_{10} and 2-methylnaphthalene-d_{10} to the sample. Add sufficient volume of the 1:1 (v/v) acetone/methylene chloride extraction solvent to cover the

sample (e.g., 30-60 mL) and cap the vessel per the manufacturer's instructions.

10.1.2.2.8.3 Place the extraction vessel in the laboratory microwave and proceed with the manufacturer's specified set-up procedure. This may include placing additional vessels containing water or other materials to ensure consistent exposure to the microwaves across extractions.

10.1.2.2.8.4 Optimize the extraction conditions per the manufacturer's instructions. The following set of conditions may serve as a starting point:

Temperature	100-115°C
Pressure	50-150 psi
Time at temperature	10-20 minutes
Cooling to room temperature	
Filter/Rinse with same solvent system	

10.1.2.2.8.5 Proceed to Section 10.2.

10.1.2.3 Medium-Level Extraction of Soil/Sediment and Waste Samples

The procedure described below is for the extraction of soil/sediment and waste samples by the ultrasonic method (Section 10.1.2.2.5). The Contractor may also use the automated or manual Soxhlet extraction, PFE procedures, or microwave extraction described in Sections 10.1.2.2.6, 10.1.2.2.7, and 10.1.2.2.8, respectively. The requirements of this analytical method shall be met at all times (i.e., sample weight used for medium-level soil/sediment and waste extractions and original CRQLs for medium-level soil/sediment and waste samples). As applicable, follow the manufacturer's instructions for the use of all extraction equipment.

NOTE: All medium-level samples of the same matrix in a Case shall 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 2.0 g or a 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.

10.1.2.3.3 After the sample is transferred to the intended extraction device, add 500 µL of the DMC spiking solution (Section 7.2.2.5) to result in the addition of 40 µg of each DMC (8.0 µg for 1,4-Dioxane-d_8), excluding the two SIM DMCs (fluoranthene-d_{10} and 2-methylnaphthalene-d_{10}), to the sample mixture.

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 10.2.1.8 if no extract concentration is to be performed.

10.1.2.4 Waste Dilution

Document the condition of each waste sample. Include such observations as color, the presence of multiple phases, the presence of any solids, and the solubility of any oily layer in methylene chloride.

- If there is an aqueous layer, measure and record the pH of that layer.
- If the sample is oily, or there is a distinct oily layer, estimate and record the volume of oily substance.

Oily waste samples are prepared using the following waste dilution procedure.

NOTE: If the sample is not amenable to the following procedure, contact SMO for direction from the EPA.

10.1.2.4.1 Measure a 0.20 g aliquot of the waste sample to a separate 20 mL vial or 10 mL volumetric flask (record weight to the nearest 0.01 g).

10.1.2.4.2 Spike the sample with 1,000 µL of the DMC spiking solution (Section 7.2.2.5), mixed with a sufficient amount of anhydrous sodium sulfate (or Hydromatrix™) to absorb any aqueous phase, and approximately 5 mL of methylene chloride to dilute the sample. Note whether the sample is miscible with the solvent. If the sample is miscible with methylene chloride, proceed to Section 10.1.2.4.3.

10.1.2.4.3 Shake the vial or flask for 2 minutes.

10.1.2.4.4 Loosely pack a disposable Pasteur pipette with 2-3 cm glass wool plugs. Filter the extract through the glass wool and rinse the glass wool several times with 1-2 mL of methylene chloride. Adjust the final extract volume to 10 mL. Proceed to Section 10.3 for the GPC cleanup (optional), as needed. Concentrate the final extract volume to the same volume used for GPC cleanup or to 10 mL if GPC cleanup was not used, prior to analysis.

NOTE: The use of a screening technique is highly encouraged for waste samples. Important decisions about characterizing a sample can be made based on these results, which can save time and prevent laboratory contamination.

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 volumes of concentrator tube or flask are permitted to increase the process efficiency. 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 –

Target Analyte List and Contract Required Quantitation Limits, Table 2.

10.2.1.2 For aqueous/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 and waste samples, directly transfer the extract to the K-D concentrator, if the extract is known to be dry. Refer to Section 10.2.1.2 if the extract is known to be wet or shows visible signs of wetness.

10.2.1.4 Rinse the original container collecting the extract (for aqueous/water, soil/sediment, and waste samples) and the column (for aqueous/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 aqueous/water extracts that do not require GPC cleanup, proceed to final concentration of extract (Section 10.2.2). Oily water sample extracts require GPC cleanup.

10.2.1.7 For aqueous/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 and waste 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 aqueous/water, soil/sediment, and waste 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. The extract final volumes specified herein are intended to enable achievement of the CRQLs in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 2, using the recommended initial sample amounts. Other volumes may be used as long as method performance criteria and CRQLs are met.

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 in 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 aqueous/water samples, and low-level soil/sediment and waste 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 extracts from the solid-phase extraction of aqueous samples for 1,4-Dioxane analysis, and from soil/sediment and waste samples that have undergone the GPC cleanup) with the extraction solvent. 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

10.2.2.2.1 Place the concentrator tube in a warm water bath (30-35°C recommended) and evaporate the solvent volume to just below 1 mL (0.50 mL for extracts from soil/sediment and waste samples that have undergone the GPC cleanup with an initial volume of 5 mL) using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). DO NOT ALLOW THE EXTRACT TO GO DRY.

10.2.2.2.2 Gas lines from the gas source to the evaporation apparatus shall be stainless steel, copper, or PTFE tubing. Plastic tubing shall not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the concentrator tube shall be rinsed down several times with methylene chloride during the operation.

10.2.2.2.3 This technique shall not be used for extracts from the solid-phase extraction for 1,4-Dioxane analysis by the SIM technique.

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 Aqueous/Water

For aqueous/water samples that did not undergo GPC cleanup, the extract shall be brought to a final volume of 1.0 mL with methylene chloride. Remove boiling chips before adjusting final volume. For aqueous/water samples that underwent GPC cleanup, the extract shall 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 and Waste

Adjust the final volume for low-level and medium-level soil/sediment and waste samples to equal V_{out} with methylene chloride. For example, if V_{out} equals 0.50 mL, then the final volume shall 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 shall be larger than the size of the molecules to be separated.

10.3.1.2 GPC must be performed for all soil/sediment and waste extracts. GPC may be performed for aqueous/water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. In addition, GPC shall 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. 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 verification; 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 shall be calibrated prior to processing samples under the contract, when the GPC calibration verification 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 retention time (RT) shift shall be less than 5% when compared to RTs in the last calibration UV traces.

10.3.3.3 Procedure for GPC UV Detector 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 shall be monitored.

10.3.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.2.4) 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 shall 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 calibration verification. 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 shall be calibrated at the frequency described in Section 10.3.3.2. The UV trace must meet the following requirements:

- Peaks shall be observed and must be symmetrical for all compounds in the calibration solution;
- Corn oil and the phthalate peaks must exhibit greater than 85% resolution;
- Phthalate and methoxychlor peaks must exhibit greater than 85% resolution;
- Methoxychlor and perylene peaks must exhibit greater than 85% resolution; and
- Perylene and sulfur peaks must not be saturated and must exhibit greater than 90% baseline resolution.

10.3.3.4.2 The solvent flow rate and column pressure shall be within the manufacturer’s specified ranges.

10.3.3.4.3 The RTs for bis(2-ethylhexyl)phthalate and perylene shall 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 shall be less than the CRQL for all target analytes in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2, except bis(2-ethylhexyl)phthalate, which shall 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 shall 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 to remove the discoloration and possible precipitated particles. If a guard column is being used, replace it with a new one. 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 shall 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 shall 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 shall 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 shall 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 shall be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration shall 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 shall 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/ECD according to the procedure in Exhibit D - Pesticides Analysis (Section 10.4). The analysis shall be performed on only one of the GC/ECD columns used for pesticides analysis.

10.3.4.3.4 The recovery of each analyte shall be determined for evaluation and reporting purposes. Calculate the Percent Recovery (%R) of each analyte using Equation 20 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

10.3.4.4 Technical Acceptance Criteria for GPC Calibration Verification

The technical criteria specified in Exhibit D – Pesticides Analysis shall be met prior to the GPC cleanup on samples, blanks, and MS/MSDs.

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 shall 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 7.2.2.4) and the UV detector calibration procedure (Section 10.3.3). The UV detector shall 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 shall 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 shall be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 (v/v) glycerol/water solution shall be diluted and loaded into several loops. Similarly, extracts containing more than the manufacturer’s recommended non-volatile residue shall 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 shall be carefully monitored to ensure 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 shall be checked to ensure the proper amount was injected on the column. If the proper amount of extract was not injected, the sample shall be reprepared, and the sample extract shall either be diluted and loaded into several loops, or the sample extract shall be injected manually.

10.3.6.2 Frequency of Sample Extract Cleanup by GPC

GPC cleanup shall be performed once for each soil/sediment and waste sample, and all associated QC samples (blanks, LCSs, and MS/MSDs) shall be subjected to this procedure. GPC cleanup on the method blank shall be performed after all associated samples have been cleaned up (GPC sequence: calibration, GPC blank, 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 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.

10.3.6.3.3 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 then 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 shall 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; and/or
- Leaks in the system or significant variances in room temperature.

NOTE: Any samples that were loaded into multiple loops shall 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 shall 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 shall be employed for the analysis of samples as were used for calibration. The same injection volume shall be used for all standards, samples, and blanks.

NOTE 1: If SIM analysis is requested for a sample, a full scan analysis shall be performed on that sample prior to the SIM analysis. If all PAHs and PCP target analytes are detected at or above the sample adjusted CRQLs in the full scan analysis, a SIM analysis is not to be performed for that sample.

NOTE 2: If any single PAH analyte or PCP exceeds the calibration range in the full scan sample analysis, do not proceed with the SIM method for any of the other target analytes scheduled for SIM analysis for that sample.

NOTE 3: If target analyte 1,4-Dioxane is detected at or above the sample adjusted CRQL in the full scan analysis, a SIM analysis is not to be performed for that sample.

Any SIM sample analyses not performed for any reasons in the above notes shall be included in the SDG Narrative.

10.4.2 Procedure for Sample Analysis by GC/MS

Separate full scan analyses on the same sample extract may be performed for the 1,4-Dioxane target analyte only and all the other target analytes, to achieve improved chromatographic performance for the later eluting target analytes. The analysis of the 1,4-Dioxane and associated internal standard and DMC may be performed on a separate instrument than that used for the analysis of all other target analytes, with the appropriate GC column (Section 6.3.2) and operating conditions.

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 7.2.2.7) to each accurately measured aliquot of aqueous/water, and low-level or medium-level soil/sediment and waste sample extract to result in 20 ng/µL concentration of each internal standard.

NOTE: The internal standard spiking solution shall 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 or 1,4-Dioxane 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 aqueous/water and low-level soil/sediment and waste 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 shall 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 µL or other selected volume of the sample extract into the GC/MS.

10.4.3 Sample Dilutions

10.4.3.1 All samples shall 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 shall 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 or 1,4-Dioxane by SIM) of each internal standard, and analyze the diluted extract. Guidance in performing dilutions 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 Dilution Factor (DF) selected shall 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 soil/sediment and waste samples is 30.0. If a low-level soil/sediment or waste 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 9.5.6 and 10.4.3, but the closing CCV is still not compliant with the criteria in Exhibit D – SVOA, Table 5, then the Contractor shall follow the procedures below.

10.4.4.1.1 Examine the sample data from the noncompliant 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 Exhibit D – SVOA, 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 shall be reanalyzed at a nominal 1:4 dilution (or further dilution), sufficient to reduce the baseline to within this factor of four criteria, 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 noncompliance 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 – Target Analyte List and Contract Required Quantitation Limits, Table 2, 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 shall 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 standard analyte mass spectra.

11.1.1.2 Establish correspondence between the RRT of the analyte in the continuing calibration standard and the sample component 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 shall 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 mid-point CS3 ICAL 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 shall 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 on the Contractor’s GC/MS (as opposed to library spectra) are required. Once obtained, these standard spectra shall be used for identification purposes, only if the Contractor’s GC/MS meets the daily instrument performance requirements for DFTPP. These standard spectra shall 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 the ions specified in the section 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%), barring the influence of interference.

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 shall 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 (2017 release or later), Wiley (2014 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 – Target Analyte List and Contract Required Quantitation Limits, unless the volatile analysis was not requested, 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. 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. 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 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.

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 shall be considered a "probable match". The compound shall 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 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 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 shall 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 Contractor 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 Contractor 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 shall 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 substance is liable to have several names or synonyms: 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 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 the percent match at or above 85% at two different RTs, the compound having the highest percent match shall 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 shall 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 (Exhibit D – SVOA, Table 9, and Exhibit D – SVOA, Table 10). The EICP area of primary characteristic ions of analytes listed in Exhibit D – SVOA, Table 8, 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 quantitation. This normally occurs when there is compound coelution, baseline noise, or matrix interferences. In these circumstances, the Contractor shall perform a manual integration. Manual integrations are performed by manually changing the area of the quantitation ion of the compound, either by drawing the baseline manually or by choosing times for setting baselines in the software. 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 shall 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 instrument operator shall 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 instrument operator shall also mark each integrated area with the letter "m" on the quantitation report. All edits and manual integrations shall be verified by a second person, who shall also initial the change(s). In addition, graphical display(s) of the EICPs of the quantitation ion displaying the original integration(s) shall be included in the raw data, in addition to

the graphical display(s) of the EICPs of the quantitation ion displaying the manual integration(s). Chromatographic baselines shall be clearly visible in the original and edited EICPs at the same scaling. This applies to all target analytes listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2.

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 The factor $[(CV_{in} \times E)/CV_{out}]$ used in Equations 4B, 5C, 6B, and 7C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations will only apply when GPC is performed for semivolatile analysis. It is applied when GPC is performed to account for the factor of loss in the GPC (i.e., 50% efficiency, expressed as 0.50).

11.2.1.6 Target Analyte Calculations

Identified target analytes shall be quantitated by the internal standard method using Equation 4B or 5C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. The internal standard used shall be that which is assigned in Exhibit D – SVOA, Table 9. The $\overline{RRF}$ from the initial calibration standard is used to calculate the concentration in the sample.

11.2.1.7 Aqueous/Water

Calculate the aqueous/water and TCLP/SPLP leachate sample concentration using Equation 4B in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.1.8 Soil/Sediment and Waste

Calculate the soil/sediment and waste sample concentration using Equation 5C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 4B and 5C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 $\overline{RRF}$ of 1.0 is to be assumed.

11.2.3 Contract Required Quantitation Limit Calculations

11.2.3.1 Aqueous/Water

Calculate the aqueous/water and TCLP/SPLP leachate sample adjusted CRQL using Equation 6B in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.3.2 Soil/Sediment and Waste

Calculate the soil/sediment and waste sample adjusted CRQL using Equation 7C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.4 Deuterated Monitoring Compound Recoveries

11.2.4.1 Calculate the amount of each DMC using Equation 22B in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.4.2 Calculate the recovery of each DMC in all samples and blanks using Equation 22 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.3 Technical Acceptance Criteria for Sample Analysis

11.3.1 The sample shall be analyzed on a GC/MS system meeting the DFTPP, initial calibration, ICV, CCV, and blank technical acceptance criteria. The sample shall undergo cleanup procedures, when required, on a GPC meeting the technical acceptance criteria for GPC calibration.

11.3.2 The sample shall be extracted and analyzed within the contract holding time.

11.3.3 The sample must have an associated method blank.

11.3.4 The %R limits for each DMC are listed in Exhibit D – SVOA, Table 11. Up to four DMCs per sample may fail to meet the recovery limits listed Exhibit D – SVOA, Table 11, but all %Rs shall be greater than zero. The %R limits for 4-Chloroaniline-d_4 (aqueous/water and soil/sediment/waste) and 1,4-Dioxane-d_8 (soil/sediment/waste) are advisory only. If the optional analysis of PAHs and PCP only by the full scan method is to be performed, up to two DMCs associated with these target analytes per sample may fail to meet the recovery limits listed in Exhibit D – SVOA, Table 11, but all %Rs shall be greater than zero. For TCLP leachate sample analysis, up to one DMC (except Pyridine-d_5) associated to the TCLP analytes may fail to meet the recovery limits listed in Exhibit D – SVOA, Table 11, but the %R shall be greater than zero. The %R for Pyridine-d_5 is advisory.

11.3.5 If the optional analysis of PAHs and PCP using the SIM technique is to be performed, both SIM DMCs shall meet the recovery limits in Exhibit D – SVOA, Table 11. For the optional analysis of 1,4-Dioxane only by the full scan method and the SIM technique, the %R limits for 1,4-Dioxane-d_8 listed in Exhibit D – SVOA, Table 11, must be met for the aqueous/water samples. The %R limits for the soil/sediment/waste samples are advisory. DMC 1,4-Dioxane-d_8 recovery is not evaluated by the SIM technique.

NOTE: The DMC recovery requirements do not apply to samples that have been diluted.

11.3.6 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 or in the ICV standard analysis in the analytical sequence.

11.3.7 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 or in the ICV standard analysis in the analytical sequence.

11.3.8 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 extract is also analyzed according to the procedures in Section 10.4.3.

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 any samples not meeting the sample technical acceptance criteria will require re-extraction and/or reanalysis.

11.4.2 Corrective actions for failure to meet technical acceptance criteria for instrument performance checks, initial calibration, ICV, and CCV shall 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 After completing the corrective actions outlined above, the Contractor shall proceed to the following corrective actions including: reanalyze the extract used for the initial analysis (i.e., reinject the same extract containing the internal standards); analyze a new aliquot of the original sample extract with freshly added internal standards; or re-extract and reanalyze the sample, as appropriate.

11.4.4.1 If the DMC recoveries do not meet the acceptance criteria in the initial (undiluted) sample extract analysis, re-extract the sample and analyze the extract.

- If the DMC recoveries meet the acceptance criteria in the re-extracted sample, it indicates that the problem was within the Contractor’s control. Therefore, only submit the data from the reanalysis.
- If the DMC recoveries do not meet the acceptance criteria in the re-extracted sample, then submit the data from both analyses. Distinguish between the initial analysis and the re-extracted analysis in all deliverables using the suffixes in Appendix B – Codes for Labeling Data.

11.4.4.2 If the internal standard compound responses do not meet the acceptance criteria in the initial (undiluted) sample extract analysis, reanalyze the extract used for the initial analysis (i.e., reinject the same extract containing the internal standards), or, in lieu of the reinjection, directly analyze a new aliquot of the original sample extract with freshly added internal standards.

- If the internal standard compound responses meet the acceptance criteria in the reanalyzed sample (reinjection or the reanalysis of the original sample extract with freshly added internal standards), it indicates that the problem was within the Contractor’s control. Therefore, only submit the data from the reanalysis.

- If the internal standard compound responses are still noncompliant after the analysis of the extract with freshly added internal standards, the Contractor shall dilute once by an appropriate dilution factor (nominally 2-10) and reanalyze the extract. If the internal standard compound responses are acceptable in the subsequent diluted analysis, submit the data from the reanalysis and the diluted analysis.

- No further corrective action is required if the internal standard compound responses do not meet the acceptance criteria in the analysis of the extract with freshly added internal standards and the subsequent diluted analysis. Submit the data from the reanalysis and the diluted analysis. Distinguish between the initial analysis, the reanalysis, and the diluted analysis in all deliverables using the suffixes in Appendix B – Codes for Labeling Data.

NOTE: If the internal standard and/or DMC performance issue appears to be caused by the presence of high levels of target analytes (i.e., above the highest calibration standard), the Contractor may analyze the sample at an appropriate dilution factor (nominally 2-10) after the initial analysis that did not meet the criteria (without first reanalyzing the undiluted sample). However, if no target analytes are measured in the upper half of the calibration range in the diluted sample, the Contractor must proceed with the rextraction and/or reanalysis of the undiluted sample extract.

11.4.4.3 If both the DMC recoveries and internal standard compound responses do not meet the acceptance criteria in the initial sample extract analysis, re-extract the sample and analyze the new extract.

- If both the DMC recoveries and the internal standard compound responses meet the acceptance criteria in the re-extracted sample, it indicates that the problem was within the Contractor’s control. Therefore, only submit the data from the reanalysis.

- If the DMC recoveries do not meet the acceptance criteria in the re-extracted sample, then submit the data from both analyses. Distinguish between the initial analysis and the re-extraction/reanalysis in all deliverables using the suffixes in Appendix B – Codes for Labeling Data.

- If the internal standard compound responses do not meet the acceptance criteria in the re-extracted sample, follow the corrective actions in Section 11.4.4.2 to perform reinjection of the re-extracted sample or reanalysis of the new aliquot of the re-extracted sample with the freshly added internal standards and the subsequent corrective actions if necessary; and submit the specified data.

11.4.4.4 If the DMC recoveries or internal standard compound responses in a sample used for the MS/MSD analyses are outside the acceptance criteria, the Contractor shall proceed to the following corrective actions:

- If the DMC recoveries in the sample used for the MS/MSD analyses are outside the acceptance criteria, then the sample shall be re-extracted/reanalyzed only if the DMC recoveries meet the acceptance criteria in both the MS and MSD analyses.

- If the internal standard compound responses do not meet the acceptance criteria, the Contractor shall proceed to the reanalysis in Sections 11.4.4.2 and 11.4.4.3 only if the internal standard compound responses meet the technical acceptance criteria in both the MS and MSD analyses.

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

11.4.5.1 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 extract. If the instrument malfunction affected the calibration, recalibrate the instrument before reanalyzing the sample extract.

11.4.5.2 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 matrix effect, take the following 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 shall be reanalyzed only if the internal standard compound RTs were within the acceptance criteria in both 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 are 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 Appendix B – Codes for Labeling Data.

11.4.6 If the required corrective actions for sample re-extraction, reanalysis, and/or dilution cannot be performed due to insufficient sample volume, the Contractor shall contact SMO.

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 aqueous/water samples, or purified sodium sulfate or Hydromatrix™ for soil/sediment and waste samples) carried through the entire analytical procedure. The volume or weight or the reference matrix shall be approximately equal to the volume of weight of samples associated with the method blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of the samples. The leachate extraction blank shall be extracted accordingly.

12.1.2.2 Frequency of Method Blank

A method blank shall 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]. A method blank shall be analyzed after the ICV or opening CCV (see sample sequence in Section 9.4.2 or 9.5.2) and prior to samples in order to ensure that the total system (i.e., introduction device, transfer lines, and GC/MS system) is free of contaminants. In addition, a method blank shall:

- Be prepared with the same procedures and reagents used to extract and cleanup the samples; and
- Be analyzed on each GC/MS system under the same conditions used to analyze associated samples.

12.1.2.3 Procedure for Method Blank

12.1.2.3.1 For aqueous/water samples, measure a 1.0 L volume of reagent water and spike with 40 µg of each DMC and, if SIM analysis of PAHs and PCP or 1,4-Dioxane is requested, 0.40 µg of each SIM DMC (Section 7.2.2.5). For soil/sediment and waste 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 according to Section 10.0. If an alternate sample aliquot volume or weight is used, add sufficient amount of the specified DMC spiking solution corresponding to the proportional change in sample volume or weight. Make similar adjustment to the volume of the DMC spiking solutions if alternate final extract volume is to be used (Section 10.1.1).

12.1.2.3.2 Under no circumstances shall 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 method blanks shall be prepared and analyzed on a GC/MS system meeting the DFTPP, initial calibration, ICV, 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 method blank must be within the acceptance limits listed in Exhibit D – SVOA, Table 11. The %R limits for 1,4-Dioxane-d_8 (soil/sediment/waste), Pyridine-d_5 (for TCLP), and 4-Chloroaniline-d_4 (aqueous/water and soil/sediment/waste) are advisory. If a DMC %D does not meet the acceptance criteria in the associated opening CCV, the same DMC is also permitted to fail to meet the recovery criteria in the method blank, up to the maximum specified in Section 9.5.5.3 (e.g., DMC %R limits of 10-130% will become 10-140%).

12.1.2.5.3 The method blank must meet the sample technical acceptance criteria listed in Sections 11.3.6 - 11.3.7.

12.1.2.5.4 The concentration of target analyte bis(2-ethylhexyl) phthalate in the method blank for low-level aqueous/water and soil/sediment samples must be less than five times the CRQL listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2. The concentration for each of the other target analytes in the method blank for low-level aqueous/water and soil/sediment samples must be less than the CRQL listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2. The concentration of each target analyte in the method blank for medium-level soil/sediment samples must be less than the CRQL listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2. The concentration of each TIC in the aqueous method blank must be less than 5.0 µg/L (0.050 mg/L for TCLP leachate) or 170 µg/kg in the solid method blank.

12.1.2.5.5 All method blanks shall 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 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 shall 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. 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 Exhibit D – SVOA, Table 11, 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 shall be re-extracted and reanalyzed.

12.1.2.6.4 If the method blank does not meet internal standard response requirements listed in Section 11.3.6, follow the corrective action procedure outlined in Section 11.4.4. 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 11.3.7), 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 (TR/COC) Record.

12.2.2 Frequency of Matrix Spike and Matrix Spike Duplicate

12.2.2.1 If requested, an MS/MSD analysis shall be performed for each group of 20 field samples of a similar matrix in an SDG. For the optional analysis by the SIM method, MS/MSD will not be required unless specifically requested by the EPA Region. An MS/MSD sample shall be analyzed for each sample matrix (water/soil) and each level (low/medium).

12.2.2.2 Samples identified as field blanks or PE samples shall not be used for MS/MSD analysis.

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

12.2.3 Procedure for Preparing Matrix Spike and Matrix Spike Duplicate

12.2.3.1 For aqueous/water samples, prepare two additional aliquots of the sample selected for spiking at the same volume used for the original sample in two continuous extractors. If a 1 L sample aliquot volume is prepared, add 500 µL of DMC spiking solution corresponding to 40 µg of each DMC (8.0 µg for 1,4-Dioxane-d_8) and 500 µL of matrix spiking solution corresponding to 40 µg of each matrix spiking analyte (16 µg for 1,4-Dioxane). If an alternate sample aliquot volume is used, add sufficient amount of the specified matrix and DMC spiking solutions corresponding to the proportional change in sample volume. Make similar adjustments to the volumes of the matrix and DMC spiking solutions if alternate final extract volume is to be used (Section 10.1.1). These additions shall be made to the samples prior to transferring to the continuous liquid-liquid extraction or solid-phase extraction apparatus. Extract, concentrate, cleanup, and analyze the MS/MSD according to the procedures for aqueous/water samples (Section 10.1.1).

NOTE 1: For analysis of PAHs and PCP only, add 500 µL of each DMC spiking solution corresponding to 40 µg of each DMC (0.40 µg of each SIM DMC) and 500 µL of matrix spiking solution corresponding to 40 µg of each matrix spiking analyte (80 µg for PCP) for the full scan analysis.

NOTE 2: For analysis of 1,4-Dioxane only for the full scan method and SIM technique (excluding SPE), add 500 µL of each DMC spiking solution corresponding to 8.0 µg of the DMC for the full scan (0.80 µg for SIM technique) and 500 µL of matrix spiking solution corresponding to 16 µg for the full scan (2.0 µg for SIM technique) of 1,4-Dioxane matrix spiking analyte, to the separate aliquots for the full scan and SIM analyses, respectively. For analysis of 1,4-Dioxane only for the full scan method and SIM technique by SPE, add 250 µL of each DMC spiking solution corresponding to 4.0 µg of the DMC for the full scan (0.40 µg for SIM technique) and 250 µL of matrix spiking solution corresponding to 8.0 µg for the full scan (1.0 µg for SIM technique) of 1,4-Dioxane matrix spiking analyte, to the separate aliquots for the full scan and SIM analyses, respectively.

12.2.3.2 For low-level soil/sediment and waste samples, prepare two additional aliquots (record weight to nearest 0.1 g) of the sample selected for spiking at the same mass used for the original sample in two 400 mL beakers. Add 60 g of anhydrous powdered sodium sulfate or 30 g of Hydromatrix™ to each aliquot and mix well. Transfer the entire sample to the intended extraction device. Add the following specified amounts of the DMC spiking solution to the transferred sample: If a 30 g sample aliquot amount is prepared, add 500 µL of DMC spiking solution and 500 µL of matrix spiking solution to each aliquot, to result in the addition of 40 µg of each DMC (8.0 µg for 1,4-Dioxane-d_8) and 40 µg of each matrix spiking analyte (16 µg for 1,4-Dioxane). If an alternate sample aliquot weight is used, add an amount of the specified spiking solutions corresponding to the proportional change in sample weight. Make similar adjustments to the volume of the DMC and matrix spiking solutions if alternate final extract volume is to be used (Section 10.1.1). 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/sediment samples.

NOTE 1: For analysis of PAHs and PCP only, add 500 µL of each DMC spiking solution corresponding to 40 µg of each DMC (0.40 µg of each SIM DMC) and 500 µL of matrix spiking solution corresponding to 40 µg of each matrix spiking analyte (80 µg for PCP).

NOTE 2: For analysis of 1,4-Dioxane only by the full scan method, add 500 µL of DMC spiking solution corresponding to 8.0 µg of the DMC and 500 µL of matrix spiking solution corresponding to 16 µg of 1,4-Dioxane matrix spiking analyte.

12.2.3.3 For medium-level soil/sediment and waste samples, prepare two additional 1.0 g aliquots (record weight to nearest 0.1 g) of the sample selected for spiking in two 20 mL vials. Add 2.0 g of anhydrous powdered sodium sulfate or 1.0 g of Hydromatrix™ to each aliquot and mix well. Transfer the entire sample to the intended extraction device. Add a sufficient amount of DMC spiking solution and the matrix spiking solution to result in the addition of 40 µg of each DMC (8.0 µg of 1,4-Dioxane-d_8) and 40 µg of each matrix spiking analyte (16 µg for 1,4-Dioxane). 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 dilution 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 shall be analyzed and reported at a 1:10 dilution only. Do not dilute the MS/MSD samples further to get either spiked or non-spiked analytes within calibration range. Sample dilutions shall be performed in accordance with Section 10.4.3.

NOTE: In cases where PAHs and PCP or 1,4-Dioxane only SIM MS/MSD analysis is requested, and the sample designated for MS/MSD analysis has PAH target analytes, PCP, or 1,4-Dioxane detected at or above the sample adjusted CRQL or any target exceeding the calibration range, during the full scan analysis, then the Contractor shall contact SMO to determine if another sample should be selected for the 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 4B and 5C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations). Calculate the recovery of each Matrix Spike analyte using Equation 23 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD sample using Equation 24A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Matrix Spike Duplicate

12.2.5.1 All MS/MSDs shall be analyzed on a GC/MS system meeting the DFTPP, initial calibration, ICV, CCV, and method blank technical acceptance criteria, and at the frequency described in Section 12.2.2. The MS/MSD shall undergo cleanup procedures when required on a GPC meeting the technical acceptance criteria for GPC calibration.

12.2.5.2 The MS/MSD sample shall be extracted and analyzed within the contract required holding time.

12.2.5.3 The internal standards in the MS/MSD sample must meet the sample technical acceptance criteria listed in Sections 11.3.6 - 11.3.7.

12.2.5.4 The percent recovery and RPD limits for the spiking analytes listed in Exhibit D – SVOA, Table 12, are advisory. No further action by the Contractor is required when these criteria are not met. There are no specified limits for the spiking analytes that are not listed in Table 12. However, the amount added, percent recovery, and RPD values for each spiking analyte shall be reported.

12.2.6 Corrective Action for Matrix Spike and Matrix Spike Duplicate

Any MS/MSD sample that does not meet the technical acceptance criteria in Sections 12.2.5.1 and 12.2.5.3 shall be reanalyzed.

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. The LCS consists of an aliquot of a clean matrix similar to the sample matrix and of the same volume or weight. The LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

12.3.2 Frequency of Laboratory Control Sample

The LCS shall be prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix, at each level (low/medium), per preparation batch. Additionally, an LCS shall be:

- By the same procedures used to extract and cleanup samples; and
- Analyzed on each GC/MS system under the same conditions used to analyze associated samples.

12.3.3 Procedure for Preparing Laboratory Control Sample

12.3.3.1 For aqueous/water samples, add 500 µL of LCS spiking solution (Section 7.2.2.8) corresponding to 40 µg of each spiking analyte (16 µg for 1,4-Dioxane), and add 500 µL of DMC spiking solution corresponding to 40 µg of each DMC (8 µg for 1,4-Dioxane-d_8), to a 1.0 L sample aliquot volume. If an alternate sample aliquot volume/weight is used, a proportionally reduced DMC spiking solution shall be added to the sample aliquot (Section 10.1.1). These additions shall be made to the samples prior to transferring to the continuous liquid-liquid extraction or solid-phase extraction apparatus. Extract, concentrate, cleanup, and analyze the LCS according to the procedures for aqueous/water samples (Section 10.1.1). Prepare separate aliquots of the LCS for PAHs and PCP by SIM, as well as for 1,4-Dioxane by the SIM technique.

NOTE 1: For analysis of PAHs and PCP only by the full scan method and SIM technique, add 500 µL of LCS spiking solution corresponding to 40 µg of each PAH spiking analyte (80 µg for PCP) for the full scan and 0.40 µg of each PAH spiking analyte (0.80 µg for PCP) for SIM analysis; and add 500 µL of each DMC spiking solution corresponding to 40 µg of each PAH and PCP (0.40 µg of each SIM DMC).

NOTE 2: For analysis of 1,4-Dioxane only for the full scan method and SIM technique (excluding SPE), add 500 µL of LCS spiking solution corresponding to 8.0 µg of the DMC for the full scan method (0.80 µg for SIM technique) and 500 µL of LCS spiking solution corresponding to 16 µg for the full scan method (2.0 µg for SIM technique) of 1,4-Dioxane LCS spiking analyte, to the separate aliquots for the full scan and SIM analyses, respectively. For analysis of 1,4-Dioxane only for the full scan method and SIM technique by SPE, add 250 µL of each DMC spiking solution corresponding to 4.0 µg of the DMC for the full scan method (0.40 µg for SIM technique) and 250 µL of the LCS spiking solution corresponding to 8.0 µg for the full scan method (1.0 µg for SIM technique) of 1,4-Dioxane LCS spiking analyte, to the separate aliquots for the full scan and SIM analyses, respectively.

12.3.3.2 For low-level soil/sediment and waste samples, measure out 30 g of a clean reference matrix (e.g., sodium sulfate, Hydromatrix™) and add the following specified amounts of the LCS and DMC spiking solutions to the sample: add 500 µL of LCS spiking solution to the aliquot, to result in the addition of 40 µg of each spiking analyte (16 µg for 1,4-Dioxane), and add 500 µL of DMC spiking solution, to result in the addition of 40 µg of each DMC (8.0 µg for 1,4-Dioxane-d_8). If an alternate sample aliquot amount is used, add sufficient amount of the LCS and DMC spiking solutions corresponding to the proportional change in sample weight. Make similar adjustments to the volumes of LCS and DMC spiking solutions if alternate final extract volume is to be used Section 10.1.1). Follow the appropriate extraction procedure in Section 10.1.2, extract, concentrate, cleanup, and analyze the LCS according to the procedures for low-level soil/ sediment samples. Prepare separate aliquots of the LCS for PAHs and PCP by SIM, as well as for 1,4-Dioxane by the SIM technique.

NOTE 1: For analysis of PAHs and PCP only, add 500 µL of LCS spiking solution corresponding to 40 µg of each spiking analyte (80 µg for PCP) and 0.40 µg of each LCS spiking analyte (0.80 µg for PCP) for SIM analysis; and add 500 µL of each DMC spiking solution corresponding to 40 µg of each PAH and PCP (0.40 µg of each SIM DMC).

NOTE 2: For analysis of 1,4-Dioxane only by the full scan method, add 500 µL of LCS spiking solution corresponding to 16 µg of 1,4-Dioxane spiking analyte, and add 500 µL of DMC spiking solution corresponding to 8.0 µg of the DMC (0.80 µg of the SIM DMC if extract separately). For analysis of 1,4-Dioxane only by the SIM technique, add 500 µL of LCS spiking solution corresponding to 2.0 µg of 1,4-Dioxane spiking analyte. Add 500 µL of SIM DMC spiking solution corresponding to 0.80 µg of the DMC.

12.3.3.3 For medium-level soil/sediment and waste samples, prepare two additional 1.0 g aliquots (record weight to nearest 0.1 g) of the sample selected for spiking in two 20 mL vials. Add 2.0 g of anhydrous powdered sodium sulfate or 1.0 g of Hydromatrix™ to each aliquot and mix well. Transfer the entire sample to the intended extraction device. Add 500 µL of LCS spiking solution to the aliquot, to result in the addition of 40 µg of each spiking analyte with a CRQL of 5,000 µg/kg (16 µg for 1,4-Dioxane). Add sufficient amount of DMC spiking solution to result in the addition of 40 µg of each DMC (8.0 µg of 1,4-Dioxane-d_8). Proceed with the appropriate extraction procedure (Section 10.1.2.3). Extract, concentrate, cleanup, and analyze the LCS according to the procedures for medium-level samples.

12.3.4 Calculations for Laboratory Control Sample

12.3.4.1 Calculate the concentrations of the LCS spiking analytes using the same equations as used for target analytes (Equations 4B and 5C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations). Calculate the recovery of each LCS analyte using Equation 26A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Calculate the DMC recoveries for the LCS using Equation 22 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.3.5 Technical Acceptance Criteria for Laboratory Control Sample

12.3.5.1 All LCSs shall be analyzed on a GC/MS system meeting the DFTPP, initial calibration, ICV, CCV, and method blank technical acceptance criteria, and at the frequency described in Section 12.3.2. The LCS shall undergo cleanup procedures when required on a GPC meeting the technical acceptance criteria for GPC calibration.

12.3.5.2 The internal standards in the LCS sample must meet the sample technical acceptance criteria listed in Sections 11.3.6 - 11.3.7.

12.3.5.3 The %R of each of the DMCs in the LCS must be within the acceptance limits listed in Exhibit D – SVOA, Table 11. The %R limits for Pyridine-d_5 (for TCLP), 1,4-Dioxane-d_8 (soil/sediment/waste) and 4-Chloroaniline-d_4 (aqueous/water and soil/sediment/waste) are advisory. If a DMC %D does not meet the acceptance criteria in the associated opening CCV, the same DMC is also permitted to fail to meet the recovery criteria in the LCS, up to the maximum specified in section 9.5.5.3 (e.g., DMC %R limits of 10-130% will become 10-140%).

12.3.5.4 There are no specified percent recovery limits for the spiking analytes.

12.3.6 Corrective Action for Laboratory Control Sample

If an LCS sample does not meet the technical acceptance criteria in Sections 12.3.5.1 and 12.3.5.2, it shall be reanalyzed. If the LCS still fails the criteria, all associated samples shall be re-extracted and re-analyzed.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed under the contract, the MDL for each semivolatile target analyte shall be determined for each instrument under the same conditions used for analysis (i.e., analytical system configuration, as well as type and dimension of GC column), prior to the start of contract analyses and verified annually thereafter. MDL determination is matrix-specific and level-specific (i.e., the MDL shall be determined for aqueous/water, aqueous/water by SIM, low-level soil/sediment, low-level soil/sediment by SIM, and medium-level soil/sediment samples. The MDL determined for aqueous/water samples shall be used for TCLP and SPLP leachates. The MDL determined for soil/sediment samples shall be used for waste samples.). An MDL study shall also be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis. Major instrument maintenance includes, but is not limited to: replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), or 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.

12.4.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.

12.4.1.2 The determined concentration of the MDL shall be less than the CRQL listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 2.

12.4.1.3 The MDLs for TCLP and SPLP are not required to be determined or reported.

12.4.1.4 The delivery requirements for the MDL values are specified in Exhibit B – Reporting and Deliverables Requirements, Table 1.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Method 522, Determination of 1,4-Dioxane in Drinking Water by Solid Phase Extraction (SPE) and Gas Chromatography/ Mass Spectrometry (GC/MS) With Selected Ion Monitoring (SIM), Revision 1, September 2008.

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3520C, Continuous Liquid-Liquid Extraction, Revision 3, December 1996.

16.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3535A, Solid Phase Extraction, Revision 1, January 1998.

16.4 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3540C, Soxhlet Extraction, Revision 3, December 1996.

16.5 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3541, Automated Soxhlet Extraction, Revision 0, September 1994.

16.6 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3545A, Pressurized Fluid Extraction (PFE), Revision 1, February 2007.

16.7 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3546, Microwave Extraction, Revision 0, February 2007.

16.8 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3550C, Ultrasonic Extraction, Revision 3, February 2007.

16.9 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3580A, Waste Dilution, Revision 1, July 1992.

16.10 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3630C, Silica Gel Cleanup, Revision 3, December 1996.

16.11 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3640A, Gel-Permeation Cleanup, Revision 1, September 1994.

16.12 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 8270E, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 6, July 2018.

16.13 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

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
Pyridine	Pyridine	Azabenzene	110-86-1
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, 1-methyl-	1-Methylnaphthalene	alpha-Methylnaphthalene	90-12-0
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
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

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

Systematic Name	EPA Registry Name	Synonym	CAS #
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
Pyridine-d5	Pyridine-d5	Pentadeuteropyridine	7291-22-7
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-Methylnaphthalene-d10 (SIM DMC)	7297-45-2

TABLE 2. DECAFLUOROTRIPHENYLPHOSPHINE KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
197	Less than 2.0% of mass 198
198	Base peak 100% relative abundance or present (see NOTE)
199	5.0 - 9.0% of mass 198
441	Less than 150% of mass 443
442	Base peak or present
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 Phenol	Bis(2-chloroethyl)ether 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 3-Methylphenol 4-Methylphenol 2,4-Dimethylphenol	4-Chloroaniline
Nitrobenzene-d_5 (DMC-7)	**2-Nitrophenol-d_4 (DMC-8)**	**2,4-Dichlorophenol-d_3 (DMC-9)**
Acetophenone N-Nitroso-di-n-propylamine Hexachloroethane Hexachlorocyclopentadiene Nitrobenzene 2,6-Dinitrotoluene 2,4-Dinitrotoluene N-Nitrosodiphenylamine 3,3'-Dichlorobenzidine	Isophorone 2-Nitrophenol	2,4-Dichlorophenol Hexachlorobutadiene 4-Chloro-3-methylphenol 2,4,6-Trichlorophenol 2,4,5-Trichlorophenol 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 1,1'-Biphenyl Dimethylphthalate Diethylphthalate Di-n-butylphthalate Butylbenzylphthalate Bis(2-ethylhexyl)phthalate Di-n-octylphthalate	*Naphthalene *1-Methylnaphthalene *2-Methylnaphthalene 2-Chloronaphthalene *Acenaphthylene *Acenaphthene	2-Nitroaniline 3-Nitroaniline 2,4-Dinitrophenol 4-Nitrophenol 4-Nitroaniline

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 *Fluorene 4-Chlorophenyl-phenylether 4-Bromophenyl-phenylether Carbazole	4,6-Dinitro-2-methylphenol	Hexachlorobenzene Atrazine *Phenanthrene *Anthracene
Pyrene-d_{10} (DMC-16)	**Benzo(a)pyrene-d_{12} (DMC-17)**	**Pyridine- d_5 (DMC-18)**
*Fluoranthene *Pyrene *Benzo(a)anthracene *Chrysene	*Benzo(b)fluoranthene *Benzo(k)fluoranthene *Benzo(a)pyrene *Indeno(1,2,3-cd)pyrene *Dibenzo(a,h)anthracene *Benzo(g,h,i)perylene	Pyridine (TCLP only)

*Included in optional TAL of PAHs and PCP only.

TABLE 4. SEMIVOLATILE DEUTERATED MONITORING COMPOUNDS AND THE ASSOCIATED TARGET ANALYTES FOR OPTIONAL ANALYSIS OF PAHS AND PCP BY SELECTED ION MONITORING

Fluoranthene-d_{10}	**2-Methylnaphthalene-d_{10}**
Fluoranthene	Naphthalene
Pyrene	1-Methylnaphthalene
Benzo(a)anthracene	2-Methylnaphthalene
Chrysene	Acenaphthylene
Benzo(b)fluoranthene	Acenaphthene
Benzo(k)fluoranthene	Fluorene
Benzo(a)pyrene	Pentachlorophenol
Indeno(1,2,3-cd)pyrene	Phenanthrene
Dibenzo(a,h)anthracene	Anthracene
Benzo(g,h,i)perylene	

TABLE 5. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL CALIBRATION, INITIAL CALIBRATION VERIFICATION, AND CONTINUING CALIBRATION VERIFICATION FOR SEMIVOLATILE ORGANIC COMPOUNDS

Analyte	ICAL/ICV Minimum RRF	Opening/ Closing CCV Minimum RRF	ICAL Maximum %RSD	ICV/Opening CCV Maximum %D[1]	Closing CCV Maximum %D
1,4-Dioxane	0.010	0.010	40.0	±40.0	±50.0
Pyridine	0.010	0.010	40.0	±40.0	±50.0
Benzaldehyde	0.010	0.010	40.0	±40.0	±50.0
Phenol	0.080	0.080	20.0	±20.0	±50.0
Bis(2-chloroethyl)ether	0.100	0.100	20.0	±20.0	±50.0
2-Chlorophenol	0.200	0.200	20.0	±20.0	±50.0
2-Methylphenol	0.010	0.010	20.0	±20.0	±50.0
3-Methylphenol	0.010	0.010	20.0	±20.0	±50.0
2,2'-Oxybis-(1-chloropropane)	0.010	0.010	20.0	±40.0	±50.0
Acetophenone	0.060	0.060	20.0	±20.0	±50.0
4-Methylphenol	0.010	0.010	20.0	±20.0	±50.0
N-Nitroso-di-n-propylamine	0.050	0.050	20.0	±30.0	±50.0
Hexachloroethane	0.100	0.100	20.0	±20.0	±50.0
Nitrobenzene	0.050	0.050	20.0	±25.0	±50.0
Isophorone	0.050	0.050	20.0	±25.0	±50.0
2-Nitrophenol	0.050	0.050	25.0	±25.0	±50.0
2,4-Dimethylphenol	0.050	0.050	20.0	±25.0	±50.0
Bis(2-chloroethoxy)methane	0.050	0.050	20.0	±20.0	±50.0
2,4-Dichlorophenol	0.060	0.060	20.0	±20.0	±50.0
Naphthalene	0.200	0.200	20.0	±20.0	±50.0
4-Chloroaniline	0.010	0.010	40.0	±40.0	±50.0
Hexachlorobutadiene	0.040	0.040	20.0	±30.0	±50.0
Caprolactam	0.010	0.010	40.0	±40.0	±50.0
4-Chloro-3-methylphenol	0.040	0.040	20.0	±25.0	±50.0
1-Methylnaphthalene	0.100	0.100	20.0	±20.0	±50.0
2-Methylnaphthalene	0.100	0.100	20.0	±20.0	±50.0
Hexachlorocyclopentadiene	0.010	0.010	40.0	±40.0	±50.0
2,4,6-Trichlorophenol	0.090	0.090	25.0	±25.0	±50.0
2,4,5-Trichlorophenol	0.100	0.100	20.0	±25.0	±50.0
1,1'-Biphenyl	0.200	0.200	20.0	±20.0	±50.0
2-Chloronaphthalene	0.300	0.300	20.0	±20.0	±50.0
2-Nitroaniline	0.050	0.050	25.0	±40.0	±50.0
Dimethylphthalate	0.300	0.300	20.0	±20.0	±50.0
2,6-Dinitrotoluene	0.080	0.080	40.0	±30.0	±50.0
Acenaphthylene	0.400	0.400	20.0	±20.0	±50.0
3-Nitroaniline	0.010	0.010	40.0	±40.0	±50.0
Acenaphthene	0.200	0.200	25.0	±20.0	±50.0
2,4-Dinitrophenol	0.010	0.010	40.0	±40.0	±50.0
4-Nitrophenol	0.010	0.010	40.0	±40.0	±50.0
Dibenzofuran	0.300	0.300	20.0	±20.0	±50.0
2,4-Dinitrotoluene	0.070	0.070	40.0	±30.0	±50.0
Diethylphthalate	0.300	0.300	20.0	±20.0	±50.0

TABLE 5. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL CALIBRATION, INITIAL CALIBRATION VERIFICATION, AND CONTINUING CALIBRATION VERIFICATION FOR SEMIVOLATILE ORGANIC COMPOUNDS (CON'T)

Analyte	ICAL/ICV/ Minimum RRF	Opening/ Closing CCV Minimum RRF	ICAL Maximum %RSD	ICV/Opening CCV Maximum %D[1]	Closing CCV Maximum %D
1,2,4,5-Tetrachlorobenzene	0.100	0.100	20.0	±20.0	±50.0
4-Chlorophenyl-phenylether	0.100	0.100	25.0	±20.0	±50.0
Fluorene	0.200	0.200	25.0	±20.0	±50.0
4-Nitroaniline	0.010	0.010	40.0	±40.0	±50.0
4,6-Dinitro-2-methylphenol	0.010	0.010	40.0	±40.0	±50.0
4-Bromophenyl-phenyl ether	0.070	0.070	20.0	±20.0	±50.0
N-Nitrosodiphenylamine	0.050	0.050	20.0	±20.0	±50.0
Hexachlorobenzene	0.050	0.050	25.0	±25.0	±50.0
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	±50.0
Anthracene	0.200	0.200	20.0	±20.0	±50.0
Carbazole	0.050	0.050	40.0	±40.0	±50.0
Di-n-butylphthalate	0.500	0.500	20.0	±25.0	±50.0
Fluoranthene	0.400	0.400	20.0	±25.0	±50.0
Pyrene	0.400	0.400	20.0	±25.0	±50.0
Butylbenzylphthalate	0.100	0.100	40.0	±40.0	±50.0
3,3'-Dichlorobenzidine	0.010	0.010	40.0	±40.0	±50.0
Benzo(a)anthracene	0.300	0.300	20.0	±30.0	±50.0
Chrysene	0.200	0.200	20.0	±30.0	±50.0
Bis(2-ethylhexyl)phthalate	0.200	0.200	40.0	±40.0	±50.0
Di-n-octylphthalate*	0.010	0.010	40.0	±40.0	±50.0
Benzo(b)fluoranthene	0.200	0.200	20.0	±25.0	±50.0
Benzo(k)fluoranthene	0.200	0.200	20.0	±25.0	±50.0
Benzo(a)pyrene	0.200	0.200	20.0	±20.0	±50.0
Indeno(1,2,3-cd)pyrene	0.200	0.200	20.0	±25.0	±50.0
Dibenzo(a,h)anthracene	0.200	0.200	20.0	±30.0	±50.0
Benzo(g,h,i)perylene	0.200	0.200	20.0	±30.0	±50.0
2,3,4,6-Tetrachlorophenol	0.040	0.040	40.0	±20.0	±50.0
Selective Ion Monitoring					
1,4-Dioxane	0.010	0.010	40.0	±40.0	±50.0
Naphthalene	0.600	0.600	20.0	±30.0	±50.0
1-Methylnaphthalene	0.300	0.300	20.0	±30.0	±50.0
2-Methylnaphthalene	0.300	0.300	20.0	±30.0	±50.0
Acenaphthylene	0.900	0.900	20.0	±30.0	±50.0
Acenaphthene	0.500	0.500	20.0	±30.0	±50.0
Fluorene	0.700	0.700	20.0	±30.0	±50.0
Phenanthrene	0.300	0.300	20.0	±30.0	±50.0
Anthracene	0.400	0.400	20.0	±30.0	±50.0
Fluoranthene	0.400	0.400	20.0	±30.0	±50.0
Pyrene	0.500	0.500	20.0	±30.0	±50.0

TABLE 5. TECHNICAL ACCEPTANCE CRITERIA FOR INITIAL CALIBRATION, INITIAL CALIBRATION VERIFICATION, AND CONTINUING CALIBRATION VERIFICATION FOR SEMIVOLATILE ORGANIC COMPOUNDS (CON'T)

Analyte	ICAL/ICV Minimum RRF	Opening/ Closing CCV Minimum RRF	ICAL Maximum %RSD	ICV/Opening CCV Maximum %D[1]	Closing CCV Maximum %D
Benzo(a)anthracene	0.400	0.400	20.0	±30.0	±50.0
Chrysene	0.400	0.400	20.0	±30.0	±50.0
Benzo(b)fluoranthene	0.200	0.200	20.0	±30.0	±50.0
Benzo(k)fluoranthene	0.200	0.200	20.0	±30.0	±50.0
Benzo(a)pyrene	0.200	0.200	20.0	±30.0	±50.0
Indeno(1,2,3-cd)pyrene	0.200	0.200	25.0	±30.0	±50.0
Dibenzo(a,h)anthracene	0.200	0.200	25.0	±30.0	±50.0
Benzo(g,h,i)perylene	0.200	0.200	25.0	±30.0	±50.0
Pentachlorophenol*	0.010	0.010	50.0	±50.0	±50.0
Deuterated Monitoring Compounds					
1,4-Dioxane-d_8	0.010	0.010	20.0	±25.0	±50.0
Pyridine-d_5	0.010	0.010	40.0	±40.0	±50.0
Phenol-d_5	0.010	0.010	20.0	±25.0	±50.0
Bis-(2-chloroethyl)ether-d_8	0.050	0.050	20.0	±25.0	±50.0
2-Chlorophenol-d_4	0.200	0.200	20.0	±20.0	±50.0
4-Methylphenol-d_8	0.010	0.010	20.0	±20.0	±50.0
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	±50.0
2-Nitrophenol-d_4	0.050	0.050	25.0	±30.0	±50.0
2,4-Dichlorophenol-d_3	0.060	0.060	20.0	±20.0	±50.0
Dimethylphthalate-d_6	0.300	0.300	20.0	±20.0	±50.0
Acenaphthylene-d_8	0.400	0.400	20.0	±20.0	±50.0
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	±50.0
4,6-Dinitro-2-methylphenol-d_2	0.010	0.010	40.0	±40.0	±50.0
Anthracene-d_{10}	0.300	0.300	20.0	±20.0	±50.0
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	±30.0	±50.0
2-Methylnaphthalene-d_{10} (SIM)	0.300	0.300	20.0	±30.0	±50.0
1,4-Dioxane-d_8 (SIM)	0.010	0.010	20.0	±40.0	±50.0

*NOTE: The maximum %D for Di-n-octylphthalate and Pentachlorophenol (SIM) is advisory for the closing continuing calibration verification standard.

[1] If a closing CCV is acting as an opening CCV, all target analytes and DMCs shall 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 - Target Analyte List and Contract Required Quantitation Limits, Table 2, 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
Pyridine	79	52,51
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(l-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
1-Methylnaphthalene	142	141
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

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

Analyte	Primary Quantitation Ion	Secondary Ion(s)
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
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	138,277
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

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

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Deuterated Monitoring Compounds		
1,4-Dioxane-d_8	96	64,34
Pyridine-d_5	84	56,54
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-Methylnaphthalene-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 Pyridine 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) Pyridine-d_5 (TCLP-DMC)	Nitrobenzene Isophorone 2-Nitrophenol 2,4-Dimethylphenol Bis(2-chloroethoxy)methane 2,4-Dichlorophenol Hexachlorobutadiene Caprolactam 4-Chloro-3-methylphenol *1-Methylnaphthalene *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-Methylnaphthalene-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)	*Fluoranthene *Pyrene Butylbenzylphthalate 3,3'-Dichlorobenzidine *Benzo(a)anthracene Bis(2-ethylhexyl)phthalate *Chrysene Pyrene-d_{10} (DMC) Fluoranthene-d_{10} (SIM-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}**
1-Methylnaphthalene 2-Methylnaphthalene Naphthalene 2,4-Dichlorophenol-d_3 (DMC) *2-Methylnaphthalene-d_{10} (DMC)	Acenaphthylene Acenaphthene Fluorene Acenaphthylene-d_8 (DMC) Fluorene-d_{10} (DMC)	Phenanthrene Anthracene Fluoranthene Pentachlorophenol Anthracene-d_{10} (DMC)
Chrysene-d_{12}	**Perylene-d_{12}**	
Fluoranthene Pyrene Benzo(a)anthracene Chrysene Pyrene-d_{10} (DMC) *Fluoranthene-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 Aqueous/Water Samples	Percent Recovery For Soil/Sediment and Waste Samples
1,4-Dioxane-d_8	15-120	15-120*
Pyridine-d_5	20-120*	-
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-Methylnaphthalene-d_{10} (SIM)	30-130	20-140
1,4-Dioxane-d_8 (SIM)	15-120	15-120*

*Limits are advisory.

TABLE 12. MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS*

Analyte	Percent Recovery Aqueous/Water	RPD Aqueous/Water	Percent Recovery Soil/Sediment and Waste	RPD Soil/Sediment and Waste
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
1,4-Dioxane	15-120	0-50	15-120	0-50

*Limits are advisory.

EXHIBIT D

PESTICIDES ANALYSIS

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EXHIBIT D - Pesticides Analysis

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EXHIBIT D - Pesticides Analysis

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1.0 SCOPE AND APPLICATION

1.1 The analytical method that follows is designed to analyze aqueous/water, leachate derived from the Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP), soil/sediment, waste, and wipe 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 – Target Analyte List and Contract Required Quantitation Limits. The method, based on the U.S. Environmental Protection Agency (EPA) Method 8081B, 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 shall be used as an analytical standard, identified and quantitated in sample analysis, and reported as heptachlor epoxide.

2.0 SUMMARY OF METHOD

2.1 Aqueous/Water, TCLP, or SPLP Leachate

A suitable sample aliquot volume [minimum 1.0 Liter (L)] is spiked with a surrogate solution and extracted using a separatory funnel, a continuous liquid-liquid extractor, or a solid-phase extraction disk. The extract is dried with anhydrous sodium sulfate (or an equivalent drying agent such as Hydromatrix™), concentrated, and may be subjected to Gel Permeation Chromatography (GPC) cleanup (optional). The extract is then solvent exchanged into hexane, a 1 or 2 milliliter (mL) aliquot of the extract is subjected to Florisil cleanup and other cleanup methods as applicable, and the final volume is adjusted to the same volume as the aliquot (1 mL or 2 mL). The extract is analyzed using a dual column (widebore and megabore) capillary GC/ECD.

2.2 Soil/Sediment

A suitable sample aliquot amount [minimum 30 grams (g)] is spiked with a surrogate solution, 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, pressurized fluid extraction, or microwave extraction. The extract is filtered (for ultrasonic extraction), concentrated, and solvent-exchanged into methylene chloride. The extract is subjected to GPC cleanup and is then solvent-exchanged into hexane. A 1 or 2 mL aliquot of the extract is subjected to Florisil cleanup and other cleanup methods as applicable. The final volume is adjusted to the same volume

as the aliquot (1 mL or 2 mL) and the extract is analyzed using a dual column (widebore and megabore) capillary GC/ECD.

2.3 Wipes

A solvent-saturated glass wool or gauze wipe sample is spiked with a surrogate solution, mixed with anhydrous sodium sulfate (or Hydromatrix™), and extracted with a 1:1 (v/v) acetone/methylene chloride solvent mixture by ultrasonic extraction or Soxhlet extraction. The extract is filtered (for ultrasonic extraction), concentrated, and solvent-exchanged into methylene chloride. The extract is subjected to GPC cleanup and is then solvent-exchanged into hexane. A 1 or 2 mL aliquot of the extract is subjected to Florisil cleanup and other cleanup methods as applicable. The final volume is adjusted to the same volume as the aliquot (1 mL or 2 mL) and the extract is analyzed using a dual column (widebore and megabore) capillary GC/ECD.

2.4 Waste

Solid waste samples are extracted and analyzed using the soil/sediment methods in Section 2.2. Alternatively, oily waste samples are prepared using a waste dilution procedure. A 0.20 g aliquot of the oily waste sample is spiked with a surrogate solution, mixed with anhydrous sodium sulfate (or Hydromatrix™), and diluted with 10 mL of hexane. A 1 or 2 mL aliquot of the extract is subjected to Florisil cleanup. The extract is then diluted to 10 mL with methylene chloride and cleaned up by GPC (optional, based on sample characteristics), solvent exchanged into hexane, and concentrated to a final extraction volume of 1 or 2 mL prior to analysis. Waste samples that have undergone TCLP/SPLP procedures are extracted and analyzed using the aqueous/water methods described in Section 2.1.

3.0 DEFINITIONS

See Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 to elevated baselines in Gas Chromatograms. The method shall 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 compounds that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending on the nature of the site being sampled. The cleanup procedures in this method shall be used to remove such interferences in order to achieve the CRQLs.

5.0 SAFETY

See Section 12.0 of Exhibit D – Introduction to 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, demonstration of equivalent performance that meets 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.

All instruments, balances, heating, and measuring equipment and devices shall be uniquely identified and labeled to allow traceability to any corresponding records of use.

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 The balance calibration shall be checked with known masses once per each day of use. This verification shall consist 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 shall be checked on a monthly basis using National Institute of Standards and Technology (NIST)-traceable known reference masses (Class ‘0’ or Class ‘1’) as defined by ASTM E617-13 or equivalent (e.g., earlier Class ‘S’ defined masses). All balances shall be checked at least once annually by a certified technician. The reference masses used by the Contractor shall 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, Tabletop (optional).

6.1.3.1 Centrifuge Tube - 12-15 mL with 19 millimeter (mm) ground-glass joint (optional).

6.1.4 Desiccator - Containing a desiccant indicator compound.

6.1.5 Erlenmeyer Flasks - 250 mL.

6.1.6 Graduated Cylinders Class A – 100 mL, 500 mL, and 1 L capacity.

6.1.7 Magnetic Stirring Bars - Polytetrafluoroethylene (PTFE) coated, at least 4 centimeters (cm) long.

6.1.8 Ovens – Drying, capable of maintaining 105°C (±5°C).

6.1.9 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.

6.1.10 pH Paper – Wide range.

6.1.11 Pasteur Pipettes – Regular and packed with glass wool plugs.

6.1.12 Pipettes (Calibrated) - Glass volumetric, l.0 mL or 2.0 mL. Manufacturer's instructions shall be followed for the calibration and maintenance of adjustable pipettes.

6.1.13 Sieve - No. 18 mesh with nominal pore size of 1 mm and a collection pan and cover.

6.1.14 Spatulas - Stainless steel or PTFE.

6.1.15 Syringes – 10 microliters (µL), 25 µL, 100 µL, and 1000 µL.

6.1.16 Vials and Caps - 10 mL (optional), with screw-cap and PTFE or aluminum foil liner; autosampler vial with 2 mL capacity for GC autosampler.

6.1.17 Volumetric Flasks, Class A – 5.0, 10, 20, 50, 100, 250, and 500 mL.

6.1.18 Weigh Dishes – Porcelain crucibles or disposable aluminum weighing pans.

6.2 Glassware/Extraction/Cleanup Equipment

6.2.1 Separatory Funnels - 2 L with PTFE stopcock.

6.2.1.1 Borosilicate Glass Wool - Rinsed with methylene chloride.

6.2.2 Continuous Liquid-Liquid Extractors - Equipped with PTFE or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.2.3 Solid-Phase Extraction System

6.2.3.1 Extraction Disks – 90 mm or 47 mm C_{18} disks.

6.2.3.2 TCLP Leachate Extraction Disks – SDB-XC.

6.2.3.3 Solid-phase Disk Extraction System – Manifold that holds three 90 mm filter standard apparatus or six 47 mm standard filter apparatus, or equivalent. Includes sample reservoirs, clamps, fritted disks, and filtration head with drip tip.

6.2.3.4 Vacuum Extraction Manifold - Equipped with flow/vacuum control.

6.2.3.5 Sample Delivery System – Equipped with transfer tube system and sample reservoir(s), or 60 mL collection tubes.

6.2.4 Sonication Equipment

6.2.4.1 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 shall 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.

6.2.4.2 Sonabox Acoustic Enclosure (or equivalent) - For use with disruptor to decrease noise level.

6.2.4.3 Vacuum Filtration Apparatus

6.2.4.3.1 Buchner Funnel.

6.2.4.3.2 Filter Paper – Whatman No. 42, or equivalent.

6.2.5 Automated Soxhlet Extraction System - With temperature-controlled oil bath. Silicone oil shall not be used because it destroys the rubber parts. The apparatus shall be used in a hood.

6.2.5.1 Cellulose or Glass Extraction Thimble, 26 mm x 60 mm.

6.2.5.2 Glass Extraction Cups.

6.2.5.3 Thimble Adapters.

6.2.5.4 Viton Seals.

6.2.6 Soxhlet Extraction, Manual

6.2.6.1 Allihn Condenser.

6.2.6.2 Cellulose or Glass Extraction Thimble, 35 mm x 90 mm.

6.2.6.3 Soxhlet Extractor body, 40 mm ID.

6.2.6.4 Round bottom flask, 500 mL.

6.2.7 Pressurized Fluid Extraction Device

6.2.7.1 Dionex Accelerated Solvent Extractor (ASE-350) or equivalent with appropriately-sized extraction cells. Currently, 100 mL cells that will accommodate greater than 30 g samples are available. 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.

6.2.7.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.2.8 Microwave Extraction System

6.2.8.1 Laboratory Microwave – Capable of maintaining sample temperature within ±2.5°C and adjusting power within 2 seconds.

6.2.8.2 Microwave Extraction Vessels – Capable of accepting up to 30 g of sample, transparent to microwave energy, and capable of withstanding temperatures of 200°C minimum and pressures of 200 psi minimum.

6.2.8.3 The laboratory shall maintain separate vessels for the digestion of metals and solvent extraction of organics and follow manufacturer’s instructions with regard to monitoring and maintaining sample temperature during microwave extraction.

6.2.9 Kuderna-Danish (K-D) Apparatus

6.2.9.1 Concentrator Tubes - 10 mL and 15 mL, graduated.

6.2.9.2 Drying Column – 400 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).

6.2.9.3 Evaporative Flasks - 500 mL.

6.2.9.4 Silicon Carbide Boiling Chips – Approximately 10/40 mesh. Heat to 400°C for 30 minutes or solvent-rinsed with methylene chloride.

6.2.9.5 Snyder Column - Three-ball macro.

6.2.9.6 Snyder Column - Two-ball micro.

6.2.9.7 Water Bath - Heated, with concentric ring cover, capable of temperature control. The bath shall be used in the hood.

6.2.10 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 shall be used in a hood.

6.2.11 Gel Permeation Chromatography Cleanup System

6.2.11.1 GPC 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, shall meet the calibration requirements in Section 10.3.1.3.

NOTE: GPC cleanup is required for all soil/sediment, waste, and wipe sample extracts, and for aqueous/water sample extracts containing higher molecular weight contaminants that interfere with the analyses of the target analytes.

6.2.11.2 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.

6.2.11.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column.

6.2.11.4 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.

6.2.11.4.1 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 verification; 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.

6.2.11.5 UV Detector - Fixed wavelength [254 nanometers (nm)] with a semi-prep flow-through cell.

6.2.11.6 Strip Chart Recorder - Recording integrator or laboratory data system.

6.2.11.7 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.

6.2.11.8 Viscometer

6.2.12 Florisil Cleanup Equipment

6.2.12.1 Florisil - 500 milligram (mg) or 1 g cartridges with stainless steel or PTFE frits.

6.2.12.2 Vacuum System for Eluting Multiple Cleanup Cartridges.

6.2.12.3 Vacuum Trap - Made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.

6.2.12.4 Vacuum Pressure Gauge.

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 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 shall be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room. Adsorbents used in trapping systems must be replaced according to the product replacement periods as recommended by the manufacturer, and at a minimum annually. 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. The instrument shall be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

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 (0.53 mm ID) fused silica GC columns may be used provided that the resolution requirements (Section 9.3.5.2) are met; 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 columns used for analysis shall be provided in the SDG Narrative. Packed GC 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 - Target Analyte List and Contract Required Quantitation Limits, Table 3.
- 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 the analytical method in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 3.
- The column can accept at least 16 times the low-point initial calibration concentration level in Exhibit D - Pesticides, Table 2, without becoming overloaded.
- The column pair selected must have dissimilar phases/chemical properties in order to separate the analytes of interest in different Retention Time (RT) order.
- The column provides equal or better resolution of the analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 3, than the columns listed in Section 6.3.2.

6.3.2.1.1 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 shall maintain documentation verifying 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 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 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 comparison/review, signed by the Laboratory Manager, certifying that:

- The alternate column performance meets the technical acceptance criteria in Section 6.3.2.1;
- 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 that interfere with the identification and/or quantitation of analytes listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 3.

6.3.2.1.4 The documentation shall be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional CLP Contracting Officer's 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 shall 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 shall clearly identify its use in the SDG Narrative in submissions to the EPA. Contractors 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.

6.3.3 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 (5% methane/argon balance), P-10 (10% methane/argon balance), 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 shall be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room. Adsorbents used in trapping systems must be replaced according to the product replacement periods as recommended by the manufacturer, and at a minimum annually.

6.3.3.2 At least annually, or as advised by the local radiation regulatory agency, each ECD shall be checked for radiation leakage from their Ni-63 source. Wipe tests shall 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 shall provide all standards to be used with the contract. These standards shall be used only after they have been certified according to the procedure in Exhibit D – Introduction to Analytical Methods, Section 11.0. The Contractor shall be able to verify that the standards are certified. Manufacturer's certificates of analysis shall 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 a contaminant or 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 10% acetone in hexane (v/v) - Prepare by adding 10 mL of acetone to 90 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.

CAUTION: DO NOT STORE CONCENTRATED MINERAL ACIDS (SULFURIC, NITRIC) WITH ORGANIC ACIDS.

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 shall be extracted with hexane and analyzed by a GC/ECD to demonstrate that it is free of interference before use or shall 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.

7.1.9 Sodium sulfite.

7.1.10 Solvents: Methylene chloride, hexane, acetone, ethyl acetate, toluene, iso-octane, petroleum ether, 2-propanol, and methanol - 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 shall be purchased with certification that it is free of interference. Methylene chloride must be certified as acid free or shall be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride shall be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.1.11 Sulfuric acid, concentrated, 95-98% (specific gravity 1.84).

CAUTION: DO NOT STORE CONCENTRATED MINERAL ACIDS (SULFURIC, NITRIC) WITH ORGANIC ACIDS.

7.1.12 Tetrabutylammonium (TBA) sulfite.

7.1.13 Glycerol.

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 prepared in hexane or isooctane, which may contain small amounts of toluene or acetone, from pure standard materials, or purchased as certified pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated, unless acceptability of the standard can be documented (Section 7.2.3.6).

7.2.2 Working Standards

7.2.2.1 Individual Standard Mixtures

7.2.2.1.1 The Calibration Standard Mixture solutions shall 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 compositions of Individual Standard Mixture A and Mixture B are listed in Exhibit D - Pesticides, Table 2, with the concentrations of each target analyte and surrogate given for the low-point standard mixtures (CS1 Standard A and CS1 Standard B) in Exhibit D - Pesticides, Table 4. 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 Exhibit D - Pesticides, Table 2) or lower for each analyte. The concentration for each analyte in the high-point standard shall 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. For TCLP analysis, the additional high point ICAL standard shall be analyzed at 2 times the CS5 concentrations for the applicable analytes and the associated surrogates.

7.2.2.1.4 The concentrations of the target analytes in each calibration standard are listed in Exhibit D - Pesticides, Table 2. 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 Limit (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 Exhibit D - Pesticides, Table 2 (e.g., if a laboratory were using a 2.5 ng/mL low standard, then the other calibration levels shall 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 shall 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 shall be 5 and 10 ng/mL, respectively.

7.2.2.2.2 The concentration of Toxaphene in the low-point standard (CS1) shall be 500 ng/mL or lower. The concentration in the high-point standard (CS5) shall 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). For TCLP analysis, the additional high point ICAL standard shall be analyzed at 2 times the CS5 concentrations for the applicable analytes and the associated surrogates.

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 shall be initiated on the GC/ECD and the sample containing the Toxaphene shall be reanalyzed.

7.2.2.3 Continuing Calibration Standard

The CCV Standards INDA and INDB or INDC shall contain the target analytes and surrogates at or near the mid-point CS3 concentration of the Initial Calibration Standard (ICAL) (Exhibit D - Pesticides, Table 2). Use the same source of target analytes (i.e., same manufacturer lot) for CCVs as were used for the preparation of initial calibration standards.

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/MSDs), Performance Evaluation (PE) samples (if required), and required blanks (method/sulfur cleanup/ instrument). Add the same source of surrogates (i.e., same manufacturer lot) for the preparation of calibration standards, initial and continuing calibration verification standards, samples, blanks, and MS/MSDs. Add the same surrogate standard spiking solution to LCSs, samples, blanks, and MS/MSDs. 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 shall be checked frequently for stability. The solution shall 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 all single component pesticides target analytes in Exhibit D - Pesticides, Table 7, in acetone or methanol at the concentrations specified. The solution shall be replaced every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.6 Laboratory Control Sample Spiking Solution

Prepare an LCS spiking solution containing all single component pesticides target analytes in Exhibit D - Pesticides, Table 7, in acetone or methanol at the concentrations specified. The LCS solution shall be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.7 Gel Permeation Chromatography Calibration and Calibration Verification Solutions

7.2.2.7.1 GPC Calibration Solution

Prepare a GPC calibration solution in methylene chloride that contains the following analytes at the minimum concentrations listed below. The solution shall 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.

7.2.2.7.2 GPC Calibration Verification Solution

Prepare the GPC calibration verification solution containing the pesticides listed in Exhibit D - Pesticides, Table 7, 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 shall be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.8 Florisil Cartridge Check Solution

Prepare a solution containing 2,4,5-trichlorophenol at 0.10 µg/mL in acetone. The solution shall be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.9 Instrument Performance Check Standards

7.2.2.9.1 Resolution Check Mixture

Prepare the Resolution Check Mixture containing the pesticides and surrogates listed in Exhibit D - Pesticides, Table 3, in hexane or iso-octane at the concentrations specified. The mixture shall be prepared every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.9.2 Performance Evaluation Mixture

Prepare the Performance Evaluation Mixture (PEM) solution containing the pesticides and surrogates listed in Exhibit D - Pesticides, Table 3, in hexane or iso-octane at the concentration specified. The PEM shall 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 Working standards shall be prepared every 6 months, or sooner if the solutions have degraded or concentrated, unless acceptability of the standard can be documented to meet the criteria specified in Section 7.2.3.6.1. Working standards shall be checked frequently for signs of degradation or evaporation. Store working standards at ≤6°C in PTFE-lined screw-cap amber bottles/vials and according to the manufacturer's documented holding time recommendations. In the absence of manufacturer's instructions, the solution shall be replaced after 6 months unless the integrity of the solution is suspected of being compromised prior to that time.

NOTE: Refrigeration of GPC calibration solutions may cause the corn oil to solidify. Before use, allow the solution to stand at room temperature until the corn oil dissolves.

7.2.3.3 Store premixed certified solutions according to the manufacturer's documented holding time and storage temperature recommendations. Once the seal is compromised (e.g., ampule is opened), stock solutions for most compounds shall be maintained under the same conditions and assigned the same shelf life as working standards (Section 7.2.3.2). Stock solutions must be replaced in the same timeframe as the working standards unless acceptability of the standard can be documented to meet the specified criteria (Section 7.2.3.6.1).

7.2.3.4 Protect all standards from light.

7.2.3.5 Samples, sample extracts, and standards shall 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 that, at a minimum, the standards shall be brought to room temperature prior to use, checked for losses, and checked to verify that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

7.2.3.6.1 Working standards shall be monitored frequently by comparison to the initial calibration. Fresh standards shall be prepared if the opening CCV criteria can no longer be met (Section 9.4.5) and the shelf life of the working standard is exceeded (Section 7.2.3.2). Standards shall be replaced upon expiration of the shelf life unless acceptability of the standard can be documented to meet all applicable SOW criteria, either by comparison to a compliant initial calibration generated from standards prepared within the shelf life of the working standards or by comparison to a freshly prepared standard.

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 Aqueous/Water Samples

Aqueous/water samples should 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. Smaller sample containers may be used if the Contractor's analytical system can accommodate small volume sample preparation accompanied by large volume injection capability.

8.1.2 Soil/Sediment and Waste Samples

Soil/sediment and waste samples should be collected in glass containers.

8.1.3 Wipe Samples

Wipe samples should be collected in 20 mL glass vials with Teflon-lined caps oversaturated in hexane so there is excess solvent in the vial.

8.2 Sample and Sample Extract Storage

8.2.1 Sample Storage

The samples shall be protected from light and refrigerated at ≤6°C, but not frozen, in an upright position from the time of receipt until 60 days after the delivery of a complete, reconciled data package to the EPA. After 60 days, the samples shall be disposed of in a manner that complies with all applicable regulations.

8.2.2 Sample Extract Storage

Sample extracts shall be protected from light and stored at ≤6°C, but not frozen, until 365 days after the delivery of a complete, reconciled data package to the EPA.

8.3 Contract Required Holding Times

8.3.1 Extraction of aqueous/water samples by separatory funnel or solid-phase extraction procedures shall be completed within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of aqueous/water samples by continuous liquid-liquid extraction shall be started within 5 days of the VTSR. Extraction of the TCLP or SPLP filtrates and leachates shall begin within 7 days of completion of the filtration and leaching procedures. Extraction of soil/sediment, waste, and wipe samples by the Soxhlet method shall be started within 10 days of the VTSR. Extraction of soil/sediment, waste, and wipe samples by methods other than Soxhlet shall be completed within 10 days of the VTSR. The waste dilution procedure of oily waste samples shall be completed within 10 days of the VTSR.

8.3.2 Analysis of sample extracts shall 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 Exhibit D - Pesticides, Table 6. 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 the GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions shall be used for the analysis of all standards, samples (including LCSs and MS/MSDs), and required blanks (method/sulfur cleanup/instrument).

9.1.1.3 The same injection volume, 1.0 µL or 2.0 µL, must be used for all standards, samples (including LCSs and MS/MSDs), 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 shall 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 LCSs and MS/MSDs) and required blanks (method/sulfur cleanup/instrument), each GC/ECD system shall 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 shall 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.

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 shall 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 shall 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 9.3.3.5 and 9.3.5.3). 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.

NOTE: The steps pertaining to Instrument Blank and PEM are also used as part of the continuing calibration verification (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 9.3.5.3). 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. 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.

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 10 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.4.2 During the initial calibration sequence, mean RTs ($\overline{RT}$s) are determined for all single component pesticides, surrogates, and the four to six 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 $\overline{RT}$ is calculated for each single component pesticide, surrogate, and Toxaphene as the average of the five values. 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. Calculate the $\overline{RT}$ for each single component pesticide, surrogate, and Toxaphene using Equation 11 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.4.4 An RT window is calculated for each single component analyte and surrogate and for the four to six major peaks of Toxaphene using Exhibit D - Pesticides, Table 5. 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 12 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. 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 12 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.4.5.1 For example, it is permitted to calculate the CF for Endrin based on peak area and to calculate the 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.

9.3.4.6 Calculate the Mean CF ($\overline{CF}$) and the Percent Relative Standard Deviation (%RSD) of the CF for each single component pesticide and surrogate over the initial calibration range using Equations 1, 2 and 3 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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.

9.3.4.8 Toxaphene shall be calibrated at a single low-point CS1 for pattern recognition. A CF is calculated for each peak in a selected set of four to six major peaks for Toxaphene using Equation 12 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.4.9 If Toxaphene is detected in a sample analysis following a single-point initial calibration, a separate five-point Toxaphene calibration shall 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 four to six major peaks for Toxaphene using Equation 12 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. The $\overline{CF}$ and the %RSD of the CFs for each selected Toxaphene peak are calculated using Equations 1, 2, and 3 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. 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 shall 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 13, 14A, 14B, and 14C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 13 and 18 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 shall 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 shall 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 and relative peak heights 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.

NOTE: Either of the two columns can be designated as the primary column; however, designation should be consistent through initial and continuing calibrations. Primary column data is submitted first in the data package and secondary column data is submitted second. These designations shall be reported on the Form DC-2.

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 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.

NOTE: Either of the two columns can be designated as the primary column; however, designation should be consistent through initial and continuing calibrations. Primary column data is submitted first in the data package and secondary column data is submitted second. These designations shall be reported on the Form DC-2.

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 18 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

9.3.5.8 The %Breakdown of DDT and Endrin in each of the PEM analyses must be ≤20.0% calculated using Equations 14A and 14B in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. The combined %Breakdown of DDT and Endrin must be ≤30.0% calculated using Equation 14C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 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 shall 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.

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 data (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 shall 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 shall be used in the calibration verification.

9.4.2.2 The instrument blank and the PEM, the last two analyses in the initial calibration sequence, are the first two injections bracketing the next 12-hour period followed by the sample and the required blank analyses. The injection of the instrument blank starts 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 shall 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 shall 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 shall end with an instrument blank and a CS3 Toxaphene Standard.

9.4.2.6 No more than 14 hours can elapse from the injection beginning the opening CCV and the injection ending the closing CCV (PEM or CS3 Standard Mixture).

All acceptable samples shall 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
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 shall 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 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 18 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 13, 14A, 14B, and 14C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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) or each toxaphene peak in the standard mixture and the corresponding $\overline{CF}$ from the initial calibration, using Equation 19 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. 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.

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 shall 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.

NOTE: Primary and secondary column designation should be consistent through initial and continuing calibrations. Primary column data is submitted first in the data package and secondary column data is submitted second. These designations shall be reported on the Form DC-2.

9.4.5.4 The 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 - 9.3.4.4.

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) shall 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 does 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 shall 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 shall be taken and a new initial calibration sequence shall 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 shall be stopped. Appropriate corrective action shall be taken to clean out the system and an acceptable instrument blank shall 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 9.4.2.4), an acceptable initial calibration shall be analyzed before samples may be analyzed. 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.

9.4.6.9 The corrective action for sample reanalysis is not required when the noncompliant analytes or surrogates, in the opening or closing CCVs bracketing a dilution, a re-extraction, or a reanalysis, are not the same analytes or surrogates for which the dilution, re-extraction, or reanalysis was intended.

10.0 PROCEDURE

The Contractor shall 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 shall 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 Aqueous/Water and TCLP/SPLP Leachate Samples

Aqueous/water and TCLP or SPLP leachate samples may be extracted by either a separatory funnel procedure, a continuous liquid-liquid extraction procedure, or a solid-phase extraction procedure. Solid-phase extraction is not recommended for samples with greater than 1% solids. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, continuous liquid-liquid extraction shall be employed. Allow the samples to warm to ambient temperature before extraction. Sample aliquot amounts other than the specified 1 L can be used for the extraction procedure, provided that the CRQLs listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits can still be achieved by using a proportionally reduced final extract volume without altering the initial calibration curve. If a smaller sample aliquot amount is selected, 500 mL for example, the surrogate standard spiking solution added to the aliquot shall be reduced accordingly (e.g., 500 µL of the surrogate standard spiking solution) with the reduced final extract volume from 10 mL to 5 mL.

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 aqueous/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 shall 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 shall 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 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 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring the pH adjustment shall 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 (e.g., 50 mL) of methylene chloride and add the rinsate to the continuous extractor.

10.1.1.2.1.7 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.

NOTE 2: Some continuous 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.

10.1.1.2.1.8 Allow to cool and then detach the distillation flask. Proceed to Section 10.2.

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 - 10.1.1.2.1.6, 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 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 shall be used. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

10.1.1.2.2.4 Some continuous 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 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.

10.1.1.3 Solid-Phase Extraction

10.1.1.3.1 Follow the manufacturer's instructions for set up, using a C_{18} disk for aqueous/water samples and a SDB-XC disk for TCLP leachate samples. The laboratory may use a filter aid or pre-filter for samples containing particulates. Solid-phase extraction is used for samples without visible solids and it is not appropriate for samples with suspended particulate matter or noticeably turbid samples.

10.1.1.3.2 If the samples have been received in 1 L bottles, the laboratory shall mark the meniscus, shake the sample, and add 1.0 mL of the surrogate standard spiking solution. 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 add 1.0 mL of the surrogate standard spiking solution. Other volumes may be used as long as method performance criteria and CRQLs are met.

10.1.1.3.3 Measure the pH of aqueous/water samples 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 pH adjustment shall be noted in the SDG Narrative. Do not adjust the pH of TCLP leachate samples prior to extraction.

10.1.1.3.4 For aqueous/water samples, wash each extraction disk with 20 mL of methylene chloride. For TCLP leachate samples, wash each extraction disk with 5 mL of acetone. Rinse down the sides of the sample reservoir and pull approximately 1 mL of methylene chloride or acetone through each disk. Allow the disks to soak for 1 minute, then pull the remaining solvent through the disks and allow them to dry.

10.1.1.3.5 For aqueous/water samples, wash each extraction disk a second time with 10 mL of acetone. For TCLP leachate samples, wash each extraction disk with 5 mL of ethyl acetate. Rinse down the sides of the sample reservoir and pull approximately 1 mL of acetone or ethyl acetate through each disk. Allow the disks to soak for 1 minute, then pull the remaining solvent through the disks and allow them to dry.

10.1.1.3.6 For aqueous/water samples, precondition each disk with 20 mL of methanol. For TCLP leachate samples, precondition each disk with 5 mL of methanol. Pull a few drops of methanol through each disk and allow the disks to soak for 1 minute. Pull the methanol through the disks, stopping when there is a thin layer of methanol remaining. For aqueous/water samples, add 20 mL of reagent water. For TCLP leachate samples, add 15 mL of reagent water. Pull the water through the disks, stopping when there is a 2-3 mm layer of water remaining. Do

not allow the disks to go dry. Any disk that goes dry shall be reconditioned with both solvents.

10.1.1.3.7 Add the samples to the sample reservoirs and filter through the extraction disks as quickly as possible. Dry the disks by continuing to draw vacuum for 3 minutes after the sample has passed through.

10.1.1.3.8 To elute the disks, remove the filter apparatus from the manifold (do not disassemble) and insert a collection tube with at least a 25 mL capacity. The drip tip shall be seated sufficiently below the neck of the tube to prevent loss by spattering. For aqueous/water samples, add 5 mL of acetone (or volume as specified by the solid-phase extraction system manufacturer) to the sample bottle or graduated cylinder to rinse the vessel. Transfer the rinsate to the extraction reservoir, rinsing as necessary. Pull a few drops through and allow the acetone to soak the disk for 20 seconds. Rinse the sample vessel with 15 mL of methylene chloride and transfer the rinsate to the extraction reservoir, rinsing as necessary. For TCLP leachate samples, elute the disks by adding 4 mL of acetone, pulling a few drops through, and allowing the acetone to soak the disk for 1 minute. Rinse the sample bottle or graduated cylinder with 2 mL of acetone. Then rinse with 5 mL of ethyl acetate and transfer the rinsate to the extraction reservoir. Rinse a second time with 5 mL of ethyl acetate or alternative solvents (i.e., hexane, acetone) and transfer the rinsate to the extraction reservoir. Draw approximately one-half the volume of solvent through the disk and allow the remainder to soak the disk for 1 minute. Completely draw the remaining solvent through the disk.

10.1.1.3.9 Proceed to Section 10.2.

10.1.2 Soil/Sediment, Waste, and Wipe Samples

Four procedures are provided for the extraction of pesticide analytes from soil/sediment, waste, and wipe samples:

- Ultrasonic extraction;
- Soxhlet extraction (automated and manual);
- Pressurized fluid extraction (PFE) – For soil/sediment and waste samples only; and
- Microwave extraction – For soil/sediment and waste samples only.

NOTE: All samples of the same matrix in a Case shall be extracted by the same procedure.

10.1.2.1 For extraction of soil/sediment and waste samples, mix samples thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves, and rocks. Decant any standing aqueous phase but contact the Sample Management Office (SMO) for EPA Regional approval before discarding. Given the types of the collected samples, soil/sediment/waste shall not require further grinding. However, the Contractor shall contact SMO if samples cannot be processed as received. The appropriate extraction methods to be used are to be determined based on the sample characteristics. The microwave extraction method shall be used only for samples with finely divided particle size (≤1 mm) and alternative extraction methods shall be used for samples with particle size >1 mm. If necessary, remove particles >1 mm by sieving and taking measures to control fugitive dust.

For soil/sediment and waste sample extractions by the ultrasonic, Soxhlet, or pressurized fluid extraction procedure, proceed to Sections 10.1.2.1.1 - 10.1.2.1.4. For soil/sediment and waste sample extraction by the microwave procedure, proceed to Section 10.1.2.5.

10.1.2.1.1 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. For example, 15 g of sample aliquot for extraction can be used along with the proportionally reduced final extract volume prior to GPC cleanup from 10.0 mL to 5.0 mL, without altering the initial calibration curve. 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.

10.1.2.1.2 Add 60 g of anhydrous powdered or granulated sodium sulfate, or 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 10.1.2.4) the use of sodium sulfate is not recommended.

10.1.2.1.3 For extraction of wipe samples, place the contents of the sample container, including the wipe and excess solvent, into a 400 mL beaker. Add 10 g of anhydrous powdered or granulated sodium sulfate, or 10 g of Hydromatrix™, and mix well.

10.1.2.1.4 Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.4) to each soil/sediment, waste, and wipe sample after it is transferred to the intended extraction device. Then immediately add 100 mL of 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.1.2.2 for ultrasonic extraction, Section 10.1.2.3 for automated or manual Soxhlet extraction, or Section 10.1.2.4 for pressurized fluid extraction. As applicable, follow the manufacturer’s instructions for use of all extraction equipment.

10.1.2.2 Ultrasonic Extraction

10.1.2.2.1 Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.4) to the transferred sample (10.1.2.1.4).

10.1.2.2.2 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 not use a microtip probe.

10.1.2.2.3 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.

10.1.2.2.4 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 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.

10.1.2.3 Soxhlet Extraction (Automated and Manual)

The Contractor may use either automated or manual Soxhlet extraction.

10.1.2.3.1 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.

10.1.2.3.1.1 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.

10.1.2.3.1.2 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.

10.1.2.3.1.3 Transfer the entire sample from the beaker (Section 10.1.2.1.2 or 10.1.2.1.3) to the thimble. Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.4) to the sample.

10.1.2.3.1.4 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.

10.1.2.3.1.5 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 shall be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

10.1.2.3.1.6 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.

10.1.2.3.1.7 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.

10.1.2.3.1.8 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.

10.1.2.3.2 Manual Soxhlet Extraction

10.1.2.3.2.1 Transfer the entire sample (Section 10.1.2.1.2 or 10.1.2.1.3) from the beaker to an extraction thimble. Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.4) to the sample. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble.

10.1.2.3.2.2 Place approximately 300 mL of the extraction solvent into a 500 mL round bottom flask containing one or two clean boiling chips.

10.1.2.3.2.3 Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles/hour. Allow the extract to cool after the extraction is complete.

10.1.2.3.2.4 Proceed to Section 10.2.

10.1.2.4 Pressurized Fluid Extraction

10.1.2.4.1 Transfer the entire sample from the beaker (Section 10.1.2.1.2) to an extraction cell of the appropriate size for the aliquot. Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.4) to the sample.

10.1.2.4.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.2.4.3 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.

10.1.2.4.4 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

10.1.2.4.5 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 shall be used to achieve the conditions in Section 10.1.2.4.4.

10.1.2.4.6 Once established, the same pressure shall be used for all samples in the same SDG.

10.1.2.4.7 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.

10.1.2.5 Microwave Extraction

10.1.2.5.1 For soil/sediment and non-oily waste samples, weigh out 30 ±0.1 g of the processed sample (Section 10.1.2) and transfer to a microwave extraction vessel. Add sufficient anhydrous powdered or granulated sodium sulfate, or Hydromatrix™ and mix well to produce a free-flowing mixture.

10.1.2.5.2 Add 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.4). Add 25 mL of the 1:1 (v/v) acetone/methylene chloride extraction solvent and cap the vessel per the manufacturer's instructions.

10.1.2.5.3 Place the extraction vessel in the laboratory microwave and proceed with the manufacturer's specified setup procedure. This may include placing additional vessels containing water or other materials to ensure consistent exposure to microwaves across extractions.

10.1.2.5.4 Optimize the extraction conditions per the manufacturer's instructions. The following set of conditions may serve as a starting point:

Temperature:	100-115°C
Pressure:	50-150 psi
Time at Temperature:	10-20 minutes
Cooling to room temperature	
Filter/Rinse with same solvent system	

10.1.2.5.5 Proceed to Section 10.2.

10.1.3 Waste Dilution

Oily waste samples are prepared using the following waste dilution procedure.

10.1.3.1 Measure a 0.20 g aliquot of the waste sample to a separate 20 mL vial or 10 mL volumetric flask (record weight to the nearest 0.01 g).

10.1.3.2 Spike the sample with 1.0 mL of the surrogate standard spiking solution (7.2.2.4), mix with 1 g of anhydrous sodium sulfate (or Hydromatrix™), and immediately add approximately 5 mL of hexane to dilute the sample.

10.1.3.3 Shake the vial or flask for 2 minutes.

10.1.3.4 Loosely pack a disposable Pasteur pipette with 2-3 cm glass wool plugs. Filter the extract through the glass wool and rinse the glass wool several times with 1-2 mL of hexane. Adjust the final extract volume to 10 mL. Proceed to Section 10.3 for Florisil cleanup, GPC cleanup (optional), and other optional cleanup procedures, as needed. Concentrate the final extract volume to the same volume used for Florisil cleanup prior to analysis.

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 volumes of concentrator tube and evaporative flask are permitted to increase the process efficiency. 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 – Target Analyte List and Contract Required Quantitation Limits, Table 3.

10.2.1.2 For aqueous/water and TCLP or SPLP leachate 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, waste, and wipe samples, directly transfer the extract to the K-D concentrator, if the extract is known to be dry. Refer to Section 10.2.1.2 if the extract is known to be wet or shows visible signs of moisture.

10.2.1.4 Rinse the original container collecting the extract (for all samples) and the column (for aqueous/water and TCLP or SPLP leachate 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 aqueous/water and TCLP or SPLP leachate samples (and less than 10 mL for soil/sediment, waste, and wipe 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 aqueous/water and TCLP or SPLP leachate sample extracts that do not require GPC cleanup, and for all sample extracts that have been through the GPC cleanup step, proceed with the hexane exchange procedure described in Section 10.2.2.

10.2.1.7 For aqueous/water and TCLP or SPLP leachate sample 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, waste, and wipe sample extracts, it is absolutely necessary prior to GPC cleanup to further reduce the volume of the 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 GPC

cleanup. Adjust the extract volume to 10 mL with methylene chloride. Proceed to Section 10.3.1 for GPC cleanup.

10.2.2 Solvent Exchange into Hexane

This procedure applies to all sample extracts.

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 sample extracts that have not been subjected to GPC cleanup, adjust the volume of the hexane extract to 10 mL. For sample extracts that have 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. The extract final volumes specified are intended to enable achievement of the CRQLs in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 3, using the recommended initial sample amounts. Other volumes may be used so long as method performance criteria and CRQLs are met.

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 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 0.2 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 aqueous/water and TCLP or SPLP leachate sample extracts 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 any sample extract that has 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 shall 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 aqueous/water and TCLP or SPLP leachate sample extracts 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 any sample extract that has already undergone GPC cleanup, adjust the volume with hexane to 1.0 or 2.0 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 (1.0 or 2.0 mL) and proceed to Section 10.4 for GC/ECD analysis. Extracts shall 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 shall not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of new tubing shall 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, Florisil cartridge cleanup, and sulfur cleanup. GPC cleanup shall be performed for all soil/sediment, waste, and wipe sample extracts. GPC cleanup may be performed for aqueous/water and TCLP or SPLP leachate sample extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. Florisil cartridge cleanup is mandatory for all extracts. Sulfur cleanup shall be performed for all sample extracts contaminated with sulfur. Method blanks shall be subjected to the same cleanup procedures as the samples (including LCSs and MS/MSDs). If a method blank, associated with all samples requiring sulfur cleanup, is not subjected to the same sulfur cleanup procedure as the associated samples, then a separate sulfur cleanup blank is required.

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 verification; 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 a UV detector connected to the GPC column.

10.3.1.3.2 Frequency of GPC Calibration

Each GPC system shall be calibrated prior to processing samples under the contract, when the GPC calibration verification 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 UV Detector 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 shall be monitored.

10.3.1.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.2.7.1) 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 shall 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 aqueous/water sample,

calculate the analyte concentrations using Equation 4C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

10.3.1.3.4 Technical Acceptance Criteria for GPC Calibration

10.3.1.3.4.1 The GPC system shall 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 must be symmetrical for all compounds in the calibration solution;
- Corn oil and phthalate peaks must exhibit greater than 85% resolution;
- Phthalate and methoxychlor peaks must exhibit greater than 85% resolution;
- Methoxychlor and perylene peaks must exhibit greater than 85% resolution; and
- Perylene and sulfur peaks must not be saturated and must 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 – Target Analyte List and Contract Required Quantitation Limits, Table 3.

10.3.1.3.4.5 A copy of the two most recent UV traces of the calibration solution shall 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 requirements in Section 10.3.1.3.4 cannot be met, the column may be cleaned by processing several 5 mL volumes of butylchloride through the system to remove the discoloration and possible precipitated particles. If a guard column is being used, replace it with a new one. It may be necessary to obtain a new lot of Bio Beads in order to correct the criteria failures.

10.3.1.3.5.2 If the flow rate and/or column pressure do not fall within the manufacturer’s specified ranges, a new column shall be prepared.

10.3.1.3.5.3 A UV trace that does not meet the criteria in Section 10.3.1.3.4 would also indicate that a new column shall be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

10.3.1.3.5.4 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 shall be routinely verified with the calibration verification solution specified in Section 7.2.2.7.2.

10.3.1.4.2 Frequency of GPC Calibration Verification

10.3.1.4.2.1 The calibration verification shall 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 shall be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration shall 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 shall 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, 4,4'-DDT, Endrin, and Dieldrin in methylene chloride at the concentrations in Exhibit D - Pesticides, Table 7.

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 shall be performed on only one of the GC columns used for sample analysis.

10.3.1.4.3.4 The recovery of each analyte shall be determined for evaluation and reporting purposes. Calculate the Percent Recovery (%R) of each analyte using Equation 20 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

10.3.1.4.4 Technical Acceptance Criteria for GPC Calibration Verification

The recovery of each analyte must be between 80-110%.

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 shall 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 GPC calibration solution (Section 7.2.2.7.1) and the GPC UV detector calibration procedure (Section 10.3.1.3.3). The UV detector shall 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 shall 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 sample sequence, 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 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 shall be diluted prior to cleanup. Any sample extract with a viscosity greater than that of 1:1 (v/v) glycerol/water solution shall be diluted and loaded into several loops. Similarly, extracts containing more than the manufacturer’s recommended non-volatile residue shall 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 shall be carefully monitored to ensure 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 shall be checked to ensure 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 shall be reprepared, and the sample extract shall be either diluted

and loaded into several loops, or the sample extract shall be injected manually.

10.3.1.6.2 Frequency of Sample Extract Cleanup by GPC

GPC cleanup shall be performed at least once for each aqueous/water and TCLP/SPLP leachate sample extract that contains high molecular weight contaminants that interfere with the analysis of the target analytes. GPC cleanup must be performed for all soil/sediment, waste, and wipe sample extracts. All associated QC samples (blanks, LCSs, and MS/MSDs) shall be subjected to this procedure. GPC cleanup on the method blank shall be performed after all associated samples have been cleaned up (GPC sequence: calibration, GPC blank, 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 shall 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 Florisil cleanup in Section 10.3.2.

NOTE: Any samples that were loaded into multiple loops shall 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 shall 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 shall 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 shall 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 7.2.2.8) 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 used for sample analysis. Determine the recovery of each analyte for evaluation and reporting purposes. Calculate the %R using Equation 20 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 shall 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% (Exhibit D - Pesticides, Table 8), 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 shall be discarded and a new lot, meeting criteria, shall 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 shall be washed with hexane/acetone [(90:10) (V/V)]. 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 shall 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) (V/V)] and 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 shall 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

A sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. If a method blank, associated with all samples requiring sulfur cleanup, is subjected to the same sulfur cleanup procedure as the associated samples, then no separate sulfur cleanup blank is required.

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 5.0 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. 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

10.4.1.1 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 CCV technical acceptance criteria. All sample extracts, required blanks, and calibration standards shall be analyzed under the same instrumental conditions. All sample extracts, required blank extracts, and standard/spiking solutions shall 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 shall be heated to at least 200°C. The optimized GC conditions shall be used.

10.4.2 Procedure for Sample Analysis by GC/ECD

The injection shall be made on-column by using either automatic or manual injection. 1.0 µL or other selected injection volumes may be used provided that all associated standards, samples, and blanks use the same injection volume. The same injection volume shall 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 or twice the selected volume. However, the same injection volume shall be used for all analyses. The TCLP leachate samples including the requested MS/MSD leachates shall be diluted with solvent by a dilution factor of 10 prior to analysis.

10.4.2.1 Analytical Sequence

All acceptable samples shall be analyzed within a valid analysis sequence as given below.

NOTE: The injection # will depend on whether initial calibration sequence 1 or 2 (Section 9.3.3.5) 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, or	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 can 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 shall 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 shall 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 three 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 shall 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.

10.4.3.4.1 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 shall be diluted to have the concentration of the same peak be between the mid-point (CS3) and high-point (CS5) standards of Toxaphene.

10.4.3.5 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 more and the less concentrated extracts shall be reported. The resulting changes in quantitation limits and surrogate recovery shall 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 shall 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 shall also be reported.

10.4.3.7 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.

10.4.3.7.1 When diluted, Toxaphene must be able to be reported at greater than 25% of full scale but less than 100% of full scale.

10.4.3.8 Samples with analytes detected at a level greater than the high calibration point shall 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 concentration after the dilution of 1:100,000, the Contractor shall contact SMO immediately.

10.4.3.10 Sample dilutions shall 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 four to six 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 shall 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 - Target Analyte List and Contract Required Quantitation Limits, Table 3, for which a concentration is reported from a GC/ECD 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.

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 1 µL injection of a full volume/weight sample extract or 5 µL injection of a reduced volume/weight sample extract. The semivolatile CRQL values in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 2, 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 aqueous/water samples prepared according to the method described in Section 10.1.1, 5 ng/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 and waste 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. For oily waste samples prepared by the waste dilution procedure described in Section 10.1.3, the corresponding sample concentration is 51,000 µg/kg for single component pesticides and 1260 mg/kg for Toxaphene. For wipe samples prepared according to the method described in Section 10.1.2, the corresponding sample concentration is 50 µg for single component pesticides and 1250 µg for Toxaphene.

11.1.2.4 In order to confirm the identification of Toxaphene, the Contractor shall 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 shall 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 <u>not</u> 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 (2017 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 shall 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 shall be analyzed along with separate reference standards for the analyte to be confirmed.

11.1.2.8 If the analyte cannot be confirmed by either procedure in Section 11.1.2.5 or 11.1.2.7, then an aliquot of the extract prepared for the GC/ECD analysis shall 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 shall 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 shall 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 shall also 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 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 or reported as final results. 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 shall 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 <u>only</u> permitted when accurate electronic integration of peaks cannot be done. If manual integration of peaks is required, it shall be documented in the SDG Narrative.

NOTE: In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC instrument operator shall identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the properly scaled raw chromatogram that clearly shows the manual integration. The GC instrument operator shall also mark each integrated area with the letter "m" on the quantitation report, and initial and date the changes. All edits and manual integrations shall be verified by a second person, who shall also initial the change(s). The printout(s) of the chromatograms displaying the original integration(s) shall be included in the raw data, in addition to the printout(s) of the chromatograms displaying the manual integration(s). This applies to all target analytes listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 3, and surrogates.

11.2.1.4 The Contractor shall quantitate each single component analyte using the average or $\overline{CF}$ 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 Except for an estimated concentration reported for Toxaphene (with an "S" lab qualifier), the quantitation of Toxaphene shall be accomplished by comparing the heights or the areas of each of the four to six major peaks of the Toxaphene in the sample with the $\overline{CF}$ for the same peaks established during the specific five-point calibration. The concentration or amount of the Toxaphene target analyte is calculated by using Equation 4C, 5D, 5E, or 5E-a in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations, where A_x is the area for each of the major peaks of the Toxaphene. The concentration of each peak in the sample chromatogram is determined and the mean concentration for the four to six major peaks is determined on each column.

NOTE: An estimated concentration (reported with an "S" lab qualifier) of the initial detection for Toxaphene using a single-point calibration standard will be quantitated using the CF, of the four to six major peaks, from the specific single-point calibration standard.

11.2.1.6 When Toxaphene is detected in a sample, using a single point calibration, a valid five-point calibration of Toxaphene shall be performed, followed by reanalysis of the sample or appropriately diluted sample (if the sample concentration of Toxaphene exceeded calibration) with the Toxaphene detected initially. If a valid five-point calibration curve is available, the $\overline{CF}$ will be used for quantitation of the Toxaphene in the sample; however, quantitation of the surrogate compounds shall use the surrogate $\overline{CF}$ from the five-point initial calibration of Individual Standard Mixture or Individual Standard Mixture A if two Individual Standard Mixtures are used.

11.2.1.7 The chromatograms of all samples (including LCSs and MS/MSDs), standards, and required blanks shall be reviewed by a qualified pesticide analyst before they are reported.

11.2.2 Target Analyte Calculations

11.2.2.1 Calculate the aqueous/water/TCLP/SPLP, soil/sediment/waste, and wipe sample concentration or amount and on-column concentration of the pesticides and surrogates by using Equation 4C, 4C-a, 5D, 5E (if wipe sample area is not provided), or 5E-a (if wipe sample area is provided) as applicable in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.2.2 The lower of the two concentrations or amounts calculated for each pesticide is reported as the final result and the analyte concentrations calculated for each GC column are reported for each analysis. The %D is calculated using Equation 25 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.2.3 The quantitation of Toxaphene shall be performed by comparing the heights or the areas of each of the four to six major peaks of the sample with the $\overline{CF}$ for the same peaks established during the initial calibration sequence. The concentration or amount of Toxaphene is calculated by using Equation 4C, 5D, 5E, or 5E-a in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations, 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 four to six major peaks is determined on each column.

11.2.2.4 The reporting requirement for Toxaphene is similar to that for the single component analytes, except that the lower mean concentration (from four to six peaks) is reported as the final result and the mean concentration is reported as the analyte result for each column analysis. The two mean concentrations are compared by calculating the %D using Equation 25 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.3 Contract Required Quantitation Limit Calculations

Calculate the aqueous/water/TCLP/SPLP, soil/sediment, waste, and wipe sample adjusted CRQL using Equation 6C, 7D, 7E (if wipe sample area is not provided), or 7E-a (if wipe sample area is provided) as applicable in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.4 Deuterated Monitoring Compound Recoveries

Not applicable to this method.

11.2.5 Surrogate Recoveries

11.2.5.1 The amounts for surrogate compounds are calculated by using Equation 22C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Use the $\overline{CF}$s (Equation 1 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations) from the initial calibration. If two Individual Standard Mixtures are used, the $\overline{CF}$s from Individual Standard Mixture A are to be used.

11.2.5.2 Calculate the surrogate recoveries for each GC column using Equation 22 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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.

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 shall be performed on each GC column.

11.3.1 Samples shall 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. Samples shall be cleaned up, when required, with GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration verification. Samples shall be cleaned-up using Florisil that meets the technical acceptance criteria for Florisil Cartridge Performance Check. Sample analysis shall 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 shall 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 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 the extract shall 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 shall 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. Any samples analyzed that do not meet the technical acceptance criteria will require re-extraction and/or reanalysis.

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 shall be reanalyzed 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, shall be checked to ensure that the proper amount was injected on the GPC column. If insufficient volume was injected, the sample shall be reprepared and reanalyzed.

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.

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 a 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 shall 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 criteria 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 Appendix B – Codes for Labeling Data.

11.4.6 If the required corrective actions for sample re-extraction, reanalysis, and/or dilution cannot be performed due to insufficient sample volume, the Contractor shall contact SMO.

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 shall 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/water samples, or purified sodium sulfate or Hydromatrix™ for soil/sediment and waste samples) carried through the entire analytical procedure. A method blank is prepared for the wipe samples using either the wipes designated for QC shipped together with the samples or the reference matrix used for the soil/sediment samples. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the method blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of the samples. The leachate extraction blank shall be extracted and reported as PLEB##.

12.1.2.2 Frequency of Method Blank

A method blank shall 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:

- Processed with the same procedures used to extract and cleanup the samples; and
- Analyzed on each GC/ECD system under the same conditions used to analyze associated samples.

12.1.2.3 Procedure for Method Blank

For aqueous/water samples, measure a 1.0 L volume of reagent water and spike with 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.4). If an alternate aqueous/water sample aliquot volume (e.g., 500 mL) is used, measure the same volume (e.g., 500 mL) of reagent water, and spike a reduced amount (e.g., 500 µL) of the surrogate standard spiking solution in the blank sample aliquot. For wipe samples, add 10 g of sodium sulfate or Hydromatrix™ to the wipe designated for QC and spike with 1.0 mL of the surrogate standard spiking solution. If no wipes are received for QC, the Contractor shall notify SMO, note the issue in the SDG Narrative, and prepare the method blank by measuring 10 g of sodium sulfate or Hydromatrix™ and spiking with 1.0 mL of the surrogate standard spiking solution. For soil/sediment and waste samples, measure 30 g of sodium sulfate

or Hydromatrix™ and spike with 1.0 mL of the surrogate standard spiking solution. If an alternate soil/sediment or waste sample aliquot amount (e.g., 15 g) is used, measure the same amount (e.g., 15 g) of the reference matrix, and spike a reduced amount (e.g., 500 µL) of the surrogate standard spiking solution in the blank sample aliquot. For oily waste samples prepared using the waste dilution procedure, measure 1.0 g of sodium sulfate or Hydromatrix™ and spike with 1.0 mL of the surrogate standard spiking solution. Extract, concentrate, clean up, and analyze the method blank according to Section 10.0. Method blanks shall be carried through any and all cleanup procedures as the samples in the same preparation batch.

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 shall be performed on each GC column.

12.1.2.5.2 All method blanks shall 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 shall undergo GPC cleanup, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration verification. Method blanks shall be cleaned up using Florisil meeting the technical acceptance criteria for Florisil.

12.1.2.5.3 Method blanks shall be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and CS3 Standards, as described in Section 10.4.2.1.

12.1.2.5.4 The concentration of each target analyte in the method blank must be less than the CRQL listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 3.

12.1.2.5.5 The method blank must meet the sample technical acceptance criteria in Sections 11.3.5 and 11.3.8.

12.1.2.5.6 Surrogate recoveries in the method blank must fall within the acceptance window in Exhibit D - Pesticides, Table 10. These limits are not advisory.

12.1.2.5.7 All method blanks shall 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 a problem, then the source of the contamination shall 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. 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 shall be re-extracted and reanalyzed.

12.1.2.6.4 If the method blank fails to meet a technical acceptance criteria 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 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 sulfur cleanup blank must be the same as the final volume of the samples associated with the sulfur cleanup blank. The sulfur cleanup 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 sulfur cleanup blank.

12.1.3.3.3 Analyze the sulfur cleanup 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 cleanup blank resulted from the extraction of a 1.0 L aqueous/water sample, calculate the concentration of each analyte using Equation 4C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Compare the results to the CRQL values in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 3. If a reduced sample aliquot amount is used for the samples and method blanks, the sulfur cleanup blank result shall be calculated using the same reduced volume.

12.1.3.4.2 See Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 shall be performed on each column.

12.1.3.5.2 All sulfur cleanup blanks shall 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 shall be bracketed at 12-hour intervals (or less) by acceptable analyses of instrument blanks, PEMs, and Individual Standard Mixtures, as described in Section 10.4.2.1.

12.1.3.5.4 The concentration of each target analyte in the sulfur cleanup blank must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 3.

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 criteria in Exhibit D - Pesticides, Table 10. 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 shall consider the analytical system to be out of control.

12.1.3.6.2 If contamination is a problem, then the source of the contamination shall 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. 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 shall be reprepared/re-extracted and reanalyzed.

12.1.3.6.4 If the sulfur cleanup blank fails to meet a technical acceptance criteria 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) 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 shall 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. If a reduced sample aliquot amount is used for samples and method blanks, the surrogate standard spiking solution concentrations shall be lowered to take into the account the proportionally reduced final extract volume to result in the same surrogate concentrations.

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 aqueous/water sample, calculate the concentration of each analyte using Equation 4C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Compare the results to the CRQL values for aqueous/water samples in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 3. If a reduced sample aliquot amount is used for the samples and method blanks, the instrument blank result shall be calculated using the same reduced volume.

12.1.4.4.2 See Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 shall be performed and reported independently for each GC column.

12.1.4.5.2 All instrument blanks shall 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 in the instrument blank must be less than the CRQL listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 3.

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 shall 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 shall be stopped, and corrective action shall 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 shall 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 shall be reinjected during a valid analytical sequence and shall be reported.

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

12.2.2.1 An MS/MSD sample shall be extracted and analyzed for every 20 or fewer field samples of a similar matrix in an SDG. MS/MSD samples shall be analyzed unless otherwise specified on the Traffic Report/Chain of Custody (TR/COC) Record. An MS/MSD analysis is not required for wipe samples.

12.2.2.2 Samples identified as field blanks or PE samples shall not be used for MS/MSD analysis.

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

12.2.3 Procedure for Preparing Matrix Spike and Matrix Spike Duplicate

12.2.3.1 For aqueous/water samples, prepare two additional aliquots of the sample selected for spiking at the same volume used for the original sample. If a 1.0 L sample aliquot volume is prepared, fortify each with 1.0 mL of the matrix spiking solution (Section 7.2.2.5). Using a syringe or volumetric pipette, add 1.0 mL of surrogate standard spiking solution to each sample (Section 7.2.2.4). If an alternate sample aliquot volume (e.g., 500 mL) is used, add a reduced volume (e.g., 500 µL) of the matrix spiking solution and a reduced volume (e.g., 500 µL) of the surrogate standard spiking solution to each MS/MSD sample, with the proportionally reduced final extract volume without GPC cleanup (e.g., half that specified at 5.0 mL). 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 and waste samples, prepare two additional aliquots of the sample selected for spiking at the same weight used for the original sample. If a 30 g sample aliquot amount is prepared, add 1.0 mL of the matrix spiking solution (Section 7.2.2.5) and 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.4). If an alternate sample aliquot amount (e.g., 15 g) is used, add a reduced volume (e.g., 500 µL) of the matrix spiking solution and a reduced volume (e.g., 500 µL) of the surrogate standard spiking solution to each MS/MSD sample, with the proportionally reduced final extract volume prior to GPC cleanup (e.g., half that specified at 5.0 mL). For oily waste samples prepared using the waste dilution procedure, add 1.0 mL of the matrix spiking solution (Section 7.2.2.5) and spike with 30 µL of the surrogate standard spiking solution (Section 7.2.2.4). 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 results will to 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 shall be analyzed and reported at a 1:10 dilution only. Do <u>not</u> dilute MS/MSD samples further to get either spiked or non-spiked analytes within calibration range. Sample dilutions shall 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 4C and 5D in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations). Calculate the recovery of each Matrix Spike analyte using Equation 23 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD sample using Equation 24A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.5 Technical Acceptance Criteria for Matrix Spike and Matrix Spike Duplicate

12.2.5.1 The requirements below apply independently to <u>each</u> GC column and to all instruments used for these analyses. Quantitation shall be performed on each GC column.

12.2.5.2 All MS/MSDs shall 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 shall 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 10.4.2.1.

12.2.5.3 The MS/MSD sample shall be extracted and analyzed within the contract required holding time.

12.2.5.4 The RT for each of the surrogates in the MS/MSD sample must be within the RT window as calculated in Section 9.3.4.4 for both GC columns.

12.2.5.5 The percent recovery and RPD limits for the spiking analytes listed in Exhibit D – Pesticides, Table 11, are advisory. No further action by the Contractor is required when these criteria are not met. There are no specified limits for the spiking analytes that are not listed in Table 11. However, the amount added, percent recovery, and RPD values for each spiking analyte shall be reported.

12.2.6 Corrective Action for Matrix Spike and Matrix Spike Duplicate

Any MS/MSD sample that does not meet the technical acceptance criteria in Sections 12.2.5.1, 12.2.5.2, and 12.2.5.4 shall be reanalyzed.

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 shall be prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix, per preparation batch. The LCS shall 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 Preparing Laboratory Control Sample

12.3.3.1 For aqueous/water samples, measure out 1.0 L of reagent water and spike with 1.0 mL of the LCS spiking solution (Section 7.2.2.6) and 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.4). If an alternate sample aliquot volume (e.g., 500 mL) is used, add a reduced volume (e.g., 500 µL) of the LCS spiking solution and a reduced volume (e.g., 500 µL) of the surrogate standard spiking solution to reagent water, with the proportionally reduced final extract volume without GPC cleanup (e.g., half that specified at 5.0 mL). Extract, concentrate, and analyze the sample according to Section 10.0.

12.3.3.2 For soil/sediment and waste 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 7.2.2.6) and 1.0 mL of surrogate standard spiking solution (Section 7.2.2.4). If an alternate sample aliquot amount (e.g., 15 g) is used, add a reduced volume (e.g., 500 µL) of the LCS spiking solution and a reduced volume (e.g., 500 µL) of the surrogate standard spiking solution to the clean reference matrix, with the proportionally reduced final extract volume prior to GPC cleanup (e.g., half that specified at 5.0 mL). For oily waste samples prepared using the waste dilution procedure, add 1.0 mL of the LCS spiking solution (Section 7.2.2.6) and spike with 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.4). Extract, concentrate, and analyze the LCS according to Section 10.0.

12.3.3.3 For wipe samples, add 10 g of sodium sulfate or Hydromatrix™ to the wipe designated for QC shipped together with the samples, and spike with 1.0 mL of the LCS spiking solution (Section 7.2.2.6) and 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.4). If no wipes are received for QC, the Contractor shall notify SMO, note the issue in the SDG Narrative, and prepare the LCS by measuring 10 g of sodium sulfate or Hydromatrix™ and spiking with 1.0 mL of the LCS spiking solution and 1.0 mL of the surrogate standard spiking solution.

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 26A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.3.4.3 Calculate the surrogate recoveries for the LCS using Equation 22 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 shall be performed on each GC column.

12.3.5.2 The LCS shall 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 shall be prepared as described in Section 12.3.3.

12.3.5.4 The LCS must meet all sample technical acceptance criteria in Section 11.3.5.

12.3.5.5 The %R for the spiking analytes in the LCS listed in Exhibit D - Pesticides, Table 12, must be within the recovery limits listed in Table 12. There are no specified limits for the spiking analytes that are not listed in Exhibit D - Pesticides, Table 12. However, the amount added and percent recovery values for each spiking analyte shall be reported.

12.3.5.6 Surrogate recoveries must fall within the acceptance criteria in Exhibit D - Pesticides, Table 10. 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.

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.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed under the contract, the MDL for each single compound pesticide target analyte and Toxaphene shall be determined for each instrument under the same conditions used for analysis (i.e., analytical system configuration, as well as type and dimension of GC column), prior to the start of contract analyses and verified annually thereafter. MDL determination is matrix-specific (i.e., the MDL shall be determined for aqueous/water and soil/sediment samples. The MDL determined for aqueous/water samples shall be used for TCLP and SPLP leachates. For wipe samples, the results of the MDL study performed for soil/sediment samples shall be used, and reported in the appropriate units. The MDL determined for soil/sediment samples shall be used for waste samples.). An MDL study shall also be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis. 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.

12.4.1.1 To determine the MDLs, the Contractor shall perform MDL studies following the procedures in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.

12.4.1.2 The determined concentration of the MDL must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 3.

12.4.1.3 The delivery requirements for the MDL values are specified in Exhibit B – Reporting and Deliverables Requirements, Table 1.

13.0 METHOD PERFORMANCE

Not Applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3520C, Continuous Liquid-Liquid Extraction, Revision 3, December 1996.

16.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3535A, Solid-Phase Extraction, Revision 1, February 2007.

16.4 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3540C, Soxhlet Extraction, Revision 3, December 1996.

16.5 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3541, Automated Soxhlet Extraction, Revision 0, September 1994.

16.6 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3545A, Pressurized Fluid Extraction (PFE), Revision 1, February 2007.

16.7 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3546, Microwave Extraction, Revision 0, February 2007.

16.8 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3550C, Ultrasonic Extraction, Revision 3, February 2007.

16.9 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3580A, Waste Dilution, Revision 1, July 1992.

16.10 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3620C, Florisil Cleanup, Revision 4, July 2014.

16.11 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3640A, Gel-Permeation Cleanup, Revision 1, September 1994.

16.12 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 8081B, Organochlorine Pesticides by Gas Chromatography, Revision 2, February 2007.

16.13 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

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
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

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'-(2,2,2-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 STANDARDS 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

Analyte	Resolution Check Mixture (RESC)	Performance Evaluation Mixture (PEM)
	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)
alpha-BHC	0.50	0.050	
beta-BHC	0.50	0.050	
delta-BHC	0.50	0.050	
gamma-BHC (Lindane)	0.50	0.050	0.020
Heptachlor	0.50	0.050	0.020
Aldrin	0.50	0.050	0.020
Heptachlor epoxide	0.50	0.050	
Endosulfan I	0.50	0.050	
Dieldrin	1.0	0.10	0.040
4,4'-DDE	1.0	0.10	
Endrin	1.0	0.10	0.040
Endosulfan II	1.0	0.10	
4,4'-DDD	1.0	0.10	0.040
Endosulfan sulfate	1.0	0.10	
4,4'-DDT	1.0	0.10	
Methoxychlor	5.0	0.50	
Endrin ketone	1.0	0.10	
Endrin aldehyde	1.0	0.10	
cis-Chlordane	0.50	0.050	
trans-Chlordane	0.50	0.050	

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 Aqueous/Water	RPD Aqueous/Water	Percent Recovery Soil/Sediment and Waste	RPD Soil/Sediment and Waste
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 Aqueous/Water/Soil/Sediment/Waste and Wipes
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

EXHIBIT D

AROCLORS ANALYSIS

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Exhibit D – Aroclors Analysis

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Exhibit D – Aroclors Analysis

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1.0 SCOPE AND APPLICATION

The analytical method that follows is designed to analyze aqueous/water, soil/sediment, waste, and wipe 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 – Target Analyte List and Contract Required Quantitation Limits. The method, based on the U.S. Environmental Protection Agency (EPA) 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 Aqueous/Water

A suitable sample aliquot volume [minimum 1.0 Liter (L)] is spiked with a surrogate solution and extracted using a separatory funnel, a continuous liquid-liquid extractor, or a solid-phase extraction disk. The extract is dried with anhydrous sodium sulfate (or an equivalent drying agent such as Hydromatrix™), concentrated, and may be subjected to Gel Permeation Chromatography (GPC) cleanup (optional). The extract is then solvent exchanged into hexane, a 1 or 2 milliliter (mL) aliquot of the extract is subjected to sulfuric acid cleanup, and the final volume is adjusted to the same volume as the aliquot (1 mL or 2 mL). The extract is analyzed using a dual column (widebore and megabore) capillary GC/ECD.

2.2 Soil/Sediment

A suitable sample aliquot amount [minimum 30 grams (g)] is spiked with a surrogate solution, 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. For microwave extraction, the sample is air-dried, spiked with a surrogate solution, and extracted with a 1:1 (v/v) acetone/methylene chloride solvent mixture. The extract is filtered (for ultrasonic extraction), concentrated, and may be subjected to GPC cleanup (optional). The extract is then solvent-exchanged into hexane. A 1 or 2 mL aliquot of the extract is subjected to sulfuric acid cleanup. The final volume is adjusted to the same volume as the aliquot (1 mL or 2 mL) and the extract is analyzed using a dual column (widebore and megabore) capillary GC/ECD.

2.3 Wipes

A hexane-saturated glass wool or gauze wipe sample is spiked with a surrogate solution, mixed with anhydrous sodium sulfate (or Hydromatrix™), and extracted with a 1:1 (v/v) acetone/methylene chloride solvent mixture by ultrasonic extraction or Soxhlet extraction. The extract is filtered (for ultrasonic extraction), concentrated, and may be subjected to GPC cleanup (optional). The extract is then solvent-exchanged into hexane. A 1 or 2 mL aliquot of the extract is subjected to sulfuric acid cleanup. The final volume is adjusted to the same volume as the aliquot (1 mL or 2 mL) and the extract is analyzed using a dual column (widebore and megabore) capillary GC/ECD.

2.4 Waste

Solid waste samples are extracted and analyzed using the soil/sediment methods in Section 2.2. Alternatively, oily waste samples are prepared using a waste dilution procedure. A 0.20 g aliquot of the oily waste sample is spiked with a surrogate solution, mixed with anhydrous sodium sulfate (or Hydromatrix™), and diluted with 10 mL of hexane. A 1 or 2 mL aliquot of the extract is subjected to sulfuric acid cleanup and other applicable procedures in Section 10.3 to a final extract volume of 1 or 2 mL prior to analysis.

3.0 DEFINITIONS

See Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 to elevated baselines in Gas Chromatograms. The method shall 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 on the nature of the site being sampled. The cleanup procedures in this method shall be used to remove such interferences in order to achieve the CRQLs.

5.0 SAFETY

See Section 12.0 of Exhibit D – Introduction to 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, demonstration of equivalent performance that meets 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.

All instruments, balances, heating, and measuring equipment and devices shall be uniquely identified and labeled to allow traceability to any corresponding records of use.

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 The balance calibration shall be checked with known masses once per each day of use. This verification shall consist 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 shall be checked on a monthly basis using National Institute of Standards and Technology (NIST)-traceable known reference masses (Class ‘0’ or Class ‘1’) as defined by ASTM E617-13 or equivalent (e.g., earlier Class ‘S’ defined masses). All balances shall be checked at least once annually by a certified technician. The reference masses used by the Contractor shall 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, Tabletop (optional).

6.1.3.1 Centrifuge Tube - 12-15 mL with 19 millimeter (mm) ground-glass joint (optional).

6.1.4 Desiccator - Containing a desiccant indicator compound.

6.1.5 Erlenmeyer Flasks - 250 mL.

6.1.6 Graduated Cylinders Class A – 100 mL, 500 mL, and 1 L capacity.

6.1.7 Magnetic Stirring Bars – Polytetrafluoroethylene (PTFE) coated, at least 4 centimeters (cm) long.

6.1.8 Ovens – Drying, capable of maintaining 105°C (±5°C).

6.1.9 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.

6.1.10 pH Paper – Wide range.

6.1.11 Pasteur Pipettes – Regular and packed with glass wool plugs.

6.1.12 Pipettes (Calibrated) - Glass volumetric, l.0 mL or 2.0 mL. Manufacturer's instructions shall be followed for the calibration and maintenance of adjustable pipettes.

6.1.13 Sieve – No. 18 mesh with nominal pore size of 1 mm and a collection pan and cover.

6.1.14 Spatulas - Stainless steel or PTFE.

6.1.15 Syringes – 10 microliters (µL), 25 µL, 100 µL, and 1000 µL.

6.1.16 Vials and Caps - 10 mL (optional), with screw-cap and PTFE or aluminum foil liner; autosampler vial with 2 mL capacity for GC autosampler.

6.1.17 Volumetric Flasks, Class A – 5.0, 10, 20, 50, 100, 250, and 500 mL.

6.1.18 Weigh Dishes – Porcelain crucibles or disposable aluminum weighing pans.

6.2 Glassware/Extraction/Cleanup Equipment

6.2.1 Separatory Funnels - 2 L with PTFE stopcock.

6.2.1.1 Borosilicate Glass Wool - Rinsed with methylene chloride.

6.2.2 Continuous Liquid-Liquid Extractors - Equipped with PTFE or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf extractor) or hydrophobic membrane-based extractor.

6.2.3 Solid-Phase Extraction System

6.2.3.1 Extraction Disks – 90 mm or 47 mm C_{18} disks.

6.2.3.2 Solid-phase Disk Extraction System – Manifold that holds three 90 mm filter standard apparatus or six 47 mm standard filter apparatus, or equivalent. Includes sample reservoirs, clamps, fritted disks, and filtration head with drip tip.

6.2.3.3 Vacuum Extraction Manifold – Equipped with flow/vacuum control.

6.2.3.4 Sample Delivery System – Equipped with transfer tube system and sample reservoir(s), or 60 mL collection tubes.

6.2.4 Sonication Equipment

6.2.4.1 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 shall 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.

6.2.4.2 Sonabox Acoustic Enclosure (or equivalent) - For use with disruptor to decrease noise level.

6.2.4.3 Vacuum Filtration Apparatus

6.2.4.3.1 Buchner Funnel.

6.2.4.3.2 Filter Paper – Whatman No. 42, or equivalent.

6.2.5 Automated Soxhlet Extraction System - With temperature-controlled oil bath. Silicone oil shall not be used because it destroys the rubber parts. The apparatus shall be used in a hood.

6.2.5.1 Cellulose or Glass Extraction Thimble, 26 mm x 60 mm.

6.2.5.2 Glass Extraction Cups.

6.2.5.3 Thimble Adapters.

6.2.5.4 Viton Seals.

6.2.6 Soxhlet Extraction, Manual

6.2.6.1 Allihn Condenser.

6.2.6.2 Cellulose or Glass Extraction Thimble, 35 mm x 90 mm.

6.2.6.3 Soxhlet Extractor body, 40 mm ID.

6.2.6.4 Round bottom flask, 500 mL.

6.2.7 Pressurized Fluid Extraction Device

6.2.7.1 Dionex Accelerated Solvent Extractor (ASE-350) or equivalent with appropriately-sized extraction cells. Currently, 100 mL cells that will accommodate greater than 30 g samples are available. 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.

6.2.7.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

6.2.8 Microwave Extraction System

6.2.8.1 Laboratory Microwave – Capable of maintaining sample temperature within ±2.5°C and adjusting power within 2 seconds.

6.2.8.2 Microwave Extraction Vessels – Capable of accepting up to 30 g of sample, transparent to microwave energy, and capable of withstanding temperatures of 200°C minimum and pressures of 200 psi minimum.

6.2.8.3 The laboratory shall maintain separate vessels for the digestion of metals and solvent extraction of organics and follow manufacturer’s instructions with regard to monitoring and maintaining sample temperature during microwave extraction.

6.2.9 Kuderna-Danish (K-D) Apparatus

6.2.9.1 Concentrator Tubes - 10 mL and 15 mL, graduated.

6.2.9.2 Drying Column – 400 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).

6.2.9.3 Evaporative Flasks - 500 mL.

6.2.9.4 Silicon Carbide Boiling Chips – Approximately 10/40 mesh. Heat to 400°C for 30 minutes or solvent-rinsed with methylene chloride.

6.2.9.5 Snyder Column - Three-ball macro.

6.2.9.6 Snyder Column - Two-ball micro.

6.2.9.7 Water Bath - Heated, with concentric ring cover, capable of temperature control. The bath shall be used in the hood.

6.2.10 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 shall be used in a hood.

6.2.11 Gel Permeation Chromatography Cleanup System

6.2.11.1 GPC 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, shall meet the calibration requirements in Section 10.3.1.3.

NOTE: Optional GPC cleanup is for all soil/sediment, waste, and wipe sample extracts, and for aqueous/water sample extracts containing higher molecular weight contaminants that interfere with the analyses of the target analytes.

6.2.11.2 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.

6.2.11.3 Guard Column (optional) - 5 cm, with appropriate fittings to connect to the inlet side of the analytical column.

6.2.11.4 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.

6.2.11.4.1 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 verification; 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.

6.2.11.5 UV Detector - Fixed wavelength [254 nanometers (nm)] with a semi-prep flow-through cell.

6.2.11.6 Strip Chart Recorder - Recording integrator or laboratory data system.

6.2.11.7 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.

6.2.11.8 Viscometer

6.2.12 Sulfuric Acid Cleanup

6.2.12.1 Syringe or calibrated Class A volumetric glass pipette, 1.0, 2.0, and 5.0 mL. Manufacturer’s instructions shall be followed for the calibration and maintenance of adjustable pipettes.

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.

6.3 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 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 shall be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room. Adsorbents used in trapping systems must be replaced according to the product replacement periods as recommended by the manufacturer, and at a minimum annually. 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. The instrument shall be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room.

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 (0.53 mm ID) fused silica GC columns may be used provided that the resolution requirements (Section 9.3.5.2) are met; 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 columns used for analysis shall be provided in the SDG Narrative. Packed GC 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 - Target Analyte List and Contract Required Quantitation Limits, Table 4.
- 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 the analytical method in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 4.

- The column can accept at least 16 times the low-point initial calibration concentration level in Exhibit D – Aroclors, Table 2, without becoming overloaded.
- The column pair selected must have dissimilar phases and must produce different patterns to aid in Aroclor confirmation despite chromatographic interferences.
- The column provides equal or better resolution of the analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 4.

6.3.2.1.1 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 shall maintain documentation verifying 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 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 comparison/review, signed by the Laboratory Manager, certifying that:

- The alternate column performance meets the technical acceptance criteria in Section 6.3.2.1;
- 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 that interfere with the identification and/or quantitation of analytes listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 4.

6.3.2.1.4 The documentation shall be made available to the EPA during on-site laboratory evaluations or sent to the EPA upon request by the EPA Regional CLP Contracting Officer's 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 shall 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 shall clearly identify its use in the SDG Narrative in submissions to the EPA. Contractors 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.

6.3.3 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 (5% methane/argon balance), P-10 (10% methane/argon balance), 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 shall be vented to outside the facility or to a trapping system that prevents the release of contaminants into the instrument room. Adsorbents used in trapping systems must be replaced according to the product replacement periods as recommended by the manufacturer, and at a minimum annually.

6.3.3.2 At least annually, or as advised by the local radiation regulatory agency, each ECD shall be checked for radiation leakage from their Ni-63 source. Wipe tests shall 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 shall provide all standards to be used with the contract. These standards shall be used only after they have been certified according to the procedure in Exhibit D – Introduction to Analytical Methods, Section 11.0. The Contractor shall be able to verify that the standards are certified. Manufacturer's certificates of analysis shall 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 a contaminant or 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 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.

7.1.4 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.

7.1.5 Nitric acid - Dilute, for sulfur removal with copper.

CAUTION: DO NOT STORE CONCENTRATED MINERAL ACIDS (SULFURIC, NITRIC) WITH ORGANIC ACIDS.

7.1.6 Sodium hydroxide solution (10 N) - Carefully dissolve 40 g of NaOH in reagent water and dilute the solution to 100 mL.

7.1.7 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 shall be extracted with hexane and analyzed by a GC/ECD to demonstrate that it is free of interference before use or shall 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.

7.1.8 Sodium sulfite.

7.1.9 Solvents: Methylene chloride, hexane, acetone, toluene, iso-octane, 2-propanol, petroleum ether, acetonitrile, and methanol - Aroclor quality or equivalent. It is recommended that each lot of solvent be analyzed to demonstrate that it is free of interference before use or shall be purchased with certification that it is free of interference. Methylene chloride must be certified as acid free or shall be tested to demonstrate that it is free of hydrochloric acid. Acidic methylene chloride shall be passed through basic alumina and then demonstrated to be free of hydrochloric acid.

7.1.10 Sulfuric acid, concentrated, 95-98% (specific gravity 1.84).

CAUTION: DO NOT STORE CONCENTRATED MINERAL ACIDS (SULFURIC, NITRIC) WITH ORGANIC ACIDS.

7.1.11 Tetrabutylammonium (TBA) sulfite.

7.1.12 Glycerol.

7.1.13 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.

7.2 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 prepared in hexane or isooctane, which may contain small amounts of toluene or acetone, from pure standard materials, or purchased as certified pre-made solutions. Prepare fresh stock standards every 6 months, or sooner if the standard has degraded or evaporated, unless acceptability of the standard can be documented (Section 7.2.3.6).

7.2.2 Working Standards

7.2.2.1 Aroclor Standard Mixtures

7.2.2.1.1 The Calibration Standard Mixture solutions shall be prepared in either hexane or iso-octane. The solutions shall be prepared every 6 months, or sooner if the solutions have degraded or concentrated.

7.2.2.1.2 The concentration of each target analyte for each calibration standard are listed in Exhibit D – Aroclors, Table 2. 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.

7.2.2.1.3 Prepare Aroclor and surrogates tetrachloro-m-xylene and decachlorobiphenyl (DCB) calibration standard solutions at a minimum of five concentration levels listed in Exhibit D – Aroclors, Table 2. The standard solutions of each target analyte plus surrogates shall be prepared individually for each Aroclor, except for Aroclor 1260 and Aroclor 1016 which may be combined in one standard mixture.

7.2.2.1.4 Prepare a single-point calibration for Aroclor 1221, 1232, 1242, 1248, 1254, 1262, and 1268 including surrogates at the lowest standard concentration in Exhibit D – Aroclors, Table 2.

7.2.2.1.5 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 shall be used for the initial calibration of the GC/ECD.

7.2.2.1.6 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 Limit (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 Exhibit D – Aroclors, Table 2 (e.g., if a laboratory were using a 50 ng/mL low standard, then the other calibration levels shall be 100, 200, 400, and 800 ng/mL).

7.2.2.2 Continuing Calibration Standard

The CCV Aroclor Standards shall 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 (Exhibit D – Aroclors, Table 2). Use the same source of target analytes (i.e., same manufacturer lot) for CCVs as were used for the preparation of initial calibration standards.

7.2.2.3 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/MSDs), Performance Evaluation (PE) samples (if required), and required blanks (method/sulfur cleanup/ instrument). Add the same source of surrogates (i.e., same manufacturer lot) for the preparation of calibration standards, initial and continuing calibration verification standards, samples, blanks, and MS/MSDs. Add the same surrogate standard spiking solution to LCSs, samples, blanks, and MS/MSDs. 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 shall be checked frequently for stability. The solution shall 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.

7.2.2.4 Matrix Spiking Solution

Prepare a matrix spiking solution containing the Aroclors in Exhibit D – Aroclors, Table 5, in acetone or methanol at the concentrations specified. The solution shall be replaced every 6 months, or sooner if the solution has degraded or concentrated.

7.2.2.5 Laboratory Control Sample Spiking Solution

Prepare an LCS spiking solution containing the Aroclors in Exhibit D – Aroclors, Table 5, in acetone or methanol at the concentrations specified. The LCS solution shall 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 shall 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.

7.2.2.6.2 GPC Calibration Verification Solution

Prepare the GPC calibration verification solution containing the Aroclors listed in Exhibit D – Aroclors, Table 5, 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 shall 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 Working standards shall be prepared every 6 months, or sooner if the solutions have degraded or concentrated, unless acceptability of the standard can be documented to meet the criteria specified in Section 7.2.3.6.1. Working standards shall be checked frequently for signs of degradation or evaporation. Store working standards at ≤6°C in PTFE-lined screw-cap amber bottles/vials and according to the manufacturer's documented holding time recommendations. In the absence of manufacturer's instructions, the solution shall be replaced after 6 months unless the integrity of the solution is suspected of being compromised prior to that time.

NOTE: Refrigeration of GPC calibration solutions may cause the corn oil to solidify. Before use, allow the solution to stand at room temperature until the corn oil dissolves.

7.2.3.3 Store premixed certified solutions according to the manufacturer's documented holding time and storage temperature recommendations. Once the seal is compromised (e.g., ampule is opened), stock solutions for most compounds shall be maintained under the same conditions and assigned the same shelf life as working standards (Section 7.2.3.2). Stock solutions must be replaced in the same timeframe as the working standards unless

acceptability of the standard can be documented to meet the specified criteria (Section 7.2.3.6.1).

7.2.3.4 Protect all standards from light.

7.2.3.5 Samples, sample extracts, and standards shall 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 that, at a minimum, the standards shall be brought to room temperature prior to use, checked for losses, and checked to verify that all components have remained in solution. Additional steps may be necessary to ensure all components are in solution.

7.2.3.6.1 Working standards shall be monitored frequently by comparison to the initial calibration. Fresh standards shall be prepared if the opening CCV criteria can no longer be met (Section 9.4.5) and the shelf life of the working standard is exceeded (Section 7.2.3.2). Standards shall be replaced upon expiration of the shelf life unless acceptability of the standard can be documented to meet all applicable SOW criteria, either by comparison to a compliant initial calibration generated from standards prepared within the shelf life of the working standards or by comparison to a freshly prepared standard.

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 Aqueous/Water Samples

Aqueous/water samples should 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. Smaller sample containers may be used if the Contractor's analytical system can accommodate small volume sample preparation accompanied by large volume injection capability.

8.1.2 Soil/Sediment and Waste Samples

Soil/sediment and waste samples should be collected in glass containers.

8.1.3 Wipe Samples

Wipe samples should be collected in 20 mL glass vials with Teflon-lined caps oversaturated in hexane so there is excess solvent in the vial.

8.2 Sample and Sample Extract Storage

8.2.1 Sample Storage

The samples shall be protected from light and refrigerated at ≤6°C, but not frozen, in an upright position from the time of receipt until 60 days after the delivery of a complete, reconciled data package to the EPA. After 60 days, the samples shall be disposed of in a manner that complies with all applicable regulations.

8.2.2 Sample Extract Storage

Sample extracts shall be protected from light and stored at ≤6°C, but not frozen, until 365 days after the delivery of a complete, reconciled data package to the EPA.

8.3 Contract Required Holding Times

8.3.1 Extraction of aqueous/water samples by separatory funnel or solid-phase extraction procedures shall be completed within 5 days of the Validated Time of Sample Receipt (VTSR). Extraction of aqueous/water samples by continuous liquid-liquid extraction shall be started within 5 days of the VTSR. Extraction of soil/sediment, waste, and wipe samples by the Soxhlet method shall be started within 10 days of the VTSR. Extraction of soil/sediment, waste, and wipe samples by methods other than Soxhlet shall be completed within 10 days of the VTSR. The waste dilution procedure of oily waste samples shall be completed within 10 days of the VTSR.

8.3.2 Analysis of sample extracts shall 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 Exhibit D – Aroclors, Table 4. 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 the GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions shall be used for the analysis of all standards, samples (including LCSs and MS/MSDs), and required blanks (method/sulfur cleanup/instrument).

9.1.1.3 The same injection volume, 1.0 µL or 2.0 µL, must be used for all standards, samples (including LCSs and MS/MSDs), 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 shall 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 shall 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 shall 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 shall be performed prior to reanalysis of samples known to contain the Aroclor.

9.3.2 Frequency of Initial Calibration

Each GC/ECD system shall 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 shall be used for both calibrations and sample analyses.

9.3.3.2 All standards and instrument blanks shall 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 shall be prepared (Section 7.2.2.1) and analyzed for that particular Aroclor, followed by a reanalysis 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 must 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, Mean Retention Times ($\overline{RT}$s) 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. 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. Calculate the $\overline{RT}$ using Equation 11 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 Exhibit D – Aroclors, Table 3. 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 Calibration Factors (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 12 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Calculate the Mean CFs ($\overline{CF}$s) for each set of Aroclor peaks and surrogates over the initial calibration range using Equation 1 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. 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 12 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Either peak area or peak height may be used to calculate the CFs used in the Percent Relative Standard Deviation (%RSD) equation.

9.3.4.7 Calculate the CFs, the $\overline{CF}$, 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 1, 2, 3, and 12 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Either peak area or peak height may be used to calculate the CFs.

9.3.4.7.1 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.

9.3.4.8 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.

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 shall be analyzed according to the procedure listed in Section 9.3.3, at the concentrations 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 shall be followed.

9.3.5.2 The identification of Aroclors by GC methods is based primarily on recognition of patterns of RTs and relative peak heights 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% (Exhibit D – Aroclors, Table 2). 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 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.

NOTE: If any of the DDT analogs elute at the same retention time as an Aroclor peak that was selected for use in quantitation, then the analyst shall 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 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 shall 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.

9.4 Continuing Calibration Verification

9.4.1 Summary of Continuing Calibration Verification

The analyses of instrument blanks and the required Aroclor CS3 standard constitute the calibration verification. Sample data (including LCS and MS/MSD) and required blank (method/sulfur cleanup/instrument) data 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

9.4.2.1 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 the 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 the opening Aroclor CCV technical acceptance criteria in Sections 9.4.5.3 and 9.4.5.4.

9.4.2.2 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 shall 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 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, 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.

9.4.2.3 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.

9.4.2.4 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.

9.4.2.5 No more than 14 hours can elapse from the injection beginning the opening CCV (instrument blank) and the injection ending the closing CCV (Aroclor Standard).

All acceptable samples shall 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
		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)

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 All standards and instrument blanks shall 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 Equation 19 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 Aroclor 1016/1260 standards and Aroclor standards of other detected Aroclors shall 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 RT of each of the Aroclor peaks and surrogates in the calibration verification standard must be within the RT windows 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 any 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 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 that originally failed the criteria and an associated instrument blank immediately after the corrective action does meet all the technical acceptance criteria.

9.4.6.4 If the Aroclor 1016/1260 standard does not meet the technical acceptance criteria listed in Sections 9.4.5.2 - 9.4.5.4, it shall 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 shall be stopped. Appropriate corrective action shall be taken and a new initial calibration sequence shall 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 shall be stopped. Appropriate corrective action shall be taken to clean out the system and an acceptable instrument blank shall 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 shall 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.

9.4.6.9 The corrective action for sample reanalysis is not required when the noncompliant analytes or surrogates, in the opening or closing CCVs bracketing a dilution, a re-extraction, or a reanalysis, are not the same analytes or surrogates for which the dilution, re-extraction, or reanalysis was intended.

10.0 PROCEDURE

The Contractor shall 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 shall 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 Aqueous/Water Samples

Aqueous/Water samples may be extracted by either a separatory funnel procedure, a continuous liquid-liquid extraction procedure, or a solid-phase extraction procedure. Solid-phase extraction is not recommended for samples with greater than 1% solids. If an emulsion prevents acceptable solvent recovery with the separatory funnel procedure, continuous liquid-liquid extraction shall be employed. Allow the samples to warm to ambient temperature before extraction. Sample aliquot amounts other than the specified 1 L can be used for the extraction procedure, provided that the CRQLs listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits can still be achieved by using a proportionally reduced final volume without altering the initial calibration curve. If a smaller sample aliquot amount is selected, 500 mL for example, the surrogate standard spiking solution added to the aliquot shall be reduced accordingly (e.g., 500 µL of the surrogate standard spiking solution) with the reduced final extract volume from 10 mL to 5 mL.

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 7.2.2.3) to all aqueous/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 shall 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 shall 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 7.2.2.3) 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 9 with 10 N sodium hydroxide or concentrated sulfuric acid, if required. Samples requiring the pH adjustment shall 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 (e.g., 50 mL) of methylene chloride and add the rinsate to the continuous extractor.

10.1.1.2.1.7 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.

NOTE 2: Some continuous 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.

10.1.1.2.1.8 Allow to cool and then detach the distillation flask. Proceed to Section 10.2.

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 - 10.1.1.2.1.6, 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 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 shall be used. Allow to cool, then detach the distillation flask. Proceed to Section 10.2.

10.1.1.2.2.4 Some continuous 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 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.

10.1.1.3 Solid-Phase Extraction

10.1.1.3.1 Follow the manufacturer's instructions for set up, using a C_{18} disk. The laboratory may use a filter aid or pre-filter for samples containing particulates. Solid-phase extraction is used for samples without visible solids and is not appropriate for samples with suspended particulate matter or noticeably turbid samples.

10.1.1.3.2 If the samples have been received in 1 L bottles, the laboratory shall mark the meniscus, shake the sample, and add 1.0 mL of the surrogate standard spiking solution. 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 add 1.0 mL of the surrogate standard spiking solution. Other volumes may be used as long as method performance criteria and CRQLs are met.

10.1.1.3.3 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 pH adjustment shall be noted in the SDG Narrative.

10.1.1.3.4 Wash each extraction disk with 20 mL of methylene chloride. Rinse down the sides of the sample reservoir and pull approximately 1 mL of methylene chloride through each disk. Allow the disks to soak for 1 minute, then pull the remaining solvent through the disks and allow them to dry.

10.1.1.3.5 Precondition each disk with 20 mL of methanol. Pull a few drops of methanol through each disk and allow the disks to soak for 1 minute. Pull the methanol through the disks, stopping when there is a thin layer of methanol remaining. Add 20 mL of reagent water and pull the water through the disks, stopping when there is a 2-3 mm layer of water remaining. Do not allow the disks to go dry. Any disk that goes dry shall be reconditioned with both solvents.

10.1.1.3.6 Add the samples to the sample reservoirs and filter through the extraction disks as quickly as possible. Dry the disks by continuing to draw vacuum for 3 minutes after the sample has passed through.

10.1.1.3.7 To elute the disks, remove the filter apparatus from the manifold (do not disassemble) and insert a collection tube with at least a 25 mL capacity. The drip tip shall be seated sufficiently below the neck of the tube to prevent loss by spattering. Add 5 mL of acetone (or volume as specified by the solid-phase extraction system manufacturer) to the sample bottle or graduated cylinder to rinse the vessel. Transfer the rinsate to the extraction reservoir, rinsing as necessary. Pull a few drops through and allow the acetone to soak the disk for 20 seconds. Rinse the sample vessel with 20 ml of acetonitrile or alternative solvents (i.e., hexane, acetone) and transfer the rinsate to the extraction reservoir, rinsing as necessary. Draw approximately one-half the volume of solvent through the disk and allow the remainder to soak the disk for 1 minute. Completely draw the remaining solvent through the disk.

10.1.1.3.8 Proceed to Section 10.2.

10.1.2 Soil/Sediment, Waste, and Wipe Samples

Four procedures are provided for the extraction of Aroclor analytes from soil/sediment, waste, and wipe samples:

- Ultrasonic extraction;
- Soxhlet extraction (automated and manual);
- Pressurized fluid extraction (PFE) – For soil/sediment and waste samples only; and
- Microwave extraction – For soil/sediment and waste samples only.

NOTE: All samples of the same matrix in a Case shall be extracted by the same procedure.

10.1.2.1 For extraction of soil/sediment and waste samples, mix samples thoroughly, especially composite samples. Discard any foreign objects such as sticks, leaves, and rocks. Decant any standing aqueous phase but contact the Sample Management Office (SMO) for EPA Regional approval before discarding. Given the types of the collected samples, soil/sediment/waste shall not require further grinding. However, the Contractor shall contact SMO if samples cannot be processed as received. The appropriate extraction methods to be used are to be determined based on the sample characteristics. The microwave extraction method shall be used only for samples with finely divided particle size (≤1 mm) and alternative extraction methods shall be used for samples with particle size >1 mm. If necessary, remove particles >1 mm from the air dried samples (Section 10.1.2.5.1) by sieving the samples and taking measures to control fugitive dust.

For soil/sediment and waste sample extractions by the ultrasonic, Soxhlet, or pressurized fluid extraction procedure, proceed to Sections 10.1.2.1.1 - 10.1.2.1.4. For soil/sediment and waste sample extraction by the microwave procedure, proceed to Section 10.1.2.5.

10.1.2.1.1 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. For example, 15 g of sample aliquot for extraction can be used along with the proportionally reduced final extract volume prior to GPC cleanup from 10 mL to 5.0 mL, without altering the initial calibration curve. 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.

10.1.2.1.2 Add 60 g of anhydrous powdered or granulated sodium sulfate, or 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 10.1.2.4) the use of sodium sulfate is not recommended.

10.1.2.1.3 For extraction of wipe samples, place the contents of the sample container, including the wipe and excess solvent, into a 400 mL beaker. Add 10 g of anhydrous powdered or granulated sodium sulfate, or 10 g of Hydromatrix™, and mix well.

10.1.2.1.4 Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.3) to each soil/sediment, waste, and wipe sample after it is transferred to the intended extraction device. Then immediately add 100 mL of 1:1 (v/v) acetone/methylene chloride. Proceed to Section 10.1.2.2 for ultrasonic extraction, Section 10.1.2.3 for automated or manual Soxhlet extraction, or Section 10.1.2.4 for pressurized fluid extraction. As applicable, follow the manufacturer's instructions for use of all extraction equipment.

10.1.2.2 Ultrasonic Extraction

10.1.2.2.1 Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.3) to the transferred sample (10.1.2.1.4).

10.1.2.2.2 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 not use a microtip probe.

10.1.2.2.3 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.

10.1.2.2.4 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 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.

10.1.2.3 Soxhlet Extraction (Automated and Manual)

The Contractor may use either automated or manual Soxhlet extraction.

10.1.2.3.1 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.

10.1.2.3.1.1 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.

10.1.2.3.1.2 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.

10.1.2.3.1.3 Transfer the entire sample from the beaker (Section 10.1.2.1.2 or 10.1.2.1.3) to the thimble. Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.3) to the sample.

10.1.2.3.1.4 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.

10.1.2.3.1.5 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 shall be pre-rinsed or pre-extracted with extraction solvent prior to initial use.

10.1.2.3.1.6 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.

10.1.2.3.1.7 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.

10.1.2.3.1.8 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.

10.1.2.3.2 Manual Soxhlet Extraction

10.1.2.3.2.1 Transfer the entire sample from the beaker (Section 10.1.2.1.2 or 10.1.2.1.3) to an extraction thimble. Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.3) to the sample. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble.

10.1.2.3.2.2 Place approximately 300 mL of the extraction solvent into a 500 mL round bottom flask containing one or two clean boiling chips.

10.1.2.3.2.3 Attach the flask to the extractor and extract the sample for 16 - 24 hours at 4 - 6 cycles/hour. Allow the extract to cool after the extraction is complete.

10.1.2.3.2.4 Proceed to Section 10.2.

10.1.2.4 Pressurized Fluid Extraction

10.1.2.4.1 Transfer the entire sample from the beaker (Section 10.1.2.1.2) to an extraction cell of the appropriate size for the aliquot. Add 1.0 mL of surrogate standard spiking solution (Section 7.2.2.3) to the sample.

10.1.2.4.2 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

10.1.2.4.3 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.

10.1.2.4.4 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

10.1.2.4.5 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 shall be used to achieve the conditions in Section 10.1.2.4.4.

10.1.2.4.6 Once established, the same pressure shall be used for all samples in the same SDG.

10.1.2.4.7 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.

10.1.2.5 Microwave Extraction

10.1.2.5.1 For soil/sediment and non-oily waste samples, weigh out 30 ±0.1 g of the processed sample (Section 10.1.2) and transfer to a microwave extraction vessel. Alternatively, air dry 40-60 g of sample on a glass tray or hexane rinsed aluminum foil in a fume hood for 48 hours and sieve the sample if necessary (10.1.2), weigh out 30 ±0.1 g of the processed sample and transfer to a microwave extraction vessel. Add sufficient anhydrous powdered or granulated sodium sulfate, or Hydromatrix™ and mix well to produce a free-flowing mixture.

10.1.2.5.2 Add 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.3). Add 25 mL of the 1:1 (v/v) acetone/methylene chloride extraction solvent and cap the vessel per the manufacturer's instructions.

10.1.2.5.3 Place the extraction vessel in the laboratory microwave and proceed with the manufacturer's specified setup procedure. This may include placing additional vessels containing water or other materials to ensure consistent exposure to microwaves across extractions.

10.1.2.5.4 Optimize the extraction conditions per the manufacturer's instructions. The following set of conditions may serve as a starting point:

Temperature:	100-115°C
Pressure:	50-150 psi
Time at Temperature:	10-20 minutes
Cooling to room temperature	
Filter/Rinse with same solvent system	

10.1.2.5.5 Proceed to Section 10.2.

10.1.3 Waste Dilution

Oily waste samples are prepared using the following waste dilution procedure.

10.1.3.1 Measure a 0.20 g aliquot of the waste sample to a separate 20 mL vial or 10 mL volumetric flask (record weight to the nearest 0.01 g).

10.1.3.2 Spike the sample with 1.0 mL of the surrogate standard spiking solution (7.2.2.3), mix with 1 g of anhydrous sodium sulfate (or Hydromatrix™), and immediately add approximately 5 mL of hexane to dilute the sample.

10.1.3.3 Shake the vial or flask for 2 minutes.

10.1.3.4 Loosely pack a disposable Pasteur pipette with 2-3 cm glass wool plugs. Filter the extract through the glass wool and rinse the glass wool several times with 1-2 mL of hexane. Adjust the final extract volume to 10 mL. Proceed to Section 10.3 for the sulfuric acid cleanup and other optional cleanup procedures, as needed. Concentrate the final extract volume to the same volume used for sulfuric acid cleanup prior to analysis.

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 volumes of concentrator tube and evaporative flask are permitted to increase the process efficiency. 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 – Target Analyte List and Contract Required Quantitation Limits, Table 4.

10.2.1.2 For aqueous/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, waste, and wipe samples, directly transfer the extract to the K-D concentrator, if the extract is known to be dry. Refer to Section 10.2.1.2 if the extract is known to be wet or shows visible signs of moisture.

10.2.1.4 Rinse the original container collecting the extract (for all samples) and the column (for aqueous/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 aqueous/water samples (and less than 10 mL for soil/sediment, waste, and wipe 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 aqueous/water, soil/sediment, waste or wipe sample extracts that do not require GPC cleanup, proceed with the hexane exchange procedure described in Section 10.2.2.

10.2.1.7 For aqueous/water sample 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, waste, and wipe sample extracts that require GPC cleanup, it is absolutely necessary to further reduce the volume of the 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 GPC cleanup. Adjust the extract volume to 10 mL with methylene chloride. Proceed to Section 10.3.1 for GPC cleanup.

10.2.2 Solvent Exchange into Hexane

This procedure applies to all sample extracts.

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 sample extracts that have <u>not</u> been subjected to GPC cleanup, adjust the volume of the hexane extract to 10 mL. For sample extracts 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 sulfuric acid cleanup or instrumental analysis. They are the Micro Snyder Column and the Nitrogen Evaporation Technique. The extract final volumes specified are intended to enable achievement of the CRQLs in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 4, using the recommended initial sample amounts. Other volumes may be used so long as method performance criteria and CRQLs are met.

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 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 0.2 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 sample extracts 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 sample extracts 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 shall 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 sample extracts 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 sample extracts that have already undergone GPC cleanup, adjust the volume with hexane to 1.0 or 2.0 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 (1.0 or 2.0 mL) and proceed to Section 10.4 for GC/ECD

analysis. Extracts shall 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 shall not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of new tubing shall 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. GPC cleanup is optional for all sample extracts. Sulfuric acid cleanup is mandatory for all sample extracts. Sulfur cleanup shall be performed for all sample extracts contaminated with sulfur. Method blanks shall be subjected to the same cleanup procedures as the samples (including LCSs and MS/MSDs). If a method blank, associated with all samples requiring sulfur cleanup, is not undergone the same sulfur cleanup procedure as the associated samples, then a separate sulfur cleanup blank is required.

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 verification; 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 shall be calibrated prior to processing samples under the contract, when the GPC calibration verification 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 UV Detector 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 shall be monitored.

10.3.1.3.3.1 Using a 10 mL syringe, load the calibration solution (Section 7.2.2.6.1) 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 shall 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 aqueous/water sample, calculate the analyte concentrations using Equation 4D in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

10.3.1.3.4 Technical Acceptance Criteria for GPC Calibration

10.3.1.3.4.1 The GPC system shall 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 must be symmetrical for all compounds in the calibration solution;
- Corn oil and phthalate peaks must exhibit greater than 85% resolution;
- Phthalate and methoxychlor peaks must exhibit greater than 85% resolution;
- Methoxychlor and perylene peaks must exhibit greater than 85% resolution; and
- Perylene and sulfur peaks must not be saturated and must 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 - Target Analyte List and Contract Required Quantitation Limits, Table 4.

10.3.1.3.4.5 A copy of the two most recent UV traces of the calibration solution shall 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 requirements in Section 10.3.1.3.4 cannot be met, the column may be cleaned by processing several 5 mL volumes of butylchloride through the system to remove the discoloration and possible precipitated particles. If a guard column is being used, replace it with a new one. It may be necessary to obtain a new lot of Bio Beads in order to correct the criteria failures.

10.3.1.3.5.2 If the flow rate and/or column pressure do not fall within the manufacturer’s specified ranges, a new column shall be prepared.

10.3.1.3.5.3 A UV trace that does not meet the criteria in Section 10.3.1.3.4 would also indicate that a new column shall be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

10.3.1.3.5.4 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 shall be routinely verified with the calibration verification solution specified in 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 shall 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 shall be checked whenever a sample causes significant discoloration of the GPC

column. Even if no darkening is visible, GPC calibration shall 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 shall 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 the Aroclor 1016 and Aroclor 1260 in methylene chloride at the concentrations in Exhibit D – Aroclors, Table 5.

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 shall be performed on only one of the GC columns used for sample analysis.

10.3.1.4.3.4 The recovery of each analyte shall be determined for evaluation and reporting purposes. Calculate the Percent Recovery (%R) of each analyte using Equation 20 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 shall 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 GPC calibration solution (Section 7.2.2.6.1) and the GPC UV detector calibration procedure (Section 10.3.1.3.3). The UV detector shall 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 shall 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 sample sequence, 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 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 shall be diluted prior to cleanup. Any sample extract with a viscosity greater than that of 1:1 (v/v) glycerol/water solution shall be diluted and loaded into several loops. Similarly, extracts containing more than the manufacturer’s recommended non-volatile residue shall 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 shall be carefully monitored to ensure 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 shall be checked to ensure 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 shall be reprepared, and the sample extract shall be either diluted and loaded into several loops, or the sample extract shall be injected manually.

10.3.1.6.2 Frequency of Sample Extract Cleanup by GPC

GPC cleanup shall be performed at least once for each aqueous/water, soil/sediment, and waste sample 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) shall be subjected to this procedure. GPC cleanup on the method blank shall be performed after all associated samples have been cleaned up (GPC sequence: calibration, GPC blank, 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 shall 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 shall 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 aqueous/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 shall be used. If the autosampler requires more than 1.0 mL of sample volume, 2.0 mL of extract shall 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 10.3.2.3.8.

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 shall 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 shall 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

A sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. If a method blank, associated with all samples requiring sulfur cleanup, is subjected to the same sulfur cleanup procedure as the associated samples, then no separate sulfur cleanup blank is required.

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 5.0 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 cleanup, 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 shall be analyzed under the same instrumental conditions. All sample extracts, required blank extracts, and standard/spiking solutions shall 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.

10.4.1.2 Set up the GC/ECD system per the requirements in Section 9.1. Unless ambient temperature on-column injection is used, the injector shall be heated to at least 200°C. The optimized GC conditions shall be used.

10.4.2 Procedure for Sample Analysis by GC/ECD

The injection shall be made on-column by using either automatic or manual injection. 1.0 µL or other selected injection volumes may be used provided that all associated standards, samples, and blanks use the same injection volume. The same injection volume shall 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 or twice the selected volume. However, the same injection volume shall be used for all analyses.

10.4.2.1 Analytical Sequence

All acceptable samples shall 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 hrs	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 hrs	Last injection past 12 hours	Any other Aroclor CS3 Standard
Another 12 hrs	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 hrs beginning of the next 12 hrs	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 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 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 can 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 shall 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 shall be analyzed at the most concentrated level that is consistent with achieving satisfactory chromatography as defined in Section 11.3.9.

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 three 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 Aroclor peak used for quantitation is greater than the concentration of the corresponding Aroclor peak in the high standard (CS5) on GC both columns, then the sample extract shall 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 shall be reported. The resulting changes in quantitation limits and surrogate recovery shall 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 shall 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 shall 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 shall 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 concentration after the dilution of 1:100,000, the Contractor shall contact SMO immediately.

10.4.3.10 Sample dilutions shall 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 - Target Analyte List and Contract Required Quantitation Limits, Table 4, 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.

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 for both columns, the Contractor shall contact SMO to determine whether GC/MS confirmation is required. The on-column concentration is calculated using Equation 4C-a in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.1.2.3.1 For aqueous/water samples prepared according to the method described in Section 10.1.1, the corresponding sample concentration is 100 µg/L.

11.1.2.3.2 For soil/sediment and waste samples prepared according to the method described in Section 10.1.2, the corresponding sample concentration is 3,300 µg/kg. For oily waste samples prepared by the waste dilution procedure described in Section 10.1.3, the corresponding sample concentration is 99,000 µg/kg. For wipe samples prepared according to the method described in Section 10.1.2, the corresponding sample concentration is 100 µg.

11.1.2.4 In order to confirm the identification of the target Aroclor, the Contractor shall also analyze a reference standard for the analyte.

11.1.2.5 To facilitate the ability of the GC/MS system to confirm the identification of the Aroclor in determined by GC/ECD analysis, the concentration of the corresponding Aroclor GC/MS standard shall be 50 ng/µL.

11.1.2.6 The Contractor is advised that library search results from the NIST (2017 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.

11.1.2.7 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 shall 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 11.1.2.5, or it shall be analyzed along with separate reference standards for the analyte to be confirmed.

11.1.2.8 If the analyte cannot be confirmed by either procedure in Section 11.1.2.5 or 11.1.2.7, then an aliquot of the extract prepared for the GC/ECD analysis shall 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 shall 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 shall 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 shall also 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 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 Aroclors, spectra of three 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 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 or reported as final results. 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 shall 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 shall be documented in the SDG Narrative.

NOTE: In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC instrument operator shall identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the properly scaled raw chromatogram that clearly shows the manual integration. The GC instrument operator shall also mark each integrated area with the letter "m" on the quantitation report, and initial and date the changes. All edits and manual integrations shall be verified by a second person, who shall also initial the change(s). The printout(s) of the chromatograms displaying the original integration(s) shall be included in the raw data, in addition to the printout(s) of the chromatograms displaying the manual integration(s). This applies to all target analytes listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 4, and surrogates.

11.2.1.4 The Contractor shall quantitate each Aroclor analyte using the average or $\overline{CF}$ from the most recent initial calibration. Do not use the analysis of the Aroclor standard used to demonstrate calibration verification for quantitation of samples.

11.2.1.5 Except for an estimated concentration reported for an Aroclor other than 1016 or 1260, the quantitation of Aroclors shall 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 or amount of the Aroclor target analytes is calculated by using Equation 4D, 5F, 5G, or 5G-a in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations, where A_x is the area for each of the major peaks of the Aroclor. The concentration of each peak in the sample chromatogram is determined and the mean concentration for five major peaks (three major peaks for Aroclor 1221) is determined on each column.

NOTE: An estimated concentration (reported with an "S" lab qualifier) 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.

11.2.1.6 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 shall 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 the surrogate $\overline{CF}$ from the initial five-point Aroclor 1016/1260 or from Aroclor 1016 if analyzed as a separate mixture.

11.2.1.7 If more than one Aroclor is observed in a sample, the Contractor shall choose different peaks to quantitate each Aroclor. A peak common to both analytes present in the sample shall not be used to quantitate either analyte.

11.2.2 Target Analyte Calculations

11.2.2.1 Calculate the aqueous/water, soil/sediment, waste, and wipe sample concentration or amount and on-column concentration of target analytes and surrogates by using Equation 4C-a, 4D, 5F, 5G (if wipe sample area is not provided), or 5G-a (if wipe sample area is provided) as applicable in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.2.2 The lower mean concentration or amount (from a minimum of three peaks for Aroclor 1221 and a minimum of five peaks for the remaining Aroclors) is reported as the final result, and the analyte concentrations calculated for each GC column are reported for each analysis. The %D is calculated using Equation 25 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.3 Contract Required Quantitation Limit Calculations

Calculate the aqueous/water, soil/sediment, waste, and wipe sample adjusted CRQL using Equation 6D, 7F, 7G (if wipe sample area is not provided), or 7G-a (if wipe sample area is provided) as applicable in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

11.2.4 Deuterated Monitoring Compound Recoveries

Not applicable to this method.

11.2.5 Surrogate Recoveries

11.2.5.1 The amounts for surrogate compounds on each column are calculated by using Equation 22C in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. 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 Equation 22 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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.

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 shall be performed on each GC column.

11.3.1 Samples shall 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 analysis shall 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 shall 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 The surrogate compounds RT shall 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 provided that no interference has affected the surrogate result calculations.

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 the extract shall 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 shall 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 shall be chosen for each Aroclor with the exception of Aroclor 1221, where three peaks shall 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 shall 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. Any samples analyzed that do not meet the technical acceptance criteria will require re-extraction and/or reanalysis.

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 shall be reanalyzed after the corrective action. Reanalyses of the MS and MSD samples are not required for any target Aroclor qualified with an "S" lab qualifier, 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, shall be checked to ensure that the proper amount was injected on the GPC column. If insufficient volume was injected, the sample shall be reprepared and reanalyzed.

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.

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 a 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 shall 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 criteria 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 Appendix B – Codes for Labeling Data.

11.4.6 If the required corrective actions for sample re-extraction, reanalysis, and/or dilution cannot be performed due to insufficient sample volume, the Contractor shall contact SMO.

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 shall 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/water samples, or purified sodium sulfate or Hydromatrix™ for soil/sediment and waste samples) carried through the entire analytical procedure. A method blank is prepared for the wipe samples using either the wipes designated for QC shipped together with the samples or the reference matrix used for the soil/sediment samples. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the method blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of the samples.

12.1.2.2 Frequency of Method Blank

A method blank shall 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:

- Processed with the same procedures used to extract and cleanup the samples; and
- Analyzed on each GC/ECD system under the same conditions used to analyze associated samples.

12.1.2.3 Procedure for Method Blank

For aqueous/water samples, measure a 1.0 L volume of reagent water and spike with 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.3). If an alternate aqueous/water sample aliquot volume (e.g., 500 mL) is used, measure the same volume (e.g., 500 mL) of reagent water, and spike a reduced amount (e.g., 500 µL) of the surrogate standard spiking solution in the blank sample aliquot. For wipe samples, add 10 g of sodium sulfate or Hydromatrix™ to the wipe designated for QC and spike with 1.0 mL of the surrogate standard spiking solution. If no wipes are received for QC, the Contractor shall notify SMO, note the issue in the SDG Narrative, and prepare the method blank by measuring 10 g of sodium sulfate or Hydromatrix™ and spiking with 1.0 mL of the surrogate standard spiking solution. For soil/sediment and waste samples, measure 30 g of sodium sulfate or Hydromatrix™ and spike with 1.0 mL of the surrogate standard spiking solution. If an alternate soil/sediment or waste sample aliquot amount (e.g., 15 g) is used, measure the same amount (e.g., 15 g) of the reference matrix, and spike a reduced amount (e.g., 500 µL) of the surrogate standard spiking solution in the blank sample aliquot. For oily waste samples prepared using the waste dilution procedure, measure 0.20 g of sodium sulfate or Hydromatrix™ and spike with 1.0 mL of the surrogate standard spiking solution. Extract, concentrate, clean up, and analyze the method blank according to Section 10.0. Method blanks shall be carried through any and all cleanup procedures as the samples in the same preparation batch.

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 shall be performed on each GC column.

12.1.2.5.2 All method blanks shall 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 shall undergo GPC cleanup, when required, on a GPC meeting the technical acceptance criteria for GPC calibration and GPC calibration verification.

12.1.2.5.3 Method blanks shall 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 each target analyte in the method blank must be less than the CRQL listed in Exhibit C – Target Analyte List and Contract Required Quantitation Limits, Table 4.

12.1.2.5.5 The method blank must meet the sample technical acceptance criteria in Sections 11.3.5 and 11.3.9.

12.1.2.5.6 Surrogate recoveries in the method blank must fall within the acceptance window in Exhibit D – Aroclors, Table 6. These limits are not advisory.

12.1.2.5.7 All method blanks shall 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 a problem, then the source of the contamination shall 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. 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 shall be re-extracted and reanalyzed.

12.1.2.6.4 If the method blank fails to meet a technical acceptance criteria 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 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 sulfur cleanup blank must be the same as the final volume of the samples associated with the sulfur cleanup blank. The sulfur cleanup 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 sulfur cleanup blank.

12.1.3.3.3 Analyze the sulfur cleanup 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 cleanup blank resulted from the extraction of a 1.0 L aqueous/water sample, calculate the concentration of each analyte using Equation 4D in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations. Compare the results to the CRQL values in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 4. If a reduced sample aliquot amount is used for the samples and method blanks, the sulfur cleanup blank result shall be calculated using the same reduced volume.

12.1.3.4.2 See Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 shall be performed on each column.

12.1.3.5.2 All sulfur cleanup blanks shall 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 shall 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 each target analyte in the sulfur cleanup blank must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 4.

12.1.3.5.5 The sulfur cleanup blank must meet all sample technical acceptance criteria in Section 11.3.5.

12.1.3.5.6 Surrogate recoveries must fall within the acceptance criteria in Exhibit D – Aroclors, Table 6. 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 shall consider the analytical system to be out of control.

12.1.3.6.2 If contamination is a problem, then the source of the contamination shall 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. 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 shall be reprepared/re-extracted and reanalyzed.

12.1.3.6.4 If the sulfur cleanup blank fails to meet a technical acceptance criteria 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) 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 shall 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. If a reduced sample aliquot amount is used for samples and method blanks, the surrogate standard spiking solution concentrations shall be lowered to take into the account the proportionally reduced final extract volume to result in the same surrogate concentrations.

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 L aqueous/water sample, calculate the concentration of each analyte using Equation 4D in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and

Equations. Compare the results to the CRQL values for aqueous/water samples in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 4. If a reduced sample aliquot amount is used for the samples and method blanks, the instrument blank result shall be calculated using the same reduced volume.

12.1.4.4.2 See Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations 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 shall be performed and reported independently for each GC column.

12.1.4.5.2 All instrument blanks shall 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 in the instrument blank must be less than the CRQL listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 4.

12.1.4.5.4 The instrument blank must meet all sample technical acceptance criteria in Section 11.3.5.

12.1.4.5.5 Instrument blanks shall 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 shall be stopped, and corrective action shall 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 shall 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 shall be re-injected during a valid analytical sequence and shall be reported.

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.

12.2.2 Frequency of Matrix Spike and Matrix Spike Duplicate

12.2.2.1 An MS/MSD shall be extracted and analyzed for every 20 or fewer field samples of a similar matrix in an SDG. MS/MSD samples shall be analyzed unless otherwise specified on the Traffic Report/Chain of Custody (TR/COC) Record. An MS/MSD analysis is not required for wipe samples.

12.2.2.2 Samples identified as field blanks or PE samples shall not be used for MS/MSD analysis.

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

12.2.3 Procedure for Preparing Matrix Spike and Matrix Spike Duplicate

12.2.3.1 For aqueous/water samples, prepare two additional aliquots of the sample selected for spiking at the same volume used for the original sample. If a 1.0 L sample aliquot volume is prepared, fortify each with 1.0 mL of the matrix spiking solution (Section 7.2.2.4). Using a syringe or volumetric pipette, add 1.0 mL of surrogate standard spiking solution to each sample (Section 7.2.2.3). If an alternate sample aliquot volume (e.g., 500 mL) is used, add a reduced volume (e.g., 500 µL) of the matrix spiking solution and a reduced volume (e.g., 500 µL) of the surrogate standard spiking solution to each MS/MSD sample, with the proportionally reduced final extract volume without GPC cleanup (e.g., half that specified at 5.0 mL). 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 and waste samples, prepare two additional aliquots of the sample selected for spiking at the same weight used for the original sample. If a 30 g sample aliquot amount is prepared, add 1.0 mL of the matrix spiking solution (Section 7.2.2.4) and 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.3). If an alternate sample aliquot amount (e.g., 15 g) is used, add a reduced volume (e.g., 500 µL) of the matrix spiking solution and a reduced volume (e.g., 500 µL) of the surrogate standard spiking solution to each MS/MSD sample, with the proportionally reduced final extract volume prior to GPC cleanup (e.g., half that specified at 5.0 mL). For oily waste samples prepared using the waste dilution procedure, add 1.0 mL of the matrix spiking solution (Section 7.2.2.4) and spike with 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.3). 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 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 shall be analyzed and reported at a 1:10 dilution only. Do <u>not</u> dilute MS/MSD samples further to get either spiked or non-spiked analytes within calibration range. Sample dilutions shall 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 4D and 5F in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations). Calculate the recovery of each Matrix Spike analyte using Equation 23 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each analyte in the MS/MSD sample using Equation 24A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 shall be performed on both GC columns.

12.2.5.2 All MS/MSDs shall 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 shall 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 sample shall be extracted and analyzed within the contract required holding time.

12.2.5.4 The RT for each of the surrogates in the MS/MSD sample 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 Exhibit D – Aroclors, Table 7. 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 sample that does not meet the technical acceptance criteria in Sections 12.2.5.1, 12.2.5.2, and 12.2.5.4 shall be reanalyzed.

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 shall be prepared, extracted, analyzed, and reported once for every 20 field samples of a similar matrix, per preparation batch. The LCS shall 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 aqueous/water samples, measure out 1.0 L of reagent water and spike with 1.0 mL of the LCS spiking solution (Section 7.2.2.5) and 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.3). If an alternate sample aliquot volume (e.g., 500 mL) is used, add a reduced volume (e.g., 500 µL) of the LCS spiking solution and a reduced volume (e.g., 500 µL) of the surrogate standard spiking solution to reagent water, with the proportionally reduced final extract volume without GPC cleanup (e.g., half that specified at 5.0 mL). Extract, concentrate, and analyze the sample according to Section 10.0.

12.3.3.2 For soil/sediment and waste 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 7.2.2.5) and 1.0 mL of surrogate standard spiking solution (Section 7.2.2.3). If an alternate sample aliquot amount (e.g., 15 g) is used, add a reduced volume (e.g., 500 µL) of the LCS spiking solution and a reduced volume (e.g., 500 µL) of the surrogate standard spiking solution to the clean reference matrix, with the proportionally reduced final extract volume prior to GPC cleanup (e.g., half that specified at 5.0 mL). For oily waste samples prepared using the waste dilution procedure, add 1.0 mL of the LCS spiking solution (Section 7.2.2.5) and spike with 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.3). Extract, concentrate, and analyze the LCS according to Section 10.0.

12.3.3.3 For wipe samples, add 10 g of sodium sulfate or Hydromatrix™ to the wipe designated for QC shipped together with the samples, and spike with 1.0 mL of the LCS spiking solution (Section 7.2.2.5) and 1.0 mL of the surrogate standard spiking solution (Section 7.2.2.3). If no wipes are received for QC, the Contractor shall notify SMO, note the issue in the SDG Narrative, and prepare the LCS by measuring 10 g of sodium sulfate or Hydromatrix™ and spiking with 1.0 mL of the LCS spiking solution and 1.0 mL of the surrogate standard spiking solution.

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 26A in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

12.3.4.3 Calculate the surrogate recoveries for the LCS using Equation 22 in Exhibit G – List of Abbreviations & Acronyms, Glossary of Terms, and Equations.

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 shall be performed on each GC column.

12.3.5.2 The LCS shall 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 shall be prepared as described in Section 12.3.3.

12.3.5.4 The LCS must meet all sample technical acceptance criteria in Section 11.3.5.

12.3.5.5 The %R for each of the analytes in the LCS must be within the recovery limits listed in Exhibit D – Aroclors, Table 8.

12.3.5.6 Surrogate recoveries must fall within the acceptance criteria in Exhibit D – Aroclors, Table 6. 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.

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.

12.4 Method Detection Limit Determination

12.4.1 Before any field samples are analyzed under the contract, the MDLs for only target analytes Aroclor 1016 and Aroclor 1260 shall be determined for each instrument under the same conditions used for analysis (i.e., analytical system configuration, as well as type and dimension of GC column), prior to the start of contract analyses and verified annually thereafter. The detection limits for target analytes other than Aroclor 1016 and Aroclor 1260 shall be reported using the MDL value for Aroclor 1016 or Aroclor 1260 (whichever is the greater value). MDL determination is matrix-specific (i.e., the MDL shall be determined for aqueous/water and soil/sediment samples. The MDL determined for soil/sediment samples shall be used for waste samples. For wipe samples, the results of the MDL study performed for soil/sediment samples shall be used and reported in the appropriate units.). An MDL study shall also be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis. 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.

12.4.1.1 To determine the MDLs for Aroclor 1016 and Aroclor 1260, the Contractor shall perform MDL studies following the procedures in Title 40 of the Code of Federal Regulations (CFR), Part 136, Appendix B, Revision 2.

12.4.1.2 The determined concentration of the MDLs for Aroclor 1016 and Aroclor 1260 must be less than the CRQLs listed in Exhibit C - Target Analyte List and Contract Required Quantitation Limits, Table 4.

12.4.1.3 The delivery requirements for the MDL values are specified in Exhibit B – Reporting and Deliverables Requirements, Table 1.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

16.1 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.

16.2 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3520C, Continuous Liquid-Liquid Extraction, Revision 3, December 1996.

16.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3535A, Solid-Phase Extraction, Revision 1, February 2007.

16.4 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3540C, Soxhlet Extraction, Revision 3, December 1996.

16.5 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3541, Automated Soxhlet Extraction, Revision 0, September 1994.

16.6 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3545A, Pressurized Fluid Extraction (PFE), Revision 1, February 2007.

16.7 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3546, Microwave Extraction, Revision 0, February 2007.

16.8 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3550C, Ultrasonic Extraction, Revision 3, February 2007.

16.9 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3580A, Waste Dilution, Revision 1, July 1992.

16.10 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3640A, Gel-Permeation Cleanup, Revision 1, September 1994.

16.11 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 3665A, Sulfuric Acid/Permanganate Cleanup, Revision 1, December 1996.

16.12 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Method 8082A, Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Revision 1, February 2007.

16.13 U.S. Government Printing Office, Title 40 of the Code of Federal Regulations, Chapter 1, Subchapter D, Part 136, Appendix B, Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.

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 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
Aroclor 1248	100	200	400	800	1600	20.0	±25.0	±50.0
Aroclor 1254	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 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 can be prepared together but the other Aroclor standards (1221 - 1268) shall 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 Aqueous/Water/Soil/Sediment and Waste**	**RPD Aqueous/Water/Soil/Sediment and Waste**
Aroclor 1016	29-135	0-15
Aroclor 1260	29-135	0-20

TABLE 8. LABORATORY CONTROL SAMPLE RECOVERY LIMITS

Analyte	**Percent Recovery Aqueous/Water/Soil/Sediment/Waste and Wipes**
Aroclor 1016	50-150
Aroclor 1260	50-150