METHOD 327 - Fugitive and Area Source Measurement of Selected Volatile Organic Hazardous Air Pollutants Using Specially Prepared Canisters

1.0 *Scope and Application*

1.1 This method describes the sampling and analysis of emissions from fugitive and area sources collected using specially prepared canisters and analyzed using a gas chromatograph (GC) coupled with a low- or high-resolution mass spectrometer (MS) for the determination of the airborne concentration of selected volatile organic hazardous air pollutants (oHAPs) such as ethylene oxide or vinyl chloride.

1.2 Applicability. The use of this method is strictly intended for determining airborne concentrations of selected speciated oHAPs to determine compliance with a fenceline emission standard and/or work practices when specified by the applicable regulation. This method includes data quality objectives (DQOs) specific to the measurement of airborne concentrations of speciated oHAPs and must not be used for other compliance purposes (i.e., measurements from ducted sources).

1.3 The analytical approach for this method uses a GC coupled with a low- or high-resolution MS, which may consist of a linear quadrupole, ion trap, or time-of-flight (TOF) system. Speciated oHAPs are identified by a combination of the retention times (RTs) and the associated mass spectra by comparing observed fragmentation patterns to reference spectral patterns and relative ion abundances established during calibration. For the speciated oHAPs, the intensity of the observed quantitation ion in the unknown sample is compared with the system response to the same ion for known amounts of the compound.

1.4 The sampling and analytical approach included in this method is based on previously published EPA guidance in Compendium Method TO-15A, which describes the sampling and analytical procedures for measuring volatile organic compounds (VOCs) in ambient air.

2.0 Summary of Method

2.1 In this method, a whole air sample is collected through a particulate filter with a flow control device into an evacuated, specially prepared canister for a length of time specified by the applicable regulation, typically 24 hours. After the air sample is collected, the canister valve is closed, the canister pressure is measured, and the canister is transported to the laboratory for analysis. Upon receipt at the laboratory, the sample collection information is verified, the canister pressure is measured, and the canister is stored at ambient laboratory temperature until analysis. For analysis, a known volume of the sample is directed from the canister into a preconcentrator to collect speciated oHAPs from the sample aliquot and to allow the majority of bulk gases (e.g., nitrogen, oxygen, argon, and carbon dioxide) and water vapor to be vented.

2.2 The laboratory, field laboratory, and field personnel must have experience with sampling trace-level oHAPs using specially prepared canisters and with operating preconcentrator/ GC/multidetector instrumentation (e.g., MS) for trace-level analysis.

2.3 This method is performance-based and includes a description of the equipment, instruments, operations, and acceptance and performance criteria. EPA developed these criteria to ensure the collection of high-quality data. Laboratories must develop their own standard operating procedure (SOP) documents describing the equipment, equipment management, targeted compounds, procedures, and quality assurance (QA) activities specific to that laboratory, instrumentation, and potentially specific for the targeted analyte.

2.4 The key steps of this method required for the collection of each sample include stringent leak testing under stop flow, using certified and clean canisters, using certified sampling devices, collecting accurate field data, and collecting field blanks and duplicates. The key steps of this method required for sample analysis include the analysis of blanks, use of high-quality reference standards, and initial and ongoing calibration checks of the instruments used.

3.0 Definitions

3.1 *Absolute pressure* means the pressure measured with reference to absolute zero pressure, usually expressed in units of kilopascal (kPa) absolute or pounds per square inch absolute (psia).

3.2 *Collocated precision* means the precision determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters and collected through two separate sampling devices with separate inlets. This determines the precision of the method including the sampling and analysis processes. Collocated precision is determined by calculating the absolute relative percent difference (RPD) for the collocated measurements (the absolute value of the difference between the two collocated sample results divided by their average value and expressed as a percentage).

3.3 *Continuing calibration verification sample (CCV*) means single level calibration samples run conducted periodically to confirm that the analytical system continues to generate sample results within acceptable agreement to the current calibration curve.

3.4 *Cryogen* means a refrigerant used to obtain sub-ambient temperatures in the preconcentrator and/or the GC oven. Typical cryogens are liquid nitrogen (boiling point [BP] -195.8 °C), liquid argon (BP -185.7 °C), and liquid carbon dioxide (BP -79.5 °C).

3.5 *Deionized water* means ASTM Type I water or equivalent.

3.6 *Diluent gas* means hydrocarbon-free (HCF) synthetic “zero” air.

3.7 *Dynamic dilution* means a technique for preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with a diluent gas (such as humidified HCF zero air) in a mixing chamber or manifold so that a flowing stream of calibration mixture is created.

3.8 *Gauge pressure* means the pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or inches of mercury (Hg). Gauge pressure is zero-

referenced against ambient air pressure; zero is equal to the local atmospheric (barometric) pressure, which is nominally 101.3 kPa (29.92 in. Hg or 14.7 psia) at sea level.

3.9 *Mass spectrometer* means an instrument that ionizes molecules and atoms (typically into electrically charged fragments), separates these ions according to their mass-to-charge ratio (m/z or m/e), and responds to the impact of the ions based on their population. MS systems suitable for this method include quadrupole, ion trap, and TOF detectors. Quadrupole and ion trap MS operating modes (i.e., full-scan, selected ion monitoring [SIM], and selected ion storage [SIS] modes) can be selected to optimize the ion mass collection range.

3.10 *Mechanical Flow Controlling Device (MFCD)* means a device that is used to ensure constant flow to an evacuated canister to near ambient pressure. MCFD are designed to maintain a constant pressure drop (and thus a constant flow rate) across a restrictive orifice by allowing a constant leak rate of sample into the canister as the canister vacuum decreases to near ambient pressure without power.

3.11 *Nominal concentration* means a requested, target, or named concentration that approximates the true, reference, or certified concentration. For example, a nominal 200 parts per trillion by volume (pptv) standard may have an actual certified concentration of 206 pptv.

3.12 *Preconcentrator* means a device used to concentrate the target compound(s) while the bulk gases are effectively removed. The target compound(s) are then desorbed and injected into a GC-MS system.

3.13 *Quantitative accuracy* means the degree of measurement accuracy required to measure the concentration of an identified compound, within a given tolerance of uncertainty, with an analytical system.

3.14 *Replicate precision* means the precision determined from repeated analysis of a gas sample from one canister, which may be evaluated by calculating the absolute RPD for pairwise measurements (N = 2) or by determining the relative standard deviation (RSD) for replicate measurements where $N \geq 3$. Replicate analyses are used to determine precision of the analysis processes and do not provide information on sampling precision.

3.15 *Second Source Calibration Verification (SSCV) Standard* means a humidified calibration standard prepared from a calibration stock gas procured from a separate supplier. An SSCV can only be prepared with a calibration stock from the same supplier if it is unavailable from another supplier and is prepared from a different lot of source material as the primary calibration stock.

3.16 *Static dilution* means a technique for preparing calibration mixtures in which standard and diluent gases are added to a fixed-volume vessel or chamber at a known ratio. Standard and diluent gas amounts may be measured gravimetrically, by volume, and/or by pressure differential from pressurized cylinders or as neat materials and blended with a known amount of diluent gas (such as humidified zero air) in a mixing chamber or manifold.

3.17 *Target concentration* means desired, estimated, or approximate concentration (see "nominal concentration" above).

3.18 *Theoretical concentration* means a reference concentration derived by applying measurements performed with calibrated instruments with known tolerances to a certified reference standard concentration value. Measurements of the target compound(s) concentrations are to be determined using a calibration that is developed based on theoretical concentrations.

3.19 *Time-of-flight (TOF) mass spectrometry* means a MS method that determines the ion's mass-to-charge ratio by measuring the time the ion takes to reach the detector.

3.20 *Wetted surfaces* mean the surfaces of the flow path, canister, valving, pumps, etc., that contact the gas undergoing collection, mixing, transfer, or analysis.

4.0 Interferences

4.1 Sample Collection. There are potential physical interferents which could impact the ability to properly time-integrate the sampling, such as leaks of the sampling system or introduction of foreign material (e.g., particulate matter [PM], insect nests, spider webs). These interferences are mitigated by closely following the sampling protocols included in this method (e.g., leak check procedures and sampling system requirements).

4.2 Canister Sampling Media Interferences. Each canister will have its own specific performance characteristics and appropriate cleaning, sampling, and handling procedures are required for attainment of acceptable initial and ongoing method performance. Failure to adhere to the cleaning and certification requirements included in this method may lead to the following interference issues:

(1) Incomplete deactivation of canister interior surfaces (e.g., canister welds) may result in active sites for adsorption or surfaces that facilitate the decomposition of labile VOCs to form other VOCs within the canister. Other potential sources of active sites include canister valves, valve stems, and ferrules. Damage to the canister interior that exposes untreated surfaces may also result in active sites.

(2) Entrained PM deposited in the canister sampling pathway can adsorb VOCs making them unavailable in the canister gas phase which interferes with collected samples. Such trapped VOCs can potentially desorb later and result in the inability to achieve canister cleanliness performance specifications and/or contaminate subsequent canister sampling events. Additionally, organic PM can react with co-sampled ozone or other oxidative species to form target VOCs. PM can also clog tiny openings in critical or restrictive orifices, which impacts collection flow rates.

(3) Under certain conditions, the composition of an air sample may change upon its introduction into the canister and over time such that the air in the canister no longer represents the air sampled. Such changes may be caused by interactions of the VOCs with the interior canister surface or between chemicals in the air matrix. The activity of the interior canister surface is

unique to each canister and is based on several factors, including variability in canister manufacturing defects, differences in canister surface deactivation treatments, the presence of PM and co-collected moisture in the canister, and artifacts from reactions of VOCs on the canister walls.

(4) Condensed water within the canister can result in corrosion of the interior surface of canisters with weak or deficient coatings and can result in the partitioning of hydrophilic polar VOCs to liquid water. Under such circumstances, concentrations of these analytes in the gas phase will be biased low until the condensation is eliminated by reduction of the canister pressure below the vapor saturation pressure of water.

4.3 Analytical Interferences. Contamination within the analytical system may come from several sources including, but not limited to, off-gassing of materials within the sample introduction or preconcentrator flow path, carryover from high-concentration samples or standards, and solvent vapors within the laboratory.

(1) Active sites within the sample introduction or preconcentration flow path are often caused by use of improper materials or degradation of deactivated surfaces.

(2) Impurities in source materials or diluent gases for internal standard (IS) gas mixtures may result in contamination of target VOCs.

(3) Water and the delivery systems used to humidify canisters or diluent gas streams may contaminate the canister contents or humidified gases.

(4) Moisture in the sample gas may interfere with VOC analysis by GC-MS. Poor or inconsistent water management during preconcentration can cause peak broadening and RT shifts that can result in peak misidentification, particularly for hydrophilic polar compounds. Water management systems that use semipermeable fluoropolymer membranes remove oxygenated and polar VOCs from the sample matrix and exhibit memory effects for several VOCs. VOCs entrained in the fluoropolymer membrane can convert to ketones and alcohols, which are transported across the membrane bidirectionally such that these ketones and alcohols can contaminate the sample stream and VOCs in the sample stream can be adsorbed into the fluoropolymer and removed from the sample stream.

(5) Carbon dioxide in the collected sample can coelute with more volatile VOCs eluting early in the GC-MS run and interfere with their quantitation.

(6) Artifacts in chromatograms, such as silanol compounds formed from the breakdown of silicon-ceramic linings of canisters and siloxane compounds from the breakdown of the stationary phase in an analytical column, can interfere with identification and quantitation of less volatile VOCs.

(7) Be cognizant of compounds that interfere with target analytes when operating in MS modes that do not provide full-scan ion spectra (i.e., selected ion monitoring [SIM] and selected ion

storage [SIS]). Such interfering coeluting compounds may share common ions, may have similar mass spectra, and may be difficult or impossible to separate from target VOCs.

5.0 Safety

This method does not address all the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate field and laboratory safety and health practices prior to use.

6.0 Equipment and Supplies

6.1 Specially Prepared Canisters. You must use specially prepared canisters at least 6 liters in volume that are suitable for trace gas analysis of the target compounds, such that they meet the requirements in Section 8.3 of this method. Canisters must be able to withstand numerous cycles of evacuation to high vacuum of 0.0067 kPa (0.002 in. Hg) and pressurization to 377 kPa (40 pounds per square inch gauge, psig).

6.2 Valves. You must use canisters with valves that are designed specifically for trace level measurements. The wetted portions of the valve must, at a minimum, be constructed of chromatographic-grade stainless steel (preferably type 316), and the valve seal surfaces must be metal to metal to minimize absorption and off-gassing of VOCs and other potential contaminants. It is recommended that valve designs have minimal internal volume and surface area to minimize the risk of contamination.

6.3 Canister Cleaning System. You must use a canister cleaning system that includes the following components.

6.3.1 Manifold constructed of chromatographic-grade stainless-steel tubing and connections for multiple canisters.

6.3.2 Oil-free vacuum pump capable of achieving vacuum of approximately 3.4 kPa absolute (1 in. Hg absolute or 0.5 psia).

6.3.3 High-vacuum pump for achieving a final canister vacuum of approximately 0.0067 kPa (0.002 in. Hg) or less.

6.3.4 Heating oven that can contain the canister and allow heating of the valve. The oven is also used to bake sampling system components.

6.3.5 Humidification system, such as humidifier impinger or bubbler, capable of achieving relative humidity (RH) of at least 50% in the cannister.

6.3.6 Programmable controller for selecting temperature and cycle time and for manually or automatically switching between evacuation and pressurization.

6.3.7 A pressure release valve to minimize the likelihood of system over pressurization.

6.3.8 Tubing and connections constructed of borosilicate glass, quartz glass, or chromatographic-grade stainless-steel (minimum type 316 or silicon-ceramic coated) to minimize dead volume of the system. You must not use butyl rubber or perfluoroalkoxy (PFA) materials. If needed for connections or seals, minimize the use of Viton and Teflon to avoid adsorption and/or off-gassing of compounds of interest or introduction of other potential interferences.

6.3.9 Purge gas such as HCF zero air or ultra-high purity (UHP)-grade cylinder nitrogen or liquid nitrogen dewar headspace.

6.3.10 Charcoal scrubber, catalytic oxidizer, or other systems for eliminating trace contaminants from the purge gas.

6.4 Sampling Device. The sampling device consists of the following equipment and for the purpose of this method, the sampling device consists of the aggregation of equipment in this section. The sampling device must be individually named with an alpha-numeric serial number that is unique.

6.4.1 A stainless-steel particulate filter with pore size of 2 to 7 micrometers (μm) installed on the sampling device inlet.

6.4.2 Sampling Probe. The internal volume of the sample probe must be less than 1% of the volume collected by the sample container with an inverted inlet (e.g., sampling cane to prevent the entry of water droplets) consisting of only chromatographic-grade stainless steel (including silicon-ceramic lined steel).

6.4.3 You must use an MFCD to regulate the flow at a constant flow rate over the 24-hour collection period into an evacuated stainless-steel canister.

6.5 Vacuum/Pressure Gauges.

6.5.1 Field Pressure Measurement Gauge. A vacuum/pressure gauge or pressure transducer with an accuracy of ± 0.25% full scale calibrated over the range of use for the application with sufficient resolution to permit precise measurement of pressure differentials must be used for field sampling purposes. The accuracy of the vacuum gauge must be measured verified on an annual basis against a National Institute of Standards and Technology (NIST)-certified standard.

6.5.2 Laboratory Canister Pressure Measurement Gauge. A vacuum/pressure gauge or pressure transducer with an accuracy of ± 0.1% full scale or 0.13 kPa, whichever is smaller, calibrated over the range of use for the application with sufficient resolution to permit precise measurement of canister pressure must be used for pressurizing field samples with HCF zero air or ultrapure nitrogen for analysis. The accuracy of the vacuum gauge must be measured verified on an annual basis against a NIST-certified standard for analysis.

6.6 Gas Regulators. Regulators for high-pressure cylinders of dilution gas, stock standard gases, and internal standard gases must be constructed of non-reactive material, such as high-purity

stainless steel, and may be lined with an appropriate material that is inert to the targeted VOC (e.g., silicon-ceramic). Do not use regulators that contain PFA materials (e.g., for seals and diaphragms) and avoid using regulators that contain Teflon products such as polytetr-rafluoroethylene (PTFE) and flouroethylenepropylene(FEP), where possible, to minimize memory effects. All regulators must be rated for the pressure and flow expected during use. Regulators must be dedicated to a specific task and labeled for use (e.g., do not use the same regulator on a high-concentration stock VOC standard cylinder and a low-concentration stock VOC cylinder).

Note: Some new regulators (e.g., stainless steel regulators) should be sufficiently passivated prior to use to prevent potential sample loss.

6.7 Reference Flow Meters.

6.7.1 A flow meter (e.g., a calibrated mass flow meter (MFM), a volumetric reference standard, or other similar measurement device) calibrated to measurement range appropriate to measure continuous flow must be used. The flow meter must not interfere with the flow measurement (i.e., the pressure drop across the flow meter may affect the flow being measured).

6.7.2 Reference flow meters must be calibrated on an annual basis and be able to measure within ±2 % of the predicted values (e.g., cubic centimeters per minute) against a NIST-traceable volumetric standard.

6.8 Tubing and Fittings. Connecting tubing and fittings for dilution and standard gases must be constructed of chromatographic-grade stainless steel (e.g., 316 type), which includes silicon-ceramic–treated stainless steel. Connections must be metal to metal. Lines may need to be heated to ensure that there is no condensation. You must not use PTFE thread sealants or Buna-N rubber components on any wetted surface in a sampling and analytical system.

6.9 Analytical Instrumentation. Conduct analyses under this method using any combination of preconcentrator, GC, and MS provided the equipment meets the performance specifications of this method.

6.9.1 Gas Chromatographic–Mass Spectrometric (GC-MS) System.

6.9.1.1 Gas Chromatograph. The GC used for analysis under this method must allow temperature programming with quick and accurate temperature ramping. If needed for separation of very light VOCs from the targeted oHAPs, the GC must be capable of sub-ambient cooling (e.g., -50 °C). Carrier gas connections must be constructed of stainless-steel or copper tubing.

6.9.1.2 Chromatographic Column. The capillary chromatographic column must be capable of achieving separation of target compounds and any potential interferences per Section 4 and maintaining retention time stability as required in Section 9.

6.9.1.3 Mass Spectrometer. The MS may be a linear quadrupole, ion trap, or TOF unit, and must have minimum resolution of 1 atomic mass unit (amu) or less. The MS must be capable of

analyzing the desired mass range every 1 second or less and operate with an acquisition rate such that at least 12 measurements are performed over a typical chromatographic peak. Quadrupole and ion trap systems employing electron impact (EI) ionization mode must provide nominal 70 volt (V) electron energy in EI mode to produce a bromofluorobenzene (BFB) mass spectrum that meets all the instrument performance acceptance criteria as specified in this method.

6.10 Calibration Gas Standard Preparation Equipment. This section discusses the equipment needed to prepare working-level standards for calibrating the GC-MS by dilution of a higher concentration stock standard gas.

6.10.1 Dynamic Dilution System Instrumentation.

6.10.1.1 The dynamic dilution system must include, at a minimum, calibrated electronic mass flow controllers (MFCs) for the diluent gas and each standard gas to be diluted, a humidifier for the diluent gas, and a manifold or mixing chamber where the diluent and standard gases can be sufficiently combined before introduction to the preconcentrator or canister. The gas dilution system must produce calibration gases whose measured values are within ± 2% of the predicted values. The predicted values are calculated based on the certified concentration of the supply gas (protocol gases, when available, are recommended for their accuracy) and the gas flow rates (or dilution ratios) through the gas dilution system.

6.10.1.2 Connection tubing for the dynamic dilution system must be constructed of chromatographic-grade or silicon-ceramic–coated stainless steel. Mixing chambers or manifolds must be constructed of chromatographic-grade or silicon-ceramic–coated stainless steel, borosilicate, or quartz glass.

6.10.1.3 The gas dilution system must be recalibrated once per calendar year using NIST-traceable primary flow standards with an uncertainty ≤ 0.25%. You must report the results of the calibration whenever the dilution system is used, listing the date of the most recent calibration, the due date for the next calibration, calibration point, reference flow device (device identification [ID], signal-to-noise [S:N] ratio, and acceptance criteria.

6.10.1.4 The gas dilution system must be verified to be non-biasing under HFC zero air and known standards at least one per calendar year for each reactive target compounds (e.g., ethylene oxide and vinyl chloride). Zero air must be flowed through all applicable MFCs, tubing, and manifold used and verified to not be detectable for the target compounds. Additionally, a known standard within the calibration range of the analytical system for each target compound must be flowed through all applicable MFCs, tubing, and manifold to allow equalization and verified to not bias the standard by ± 15% of the concentrations in the reference sample. The equalization time for the bias verification must be used at a minimum for the development of standards.

6.10.1.5 The gas dilution system must be verified daily or per use (whichever is less stringent) per Section 3.2 of Method 205 using any available protocol gas and corresponding reference method.

6.10.2 Static Dilution System Instrumentation.

6.10.2.1 The static dilution system must include, at a minimum, a calibrated pressure transducer or pressure gauge to measure the partial pressures of each standard gas to be diluted and the balance gas, and a manifold to introduce the gases into the working standard canister or vessel. Pressure transducer(s) or pressure gauge(s) used for static dilution must have an accuracy of ± 0.1% full scale or 0.13 kPa, whichever is smaller, calibrated over the range of use for the application with sufficient resolution to permit precise measurement of pressure differentials.

6.10.2.2 Connection tubing for the static dilution system must be constructed of chromatographic-grade or silicon-ceramic–coated stainless steel. Manifolds must be constructed of chromatographic-grade or silicon-ceramic–coated stainless steel, borosilicate, or quartz glass.

6.10.2.3 The static gas dilution system must be recalibrated once per calendar year using NIST-traceable primary pressure gauge with an uncertainty ≤ 0.1%. You must report the results of the calibration whenever the dilution system is used, listing the date of the most recent calibration, the due date for the next calibration, calibration point, reference flow device (ID, S:N ratio), and acceptance criteria.

6.10.2.4 The gas dilution system must be verified to be non-biasing under HFC zero air and known standards at least one per calendar year for each reactive target compounds (e.g., ethylene oxide and vinyl chloride). Zero air must be flowed through all applicable tubing and manifold used and verified to not be detectable for the target compounds. Additionally, a known standard within the calibration range of the analytical system for each target compound must be flowed through all applicable tubing and manifold into the standard canister or vessel and verified to not bias the standard by ± 15% of the concentrations in the reference sample.

6.11 Calibrated Hygrometer.

6.11.1 The calibrated hygrometer must be capable of a 1% RH resolution with a yearly calibration to a NIST-traceable accuracy of ± 3% RH within the range of 20% to 80% RH.

6.11.2 The calibration hydrometer calibration must be verified weekly or per use (whichever is less stringent) at a single point that is approximatively 40 to 50% RH to within ± 5% using a second calibrated hygrometer or a saturated salt solution.

7.0 Reagent and Standards

7.1 You must use only NIST-certified or NIST-traceable calibration standards, standard reference materials, and reagents that are stable through certification and recertification for the tests and procedures required by this method. You must use standards and reagents within their expiration period and evaluate working-level standards prepared in canisters within 30 days of preparation. The concentrations of the target compounds in the mixture must be commensurate with the anticipated dilution factor achievable by the laboratory needed to dilute the mixture to the desired working range. You must retain and report the gas standard certificates of analysis.

7.2 Carrier Gas. Use helium, hydrogen, or nitrogen as the carrier gas in the GC. Carrier gas must be ultrapure (99.999% pure or better).

7.3 HCF Zero Air. Purchase HCF zero air in high-pressure cylinders from reputable gas vendors or prepare HCF zero air by passing ambient air through molecular sieves, catalytic oxidizers, and subsequent charcoal filters or similar substrate. HFC zero air must contain impurities less than 20 pptv or undetected (whichever is more stringent) per compound of interest.

7.5 Nitrogen. Use ultrapure (99.999% pure or better) nitrogen from cylinders procured from commercial gas vendors or from the headspace gas from a liquid nitrogen dewar.

7.6 Cryogens. Cryogens (e.g., liquid nitrogen, liquid argon, and liquid carbon dioxide) specified by the instrument manufacturer, if needed.

7.7 Water for Canister Humidification. ASTM Type I (resistivity ≥ 18 megaohm-centimeter [MΩ·cm]) or equivalent.

8.0 Sample Collection and Preparation

This section presents the sample collection and handling procedures of this method with the initial and ongoing performance evaluation of materials used in sampling and analysis. This method allows the user to choose the materials used for sampling. You must record the exact materials used when conducting this method and include that information in any report associated with sampling according to this method.

8.1 Sampling Device Performance Tests. Prior to initial field deployment and as directed in this section, you must verify that all equipment used to conduct this method meets the performance criteria specified in this section. The primary objectives of the performance tests in this section are to characterize the sampling system and to verify that the sampling system used meets the criteria in the method. The sampling system performance tests include the following:

(a) Flow control verification test,

(b) Flow control flow check,

(c) Sampling device leak check,

(d) Sampling device bias check, and

(e) Sampling device standard check.

8.1.1 Flow Control Verification Test. Prior to initial field deployment and at least every six months, you must verify that the sampling device's ability to control flow to the canister is acceptable. Assemble an evacuated canister with the sampling device including filter connected to a certified flow meter. Figure 1 of Section 17 of this method provides an illustration of the apparatus for characterizing the flow control device.

8.1.1.1 Open the evacuated canister, monitor and record (manually or electronically) the canister pressure downstream of the flow control device and the flow upstream of the flow control device on an hourly basis over the period of 24-hours.

8.1.1.2 The flow control verification test is considered acceptable when the sampling apparatus maintains a constant flow rate for 24-hours and until at least 75% of the canister volume is collected, which is equivalent to approximately 28 kPa (7 in. Hg or 4 psia) below atmospheric pressure.

8.1.1.3 Record the average flow rate during this test. This value will be the reference flow rate for the sampling device until the next verification test. Maintain the results as part of a laboratory record associated with the sampling device.

8.1.2 Flow Control Flow Check. Prior to and after each field sampling event, establish or verify the flow rate of the sampling apparatus. This verification must occur in the field immediately prior to and after each field event.

8.1.2.1 Assemble an evacuated canister and the sampling device connected to a certified flow meter in the same manner used for the flow control verification test discussed above.

8.1.2.2 Open the evacuated canister, allow sufficient time for the system to stabilize, and record the flowrate upstream of the flow control device. Collect two additional flow rate measurements.

8.1.2.3 Calculate the average flowrate. The flow control flow check is considered valid if within +/- 10% of the reference flow rate.

8.1.2.4 If the flow rate has changed and is outside the desired range, you must adjust the controller and repeat the flow check.

8.1.3 Sampling Device Leak Check. You must demonstrate the sampling device and sampling system are leak-free immediately before you begin sampling.

8.1.3.1 Install the sampling device on an evacuated canister equipped with a MFCD and tightly cap the inlet to the sampling device.

8.1.3.2 Open the canister valve fully, and then re-close the valve and observe the vacuum/pressure gauge for a minimum of 2 minutes.

8.1.3.3 If you observe an increase in pressure, the sampling device does not qualify as leak-free. If no changes are observed, record the data and time of the leak check on the Field Data Page (see Figure 4 in Section 17 of this method for an example).

8.1.4 Sampling Device Bias Check. You must demonstrate that sampling device is non-biasing under zero-air and known-standard conditions. For the procedures in Sections 8.1.5 and 8.1.6 of

this method, you must use only canisters that have been qualified as specified in Section 8.3 of this method.

8.1.5 Zero-Air Challenge. You must conduct the sample bias test at least every six months, and after cleaning, replacement of components, or collection of potentially contaminating samples. The volume of air analyzed for the zero-air and reference standard gas must be consistent with the laboratory's typical canister sample injection volume.

8.1.5.1 Provide humidified (> 40% RH) HCF zero air through the sampling device into the canister, and then analyze the sample according to Section 11 of this method and record the concentration measurement and maintain the results as part of a laboratory record associated with the sampling device.

8.1.5.2 Provide humidified (> 40% RH) reference standard air through the sampling device into a canister, then analyze the sample according to Section 11 of this method and record the concentration measurement and maintain the results as part of a laboratory record associated with the sampling device.

8.1.5.3 The results must show that the concentration of the target compounds in the zero-air challenge sample collected through the sampling unit is not greater than 20 pptv higher than the native concentration of the target compounds in the reference sample. If a sampling device does not meet this performance criteria, take action to remove the contamination attributable to the sampling unit (e.g., purging with humidified HCF zero air overnight or longer) and repeat the zero-air challenge. You must not use a sampling device that has not met the standards in this section.

Note: If extended purging durations are not adequate to eliminate contaminants, then disassemble and clean according to Section 8.4 of this method. If the unit cannot be cleaned to meet the specifications, retire the unit from use or repurpose for source sampling.

8.1.6 Sampling Device Standard Check. You must conduct the sampling device standard check prior to initial use and at least every six months, and after replacement of components, or collection of potentially contaminating samples. For the procedures specified below, you must use only canisters that have been qualified as specified in Section 8.3 of this method.

8.1.6.1 Collect a humidified (> 40% RH) known-standard challenge gas through the sampling device and into a canister. The challenge gas must contain the target oHAPs at 100 to 500 pptv each and you must choose the selected challenge concentration considering the expected measured concentration at the deployment location(s).

8.1.6.2 Analyze the sample according to Section 11 of this method and record the concentration measurement and maintain the results as part of a laboratory record associated with the sampling device. The results must demonstrate that each oHAP in the sample collected through the sampling device must be within ± 15% of the concentrations in the reference sample. For compounds exceeding this criterion, you must take steps to eliminate the bias (e.g., cleaning as

specified in Section 8.6.1 of this method or replacement of compromised parts) and repeat the known-standard challenge.

8.1.6.3 Following successful completion of the known-standard challenge, flush the sampling device or system with humidified (> 50% RH) HCF zero air or ultrapure nitrogen for a minimum of 24 hours before field deployment.

8.2 Qualification of Analytical Instrumentation. Prior to initial use and as directed in this section, you must verify that the analytical equipment used in performing this method meets the performance criteria in this section. The primary objectives of these performance tests are to characterize the analytical instrumentation and verify that the analytical instrumentation meets the criteria in this method. The analytical instrumentation performance tests consist of the following:

(a) Analytical zero-air verification,

(b) Analytical known-standard challenge for analytical instrumentation, and

(c) Autosampler verification.

8.2.1 Analytical Zero-Air Verification. Prior to initial use and as part of an instrument's annual calibration, you must demonstrate that the analytical instrumentation (preconcentrator, GC-MS system, and all connections) is non-biasing under zero-air. The volume of air analyzed must be consistent with the laboratory's typical canister sample injection volume.

8.2.1.1 Use the analytical instrumentation to analyze humidified (40 to 50% RH) HCF zero air from a known clean source (e.g., certified clean canister, clean cylinder gas, zero-air generator) at the installation prior to initial use of the instrument.

8.2.1.2 Examine chromatograms for interferences and other chromatographic artifacts such as nontarget peak responses, large peaks or rises in the chromatogram due to undifferentiated compounds, and baseline anomalies. The analysis must show that the concentration of any detected target compounds in the zero-air challenge sample is < 20 pptv or undetected (whichever is more stringent) per compound of interest.

8.2.1.3 If you identify exceedances of target compounds in the zero-air challenge, take steps (e.g., analyzing replicates of humidified clean gas until the contamination is eliminated) to remove the contamination attributable to the analytical instrumentation by following the manufacturer's instructions.

8.2.1.4 You must repeat the analytical zero-air verification to ensure that you have mitigated any problems before using the analytical instrumentation.

8.2.2 Analytical Known-Standard Challenge for Analytical Instrumentation. Prior to initial use and as part of an instrument's annual calibration, you must demonstrate that the analytical instrumentation (preconcentrator, GC-MS system, and all connections) is non-biasing under

known standards. The volume of air analyzed must be consistent with the laboratory's typical canister sample injection volume.

8.2.2.1 Analyze a humidified (40 to 50% RH) reference standard in duplicate containing all target compounds at approximately 100 to 500 pptv each, chosen in consideration of the expected concentration at the deployment locations.

8.2.2.2 The results must demonstrate that the target compounds in the sample collected through the sampling device are within ± 15% of the expected concentrations in the sample.

8.2.2.3 Compounds demonstrating poor response as indicated by peak absence or minimal peak area may be a result of active sites in the analytical system, cold spots in transfer lines, gas impurities, improper choice of preconcentrator sorbent traps or GC columns, system leaks, and/or poor moisture management. If you identify problems, consult the instrument manufacturer to determine the necessary steps to eliminate the bias.

8.2.3 Autosampler Verification. Prior to initial use and as part of an instrument's annual calibration, you must demonstrate that the auto sampling equipment is non-biasing under zero-air.

8.2.3.1 If you use an autosampler to facilitate analysis of multiple canisters, you must test all ports, transfer lines, and connections of the autosampler after you have calibrated the analytical system and prior to conducting the canister, sampling device and system qualifications, or upon replacement of transfer lines or after analysis of potentially contaminating samples.

8.2.3.2 Connect humidified (40 to 50% RH) HCF zero air to each port and verify that the concentration for each target compound is < 20 pptv or undetected (whichever is more stringent) per compound of interest using the procedures in Section 11 of this method.

8.2.3.3 After the zero-air test, challenge each port of the autosampler with a reference standard (approximately 100 to 500 pptv) to verify that the autosampler is not causing bias using the procedures in Section 11 of this method). The concentration of each target compound must be within ± 15% of the theoretical concentration of the reference standard.

8.3 Qualification of Canisters. Prior to initial use and as directed in this section, sampling canisters must meet the performance criteria in this section. The primary objectives of these performance tests are to ensure canisters are well characterized and to verify they are non-biasing. The performance criteria in this section are specific to the application of fenceline measurements for regulatory purposes at stationary sources. The performance test consists of the following:

(a) Canister design,

(b) Canister leak check,

(c) Canister zero-air verification, and

(d) Canister known-standard verification.

8.3.1 Canister Design.

8.3.1.1 You must use specially prepared canisters at least 6-liters volume in size that are suitable for trace gas analysis of the target compounds. The canister must include a fixed on/off valve made from chromatographic-grade stainless with metal valve seal surfaces. Each canister must also include a permanent alpha-numeric serial number for identification purposes. Alternative canister volumes may be used, subject to approval by the Administrator.

Note: Specially prepared canisters are commercially available with a modest range of options for surface preparation of the canister interior surfaces, valves, and connections. Currently, canister interior surfaces are typically passivated by electropolishing or coating with a silicon-ceramic film. EPA does not require a specific treatment or design and any canister type may be used for this method contingent on meeting the performance criteria in this section; however, silicon-ceramic coated canisters have demonstrated superior performance when used to sample reactive compounds, (e.g., ethylene oxide).

8.3.1.2 Canisters should be handled with care to ensure that the interior canister surface is not compromised, the valve-to-canister connection remains intact, and weld integrity is maintained. Excessive torque on unbraced canister valve stems when making connections may cause damage and potentially leaks in the valve stem weld or at the ferrule sealing the canister valve and canister stem. Shocks resulting in dents to the surface of the canister may damage welds or create small cracks in the interior canister surface that may expose active sites. You must not use any canister with dents or compromised welds.

8.3.1.3 You must maintain a record of the results for all canisters used for this method. It is recommended that you evaluate the results for any potential trends that could result in erroneous data.

8.3.2 Canister Leak Check. You must qualify each canister as being acceptably leak-tight to ensure sample validity. Qualify new canisters before initial use and qualify all canisters used for sampling at least annually.

8.3.2.1 Leak Check. In conducting the canister leak check, you can either evacuate the canister to high vacuum $\leq$ 0.0067 kPa absolute (0.002 in. Hg or 0.001 psia) or pressurize the canister with clean fill gas to $\geq$ 203 kPa absolute (60 in. Hg or 29.4 psia).

8.3.2.2 After establishing the target pressure in the canister, close the valve and attach a vacuum/pressure gauge.

8.3.2.3 Open the valve and record the initial pressure reading.

8.3.2.4 Close the valve, remove the vacuum/pressure gauge, and loosely cap the canister using a cap fitting to ensure that leakage through the valve is accurately assessed while avoiding potential entry of debris into the valve during storage.

8.3.2.5 After a minimum of three days in storage, reinstall the vacuum/pressure gauge, open the valve, and record the canister pressure reading.

8.3.2.6. Determine the pressure decay rate as the absolute value of the difference between the initial and post-storage canister pressures. You must remove the canister from service if the pressure decay rate exceeds 0.69 kPa/storage day (0.2 in. Hg or 0.1 psia/storage day).

8.3.3 Canister Zero-Air Verification. You must qualify each canister as being acceptably non-biasing under zero-air conditions to ensure sample validity. Qualify new canisters before initial use and qualify all canisters used for sampling at least once every 6 months.

8.3.3.1 Pressurize the clean evacuated canister with humidified (> 50% RH) HCF zero air. Do not use ultrapure nitrogen to pressurize the canister because the inert nitrogen atmosphere does not permit reactions within the canister that may occur under sampling conditions.

8.3.3.2 Allow the canister to equilibrate for a minimum of 24 hours.

8.3.3.3 After the equilibration period, conduct an initial cleanliness analysis as specified in Section 8.4 of this method.

8.3.3.4 Store the canister for a holding period equal to or exceeding the typical laboratory holding time, nominally 7 days from the canister fill date.

8.3.3.5 After the holding period, conduct a subsequent cleanliness analysis as specified in Section 8.5 of this method.

8.3.3.6 The results of both the initial and subsequent cleanliness analysis must meet the cleanliness criteria specified in Section 8.5 of this method to be used for sampling. You must reclean and retest canisters that fail the zero-air challenge.

Note: If necessary, use more aggressive cleaning techniques such as water rinses or other rinses as specified by manufacturers. If a canister continues to fail the zero-air challenges, remove the canister from service.

8.3.4 Canister Known-Standard Verification. You must qualify each canister as being acceptably non-biasing under known-standard conditions to ensure sample validity. Qualify new canisters before initial use and qualify all canisters used for sampling at least every 6 months.

8.3.4.1 Fill the clean evacuated canister with a humidified (40 to 50% RH) standard gas in HCF zero air with each target compound at approximately 100 to 500 pptv. Choose the selected challenge concentration based on the concentration expected to be measured during the sampling event.

8.3.4.2 Allow the canister to equilibrate for a minimum of 24 hours.

8.3.4.3 After the equilibration period, conduct an initial analysis according to Section 11 of this method.

8.3.4.4 Store the canister for a holding period equal to or exceeding the typical laboratory holding time, nominally 7 days from the canister fill date.

8.3.4.5 After the holding period, conduct a subsequent analysis.

8.3.4.6 The results of both the initial and subsequent analysis must show that the measured concentrations of the target analytes are within ± 30% of the theoretical spiked concentration for each target compound. You must reclean and retest canisters that fail the known-standard verification.

8.4 Canister Cleaning. Clean canisters using repeated cycles of evacuation and pressurization. Table 1 in Section 17 of this method summarizes the canister cleaning procedures.

8.4.1 Gas Source for Canister Cleaning, Pressurization, and Flushing.

8.4.1.1 Verify, by direct analysis, the cleanliness of the purge gas upon initial setup. The analysis must show that the concentration of the individual target compounds is ≤ 20 pptv or undetected (whichever is more stringent) per compound of interest at 101.3 kPa absolute (29.92 in. Hg or 14.7 psia).

8.4.1.2 Humidify the purge gas to >50% RH and measure the humidity by placing a calibrated hygrometer probe in the humidified gas stream.

8.4.1.3 If using a bubbler-type humidifier, ensure that the downstream pressure is lower than the humidifier upstream pressure to avoid backflow of the water.

8.4.2 Pre-Evacuation of Canisters. You may need to repeat the pre-evacuation process for canisters that contain VOCs at higher concentrations.

8.4.2.1 Pre-evacuate canisters to be cleaned prior to connection to the canister cleaning system. To reduce the potential for contamination of the system, attach the canisters to an oil-free roughing pump and evacuate to approximately 7 kPa absolute (28 in. Hg vacuum or 1.0 psia) with the exhaust of the pump directed to a fume hood or passed through a charcoal trap.

8.4.2.2 Refill canisters to ambient pressure with HCF zero air.

8.4.2.3 Attach the canisters to the cleaning system after completing the pre-evacuation and refilling steps.

8.4.3 Canister Heating During Cleaning.

8.4.3.1 Heat canisters by placing them in an enclosed oven during cleaning to facilitate removal of compounds. Do not use heat bands or heating jackets.

8.4.3.2 Table 1 of Section 17 of this method specifies the temperatures to use for canister cleaning procedures.

8.4.4 Canister Evacuation and Pressurization Cycling.

8.4.4.1 Evacuate canisters to minimally 7 kPa absolute (28 in. Hg vacuum or 1 psia) and maintain this vacuum for a at least 1 minute.

8.4.4.2 Pressurize canisters to 414kPa absolute (≤ 30 psig) with humidified (> 50% RH) HCF zero air and maintain this pressure for a minimum of 1 minute.

8.4.4.3 Repeat the cycle of canister evacuation and pressurization specified in Sections 8.4.4.1 and 8.4.4.2 of this method at least 5 times. You may need to perform 10 to 20 cycle repetitions or use other ancillary procedures to remove stubborn interferents or oxygenated compounds such as ketones, alcohols, and aldehydes (U.S. EPA, 2016b).

8.5 Verification of Canister Cleanliness Prior to Sample Collection.

8.5.1 After cleaning, pressurize each canister from the batch with humidified HCF zero air and maintain that pressure for at least 24 hours.

8.5.2 Connect each canister to the analytical system and measure the concentration of each target compound according to the procedures in Section 11 of this method.

8.5.3 The canister background concentration for each target compound must be ≤ 20 pptv (0.02 ppbv) or undetected (whichever is more stringent) when a canister is filled to standard ambient pressure (101.3 kPa absolute or 14.7 psia).

8.5.4 Canisters that meet the blank criteria are suitable to be evacuated for use. If a canister fails to meet the criteria, you must not use that canister until it has been re-cleaned and has met the requirements in Section 8.5.3 of this method.

8.5.5 Prior to field deployment, evacuate canisters to ≤ 0.0067 kPa (≤ 0.002 in. Hg or 0.001 psia)

8.6 Cleaning of Sampling Components.

8.6.1 Follow the manufacturer's instructions for cleaning components such as flow controllers and sampling unit parts, when necessary.

Note: Disassembly of such instruments may void warranties or calibrations.

8.6.1.1 Flush the sampling units with humidified HCF zero air to remove contamination for at least 15 minutes.

8.6.1.2 Disassemble sampling components and visually inspect for cracks, abrasions, and residue prior to sonicating in deionized water for at least 30 minutes.

8.6.1.3 After flushing/sonication, rinse the components with clean deionized water and dry the components in an enclosed oven set to at least 50 °C for a minimum of 12 hours.

8.6.1.4 Following drying, reinspect components for defects, reassemble, and flush the sampler with humidified HCF zero air or ultrapure nitrogen for at least 12 hours.

Note: To avoid damage to deactivated stainless-steel components due to oxidation in the presence of oxygen-containing atmospheres (e.g., HCF zero air), you should not heat components treated with silicon-ceramic coatings above 80 °C unless evacuated or under an inert atmosphere (e.g., nitrogen).

8.7 Sample Collection. Persons collecting field samples should be familiar with all aspects of this sampling protocol. It is suggested that those collecting these measurements for regulatory purposes develop site-specific SOPs to ensure samples are collected consistently and those doing the sampling are sufficiently trained on this method and the SOP.

8.7.1 Pre-Sampling Activities.

8.7.1.1 Clean canisters and verify that the canisters meet cleanliness and vacuum criteria specified in Sections 8.3 through 8.5 of this method.

8.7.1.2 If canisters were previously cleaned and stored under pressure while awaiting use, you must evacuate the canisters prior to field deployment. If canisters were stored under vacuum, you must verify that the canisters continue to meet vacuum threshold requirements.

8.7.1.3 Clean and verify the cleanliness and flowrates of sample devices that you will use for sampling, and ensure that a clean particulate filter is placed in the inlet of the sampling device.

8.7.1.4 Establish sample codes (unique identifiers) and develop field data page and/or chain of custody (COC)/sample collection data form(s).

8.7.1.5 If shipping equipment into the field, make sure you have the proper number of canisters and sampling devices for the number of samples required for the sampling location and QC samples, allowing for sufficient timing for samples to arrive at the site.

8.7.1.6 Develop a unique sampling location ID. The sampling location must meet any requirements set in the applicable regulation and be in a secure location that protects the canister and sampling inlet from unwanted tampering or damage. The sampling location must also be located away from the immediate vicinity of any biasing sources (e.g., outdoor smoking areas; vehicle exhaust; heating, ventilation, and air conditioning units/building exhaust; outdoor fuel

storage areas; shelter roofing materials; or exhaust from other sample collection devices). In general, horizontal distances should be > 10 meters (m) from biasing sources.

8.7.2 Sample Setup Activities.

8.7.2.1 You must place the canister in a location that protects the canister and sampling inlet from unwanted tampering, damage, or theft.

8.7.2.2 Protect the canister and sampling inlets by placing the canister under shelter, if possible. Do not restrict air flow around inlets and do not locate inlets under building overhangs.

8.7.2.3 Do not place the canister near vegetation or structures that block or significantly restrict air flow to the MFCD inlet or manifold. Ensure that rain cannot be drawn directly into the MFCD, and the inlet heights must be approximately 1.5 to 3 m above ground level.

8.7.3 Sample Setup and Deployment. Perform the following steps at the time of sample setup and deployment.

8.7.3.1 Based on the applicable standard, determine the appropriate number and placement of sampling locations at the fenceline. The applicable standard will define the sampling schedule (e.g., one sampling event over a 5-day period) and the sampling period. All sampling locations must initiate sampling within 60 minutes of each other.

8.7.3.2 You must document all activities associated with sampling on the field data page. (See Figure 4 in Section 17 of this method for an example field data page.) You may choose to use this field data page as the COC, or you may choose to establish a separate COC form. The chain of custody will accompany the canisters during shipment and collection to document sample handling and transport.

8.7.3.4 Verify that each canister has been cleaned and blanked within the last 30 days. Label each canister with a sample ID code and record the canister and sample ID on the field data page. You must not use a use a canister for sampling that has not been cleaned and blanked within 30 days of sampling.

8.7.3.5 Verify the sample device is in working order and calibrate/verify the flow rate setting, if applicable, with a reference flow meter. Record the sample device ID, expected flowrate, and the reference flowrate if calibrated/verified in the field, including the reference flow meter if applicable.

8.7.3.6 Attach the sampling device to the canister and locate at the appropriate sampling location. Record the sampling location ID, latitude, longitude, date, and time that you installed the canister on the field data page.

8.7.3.7 Measure and record the canister vacuum using the field pressure measurement gauge, and verify that the canister has not leaked and has sufficient vacuum to collect the sample. You must

replace the canister if the initial pressure is not within -1 in. Hg absolute zero (-3.39 kPa or -0.5 psi).

8.7.3.8 Conduct leak checks as specified in Section 8.3.2 of this method and record the results on the field data page.

8.7.3.9 Open the canister valve. Record the date and time that you opened the valve as the start time, and record the initial canister vacuum/pressure and any other comments such as unusual events or conditions that may impact sample results on the field data page.

8.7.3.10 Sample for the period as defined in the applicable standard (e.g., 24 hours +/- 1 hour).

8.7.3.11 At the end of the sampling period, close the valve. Record the date and time that you closed the valve as the end time.

8.7.3.12 Remove the sampling device and attach the field pressure measurement gauge.

8.7.3.13 Open the canister valve and measure and record the final canister vacuum/pressure and any other comments such as unusual events or conditions that may impact sample results on the field data page. Flag any canisters with a final pressure greater than -3 in. Hg gauge pressure (-10.2 kPag or -1.5 psig).

8.7.3.14 Disconnect the field canister pressure measurement gauge and replace with a cap.

8.7.3.15 If applicable, verify the sample device is still in working order and verify the flow rate setting with a reference flow meter. Record the final flowrate on the field data page.

8.7.4 Field Duplicates. For each sampling day, you must include the collection of a separate co-located sample for at least one sampling location. The collocated duplicate must be sampled using a discrete MFCD. The collection of the field duplicates must follow the same procedure and occur at the same time as the co-located field sample.

8.7.5 Canister Field Blanks. For each sample day, you must collect canister field blanks. A canister blank is prepared by filling a canister with humidified clean diluent gas (prepared in the same manner as the method blank (MB) described in Section 9.3.2 of this method) to approximately -15 in. Hg ± 1 in. Hg . Record the pressure and transport to the field site(s) to accompany field-collected canisters. Canister field blanks are to be treated identically to field-collected samples in the field and laboratory including pressure checks, MFCD leak checks, etc. The field blanks are analyzed by interspersing them among the field samples.

8.7.6 Canister Field Spike. For each sample day, you must collect a canister field spike. A canister field spike is prepared by filling a canister with humidified standard gas at a concentration in the lower third of the calibration curve for the target compound to approximately -15 in. Hg ± 1 in. Hg. The field spike canister is transported to the field site to accompany field-collected canisters and treated identically to field-collected samples in the field and laboratory, including pressure checks, MFCD leak checks, etc. The field spikes are analyzed

by interspersing them among the field samples. Field spike acceptance criteria should be within ± 30% of the theoretical spiked concentrations.

8.7.7 Prepare and secure the canisters for transport. You must ship canisters in protective hard-shell boxes and/or sturdy cardboard boxes to ensure canister longevity. Do not use boxes that have lost integrity or rigidity.

8.8 Method Detection Limit (MDL) Determination. Determine the MDL under the analytical conditions selected (see Section 11 of this method) using the procedures in this section.

8.8.1 Prepare at least seven blank samples according to the procedures Section 9.3.2 of this method using sampling media (i.e., canisters) that have been deployed in the field, and cleaned per Section 8.4 of this method. The blank samples must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates according to the procedures in Section 11 of this method.

8.8.2 Prepare at least seven spike samples according to the procedures in either Section 10.2 or 10.3 of this method, at a concentration of the target compound within a factor of five of the expected detection limits. The spike samples must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates according to the procedures in Section 11 of this method.

8.8.3 Compute the standard deviation for the replicate blank samples concentrations and multiply this value by 3.14 to determine the blank MDL (MDL_b).

8.8.4 Compute the standard deviation for the replicate spike sample concentrations and multiply this value by 3.14 to determine the spike MDL (MDL_s).

8.8.5 Select the greater of MDL_b or MDL_s as the MDL for the compound of interest. The results must demonstrate that the method is able to detect analytes such as ethylene oxide at concentrations less than 20 pptv and at least $1/10^{th}$ of the lowest concentration of interest (i.e., action-level), whichever is larger. If the MDL does not meet the concentration requirement, perform corrective action and repeat the MDL determination.

8.8.6 MDL determinations must be repeated at least annually or whenever significant changes have been made to the sampling or analytical system.

Note: The MDL calculation is based on single-tailed 99^{th} percentile t static at six degrees of freedom. Additional blank or spike samples would increase the degrees of freedom.

9.0 Quality Control

Table 9-1 in this section lists the quality control (QC) parameters and performance specifications for this method.

9.1 Second Source Calibration Verification (SSCV) Standard.

9.1.1 Prepare a humidified SSCV standard in a canister at a concentration in the lower third of the calibration curve. The SSCV standard must contain all compounds in the calibration mixture. The SSCV standard must be prepared independently from the calibration standards using a certified secondary source calibration standard.

9.1.2 Analyze the SSCV after the initial calibration (ICAL). Recovery of each target oHAP in the SSCV standard must be within ± 30% of the theoretical concentration.

9.2 Continuing Calibration Verification (CCV) Standard. Prepare a humidified CCV standard as a dilution of a certified standard in a canister at a concentration in the lower third of the calibration curve. This certified standard must be prepared from the same standard used for the ICAL standards.

9.2.1 Analyze a CCV for each target oHAP prior to analyzing samples, after every 10 sample injections, and at the end of the analytical sequence. Prepare a humidified CCV standard as a dilution of a certified standard in a canister at a concentration in the lower third of the calibration curve. This certified standard must be prepared from the cylinder used for the ICAL standards.

9.2.2 The internal standard (IS) area responses for each CCV standard must meet the criteria outlined in Section 10.8.1.5 of this method, and the quantitated concentrations of the target compounds for each CCV standard must be within ± 30% of the theoretical concentrations as determined using Equation 3 in Section 12 of this method.

9.2.3 If the CCV is not within specifications, you must invalidate any results after the last successful CCV. You must investigate and address CCV failures and initiate corrective actions, including, for example, reanalyzing the CCV, preparing and analyzing a new CCV or standard canister, and performing a new ICAL

9.3 Blank Analyses. Analysis of all blanks must demonstrate each target compound is < 20 pptv 14.7 psia or undetected (whichever is more stringent) per compound of interest. Unless otherwise stated, the volume used for analysis of blanks must match the volume of sample to be analyzed.

9.3.1 Instrument Blanks (IB). Analyze an IB at the beginning of the sequence and prior to analysis of the ICAL standard and daily CCV standard.

9.3.2 Method Blanks (MB). Analyze a laboratory MB prior to and following the ICAL in an ICAL sequence and prior to analyzing the CCV standard. The MB consists of a canister filled with humidified (40 to 50% RH) clean diluent gas and is analyzed via the same instrument method as the standards and field samples in the analytical sequence. Your MB must be the same diluent used for sample dilution.

9.3.3 Canister Field Blank. Analyze the canister field blank as part of the same analytical sequence as the accompanying field samples.

9.3.4 Calibration Blank (CB). Analyze the CB when the ICAL is established and when preparing any new CCV standard using the same instrument method that was used for standards and field samples when establishing the ICAL. The CB consists of a canister filled with the humidified (40 to 50% RH) clean diluent gas sourced through the dilution system employed to prepare standards. For laboratories that do not employ a dynamic or automated static dilution system, the CB consists of a humidified (40 to 50% RH) canister of the gas used to dilute the calibration standard.

9.4 Duplicate samples must be analyzed and reported as part of this method. They are used to evaluate sampling and/or analytical precision.

9.4.1 Field Duplicate. The level of agreement between duplicate field samples is a measure of the precision achievable for the entire sampling and analysis. Analyze the field duplicate during the same analytical sequence as the accompanying field sample. The RPD of the precision measurements should agree within ± 30% when both measurements are ≥ 5 times the MDL. Flag associated results to indicate if the RPD indicates poor method precision.

9.4.2 Replicate Analysis. The level of agreement between replicate samples is a measure of precision achievable for the analysis. Analyze at least one replicate analysis for each set of field-collected samples. The RPD of the precision measurements should agree within ± 25% when both measurements are ≥ 5 times the MDL. Flag associated results to indicate if the RPD indicates poor method precision.

Table 9-1. Quality Control Parameters and Performance Specifications

Parameter	Description and Details	Required Frequency	Acceptance Criteria	Corrective Action
Analytical zero-air verification	Test of instrumentation to demonstrate cleanliness (positive bias) by analyzing humidified zero air; performed by connecting the clean humidified gas sample to the pre concentrator to verify that the analytical instrument and all connections are sufficiently clean.	At installation prior to initial use of the instrument.	Analysis must show that any detected target compounds in the zero-air challenge sample are at response levels that are expected to be < 20 pptv or not detected.	Take steps to remove contamination attributable to the analytical instrumentation by following the manufacturer's instructions (e.g., analyzing replicates of humidified clean gas).

Parameter	Description and Details	Required Frequency	Acceptance Criteria	Corrective Action
Analytical known-standard challenge for analytical instrumentation	Test to demonstrate that the analytical instrumentation (preconcentrator and GC-MS system) is not causing loss of compounds (negative bias).	At installation prior to initial use of the instrument and with instrument's annual calibration.	Verifies that all target compounds are detected by the system, that they respond consistently upon repeated injection, and that they exhibit sufficient response to be quantifiable at low concentrations (see Section 8.2.2 of this method).	Check for cold spots in transfer line, gas impurities, sorbent traps, GC column, system leaks, and/or poor moisture management. Consult instrument manufacturer for steps to eliminate bias, as necessary.
Zero-air challenge of autosamplers associated with analytical instrument systems	After establishing the ICAL, each port of the autosampler is tested to demonstrate cleanliness (positive bias) by analyzing humidified zero air; performed by connecting the clean humidified gas sample to the port to verify that transfer lines and all connections are sufficiently clean.	Prior to initial use, upon replacement of transfer lines, or after analysis of potentially contaminating samples.	Each target VOC's concentration must be < 20 pptv or preferably not detected (see Section 8.2.3 of this method).	(1) Heat and purge any lines, and/or (2) Rinse with deionized water, dry, and purge any lines that fail.

Parameter	Description and Details	Required Frequency	Acceptance Criteria	Corrective Action
Known-standard challenge of autosamplers associated with analytical instrument systems	After establishing the ICAL, each port of the autosampler is tested with a reference standard (approximately 100 to 500 pptv) to demonstrate that the autosampler is not causing bias (typically loss of compounds or negative bias).	Prior to initial use and upon replacement of transfer lines.	Each target VOC's concentration within ± 15% of theoretical concentration (see Section 8.2.3 of this method).	(1) Heat and purge any lines, and/or (2) Rinse with deionized water, dry, and purge any lines that fail.
Canister leak check	Verification that canisters are leak-free by performing a pressure decay test of a canister pressurized to approximately 203 kPa absolute (29.4 psia) over the course of several days.	Prior to initial use and annually thereafter.	A pressure change ≥ 0.69 kPa/day (see Section 8.3.2 of this method).	(1) Remove from service, and (2) Repair canister connections and/or valve.
Canister zero-air verification	Test of canisters to determine that they are and remain acceptably clean (show acceptably low positive bias) over the course of 7 days, by filling with humidified zero air (not nitrogen).	Initially upon receipt in the laboratory and every 6 months thereafter.	Upon initial analysis after a minimum of 24 hours and after 7 days, each target VOC's concentration ≤ 20 pptv at 101.3 kPa absolute (14.7 psia).	(1) Clean and retest canisters that fail the zero-air verification. (2) Remove canisters from service that cannot pass the zero-air verification after the cleaning process.

Parameter	Description and Details	Required Frequency	Acceptance Criteria	Corrective Action
Known-standard challenge of canisters for qualification	Test of canisters to determine bias by filling with a known reference standard (approximately 100 to 500 pptv) prepared in humidified zero air (not nitrogen) and analyzing.	Initially upon receipt in the laboratory and every 3 years thereafter.	Upon initial analysis after a minimum of 24 hours and subsequent analysis at 30 days or typical laboratory holding time, each target VOC's concentration must remain within ± 30% of theoretical concentration (see Section 8.3.4 of this method).	(1) Clean and retest canisters that fail the known-standard verification. (2) Remove canisters from service that cannot pass known-standard verification after the cleaning process.
Zero-air challenge of sampling devices	Assessment of positive bias of sampling system by collecting humidified zero air through the sampling device/system and comparing it to the reference sample collected upstream of the sampling device/system.	Prior to initial field deployment and every six months thereafter, following maintenance (component replacement), or after collection of potentially contaminating samples.	Analysis must show that the target compounds in the zero-air challenge sample collected through the sampling unit are not > 20 pptv higher than the concentration in the reference sample (see Section 8.1.5 of this method).	(1) Take steps to remove the contamination attributable to the sampling unit (e.g., purging with HCF zero air overnight or longer). (2) Disassemble and clean. See Section 8.6 of this method.

Parameter	Description and Details	Required Frequency	Acceptance Criteria	Corrective Action
Known-standard challenge of sampling devices/systems	Assessment of bias of sampling system by collecting a known reference standard (approximately 100 to 500 pptv) through the sampling device/system and comparing it to the reference standard collected upstream of the sampling device/system.	Prior to initial field deployment and at least every six months thereafter, following maintenance (component replacement), or after collection of potentially contaminating samples or damaging sample matrices that may impact the activity of the flow path surfaces.	Each target VOC's concentration within ± 15% of concentrations in the reference sample.	(1) Take steps to remove the contamination attributable to the sampling unit (e.g., purging with HCF zero air overnight or longer). (2) Disassemble and clean. See Section 8.6 of this method.
Purge gas check	Analysis of canister cleaning purge gas to ensure contaminants are acceptably low.	Verified upon initial setup and in the event of changes in gas sourcing or after the replacement of scrubbers such as hydrocarbon traps and moisture traps, or following maintenance of zero-air generator.	Each target VOC's concentration < 20 pptv (see Section 8.4.1 of this method).	Replace hydrocarbon trap, catalytic oxidizer, contaminated tubing, etc.
Canister cleaning blank check	Analysis of a sample of humidified diluent gas in a canister after cleaning to ensure acceptably low levels of VOCs in the cleaned canisters.	Every canister from each batch of cleaned canisters.	Upon analysis 24 hours after filling, each target VOC's concentration must meet the canister blank acceptance criterion in Table 2 in Section 17 of this method (i.e., ≤ 20 pptv at 101.3 kPa absolute, 14.7 psia) (see Section 8.5 of this method).	(1) Reclean canister, and/or (2) Disassemble and clean the components according to Section 8.6 of this method.

Parameter	Description and Details	Required Frequency	Acceptance Criteria	Corrective Action
Holding time	Duration from end of sample collection or canister preparation to analysis.	Each field-collected or laboratory QC (standard or blank) canister.	≤ 7 days	(1) Reprepare any lab standard or blank. (2) Flag the results of any sample analyzed outside of holding time.
Bromofluorobenzene instrument tune performance check	Injection of 1 to 2 nanograms (ng) BFB for tune verification of quadrupole or ion trap MS detector.	Prior to ICAL and prior to each day's analysis.	Abundance criteria for BFB listed in Table 5 in Section 17 of this method (see Section 10.7.2 of this method)	(1) Retune, and/or (2) Perform maintenance.
Retention time (RT)	RT of each IS and target compound.	All qualitatively identified compounds and internal standards.	IS compounds and target oHAP within ± 2 seconds of most recent calibration check.	Flag data for possible invalidation.
Samples – internal standards (IS)	Deuterated or other compounds not typically found in ambient air co-analyzed with samples to monitor instrument response and assess matrix effects.	All laboratory QC samples, and field-collected samples.	Area response for each IS compound must be within ± 30% of the average response as determined from the most recent calibration check.	Flag data for possible invalidation.

Parameter	Description and Details	Required Frequency	Acceptance Criteria	Corrective Action
Initial calibration (ICAL)	Analysis of a minimum of five calibration levels covering approximately 20 to 5000 pptv.	Before sample analysis, following failed BFB tune check (as applicable), failed IS criteria, or failed CCV criteria; annually, or when changes/maintenance to the instrument affect calibration response.	Average Relative Response Factor (RRF) ≤ 30% RSD and each calibration level within ±30% of theoretical concentration; Relative Retention Times (RRTs) for target peaks within 0.06 units from mean RRT.	(1) Repeat calibration standard analysis. (2) Repeat linearity check. (3) Prepare new calibration standards as necessary and repeat analysis.
Second source calibration verification (SSCV)	Analysis of a secondary source standard in the lower third of the calibration curve to verify ICAL accuracy for each target analyte.	Immediately after each ICAL.	Measured concentrations of VOCs must be within ±30% of theoretical concentration (see Section 9.1 of this method).	(1) Repeat SSCV analysis. (2) Reprepare and reanalyze SSCV standard.
Continuing calibration verification (CCV)	Analysis of a known standard in the lower third of the calibration curve to verify ongoing instrument calibration for each target analyte.	Prior to analyzing samples in an analytical sequence and at the end of a sequence, unless the sequence begins with an ICAL; recommended after every 10 sample injections.	Measured concentrations of VOCs within ± 30% of theoretical concentration (see Section 9.2 of this method).	(1) Repeat CCV analysis. (2) Repeat ICAL.

Parameter	Description and Details	Required Frequency	Acceptance Criteria	Corrective Action
Instrument blank (IB)	Analysis of an injection where no sample or standard is introduced to the preconcentrator to preliminarily demonstrate the carrier gas and instrument are sufficiently clean to begin analysis.	Prior to ICAL and at the beginning of an analytical sequence.	Each target VOC's concentration must be < 20 pptv (see Section 9.3.1 of this method).	(1) Repeat IB analysis. (2) Bakeout preconcentrator system and repeat IB analysis. (3) Replace contaminated tubing/traps as needed.
Method blank (MB)	Canister filled with clean, humidified diluent gas; indicates that target VOCs and potential interferences are at acceptably low levels in the system as a whole; the MB is to help assess overall quality of the data.	Prior to and following the ICAL and daily following the IB/BFB and prior to the initial daily CCV/SSCV.	This must demonstrate acceptably low carryover in the analytical system prior to analysis of samples; each target VOC's concentration must be < 20 pptv (see Section 9.3.2 of this method).	(1) Repeat analysis. (2) Reprepare the MB canister and reanalyze. (3) Check the system for leaks.
Calibration blank (CB)	Canister filled with clean, humidified diluent gas sourced through the standard preparation dilution system; indicates that diluent gas and dilution apparatus do not contribute target VOCs, imparting a positive bias to the ICAL	Prepare one CB with each set of calibration standard canisters and analyze with each ICAL	CB must be sufficiently clean such that little or no positive bias is imparted to the calibration (see Section 9.3.3 of this method).	(1) Reanalyze CB. (2) Reprepare CB and ICAL canister standards.

Parameter	Description and Details	Required Frequency	Acceptance Criteria	Corrective Action
Method precision	Duplicate samples: precision is determined from the analyzed concentrations of collocated samples.	Applicable to the collection of samples: one per sampling day.	Precision ≤ 30% RPD of target VOCs in the compared samples when both measurements are ≥ fivefold MDL (see Section 9.4 of this method).	(1) Check for preconcentrator volume measurement error. (2) Reanalyze primary sample and collocated duplicate. (3) Flag data for possible invalidation.
Instrument precision	Precision is determined from repeated analyses of a sample from a single canister; replicate analyses are used to determine precision of the analysis processes and do not provide information on sampling precision.	One replicate analysis to be performed with each sampling day.	Precision ≤ 25% RPD for target VOCs when both measurements are ≥ fivefold MDL (see Section 9.4 of this method).	(1) Check for preconcentrator volume measurement error. (2) Reanalyze primary sample and collocated duplicate. (3) Flag data for possible invalidation.
Preconcentrator leak check	Pressurize or evacuate the canister connection to verify as leak-free.	Each canister connected to the instrument prior to analysis.	< 3.4 kPa (0.5 psi) change per minute or as recommended by the manufacturer (see Section 11.4.2 of this method).	Check the tightness of all fittings and recheck.

10.0 Calibration and Standardization

10.1 Humidification of Canisters.

10.1.1 Calculate the volume of water you must add to standard and blank canisters to achieve 40 to 50% RH at ambient laboratory temperature. (See Equation 6 in Section 12 of this method).

10.1.2 Use a bubbler or impinger within the dilution gas stream, add water to the canister, or use a combination of these two methods to add the calculated volume of deionized water to the canister necessary to achieve internal RH of approximately 40 to 50% at ambient laboratory temperature. For direct injection of water into a canister with a syringe, install a high-pressure PTFE-sealed septum on the canister. For canisters that are to be connected to a gas source for pressurization via a dynamic or static dilution system, you can add the deionized water to the valve opening of the evacuated canister prior to connecting to the dilution system. Do not add water to the canister using a syringe via rubber septum or other materials that may introduce target or interfering compounds.

10.2 Dynamic Dilution.

10.2.1 Gas Dilution System. The gas dilution system must produce calibration gases whose measured concentration values are within ± 2% of the predicted values. The predicted values are calculated based on the certified concentration of the supply gas (Protocol gases, when available, are recommended for their accuracy) and the gas flow rates (or dilution ratios) through the gas dilution system.

10.2.2 The gas dilution system must be calibrated and verified per Section 6.10.1 of this method.

10.2.3 Standards Preparation by Dynamic Dilution.

10.2.3.1 Prior to use, power on the dynamic dilution system and allow the diluent and stock gases to flow through the respective MFC at operating flow rates. Allow gases to flow for at least the minimum time used during the yearly bias check in Section 6.10.1.3 of this method, to ensure the concentrations of the oHAPs in the blended gas are stable prior to transferring to the humidified canister (or directly to the preconcentrator).

10.2.3.2 You must prepare humidified (40 to 50% RH) standards in canisters from low concentration to high concentration. When changing stock gas flow rate(s) to prepare a different concentration, allow the calibration gas sufficient time to flow through the system prior to preparation of the working calibration canister (or delivering the working standard directly to the preconcentrator).

10.2.3.3 The final pressure of the calibration standard canister must not exceed the maximum pressure permitted by the preconcentrator.

10.2.2.4 Calculate the final concentration of the diluted standard using Equation 7 in Section 12 of this method.

10.3 Static Dilution.

10.3.1 Static Gas Dilution System. The gas dilution system shall produce calibration gases whose measured values are within ± 2% of the predicted values. The predicted values are calculated based on the certified concentration of the supply gases (Protocol gases, when available, are

recommended for their accuracy) and their partial pressure measurements (or dilution ratios) in the prepared standard canister.

10.3.2 Static Dilution by Addition of Partial Pressures into a Canister.

10.3.2.1 Connect a pressure transducer or gauge to an evacuated canister to monitor the canister pressure as you add gases. The pressure transducer or gauge must meet the requirements in Section 6.5 of this method.

10.3.2.2 Add stock and diluent gases separately through a manifold or by direct connection of the gas to the standard canister or vessel.

10.3.2.3 Measure the canister pressure before and after standard and diluent gases are bled into the canister, and input these pressures into the calculation of the dilution factor and final concentrations.

10.3.2.4 Calculate the final concentration of each target compound in the diluted standard using Equation 8 in Section 12 of this method.

10.4 Storage of Standards. Standards prepared in canisters at ambient laboratory conditions must be stored in locations that are free of potential contaminants for up to 7 days.

10.5 Pre-Concentration System Operation. Condition preconcentrator traps when first installed to eliminate contaminants that act as interferences or chromatographic artifacts, per manufacturer recommendation. After the recommended conditioning procedure is completed, analyze the IBs and MBs to verify the preconcentrator system meets the method criteria.

Note: For preconcentrator traps that contain multiple types of sorbent beds, the oven temperature must not exceed the lowest conditioning temperature of the sorbents contained in the trap.

10.6 GC-MS System. Optimize GC conditions for compound separation and sensitivity as indicated by baseline separation for the targeted compounds by establishing GC carrier gas flow rates, oven temperature program, and instrument run time based on the manufacturer's recommendations and customize, as needed, to separate the desired target oHAPs.

10.7 MS Tuning/Optimizing and Verification.

10.7.1 General. Tune/optimize the MS (quadrupole, ion trap, or TOF MS) to demonstrate acceptable performance across the selected ion mass range according to the manufacturer's specifications upon initial installation of the instrument and following significant preventive maintenance or repair activities that impact the performance of the GC-MS system (e.g., cleaning the ion source or analyzer; trimming or replacing the capillary column; and adjusting MS tune or optimization parameters).

10.7.2 BFB Tuning Check. Before the ICAL and at least once during every 24-hour period of analyzing samples, blanks, or calibration standards thereafter, you must conduct a BFB tuning check for linear quadrupole or ion trap MS instruments. The BFB tuning check may be combined with the IB.

10.7.2.1 Introduce 1 to 2 ng of BFB into the preconcentrator and analyze the standard using the preconcentrator parameters established and used for the analysis of calibration standards, QC samples, and field samples. You must also use the method integration and analysis parameters employed for routine analysis of standards, QC samples, and field samples.

10.7.2.2 The BFB tuning check must show that the GC-MS system meets the mass spectral ion abundance criteria listed in Table 2 in Section 17 of this method for the target compounds before you can use the system for any analysis. If the GC-MS system cannot meet the BFB tuning criteria, adjust the tuning of the MS or take corrective actions. You must not use this system until the abundance criteria has been met.

10.8 Internal Standards and Calibration.

Method users must meet acceptance criteria for the calibration and QC listed in the following section for the suite of target compounds.

10.8.1 Selection and Use of Internal Standards (IS).

10.8.1.1 Select IS compound(s) to be used for oHAP analysis. At a minimum, you must use a single IS compound. IS compounds must have similar retention times to the compounds being detected. Typical IS compounds include bromochloromethane; 1,4-difluorobenzene; chlorobenzene-d_5; 1,2-dichloroethane-d_4; hexane-d_{14}; toluene-d_8; and 1,2-dichlorobenzene-d_4.

10.8.1.2 If using purchased IS stock gases, evaluate the IS upon receipt for the presence of contaminants that may interfere with the quantitation of target compounds by analyzing increasing volumes of the IS (e.g., 25, 50, 100, 250 milliliters [mL]) and examining the results for compound contaminants whose responses increase proportionally with the increasing volume of IS analyzed. Do not use IS gas standards that fail the MB acceptance criteria.

10.8.1.3 You must add the IS through a dedicated non-sample port in the preconcentrator at the same concentration for each injection (e.g., standard, sample, blank) to monitor instrument sensitivity and assess potential matrix effects. Choose the concentration of IS added to each injection such that the peak area response for the IS compound approximates the area responses for target compounds in the lower half of the calibration curve range, but that minimally provides a peak that is on scale and does not exceed the area response of the highest calibration standard.

10.8.1.4 Internal Standard Retention Time (RT). Each IS compound in each sample injection must be within ±2 seconds of the RT for each IS compound in the most recent calibration.

10.8.1.5 Internal Standard Response. The area response for each IS compound in each injection (e.g., calibration standard, field sample, blank, CCV) must be within ± 30% of the mean area

response of the IS compound determined from the ICAL determined using Equation 10 in Section 12 of this method or most recent calibration check, whichever is most appropriate.

10.8.1.6 Choose the quantitation ion for each IS compound as the most abundant ion (base peak) unless there is a spectral interference from a coeluting or nearby compound or interference that impacts the quantitation of the base peak. In such cases, select another abundant ion that is distinguishable from the other compounds for quantitation.

10.8.1.7 You must invalidate then reanalyze any samples for which the IS area response differs by more than 30% from the mean IS area response.

10.8.2 Establishing Calibration. Calibrate the GC-MS initially, annually, whenever CCV standards exceed acceptance criteria, or when the system is out of control as indicated by IS responses. Prior to calibration, analyze a sufficient number of humidified (40 to 50% RH) HCF zero air blanks or humidified check standards to verify that instrument sensitivity is stable, as indicated by IS response.

10.8.2.1 Preparation for Calibration.

10.8.2.1.1 Prepare the calibration curve by preparing standards that bracket the expected concentration levels at the sampling location(s).

10.8.2.1.2 You must include at least five levels in the ICAL to approximate concentrations of target oHAPs expected at the deployment location(s), including one level within a factor of five of the detection limits of the compounds of interest, and another level within 10% of the compound specific action-level, as defined in the applicable standard.

Note: To establish the calibration curve, the theoretical concentrations of the working calibration standards must be calculated using the certified concentration from the gas vendor or neat standard provider. Certificates of analysis for stock standard gas mixtures typically include both a nominal (or "requested") concentration (e.g., 100 ppbv) for each analyte and a certified concentration (e.g., 108 ppbv), which should be within a specified tolerance (e.g., ± 10%). These tolerances may permit the certified concentration to differ from the nominal concentration by 10% to 20%, resulting in final theoretical concentration errors for the working-level standards when the nominal concentration is input into standard concentration calculations instead of the certified concentration. Calibration standards prepared with neat materials must account for the standard purity when calculating the working standard concentrations.

10.8.2.2 Calibration Curve.

10.8.2.2.1 Following analysis of all calibration standards, prepare a calibration curve for each target analyte by determining the relative response factor (RRF) of each concentration level. Following data acquisition for the calibration standards, calculate the RRF of each target compound in each calibration level using Equation 11 in Section 12 of this method.

10.8.2.2.2 Choose the quantitation ion for each target compound as the most abundant ion (base peak) unless there is a spectral interference from a coeluting or nearby compound or interference that impacts the quantitation of the base peak. In such cases, select another abundant ion that is distinguishable from the other compounds for quantitation.

10.8.2.2.3 The %RSD of the RRF for each target compound must be ≤ 30%.

10.8.2.2.4 The calculated concentration for each target compound(s) at each calibration level must be within ± 30% of the theoretical concentration when quantitated against the resulting calibration curve.

11.0 Analytical Procedures

11.1 Measurement of Canister Receipt Pressure.

11.1.1 Upon receipt at the laboratory, review the sample collection information documented on the field data page and/or COC form(s) for completeness and accuracy. Compare the canister label with the sample collection data sheet and verify that the canister and sample IDs are correct.

11.1.2 Measure and record the canister pressure using a calibrated vacuum/pressure gauge or transducer. The measured canister absolute pressure must be within ±3.5 kPa (1 in. Hg or 0.5 psi) of that measured upon collection in the field. Pressure differences exceeding this criterion indicate the canister has leaked and you must flag the results as invalid.

11.2 Dilution of Canister Samples. A canister must be pressurized to provide sufficient pressure for removing an aliquot from the canister for analysis. Pressurize the canister with diluent gas to a pressure less than or equal to the final pressure of the standard gas canisters.

Note: Minimum sample pressures will depend on the size of the canister and the capability of the preconcentrator to remove the desired aliquot of the sample and will be indicated by the instrument manufacturer.

11.2.2 Measure the canister pressure using a calibrated vacuum/pressure gauge or pressure transducer just prior to dilution and immediately following dilution and calculate the canister dilution correction factor (CDCF) from the two absolute pressure readings (see Equation 12 in Section 12 of this method).

11.2.3 You must allow diluted canisters to equilibrate for a minimum of 12 hours before analysis.

11.3 Sample Preconcentration. Draw a measured aliquot of the whole air sample (typically 100 to 1000 mL) from the sample canister by vacuum through a preconcentrator to minimize the moisture and bulk atmospheric gases (e.g., oxygen, nitrogen, argon, and carbon dioxide) from the sample aliquot prior to introduction of the target compounds to the GC.

Note: Preconcentrator instrument manufacturers will typically indicate the optimum factory default settings for the sample aliquot volume, trapping time, trapping temperature, gas flows, and additional preconcentration parameters. Adjust each of these variables as needed for the target compounds.

11.4 Sample Analysis. You must analyze samples using the same acquisition methods you used for establishing calibration (i.e., preconcentrator operation parameters, GC oven program, MS parameters, and integration methods). Field-collected samples and QC samples must be at ambient laboratory temperature for analysis. You must use approximately the same sample aliquot volume for all samples unless dilution is required. Adjustment of this sample aliquot volume requires adjustment of a dilution factor to account for the difference in relative analyzed volume, as discussed in Section 11.4.4 of this method.

11.4.1 Leak Check of Preconcentrator Connections.

11.4.1.1 Prior to beginning an analytical sequence, including an ICAL sequence, verify each canister connection as leak-free through the preconcentrator.

11.4.1.2 During the leak check, connect canisters to the autosampler or sample introduction lines and maintain the canister valves in the closed position.

11.4.1.3 Evacuate each port of the autosampler or sample introduction line and monitor for a change in pressure for 1 minute. The pressure must not change by more than 0.5 psig/minute.

11.4.1.4 If a sample line fails the leak check, implement corrective actions (e.g., rechecking the tightness of all fittings) and then retest. Do not perform analysis using any canister connection that does not pass the leak check.

11.4.1.5 Following the successful leak check, evacuate all autosampler ports or sample introduction lines, open the canister valves, and document the leak check results in the analysis records.

11.4.2 Sample Introduction.

11.4.2.1 Prior to each sample analysis sequence, you must connect each sample canister to the preconcentration unit through a port and verify each canister as having a leak-free connection.

11.4.2.2 Accurately measure the sample aliquot volume for analysis by metering the sample with an MFC or with the combination of a fixed-volume vessel and a pressure transducer. Sample introduction volume measurements must be made by the same device as the calibration standards to ensure that analyzed volumes of samples and standards are consistent.

11.4.3 Analysis of Field Samples. Perform the following steps for readying the system and performing the GC-MS analytical sequence. Once these checks meet criteria (summarized in Table 9-1 of this method), verify the instrument calibration by analysis of a CCV and begin sample analysis.

11.4.3.1 Perform an air/water check of the MS prior to any analyses to ensure that the system is acceptably leak-free.

11.4.3.2 Conduct a thorough system bakeout per the manufacturer's instructions for the preconcentrator and ramp the GC column temperature.

11.4.3.3 Analyze a preliminary IB or perform the BFB instrument tuning check.

11.4.3.4 Analyze a laboratory MB to demonstrate that the system is acceptably clean and that each target compound is < 20 pptv or undetected (whichever is more stringent) per compound of interest.

11.4.3.5 Analyze a CCV to verify the instrument calibration.

11.4.3.6 Analyze field samples and additional CCV standards (every 10 samples) and MBs to complete the sequence, ending with a CCV, as discussed in Section 9.2 of this method.

11.4.4 Sample Dilution. If the on-column concentration of any compound in any sample exceeds the calibration range, you must dilute the sample for reanalysis by either reducing the sample aliquot volume for an effective dilution or adding diluent gas to the sample canister to physically dilute the sample.

11.5 Compound Identification.

11.5.1 After completing data acquisition, examine each chromatogram. Chromatographic peaks for the target compounds must be appropriately resolved, and integration must not include peak shoulders or inflections indicative of a coelution. If a peak has not been integrated properly, you may choose to manually integrate the peak. If a peak has been manually integrated, you must flag the results and report how and why the peak was manually integrated,

Note: Deconvolution techniques may be available to the operator to help resolve compound coelutions, depending on the particular instrument and chromatography software package that is in use.

11.5.2 Identify target compounds qualitatively based on their RT and the relative abundance of their characteristic ions from the MS by satisfying the following four criteria. If any of the four criteria are not met, the compound cannot be positively identified.

11.5.2.1 The RT of the compound must be within the RT window of ± 2 seconds of the most recent calibration check.

11.5.2.2 The relative abundance ratio of qualifier ion response to target ion response for at least one qualifier ion must be within ± 30% of the average relative abundance ratio from the ICAL.

11.5.2.3 The S:N ratio of the target and qualifier ions must be > 3:1.

11.5.2.4 The target and qualifier ion peaks must be co-maximized (i.e., peak apexes within one scan of each other).

11.6 Compound Quantitation. After determining the peak areas, initiate the quantitation process using the software package of choice to provide quantitative results compound by relating the area response ratio of each target ion for each target compound to the RRF daily CCV.

11.6.2 Dilution Correction Factors.

11.6.2.1 Calculate an instrument dilution correction factor (IDCF) if you analyzed an aliquot from the sample canister that is different from the typical analysis volume (as described in Section 11.4.4 of this method for performing effective dilution) using Equation 14 in Section 12 of this method.

11.6.2.2 Use Equation 15 in Section 12 of this method to determine the final concentration of each target compound in air by multiplying the instrument-detected concentration by the CDCF (see Section 11.2 of this method) and the IDCF.

Note: The MDL reported with the final concentration data will be corrected by multiplying the MDL by the CDCF and IDCF applied to the sample concentrations.

12.0 Data Analysis and Calculations

12.1 Nomenclature. Report results in International System of Units (SI units) unless the regulatory authority for testing specifies English units. The calculations in this method use the following nomenclature.

AIS = peak area for quantitation ion of the assigned IS compound.

As = peak area for quantitation ion of the target compound.

C_{acc} = acceptance limit concentration at measured canister pressure (pptv).

C_{atm} = 20 pptv, acceptance limit concentration at standard atmospheric pressure.

CCCV = measured concentration of the CCV for each target compound (pptv).

C_D = instrument-detected analyte concentration (pptv).

CDCF = canister dilution correction factor.

C_f = final diluted standard concentration (pptv).

C_F = concentration of the target compound in air (pptv).

CIS = concentration of the assigned IS compound (pptv).

Cs = certified concentration of stock standard (pptv).

Cs = concentration of the target compound (pptv).

$C_{theoretical}$ = theoretical concentration of the CCV for each target compound(pptv).

D = sampling duration (min).

dls = density of the neat standard (grams [g]/mL) at temperature of preparation.

Dsat = saturation vapor density of water (milligrams/microliter [mg/µL]) at ambient laboratory temperature (refer to Table 3 in Section 17 of this method).

Dw = density of water (1 mg/µL).

F = flow rate (mL/min) at local conditions.

Fd = flow of diluent gas (mL/min).

Fs = flow of stock standard (mL/min).

IDCF = instrument dilution correction factor.

m = mass of the gas added (g).

m_{std} = mass of standard material (g).

MW = molecular weight of the gas (g/mol).

n = number of concentration values used to generate the calibration (minimum of 5).

p = purity of neat material as listed on the certificate of analysis (as a decimal).

P_a = atmospheric pressure (kPa absolute) at time of sampling.

P_c = final absolute canister pressure (kPa absolute).

P_i = absolute pressure of a canister sample, cleaning batch blank, etc. prior to dilution kPa absolute.

Pd = pressure of the canister following dilution (kPa).

Pda = final absolute pressure of manifold and canister after adding diluent (kPa).

Pdb = absolute pressure of manifold and canister before adding diluent (kPa).

Pf = final absolute pressure of canister after adding standard and diluent gases (kPa).

Pi = pressure of the canister immediately preceding dilution (kPa).

Ps = standard ambient pressure (101.3 kPa absolute).

Psa = absolute pressure of canister after adding standard gas (kPa).

Psb = absolute pressure of canister before adding standard gas (kPa).

P_{std} = 101.3 kPa absolute, standard atmospheric pressure.

R = gas constant, 8.314 L-kPa/mol·K.

RHd = desired RH level expressed as a decimal.

RPD = relative percent difference.

RRF = relative response factor.

RRF_i= relative response factor for the compound.

$\%RSD$ = percent relative deviation

$\overline{\text{RRF}}$ = average RRF for the compound.

$\overline{\text{RT}}$ = average RT for the IS compound (min).

RT_i = RT for the IS compound for each calibration level (min).

SD_{RRF}= standard deviation of the relative response factors.

T = standard temperature, 293.15 K.

V = volume of the canister (mL) at standard conditions (101.3 kPa absolute and 20 °C).

Vc = nominal internal volume of canister (L).

V_{calc} = approximately calculated volume of gas contained in the canister (L).

V_{can} = nominal canister volume (L).

Vls = liquid volume of neat standard material at temperature of preparation (mL).

V_t = total volume of standard and diluent gases at 20 °C and 101.3 kPa absolute (L).

Vw = water volume to add to canister (µL).

X_1 = target compound concentration measured in first measurement of the precision pair (pptv).

X_2 = target compound concentration measured in second measurement of the precision pair (pptv).

$\overline{Y}$ = average area response for the given IS compound.

Yi = area response for the IS for each calibration level.

$\%D_{CCV}$ = percent difference of the measured concentration of each target compound in the CCV standard from the theoretical concentration.

$\%Recovery_{CCV}$ = percent recovery of measured versus actual concentration.

12.2 Canister Final Air/Nitrogen Volume (V_{calc}).

$$V_{calc} = \left(\left(\frac{P_i - P_{std}}{P_{std}}\right) * V_{can}\right) + V_{can} \quad \text{Eq. 1}$$

12.3 Acceptable Concentration Criterion (C_{acc}).

$$C_{acc} = C_{atm} * \left(\frac{P_{std}}{P_i}\right) \quad \text{Eq. 2}$$

12.4 Percent Difference of the Measured Concentration of Each Target Compound in the CCV Standard (%DCCV) from the Theoretical Concentration.

$$\%D_{CCV} = \frac{C_{CCV} - C_{theoretical}}{C_{theoretical}} \times 100 \quad \text{Eq. 3}$$

12.5 Percent Recovery ($\%Recovery_{CCV}$).

$$\%Recovery_{CCV} = \frac{C_{CCV}}{C_{theoretical}} \times 100 \quad \text{Eq. 4}$$

12.6 Relative Percent Difference (RPD).

$$RPD = \left|\frac{X_1 - X_2}{\left(\frac{X_1 + X_2}{2}\right)}\right| \times 100 \quad \text{Eq. 5}$$

12.7 Water Volume to Add to Canister (V_w).

$$V_w = D_{sat} \cdot RH_d \cdot V_c \cdot \frac{P_c}{P_s} \cdot \frac{1}{D_w} \quad \text{Eq. 6}$$

Note: The equation assumes the density of water to be 1 g/mL and that 100% of the added water to the canister is in the gas phase. The equation does not correct the density of water for the ambient temperature.

12.8 Final Concentration of the Diluted Standard (C_f) – Dynamic Dilution.

$$C_f = \frac{C_s \cdot F_s}{F_s + F_d} \quad \text{Eq. 7}$$

Note: If you combine multiple gas standards for dilution, the equation denominator is the sum of all gas flows combined for preparing the dilution.

12.9 Final Concentration of the Diluted Standard (C_f) – Static Dilution.

$$C_f = \frac{C_s \cdot (P_{sa} - P_{sb})}{P_f} \quad \text{Eq. 8}$$

12.10 Average Retention Time ($\overline{RT}$).

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n} \quad \text{Eq. 9}$$

12.11 Average Area Response for the Given IS Compound ($\bar{Y}$).

$$\bar{Y} = \sum_{i=1}^{n} \frac{Y_i}{n} \quad \text{Eq. 10}$$

12.12 Relative Response Factor (RRF).

$$RRF = \frac{A_s \cdot C_{IS}}{A_{IS} \cdot C_s} \quad \text{Eq. 11}$$

12.13 Canister Dilution Correction Factor (CDCF).

$$CDCF = \frac{P_d}{P_i} \quad \text{Eq. 12}$$

12.14 Instrument-Detected Analyte Concentration (C_D).

$$C_D = \frac{A_t \cdot C_{IS}}{A_{IS} \cdot RRF} \quad \text{Eq. 13}$$

12.15 Instrument Dilution Correction Factor (IDCF).

$$IDCF = \frac{V_{nom}}{V_{inj}} \quad \text{Eq. 14}$$

12.16 Concentration of the Target Compound in Air (C_F).

$$C_F = C_D \cdot CDCF \cdot IDCF \quad \text{Eq. 15}$$

12.17 Standard Deviation of the Response Factors (SD_{RF})

$$SD_{RRF} = \sqrt{\frac{\sum_{i=1}^{n}(RRF_i - \overline{RRF})^2}{(n-1)}} \quad \text{Eq. 16}$$

12.18 Percent Relative Deviation

$$\%RSD = SD_{RRF} \div \overline{RRF} \times 100 \quad \text{Eq 17}$$

13.0 Method Performance

Table 9-1 of this method lists the QC parameters and performance specifications for this method. The method performance will be determined by the specific performance of each specific target compound, laboratory, and the associated equipment.

14.0 Pollution Prevention

[Reserved]

15.0 Waste Management

[Reserved]

16.0 References

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17.0 Tables, Diagrams, Flow Charts, etc.

Table 1. Canister Cleaning Parameters

Canister Type	Pre-evacuate Canister	Minimum Air Purge Gas Temperature	Humidity	Minimum No. of Pressure/ Evacuation Cycles	Cycle Time
All	Yes	80 °C	50%	5	Varies by system

[a] Higher purge gas temperatures may be required depending on the canister type - do not exceed the manufacturer's recommended maximum temperatures for component parts such as valves and gauges.

Table 2. BFB Tuning Check Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria[a]
50	8.0% to 40.0% of *m/z* 95
75	30.0% to 66.0% of *m/z* 95
95	Base peak, 100% relative abundance
96	5.0% to 9.0% of *m/z* 95
173	< 2.0% of *m/z* 174
174	50.0% to 120.0% of *m/z* 95
175	4.0% to 9.0% of *m/z* 174
176	93.0% to 101.0% of *m/z* 174
177	5.0% to 9.0% of *m/z* 176

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

Table 3. Water Saturation Vapor Density at Various Temperatures

Temperature (°C)	Water Saturation Vapor Density (mg/L)[a]
15	12.8
16	13.6
17	14.4
18	15.3
19	16.3
20	17.3
21	18.3
22	19.4
23	20.6
24	21.8
25	23.1
26	24.4
27	25.9
28	27.3
29	28.9
30	30.5
31	32.2
32	34.0
33	35.8

[a]Values are generated according to the following formula (Nave, 2017): $vapor\ density\ (mg/L) = 5.018 + 0.32321 * T + 8.1847\times10^{-3} * T^2 + 3.1243\times10^{-4} * T^3$, where: T = temperature in °C.

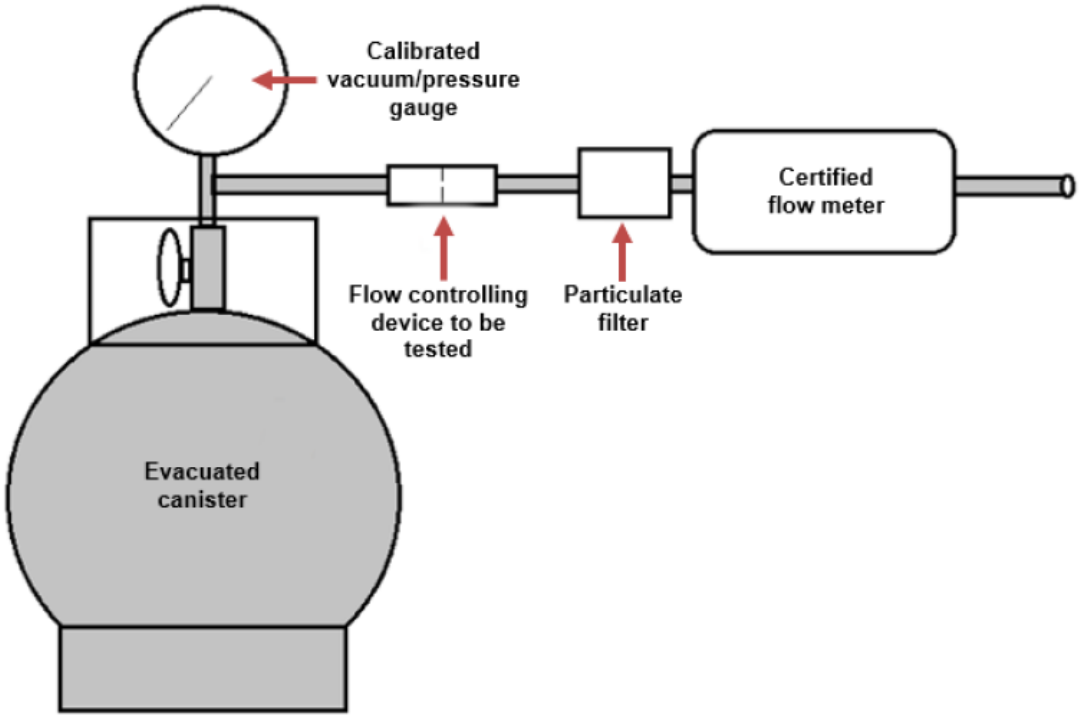

Figure 1. Apparatus for Characterizing the Flow Control Device

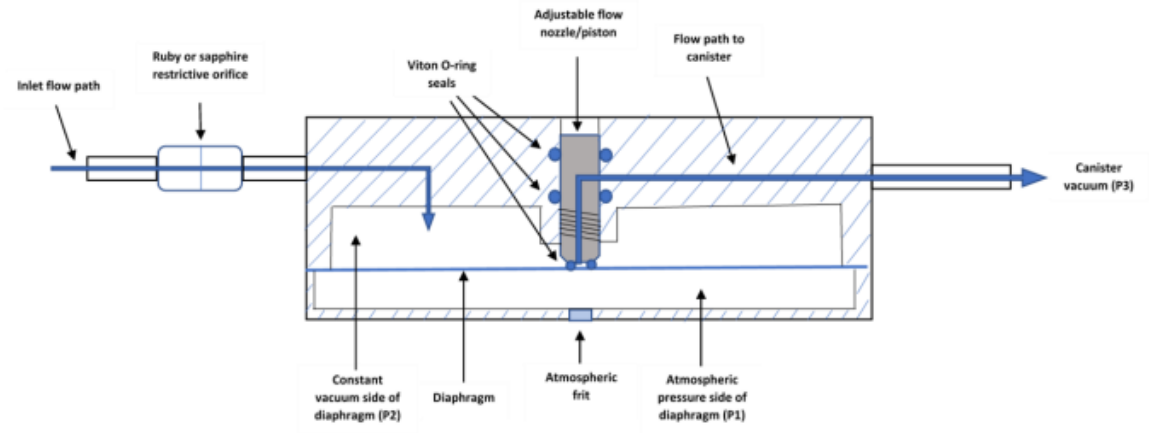

Figure 2. Mechanical Flow Control Device

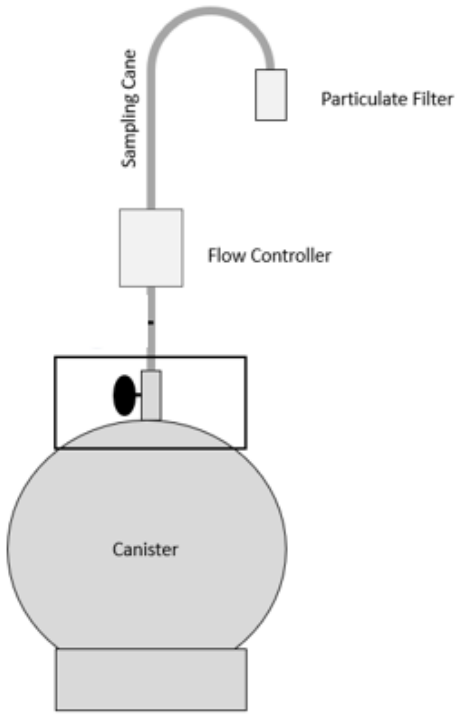

Figure 3. Method 327 Sampler

Method 327 Field Data Page

Sampling Personnel			
Sampling Location ID			
Longitude		Latitude	

Sampling Equipment Information

Sampling Canister ID	
Sampling Canister Received Date	
Sampling Canister Clean Date	
Sampling Canister Pressure Reading	
Sampling Device ID	
Reference Flow Meter S/N (if applicable)	
Reference Flow Meter Calibration Date	
Sampling Device Expected Flow Rate	
Sampling Device Actual Flow Rate (if applicable)	
Sampling Device Flow Adjusted (Yes/No)	

Sampling Information

Sample Date	
Leak Check (Date/Time)	
Leak Check Results (Pass/Fail)	
Start Time	
Start Vacuum/Pressure	
Comments:	
End Time	
End Vacuum/Pressure	
Comments:	

Custody Transfer

Relinquished/Received	Name	Signature	Date
Comments:			

Figure 4. Example Field Data Page