EXHIBIT D

INTRODUCTION TO ORGANIC ANALYTICAL METHODS

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Exhibit D – Introduction to Organic Analytical Methods

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1.0 INTRODUCTION

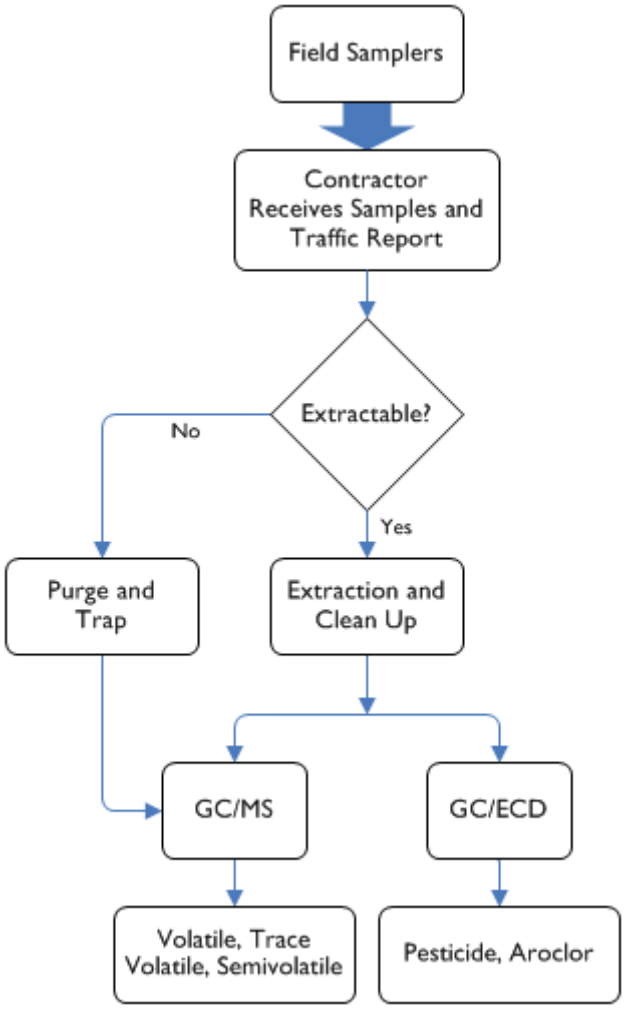
The organic analytical service provides a contractual framework for laboratories. This framework applies U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) analytical methods for the isolation, detection, and quantitative measurement of trace volatiles, low-medium volatiles,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

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

2.0 ORGANIC METHODS FLOW CHART

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

Figure 1 - Organic Methods Flow Chart



3.0 GLASSWARE CLEANING

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

4.0 STANDARD STOCK SOLUTIONS

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

5.0 VERIFICATION OF AQUEOUS/WATER SAMPLE CONDITION

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

6.0 SAMPLE CHARACTERIZATION

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

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

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

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

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

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

7.0 SAMPLE MIXING

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

8.0 SAMPLE DILUTIONS

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

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

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

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

9.0 MANUAL INTEGRATIONS

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

10.0 RAW DATA REQUIREMENTS

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

11.0 ANALYTICAL STANDARDS REQUIREMENTS

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

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

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

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

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

EQ. 1 Weight of Impure Compound

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

WHERE,

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

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

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

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

11.2 Purchase of Chemical Standards Already in Solution

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

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

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

11.3 Documentation of the Verification and Preparation of Chemical Standards

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

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

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

12.0 SAFETY

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

13.0 POLLUTION PREVENTION

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

14.0 WASTE MANAGEMENT

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

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EXHIBIT D

GENERAL ORGANIC ANALYSIS

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Exhibit D –General Organic Analysis

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1.0 SCOPE AND APPLICATION

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

2.0 SUMMARY OF METHOD

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

3.0 DEFINITIONS

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

4.0 INTERFERENCES

Not applicable.

5.0 SAFETY

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

6.0 EQUIPMENT AND SUPPLIES

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

6.1 Percent Solids Determination

6.1.1 Disposable weigh boats with covers

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

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

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

6.2 TCLP and SPLP Leaching

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

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

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

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

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

6.2.5 Beaker – 500 mL.

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

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

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

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

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

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

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

6.2.12 Magnetic stirrer with fluoropolymer-coated stir bar.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

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

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

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

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

7.1.5 Glacial Acetic Acid – reagent grade.

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

7.1.7 Extraction Fluids

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

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

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

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

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

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

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

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

8.2 Sample Storage

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

8.2.1 Unused Sample Storage

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

8.2.2 Leachate Sample Storage

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

8.2.3 Container Storage

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

8.2.4 Temperature Records

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

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

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

8.3 Contract Required Holding Time

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

9.0 CALIBRATION AND STANDARDIZATION

Not applicable.

10.0 PROCEDURE

10.1 Percent Solids Determination

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

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

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

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

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

EQ. 1 Percent Solids

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

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

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

10.2 TCLP and SPLP Extraction Procedures

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

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

10.2.1 Preliminary Evaluation

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

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

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

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

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

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

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

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

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

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

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

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

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

EQ. 2 Extraction Percent Solids

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

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

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

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

10.2.1.1.2.11 Calculate the Percent Dry Solids using the following equation:

EQ. 3 Percent Dry Solids

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

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

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

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

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

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

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

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

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

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

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

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

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

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

10.2.2 TCLP Sample Extraction

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

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

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

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

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

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

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

EQ. 4 Weight of Extraction Fluid

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

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

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

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

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

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

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

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

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

10.2.3 Zero Headspace Extraction

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

10.2.3.1 Maintaining the ZHE Apparatus

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

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

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

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

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

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

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

10.2.3.2 Zero Headspace Extraction of Volatile Compounds

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

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

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

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

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

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

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

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

EQ. 5 Sample Size

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

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

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

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

EQ. 6 Weight of Extraction Fluid

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

EQ. 7 Final Concentration

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

WHERE,

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

10.2.4 SPLP Sample Extraction

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

11.0 DATA ANALYSIS AND CALCULATIONS

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

12.0 QUALITY CONTROL

12.1 Leachate Extraction Blank

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

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

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

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

12.2 Summary of Quality Control Operations

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

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

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

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

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1. QUALITY CONTROL OPERATIONS

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

EXHIBIT D

TRACE CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS ANALYSIS

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

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

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

2.0 SUMMARY OF METHOD

2.1 Water

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

2.2 Soil/Sediment

Not applicable to this method.

2.3 Wipes

Not applicable to this method.

2.4 Waste

Not applicable to this method.

2.5 Non-Target Compounds

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

3.0 DEFINITIONS

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

4.0 INTERFERENCES

4.1 Method Interferences

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

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

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

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

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

4.2 Matrix Interferences

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

5.0 SAFETY

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

6.0 EQUIPMENT AND SUPPLIES

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

6.1 General Laboratory Equipment

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

6.1.2 Pasteur Pipettes - Disposable.

6.1.3 pH Paper - Wide range.

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

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

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

6.1.7 Vials and Caps - Assorted sizes.

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

6.2 Glassware/Extraction/Cleanup Equipment

Not applicable to this method.

6.3 Analytical Instrumentation

6.3.1 Gas Chromatograph

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

6.3.2 Gas Chromatography Columns

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

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

6.3.2.1 A capillary column is considered equivalent if:

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

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

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

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

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

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

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

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

6.3.3 Mass Spectrometer

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

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

6.3.3.1 Gas Chromatograph/Mass Spectrometer Interface

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

recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.3.4 Purge-and-Trap Device

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

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

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

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

6.3.4.3 Alternate sorbent traps may be used if:

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

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

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

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

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

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

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

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

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

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

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

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

6.4 Data System/Data Storage

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

7.0 REAGENTS AND STANDARDS

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

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

7.1 Reagents

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

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

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

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

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

7.2 Standards

7.2.1 Stock Standard Solutions

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

7.2.2 Working Standards

7.2.2.1 Initial and Continuing Calibration Solutions

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

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

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

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

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

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

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

7.2.2.2 Instrument Performance Check Solution

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

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

7.2.2.3 Deuterated Monitoring Compound Spiking Solution

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

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

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

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

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

7.2.2.4 Matrix Spiking Solution

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

7.2.2.5 Internal Standard Spiking Solution

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

7.2.3 Storage of Standard Solutions

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

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

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