EXHIBIT D

ANALYTICAL METHOD FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS (VOC) IN AIR COLLECTED IN SPECIALLY-PREPARED CANISTERS AND ANALYZED BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

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Exhibit D – Analytical Method for the Analysis of VOCs in Air

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1.0 SCOPE AND APPLICATION

1.1 This method is based on more than 30 years of USEPA's experience in determination of air toxics. Measurement of organic pollutants in ambient air is often difficult, in part because of the variety of organic substances of potential concern, the variety of potential techniques for sampling and analysis, and the lack of standardized and documented methods. As a result, the National Risk Management Research Laboratory (NRMRL) developed a Second Edition of the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* to assist Federal, State, and local regulatory personnel in developing and maintaining necessary expertise and up-to-date monitoring technology for characterizing organic pollutants in the ambient air. This method is based upon Method TO-15 as published in the January 1999 edition.

1.2 The analytical method that follows is designed to analyze air samples for volatile organic compounds on the Target Compound List (TCL) in Exhibit C. The method includes specifications for canister cleaning, sample collection, sample preconcentration and analysis to determine the approximate concentration of volatile organic constituents in the sample. The actual analysis is based on a preconcentration Gas Chromatograph/Mass Spectrometer (GC/MS) method for air samples. In addition, if required, samples will be analyzed for a select group of compounds using Selected Ion Monitoring (SIM) technique. If a SIM analysis is required, a full scan GC/MS analysis should be performed first. All sample results at or below the Contract Required Quantitation Limit (CRQL) shall be re-analyzed using SIM mode. If all required analytes are detected during full scan GC/MS analysis, then a SIM analysis is not to be performed and this should be documented in the SDG narrative. Laboratories which possess instruments that can perform SCAN and SIM analyses concurrently need not perform separate analyses as long as all requirements are met for both analyses.

1.3 This method also allows for the optional determination of tentatively identified compounds (TICs). If TICs are needed, the data user should notify the laboratory prior to sampling and specify the number of unknowns to be reported. Note the target compounds are reported in both ppbv and $\mu g/m^3$. Since conversion from ppbv to $\mu g/m^3$ requires knowledge of the molecular weight, TICs can only be reported in ppbv.

1.4 This method documents sampling and analytical procedures for the measurement of 66 volatile organic compounds (VOCs) that are a subset of the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. Table 1 contains the list of the target VOCs along with their CAS number, boiling point, vapor pressure and molecular weight.

1.5 This method applies to ambient concentrations of VOCs and typically requires VOC enrichment by concentrating up to one liter of a sample volume to achieve a Contract Required Quantitation Limit (CRQL) of 0.5 ppbv using SCAN GC/MS. The use of Selected Ion Monitoring (SIM) GC/MS can lower the CRQL to 0.05 ppbv.

1.6 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to

losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations within the 30-day specified holding time (see Section 8).

1.7 This method uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme which is generally more desirable than the use of single or even multiple specific detectors. In addition, this method establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. This method includes enhanced provisions for inherent quality control. The method uses internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

2.0 SUMMARY OF METHOD

2.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

2.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

2.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Samples must be analyzed within 30 days from collection.

2.4 To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

2.5 As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

2.6 Other water management approaches including commercially available water management systems are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Sections 11 and 12. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

2.7 The analytical strategy for this method involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring a select number of ions [Selected Ion Monitoring (SIM) mode] based on a subset of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the quantitation ion is compared with the system response to the quantitation ion for known amounts of the compound. This establishes the compound concentration that exists in the sample.

2.8 Results for target compounds are reported in both ppbv and $\mu g/m^3$. If TICs are requested, they are reported in ppbv only. The laboratory must document any analytical or technical problems encountered in the SDG Narrative. Laboratories are encouraged to be very detailed in the Narrative.

3.0 DEFINITIONS

3.1 Gauge Pressure — Pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

3.2 Absolute Pressure — Pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.

3.3 Cryogen — A refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogens are liquid nitrogen (bp: -195.8°C), liquid argon (bp: -185.7°C), and liquid carbon dioxide (bp: -79.5°C).

3.4 Dynamic Calibration — Calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

3.5 Dynamic Dilution — Means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

3.6 MS-SCAN — Mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

3.7 MS-SIM — Mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

3.8 Qualitative Accuracy — The degree of measurement accuracy required to correctly identify compounds with an analytical system.

3.9 Quantitative Accuracy — The degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

3.10 Replicate Precision — Precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage (see Section 12 for performance criteria for replicate precision).

3.11 Laboratory Control Sample – For the purpose of this SOW, a replicate of the Continuing Calibration Verification standard that is analyzed immediately after the method blank in the analytical sequence.

3.12 Duplicate Precision — precision determined from the analysis of the Continuing Calibration Verification standard and the Laboratory Control Sample taken from the same standard canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

3.13 Laboratory Control Sample Accuracy — the concentration determined by analysis of a laboratory control sample divided by the nominal value expressed as a percentage (see Section 12 for performance criteria for laboratory control sample).

4.0 INTERFERENCES

4.1 Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column, mitigates this problem.

4.2 Interferences in canister samples may result from improper use or from contamination of:

- canisters due to poor manufacturing practices,
- canister cleaning apparatus,
- sampling or analytical system.

Attention to the following details will help to minimize the possibility of contamination of canisters.

4.2.1 Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after “aging” for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

4.2.2 Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

4.2.3 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

4.2.4 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake-out and purging of the entire system may be required.

4.3 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to eliminate the presence of methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all Gas Chromatography (GC) carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

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. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should 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 maybe achieved using equipment and supplies other than those specified here, but demonstration of equivalent performance meeting the requirements of this 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 Analytical Apparatus

6.1.1 Sampling/Concentrator System

6.1.1.1 Electronic Mass Flow Controllers

Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

6.1.1.2 Vacuum Pump

General purpose laboratory pump, capable of reducing the downstream pressure of the flow controller to provide the pressure differential necessary to maintain controlled flow rates of sample air.

6.1.1.3 Stainless Steel Tubing and Stainless Steel Fittings

Coated with fused silica to minimize active adsorption sites.

6.1.1.4 Stainless Steel Cylinder Pressure Regulators. Standard, two-stage cylinder regulators with pressure gauges.

6.1.1.5 Gas Purifiers

Used to remove organic impurities and moisture from gas streams.

6.1.1.6 Six-port Gas Chromatographic Valve

For routing sample and carrier gas flows.

6.1.1.7 Multisorbent Concentrator

[Note: Guidance on the performance and selection of sorbents used in systems containing a solid sorbent preconcentrator with a cryofocusing trap are described in EPA Compendium Methods TO-15 and TO-17.]

Solid adsorbent packing with various retentive properties for adsorbing trace gases are commercially available from several sources. The packing contains more than one type of adsorbent packed in series. The following solid multisorbent concentrators or equivalent may be used.

6.1.1.7.1 A pre-packed solid adsorbent trap (Supelco 2-0321 or equivalent) containing 200 mg Carbopack B (60/80 mesh) and 50 mg Carbosieve S-III (60/80 mesh) retains VOCs and allows some water vapor to pass through.

6.1.1.7.2 A multisorbent containing Tenax/Ambersorb 340/Charcoal or equivalent trap approximately 20% of the initial water content in the sample after sampling 500 mL of air. Additional water reduction by a factor of 8 can be attained at temperatures of 45°C or higher (determined by using atomic emission detection of hydrogen atoms plotted versus purge gas volume.) Still further water reduction is possible using a two-stage concentration/dryer system.

6.1.1.8 Cryogenic Concentrator. Complete units are commercially available from several vendor sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

6.1.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System

6.1.2.1 Gas Chromatograph. The gas chromatographic (GC) system must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g., -50°C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from the focusing trap in a two stage system obviates the need for retrapping of compounds on the column. The system must include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber components must not be used.

6.1.2.2 Chromatographic Columns. 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given in the Technical Acceptance criteria in Sections 9, 11 and 12.

6.1.2.3 Mass Spectrometer. Either a linear quadrupole or ion trap mass spectrometer can be used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed. The system must be capable of SIM or equivalent. The instrument must be vented to the outside of the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.1.2.3.1 Linear Quadrupole Technology. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radio frequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrapole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

6.1.2.3.2 Ion Trap Technology. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one shet (ring electrode) and a hyperboloid of two shets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) is applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r, from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z, along the ion traps axis), and if the field were static the ions would eventually strike an electrode.

However, in an RF field, the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable.

The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

6.1.2.4 GC/MS Interface. Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points for each of the analytes of interest and can be used to achieve all acceptable performance criteria may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass, glass-lined, or fused silica-lined materials are recommended. Glass and fused silica should be deactivated.

6.1.2.5 Data System. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching 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 a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of 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 operational data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

6.1.2.6 Off-line Data Storage Device. Device must be capable of rapid recording and retrieval of data and must be suitable for long-term, off-line data storage.

6.2 Calibration System and Manifold Apparatus

6.2.1 Calibration Manifold. Stainless steel, glass, or high purity quartz manifold, (e.g., 1.25-cm I.D. x 66-cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heated to ~50°C.

6.2.2 Humidifier. 500-mL impinger flask containing HPLC grade deionized water.

6.2.3 Electronic Mass Flow Controllers. One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders in use for calibration.

6.2.4 PTFE Filter(s). 47-mm PTFE filter for particulate collection.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures. Best source (see Section 7.2).

7.1.2 Helium and Air. Ultra-high purity grade in gas cylinders. He is used as carrier gas in the GC.

7.1.3 Liquid Nitrogen, Liquid Argon, or Liquid Carbon Dioxide. Used to cool secondary trap.

7.1.4 Deionized Water. High performance liquid chromatography (HPLC) grade, ultra-high purity (for humidifier).

7.2 Standards

7.2.1 Introduction

7.2.1.1 When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Manufacturer’s certificates of analysis must be retained to track the expiration date.

7.2.1.2 The neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

7.2.1.3 Cylinder(s) containing approximately 10 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder. Refer to manufacturer's specifications for guidance on purchasing and mixing VOCs in gas cylinders.

7.2.2 Preparing Working Standards

7.2.2.1 Instrument Performance Check Standard

Prepare a standard solution of BFB in humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the optimized concentration parameters.

7.2.2.2 Calibration Standards Scan Mode

Prepare five working initial calibration standards in humidified zero air at a concentration which will allow collection at the 0.5, 2, 5, 10, and 25 ppbv level for each component under the optimized concentration parameters. Continuing Calibration Verification working standard for Scan Mode shall be prepared containing all the target compounds at the 10 ppbv calibration level.

7.2.2.3 Calibration Standards SIM Mode

Prepare initial calibration standards at a minimum of five concentration levels that are applicable to the sensitivity of the instrument. For most operations, the calibration concentrations are to be prepared at 0.05, 0.1, 0.2, 0.4 and 0.8 ppbv for each target compound of interest. Continuing Calibration Verification working standards for SIM Mode shall be prepared containing each target compounds of interest at the 0.4 ppbv calibration level.

7.2.2.4 Internal Standard Spiking Mixture Scan Mode

Prepare an internal standard spiking mixture containing bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses using the apparatus or by equivalent means. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

7.2.2.5 Internal Standard Spiking Mixture SIM Mode

Prepare an internal standard spiking mixture containing the compounds listed in Section 7.2.2.4 at 0.4 ppmv each in humidified zero air to be added to the sample or calibration standard. Just prior to SIM analysis, a sufficient volume of the internal standard spiking mixture shall be added into 500 mL of sample to result in a concentration of 0.4 ppbv in each sample. Laboratories using instruments that allow for simultaneous SCAN and SIM analysis may use alternate internal standards for the SIM analysis. Alternate internal standards must be approved by EPA and noted in the SDG narrative. All technical acceptance criteria for internal standards response and retention time must be met for the alternate internal standards.

7.2.3 Standard Preparation by Dynamic Dilution Technique

7.2.3.1 Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

7.2.3.2 Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

EQ. 1 Concentrations of Target Compounds in the Manifold

$$\text{Manifold Conc.} = \frac{(\text{Original Conc.})(\text{Std . Gas Flow rate})}{(\text{Air Flow rate}) + (\text{Std. Gas Flow rate})}$$

7.2.3.3 Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

$$\text{Manifold Conc.} = \frac{(10\ \text{ppm})(1\ \text{mL/min})(10\ 00\ \text{ppb/1 ppm})}{(1000\ \text{mL/min}) + (1\ \text{mL/min})} = 10\ \text{ppb}$$

7.2.4 Standard Preparation by Static Dilution Bottle Technique

NOTE: Standards may be prepared in canisters by spiking the canister with a mixture of components prepared in a static dilution bottle. This technique is used specifically for liquid standards.

7.2.4.1 The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in milliliters.

7.2.4.2 The flask is flushed with helium by attaching tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

7.2.4.3 The flask is placed in a 60°C oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60°C.

7.2.4.4 The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

7.2.4.5 Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

7.2.4.6 Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

7.2.4.7 The concentration of each component in the flask is calculated using the following equation:

EQ. 2 Component Concentration Injected into the Flask

$$\text{Concentration, mg/L} = \frac{(Va)(d)}{Vf}$$

Where:

Va = Volume of liquid neat standard injected into the flask, µL.
d = Density of the liquid neat standard, mg/µL.
Vf = Volume of the flask, L.

7.2.4.8 To obtain concentrations in ppbv, Equation 4 in Section 7.2.5.7 can be used.

NOTE: In the preparation of standards by this technique, the analyst should make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask. Precautions should also be taken to avoid a significant decrease in pressure inside the flask after withdrawal of aliquot(s).

7.2.5 Standard Preparation Procedure in High Pressure Cylinders

NOTE: Standards may be prepared in high pressure cylinders. A modified summary of the procedure is provided below.

7.2.5.1 The standard compounds are obtained as gases or neat liquids (greater than 98 percent purity).

7.2.5.2 An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

7.2.5.3 Predetermined amounts of each neat standard compound are measured using a microliter or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

7.2.5.4 The cylinder is pressurized to 1000 psig with zero nitrogen.

NOTE: User should read all SOPs associated with generating standards in high pressure cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.

7.2.5.5 The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of aliquots into the GC system.

7.2.5.6 If the neat standard is a gas, the cylinder concentration is determined using the following equation:

EQ. 3 Cylinder Concentration

$$\text{Concentration, ppbv} = (\text{Vol. standard})/\text{Vol. dil gas}) \times 10^9$$

NOTE: Both values must be expressed in the same units.

7.2.5.7 If the neat standard is a liquid, the gaseous concentration can be determined using the following equation:

EQ. 4 Gaseous Volume of Inject Compound

$$V = \frac{nRT}{P} \qquad n = \frac{(m1)(d)}{MW}$$

Where:

V = Gaseous volume of injected compound at EPA standard temperature (25°C) and pressure (760 mm Hg), L.

n = Moles.

R = Gas constant, 0.08206 L-atm/mole °K.

T = 298°K (standard temperature).

P = 1 standard pressure, 760 mm Hg (1 atm).

mL = Volume of liquid injected, mL.

d = Density of the neat standard, g/mL.

MW = Molecular weight of the neat standard expressed, g/g-mole.

The gaseous volume of the injected compound is divided by the cylinder volume at STP and then multiplied by 10^9 to obtain the component concentration in ppbvg units.

7.2.6 Standard Preparation by Water Methods

NOTE: Standards may be prepared by a water purge and trap method and summarized as follows.

7.2.6.1 A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

7.2.6.2 The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

NOTE: Extra effort should be made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.

7.2.6.3 A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

7.2.6.4 This water is transferred into the sparge vessel and purged with nitrogen for 10 mins at 100 mL/min. The sparging vessel is maintained at 40°C.

7.2.6.5 At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (approximately 29 psia).

7.2.6.6 The canister is allowed to equilibrate overnight before use.

7.2.7 Preparation of Standards by Permeation Tubes

7.2.7.1 Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

7.2.7.2 The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of more than 250 compounds.

7.3 Storage of Standards

7.3.1 Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

7.3.2 It is required that a storage logbook be kept to document storage time.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE AND HOLDING TIMES

8.1 Collection and Storage of Samples in Canisters

8.1.1 Samples are collected in leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces. All canisters must be certified as free from contaminants prior to sampling.

8.1.2 Each canister shall have a unique identification number and the laboratory must keep records of each canister's use for the life of the contract.

8.1.3 Canisters shall be stored at room temperature [22° (± 3°C)] in a contaminant free area. The temperature of the storage area must be recorded on a daily basis.

8.1.4 Samples must be analyzed within 30 days of collection.

8.2 Canister Cleaning Procedures

The canister cleaning procedures given in this section require that canister pressure be reduced to <0.05mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (< 0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2mm Hg. Canister cleaning as described in this section requires components with special features. The vacuum gauge must be capable of measuring 0.05mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components. An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

8.2.1 Canister Cleaning and Certification

8.2.1.1 All canisters must be clean and free of any contaminants before sample collection.

8.2.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air.

NOTE: The canister cleaning system can be used for this task.

The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

8.2.1.3 A canister cleaning system should be assembled. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to < 0.05 mm Hg for at least 1 hour.

NOTE: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.

Air released/evacuated from canisters should be diverted to a fume hood.

8.2.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

8.2.1.5 The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.2.1.3 through 8.2.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

8.2.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of any target VOCs). The check can then be reduced to a lower percentage of canisters.

8.2.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg (Section 8.2) and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the inlet of each canister for field notes and chain-of-custody purposes. An alternative to evacuating the canister at this point is to store the canisters and reevacuate them just prior to the next use.

NOTE: The Contractor must supply documentation (Form I VOA-Canister) with the canisters and in the data packages, showing that all canisters have been cleaned and certified down to the requested detection limits. The GC/MS documentation for clean canister certification is also to be included in the Data Package.

8.2.1.8 As an option to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100°C during evacuation of the canister to ensure that higher molecular weight compounds are not retained on the walls of the canister.

NOTE: For sampling more complex VOC mixtures the canisters should be heated to higher temperatures during the cleaning procedure although a special high temperature valve would be needed.

Once heated, the canisters are evacuated to <0.05 mm Hg (see Section 8.2) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are re-evacuated to <0.05 mm Hg and remain in the evacuated state until used. As noted in Section 8.2.1.7, re-evacuation can occur just prior to the next use.

8.2.2 Cleaning Sampling System Components

8.2.2.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

8.2.2.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

8.2.2.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

8.2.3 Zero Air Certification

NOTE: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv each of target compounds) have occurred when challenged with the test gas stream.

8.2.3.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas sampling canister, as follows.

8.2.3.2 The calibration system and manifold are assembled. The sampler (without an evacuated gas canister) is connected to the manifold and the zero air cylinder is activated to generate a humid gas stream (2 L/min) to the calibration manifold.

8.2.3.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to the water management system/VOC preconcentrator of an analytical system.

NOTE: The exit of the sampling system (without the canister) replaces the canister.

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocussed on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocussed prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 9) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.2.4.

8.2.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System

8.2.4.1 Assemble the dynamic calibration system and manifold.

8.2.4.2 Verify that the calibration system is clean (less than 0.2 ppbv of any target compounds) by sampling a humidified gas stream, *without* gas calibration standards, with a previously certified clean canister (see Section 8.1).

8.2.4.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of any targeted compounds is found.

8.2.4.4 For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

8.2.4.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold.

8.2.4.6 Sample the dynamic calibration gas stream with the sampling system.

8.2.4.7 Concurrent with the sampling system operation, real-time monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system to provide reference concentrations of generated VOCs.

8.2.4.8 At the end of the sampling period (normally the same time period used for experiments), the sampling system canister is analyzed and compared to the reference GC/MS analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

8.2.4.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Conditions

9.1.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature.

Oven temperature programming starts above ambient.

9.1.1.1 Sample Collection Conditions

Cryogenic Trap	Adsorbent Trap
Set point: -150°C	Set point: 27°C
Sample volume - up to 100 mL	Sample volume - up to 1,000 mL
Carrier gas purge flow - none	Carrier gas purge flow-selectable
	Dry purge (optimum) 1300 mL N

NOTE: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume to be used. The addition of a dry purging step allows for further water removal from the adsorbent trap. Other sample collection conditions may be used to pre-concentrate the sample provided technical criteria for all standards, samples and quality control samples are met.

9.1.1.2 Desorption Conditions

Cryogenic Trap	Adsorbent Trap
Desorb Temperature: 120°C	Desorb Temperature 220°C
Desorb Flow Rate - 3 mL/min He	Desorb Flow Rate - 3 mL/min He
Desorb Time < 60 sec	Desorb Time < 60 sec

The adsorbent trap conditions may depend on the specific solid adsorbents chosen (see manufacturers' specifications).

9.1.1.3 Trap Reconditioning Conditions

Cryogenic Trap	Adsorbent Trap
Initial bake out: 120°C (24 hrs)	Initial bake out Variable (24 hrs)
After each run: 120°C (5 min)	A trap bake-out at 260°C for 5

9.1.2 Gas Chromatograph (GC)

9.1.2.1 Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

9.1.2.2 The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 µm film thickness fused silica column with refocusing on the column:

Item	Condition
Carrier Gas	Helium
Flow Rate	Generally 1-3 mL/min as recommended by manufacturer
Temperature Program	
Initial Temperature	-50°C
Initial Hold Time	2 min
Ramp Rate	8°C/min
Final Temperature	200°C
Final Hold Time	Until all target compounds elute

9.1.3 Mass Spectrometer (MS)

The following are the recommended mass spectrometer conditions:

Item	Condition
Electron Energy	70 Volts (nominal)
Mass Range	35-300 amu
Scan Time	To give at least 10 scans per peak, not to exceed 1 second per scan

NOTE: For SIM analyses, the laboratory is to use the appropriate primary ion and secondary ion listed in Table 2.

9.2 GC/MS Calibration (Tuning) and Ion Abundance

9.2.1 Summary of GC/MS 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 It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

9.2.2 Frequency of GC/MS Performance Check

9.2.2.1 Prior to the analyses of any samples, blanks, or laboratory control samples or calibration standards, the laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation. The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

NOTE: BFB may not be added to any calibration standard or continuing calibration verification standard to create a single injection of a calibration standard and a tune solution.

9.2.3 Procedure for GC/MS Performance Check

9.2.3.1 The analysis of the instrument performance check standard is performed as follows:

- By trapping 50 ng of BFB under the optimized preconcentration parameters.
- The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system.

9.2.3.2 The mass spectrum of BFB must be acquired in the following manner:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.
- Background subtraction is conducted using a single scan prior to the elution of BFB.

9.2.3.3 Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

9.2.4 Technical Acceptance Criteria for GC/MS Performance Check

9.2.4.1 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and 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 elution of BFB. Do not background subtract part of the BFB peak.

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

9.2.4.2 Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3.

9.2.5 Corrective Action for GC/MS Performance Check

9.2.5.1 If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, 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, including LCS 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 but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the range of the initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. The initial calibration range is 0.5 to 20 ppbv, in which the five concentrations are 0.5, 2.0, 5.0, 10 and 25 ppbv. One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

NOTE: For analysis using SIM technique, the GC/MS system must be calibrated at a minimum of five concentrations (Section 7.2.2.3), prior to the analysis of samples and required blanks, to determine instrument sensitivity and linearity. The calibration standards contain all target compounds and internal standards requiring analysis.

9.3.2 Frequency of Initial Calibration

9.3.2.1 Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met.

9.3.2.2 If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed. If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard

9.3.3 Procedure for Initial Calibration

9.3.3.1 Verify that the GC/MS system meets the instrument performance criteria in Section 9.2.4. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 9.2.2 or with GC operating conditions such that all associated performance criteria are met, including the separation criteria in Section 9.1.2.1.

9.3.3.2 Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques described under Section 7.2 or equivalent.

9.3.3.3 A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be equal to the CRQL for the each Target Compounds.

9.3.3.4 Add sufficient amount of the internal standard solution (Section 7.2.2.4) to each of the five aqueous calibration standard solutions (Section 7.2) for a concentration of 10.0 ppbv at the time of purge. Analyze each calibration standard according to Section 10.

9.3.3.5 The calibration range should be chosen so that linear results are obtained as defined in Sections 9.3.1 and 9.3.5.

9.3.4 Calculations for Initial Calibration

9.3.4.1 Calculate the Relative Retention Times (RRT) for each target compound over the initial calibration range using Equation 5.

EQ. 5 Relative Retention Time

$$RRT = \frac{RT_c}{RT_{is}}$$

Where:

RT_c = Retention time of the target compound, seconds

RT_{is} = Retention time of the internal standard, seconds.

9.3.4.2 Mean of the Relative Retention Times ($\overline{\overline{RRT}}$). Calculate the mean of the relative retention times ($\overline{RRT}$) for each analyte target compound over the initial calibration range using Equation 6:

EQ. 6 Mean Relative Retention Time

$$\overline{\overline{RR}} = \sum_{i=1}^{n} \frac{RRT}{n}$$

Where:

$\overline{\overline{RRT}}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT = Relative retention time for the target compound at each calibration level.

9.3.4.3 Tabulate Primary Ion Area Response (Y) for Internal Standard. Tabulate the area response (Y) of the primary ions (see Table 2) and the corresponding concentration for each compound and internal standard.

9.3.4.4 Mean Area Response ($\bar{Y}$) for Internal Standard. Calculate the mean area response ($\bar{Y}$) for each internal standard compound over the initial calibration range using the following equation:

EQ. 7 Mean Area Response

$$\bar{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

Where:

$\bar{Y}$ = Mean area response.

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

9.3.4.5 Mean Retention Times ($\overline{\overline{RT}}$). Calculate the mean of the retention times for each internal standard over the initial calibration range using the following equation:

EQ. 8 Mean Retention Time

$$\overline{\overline{RT}} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

Where:

$\overline{\overline{RT}}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds.

9.3.4.6 Calculate the Relative Response Factor (RRF) for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using Equation 9.

NOTE: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.

EQ. 9 Relative Response Factor

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

Where:

RRF = Relative response factor

A_x = Area of the primary ion for the compound to be measured, counts.

A_{is} = Area of the primary ion for the internal standard, counts.

C_{is} = Concentration of internal standard spiking mixture, ppbv.

C_x = Concentration of the compound in the calibration standard, ppbv

Unless otherwise stated, the area response of the primary characteristic ion is the quantitation ion. The primary characteristic ions used for quantitation are listed in Table 2. If an interference prevents the use of a primary ion for a given internal standard, use a secondary ion listed in the same table. Assign the target compounds to an internal standard according to Table 3.

NOTE: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.

9.3.4.7 Mean Relative Response Factor. Calculate the mean RRF for each compound by averaging the values obtained at the five concentrations using the following equation:

EQ. 10 Mean Relative Response Factor

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

Where:

$\overline{RRF}$ = Mean relative response factor

x_i = RRF of the compound at concentration.

n = Number of concentration values, in this case, 5

9.3.4.8 Percent Relative Standard Deviation (%RSD). Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

EQ. 11 Percent Relative Standard Deviation

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

and

EQ. 12 Standard Deviation of Initial Response Factors

$$SD_{RRF} = \sqrt{\sum_{i=1}^{N} \frac{(RRF_i - \overline{RRF})^2}{N - 1}}$$

Where:

SD_{RRF} = Standard deviation of initial response factors (per compound).

RRF = Relative response factor at a concentration level i.

$\overline{RRF}$ = Mean of initial relative response factors (per compound).

9.3.5 Technical Acceptance Criteria for the Initial Calibration

9.3.5.1 All initial calibration standards must be analyzed at the concentration levels described in Section 7.2.2, and at the frequency described in Section 9.3.2 on a GC/MS system meeting the GC/MS Performance Check technical acceptance criteria.

9.3.5.2 The RRF at each calibration concentration for each target compound must be greater than or equal to the compound's minimum acceptable RRF listed in Table 5.

9.3.5.3 The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions.

NOTE: This exception may not be acceptable for all projects. Many projects may have a specific target list of compounds which would require the lower limit for all compounds.

Up to two compounds may fail the criteria listed in Section 9.5.5.1 and up to two compounds may fail the criteria listed in Section 9.3.5.3 and still meet the minimum RRF and %RSD requirements. However, these compounds must have a minimum RRF greater than or equal to 0.01, and the %RSD must be less than or equal to 40%.

9.3.5.4 The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound.

9.3.5.5 The area response Y of at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range for each internal standard.

9.3.5.6 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.

9.3.5.7 The retention time shift for each of the internal standards at each calibration level must be within 30 seconds of the mean retention time over the initial calibration range for each internal standard.

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 preconcentrator or take other corrective actions to meet the initial calibration technical acceptance criteria.

9.3.6.2 Initial calibration technical acceptance criteria *must* be met before any samples, including Laboratory Control Samples or required blanks are analyzed. Any samples or required blanks analyzed when initial calibration technical acceptance criteria have not been met will require re-analysis at no additional cost to USEPA.

9.4 Initial Calibration Verification

9.4.1 The initial calibration verification standard (ICV) must be analyzed to verify the initial calibration standards and to demonstrate equivalency between the second source standard and the initial calibration response. The ICV must be made from standard obtained from a certified second source that is traceable to a different lot or manufacturer than the source of the calibration standards.

9.4.2 Prior to the analysis of samples and required blanks and immediately after the Instrument Performance Check and initial calibration standard sequence, the initial calibration must be verified by analyzing the ICV containing all the target compounds at the 10 ppbv calibration level and internal standards to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method.

NOTE: For the analysis using SIM technique the initial calibration of the GC/MS system must be verified by analyzing an ICV standard, prior to the analysis of samples and required blanks. The ICV standard for SIM technique must include the required target analytes and internal standards.

9.4.3 Frequency of Internal Standard Verification Standard

9.4.3.1 The initial calibration curve must be verified by the ICV. After the laboratory has determined the initial calibration has met the technical acceptance criteria specified in Section 9.3.5, and prior to any sample analysis, the ICV standard must be analyzed. It is recommended an instrument blank be analyzed between the last initial calibration standard and the ICV standard. The ICV standard must be analyzed under a compliant BFB instrument performance check standard.

NOTE: For Selected Ion Monitoring technique (SIM), a BFB standard must be analyzed using the SCAN mode prior the SIM analysis. The instrument settings, other that those needed to be adjusted for the SIM analysis, would be required to remain the same. A 24-hour BFB clock would be required for all SIM analyses. The 24 hour time period begins at the moment of injection of the BFB standard prior to the first initial calibration standard.

9.4.3.2 If time remains in the 24-hour time period after meeting the technical acceptance criteria for the initial calibration and ICV, samples may be analyzed following the analysis of a method blank. Quantitate all sample and blank results using the mean RRF obtained from the initial calibration standard.

9.4.3 Procedure for Initial Calibration Verification

9.4.3.1 The ICV must be prepared at the mid-level calibration standard concentration (10 ppbv) and analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 9.5. For SIM, the ICV should be at 0.4 ppbv.

9.4.4 Calculations for Initial Calibration Verification

9.4.4.1 Calculate an RRF for each target compound according to Section 9.3.4.6.

Perform the following calculations.

NOTE: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.

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

EQ. 13 Percent Difference

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

Where:

RRF_c = RRF of the compound in the initial calibration standard.

$\overline{RRF}$ = Mean RRF of the compound in the most recent initial calibration.

9.4.5 Technical Acceptance Criteria for Initial Calibration Verification (ICV)

9.4.5.1 The initial calibration verification standard must be analyzed at the concentration level and frequency described in Section 9.4.3 and on a GC/MS system meeting the BFB instrument performance check criteria (See Section 9.2). The %D for each target compound in an ICV standard must be within ±20 percent in order to proceed with the analysis of samples and blanks.

9.4.5.2 For an ICV, up to ten percent of compounds may fail the ICV requirements for the minimum RRF criteria and Percent Difference criteria. However, these compounds must have a minimum RRF greater than or equal to 0.010 and the Percent Difference must be within the inclusive range of ±40.0%.

NOTE: The ICV criteria in Section 9.4.5.1 and 9.4.5.2 also apply to analysis using SIM technique.

9.4.6 Corrective Action for Initial Calibration Verification (ICV)

9.4.6.1 If the initial calibration verification technical acceptance criteria are not met, the ICV standard and the initial calibration standard may not be equivalent. It may be necessary to prepare a new aliquot of the second source standard or calibration standard and recalibrate the instrument or take other corrective actions to meet the ICV technical acceptance criteria. Initial calibration verification acceptance criteria *must* be met before any samples, including Laboratory Control Samples or required blanks are analyzed.

9.5 Continuing Calibration Verification

9.5.1 Summary of Opening Continuing Calibration Verification (CCV)

Prior to the analysis of samples and required blanks and after the Instrument Performance Check and initial calibration technical acceptance criteria have been met, each GC/MS system must be routinely checked by analyzing an opening CCV containing all the target compounds at the 10 ppbv calibration level and internal standards to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the analytical method.

NOTE: For the analysis using SIM technique the calibration of the GC/MS system must be routinely checked by analyzing a CCV standard, prior to the analysis of samples and required blanks, and after initial calibration technical acceptance criteria have been met. The continuing calibration standard for SIM technique must include the required target analytes and internal standards.

9.5.2 Frequency of Continuing Calibration Verification

9.5.2.1 A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed. The 24-hour time period begins with the injection of BFB, followed by the injection of the opening CCV solution. BFB may NOT be added to any calibration standard or calibration verification solution to create a single injection of a calibration standard and a tune solution.

NOTE: For analysis by Selected Ion Monitoring technique (SIM), the 24 hour time period begins at the moment of injection of the BFB instrument performance check in SCAN mode. Following the analysis of the BFB, the instrument is adjusted to SIM mode for the analysis of the first initial calibration standard or the CCV standard, if initial calibration has already been analyzed.

9.5.2.2 If time remains in the 24-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. A method blank is required prior to sample analysis.

9.5.2.3 Quantitate all sample and blank results using the mean RRF obtained from the initial calibration standard.

9.5.3 Procedure for Continuing Calibration Verification (CCV)

9.5.3.1 The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 9.3.

9.5.4 Calculations for Continuing Calibration Verification

9.5.4.1 Calculate an RRF for each target compound according to Section 9.3.4.6.

Perform the following calculations.

NOTE: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.

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

EQ. 14 Percent Difference

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

Where:

RRF_c = RRF of the compound in the continuing calibration standard

$\overline{RRF}$ = Mean RRF of the compound in the most recent initial calibration

9.5.5 Technical Acceptance Criteria for Continuing Calibration Verification

9.5.5.1 The daily calibration standard must be analyzed at the concentration level and frequency described in Section 9.5 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 9.2). The %D for each target compound in a daily calibration sequence must be within ±30 percent in order to proceed with the analysis of samples and blanks.

9.5.5.2 For an opening CCV, up to ten percent of compounds may fail the CCV requirements for the minimum RRF criteria and Percent Difference criteria. However, these compounds must have a minimum RRF greater than or equal to 0.010 and the Percent Difference must be within the inclusive range of ±40.0%.

NOTE: For analysis using SIM technique, the criteria in Section 9.5.5. 1 and 9.5.5.2 apply.

9.5.6 Corrective Action for Continuing Calibration Verification

9.5.6.1 If the daily calibration technical acceptance criteria are not met, inspect the system for problems. If it is necessary to clean the ion source, change the column, take other corrective actions to meet the daily calibration technical acceptance criteria, a new initial calibration must be prepared and verified before samples may be analyzed. Daily calibration acceptance criteria *must* be met before any samples, including Laboratory Control Samples or required blanks, are analyzed. It will be necessary to rerun the ICV and all affected samples following the new initial calibration.

10.0 PROCEDURE

10.1 Air Sample Analysis

10.1.1 An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and analyzed by GC/MS under conditions stated in Sections 9.1 and 9.2. If using the multisorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

NOTE: The analyst should be aware that pressurized samples of high humidity samples will contain condensed water. As a result, the humidity of the sample released from the canister during analysis will vary, being lower at the higher canister pressures and increasing in humidity as the canister pressures decreases. Storage integrity of water soluble compounds may also be affected.

10.1.2 If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration verification standard. If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

10.1.3 Procedure for Instrumental Analysis

Perform the following procedure for analysis.

10.1.3.1 All canister samples should be at temperature equilibrium with the laboratory.

10.1.3.2 Check and adjust the mass flow controllers to provide correct flow rates for the system.

10.1.3.3 Connect the sample canister to the inlet of the GC/MS analytical system. The desired sample flow is established through the six-port chromatographic valve and the preconcentrator to the downstream flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

10.1.3.4 Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port value is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

10.1.3.5 Use the arrangement (i.e., a gastight syringe or some alternate method) to introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500 mL, will result in 10 ppbv of each internal standard in the sample.

10.1.3.6 For SIM technique add sufficient internal standard equivalent to 0.4 ppbv in the samples and blanks (Section 7.2.2.5).

10.1.3.7 After the sample and internal standards are preconcentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

10.1.3.8 Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

10.1.3.9 Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

10.1.3.10 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book and in the SDG narrative.

10.1.3.11 Samples must be diluted if the compound concentrations are outside of the calibration range of the instrument.

10.1.3.12 Add the air source to the sample for the dilution as that used for the preparation of the method blanks, that being humidified, ultra-pure zero air.

10.1.3.13 The laboratory must report data for both the undiluted sample and the diluted sample. The laboratory may not submit more than two sets of diluted sample data.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Identification

11.1.1 Identification of Target Compounds

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

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

11.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within ±0.06 RRT units of the RRT of the corresponding continuing calibration standard component. For reference, the standard must be run in the same 24-hour time period as the sample. If samples are analyzed during the same 24-hour time period as the initial calibration standards, use the RRT values from the 10 ppbv standard. Otherwise, use the corresponding opening Continuing Calibration Verification (CCV) standard. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, then the RRT should be assigned by using Extracted Ion Current Profiles (EICP) or ions unique to the component of interest.

11.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the Contractor's GC/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 run used to obtain reference retention times (RRTs).

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

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.

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

Ions greater than 10% in the sample spectrum but not presenting 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 Contract Required Quantitation Limit (CRQL), report the actual value followed by a "J" (e.g., "3J").

11.1.1.5 If a compound cannot be verified by all of the spectral identification criteria listed in Section 11.1.1.4, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the Contractor shall report that identification and proceed with quantitation.

11.1.2 Qualitative Identification of Non-Target Compounds (Optional)

11.1.2.1 A library search shall be executed for non-target sample components for the purpose of tentative identification. The NIST (2002 release or later), Wiley (1991 release or later), or equivalent mass spectral library, shall be used as the reference library.

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

11.1.2.3 Up to 30 non-alkane Tentatively Identified Compounds (TICs) of greatest apparent concentration shall be reported on Form 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 CnH2n+2 (straight-chain or branched) or CnH2n (cyclic) that contains only C-H and C-C single bonds. The concentrations of each of the alkanes are to be summed and reported as a single result for the "total alkanes". 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 tentative identified compounds on Form I VOA-TIC. Carbon dioxide and compounds with responses less than 10% of the internal standard in which they are to be qualified (as determined by inspection of the peak areas or height) are not to be reported (nor are they to be counted as part of the 30 compounds that are to be reported).

11.1.2.4 Rules for Making Tentative Identification

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

11.1.2.4.2 If the library search produces more than one compound at or above 85%, report the compound with the highest percent match (report first compound if the percent match is the same for two or more compounds), unless the mass spectral interpretation specialist feels there is just evidence not to report the compound with the highest match. Do not report 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 an internal standard, or volatile target analyte.

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

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

11.1.2.4.5 If the library search produces no matches at or above 85%, the mass spectral interpretation specialist 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.).

11.2 Calculations

11.2.1 Target Compounds

11.2.1.1 Identified target compounds shall be quantified by the internal standard method using Equation 15. The Mean Relative Response Factor (Mean $\overline{RRF}$) from the initial calibration standard is used to calculate the concentration in the sample.

11.2.1.2 Concentration

EQ. 15 Air Concentration Calculation

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

Where:

C = Compound concentration, ppbv.

A_x = Area of the characteristic ion for the compound to be measured, counts.

A_{is} = Area of the characteristic ion for the specific internal standard, counts.

C_{is} = Concentration of the internal standard spiking mixture, ppbv

$\overline{RRF}$ = Mean relative response factor from the initial calibration.

DF = Dilution factor calculated as described in section 2. If no dilution is performed, DF = 1.

NOTE: The equation above is valid under the condition that the volume (~500 µL) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (~500 mL) of field and QC sample introduced into the trap is the same for each analysis.

Conversion of concentration ppbv to concentration µg/m3:

$$\text{Concentration (ppbv)} = \text{Concentration (ug/m}^3\text{)} \times 24.46/\text{MW @ 25°C}$$

For the reverse conversion:

$$\text{Concentration (ug/m}^3\text{)} = \text{Concentration (ppbv)} \times \text{MW}/24.46 \text{ @ 25°C}$$

Where:

MW = molecular weight (Table 1)

[Assumes standard temperature.]

These conversion equations depend on the ambient air temperature at time of collection conversion (usually about 20 to 25 degrees Centigrade).

At an ambient air pressure of 1 atmosphere, the equation is:

$$\text{ppbv} = (\mu g/m^3)(^\circ K)(0.08205)/MW$$

and for the reverse conversion:

$$\mu g/m^3 = (\text{ppbv})(MW)/[(0.08205)\ (K)]$$

Where:

ppbv = Air pollutant concentration, in parts per billion by volume.

$\mu g/m^3$ = Micrograms of pollutant per cubic meter of air.

K = Atmospheric temperature in degrees Kelvin = 273.15 + °C.

0.08205 = Universal gas law constant in (atm·liter)/(gmol·°K).

MW = Molecular weight of the air pollutant (dimensionless).

atm = absolute atmospheric pressure in atmospheres.

gmol = the amount of a compound equal in grams to its molecular weight (mole).

11.2.2 Quantitation of Non-Target Compounds (Optional)

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

11.2.2.2 The formula for calculating non-target compound concentrations is the same as in Section 11.2.1.2.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 as "J" (estimated due to the lack of a compound-specific RRF), and "N" (presumptive evidence of presence when a TIC is tentatively identified as a specific compound), indicating the quantitative and qualitative uncertainties associated with this non-target compound. An estimated concentration must be calculated for all TICs, as well as those identified as unknowns.

11.2.3 Internal Standard Responses and Retention Times (RTs)

Internal standard responses and RTs in all samples 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 24-hour time period as the initial calibration standards, compare the internal standard responses and RTs against the 10 ppbv calibration standard.

The EICP of the internal standards must be monitored and evaluated for each sample including LCS/LCSD and blanks.

11.3 Technical Acceptance Criteria for Sample Analysis

NOTE: If sample analysis is performed in the time remaining from a instrument performance check standard (BFB) associated with an initial calibration (ICAL), the internal area responses and the RTs in the 10 ppbv standard from the ICAL shall be used for to evaluate the samples.

11.3.1 The field sample must be analyzed on a GC/MS system meeting the BFB tuning criteria in Section 9.2, the initial calibration criteria in Section 9.3, and continuing calibration criteria in Section 9.5 at the frequency described in each section.

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

11.3.3 The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

11.3.4 All of the target analyte peaks should be within the initial calibration range. If a sample requires dilution, compounds reported in the original analysis may be reported above the initial calibration range but at least one of the two sample analyses must meet this criteria.

11.3.5 The EICP area for each of the internal standards in the sample must be within the range of ±40 percent of its response in the most recent opening CCV standard analysis.

11.3.6 The retention time for each internal standard must be within 0.5 minutes of the retention time of the internal standard in the most recent valid calibration.

11.4 Corrective Action for Sample Analysis

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

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

11.4.3 If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

NOTE: Analysis involving dilution should be reported with a dilution factor and nature of the dilution gas.

11.4.4 Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 0.5 minutes from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

11.4.5 If the area response for any internal standard changes by more than ±40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

11.4.6 The laboratory must report data for both the initial analysis and the reanalysis. The laboratory may not submit more than two sets of diluted sample data.

12.0 QUALITY CONTROL (QC)

12.1 Blank Analyses

12.1.1 Summary

There are two types of blanks required by this method:

12.1.1.1 Method Blank - The purpose of the method blank is to determine the levels of contamination associated with processing and analysis of samples. To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis. A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

12.1.1.2 Instrument Blank – is analyzed after a sample/dilution that contains a target compound exceeding the initial calibration range. The results from the instrument blank analysis indicate whether there is contamination from a previous sample.

NOTE: If the Contractor during the analytical sequence determines that an instrument blank needs to be analyzed for any reason within an analytical sequence, the instrument blank is to meet the requirements in Section 12.1.5 to be acceptable. The samples must be labeled as an instrument blank and the reason for analyzing the blank documented in the case narrative.

12.1.2 Frequency of Blank Analyses

12.1.2.1 The laboratory method blank must be analyzed at least once during every 24-hour time period on each Gas Chromatograph/Mass Spectrometer (GC/MS) system used for volatile analysis.

12.1.2.2 The method blank **must** be analyzed after the Continuing Calibration Verification (CCV) and before any samples, including Laboratory Control Samples or dilutions, are analyzed. The method blank must be analyzed after the initial calibration sequence (including the ICV)and prior to sample analysis, if samples are to be analyzed before the 24-hour period expires.

12.1.2.3 If the Contractor is using an autosampler, and a subsequent sample analysis demonstrates the system is not contaminated (e.g. the sample analysis meets the technical acceptance criteria for the method blank), this may be used as proof the system is not contaminated in lieu of an instrument blank. If the instrument blank or sample analysis does not meet the criteria, the system is considered contaminated, and must be decontaminated. Until an instrument blank meets the method blank technical acceptance criteria, any samples analyzed since the original contaminated sample will require reanalysis at no additional cost to USEPA. This criteria apply to both SCAN and SIM analyses.

NOTE: Only the instrument blank that demonstrates that the system is clean shall be reported. Instrument blanks analyzed during the instrument decontamination process that exceed the requirements listed in Section 11.3 should not need to be reported.

12.1.3 Procedure for Blank Analysis

12.1.3.1 Fill a cleaned and evacuated canister with humidified zero air (RH > 20 percent, at 25°C). Pressurize the contents to 2 atm. The blank sample should be analyzed using the same procedure outlined under Section 10.1.

12.1.3.2 For SIM technique add sufficient internal standard equivalent to 0.4 ppbv in the samples and blanks (Section 7.2.2.5).

12.1.4 Calculations for Blank Concentration

12.1.4.1 Method blanks are analyzed using the same procedure as field samples. Analyte concentrations are calculated using Equation 15. If TICs are requested, labs are required to report TIC in associated blanks.

12.1.5 Technical Acceptance Criteria for Blank Analyses

12.1.5.1 A blank canister should be analyzed daily.

12.1.5.2 A method blank should be analyzed daily after the calibration verification standard and prior to sample analysis or; after the initial calibration sequence (including the ICV) and prior to sample analysis, if samples are to be analyzed before the 24-hour period expires for an ICAL.

12.1.5.3 The retention time for each of the internal standards must be within ±0.5 minutes between the blank and the most recent valid calibration.

12.1.5.4 The blank should not contain any target analyte at a concentration greater than half of the CRQL and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte. There should be no Tentatively Identified Compound (TIC) present with areas greater than the closest eluting internal standard.

12.1.6 Corrective Action for Blank Analyses

12.1.6.1 If the blanks do not meet the technical acceptance criteria, the analyst should consider the analytical system to be out of control. It is the responsibility of the analyst to ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds. If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

12.1.6.2 Any method blank that has target compounds detected at levels above the CRQL or has failed to meet the technical acceptance criteria described in Section 12.1.5.3 must be reanalyzed. Further, all samples following a failed method blank or instrument blank in an analytical sequence must be re-analyzed in a verified calibration sequence and following an acceptable blank.

12.2 Laboratory Control Sample

12.2.1 The Laboratory Control Sample (LCS) is a replicate of the Continuing Calibration Verification standard that is analyzed immediately after the method blank in the analytical sequence.

12.2.2 The LCS must be prepared from the same standard and at the same concentration as the CCV (10 ppbv midpoint of calibration curve). All compounds in the target compound list must be present in the LCS. The LCS is prepared using the same procedures used in Section 7.2 to prepare the calibration standards (e.g. dynamic dilution, static dilution bottle technique, etc.)

12.2.2.1 For SIM technique the LCS must be prepared with a concentration at the (0.4 ppbv) of the calibration curve. All compounds in the SIM target compound list must be present in the LCS.

12.2.3 Laboratory Control Sample Analyses

12.2.3.1 The LCS is designed to assess the analytical precision by measuring the Relative Percent Difference (RPD) between the LCS and CCV. There are several factors which may affect the precision of the measurement (See Section 12.4.2).

12.2.4 Frequency of Laboratory Control Sample Analysis

12.2.4.1 LCS is analyzed immediately following the method blank and prior to sample analysis within every 24-hour analytical sequence.

12.2.5 Calculations for LCS

12.2.5.1 Calculate the concentrations of the LCS compounds using the same equations as used for target compounds (Equation 15 from Section 11.2.1). Calculate the recovery of each LCS compound as follows:

EQ. 16 LCS Spike Recovery Calculation

$$\%\ \text{LCS Recovery} = \frac{\text{Found Conc.}}{\text{True Conc.}} \times 100$$

12.2.5.2 Duplicate Precision

The Relative Percent Difference (RPD) shall be calculated for each analyte for the LCS and CCV using the following equation:

EQ. 17 Relative Percent Difference

$$RPD = \frac{\left|X_{LCS} - X_{CCV}\right|}{((X_{LCS} + X_{CCV})/2)} \times 100$$

Where:

x_{LCS} and x_{CCV} = The results for the analyte in the LCS and CCV respectively.

12.2.6 Technical Acceptance Criteria for LCS

12.2.6.1 The LCS must be analyzed on a GC/MS system meeting the BFB, initial calibration and continuing calibration verification technical acceptance criteria, blank technical acceptance criteria, and at the frequency described in Section 12.2.4.

12.2.6.2 The area response for each internal standard (IS) in the LCS must be within ±40 percent of the mean area response of the IS in the most recent valid calibration.

12.2.6.3 The retention time for each of the internal standards must be within ±0.5 minutes between the LCS and the most recent valid calibration.

12.2.6.4 The limits for LCS compound are ±30% (eg. 70 – 130% recovery). Ten percent of the LCS compounds may be outside of this limit as long as their recovery is ± 40%.

12.2.6.5 The precision between the recovery of compounds in the LCS and the CCV must be less than or equal to 25% RPD.

12.2.7 Corrective Action for LCS

12.2.7.1 If the LCS recovery and precision recovery are not met, the laboratory must perform maintenance as needed. If the criteria are still not met, the analytical system must be recalibrated and associated samples must be re-analyzed at no additional cost to the USEPA.

12.3 Method Detection Limit (MDL) Determination

12.3.1 The procedure chosen to define the method detection limit is that given in the *Code of Federal Regulations* (40 CFR 136 Appendix B).

12.3.2 The method detection limit is defined for each system in the SCAN mode by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit by SCAN mode, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values).

12.3.3 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. The MDLs must be verified annually thereafter (see Section 12.3.4 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 or source, mass filters (e.g., quadrupole, ion trap, etc.), electron multiplier (or similar device), GC column, and replacement or overhaul of preconcentrator.

12.3.4 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 for air samples is achieved by analyzing a single ultra zero air blank (see method blank in Section 12.1) 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 less than or equal to the clean canister certification criteria specified in Method TO-15. The resulting mass spectra of each target compound must meet the qualitative identification criteria outlined in Section 11.1.1.4.

12.3.5 The determined concentration of the MDL must be less than or equal to the 0.2 ppbv using SCAN mode of analysis.

12.4 Replicate Sample Precision

12.4.1 Relative Percent Difference (RPD)

The measure of precision between replicate samples from two different canisters expressed as the absolute value of the difference between sample replicate measurements divided by the average value and expressed as a percentage as follows:

EQ. 18 Relative Percent Difference

$$RPD = \frac{|X_1 - X_2|}{((X_1 + X_2)/2)} \times 100$$

Where:

x_1 = First measurement value

x_2 = Second measurement value

12.4.2 There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar VOCs. A primary influence on precision is the concentration level of the compound of interest in the sample, i.e., the precision degrades as the concentration approaches the detection limit. A conservative measure was obtained from replicate analysis of "real world" canister samples from the TAMS and UATMP networks. These data suggest that a replicate precision value of 25 percent can be achieved for each of the target compounds.

13.0 METHOD PERFORMANCE

13.1 Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

13.1.1 The performance criteria for a system to qualify under this method are as follows:

- All technical criteria for the analysis of samples, standards and quality control samples
- Establish the CRQL ≤0.5 ppbv for SCAN analysis, CRQL ≤ 0.05 ppbv for selected SIM analysis

- MDL concentration determined must be less than or equal to the 0.2 ppbv using SCAN mode of analysis.
- Routinely meet the clean canister criteria for all SUMMA Canisters.
- Mass spectra of each target compound must meet the qualitative identification criteria.
- Audit accuracy ≤ 30% for all target compounds (Requirements for an Audit Samples will be specified in the Task Order Agreement.)

13.1.2 Either SIM or SCAN modes of operation can be used to achieve these criteria and the choice of mode will depend on the number of target compounds, the decision of whether or not to determine tentatively identified compounds along with other VOCs on the target list, as well as on the analytical system characteristics.

13.1.3 Specific criteria for each compound on the target compound list must be met by the analytical system. These criteria were established by examining summary data from EPA's Toxics Air Monitoring System Network and the Urban Air Toxics Monitoring Program network. Details for the determination of each of the criteria follow.

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 operations. 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 waste cannot be feasibly reduced at the source, USEPA recommends recycling as the best option.

14.2 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 release 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

National Risk Management Research Laboratory (NRMRL). *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. Method TO-15. 2nd edition. January 1999.

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

American Chemical Society. *Less is Better. Laboratory Chemical Management for Waste Reduction*. 1985.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1

Target Compound Physical Properties

No	Compound	CAS No.	BP °C	Vapor Pressure, mm Hg	Molecular Weight
1	Propylene	115-07-1	-48	8664	42.1
2	Dichlorodifluoromethane (Freon 12)	75-71-8	-29.8	4390	120.9
3	Dichlorotetrafluoroethane (Freon 114)	76-14-2	4.1	1430	170.9
4	Chloromethane	74-87-3	-23.7	4310	50.5
5	Vinyl chloride	75-01-4	-14.0	2600	62.5
6	1,3-Butadiene	106-99-0	-4.5	2100	54
7	Bromomethane	74-83-9	3.6	1420	94.9
8	Chloroethane	75-00-3	12.5	1010	64.5
9	Ethanol	64-17-5	78.5	47	46.1
10	Trichlorofluoromethane (Freon 11)	75-69-4	23.7	690	137.4
11	1,1-Dichloroethene	75-35-4	31.7	500	97
12	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	48	284	187.4
13	Acetone	67-64-1	56.5	185	58.1
14	2-Propanol (Isopropanol)	67-63-0	82.5	42.7	60.1
15	Carbon disulfide	75-15-0	46.5	260	76
16	Methylene chloride	75-09-2	40.0	349	84.9
17	trans-1,2-Dichloroethene	156-60-5	48.0	395	96.9
18	n-Hexane	110-54-3	69.0	120	86.2
19	Methyl tert-butyl ether	1634-04-4	55.2	249	86
20	1,1-Dichloroethane	75-34-3	57.0	230	99
21	cis-1,2-Dichloroethene	156-59-2	60.3	273	96.9
22	2-Chloro-1,3-butadiene (Chloroprene)	126-99-8	59.4	226	88.5
23	2-Butanone	78-93-3	79.6	77.5	72
24	Tetrahydrofuran	109-99-9	66.0	129	72.1
25	Chloroform	67-66-3	61.2	160	119
26	1,1,1-Trichloroethane	71-55-6	74.1	100	133.4
27	Cyclohexane	110-82-7	80.7	98	84.2
28	Carbon tetrachloride	56-23-5	76.7	90.0	153.8
29	Ethyl Acetate	141-78-6	77.0	95	88.1
30	Vinyl Acetate	108-05-4	72.2	83.0	86
31	Benzene	71-43-2	80.1	76.0	78
32	1,2-Dichloroethane	107-06-2	83.5	61.5	99
33	n-Heptane	142-82-5	98.4	45.7	100.2
34	1,4-Dioxane	123-91-1	101	37.3	88
35	Trichloroethene	79-01-6	87.0	20.2	131.4
36	1,2-Dichloropropane	78-87-5	97.0	42.0	113
37	Bromodichloromethane	75-27-4	90.6	50	163.8
38	cis-1,3-Dichloropropene	10061-01-5	112	27.8	111
39	4-Methyl-2-pentanone	108-10-1	117.5	15.7	100.2
40	Toluene	108-88-3	111	22.0	92
41	trans-1,3-Dichloropropene	10061-02-6	112	23	111
42	1,1,2-Trichloroethane	79-00-5	114	19.0	113.4
43	Tetrachloroethene	127-18-4	121	14.0	165.8
44	2-Hexanone	591-78-6	117	6.0	100.2
45	Dibromochloromethane	124-48-1	119	5	208.2
46	1,2-Dibromoethane	106-93-4	132	11.0	187.9
47	n-Octane	111-65-9	125.6	14	114.2
48	Chlorobenzene	108-90-7	132	8.8	112.6
49	Ethylbenzene	100-41-4	136	7.0	106.2
50	o-Xylene	95-47-6	144	5.0	106.2

No	Compound	CAS No.	BP °C	Vapor Pressure, mm Hg	Molecular Weight
51	m,p-Xylene	179601-23-1	142	6.7	106.2
52	Styrene	100-42-5	145	6.6	104
53	Bromoform	75-25-2	149	5.6	252.8
54	Cumene	98-82-8	153	3.2	120
55	1,1,2,2-Tetrachloroethane	79-34-5	146	5.0	167.9
56	Propylbenzene	103-65-1	159	3.4	120.2
57	4-Ethyltoluene	622-96-8	162	3	120.2
58	1,3,5-Trimethylbenzene	108-67-8	165	1.9	120.2
59	1,2,4-Trimethylbenzene	95-63-6	169	2.0	120.2
60	Benzyl Chloride	100-44-7	179	1.0	126.6
61	1,3-Dichlorobenzene	541-73-1	173	2.2	147
62	1,4-Dichlorobenzene	106-46-7	173	0.60	147
63	1,2-Dichlorobenzene	95-50-1	180.5	1.2	147
64	Hexachlorobutadiene	87-68-3	215	0.40	260.8
65	1,2,4-Trichlorobenzene	120-82-1	213	0.18	181.5

Table 2

Characteristic Masses (Ions) Used for Quantifying Target Compounds

No	Compound	CAS No.	Primary Ion	Secondary Ion(s)
1	Propylene	115-07-1	41	39, 42
2	Dichlorodifluoromethane (Freon 12)	75-71-8	85	87
3	Dichlorotetrafluoroethane (Freon 114)	76-14-2	85	135, 87, 137
4	Chloromethane	74-87-3	50	52
5	Vinyl chloride	75-01-4	62	64
6	1,3-Butadiene	106-99-0	39	54
7	Bromomethane	74-83-9	94	96
8	Chloroethane	75-00-3	64	66
9	Ethanol	64-17-5	45	46
10	Trichlorofluoromethane (Freon 11)	75-69-4	101	103
11	1,1-Dichloroethene	75-35-4	96	61, 98
12	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	101	85, 151
13	Acetone	67-64-1	43	58
14	2-Propanol (Isopropanol)	67-63-0	45	43
15	Carbon disulfide	75-15-0	76	78
16	Methylene chloride	75-09-2	84	49, 51, 86
17	trans-1,2-Dichloroethene	156-60-5	96	61, 98
18	n-Hexane	110-54-3	57	41, 43
19	Methyl tert-butyl ether	1634-04-4	73	43, 57
20	1,1-Dichloroethane	75-34-3	63	65, 83, 85, 98, 100
21	cis-1,2-Dichloroethene	156-59-2	96	61, 98
22	2-Chloro-1,3-butadiene (Chloroprene)	126-99-8	88	53, 90
23	2-Butanone	78-93-3	43	57, 72*
24	Tetrahydrofuran	109-99-9	42	41, 72, 71
25	Chloroform	67-66-3	83	85
26	1,1,1-Trichloroethane	71-55-6	97	99, 117, 119
27	Cyclohexane	110-82-7	56	69, 84
28	Carbon tetrachloride	56-23-5	117	119, 121
29	Ethyl Acetate	141-78-6	43	61
30	Vinyl Acetate	108-05-4	43	86
31	Benzene	71-43-2	78	- - -
32	1,2-Dichloroethane	107-06-2	62	64, 100, 98
33	n-Heptane	142-82-5	57	41, 43, 71
34	1,4-Dioxane	123-91-1	88	58
35	Trichloroethene	79-01-6	130	95, 97, 132
36	1,2-Dichloropropane	78-87-5	63	65, 114
37	Bromodichloromethane	75-27-4	83	85
38	cis-1,3-Dichloropropene	10061-01-5	75	77
39	4-Methyl-2-pentanone	108-10-1	43	58, 100
40	Toluene	108-88-3	91	92
41	trans-1,3-Dichloropropene	10061-02-6	75	77
42	1,1,2-Trichloroethane	79-00-5	97	83, 85, 99, 132, 134
43	Tetrachloroethene	127-18-4	164	129, 131, 166
44	2-Hexanone	591-78-6	43	58, 57, 100
45	Dibromochloromethane	124-48-1	129	208, 206
46	1,2-Dibromoethane	106-93-4	107	109
47	n-Octane	111-65-9	57	41, 43, 85
48	Chlorobenzene	108-90-7	112	114
49	Ethylbenzene	100-41-4	106	91
50	o-Xylene	95-47-6	106	91
51	m,p-Xylene	179601-23-1	106	91
52	Styrene	100-42-5	104	78, 103
53	Bromoform	75-25-2	173	171, 175, 250, 252, 254
54	Cumene	98-82-8	105	120
55	1,1,2,2-Tetrachloroethane	79-34-5	83	131, 133, 166

No	Compound	CAS No.	Primary Ion	Secondary Ion(s)
56	Propylbenzene	103-65-1	91	120
57	4-Ethyltoluene	622-96-8	105	120
58	1,3,5-Trimethylbenzene	108-67-8	105	120
59	1,2,4-Trimethylbenzene	95-63-6	105	120
60	Benzyl Chloride	100-44-7	91	126
61	1,3-Dichlorobenzene	541-73-1	146	111, 75
62	1,4-Dichlorobenzene	106-46-7	146	111, 75
63	1,2-Dichlorobenzene	95-50-1	146	111, 75
64	Hexachlorobutadiene	87-68-3	225	227, 223
65	1,2,4-Trichlorobenzene	120-82-1	180	182, 145
	INTERNAL STANDARDS			
	Bromochloromethane	74-97-5	128	49, 130, 51
	1,4-Difluorobenzene	540-36-3	114	63, 88
	Chlorobenzene-d5	3114-55-4	117	82, 119

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

Table 3

Required BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria1
50	15.0 to 40.0 % of mass 95
75	30.0 to 80.0 % of mass 95
95	Base Peak, 100 % Relative Abundance
96	5.0 to 9.0 % of mass 95 (see NOTE)
173	Less than 2.0 % of mass174
174	50.0 to 120.0 % of mass 95
175	5.0 to 9.0 % of mass 174
176	93.0 to 101.0 % of mass 174
177	5.0 to 9.0 % of mass 176

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

Table 4

Volatile Target Compounds with Corresponding Internal Standards for Quantitation

Bromochloromethane	1,4-Difluorobenzene (IS)	Chlorobenzene-d5 (IS)
Propylene	Chloroform	n-Octane
Dichlorodifluoromethane	1,1,1-Trichloroethane	Chlorobenzene
Dichlorotetrafluoroethane	Cyclohexane	Ethylbenzene
Chloromethane	Carbon tetrachloride	o-Xylene
Vinyl chloride	Ethyl Acetate	m- and p-Xylenes
1,3-Butadiene	Vinyl Acetate	Styrene
Bromomethane	Benzene	Bromoform
Chloroethane	1,2-Dichloroethane	Cumene
Ethanol	n-Heptane	1,1,2,2-Tetrachloroethane
Trichlorofluoromethane	1,4-Dioxane	Propylbenzene
1,1-Dichloroethene	Trichloroethene	4-Ethyltoluene
1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichloropropane	1,3,5-Trimethylbenzene
Acetone	Bromodichloromethane	1.2.4-Trimethylbenzene
2-Propanol (Isopropanol)	cis-1,3-Dichloropropene	Benzyl Chloride
Carbon disulfide	4-Methyl-2-pentanone	1,3-Dichlorobenzene
Methylene chloride	Toluene	1,4-Dichlorobenzene
trans-1,2-Dichloroethene	trans-1,3-Dichloropropene	1,2-Dichlorobenzene
n-Hexane	1,1,2-Trichloroethane	Hexachlorobutadiene
Methyl tert-butyl ether	Tetrachloroethene	1,2,4-Trichlorobenzene
1,1-Dichloroethane	2-Hexanone	
cis-1,2-Dichloroethene	Dibromochloromethane	
2-Chloro-1,3-butadiene (Chloroprene)	1,2-Dibromoethane	
2-Butanone		
Tetrahydrofuran		

Table 5

Relative Response Factor, Initial Calibration, and Initial Calibration Verification Criteria for Volatile Organic Compounds

Volatile Compound	Minimum RRF [1]	Maximum %RSD [1]	ICV Maximum Difference [2]
Propylene	0.010	30.0	± 20.0
Dichlorodifluoromethane	0.010	30.0	± 20.0
Dichlorotetrafluoroethane	0.010	30.0	± 20.0
Chloromethane	0.010	30.0	± 20.0
Vinyl chloride	0.100	30.0	± 20.0
1,3-Butadiene	0.100	30.0	± 20.0
Bromomethane	0.100	30.0	± 20.0
Chloroethane	0.010	30.0	± 20.0
Ethanol	0.010	30.0	± 20.0
Trichlorofluoromethane	0.010	30.0	± 20.0
1,1-Dichloroethene	0.100	30.0	± 20.0
1,1,2-Trichloro-1,2,2-trifluoroethane	0.010	30.0	± 20.0
Acetone	0.010	30.0	± 20.0
2-Propanol (Isopropanol)	0.010	30.0	± 20.0
Carbon disulfide	0.010	30.0	± 20.0
Methylene chloride	0.010	30.0	± 20.0
trans-1,2-Dichloroethene	0.010	30.0	± 20.0
n-Hexane	0.100	30.0	± 20.0
Methyl tert-butyl ether	0.010	30.0	± 20.0
1,1-Dichloroethane	0.200	30.0	± 20.0
cis-1,2-Dichloroethene	0.010	30.0	± 20.0
2-Chloro-1,3-butadiene (Chloroprene)	0.010	30.0	± 20.0
2-Butanone	0.010	30.0	± 20.0
Tetrahydrofuran	0.100	30.0	± 20.0
Chloroform	0.200	30.0	± 20.0
1,1,1-Trichloroethane	0.100	30.0	± 20.0
Cyclohexane	0.010	30.0	± 20.0
Carbon tetrachloride	0.100	30.0	± 20.0
Ethyl Acetate	0.010	30.0	± 20.0
Vinyl Acetate	0.010	30.0	± 20.0
Benzene	0.400	30.0	± 20.0
1,2-Dichloroethane	0.100	30.0	± 20.0
n-Heptane	0.100	30.0	± 20.0
1,4-Dioxane	0.005	30.0	± 20.0
Trichloroethene	0.300	30.0	± 20.0
1,2-Dichloropropane	0.010	30.0	± 20.0
Bromodichloromethane	0.200	30.0	± 20.0
cis-1,3-Dichloropropene	0.200	30.0	± 20.0
4-Methyl-2-pentanone	0.010	30.0	± 20.0
Toluene	0.400	30.0	± 20.0
trans-1,3-Dichloropropene	0.100	30.0	± 20.0
1,1,2-Trichloroethane	0.100	30.0	± 20.0
Tetrachloroethene	0.100	30.0	± 20.0
2-Hexanone	0.010	30.0	± 20.0
Dibromochloromethane	0.100	30.0	± 20.0
1,2-Dibromoethane	0.010	30.0	± 20.0
n-Octane	0.100	30.0	± 20.0
Chlorobenzene	0.500	30.0	± 20.0
Ethylbenzene	0.100	30.0	± 20.0
o-Xylene	0.300	30.0	± 20.0
m,p-Xylene	0.300	30.0	± 20.0
Styrene	0.300	30.0	± 20.0
Bromoform	0.050	30.0	± 20.0
Cumene	0.050	30.0	± 20.0

Volatile Compound	Minimum RRF [1]	Maximum %RSD [1]	ICV Maximum Difference[2]
1,1,2,2-Tetrachloroethane	0.300	30.0	± 20.0
Propylbenzene	0.010	30.0	± 20.0
4-Ethyltoluene	0.100	30.0	± 20.0
1,3,5-Trimethylbenzene	0.100	30.0	± 20.0
1,2,4-trimethylbenzene	0.100	30.0	± 20.0
Benzyl Chloride	0.050	30.0	± 20.0
1,3-Dichlorobenzene	0.600	30.0	± 20.0
1,4-Dichlorobenzene	0.500	30.0	± 20.0
1,2-Dichlorobenzene	0.400	30.0	± 20.0
Hexachlorobutadiene	0.050	30.0	± 20.0
1,2,4-Trichlorobenzene	0.200	30.0	± 20.0

[1] Up to two compounds in the initial calibration may fail the criteria and still meet the minimum RRF and %RSD requirements. However, these compounds must have a minimum RRF greater than or equal to 0.01, and the %RSD must be less than equal than or equal to 40%.

[2] Up to ten percent of compounds may fail the ICV requirements for the minimum RRF criteria and Percent Difference criteria. However, these compounds in the ICV must have a minimum RRF greater than or equal to 0.010 and the Percent Difference must be within the inclusive range of ±40.0%.

Table 6

Percent Difference and Relative Percent Difference Criteria for Volatile Organic Compounds in the Continuing Calibration Verification Standard and Laboratory Control Sample

Volatile Organic Compound Standards	Maximum Difference[1]	LCS/CCV RPD[2]
Continuing Calibration Standard	± 30.0	≤ 25.0
Laboratory Control Sample	± 30.0	≤ 25.0

[1] Up to ten percent of compounds may fail the CCV and LCS requirement for the minimum RRF criteria and Percent Difference criteria. However, these compounds in the CCV must have a minimum RRF greater than or equal to 0.010 and the Percent Difference must be within the inclusive range of ±40.0%.

[2] Ten percent of the compounds may fail the CCV and LCS requirement for the maximum RPD criteria. However, these compounds in the LCS and CCV must have an RPD less than 40%.