EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF TRACE CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS

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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 compounds listed in the Target Compound List (TCL) in Exhibit C (Trace Volatiles). 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 EPA Method 524.2. The sample preparation and analysis procedures included in this method are based on purge-and-trap Gas Chromatograph/Mass Spectrometer (GC/MS) techniques.

In addition, if requested, samples will be analyzed for a select group of compounds by GC/MS, using the Selected Ion Monitoring (SIM) technique. If trace SIM is requested for 1,4-dioxane, 1,2-dibromoethane, and 1,2-dibromo-3-chloropropane, a full scan analysis using the trace method should be performed first. If the three target compounds are detected at or above the CRQL (for trace level) during the full scan analysis using the trace method, then a SIM analysis is not to be performed and this should be documented in the Sample Delivery Group (SDG) Narrative.

1.2 Problems that have been associated with the following compounds analyzed by this method include:

- Chloromethane, vinyl chloride, bromomethane, and chloroethane may display peak broadening if the compounds are not delivered to the GC column in a tight band.
- Acetone, hexanone, 2-butanone, 4-methyl-2-pentanone, and 1,4-dioxane have poor purge efficiencies.
- 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 purge-and-trap systems and/or active sites in trapping materials.
- Chloromethane may be lost if the purge flow is too fast.
- Bromoform is one of the compounds 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 An inert gas is bubbled through a 25 mL sample contained in a specially designed purging chamber at ambient temperature causing the purgeables to be transferred from the water/aqueous phase to the vapor phase. 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 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 purgeables onto a Gas Chromatograph (GC) wide-bore capillary column. The GC is temperature programmed to separate the purgeables, which are then detected with a Mass Spectrometer (MS).

2.2 Deuterated Monitoring Compounds (DMCs) and internal standards are added to all samples and blanks. The target compounds and DMCs are identified in the samples and blanks by analyzing standards that contain all target compounds, DMCs, and internal standards under the same conditions and comparing resultant mass spectra and GC Retention Times (RTs). A Mean Relative Response Factor ($\overline{RRF}$) is established for each target compound and DMC during the initial calibration. The mass spectra response from the Extracted Ion Current Profile (EICP) for the primary quantitation ion produced by that compound is compared to the mass spectral response for the primary quantitation ion produced by the associated internal standard compound. Each identified target compound and DMC is quantitated by comparing the instrument response for the compound in the sample or blank with the instrument response of the associated internal standard, while taking into account the $\overline{RRF}$, the sample volume, and any sample dilutions.

2.3 Non-target compounds are identified by comparing the resultant mass spectra from the non-target compounds to mass spectra contained in the NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library. Non-target compounds are quantitated by comparing the mass spectra response from the total ion chromatograms to the mass spectra response of the nearest internal standard compound. An RRF of 1 is assumed.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Method Interferences

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 running laboratory method and instrument blanks as described in Section 12. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.2 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 in which the atmosphere is demonstrated to be free of all potential contaminants that will interfere with the analysis.

4.3 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.

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

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Office of Safety and Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analyses.

5.2 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene; carbon tetrachloride; chloroform; vinyl chloride; and 1,4-dioxane. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, catalog, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of the analytical method 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 Glassware

6.1.1 Syringes - 25 mL, gas-tight with shut-off valve. Micro syringes - 10 µL and larger, 0.006 inch (0.15 mm) ID needle.

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

6.1.3 Pasteur Pipets - Disposable.

6.1.4 Vials and Caps - Assorted sizes.

6.1.5 Volumetric Flasks, Class A with ground-glass stoppers.

6.1.6 Bottles - 15 mL, screw-cap, with polytetrafluoroethylene (PTFE) cap liner.

6.2 pH Paper - Wide range.

6.3 Balances

Balances must be analytical and capable of accurately weighing ±0.0001 g. The balance must be calibrated with Class S weights or known reference weights once per each 12-hour work shift. The balance must be calibrated with Class S weights at a minimum of once per month. The balance must also be annually checked by a certified technician.

6.4 Purge-and-Trap Device

The purge-and-trap device consists of three separate pieces of equipment: the sample purge chamber, the trap, and the desorber. This device either manually or automatically 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 purge device also purges the volatile organic compounds (VOCs) using an inert gas stream and traps the released VOCs for subsequent desorption into the Gas Chromatograph (GC). Such systems are commercially available from several sources and shall meet the following specifications.

6.4.1 The sample purge chamber must be designed to accept 25 mL samples with a water column at least 10 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.

6.4.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch (2.667 mm). The trap must be packed to contain the following minimum lengths of absorbents: (starting from inlet) 0.5 cm silanized glass wool, 1 cm methyl silicone, 8 cm of 2,6-diphenylene oxide polymer (Tenax-GC, 60/80 mesh), 8 cm of silica gel (Davison Chemical, 35/60 mesh, grade 15 or equivalent), 7 cm of coconut charcoal, and 0.5 cm silanized glass wool. A description of the trap used for analysis shall be provided in the SDG Narrative.

6.4.3 The desorber must be capable of rapidly heating the trap to 180°C. 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.

6.4.4 Trap Packing

6.4.4.1 2,6-Diphenylene Oxide Polymer, 60/80 mesh chromatographic grade (Tenax GC or equivalent).

6.4.4.2 Methyl Silicone Packing, 3.0% OV-1 on Chromosorb W, 60/80 mesh (or equivalent).

6.4.4.3 Silica Gel, 35/60 mesh,(or equivalent).

6.4.4.4 Coconut Charcoal.

6.4.4.5 Alternate sorbent traps may be used if:

- The trap packing materials do not introduce contaminants that interfere with identification and quantitation of the compounds listed in Exhibit C (Trace Volatiles);
- The analytical results generated using the trap meet the initial calibration and continuing calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Trace Volatiles); or
- The trap can accept up to 1000 ng of each compound listed in Exhibit C (Trace Volatiles) without becoming overloaded.

6.4.4.5.1 The alternate trap must be designed to optimize performance. Follow the manufacturer's instructions for the use of its product. Before use of any trap other than the one specified in Section 6.4.2, the Contractor must first meet the criteria listed in Section 6.4.4.5. 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.

6.4.4.5.2 The Contractor must maintain documentation that the alternate trap meets the criteria listed in Section 6.4.4.5. The minimum documentation requirements are as follows:

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

6.4.4.5.2.2 Reconstructed ion chromatograms and data system reports generated on the Contractor's Gas Chromatograph/Mass Spectrometer (GC/MS) used for Contract Laboratory Program (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 continuing calibration verification standards analyzed using the trap specified in Section 6.4.4.

6.4.4.5.2.3 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 compounds listed in Exhibit C (Trace Volatiles).

6.4.4.5.2.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the Regional USEPA CLP Project Officer (CLP PO).

6.4.5 The purge-and-trap apparatus may be assembled as a separate unit or be an integral unit coupled with a GC.

6.5 Gas Chromatograph/Mass Spectrometer (GC/MS) System

6.5.1 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 purge-and-trap system as specified in Section 6.4 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 column oven must be cooled to 10°C if adequate separation of gaseous compounds is not achieved (Section 9.1.2.3); therefore, a subambient oven controller is required.

6.5.2 Gas Chromatography Columns

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

6.5.2.1 Minimum length 30 m x 0.53 mm ID VOCOL (Supelco) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.2 Minimum length 30 m x 0.53 mm ID DB-624 (J & W Scientific) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.3 Minimum length 30 m x 0.53 mm ID AT-624 (Alltech) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.4 Minimum length 30 m x 0.53 mm ID Rtx-624 (Restek) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.5 Minimum length 30 m x 0.53 mm ID BP-624 (SGE) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.2.6 Minimum length 30 m x 0.53 mm ID CP-Select 624CB (Chrompack) or equivalent fused silica widebore capillary column with 3 µm film thickness.

6.5.3 A capillary column is considered equivalent if:

- The column does not introduce contaminants that interfere with the identification and quantitation of the compounds listed in Exhibit C (Trace Volatiles);
- The analytical results generated using the column meet the initial calibration and continuing calibration verification technical acceptance criteria listed in the analytical method, and the CRQLs listed in Exhibit C (Trace Volatiles);
- The column can accept up to 1000 ng of each compound listed in Exhibit C (Trace Volatiles) without becoming overloaded; and
- The column provides equal or better resolution of the compounds listed in Exhibit C (Trace Volatiles) than the columns listed in Section 6.5.2.

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

6.5.3.2 The Contractor must maintain documentation that the column met the criteria in Section 6.5.3. The minimum documentation is as follows:

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

6.5.3.2.2 Reconstructed ion chromatograms and data system reports generated on the GC/MS used for the CLP analyses:

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

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

- The alternate column performance meets the technical acceptance criteria in Sections 9.3.5 and 9.4.5;
- The low-point initial calibration standard analysis has adequate sensitivity to meet the volatile CRQLs;
- The high-point initial calibration standard analysis was not overloaded; and
- The column does not introduce contaminants that interfere with the identification and/or quantitation of compounds listed in Exhibit C (Trace Volatiles).

6.5.3.4 The documentation must be made available to USEPA during on-site laboratory evaluations or sent to USEPA upon request of the USEPA Regional CLP PO.

6.5.4 **PACKED COLUMNS CANNOT BE USED.**

6.5.5 Mass Spectrometer (MS)

The MS must be capable of scanning from 35-300 amu 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 4-bromofluorobenzene (BFB) GC/MS performance check technical acceptance criteria in Table 1.

NOTE: To ensure sufficient precision of mass spectral data, the MS scan rate must 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 system must be capable of Selected Ion Monitoring (SIM). The instrument must be vented to outside the facility or to a trapping system which prevents the release of contaminants into the instrument room.

6.5.6 GC/MS 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 compounds 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.

6.5.7 Data System

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 (2002 release or later), Wiley (1991 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.

6.5.8 Data Storage Device

Data storage devices must be suitable for long-term, off-line storage of data.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

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.

7.1.1 Reagent Water - Reagent water is defined as water in which an interferant is not observed at or above the Contract Required Quantitation Limit (CRQL) for each compound 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 lb) of activated carbon.

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

7.1.1.3 Reagent water may 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 one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle, seal with a polytetrafluoroethylene (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 compounds listed in Exhibit C (Trace Volatiles).

7.2 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 E. 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.

Standard solutions purchased from a chemical supply house as ampulated extracts in glass vials may be retained and used until the expiration date provided by the manufacturer. If no manufacturer's expiration date is provided, the standard solutions as ampulated extracts may be retained and used for 2 years from the preparation date. Standard solutions prepared by the Contractor that are immediately ampulated in glass vials may be retained for 2 years from preparation date. Upon breaking the glass seal, the expiration times listed in Sections 7.2.1.1 to 7.2.2.2 will apply. The Contractor is responsible for assuring that the integrity of the standards has not degraded (Section 7.2.3.5).

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 purchased or prepared in methanol from pure standard materials.

7.2.1.1 Prepare fresh stock standards every 6 months, or sooner if standard has degraded or evaporated.

7.2.2 Working Standards

7.2.2.1 Instrument Performance Check Solution

Prepare the instrument performance check solution containing 4-bromoflurobenzene (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 BFB on-column). The BFB must be analyzed using the same GC and Mass Spectrometer (MS) run conditions as is used for the calibration analysis.

7.2.2.2 Calibration Standard Solution

Prepare single or multiple working calibration standard solution(s) containing all of the purgeable target compounds [Exhibit C (Trace Volatiles)]in methanol. Prepare fresh calibration standards every month, or sooner if the standard has degraded.

7.2.2.3 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 solution to 25 mL of samples, blanks, and calibration standards to result in a 5.0 µg/L concentration. Prepare a fresh internal standard solution every month, or sooner if the standard had degraded. If analysis using the Selected Ion Monitoring (SIM) technique is required, add sufficient amount of the internal standard solution to 25 mL of samples, blanks, and calibration standards to result in a 0.50 µg/L concentration of each internal standard.

7.2.2.4 Deuterated Monitoring Compound (DMC) Spiking Solution

Prepare a DMC spiking solution in methanol (or in deuterated methanol) containing the compounds listed below: DMCs are to be added to each sample and blank, as well as initial calibration standards and Continuing Calibration Verification (CCV) standards. For samples and blanks, add sufficient amount of DMC solution to each 25 mL of sample to result in a concentration of 5.0 µg/L of each non-ketone DMC, 50 µg/L for each ketone DMC, and 250 µg/L for 1,4-dioxane-d_8 DMC. If SIM analysis is required, add sufficient amount of DMC solution to each sample and blank to result in a concentration of 0.50 µg/L for each non-ketone DMC, and 25 µg/L for 1,4-dioxane-d_8 DMC. For calibration standards, add sufficient amounts of DMC solution to each 25 mL aliquot of calibration standard to result in the concentrations listed in Section 7.2.2.6.2 (initial calibration) and Section 7.2.2.6.4 (CCV). Prepare a fresh DMC solution every month, or sooner if the standard has degraded.

<u>Compound</u>
Vinyl chloride-d_3
Chloroethane-d_5
1,1-Dichloroethene-d_2
2-Butanone-d_5
Chloroform-d
1,2-Dichloroethane-d_4
Benzene-d_6
1,2-Dichloropropane-d_6
Toluene-d_8
trans-1,3-Dichloropropene-d_4
2-Hexanone-d_5
1,4-Dioxane-d_8
1,1,2,2-Tetrachloroethane-d_2
1,2-Dichlorobenzene-d_4

7.2.2.5 Matrix Spiking Solution

If Matrix Spike and Matrix Spike Duplicate (MS/MSD) analysis is requested at the time of scheduling, prepare a spiking solution in methanol that contains the following compounds 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.

7.2.2.6 Initial and Continuing Calibration Standard

7.2.2.6.1 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 7.2.2.6.2 or 7.2.2.6.4.

7.2.2.6.2 Prepare five aqueous initial calibration standard solutions containing all of the purgeable target compounds, and the DMCs at the suggested following levels: all non-ketone target compounds and associated DMCs (see Table 7), except 1,4-dioxane, at 0.50, 1.0, 5.0, 10, and 20 µg/L; all ketones and their associated DMCs (see Table 7) at 5.0, 10, 50, 100, and 200 µg/L; and 1,4-dioxane and its associated DMC (see Table 7), 1,4-dioxane-d_8 at 20, 40, 250, 400, and 800 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.

If analysis by the SIM technique is requested for 1,4-dioxane, prepare calibration standards containing 1,4-dioxane and its associated DMC (see Table 8) at concentrations of 2.0, 4.0, 25, 40, and 80 µg/L. If analysis by the SIM technique is requested for all other compounds of interest, prepare calibration standards containing the compounds of interest and their associated DMCs (see Table 8) at concentrations of 0.050, 0.10, 0.50, 1.0, and 2.0 µg/L.

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

7.2.2.6.4 For CCV (beginning and ending CCV), the aqueous CCV standard shall be at a concentration equivalent to the mid-level calibration standard listed in Section 7.2.2.6.2 (i.e., 5.0 µg/L for non-ketones, 50 µg/L for ketones, 250 µg/L for 1,4-dioxane, 25 µg/L for 1,4-dioxane by the SIM technique, and 0.50 µg/L for other compounds analyzed by the SIM technique).

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

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, and protect the standards from light.

7.2.3.2 Aqueous standards may be stored up to 24 hours if held in PTFE-sealed screw-cap vials with zero headspace at 4°C (±2°C) and protected from light. If not so stored, they 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 purge-and-trap device. If standards are purchased and stored as ampulated vials, they may be stored indefinitely.

7.2.3.3 If standards are purchased and stored in ampulated vials, they may be stored up to 2 years after the preparation date.

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

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

7.2.4 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.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection and Preservation

8.1.1 Water samples may be collected in glass containers having a total volume of at least 40 mL with a polytetrafluoroethylene (PTFE)-lined septum and an open top screw-cap. Headspace should be avoided. The specific requirements for site sample collection are outlined by the Region. If Selected Ion Monitoring (SIM) is requested, an additional sample aliquot will be collected.

8.1.2 The containers must be filled in such a manner that no air bubbles pass through the sample as the container is being filled. Seal the vial so that no air bubbles are entrapped in it.

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

8.1.4 All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until analysis.

8.1.5 If SIM analysis is requested, a total of four vials per field sample is the recommended amount of vials the contractor should receive. If SIM analysis is not requested then a total of two vials per field sample is the recommended amount of vials the Contractor should receive. An additional two vials are required if Matrix Spike and Matrix Spike Duplicates (MS/MSDs) are to be performed on that sample.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days, the samples may be disposed of in a manner that complies with all applicable regulations.

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

8.2.3 All volatile samples in a Sample Delivery Group (SDG) must be stored together in the same refrigerator.

8.2.4 Storage blanks shall be stored with samples until all samples within an SDG are analyzed.

8.2.5 Samples, sample extracts, and standards must be stored separately.

8.2.6 Trace volatile standards must be stored separately from semivolatile, pesticide, and Aroclor standards.

8.3 Temperature Records for Sample Storage

8.3.1 The temperature of all sample storage refrigerators shall be recorded daily.

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

8.3.3 Corrective action Standard Operating Procedures (SOPs) shall be posted on the refrigerators.

8.4 Contract Required Holding Times

Analysis of water samples must be completed within 10 days of Validated Time of Sample Receipt (VTSR). As part of USEPA's Quality Assurance (QA) program, USEPA may provide Performance Evaluation (PE) samples as standard extracts which the Contractor is required to prepare per the instructions provided by USEPA. PE samples must be prepared and analyzed concurrently with the samples in the SDG. The contract-required 10-day holding time does not apply to PE samples received as standard extracts.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Purge-and-Trap

9.1.1.1 The following are the recommended purge-and-trap analytical conditions. The conditions below are suggested, but other conditions may be used, provided that all technical acceptance criteria are met for all standards, samples, and blanks:

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

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

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

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

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

- The system does not introduce contaminants that interfere with identification and quantitation of compounds listed in Exhibit C (Trace Volatiles);
- The analytical results generated when using the moisture reduction/water management system meet the initial calibration and continuing calibration verification technical acceptance criteria listed in the analytical method and the Contract Required Quantitation Limits (CRQLs) listed in Exhibit C (Trace Volatiles);
- 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 (GC)

9.1.2.1 The following are the recommended GC analytical conditions. The conditions are recommended unless otherwise noted:

<u>Capillary Columns</u>

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 compounds listed in Exhibit C (Trace Volatiles) elute (required)

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

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

9.1.3 Mass Spectrometer (MS)

The following are the required MS analytical conditions:

Electron Energy:	70 volts (nominal)
Mass Range:	35-300 amu
Ionization Mode:	Electron Ionization (EI)
Scan Time:	To give at least five scans per peak, not to exceed 2 sec. per scan for capillary column.

9.2 Instrument Performance Check -- 4-bromofluorobenzene (BFB)

9.2.1 Summary of Instrument Performance Check

9.2.1.1 The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant such as perfluoro-tri-n-butylamine (FC-43) or perfluorokerosene (PFK). The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution (Section 7.2.2.1).

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

This requirement does not apply when samples are analyzed by the Selected Ion Monitoring (SIM) technique.

9.2.2 Frequency of Instrument Performance Check

The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples, blanks, or standards are to be analyzed. The 12-hour time period for GC/MS performance check, calibration standards (initial calibration or continuing calibration verification), blank, and sample analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. However, in cases where a closing Continuing Calibration Verification (CCV) can be used as an opening CCV for the next 12-hour period, then an additional BFB tune is not required, and the 12-hour period begins with the injection of the CCV. The time period ends after 12 hours have elapsed according to the system clock.

9.2.3 Procedure for Instrument Performance Check

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

- As an injection of up to 50 ng of BFB into the GC/MS.
- By adding a sufficient amount of BFB solution to the mid-level calibration standard (5.0 µg/L for non-ketones and 50 µg/L for ketones) to result in a 2.0 µg/L concentration of BFB.
- By adding a sufficient amount of BFB solution (Section 7.2.2.1) to 25 mL of reagent water to result in a 2.0 µg/L concentration of BFB.

9.2.4 Technical Acceptance Criteria for Instrument Performance Check

9.2.4.1 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan, the scan immediately preceding, and the scan immediately following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the beginning of the elution of BFB. Do not background subtract part of the BFB peak.

NOTE: All subsequent standards, samples, and blanks associated with a BFB analysis must use identical GC/MS instrument run conditions.

9.2.4.2 The analysis of the instrument performance check solution must meet the ion abundance criteria given in Table 1.

9.2.5 Corrective Action for 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, clean the quadrupole rods, or take other corrective actions to achieve the technical acceptance criteria.

9.2.5.2 BFB technical acceptance criteria **must** be met before any standards, samples, or required blanks are analyzed. Any samples or required blanks analyzed when tuning technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.3 Initial Calibration

9.3.1 Summary of Initial Calibration

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

NOTE: For analysis using the SIM technique, the GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.2.6.2), prior to the analysis of samples and required blanks, to determine instrument sensitivity and linearity.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be calibrated upon award of the contract, whenever the Contractor takes corrective action that may change or affect the initial calibration criteria (i.e., ion source cleaning or repair, column replacement, etc.), or if the CCV technical acceptance criteria have not been met.

9.3.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples and blanks may be analyzed. It is not necessary to analyze a CCV standard within this 12-hour time period. A method blank is required. Quantitate all samples and blank results using the Mean Relative Response Factor ($\overline{RRF}$) from the initial calibration. Compare Quality Control (QC) criteria such as internal standard area response change and Retention Time (RT) shift to the initial calibration standard that is the same concentration as the CCV.

9.3.3 Procedure for Initial Calibration

9.3.3.1 Assemble a purge-and-trap device that meets the specifications in Section 6.4. Condition the device as described in Section 9.1.1.

9.3.3.2 Connect the purge-and-trap device to the GC. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 9.1.2.

9.3.3.3 All samples, blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.3.3.4 Add sufficient amount of the internal standard solution (Section 7.2.2.3) to each of the five aqueous calibration standard solutions (Section 7.2.2.6.2) containing the DMCs (Section 7.2.2.4) at the time of purge. Analyze each calibration standard according to Section 10.

9.3.4 Calculations for Initial Calibration

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

9.3.4.1 Calculate the RRF for each purgeable target compound and DMC using Equation 1. See Table 3 to associate purgeable target compounds and DMCs with the proper internal standard. See Table 4 for primary quantitation ions to be used for each purgeable target compound, DMC, and internal standard compound.

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

EQ. 1 Relative Response Factor Calculation

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

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured (Table 4).

A_{is} = Area of the characteristic ion (EICP) for the specific internal standard (Table 4).

C_{is} = Concentration of the internal standard.

C_x = Concentration of the compound to be measured.

9.3.4.2 The $\overline{RRF}$ must be calculated for all compounds.

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

EQ. 2 Percent Relative Standard Deviation Calculation

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

Where,

SD_{RRF} = Standard deviation of initial calibration RRFs (per compound) from EQ. 3.

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

9.3.4.4 Equation 3 is the general formula for Standard Deviation (SD) for a statistically small set of values.

EQ. 3 Standard Deviation Calculation

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

Where,

X_i = Each individual value used to calculate the mean.

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

n = Total number of values.

9.3.4.5 Equation 4 is the general formula for the mean of a set of values.

EQ. 4 Mean Value Calculation

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

Where,

X_i = Value.

$\overline{X}$ = Mean value.

n = Number of values.

9.3.5 Technical Acceptance Criteria For Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.2.6.2, 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 instrument manufacturer's instrument operating manual to determine how saturation is indicated for your instrument.

9.3.5.3 The RRF at each calibration concentration for each purgeable target and DMC that has a required minimum RRF value must be greater than or equal to the compound's minimum acceptable RRF listed in Table 2.

9.3.5.4 The %RSD for each target or DMC listed in Table 2 must be less than or equal to that value listed.

9.3.5.5 Up to two target compounds and DMCs (excluding those with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.3.5.3 but these compounds must still meet the minimum RRF requirements of 0.010. Up to two target compounds and DMCs (excluding those with maximum %RSD requirements of 40.0%) may fail to meet the criteria listed in Section 9.3.5.4 but these compounds must still meet the maximum %RSD requirements of 40.0%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8, which must have a minimum RRF greater than or equal to 0.0050 and the %RSD must be less than or equal to 50.0%.

9.3.5.6 For analysis using the SIM technique, all target compounds and DMCs must meet a minimum RRF criterion of 0.010 and have a %RSD less than or equal to 50%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8, which must meet a minimum RRF of 0.0050.

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 purge-and-trap device, or take other corrective actions to achieve the technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria **MUST** be met before any samples or required blanks are analyzed. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

9.4 Continuing Calibration Verification

9.4.1 Summary of Opening and Closing Continuing Calibration Verification (CCV)

Prior to the analysis of samples and required blanks and after BFB tune and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing an opening CCV containing all the purgeable target compounds, DMCs, and internal standards to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method. After all samples and blanks have been analyzed and before the end of the 12-hour time period a closing CCV using the same standard conditions as for the opening CCV is required.

NOTE: For analysis using the SIM technique, prior to the analysis of samples and required blanks, and after initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing a CCV standard (25 µg/L for 1,4-dioxane and its associated DMC, and 0.50 µg/L for all other target compounds and associated DMCs).

9.4.2 Frequency of Continuing Calibration Verification

9.4.2.1 The 12-hour time period begins with the injection of BFB, followed by the injection of the opening CCV solution. BFB may be added to the CCV solution, in which case only one injection is necessary. If a closing CCV meets the technical acceptance criteria for an opening CCV (Sections 9.4.5.2 and 9.4.5.3) and samples are analyzed within that subsequent 12-hour time period, then an additional BFB tune is not required and the 12-hour time period begins with that calibration verification. If the closing CCV does not meet the technical acceptance criteria for an opening CCV, then a BFB tune followed by an opening CCV is required and the next 12-hour time period begins with the BFB tune.

9.4.2.2 If time remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. A method blank is required. Quantitate all sample and blank results using the $\overline{RRF}$ from the initial calibration.

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

9.4.3 Procedure for Continuing Calibration Verification

9.4.3.1 Set up the purge-and-trap GC/MS system per the requirements in Section 9.1.

9.4.3.2 All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis.

9.4.3.3 Add sufficient amount of internal standard solution (Section 7.2.2.3) to the 25 mL syringe or volumetric flask containing the CCV (7.2.2.6.4). Analyze the CCV according to Section 10.

9.4.4 Calculations for Continuing Calibration Verification

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

9.4.4.2 Calculate the Percent Difference (%Difference) between the CCV RRF and the most recent initial calibration $\overline{RRF}$ for each purgeable target and DMC using Equation 5.

EQ. 5 Percent Difference Calculation

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

Where,

RRF_C = Relative Response Factor from current CCV standard.

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

9.4.5 Technical Acceptance Criteria for Opening and Closing Continuing Calibration Verification (CCV)

9.4.5.1 The concentration of the trace volatile organic target compounds and DMCs in the opening and closing CCV must be at or near the mid-point concentration level of the calibration standards, (5.0 µg/L for non-ketones, 50 µg/L for ketones, and 250 µg/L for 1,4-dioxane). The opening and closing CCV must be analyzed at the frequency described in Section 9.4.2 on a GC/MS system meeting the BFB (Section 9.2.4) and the initial calibration (Section 9.3.5) technical acceptance criteria.

NOTE: For analysis using the SIM technique, the concentration of 1,4-dioxane and the DMC 1,4-dioxane-d_8 in the opening and closing CCV standard must be at or near the mid-point concentration level of the calibration standards (25 µg/L). The concentration for the remaining target compounds and DMCs must be 0.50 µg/L. The opening and closing CCV standard must be analyzed at the frequency described in Section 9.4.2 on a GC/MS system meeting the initial calibration technical acceptance criteria.

9.4.5.2 For an opening CCV, The RRF for each purgeable target and DMC must be greater than, or equal to, the compound's minimum acceptable RRF listed in Table 4. For a closing CCV, The RRF for each purgeable target and DMC must be at least 0.010 (except for 1,4-dioxane and its associated DMC, 1,4-dioxane-d_8, which must be at least 0.0050).

9.4.5.3 For an opening CCV, the RRF Percent Difference for each purgeable target compound and DMC listed in Table 2 must be within the inclusive range of the value listed. For a closing CCV, the RRF Percent Difference for each purgeable target and DMC must be in the inclusive range of 50.

9.4.5.4 For an opening CCV, up to two target compounds and DMCs (excluding those compounds with minimum RRF requirements of 0.010) may fail to meet the criteria listed in Section 9.4.5.2 but these compounds must still meet the minimum RRF requirements of 0.010. Up to two target compounds and DMCs (excluding those compounds with maximum Percent Difference requirements of ±40.0%) may fail to meet the requirements listed in Section 9.4.5.3 but these compounds must still meet the maximum Percent Difference requirements of ±40.0%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8, which must have a minimum RRF greater than or equal to 0.0050 and the Percent Difference must be within the inclusive range of ±50.0%. For a closing CCV, all target compounds and DMCs must meet the requirements listed in Sections 9.4.5.2 and 9.4.5.3.

9.4.5.5 For analysis using the SIM technique, all target compounds and DMCs must meet a minimum RRF criterion of 0.010 and have a maximum Percent Different of ±50%. The exceptions are 1,4-dioxane and 1,4-dioxane-d_8 which must meet a minimum RRF of 0.0050.

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

9.4.6 Corrective Action for Opening and Closing Continuing Calibration Verification (CCV)

9.4.6.1 If the opening CCV technical acceptance criteria are not met, recalibrate the GC/MS instrument according to Section 9.3. If the closing CCV technical acceptance criteria are not met, then all samples and blanks analyzed within that 12-hour time period must be reanalyzed at no additional cost to USEPA. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the CCV technical acceptance criteria.

9.4.6.2 Opening CCV technical acceptance criteria MUST be met before any samples or required blanks are analyzed. Any samples or required blanks analyzed when opening CCV technical acceptance criteria have not been met will require reanalysis at no additional cost to USEPA.

10.0 PROCEDURE

10.1 Summary of Sample Analysis

10.1.1 This method is designed for analysis of samples that contain trace concentrations of the target compounds listed in Exhibit C (Trace Volatiles). It is expected that the samples will come from drinking water and well/groundwater type sources around Superfund sites. If, upon inspection of a sample, the Contractor suspects that the sample is not amenable to this method, contact the Sample Management Office (SMO). SMO will contact the Region for instructions.

NOTE: If SIM analysis is requested for a sample, a full scan analysis at trace level must be performed on that sample prior to SIM analysis. For all SIM target compounds detected at or above CRQLs during the full scan analysis, a SIM analysis is not to be performed for that target compound. Any SIM analyses not performed for this reason must be noted in the Sample Delivery Group (SDG) Narrative.

10.1.2 Prior to the analysis of samples, establish the appropriate purge-and-trap Gas Chromatograph/Mass Spectrometer (GC/MS) operating conditions, as outlined in Section 9.1, analyze the instrument performance check solution (Section 9.2), and calibrate the GC/MS system according to Sections 9.3 through 9.4.6. Also prior to sample analysis, a method blank must be analyzed that meets blank technical acceptance criteria in Section 12.1.5. All samples, required blanks, and standard/spiking solutions must be allowed to warm to ambient temperature before analysis. All samples, required blanks, and calibration standards must be analyzed under the same instrument conditions.

10.1.3 If insufficient sample volume (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact SMO to apprise them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.2 Procedure for Sample Analysis

10.2.1 If the autosampler can automatically sample the appropriate volume then Sections 10.2.2 - 10.2.4 are performed by the autosampler. The pH determination procedure listed in Section 10.2.3 must still be performed manually.

10.2.2 Remove the plunger from a 25 mL syringe that has a closed syringe valve attached. 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 25.0 mL. This process of taking an aliquot destroys the validity of the sample for future analysis, unless the excess sample is immediately transferred to a smaller vial with zero headspace and stored at 4°C (±2°C).

10.2.3 For analysis by the Selected Ion Monitoring (SIM) technique, add a sufficient amount of the Deuterated Monitoring Compound (DMC) standard solution (Section 7.2.2.4) and a sufficient amount of internal standard spiking solution (Section 7.2.2.3) through the valve bore of the syringe, then close the valve. Invert the syringe 3 times.

Add a sufficient amount of the DMC standard solution (Section 7.2.2.4) and a sufficient amount of internal standard spiking solution (Section 7.2.2.3) through the valve bore of the syringe, then close the valve. Invert the syringe 3 times.

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

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

10.2.5 Close both valves and purge the sample for 11.0 (±0.1) minutes at ambient temperature.

10.2.6 Sample Desorption - After the 11-minute purge, attach the trap to the GC, adjust the purge-and-trap system to the desorb mode, initiate the temperature program sequence of the GC and start data acquisition. Introduce the trapped material to the GC column by rapidly heating the trap to 180°C while backflushing the trap with inert gas at 15 mL/minute for 4.0 ±0.1 minutes. While the trapped material is being introduced into the GC, empty the sample purger 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 purger with a detergent solution, rinse it with reagent water, and then dry it in an oven at 105°C.

10.2.7 Trap Reconditioning - After desorbing the sample, recondition the trap for a minimum of 7.0 ±0.1 minutes at 180°C by returning the purge-and-trap system to purge mode.

10.2.8 Gas Chromatography - Hold the column temperature at 10°C for 1.0 - 5.0 minutes, then program at 6°C/minute to 160°C and hold until 3 minutes after all target volatile compounds have eluted.

NOTE: Once an initial hold time has been chosen and the GC operating conditions optimized, the same GC condition must be used for the analysis.

10.2.9 Termination of Data Acquisition - 3 minutes after all the purgeable target compounds 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 Extracted Ion Current Profiles (EICPs).

10.2.10 Dilutions

10.2.10.1 An original undiluted analysis must be made and results reported for all samples. If the peak response for any target compound in any sample exceeds the peak response in the highest standard in the initial calibration, a new aliquot of that sample must be diluted and purged. Guidance for performing dilutions and exceptions to this requirement are given in Sections 10.2.10.2 - 10.2.10.8.

NOTE 1: If the laboratory has evidence or highly suspects, because of sample color or other physical properties, that a sample may contain high concentrations of either target or non-target compounds, then SMO shall be contacted immediately. SMO will seek Regional recommendations for diluted analysis.

NOTE 2: 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 a Relative Response Factor (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.

10.2.10.2 Use the results of the original analysis to determine the approximate Dilution Factor (DF) required to get the largest analyte peak within the calibration range.

10.2.10.3 The DF chosen must keep the concentration of the trace volatile target compounds that required dilution in the upper half of the initial calibration range.

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

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

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

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

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

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

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

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

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

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

10.2.10.7.3 Replace the syringe plunger and compress the water.

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

10.2.10.7.5 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 3 times. Analyze according to Section 10.2.

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

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification of Target Compounds

11.1.1 The compounds listed in the Target Compound List (TCL) [Exhibit C (Trace Volatiles)], shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

- Elution of the sample component at the same Gas Chromatograph (GC) Relative Retention Time (RRT) as the standard component; and
- Correspondence of the sample component and calibration standard component mass spectra.

11.1.2 For establishing correspondence of the GC RRT, the sample component RRT must be within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the 12-hour time period as the initial calibration, use the RRT values from the 5.0 µg/L standard [0.50 µg/L standard for Selected Ion Monitoring (SIM) analysis]. Otherwise, use the corresponding opening Continuing Calibration Verification (CCV) standard. For SIM analysis, use the RRT values of the median concentration standard. If coelution of interfering compounds prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned using the Extracted Ion Current Profile (EICP) for ions unique to the component of interest.

11.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/Mass Spectrometer (MS) are required. Once obtained, these standard spectra may be used for identification purposes, only if the Contractor's GC/MS meets the daily instrument performance requirements for 4-bromofluorobenzene (BFB). These standard spectra may be obtained from the standard analysis that was also used to obtain the RRTs.

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

11.1.4.1 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.

11.1.4.2 The relative intensities of ions specified in Section 11.1.4.1 must agree within ±20% between the standard and sample spectra (i.e., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30-70%).

11.1.4.3 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. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the adjusted Contract Required Quantitation Limit (CRQL), report the actual value followed by a "J" (e.g., "0.3J").

11.1.4.4 If a compound cannot be verified by all of the spectral identification criteria listed in Section 11.1.4, 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.

11.2 Qualitative Identification of Non-Target Compounds

11.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST (2002 release or later) or equivalent mass spectral library, shall be used as the reference library.

11.2.2 All organic compounds that have not been positively identified as volatile target analytes using the procedures detailed in Section 11.1, or that are not Deuterated Monitoring Compounds (DMCs) or internal standards shall be tentatively identified via a forward search of the NIST, Wiley, or equivalent mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalizations which would misrepresent the library or unknown spectra when compared to each other.

11.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form I VOA-TIC. 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" on Form I VOA-TIC. An alkane is defined as any hydrocarbon with the generic formula C_nH_{2n+2} (straight-chain or branched) or C_nH_{2n} (cyclic) that contains only C-H and C-C single bonds. The concentrations of each of the alkanes is to be summed and reported as a single result for the "total alkanes". Documentation for the tentative identification of each alkane shall be supplied in the hard copy deliverable packages. The alkanes are not to be counted as part of the 30 compounds individually reported as TICs on Form I VOA-TIC. Carbon dioxide and compounds with responses less than 10% of the internal standard in which they are to be quantified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.2.4 Rules for making tentative identification:

11.2.4.1 For compounds to be reported, as per the instructions in Section 11.2.3, identification (as generated by the library search program) of those receiving a library search match of 85% or higher should be considered a "probable match". The compound should be reported with the identification generated by the search program unless the mass spectral interpretation specialist feels there is just evidence not to report the compound as identified by the library search program.

11.2.4.2 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 target analyte list, unless the library search produces only one compound having a match of greater than 85%, and that compound is identified as a DMC, internal standard, or volatile target analyte.

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

11.2.4.4 If the mass spectral interpretation specialist has just evidence to support reporting a compound with a tentative identification of something other than that generated by the library search program (with a library search result of 85% or greater), the laboratory shall include in the Sample Delivery Group (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 tentatively identified compound has obvious isomer analogs, the laboratory shall include in the SDG narrative a statement indicating that the exact isomer configuration, as reported, may not be absolutely accurate.

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

11.3 Calculations

11.3.1 Target Compounds

11.3.1.1 Identified target compounds shall be quantified by the internal standard method using Equation 6. The internal standard used shall be that which is assigned in Table 3. The Mean Relative Response Factor ($\overline{RRF}$) from the initial calibration standard is used to calculate the concentration in the sample. When a target compound concentration is below its CRQL but the spectra meets the identification criteria, report the concentration with a "J". For example, if the CRQL is 0.50 µg/L and a concentration of 0.30 µg/L is calculated, report as "0.30 J". Report ALL sample concentration data as UNCORRECTED for blanks.

EQ. 6 Water Concentration Calculation

$$\text{Concentration in ug/L} = \frac{(A_x)\ (I_s)\ (DF)}{(A_{is})\ (\overline{RRF})\ (V_o)}$$

Where,

A_x = Area of the characteristic ion (EICP) for the compound to be measured. The primary quantitation ions for the target compounds, internal standards, and the DMCs are listed in Table 4.

A_{is} = Area of the characteristic ion (EICP) for the internal standard. The target compounds are listed with their associated internal standards in Table 3.

I_s = Amount of internal standard added in ng.

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

V_o = Total volume of water purged, in mL.

DF = Dilution Factor. The DF for analysis of water samples for volatiles by this method is defined as the ratio of the number of mL of water purged (i.e., V_o above) to the number of mL of the original water sample used for purging. For example, if 5.0 mL of sample is diluted to 25.0 mL with reagent water and purged, DF = 25.0 mL/5 mL = 5.0. If no dilution is performed, DF = 1.0.

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

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

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

11.3.1.4 The requirements listed in Sections 11.3.1.5 and 11.3.1.6 apply to all standards, samples, and blanks.

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

11.3.1.6 In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report, and shall include the integration scan range. In addition, a hardcopy printout of the EICP of the quantitation ion displaying the manual integration shall be included in the raw data. This applies to all compounds listed in Exhibit C (Trace Volatiles), internal standards, and DMCs.

11.3.2 Non-Target Compounds

11.3.2.1 An estimated concentration for non-target compounds tentatively identified shall be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

11.3.2.2 Equation 6 is also used for calculating non-target compound concentrations. Total area counts (or peak heights) from the total Reconstructed Ion Chromatograms (RICs) are to be used for both the non-target compound to be measured (A_x) and the internal standard (A_{is}). An RRF of 1.0 is to be assumed. The value from this quantitation shall be qualified by a "J" (estimate due to lack of a compound-specific RRF), and "N" (presumptive evidence of presence), indicating the qualitative and quantitative uncertainties associated with this non-target compound. An estimated concentration must be calculated for all TICs, as well as those identified as unknowns.

11.3.3 CRQL Calculation

Calculate the adjusted CRQL for trace volatiles by using Equation 7.

EQ. 7 Water Adjusted CRQL Calculation

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

Where,

Contract CRQL = Exact CRQL values in Exhibit C of the Statement of Work (SOW).

V_o = Total volume of water purged in mL.

NOTE: Must not exceed the contract sample volume.

V_c = Contract sample volume in mL (25 mL).

DF = Same as EQ. 6.

11.3.4 Deuterated Monitoring Compound (DMC) Recoveries

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

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

EQ. 8 DMC Percent Recovery Calculation

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

Where,

Q_d = Concentration or amount determined by analysis.

Q_a = Concentration or amount added to sample/blank.

DF = Same as EQ. 6.

11.3.5 Internal Standard Responses and Retention Times (RTs)

Internal standard responses and RTs in all samples and blanks must be evaluated during or immediately after data acquisition. Compare the sample/blank internal standard responses and RTs to the opening CCV internal standard responses and RTs. For samples and blanks analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and RTs against the initial calibration standard with non-ketone concentrations of 5.0 µg/L, ketone concentrations of 50 µg/L, and a 1,4-dioxane concentration of 250 µg/L (25 µg/L concentration of 1,4-dioxane and 0.5 µg/L concentration for other compounds analyzed by SIM). The EICP of the internal standards must be monitored and evaluated for each sample and blank.

11.4 Technical Acceptance Criteria for Sample Analysis

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

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

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

11.4.4 The Percent Recovery (%R) of each of the DMCs in the sample must be within the acceptance windows in Table 5. The recovery limits for 1,4-dioxane-d_8 are advisory. Up to three DMCs, excluding 1,4-dioxane-d_8, per sample may fail to meet the recovery limits listed in Table 5. For SIM analysis, all DMCs must meet the recovery limits listed in Table 5.

11.4.5 The EICP area for each of the internal standards in the sample must be within the range of 60.0% and 140% of its response in the most recent opening CCV standard analysis.

11.4.6 The RT shift for each of the internal standards in the sample must be within ±0.33 minutes (20.0 seconds) of its RT in the most recent opening CCV standard analysis.

11.4.7 Excluding those ions in the solvent front, no ion may saturate the detector. No peak response of any target compound in any sample should exceed the peak response of the highest standard in the initial calibration, unless a more diluted aliquot of the sample is also analyzed according to the procedures in Section 10.2.10.

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

11.4.8.1 Analyze an instrument blank immediately after the contaminated sample. If an autosampler is used, an instrument blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The instrument blanks must meet the technical acceptance criteria for blank analysis (Section 12.1.5);

or

Monitor the analyzed sample immediately after the contaminated sample for all the compounds that were in the contaminated sample and that exceeded the limits above. The maximum carryover criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds, or above 2 µg/L for the non-target compounds that exceeded the limits in the contaminated sample. If an autosampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample must also meet the maximum carryover criteria.

11.5 Corrective Action for Sample Analysis

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

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

11.5.3 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 purge-and-trap transfer lines, to recalibrate the instrument, or take other corrective action procedures to meet the technical acceptance criteria.

11.5.4 Sample reruns performed as a result of suspected matrix interference beyond the scope of the method will be evaluated on a case-by-case basis for payment purposes by the USEPA Contract Laboratory Program Project Officer (CLP PO). Send a copy of the SDG Narrative (including the Contract Number), a description of the situation, and the requested action to the CLP PO.

11.5.5 If the contractor needs to analyze more than one sample dilution other than the original analysis to have all the target compounds within the initial calibration range, contact the Sample Management Office (SMO). SMO will contact the Region for instruction.

11.5.6 All samples to be reported to USEPA must meet the maximum carryover criteria in Section 11.4.8. If any sample fails to meet these criteria, each subsequent analysis must be checked for cross contamination. The analytical system is considered contaminated until a sample has been analyzed that meets the maximum carryover criteria or an instrument blank has been analyzed that meets the technical acceptance criteria for blanks. If an instrument blank is not analyzed between consecutive samples that have the same compound with a concentration exceeding the calibration range, then the second sample must be appropriately diluted as in Section 10.2.10 and analyzed. If in the dilution this compound is detected at levels at or below the adjusted CRQL, then all samples analyzed after the second sample that fail to meet maximum carryover criteria must be reanalyzed. If in the dilution this compound is detected within the calibration range, then no further corrective action is needed.

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Summary of Blank Analyses

There are three different types of blanks required by this method.

12.1.1.1 Method Blank - 25 mL of reagent water spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and Deuterated Monitoring Compound (DMC) solution (Section 7.2.2.4), and carried through the entire analytical procedure. The purpose of the method blank is to determine the levels of contamination associated with processing and analysis of samples.

12.1.1.2 Storage Blank - Upon receipt of the first samples in a Sample Delivery Group (SDG), two 40 mL screw-cap VOA vials with a polytetrafluoroethylene (PTFE)-faced silicone septum are filled with reagent water (80 mL total). The vials are stored with the samples in the SDG under the same conditions. A 25.0 mL aliquot of this reagent water is spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and DMC solution (Section 7.2.2.4), and analyzed after all samples in the SDG have been analyzed. The storage blank indicates whether contamination may have occurred during storage of samples.

12.1.1.3 Instrument Blank - 25 mL of reagent water spiked with sufficient amount of internal standard spiking solution (Section 7.2.2.3) and DMC 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 compound exceeding the calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample.

12.1.2 Frequency of Blank Analyses

12.1.2.1 The method blank must be analyzed at least once during every 12-hour time period on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used for trace volatile analysis (see Section 9.2.2 for the definition of the 12-hour time period).

12.1.2.2 The method blank must be analyzed after the Continuing Calibration Verification (CCV) and before any samples or storage blanks are analyzed. The method blank must be analyzed after the initial calibration sequence if samples are analyzed before the 12-hour time period expires. A method blank must be analyzed in each 12-hour time period in which samples (including dilutions) and storage blanks from an SDG are analyzed.

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

12.1.2.4 The Contractor must demonstrate that there is no carryover from contaminated samples before data from subsequent analyses may be used. Samples may contain target compounds at levels exceeding the initial calibration range or non-target compounds at concentrations greater than 100 µg/L, or ions from a compound that saturate the detector (excluding the compound peaks in the solvent front). An instrument blank must be analyzed immediately after the contaminated sample (also in the same purge inlet if an autosampler is used), or a sample that meets the maximum carryover criteria in Section 11.4.8 must be analyzed. For these purposes, if the instrument blank meets the technical acceptance criteria for blank analysis or the sample meets the maximum carryover criteria, the system is considered to be uncontaminated. If the instrument blank or sample does not meet the criteria (i.e., contaminated), the system must be decontaminated. Until an instrument blank meets the blank technical acceptance criteria or a sample meets the maximum carryover criteria, any samples analyzed since the original contaminated sample will require reanalysis at no additional cost to USEPA.

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 12.1.5.6) must be reported. Instrument blanks analyzed during the instrument decontamination process that exceed the requirements listed in Section 11.4.8 do not need to be reported.

12.1.3 Procedure for Blank Analyses

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

12.1.3.2 Under no circumstances should blanks be analyzed at a dilution (i.e., blanks should always have a DF=1.0).

12.1.4 Calculations for Blank Analyses

Perform data analysis and calculations according to Section 11.

12.1.5 Technical Acceptance Criteria for Blank Analyses

12.1.5.1 All blanks must be analyzed on a GC/MS system meeting the 4-bromofluorobenzene (BFB), initial calibration, and continuing calibration verification technical acceptance criteria, and at the frequency described in Section 12.1.2.

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

12.1.5.3 The Percent Recovery (%R) of each of the DMCs in the blank must be within the acceptance windows in Table 5. The recovery limits for 1,4-dioxane-d_8 are advisory.

12.1.5.4 The Extracted Ion Current Profile (EICP) area for each of the internal standards in the blank must be within the range of 60.0% and 140% of its response in the most recent opening CCV standard analysis.

12.1.5.5 The Retention Time (RT) shift for each of the internal standards in the blank must be within ±0.33 minutes (20.0 seconds) of its RT in the most recent opening CCV standard analysis.

12.1.5.6 The concentration of each target compound found in the storage and method blanks must be less than the Contract Required Quantitation Limit (CRQL) listed in Exhibit C (Trace Volatiles), except for methylene chloride, acetone, and 2-butanone, which must be less than 2 times the respective CRQL. The concentration of each target compound in the instrument blank must be less than its CRQL listed in Exhibit C (Trace Volatiles). The concentration of non-target compounds in all blanks must be less than 2.0 µg/L.

12.1.5.7 All blanks (storage/instrument/method) must be analyzed at the original concentration only (i.e., DF=1.0).

12.1.6 Corrective Action for Blank Analyses

12.1.6.1 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. If a Contractor's blanks exceed the criteria in Section 12.1.5.6, the Contractor must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds.

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

12.1.6.3 Any instrument blank that fails to meet the technical acceptance criteria described in Section 12.1.5.6 requires reanalysis of the samples analyzed after the instrument blank having any target compounds detected at levels above the CRQLs at no additional cost to USEPA.

12.1.6.4 If the storage blank does not meet the technical acceptance criteria for blank analyses in Sections 12.1.5.1 to 12.1.5.6, correct system problems and reanalyze the storage blank. If the storage blank does not meet the criteria in Section 12.1.5.6, reanalyze the blank to determine whether the contamination occurred during storage or during analyses. If upon reanalysis, the storage blank meets the criteria in Section 12.1.5.6, the problem occurred during the analysis and the reanalyzed storage blank results must be reported. If upon reanalysis the storage blank did not meet the criteria in Section 12.1.5.6, the problem occurred during storage. The Laboratory Manager or their designee must address the problem in the SDG Narrative and discuss the corrective actions implemented to prevent future occurrences.

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

12.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.2.1 Summary of MS/MSD

In order to evaluate the effects of the sample matrix on the method used for trace volatile analysis, USEPA has prescribed a mixture of volatile target compounds to be spiked into two aliquots of a sample, and analyzed in accordance with the appropriate method, upon request.

12.2.2 Frequency of MS/MSD

12.2.2.1 An MS/MSD shall be analyzed if requested by the Region [through the Sample Management Office (SMO)] or specified on the Traffic Report/Chain of Custody Record (TR/COC). If requested, a MS/MSD must 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 Selected Ion Monitoring (SIM) technique.

12.2.2.2 As part of USEPA's Quality Assurance/Quality Control (QA/QC) program, water rinsate samples and/or field/trip blanks (field QC) may be delivered to a laboratory for analysis. The Contractor shall not perform MS/MSD analysis on any of the field QC samples.

12.2.2.3 If the USEPA Region requesting MS/MSD designates a sample to be used as an MS/MSD, then that sample must be used. If there is insufficient sample, less than the required amount, remaining to perform an MS/MSD, then the Contractor shall choose another sample to perform an MS/MSD analysis. At the time the selection is made, the Contractor shall notify SMO that insufficient sample was received and identify the USEPA sample selected for the MS/MSD analysis. SMO shall contact the Region for confirmation immediately after notification. The rationale for the choice of a sample other than the one designated by the Region shall be documented in the SDG Narrative.

12.2.2.4 If an insufficient number of sample vials were received to perform an MS/MSD, and MS/MSD are required, then the Contractor shall immediately contact SMO to inform them of the problem. SMO will contact the Region for instructions. The Region will either approve that no MS/MSD is required, or require that a reduced sample aliquot be used for the MS/MSD analysis. SMO will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.

12.2.2.5 If it appears that the Region has requested MS/MSD analysis at a greater frequency than specified in Section 12.2.2.1, the Contractor shall contact SMO. SMO will contact the Region to determine which samples should have an MS/MSD performed on them. SMO will notify the Contractor of the Region's decision. The Contractor shall document the decision in the SDG Narrative. If this procedure is not followed, the Contractor will not be paid for MS/MSD analysis performed at a greater frequency than required by the contract.

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

12.2.2.7 When a Contractor receives a PE sample as part of a larger SDG, a sample other than the PE sample must be chosen for the requested MS/MSD analysis when the Region did not designate samples to be used for this purpose.

12.2.3 Procedure for Preparing MS/MSD

12.2.3.1 If requested, add 10 µL of the matrix spiking solution (Section 7.2.2.5) to each of the 25 mL aliquots of the sample chosen for spiking. Process the samples according to Section 10.1. Disregarding any dilutions, this is equivalent to a concentration of 5 µg/L of each Matrix Spike compound.

12.2.3.2 MS/MSD samples must be analyzed at the same concentration as the most concentrated aliquot for which the original sample results will be reported. Sample dilutions must be performed in accordance with Section 10.2.10. Do **not** further dilute MS/MSD samples to get **either** spiked **or** non-spiked analytes within calibration range.

12.2.4 Calculations for MS/MSD

12.2.4.1 Calculate the concentrations of the Matrix Spike compounds using the same equations as used for target compounds (Equation 6). Calculate the recovery of each Matrix Spike compound as follows:

EQ. 9 Matrix Spike Recovery Calculation

$$\text{Matrix Spike Recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100$$

Where,

SSR = Spiked Sample Result.

SR = Sample Result.

SA = Spike Added.

12.2.4.2 Calculate the Relative Percent Difference (RPD) of the recoveries of each compound in the MS/MSD as follows:

EQ. 10 Relative Percent Difference Calculation

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

Where,

MSR = Matrix Spike Recovery.

MSDR = Matrix Spike Duplicate Recovery.

12.2.5 Technical Acceptance Criteria for MS/MSD

12.2.5.1 If requested, all MS/MSD must be prepared and analyzed at the frequency described in Section 12.2.2. All MS/MSDs must be analyzed on a GC/MS system meeting the BFB, initial calibration, and continuing calibration verification technical acceptance criteria, and the blank technical acceptance criteria.

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

12.2.5.3 The RT shift for each of the internal standards in the MS/MSD must be within ±0.33 minutes (20 seconds) of its RT in the most recent opening CCV standard analysis.

12.2.5.4 The limits for Matrix Spike compound recovery and RPD are given in Table 6. As these limits are only advisory, no further action by the laboratory is required. However, frequent failures to meet the limits for recovery or RPD warrant investigation by the laboratory, and may result in questions from USEPA.

12.2.6 Corrective Action for MS/MSD

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

12.3 Method Detection Limit (MDL) Determination

12.3.1 Before any field samples are analyzed under the contract, the MDL for each volatile target compound shall be determined on each instrument used for analysis. MDL determination is level-specific (i.e., the MDL shall be determined for trace and trace SIM levels). The MDLs must be verified annually thereafter (see Section 12.3.2 for MDL verification procedures), until the contract expires or is terminated, or after major instrument maintenance. Major instrument maintenance includes, but is not limited to, cleaning or replacement of the mass spectrometer source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device), GC column, and replacement or overhaul of the purge-and-trap device.

12.3.2 To determine the MDLs, the Contractor shall run an MDL study following the procedures specified in 40 CFR Part 136. The Contractor shall analyze the MDL samples on each instrument used for field sample analyses. MDL verification is achieved by analyzing a single reagent water blank spiked with each volatile target compound at a concentration equal to 1-4 times the analytically determined MDL. Each target compound must produce a response and meet the criteria in Section 11.1. The resulting mass spectra of each target compound must meet the qualitative identification criteria outlined in Sections 11.1.1 through 11.1.4.3.

12.3.3 The determined concentration of the MDL must be less than the CRQL.

12.3.4 All documentation for the MDL studies shall be maintained at the laboratory and provided to USEPA upon written request.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

14.1 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 operation. USEPA 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, USEPA recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington D.C., 20036, (202) 872-4386.

15.0 WASTE MANAGEMENT

USEPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

US Environmental Protection Agency. Purge-and-Trap for Aqueous Samples. Method 5030C. Revision 3. May 2003.

US Environmental Protection Agency. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Method 8260B. Revision 2. December 1996.

US Environmental Protection Agency. Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry. Method 524.2. August 1992.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

4-bromofluorobenzene Key Ions and Abundance Criteria

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

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% that of m/z 95.

Table 2

Technical Acceptance Criteria for Initial and Opening Continuing Calibration Verification for Trace Volatile Organic Compounds

Volatile Compound	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
Dichlorodifluoromethane	0.010	40.0	±40.0
Chloromethane	0.010	40.0	±40.0
Vinyl chloride	0.100	30.0	±30.0
Bromomethane	0.100	30.0	±30.0
Chloroethane	0.010	40.0	±40.0
Trichlorofluoromethane	0.010	40.0	±40.0
1,1-Dichloroethene	0.100	30.0	±30.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	40.0	±40.0
Acetone	0.010	40.0	±40.0
Carbon disulfide	0.010	40.0	±40.0
Methyl acetate	0.010	40.0	±40.0
Methylene chloride	0.010	40.0	±40.0
trans-1,2-Dichloroethene	0.010	40.0	±40.0
Methyl tert-butyl ether	0.010	40.0	±40.0
1,1-Dichloroethane	0.200	30.0	±30.0
cis-1,2-Dichloroethene	0.010	40.0	±40.0
2-Butanone	0.010	40.0	±40.0
Bromochloromethane	0.050	30.0	±30.0
Chloroform	0.200	30.0	±30.0
1,1,1-Trichloroethane	0.100	30.0	±30.0
Cyclohexane	0.010	40.0	±40.0
Carbon tetrachloride	0.100	30.0	±30.0
Benzene	0.400	30.0	±30.0
1,2-Dichloroethane	0.100	30.0	±30.0
1,4-Dioxane	0.0050	50.0	±50.0
Trichloroethene	0.300	30.0	±30.0
Methylcyclohexane	0.010	40.0	±40.0
1,2-Dichloropropane	0.010	40.0	±40.0
Bromodichloromethane	0.200	30.0	±30.0
cis-1,3-Dichloropropene	0.200	30.0	±30.0
4-Methyl-2-pentanone	0.010	40.0	±40.0
Toluene	0.400	30.0	±30.0
trans-1,3-Dichloropropene	0.100	30.0	±30.0
1,1,2-Trichloroethane	0.100	30.0	±30.0
Tetrachloroethene	0.100	30.0	±30.0
2-Hexanone	0.010	40.0	±40.0
Dibromochloromethane	0.100	30.0	±30.0
1,2-Dibromoethane	0.010	40.0	±40.0
Chlorobenzene	0.500	30.0	±30.0
Ethylbenzene	0.100	30.0	±30.0
m,p-Xylene	0.300	30.0	±30.0
o-Xylene	0.300	30.0	±30.0
Styrene	0.300	30.0	±30.0
Bromoform	0.050	30.0	±30.0

Table 2

Technical Acceptance Criteria for Initial and Opening Continuing Calibration Verification for Trace Volatile Organic Compounds (Con't)

Volatile Compound	Minimum RRF[1]	Maximum %RSD	Maximum %Diff[1]
Isopropylbenzene	0.010	40.0	±40.0
1,1,2,2-Tetrachloroethane	0.100	30.0	±30.0
1,3-Dichlorobenzene	0.400	30.0	±30.0
1,4-Dichlorobenzene	0.400	30.0	±30.0
1,2-Dichlorobenzene	0.400	30.0	±30.0
1,2-Dibromo-3-chloropropane	0.010	40.0	±40.0
1,2,4-Trichlorobenzene	0.200	30.0	±30.0
1,2,3-Trichlorobenzene	0.200	30.0	±30.0
Deuterated Monitoring Compounds			
Vinyl chloride-d_3	0.010	30.0	±30.0
Chloroethane-d_5	0.010	40.0	±40.0
1,1-Dichloroethene-d_2	0.010	30.0	±30.0
2-Butanone-d_5	0.010	40.0	±40.0
Chloroform-d	0.010	30.0	±30.0
1,2-Dichloroethane-d_4	0.010	30.0	±30.0
Benzene-d_6	0.010	30.0	±30.0
1,2-Dichloropropane-d_6	0.010	40.0	±40.0
Toluene-d_8	0.010	30.0	±30.0
trans-1,3-Dichloropropene-d_4	0.010	30.0	±30.0
2-Hexanone-d_5	0.010	40.0	±40.0
1,4-Dioxane-d_8	0.0050	50.0	±50.0
1,1,2,2-Tetrachloroethane-d_2	0.010	30.0	±30.0
1,2-Dichlorobenzene-d_4	0.010	30.0	±30.0

[1]For a closing CCV, all target compounds and DMCs must meet a minimum RRF of 0.010 and a maximum percent difference of ±50.0, except for 1,4-dioxane and 1,4-dioxane-d_8, which must meet a minimum RRF of 0.0050 and a maximum Percent Difference of ±50.0.

Table 3

Trace Volatile Target Compounds and Deuterated Monitoring Compounds with Corresponding Internal Standards for Quantitation

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

Table 4

Characteristic Ions for Trace Volatile Target Compounds

Target Compound	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
1,4-Dioxane	88	43,58
Trichloroethene	95	97, 132, 130
Methylcyclohexane	83	55, 98
1,2-Dichloropropane	63	112
Bromodichloromethane	83	85, 127
cis-1,3-Dichloropropene	75	77
4-Methyl-2-pentanone	43	58, 100
Toluene	91	92
trans-1,3-Dichloropropene	75	77
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Tetrachloroethene	164	129, 131, 166
2-Hexanone	43	58, 57, 100
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Chlorobenzene	112	77, 114
Ethylbenzene	91	106
m,p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78

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

Table 4

Characteristic Ions for Trace Volatile Target Compounds (Con't)

Analyte	Primary Quantitation Ion	Secondary Ion(s)
Bromoform	173	175, 254
Isopropylbenzene	105	120, 77
1,1,2,2-Tetrachloroethane	83	85, 131
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene	146	111, 148
1,2-Dibromo-3-chloropropane	75	157, 155
1,2,4-Trichlorobenzene	180	182, 145
1,2,3-Trichlorobenzene	180	182, 145
Deuterated Monitoring Compounds		
Vinyl chloride-d_3	65	67
Chloroethane-d_5	69	71, 51
1,1-Dichloroethene-d_2	63	98, 65
2-Butanone-d_5	46	77
Chloroform-d	84	86, 47, 49
1,2-Dichloroethane-d_4	65	67, 51
Benzene-d_6	84	82, 54, 52
1,2-Dichloropropane-d_6	67	65, 46, 42
Toluene-d_8	98	100, 42
trans-1,3-Dichloropropene-d_4	79	81, 42
2-Hexanone-d_5	63	46
1,4-Dioxane-d_8	96	51, 66
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 5

Deuterated Monitoring Compound Recovery Limits

Compound	Percent Recovery Limits
Vinyl chloride-d_3	65-131
Chloroethane-d_5	71-131
1,1-Dichloroethene-d_2	55-104
2-Butanone-d_5	49-155
Chloroform-d	78-121
1,2-Dichloroethane-d_4	78-129
Benzene-d_6	77-124
1,2-Dichloropropane-d_6	79-124
Toluene-d_8	77-121
trans-1,3-Dichloropropene-d_4	73-121
2-Hexanone-d_5	28-135
1,4-Dioxane-d_8	50-150
1,1,2,2-Tetrachloroethane-d_2	73-125
1,2-Dichlorobenzene-d_4	80-131

NOTE: The recovery limits for any of the compounds listed above may be expanded at any time during the period of performance if USEPA determines that the limits are too restrictive. The recovery limits for 1,4-dioxane-d_8 are advisory.

Table 6

Matrix Spike Recovery and Relative Percent Difference Limits

Compound	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

Table 7

Volatile Deuterated Monitoring Compounds and the Associated Target Compounds

Chloroethane-d_5 (DMC)	**1,2-Dichloropropane-d_6 (DMC)**	**1,2-Dichlorobenzene-d_4 (DMC)**
Dichlorodifluoromethane	Cyclohexane	Chlorobenzene
Chloromethane	Methylcyclohexane	1,3-Dichlorobenzene
Bromomethane	1,2-Dichloropropane	1,4-Dichlorobenzene
Chloroethane	Bromodichloromethane	1,2-Dichlorobenzene
Carbon disulfide		1,2,4-Trichlorobenzene
		1,2,3-Trichlorobenzene

1,4-Dioxane-d_8 (DMC)	**trans-1,3-Dichloropropene-d_4 (DMC)**	**Chloroform-d (DMC)**
1,4-Dioxane	cis-1,3-Dichloropropene	1,1-Dichloroethane
	trans-1,3-Dichloropropene	Bromochloromethane
	1,1,2-Trichloroethane	Chloroform
		Dibromochloromethane
		Bromoform

2-Butanone-d_5 (DMC)	**1,1-Dichloroethene-d_2 (DMC)**	**2-Hexanone-d_5 (DMC)**
Acetone	trans-1,2-Dichloroethene	4-Methyl-2-pentanone
2-Butanone	cis-1,2-Dichloroethene	2-Hexanone

Vinyl chloride-d_3 (DMC)	**Benzene-d_6 (DMC)**	**1,1,2,2-Tetrachloroethane-d_2 (DMC)**
Vinyl chloride	Benzene	1,1,2,2-Tetrachloroethane
		1,2-Dibromo-3-chloropropane

1,2-Dichloroethane-d_4 (DMC)		**Toluene-d_8 (DMC)**
Trichlorofluoromethane		Trichloroethene
1,1-Dichloroethene		Toluene
1,1,2-Trichloro-1,2,2-trifluoroethane		Tetrachloroethene
Methyl acetate		Ethylbenzene
Methylene chloride		o-Xylene
Methyl tert-butyl ether		m,p-Xylene
1,1,1-Trichloroethane		Styrene
Carbon tetrachloride		Isopropylbenzene
1,2-Dibromoethane		
1,2-Dichloroethane		

Table 8

Volatile Deuterated Monitoring Compounds and the Associated Target Compounds for Selected Ion Monitoring Analysis

1,4-Dioxane-d_8 (DMC)	**1,1,2,2-Tetrachloroethane-d_2 (DMC)**	**1,2-Dichloroethane-d_4 (DMC)**
1,4-Dioxane	1,2-Dibromo-3-chloropropane	1,2-Dibromoethane