Other Test Method 50 (OTM-50) Sampling and Analysis of Volatile Fluorinated Compounds from Stationary Sources Using Passivated Stainless-Steel Canisters

Background on OTM-50

The posting of a test method on the Other Test Methods (OTM) portion of the Air Emission Measurement Center (EMC) website is neither an endorsement by EPA regarding the validity of the test method nor a regulatory approval of the test method. The purpose of the OTM portion of the EMC website is to promote discussion of developing emission measurement methodologies and to provide regulatory agencies, the regulated community, and the public at large with potentially helpful tools. OTMs are test methods which have not yet been subject to the Federal rulemaking process. Each of these methods, as well as the available technical documentation supporting them, have been reviewed by the EMC staff and have been found to be potentially useful to the emission measurement community. The types of technical information reviewed include field and laboratory validation studies; results of collaborative testing; articles from peer-reviewed journals; peer review comments; and quality assurance (QA) and quality control (QC) procedures in the method itself. The EPA strongly encourages the submission of additional supporting field and laboratory data as well as comments regarding these methods.

These methods may be considered for use in federally enforceable State and local programs [e.g., Title V permits, State Implementation Plans (SIP)] provided they are subject to an EPA Regional SIP approval process or permit veto opportunity and public notice with the opportunity for comment. The methods may also be candidates to be alternative test methods (ALT) to meet Federal requirements under 40 CFR Parts 60, 61, and 63. However, they must be approved by the delegated authority as an ALT under Parts 60.8, 61.13, or 63.7(f) before a source may use them for this purpose. Consideration of a method's applicability for a particular purpose should be based on the stated applicability as well as the supporting technical information. The methods are available for application without EPA oversight for other non-EPA program uses including state permitting programs and scientific and engineering applications. As many of these methods are submitted by parties outside the Agency, the EPA staff may not necessarily be the technical experts on these methods. Therefore, technical support from EPA for these methods is limited, but the table at the end of this introduction contains contact information for the authors and developers so that you may contact them directly. Also, be aware that these methods are subject to change based on the review of additional validation studies or on public comment as a part of promulgation as a federal test method, the Title V permitting process, or inclusion in a SIP.

Development of methods to measure per- and polyfluoroalkyl substances (PFAS) is an ongoing process for EPA. Measurement methods that have been evaluated for identifying and quantifying PFAS or volatile fluorinated compounds (VFCs) releases from stationary air emission sources are limited and under development. The current lack of standardized methods to measure PFAS and VFC emissions and the limited availability of data on the performance of methods to measure VFCs introduce uncertainty in the understanding of the release of PFAS and VFCs into the air from these sources. The lack of validated stationary source measurement methods for VFCs also leads to inconsistent findings, incomparable measurements, and lack of coordination between policy makers, facilities, and control technology development. This OTM provides a consistent method for use by the facilities, stationary source test teams, research laboratories, and other stakeholders to measure a common list of VFCs emitted from

vents and stacks. This OTM includes performance based PFAS measurement tools and performance criteria developed through field application of this method.

The analytical method embedded in OTM-50 may support a variety of monitoring applications, which include the analysis of multiple short-chain VFCs indicative of incomplete decomposition of PFAS from thermal treatment control technologies. Posting this method, in and of itself, does not establish a requirement, although the use of this method may be specified by the EPA, state, or local authorities through independent actions. Terms such as "must" or "required," as used in this document, refer to procedures that are to be followed to conform with the method. References to specific brands and catalog numbers are included only as examples and do not imply endorsement of the products. Such reference does not preclude the use of equivalent products from other vendors or suppliers.

OTM-50 is a draft method under evaluation that will be updated as necessary when more data from stakeholders becomes available. Due to the need for consistency, this method is being released as an OTM by EMC to promote consistency with what we believe is the current best practices to sample and analyze the VFCs targets from stationary sources. We solicit feedback, comments, and additional data coming from the application of this method as we work to adjust this method in anticipation of potentially developing a reference method for VFCs from air emission sources.

Note: Please submit a copy, either electronic or paper, of any test report from application of this OTM to EPA's Measurement Technology Group.

- **Electronic copies should be submitted via email with the subject line "OTM-50" to: EMC@epa.gov**

- **Paper copies should be mailed to:**
  Measurement Technology Group
  Office of Air Quality Planning and Standards
  U.S. Environmental Protection Agency (PO Box 12055, Mail Code E143-02)
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Other Test Method 50 (OTM-50): Sampling and Analysis of Volatile Fluorinated Compounds from Stationary Sources Using Passivated Stainless-Steel Canisters.

1.0 Scope and Application

1.1 Applicability

1.1.1 OTM-50 is a performance-based method applicable to the collection and quantitative analysis of specific volatile fluorinated compounds (VFCs). The target list originates from known industrial products and products of incomplete thermal destruction. This method can be used to collect and analyze gas samples into 6-liter passivated silicon ceramic lined stainless-steel canisters, or equivalent, from stationary sources for the purpose of determining the concentration of target VFCs in Table OTM-50-1. Gaseous emissions samples collected by this method are intended to be sampled from industrial source ducts, vents, stacks, etc. Samples may be collected directly from the non-combustion stacks or vents when the moisture is relatively low (<3% volume/volume (v/v)), when sample gas temperatures are <250 °F, and when acid gases are not present. To collect samples outside these criteria, sample conditioning including moisture, acid gas, and temperature management, as described in this method, is required.

1.1.2 The test method is applicable to VFC concentrations in undiluted samples ranging from the detection limit to approximately 1000 µg/m^3, 300 parts-per-billion by volume (ppbv). Above this concentration, smaller aliquots of sample gas may be analyzed, or samples may be diluted with dry ultra-high-purity nitrogen or air. Performance results apply only to target compounds listed in this method that have been determined to be stable when stored in canisters. Other VFCs may be determined by this method after completion of verification studies that include qualitative identification and subsequent validation as specified in Section 11.5 of this method and demonstrates that acceptance criteria for all categories of quality controls can be met.

1.2 Scope

This method describes the sampling and sample analysis used to measure individual VFCs from stationary source air emissions. OTM-50 incorporates by reference some of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and sample preparation) from other methods that are essential to conduct OTM-50. To obtain reliable samples, source sampling teams should be trained and have experience with the following additional EPA test methods: Method 1; Method 2; Method 3; Method 4. Laboratory analysis teams should be trained and experienced in the use of gas chromatography coupled with mass spectrometry (GC/MS) as described in EPA compendium Method TO-15A and ASTM D5466-21, Standard Test Method D5466-21.

1.3 Performance Based

This method provides some flexibility for analysis of VFCs. The laboratory may select GC columns, GC conditions, and MS conditions different from those used to develop the method. Users may modify the sample preparation portions of this method to overcome interferences or to substitute superior materials and equipment, provided they use GC/MS as the basis for separation and quantitation of method target compounds and meet all performance criteria in Section 9 of this method.

1.4 Method Sensitivity

The VFCs in this method have been successfully measured at concentrations below one microgram per cubic meter ($\mu g/m^3$) or sub-ppbv concentration.

2.0 Summary of Method

2.1 This method involves collection of VFCs in evacuated passivated silicon ceramic lined stainless-steel canisters, or equivalent. Field sampling and recovery staff must be trained in the best practices for extracting representative gas samples from an emission vent or stack, conditioning the gas if necessary to manage moisture and acid gases, and collecting the gas sample in passivated stainless-steel canisters.

2.2 Gas samples are collected from a sampling manifold using evacuated canisters equipped with a critical orifice for sample flow control. Samples are collected directly from the manifold with or without a water and acid gas management system.

2.3 Water and acid gas management in the sampling system is described in this method.

2.4 This method provides procedures for the preparation, blanking, evacuation, and shipping of passivated canisters prior to sample collection.

2.5 Sample transport, preservation and storage are also described.

2.6 Measurements of stack carbon dioxide (CO_2) are also required. The volumetric concentration of CO_2 is important information for the proper preparation of calibration standards and analytical laboratory method optimization.

2.7 The source moisture concentration is necessary to determine what sampling train configuration is appropriate. The volumetric moisture concentration is also needed to calculate results on both a wet and dry basis.

2.8 Water and CO_2 measurements in conjunction with stack or duct volumetric flows are required as part of this method.

2.9 VFCs are identified and quantified in gas samples from canisters by GC/MS.

2.10 Additional volatile compounds present in canister samples that are not on the target list are reported with their best-available matches to mass spectral reference libraries.

3.0 Method Definitions and Abbreviations

3.1 Blanking means the confirmatory analysis of cleaned passivated canisters before they are sent to the field for sampling.

3.2 Calibration standard means a traceable standard gas or gas mixture of known concentration used for routine calibration of measurement instruments.

3.3 Canister means a passivated silicon ceramic lined stainless-steel container, or equivalent, able to be pressurized to at least 2 atmospheres.

3.4 Continuing calibration verification standard (CCV) means a dilution of the calibration standard prepared at a concentration in the lower third of the calibration curve. The CCV is run periodically to confirm that the analytical system continues to generate sample results within acceptable agreement to the current calibration curve.

3.5 COC means sample chain of custody documentation. See example in Figure OTM-50-6.

3.6 Diluent gas means a zero air or ultra-high purity nitrogen gas that is free of hydrocarbons and fluorocarbons at the method detection limit, or otherwise meets the method blank acceptance criteria for the respective VFCs.

3.7 Focusing trap means a temperature-controlled sorbent integrated into the analytical system allowing the preconcentration of sample gas to ensure efficient transfer/injection into the GC analytical column.

3.8 Full scan ion chromatogram means the chromatogram peak pattern produced from a mass spectrometer detector collecting full scan spectral information over a sample analysis run.

3.9 LB means laboratory blank. The LB is a canister filled with clean diluent gas added to the canister through the dilution system employed to prepare standards. For laboratories that do not employ a dynamic or automated static dilution system, the LB consists of a canister containing humidified gas and internal standards the same as used to dilute and prepare the calibration standards.

3.10 GC means gas chromatography or chromatograph.

3.11 MDL means the method detection limit determined using replicate precision following the procedures in 40 CFR Part 136, Appendix B.

3.12 MS means mass spectrometry or spectrometer.

3.13 MS-SCAN means the mode of operation of a mass spectrometer that measures all ions over a given mass range.

3.14 MS-SIM means the selected ion monitoring mode of operation of a mass spectrometer detector that measures a single ion or a selected small number of discrete ions for each analyte (i.e., Table OTM-50-2).

3.15 PFA means perfluoroalkoxy polymer material.

3.16 PLOT means porous layer open tubular. This type of GC column contains an immobilized stationary phase and is used to analyze fixed gases and light hydrocarbons. A PLOT column was used to develop the GC/MS method for the target analytes in Table OTM-50-1.

3.17 QRL means quantitative reporting limit, the minimum quantitative concentration that meets the criteria in Section 9.2.3.7.

Note: The QRL is based on the lowest calibration standard concentration of each target compound used during calibration. The QRL is affected by sample size, dilution, aliquots, and can vary for each sample.

3.18 VFC means volatile fluorinated compound. A fluorinated organic molecule with a vapor pressure greater than 1.3 kPa (10 Torr) at 25° C (boiling point of approximately 100 °C or lower).

3.19 VOC means volatile organic compound. VOCs are organic compounds that have vapor pressures greater than 1.3 kPa (10 Torr) at 25° C and 100 kPa (760 mm Hg) (U.S. EPA Method TO-15).

4.0 Interferences

4.1 Gas samples from stationary combustion sources contain significant quantities of CO_2 and condensed water or water vapor which interfere with VFC compounds in this method.

4.2 Water in the sample gas was found to coelute with analytes on certain chromatography columns used to evaluate this method and affected the response of those analytes. Poor or inconsistent water management during preconcentration can cause peak broadening and retention time shifts.

4.3 Acid gases and water condensed in canisters can result in corrosion of the interior surface of the canisters, resulting in reactive surfaces that compromise target compounds.

4.4 CO_2 in the collected sample may coelute and/or interfere with the quantitation of target compounds in this method.

4.5 Interferences can include target analytes as well as other VOCs that coelute and may have similar mass spectra as the target analytes. If coeluting compounds have common ions, the common ions should not be used as the target's quantifying or qualifying ions.

4.6 Contamination in the sampling system and canisters may interfere if sampling equipment is not properly cleaned before use.

5.0 Safety

5.1 This method does not purport to include all safety issues or procedures needed when collecting canister samples from stationary vents and stacks. Precautions typical of field air sampling projects are required. Tripping, falling, electrical, and weather safety considerations must all be included in plans to collect source canister samples.

5.2 This method may require work with hazardous materials and in hazardous conditions, like those associated with other stack sampling methods and procedures. The user is encouraged to establish safety procedures before using this method. Among other precautions, the user should become familiar with the safety recommendations in the gas analyzer's manual. Leak checks of the sampling system, proper exhaust ventilation, and safe gas cylinder handling are a few ways to mitigate exposure to harmful compounds.

5.3 Gases, including dilution gas and calibration standards in high-pressure cylinders, are used in this method. Exercise extreme care in working with high-pressure gas cylinders.

5.4 Exposure to suspected carcinogens or other compounds with serious health risks should be avoided in all circumstances. Refer to the safety data sheet (SDS) of each specific compound for safe handling instructions.

5.5 This method does not address all potential safety risks associated with its operation. All individuals performing this method must follow safety and health practices consistent with applicable legal requirements and prudent practices for each application.

6.0 Equipment and Supplies

All equipment and sample containers must be cleaned as specified in Section 8.4 to ensure that they will not contaminate samples.

6.1 Field Sample Collection Equipment

6.1.1 Heated sample probe, controllable to at least 150 °C (300 °F), with silanized stainless-steel or borosilicate glass liner.

6.1.2 Heated filter, controllable to at least 150 °C (300 °F), consisting of borosilicate glass housing, filter support (e.g., inconel, stainless, titanium) and glass fiber filters (GFF) or quartz fiber filters (QFF) for particulate matter (PM) removal.

6.1.3 Silanized stainless-steel compression fittings to connect the filter exit to the bypass line and the sampling canister critical orifice. Also referred to as the critical orifice tee.

6.1.4 Heated PFA line, controllable to ≥150 °C, for connecting the filter exit to the critical orifice tee.

6.1.5 Heating jacket, controllable to at least 150 °C (300 °F), to heat all fittings, including the critical orifice, between the exit of the heated PFA line and the canister sampling valve.

6.1.6 Silanized critical orifices for controlling sample flow rate, e.g., an orifice to give 83 mL/min to produce a 5 L sample in one hour.

6.1.7 Impinger conditioning system with the following components:

6.1.7.1 Four glass, 30 – 50 mL threaded joint impingers. Two tapered and two open tube stems are used. An optional “knock out” impinger with a modified stem may be used for high moisture conditions.

Note: compression fitted GL 18 threaded caps have been used.

6.1.7.2 Insulated ice bath to contain impingers.

6.1.7.3 Unheated PFA line to connect the impinger conditioning system exit to the critical orifice tee.

6.1.7.4 PFA tubing connected between the critical orifice and bypass pump.

Note: PFA line to the bypass pump can be unheated.

6.1.8 Leak free, flow controllable sample bypass pump.

6.1.9 Rotameter (0-5 Lpm) positioned at the bypass pump outlet.

6.1.10 Passivated silicon ceramic lined stainless-steel canisters, or equivalent.

Note: The suitability of electropolished (SUMMA) canisters has not been evaluated for this method. To use other types of canisters, the laboratory will need to demonstrate that they can meet all the performance criteria for sampling and analysis in this method.

6.1.11 Relative humidity (0-100% RH) and temperature (≥ 180 °C) measurement probe.

6.1.12 Vacuum gauge to measure canister pressures to 101 kPa (30 in. Hg) vacuum.

6.2 Laboratory Analysis Equipment

6.2.1 Canister cleaning system. Canister cleaning systems are commercially available or may be custom built. An example is shown in Figure OTM-50-4. A system that includes the following components should be used:

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

6.2.1.2 High-vacuum pump for achieving a final canister vacuum of approximately 0.0067 kPa (0.05 mm Hg or 50 mTorr) or less.

6.2.1.3 Oven that can contain the canister and allow heating of the valve.

6.2.1.4 Humidification system such as an impinger humidifier or bubbler capable of achieving relative humidity of at least 50% in a canister.

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

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

6.2.1.7 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. Do not use butyl rubber or PFA materials. If needed for connections or seals, minimize the use of fluoropolymers and fluoroelastomers to avoid adsorption and/or off-gassing of compounds of interest or introduction of other potential interferences.

6.2.1.8 Charcoal scrubber and catalytic oxidizer system for eliminating trace contaminants from the purge gas.

6.2.1.9 Electronic pressure transducer or absolute pressure gauge to measure the pressure and vacuum in the manifold.

6.2.2 Standard and sample dilution laboratory equipment.

6.2.2.1 Dynamic gas dilution system with the following minimal components:

6.2.2.1.1 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 combined before introduction into a canister.

6.2.2.1.2 Connection tubing for the dynamic dilution system must be constructed of chromatographic-grade stainless-steel (minimum type 316) or silicon-ceramic coated stainless-steel.

6.2.2.1.3 Mixing chambers or manifolds must be constructed of chromatographic-grade or silicon-ceramic coated stainless-steel, borosilicate, or quartz glass.6.2.2.2 Static Dilution System

6.2.2.2 Static gas dilution system with the following minimal components:

6.2.2.2.1 Calibrated pressure transducer or pressure gauge to measure the partial pressures of each standard gas to be diluted and the diluent gas, preferably zero air, as well as a manifold to introduce the gases into the working standard canister or vessel, a humidifier for the diluent gas, and a manifold or mixing chamber where the diluent and standard gases can be combined before introduction into a canister.

6.2.2.2.2 Connection tubing for the static dilution system must be constructed of chromatographic-grade stainless-steel (minimum type 316).

6.2.3 Sample analysis laboratory equipment.

6.2.3.1 Canister auto-sampler capable of being leak checked.

6.2.3.2 Sample pre-concentrator unit.

Note: Complete GC-pre-concentrator units are commercially available as an integral part of the GC/MS hardware. The characteristics of current concentrators include rapid heating of the concentrator to release trapped target compounds into a small carrier gas volume. Pre-concentrator units also have water removal capabilities to help control the humidity of the sample prior to injection into the GC.

6.2.3.3 GC, including standard features such as gas flow regulators and automatic control of valves and oven parameters. Temperature programming and electronic carrier gas pressure control (EPC) systems are required. The GC must be capable of operating with gas chromatographic columns, including porous layer open tubular (PLOT) and high-resolution bonded-phase capillary columns.

Note: Depending on the choice of column (e.g., film thickness) and the volatility of the target compounds, it may be necessary to cool the GC oven to sub-ambient temperatures at the start of the chromatographic run to allow resolution of very volatile organic compounds.

6.2.3.4 Carrier gas lines supplying the GC must be constructed from clean stainless-steel or copper tubing with non-polytetrafluoroethylene (PTFE) thread sealants. Flow controllers, cylinder regulators, or other pneumatic components fitted with rubber components are not suitable.

6.2.3.5 Chromatographic columns. GC columns that provide adequate separation of sample components to meet identification and quantitation performance requirements in Section 9 of this method are required.

Note: PLOT columns or equivalent have been shown to meet this requirement.

6.2.4 Mass spectrometer system. Linear quadrupole, magnetic sector, ion trap or time-of-flight mass spectrometers may be used provided they meet specified performance criteria with the following components:

6.2.4.1 MS system must be capable of up to 70 volts (nominal) electron energy in the electron ionization mode.

6.2.4.2 MS system detector must be capable of collecting data over the range of monitored masses (amu) every 1 second or less.

6.2.4.3 MS system detector and data handling system must be capable of producing a full scan mass spectra (MS-SCAN) or selected ion monitoring spectra (MS-SIM) that meet all the instrument performance acceptance criteria in Section 9.

6.2.5 Cylinder 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 VFC (e.g., silicon-ceramic). Do not use regulators that contain PFA materials (e.g., for seals and diaphragms) and do not use regulators that contain fluoropolymer products such as PTFE, Viton, and fluorinated ethylene propylene (FEP), where possible. 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 VFC standard cylinder and a low-concentration stock VFC cylinder).

6.3 Oven

An oven is used to bake sampling system components.

Note: A vacuum oven can help remove residual VFCs and other VOCs. Items such as impingers, tubing, and filter housings can be baked after washing to dry and remove volatile contaminants.

7.0 Reagents and Standards

7.1 Cylinder gas, research-grade helium, 99.9999-percent pure.

7.2 Cylinder gas, research plus or ultra-high-purity (UHP) nitrogen, typically 99.9999-percent pure.

7.3 Cylinder gas, scientific or zero grade air, typically total hydrocarbons (THC) less than 0.1 ppm.

7.4 Cylinder gas, CO_2 for matrix matching. Vendor certified accurate to ±5 percent.

7.5 Methanol, reagent grade.

7.6 Target VFC calibration standard(s). VFC compressed gas phase standard calibration mixture(s) in nitrogen accurate to ±10 percent or better at a concentration of approximately 1 ppmv are diluted to generate calibration mixtures that span the range of source concentrations to be measured.

7.7 Deionized water (DI), ultra-pure, carbon filtered water (resistivity >18 MΩ).

7.8 Cryogens, (e.g., liquid nitrogen, liquid argon, and/or liquid CO_2) specified by the instrument manufacturer, as needed.

8.0 Sample Collection, Preservation, and Storage

Sample train configuration. Two basic sampling train configurations are applied, the Direct VFC Sampling System or the VFC Canister Sampling System with Water/Acid Gas Management, depending on the source gas characteristics described below.

8.1 Direct VFC Sampling System

8.1.1 For emissions streams where the stack moisture is ≤3% v/v and acid gases are not present, the Direct VFC Sampling System is used. A diagram of the Direct VFC Sampling System is shown in Figure OTM-50-1.

8.1.2 The Direct VFC Sampling System is configured by connecting a heated transfer probe, a heated filter, a heated transfer line, and the heated critical orifice and connecting fittings to a bypass pump. The bypass vacuum pump is used to extract and deliver a representative gaseous sample from the source through the critical orifice tee, which directs a portion of the sample gas through the critical orifice to the cleaned and evacuated canister. Excess source gas can be vented from the bypass pump back to the stack, or vent, or treated to remove any VOCs and vented to the atmosphere.

8.2 VFC Canister Sampling System with Water/Acid Gas Management

8.2.1 For emissions streams where stack moisture is >3% v/v or acid gas levels are a concern (e.g., combustion/incineration emissions), the VFC Canister Sampling System with Water/Acid Gas Management is used. A diagram of this sampling system is shown in Figure OTM-50-2.

8.2.2 The VFC Canister Sampling System with Water/Acid Gas Management is configured by connecting a heated transfer probe, a heated filter, an impinger conditioning system, an unheated transfer line and the unheated critical orifice and connecting fittings to a bypass pump used to extract and deliver a representative gaseous sample from the source to the critical orifice. The outlet of the critical orifice directs a portion of the sample gas to a passivated canister. Excess source gas is vented from the bypass pump back to the stack or vent or treated to remove VOC and vented to the atmosphere.

8.3 VFC Canister Sampling System with Multiple Canisters

8.3.1 A diagram of the VFC Canister Sampling System with Multiple Canisters is shown in Figure OTM-50-3. The purpose of this configuration is to enable the collection of multiple canister samples concurrently. This may be added to the train equipment configurations in Sections 8.1.2 or 8.2.2 and used to collect paired samples for measurement precision determination. Additionally, this configuration may be used to collect samples of varied sample volumes. Varied sample volumes may be useful when high VFC concentrations may be present, and a much smaller sample volume may be desired. Otherwise, a high dilution may be needed to bring concentrations into analysis calibration range.

8.4 Sampling Train Cleaning

Clean glassware and sampling apparatus thoroughly before use. This section provides a recommended procedure, but any protocol that consistently results in a contamination-free sampling train meeting the blank criteria in Table OTM-50-3 is acceptable.

8.4.1 Glassware (including impingers, stems, and caps) and filter frits.

8.4.1.1 Soak in hot soapy water (Alconox® or equivalent) at 50 °C or higher.

8.4.1.2 Rinse three times with hot tap water.

8.4.1.3 Rinse three times with DI water.

8.4.1.4 Rinse three times with methanol.

8.4.1.5 Bake glassware in a vacuum oven at 65 – 100 °C (150 – 212 °F) with greater than 67 kPa (20 in. Hg) vacuum for a minimum of 2 hours.

8.4.1.6 While in the field and for subsequent sampling runs, rinse impingers with DI water and refill the impingers between runs. The probe liner and filter may be used for all three field runs.

8.4.2 Coated stainless-steel fittings, orifices, and transfer line (probe liner).

8.4.2.1 Soak in methanol for at least five minutes. Decant and repeat three times.

8.4.2.2 Soak in water for at least five minutes. Decant and repeat three times.

8.4.2.3 Bake in a vacuum oven (the parts that can fit in) at 65 – 100 °C (150 – 212 °F) with greater than 67 kPa (20 in. Hg) vacuum for a minimum of two hours.

Note: The transfer line may not be easily soaked or baked due to its length. If the line cannot be baked, rinse with the methanol, air dry, and then purge at the probe maximum temperature with nitrogen or zero air for a minimum of one hour.

8.4.3 Heated sample lines.

8.4.3.1 Heat PFA sample lines to the maximum operating temperature (≥150 °C/300 °F) and flush with nitrogen or zero air for approximately two hours.

8.4.3.2 Sample lines used for previous sampling can be heated and flushed as in Section 8.4.3.1 before re-use. A line that may be highly contaminated can be rinsed with methanol then heated and flushed as in Section 8.4.3.1. Alternatively, new PFA sample tubing may be used inside a larger diameter heated tube such that the new tubing can be replaced after each use. If this option is chosen, follow the cleaning procedure in Section 8.4.3.1.

8.5 Sample Collection System Setup

8.5.1 Determine which sampling system configuration is appropriate for sampling (Section 8.1, 8.2, or 8.3).

8.5.1.1 Determine stack gas moisture content. This may be accomplished in multiple ways. If the source is a combustion source, the moisture content is assumed to be >3% v/v and water/acid gas management is required (Section 8.2). For non-combustion sources where direct sampling is preferred (Section 8.1), the stack moisture may be determined using a high temperature relative humidity (RH) probe.

8.5.1.2 For non-combustion sources, determine if acid gases are suspected or are present based on process knowledge. No testing is required for this determination.

8.5.1.3 For gases from sources where the moisture is >3% v/v and/or acid gases are present, the VFC Sampling System with Water/Acid Gas Management described in Section 8.2 is used (Figure OTM-50-2).

8.5.1.4 For gases from sources where the moisture is confirmed to be ≤3% v/v and acid gases are not suspected, the Direct VFC Sampling System described in Section 8.1 may be used (Figure OTM-50-1).

8.5.1.5 In situations where the emissions stream may contain unknown concentrations or VFC concentrations above the analysis calibration range, the VFC Canister Sampling System with Multiple Canisters described in Section 8.3 may be used (Figure OTM-50-3).

8.5.2 Prepare the VFC Canister Sampling System with Water/Acid-Gas Management impinger conditioning system.

8.5.2.1 Pour approximately 15 mL of ultrapure DI water into each of the first three impingers (about 1/3 full). Place an empty knockout impinger in the fourth position, place the impingers in an ice bath, and connect the fourth impinger to the tee with the sampling orifice using PFA or stainless-steel tubing (see Figure OTM-50-2). The first impinger uses a plain open tube stem, the second and third stems have tapered ends, and the fourth impinger uses a plain open tube stem.

Note: An additional “knock out” impinger may be placed before the first impinger for moisture above 8% or longer run times to increase moisture capture capacity.

8.5.3 Prepare the Direct VFC Sampling System.

8.5.3.1 If the conditions listed in Section 8.1 for direct sampling are met, the canister sample can be collected directly from the source without the impinger water/acid gas management system using the Direct VFC Sampling System, as described in Section 8.1 and shown in Figure OTM-50-1.

Note: Care should be taken to avoid the use of fluoropolymer materials. The actual volume of sample collected is limited to minimize the potential for moisture condensation within the canister during sampling as well as storage and shipment.

8.5.4 Connect the sample probe liner to the heated glass filter housing with a QFF or GFF. Connect the exit of the heated glass filter housing to the impinger conditioning system if water/acid gas management is needed. Then connect the appropriate transfer line in series with the critical orifice tee and the tubing to the bypass pump. The bypass pump draws the sample gas from the source, through the filter and impingers, if needed, and past the critical orifice tee. The bypass pump flow rate must be held constant between 1-2 Lpm to ensure it is not less than the expected sample rate into the canister(s).

8.5.5 Connect the critical orifice assembly to the bypass line.

Note: If an analyte is known or suspected to have a concentration above the calibration range or the concentrations of the analytes are not known, two canisters may be sampled at the same time in the sampling setup by placing a second sample tap inline after the first, see Figure OTM-50-3. The second canister is used to collect a low volume, e.g., 500 mL, following the first canister that collects the 4 – 5 L sample. Sample dilution for high concentration analytes occurs when the 500 mL gas sample is brought up to pressure for analysis.

8.5.6 Heat the sampling train once the sample extraction system assembly is complete.

8.5.6.1 For direct VFC sampling without water and acid gas management, heat and maintain the probe and train temperature, including the critical orifice at 5 °C to 10 °C above the source temperature but not to exceed 120 °C.

8.5.6.2 For sampling using water and acid gas management, heat and maintain the probe and filter assembly only to 120 °C. For this configuration the sample orifice in not heated.

Note: A staged heating cycle is recommended by heating the extraction system to approximately half the final sampling temperature, allowing the assembly to equilibrate, then heating to the final temperature.

8.5.7 Operate the bypass pump at a flow rate of approximately 1 Lpm. Do not exceed 2 Lpm.

Note: The bypass pump extracts sample gas from the source and sample gas temperature affects extraction manifold temperature management.

8.6 Canister Sample Collection

Once the train has been assembled and the required heated components are operational and have reached the desired heating temperature, collect the source emissions sample as described in this section.

8.6.1 Leak check the system to ensure the sampling setup does not contain leaks. Once the system setup is complete and sampling taps (inlet to orifice fitting that attaches to canister) are plugged, seal the end of the sample probe. The bypass pump flow rate should drop to 0 Lpm. If the flow is not stopped, the system's connections need to be checked and adjusted until the flow can drop to 0 Lpm when the sampling probe is plugged. Be sure to unplug the probe end before turning off the bypass pump.

8.6.2 Collect the sample.

8.6.2.1 Confirm the initial canister vacuum. Prior to connecting the canister to the sampling train, attach a vacuum gauge and open the valve. Record the initial pressure (it should register 101 kPa (30 in. Hg), vacuum). Close the valve and remove the vacuum gauge.

8.6.2.2 Attach the canister to the sampling train at the critical orifice.

8.6.2.3 Insert the probe/filter assembly into the sampling duct. Position the probe at the first traverse point.

8.6.2.4 Start the bypass pump and purge the sampling line for at least two minutes.

Note: The intent is to ensure that the sample gas has fully flushed the dead volume between the probe and critical orifice location. The actual dead volume and the bypass flow rate determines the amount of time needed to fully flush the dead volume (≥7 volume exchanges).

8.6.2.5 Open the canister valve, record the start time/start timer, and collect the sample for approximately 60 minutes.

Note: A critical orifice flowrate of approximately 83 cc/minute used for a 60 min sample time will result in a nominal total sample volume of up to 5 L. This results in a calculated and observed final pressure of 17-24 kPa (5-6 in. Hg) vacuum in a 6 L canister.

Note: For anticipated high VFC concentrations that require dilution for analysis, smaller sample volumes (e.g., 500 cc) may be collected by using an orifice with a lower flowrate. This smaller sample volume is collected in a separate canister concurrently with the 5 L sample (see Section 8.3).

8.6.2.6 Collect the sample gas at a minimum of at least three discreet duct or stack traverse points, sampling for an equal amount of time at each traverse point.

Note: EPA Method 1 multiple sampling point traverse criteria are not required. However, every effort should be made to collect a representative sample. As a result, a minimum of three discreet duct or stack traverse points are required.

8.6.2.7 When the run is complete, close the canister valve, record the stop time, perform a post-test leak check (see Section 8.6.1), and disconnect the canister from the train.

8.6.2.8 Confirm the final canister vacuum.

8.6.2.8.1 Attach the vacuum gauge to the canister and open the canister valve.

8.6.2.8.2 Record the final pressure.

8.6.2.8.3 Compare the final pressure and associated sample volume (Eq. 19) to the theoretical volume sampled from the sample time and orifice flow rate (Eq. 20). A RPD > 20% indicates a potential leak or a clogged orifice and requires resampling (See also Section 9.1.2).

Note: The pressure should be approximately 17-34 kPa (5-10 in. Hg) vacuum for a 4 to 5 L gas sample collected in the 6 L canister.

8.6.2.9 Close the valve, remove the gauge, and replace the canister inlet cap.

8.6.3 Additional measurements, including but not limited to stack CO_2 (if present), stack moisture, and stack flow are required to enable full reporting of emissions data. CO_2, if present, can cause analytical interferences and is integral to the stack flow determinations.

Note: OTM-50 may be performed as part of emission tests at combustion sources which include measurement of CO_2, moisture, and flow using EPA Methods 1-4. If CO_2 stack concentration is not available, alternative approaches for measuring CO_2 must be performed. Acceptable alternative approaches to measure CO_2 include Method 320, plant/facility CEMs, or analysis of Tedlar bag samples.

8.6.4 Collect the following data/minimal information for each sample. An example field data sheet is provided in Figure OTM-50-5.

For each run:

- Run number
- Canister identification (ID)
- Orifice ID and calibrated flow rate
- Initial vacuum
- Pretest leak check

- Run start time
- Traverse point locations and duration
- Probe temperature
- Filter temperature
- Heated line temperature (if applicable)
- Fittings/orifice temperature (if applicable)
- Bypass pump flow
- Run end time
- Post test leak check
- Final vacuum
- Volume sampled as determined by final canister vacuum (Eq. 19)
- Volume sampled as determined by calibrated orifice flow rate and sample duration (Eq.20)

Additional data:

- Stack CO_2
- Stack H_2O
- Stack/duct temperature
- Stack/duct diameter/dimensions
- Stack flow
- Absolute (station) barometric pressure

8.6.5 Complete the chain of custody (COC) form. The information contained in the COC is important to the analytical laboratory, as it also provides details necessary to inform the sample analysis in addition to the standard custody transfer information. The following is a listing of the minimum information to be documented on the COC. Complete the COC sheets, make copies, and place the originals in the shipping boxes. An example COC form is provided in Figure OTM-50-6.

- Canister ID
- Date sampled
- Canister pressure after sampling/as transferred
- Volume sampled (as calculated by 12.2.19)
- Estimated/measured CO_2 concentration, if any
- Absolute (station) barometric pressure at sampling location

- Comment/instructions (any high levels, other precautions, pertinent information)
- Canister pressure as received by analytical laboratory
- Absolute (station) barometric pressure at laboratory location
- Volume sampled (as calculated by 12.2.18)
- Who is relinquishing the sample(s) and date
- Who is receiving the sample(s) and date
- Date analyzed

8.6.6 Once the canisters have been sampled, place them in their individual protective containers and then in a shipping box.

8.6.7 Store canisters in a dry location at ambient laboratory temperature.

8.6.8 Ship canisters to laboratory for analysis.

8.6.9 Upon receipt of the canisters at the laboratory, measure and record the canister pressure. Compare the final pressure and associated sample volume (Eq. 19) with the theoretical volume sampled in the field from the sample time and orifice flow rate provided on the COC. The relative agreement serves to identify potential leaks.

8.6.10 Samples must be analyzed within 30 days.

9.0 Quality Control

It is the laboratory's responsibility to establish the conditions for optimum sample analysis to meet the performance criteria in this method. This performance-based method offers some flexibility; however, you may not change the fundamental procedures of proportional sampling followed by GC/MS analysis. Quality control (QC) procedures include the initial demonstration of capability (IDC) and ongoing QC requirements. This section describes each QC parameter, its required frequency, and the performance criteria that must be met to satisfy method objectives. The analysis QC criteria discussed in the following sections are summarized in Table OTM-50-4. These QC requirements are considered the minimum for an acceptable QC program. Laboratories are encouraged to institute additional QC practices to meet their specific needs and continually improve their analysis performance. At a minimum, laboratories must evaluate the changes they've made to demonstrate that performance-based requirements and criteria have been met with their alternatives. Allowable changes to this method may be evaluated using a native target list of compounds spiked into canister(s) to re-demonstrate that the performance criteria are achieved.

9.1 Sampling Quality Control

9.1.1 Determine the sampling system background. At least one sampling system background determination must be performed for each test campaign. A canister sample is collected using the procedures in this section. The sampling system background sample must be collected in the field prior

to the collection of actual samples. A post testing sampling system background determination is also recommended.

9.1.1.1 Setup, heat, and leak check the sampling system as described in Sections 8.5 and 8.6.

9.1.1.2 Connect and deliver a flow of UHP nitrogen or zero air to the inlet of the sample probe at a flow rate slightly exceeding that of the sampling system bypass flow rate. Purge the system for at least two minutes.

9.1.1.3 Collect the sample as described in Section 8.6. Collect a 4 to 5 L sample in a 6 L canister.

9.1.1.4 Submit the canister for analysis as a sample. The performance criteria are listed in Table OTM-50-4.

9.1.2 Check the field integrity of collected samples. Perform the comparison of sample volumes required in Section 8.6.2.8. Flag data that differ between the two approaches by ≥20% RPD and indicate if leakage is suspected and invalidate the sample with a similar explanation.

Note: For high concentration small volume canister samples, volume differences >20% RPD may be acceptable due to differences in pressure measurement equipment.

9.1.3 Check the laboratory integrity of collected field samples. Upon receipt in the laboratory perform the comparison of sample volumes required in Section 11.1.2. Flag data that differs between the two approaches by more than 5% RPD and indicate leakage is suspected or invalidate the data with a similar explanation.

9.1.4 Provide COC information. Refer to Section 8.6.5 for the minimum information to provide. An example COC form is presented in Figure OTM-50-6.

9.2 Analysis Quality Control

9.2.1 Gas dilution systems.

9.2.1.1 Gas dilution systems used to generate calibration gases shall be capable of producing standards whose measured values are within ±3 percent of predicted values. The predicted values are determined based on the certified (tag) concentration of the compressed gas cylinder and the gas flow rates or dilution ratios used in the gas dilution system.

9.2.1.2 Annual evaluations are required to verify that the gas dilution system is contamination-free and not biasing samples. Perform gas dilution system evaluations by generating and analyzing blank samples using humidified zero air. Gas dilution blank samples must meet the blank sample criteria in Table OTM-50-4.

9.2.1.3 Perform mass flow or pressure gauge audits on a yearly basis to verify the accuracy of the system used to dilute calibration standards and samples.

9.2.1.4 Dynamic gas dilution systems must be recalibrated once per year using NIST traceable primary flow standards with an uncertainty of ≤ 0.25 %.

9.2.1.5 Static gas dilution systems must be recalibrated once per year using a NIST traceable primary pressure gauge with an uncertainty of ≤ 0.1 %.

9.2.1.6 Static gas dilution systems must have pressure transducer(s) with an accuracy of ± 0.1 % full scale or 0.13 kPa, whichever is smaller, calibrated over the range of use for the application to permit precise measurement of pressure differentials for the diluent gas.

9.2.1.7 Maintain records of calibration results, listing the date of the most recent calibration, the reference flow or calibration device identification and serial number as well as the measured performance that demonstrates meeting the uncertainty criteria.

9.2.2 GC/MS systems must be leak checked by monitoring the mass spectrometer vacuum or performing an air/water background check prior to sample analysis to verify that there are no leaks in the analytical instrument system. Air to water ratios should be below the manufacturer's recommended levels for operation.

9.2.3 Initial demonstration of capability (IDC). Each analyst using this method must demonstrate and document their ability to perform the method by performing the following actions: demonstration of low system background; determination and confirmation of MDL; demonstration of precision and accuracy; and confirmation of QRL. The IDC must be successfully performed prior to analyzing field samples by meeting the QC requirements in Table OTM-50-4. Prior to conducting the IDC, the analyst must meet the calibration requirements outlined in Section 10. The same calibration range used during the IDC must be used for the analysis of field samples.

Note: Failure to meet the performance criteria in Table OTM-50-4 for a target compound during the IDC or subsequent calibrations invalidates that specific compound for quantitative analysis but does not invalidate other compounds that met the performance criteria.

9.2.3.1 Initial calibration (ICAL). The ICAL consists of a multipoint curve with a minimum of five levels of known VFC concentrations described in Section 10.7.1 of this method. A specific calibration model is not required; a calibration using the average RRFs, linear, or quadratic regressions may all be used. Irrespective of the selected calibration model, the calculated concentration for each VFC at each calibration level must be within ±20% of the theoretical concentration.

9.2.3.1.1 If calibration acceptance criteria are not met, you must perform corrective action such as reanalyzing the calibration standards, restricting the range of calibration, preparing an additional multi-point calibration curve to cover the extended range, or performing instrument maintenance. If the cause for failure to meet the criteria is due to contamination or standard degradation, prepare fresh calibration standards and repeat the ICAL.

9.2.3.2 Demonstration of low system background. Confirm that the LB is free from contamination as defined in Table OTM-50-4.

9.2.3.3 Initial MDL determination.

9.2.3.3.1 Perform an MDL determination following the requirements in 40 CFR Part 136 Appendix B. The MDL determination includes analyzing seven LBs filled with clean air and seven canisters filled with the VFC standard spiked within 2 to 10 times of the expected MDL.

9.2.3.3.2 Analyze each canister in a manner identical to the field samples. The MDL study establishes the lowest detectable concentrations that are statistically different from the LB at 99% confidence.

9.2.3.4 MDL confirmation. Prepare a canister spiked with VFCs used for calibration (native target compounds) at the VFC specific MDLs. Analyze this canister to confirm that target compounds meet the qualitative retention time identification criteria in Table OTM-50-4.

9.2.3.5 Demonstration of precision. Prepare and analyze a canister spiked at the midpoint of the ICAL curve seven times. Analysis results from these seven replicates must have a percent relative standard deviation (%RSD) of the concentrations no greater than 25% for all method analytes (Table OTM-50-4).

9.2.3.6 Demonstration of accuracy. Using the same set of replicate data generated for Section 9.2.3.5, calculate the average percent recovery. The average percent recovery for each analyte must be within ±30% of the concentration prepared in Section 9.2.3.5.

9.2.3.7 Lowest calibration concentration confirmation. Establish a target concentration for the QRL based on the intended use of the method. Lowest calibration concentrations must be no lower than three times the MDL determined in 9.2.3.3.

9.2.3.7.1 The lowest calibration concentration may be established by a laboratory to meet project specific objectives. If there is a regulatory or programmatic lowest quantitative reporting requirement, the laboratory calibration curve must be set at or below this level.

9.2.3.7.2 Assess the results from the lowest calibration concentration canister sample and determine if it meets accuracy criteria of ±30% of each target compound spike concentration.

9.2.3.8 In all cases where method modifications are implemented, the analyst must perform the procedures outlined in the IDC (Section. 9.2.3) and verify that all QC acceptance criteria are met (see Table OTM-50-4).

9.2.3.9 Record and archive results in tables with associated QC narratives demonstrating acceptable performance criteria. IDC results must be made available upon request.

9.3 Sample Analysis Quality Control

9.3.1 Perform LB analysis.

9.3.1.1 Prepare and analyze an LB at the beginning of every sample sequence.

9.3.1.2 LB/artifact levels must meet the requirements in Table OTM-50-4. If the LB does not meet requirements, perform corrective actions, and re-analyze an LB to ensure QC requirements are met.

9.3.1.3 Analyze the LB using the same concentrator instrument settings and GC/MS operating conditions as used for the ICAL and field samples (see Section 10.4). The blank volume used for analysis must match the nominal volume of sample to be analyzed. Table OTM-50-4 lists the performance criteria for blank acceptance.

9.3.2 Selection of internal standards (IS).

9.3.2.1 Internal standard(s) (IS) are used to check daily calibration responses. Use standard gaseous mixtures with certified concentrations of IS compounds in ultrapure nitrogen. IS compounds chosen should represent the molecular weight range of the desired target compounds and may be isotopically labelled analogs of target analytes or VOCs that are not expected to be found in field samples.

9.3.2.2 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.

Note: This evaluation may be performed by analyzing increasing volumes of the IS (e.g., 25, 50, 100, 250 mL) and examining the results for compound contaminants whose responses increase proportionally with the increasing volume of IS analyzed. The analyst may also compare blank analyses with and without the IS to look for contaminants that may interfere with quantitation. Do not use IS gas standards that fail the LB acceptance criteria.

9.3.2.3 Internal standard retention time. Each IS compound in each sample injection must be within ±5 seconds of the mean RT for each IS compound in the most recent calibration.

9.3.2.4 Internal standard response. The area response for each IS compound in each injection (e.g., calibration standard, field sample, blank, CCV) must be within ±40% of the mean area response of the IS compound determined from the ICAL determined using Eq. 10 in Section 12 or the most recent calibration check, whichever is most appropriate.

9.3.3 Continuing calibration verification (CCV) standard.

9.3.3.1 Prepare a humidified CCV standard in a canister at a concentration in the lower third of the calibration curve. Prepare the CCV standard independently from a secondary certified calibration standard (if available). If secondary certified calibration standards are unavailable, individual targeted VFCs can be purchased and prepared at nominal concentrations from the pure/neat compounds. The CCV standard must contain all compounds in the calibration mixture.

9.3.3.2 Following each successful ICAL, analyze a CCV standard to verify the ICAL for each target compound. Recovery of each target compound in the CCV standard must be within ±20% of the theoretical concentration.

9.3.3.3 Analyze a daily CCV at the beginning of each analytical sequence. The difference between the quantitated concentrations of the target compounds ($\%D_{ccv}$) and the theoretical concentrations should be within ±20% using Eq. 3 in section 12.

9.3.3.3.1 Failure to meet the ±20% agreement requires corrective action such as instrument maintenance, repreparation of the CCV, and recalibration.

9.3.3.3.2 Using the daily CCV to calculate sample concentrations requires the daily CCV VFC RRFs to agree with the ICAL VFC average RRF within ±20% relative percent difference.

9.3.3.4 Analyze a CCV at the end of the analytical sequence and after every ten samples, whichever is more frequent. Sequence continuing and ending CCV VFC concentrations must be within ±20% of their theoretical value to be considered valid. If a sequence continuing or ending CCV fails to meet this criterion perform corrective action and reanalyze all samples not bracketed by a passing CCV for the failing compound(s).

9.3.4 Replicate field sample. Each analytical sequence must include analysis of one replicate field sample. Target compounds with concentrations >3x the MDL must agree within ±25% RPD in the replicate field samples.

9.3.5 Canister cleaning batch blanks. One canister from every cleaning batch will be analyzed as an LB to ensure that the cleaning procedure is adequately removing contaminants that may interfere with quantitation. A canister cleaning apparatus with features equivalent to Figure OTM-50-4 must be used for canister cleaning.

10.0 Calibration and Standardization

Calibration gas standard preparation may be performed using dynamic gas dilution systems or static dilution systems. Standards prepared in canisters at ambient laboratory conditions must be stored in locations that are free of potential contaminants for a period not to exceed 30 days.

Note: Alternative approaches for generation of calibration standards are acceptable if the following criteria are met: the calibration concentration is of known accuracy, the calibration range spans the sample concentrations and humidity, and CO_2 is accurately maintained.

10.1 VFC Standard Calibration Preparation

10.1.1 Evacuate clean passivated stainless-steel canisters, or equivalent, to 50 mTorr then inject 50 µL of DI water using a 100-microliter glass displacement syringe.

10.1.2 Prepare VFC calibration standards by diluting individual neat standards and/or from vendor certified pressurized cylinders containing a mixture of the VFC standard targets in nitrogen. Vendor certified standard gasses must be accurate to 5%. The VFC calibration standards should be diluted using a scientific grade air or zero air.

10.1.3 Determine the calibration concentration range needed to span the measured sample concentrations. An example calibration range is approximately 0.5, 2.5, 5.0, 10.0, and 20.0 ppbv for each compound except CF_4, which may be calibrated using 10-fold higher standard concentrations due lower injection volumes needed to avoid breakthrough. The lowest calibration standard used to establish the ICAL must be at least three times the estimated MDL. The calibration range may be extended, or samples may be diluted to bracket the expected concentration of field samples.

10.1.4 Use individual canister calibration standards and the same injection volume to generate calibration curves. Individual canisters must be prepared for each calibration level unless demonstrated that an effective dilution method is consistent with an individual standards calibration described in 9.2.3.1.1.

10.1.5 Use either a dynamic or static gas dilution system, or equivalent technique, to blend the VFC calibration gas with zero air (see Sections 10.2 and 10.3).

10.1.6 After preparation, allow the pressurized calibration standard canisters to equilibrate at ambient laboratory temperature for a minimum of 12 hours prior to instrumental analysis.

10.2 Calibration Standard Preparation using Dynamic Gas Dilution Systems

10.2.1 Calibration gases may be generated by dynamic dilution of a certified compressed gas cylinder containing VFC targets in nitrogen to make a working standard that is diluted with a gas stream of humidified zero air in the heated mixing chamber to generate various concentrations of calibration standards.

10.2.2 After allowing the nominal standard mixture to flow and equilibrate with humidified zero air for a minimum of 30 minutes in the mixing chamber, sample the gas standard mixture with a canister.

10.2.3 The final pressure of the calibration standard canister must not exceed the maximum pressure permitted by the GC/MS pre-concentrator unit.

10.2.4 Calculate the final concentration of each target compound in the diluted standard using Equation 7 in Section 12 of this method.

10.3 Calibration Standard Preparation using Static Gas Dilution Systems – Dilution by Addition of Partial Pressures into a Canister

10.3.1 Connect a pressure transducer or gauge to a clean evacuated canister to monitor the canister pressure as gases are added. The pressure transducer or gauge must meet the requirements in Section 9.2.1.6.

10.3.2 Add the VFC calibration standard and the zero air diluent gases separately through a manifold or by direct connection of the gas to the standard canister or vessel.

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

10.4 MS Tuning/Optimizing and Verification

10.4.1 Tune/optimize the 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, or adjusting MS tune or optimization parameters). Once optimized, the MS tune should be verified according to the manufacturer's specifications prior to initial calibration. The purpose of MS tuning is to demonstrate acceptable performance across the selected ion mass range, where acceptable performance demonstrates accuracy of mass assignments, unit mass resolution, and to some extent sufficient responses and adequately low vacuum leak rates.

10.4.2 Optional tune verification using bromofluorobenzene (BFB). Most modern MS systems include an automatic tuning optimization routine that is operated through the instrument software. Analysts may choose to use a BFB tune verification and criteria (Table OTM-50-4) to ensure acceptable MS response ratios up to approximately 200 amu. For a detailed BFB tune verification protocol, refer to EPA Method TO-15A.

10.5 Use of Internal Standards (IS)

10.5.1 Add the IS through a dedicated non-sample port in the pre-concentrator at the same concentration for each injection (e.g., standard, sample, blank) to monitor instrument sensitivity and assess potential matrix effects. The concentration of IS added to each injection should be in the lower middle portion of the calibration range (e.g., 5 ppbv) but must not exceed the concentration of the highest calibration level (e.g., 20 ppbv).

10.5.2 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.

10.5.3 Flag samples in which IS area response differs by more than 40% from the mean IS area response and/or in which the IS retention times different by more than ±5 seconds of the average RT for each IS in the most recent calibration. Perform corrective actions and reanalyze the samples (see Table OTM-50-4).

10.6 Pre-Concentration System Operation

10.6.1 Condition pre-concentrator focusing traps as specified by the manufacturer when first installed to reduce interferences and chromatographic artifacts to a level where they are below the desired detection limit and do not impact quantitation.

Note: Pre-concentrator focusing traps that contain multiple types of sorbent beds may need to be conditioned at multiple temperatures starting from the lowest to the highest recommended temperature.

10.6.2 Perform a leak check of the canister lines on the pre-concentrator system prior to opening the canister valves.

10.6.3 Analyze an LB to verify the pre-concentrator system meets the method criteria in Table OTM-50-4.

10.7 Instrument ICAL and Recalibration Procedure

10.7.1 Perform ICAL following the procedures in this section. The instrument must be calibrated for each target compound prior to sample analysis. Recalibrate following the procedures in this section when CCV results fail performance requirements (Section 9.3.3, Table OTM-50-4).

10.7.2 Prepare the VFC calibration standards using procedures in Sections 10.1-10.3. A minimum of five concentration levels that span the minimum quantifiable concentration up to 20 ppbv may be used.

10.7.3 Prepare analytical sequence for instrument calibration.

10.7.3.1 Run one LB prior to the calibration standards.

Note: Instrument blanks may be run before the LB to flush the system after high concentration standards or samples have been run.

10.7.3.2 Establish the ICAL using individual standards in separate canisters at each level of the calibration curve and injecting the same volume from each canister. Subsequent calibrations may employ various gas volumes from a single canister if the resulting effective dilution calibration curve meets the performance criteria for calibration.

10.7.3.3 Run calibration standards from the lowest to highest concentration.

10.7.3.4 Analyze a LB after the highest calibration standard. This LB verifies that the GC/MS system contains no carryover. LB concentrations are acceptable if they are <3x MDL or ≤ 50 % of the project required reporting limit for each target compound, whichever is higher.

10.7.3.5 Run a CCV after the LB.

10.7.4 Review all retention times, chromatographic peak shapes, and integrations for the calibration standard compounds to ensure proper quantification of VFCs. Adjust analytical method parameters to remedy any observed issues and rerun and/or reprocess data from 10.7.3 as necessary.

Note: Due to the similar boiling points of many of the compounds in the target list, it may not be possible to chromatographically resolve all of them. Unique quantifying and qualifying ions should be selected, if possible. Manual integration may be used to correct for improper integrations performed by the software but must be flagged for data points in the calibration curve.

10.7.5 Once the calibration standards are analyzed, generate a calibration curve for each VFC target compound. The use of the daily CCV RRF for quantitation is preferred if using a linear calibration curve. When using the daily CCV for VFC quantitation calculate an average RRF using equation 12 in Section 12.

10.8 Validation of Target Quantitation in the Presence of CO_2

10.8.1 Depending on the field sample concentration and analytical strategies utilized, CO_2 may interfere with one or more target compounds. The analyst must demonstrate that the response of the target analytes is not affected by the amount of CO_2 in the canister samples during IDC and prior to each sample analysis.

Note: CO_2 concentrations as high as 10-12% may be present in some source samples, leading to canister samples with 3-4% CO_2 levels after dilution/pressurization.

10.8.2 Prepare two additional calibration standards at the lowest and highest points on the calibration curve generated in Section 10.1 and dilute the canisters with CO_2 to final concentrations equal to or higher than the expected CO_2 concentration in the field samples. Use the stack equivalent concentration of CO_2 determined using an ancillary measurement described in Section 8.6.3 to determine the percentage of CO_2 to add to these calibration standards.

Note: If the samples are pressurized/diluted prior to analysis, the standards need only to be made to the expected CO_2 concentration after pressurization/dilution.

10.8.3 Analyze the two standards containing CO_2 using the same injection volume that will be used to analyze samples. If variable injection volumes are used to generate the calibration curve, the CO_2 standards must be prepared in a way to yield the expected concentration at the injection volume used for sample canisters.

10.8.4 Recovery of each target compound in the two standards containing CO_2 must be within ±30% of the true value for the compound. If either of the two CO_2 spiked canister analyses generate VFC values exceeds ±30% for a given target compound, a quantitative value must be flagged for that VFC with an explanation about CO_2 interference (see Table OTM-50-4).

Note: Pre-concentrator settings, purge times and/or GC/MS operating conditions may be optimized to decrease the impact of CO_2 interference at high concentration levels to avoid invalidating results for coeluting target compounds.

11.0 Analysis Procedure

In general, a fixed aliquot of gas sample is pulled from each canister and the sample is pre-concentrated onto a focusing trap. Water may be removed by the system prior to or during this stage. After sample concentration, the focusing trap is rapidly heated and flushed with carrier gas to desorb the VFCs onto the GC column where they are separated into individual VFC components or simplified mixtures of components and analyzed by mass spectrometry. VFC quantification is performed using an internal calibration standard including calibration for target analytes with native standards.

11.1 Preparing Samples for Analysis

11.1.1 Receive canister samples from the field and cross check COC forms with canister identification numbers. Resolve any disparities before analyzing canisters.

11.1.2 Measure and record the vacuum from field samples. The sample canisters should measure 17 kPa (5 in. Hg) or greater vacuum. Calculate the volume sampled in the field from the laboratory measured pressure (Eq. 19) and compare with the field sampled volume (see 9.1.3). Flag data that differs between the two approaches by more than >5% RPD and indicate leakage is suspected or invalidate the data with a similar explanation.

11.1.3 Canisters may be pressurized for analysis with zero air, research plus nitrogen, or UHP nitrogen. Minimum sample pressures will depend on the size of the canister and the capability of the pre-concentrator to remove the desired aliquot of the sample. This will be dependent on the instrument manufacturer.

Note: Field sample canisters are typically pressurized to dilute the contents by a factor of two or more to reduce the interference of CO_2 and water.

11.1.4 Measure and record the final canister pressure. Calculate the dilution factor resulting from sample pressurization using Eq. 11 in Section 12 of this method.

11.1.5 Allow each pressurized canister to sit for a minimum of 12 hours to equilibrate before analysis. Canisters have a maximum hold time of 30 days prior to analysis.

11.2 Field Sample Analysis

11.2.1 Organize and load the canister samples for instrumental analysis.

Note: Carbon tetrafluoride (CF_4) and trifluoromethane analyses may need to be performed using a multi-media cold trap or a separate (smaller) aliquot of gas from the sample canister to optimize the preconcentration procedure for the extreme volatility of CF_4.

11.2.1.1 Record sample names or identifiers, canister pressure, sample description, and total milliliters (mL) used for analysis in laboratory notebooks. Field samples must be analyzed using the same injection volume used for calibration standards.

11.2.1.2 Connect samples to instrument sampler/autosampler and check for leaks.

11.2.1.3 If the system is leak free, open the canister valves prior to starting the analytical sequence. If a leak is detected, re-tighten the connection and perform another leak check. Do not open the canister valve if the leak check fails.

11.2.2 Generate an analytical sequence and sample batch that at a minimum includes the following samples:

11.2.2.1 One LB at the beginning of the sequence.

11.2.2.2 A daily CCV after the LB.

11.2.2.3 Field samples, including one duplicate analysis of a field sample.

11.2.3 Run the sample sequence.

11.2.4 At the conclusion of data acquisition, use the same software settings established during the calibration procedure to qualitatively identify analyte peaks in the predetermined retention time windows. Confirm the identity of each analyte by comparing its retention time with that of the corresponding target analyte peak in an ICAL standard or CCV.

11.2.5 Confirm that the ions are consistent with the continuing calibration results. The signals for all characteristic masses shall be present and reach a maximum within the same two consecutive scans. The retention time difference between the target compound in the sample and the CCV shall agree within ±6 scans or ±6 seconds (whichever is greater) of this difference in the CCV standard.

11.2.6 After the entire sequence has been analyzed on the instrument, review the analytical results (chromatograms, peak integrations, and instrument reports) as described in Section 9 for completeness and performance requirements prior to data reporting.

11.2.7 Reanalyze samples that failed performance criteria. Dilute samples as necessary to measure target analytes within the calibration range.

11.2.8 Record and report deviations to performance criteria and actions to report compliant data.

11.2.9 If any target compounds fail to meet quality requirements during the IDC, calibration, or analysis, the failure only invalidates that specific compound or compounds from quantitative analysis. Results are still valid for compounds that meet performance specifications in this method.

11.2.10 Calculate the concentration (ppbv) of each target compound in the sample canister using Eq. 13 of this method.

11.2.11 Source gas volume calculations. Carry out calculations for stack gas velocity, volumetric flow rate, sampling volume, moisture, proportional sampling rate using equations 15 through 19 in Section 12 of this method.

11.2.12 Calculate and report wet and dry gas concentrations found in source/vent samples correcting for sample dilutions using Eq. 16 or Eq.17 in units of ppbv and µg/dscm using Eq. 18 in Section 12 of this method.

11.2.13 Record and report sample specific MDLs inclusive of sample-specific dilutions, final volumes, aliquots, etc.

11.3 Reporting of Unknown Peaks

GC/MS full scan results acquired through the application of OTM-50 sampling and analysis procedures are processed to identify unknown compounds in chromatographic peaks that do not correspond to target compounds in OTM-50.

11.3.1 Identify unknown peaks. Report the retention time and the associated integrated area for unknown peaks in a sample that (1) is not attributed to a target compound or internal standard and (2) the integrated area is greater than or equal to 5% of the integrated peak area of the IS. If multiple IS are used, the area of the IS nearest in retention time to the unknown peak should be used.

11.3.2 Generate unknown mass spectrum. The mass spectrum at the peak maximum or averaged across the width of the peak may be used for spectral matching. If background ions are present, a background subtraction may be performed; however, library matches for both the original and background subtracted spectra must be reported.

11.3.3 For each unknown mass spectrum, perform spectral matching to evaluated libraries of reference data (i.e., NIST/EPA/NIH Mass Spectral Library).

11.3.4 For each unknown peak, provide the following information:

1. Visualization of chromatographic peak

2. Retention time

3. Integrated peak area

4. The top five spectral matches (as IUPAC compound) based on match factor (no minimum) with each match's respective match factor and the name of the reference library the match comes from

5. The unknown spectrum from the sample that was searched

6. For compounds that have a top match greater than or equal to 80%, the library spectrum for the top match.

12.0 Data Analysis and Calculations

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

$$V_{calc} = (((P_{clean} - P_{std})/P_{std}) * V_{can}) + V_{can} \quad \text{Eq. 1}$$

Where:
P_{clean} = absolute pressure of canister cleaning batch blank, kPa absolute.
P_{std} = 101.3 kPa absolute, standard atmospheric pressure.
V_{can} = volume of the canister (mL) at standard conditions (101.3 kPa absolute and 25 °C).

12.2 Acceptance Concentration Criterion for Blank/Zero Air (C_{acc}) (Section 7.3)

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

Where:

C_{acc} = acceptance limit concentration at measured canister pressure (pptv).
C_{atm} = 20 pptv, acceptance limit concentration at standard atmospheric pressure.
P_{std} = 101.3 kPa absolute, standard atmospheric pressure.
P_{clean} = absolute pressure of canister cleaning batch blank, kPa absolute.

12.3 Percent Difference of the Measured Concentration of Each Target VFC in the CCV Standard from The Theoretical Concentration (Section 9.3.3.3)

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

Where:
$\%D_{CCV}$ = percent difference of the measured concentration of each target VFC in the CCV standard from the theoretical concentration.
C_{CCV} = measured concentration of the CCV for each target VFC (pptv).
$C_{theoretical}$ = theoretical concentration of the CCV for each target VFC (pptv).

12.4 Percent Recovery ($\%Recovery_{CCV}$) (Section 9.2.3.6)

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

Where:
$\%Recovery_{CCV}$ = percent recovery of measured versus actual concentration.
$C_{theoretical}$ = theoretical concentration of the CCV for each target VFC (pptv).

12.5 Relative Percent Difference (RPD) (Section 9.3.3.3)

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

Where:
RPD = relative percent difference.
X_1 = target VFC concentration measured in first measurement of the precision pair (pptv).
X_2 = target VFC concentration measured in second measurement of the precision pair (pptv).

12.6 Water Volume to Add to Canister (V_w) (reserved for ambient use of this method)

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

Where:
V_w = water volume to add to canister (µL).

D_{sat} = saturation vapor density of water (mg/µL) at ambient laboratory temperature (refer to Table OTM-50-5 in Section 17 of this method).
RH_d = desired RH level expressed as a decimal.
V_c = nominal internal volume of canister (L).
P_c = final absolute canister pressure (kPa absolute).
P_s = standard ambient pressure (101.3 kPa absolute).
D_w = density of water (1 mg/µL).

12.7 Final Concentration of the Diluted Standard (C_f) – Dynamic Dilution (Section 10.2.4)

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

Where:
C_f = final concentration of the diluted standard.
C_s = certified concentration of stock standard (pptv).
F_d = flow of diluent gas (mL/min).
F_s = flow of stock standard (mL/min).

12.8 Final Concentration of the Diluted Standard (C_f) – Static Dilution (Section 10.3.3)

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

Where:
C_s = certified concentration of stock standard (pptv).
P_{sa} = absolute pressure of canister after adding standard gas (kPa).
P_{sb} = absolute pressure of canister before adding standard gas (kPa).
P_f = final absolute pressure of canister after adding standard and diluent gases (kPa).

12.9 Average Retention Time ($\overline{RT}$) (Not used in current method)

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

Where:
$\overline{RT}$ = average RT for the IS compound (min).
RT_i = RT for the IS compound for each calibration level (min).
n = number of units used to generate a sum.

12.10 Average Relative Response for a Target Compound ($\overline{RRS}$) (Section 9.2.3.1)

$$\overline{RRS} = \sum_{i=1}^{n} \frac{RRS_i}{n} \quad \text{Eq. 10}$$

Where:
$\overline{RRS}$ = average relative response factor for a target compound.
RRS_i = response factor for a target compound at calibration concentration i.

n = number of units used to generate a sum.

12.11 Dilution factor for sample pressurization (Section 11.1.4)

$$DF_C = \frac{P_d}{P_i} \quad \text{Eq. 11}$$

Where:
DF_C = canister dilution correction factor.
P_d = pressure of the canister following dilution (kPa).
P_i = absolute pressure of the canister immediately preceding dilution (kPa).

12.12 Relative Response Factor (RRF), (Section 9.2.3.1 and 10.7.5)

$$RRF = \frac{A_S \cdot C_{IS}}{A_{IS} \cdot C_S} \quad \text{Eq. 12}$$

Where:
A_s = peak area for quantitation ion of the target compound.
A_{IS} = peak area for quantitation ion of the assigned IS compound.
C_s = certified concentration of stock standard (pptv).
C_{IS} = concentration of the assigned IS compound (pptv).

12.13 Instrument-Detected Analyte Concentration (C_D) in ppbv

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

Where:
C_D = instrument-detected analyte concentration (pptv).
A_{IS} = peak area for quantitation ion of the assigned IS compound.

12.14 Instrument Dilution Correction Factor (DF_I) (Not used in this method)

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

12.15 Concentration, in ppb, of the Target Compound in canister as received Stack Gas (C_F), (Section 11.2.12)

$$C_{ar} = C_D \cdot DF_C \cdot DF_I \quad \text{Eq. 15}$$

Where:
C_{ar} = concentration of the target compound in stack gas as received (pptv).
C_D = measured concentration of the target VFC in the canister as analyzed sample.

12.16 Concentration, in ppb, of the Target Compound in Stack Gas Wet (C_{SW}), (Section 11.2.12)

$$C_{SW} = C_{ar} \times (100 - (B_{WS} - 1))/100 \quad \text{Eq. 16}$$

Where:
Csw = the concentration of a target compound in the stack or vent not corrected for moisture
B_{WS} = stack moisture percent volume.
C_{ar} = from Eq. 15.

12.17 Concentration, in ppb, of the Target Compound in Stack Gas Dry (C_D), (Section 11.2.12)

$$C_D = C_{SW} \div (100 - B_{WS})/100 \quad \text{Eq. 17}$$

Where:
Csw = from Eq. 16
B_{WS} = stack moisture percent volume.

12.18 Concentration of the Target Compound in Stack Gas (Wet or Dry), (Section 11.2.12)

$$EGC = C_{SW} \times \text{mol weight (g/mole)}/24.06 \quad \text{Eq. 18}$$

Or

$$EGC = C_D \times MW/24.06 \quad \text{Eq. 18}$$

Where:
EGC = emission gas concentration in µg/m3 @ 20 °C,
Csw from Eq. 16
C_D = from Eq. 17
MW = target compound molecular weight (g/mole)

12.19 Canister Volume Sampled (L) in the Field from Final Sample Vacuum (Section 8.6.28 and 8.6.4)

$$V_c = P_g/101.3 \text{ kPa} \times C_v \quad \text{Eq. 19}$$

Where:
V_c = volume sampled (L)
P_g = measured canister vacuum (kPa)
C_v = canister volume (L)

12.20 Canister Volume Sampled (L) in the Field from Calibrated Orifice Flow Rate and Sample Duration (Section 8.6.28 and 8.6.4)

$$V_c = (FR_o \times T_s)/1000 \quad \text{Eq. 20}$$

Where:
FR_o = calibrated orifice flow rate (cc/min)
T_s = total sample time (min)

13.0 Method Performance

Data to support OTM-50 Method Performance to date are limited; however, EPA/ORD research, including field evaluation testing, has resulted in data that support the specified OTM-50 method performance criteria. Method performance criteria such as: MDLs and PQLs/QRLs (Table OTM-50-2), calibration bias (Table OTM-50-6), analytical precision (Table OTM-50-7), and standard stability (Table OTM-50-8) have all been investigated.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Bibliography

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17.0 Tables, Diagrams, Flowcharts and Validation Data

Table OTM-50-1. Volatile Fluorinated Compound Target List

Compound Name	CAS #	Chemical Formula
Carbon tetrafluoride	75-73-0	CF_4
Hexafluoroethane (FC-116)	76-16-4	C_2F_6
Tetrafluoroethene	116-14-3	C_2F_4
Trifluoromethane (HFC-23)	75-46-7	CHF_3
Octafluoropropane	76-19-7	C_3F_8
Difluoromethane (HFC-32)	75-10-5	CH_2F_2
Fluoromethane (HFC-41)	593-53-3	CH_3F
Pentafluoroethane (HFC-125)	354-33-6	C_2HF_5
Hexafluoropropene	116-15-4	C_3F_6
Hexafluoropropene oxide (HFPO)	428-59-1	C_3F_6O
Decafluorobutane	355-25-9	C_4F_{10}
Dodecafluoropentane	678-26-2	C_5F_{12}
Tetradecafluorohexane	355-42-0	C_6F_{14}
1H-Perfluoropentane	375-61-1	C_5HF_{11}
Hexadecafluoroheptane	335-57-9	C_7F_{16}
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether (E1)	3330-15-2	$C_5HF_{11}O$
1H-Perfluorohexane	355-37-3	C_6HF_{13}
1H-Perfluoroheptane	375-83-7	C_7HF_{15}
2H-Perfluoro-5-methyl-3,6-dioxanonane (E2)	3330-14-1	$C_8HF_{17}O_2$
1H-Perfluorooctane	335-65-9	C_8HF_{17}
Octadecafluorooctane	307-34-6	C_8F_{18}
1H-Nonafluorobutane	375-17-7	C_4HF_9
1H-Heptafluoropropane	2252-84-8	C_3HF_7
1,1,1,2-Tetrafluoroethane (HFC-134a)	811-97-2	$C_2H_2F_4$
1,1,1-Trifluoroethane (HFC-143a)	420-46-2	$C_2H_3F_3$
Chlorodifluoromethane (HCFC-22)	75-45-6	$CHClF_2$
Chlorotrifluoromethane (CFC-13)	75-72-9	CF_3Cl
Octafluorocyclobutane (FC-C318)	115-25-3	C_4F_8
Octafluorocyclopentene (FC-C1418)	559-40-0	C_5F_8
Trichloromonofluoromethane (CFC-11)	75-69-4	CCl_3F

Table OTM-50-2. Detection and Quantitative Reporting Limits

Target Compound	CAS #	Canister Concentration (ppbv)[1]	MDL (ppbv)	MDL (µg/m³)	QRL (ppbv)	QRL (µg/m³)
Carbon tetrafluoride	75-73-0	0.125	0.030	0.109	0.09	0.327
Hexafluoroethane (FC-116)[2]	76-16-4	0.0125	0.0125	0.072	0.037	0.215
Tetrafluoroethene	116-14-3	0.0125	0.011	0.044	0.033	0.132
Trifluoromethane (HFC-23)[4]	75-46-7	0.0125	0.050	0.145	0.15	0.435
Octafluoropropane[2]	76-19-7	0.0125	0.0125	0.098	0.037	0.293
Difluoromethane (HFC-32)	75-10-5	0.0125	0.016	0.034	0.048	0.102
Fluoromethane (HFC-41)	593-53-3	0.050	0.019	0.027	0.057	0.081
Pentafluoroethane (HFC-125)[2]	354-33-6	0.0125	0.0125	0.062	0.037	0.187
Hexafluoropropene[2]	116-15-4	0.0125	0.0125	0.078	0.037	0.233
Hexafluoropropene oxide (HFPO)	428-59-1	0.050	0.021	0.146	0.063	0.438
Decafluorobutane[2]	355-25-9	0.0125	0.0125	0.124	0.037	0.371
Dodecafluoropentane[3]	678-26-2	0.025	0.023	0.271	0.069	0.813
Tetradecafluorohexane	355-42-0	0.0125	0.016	0.225	0.048	0.675
1H-Perfluoropentane	375-61-1	0.0125	0.016	0.180	0.048	0.54
Hexadecafluoroheptane[2]	335-57-9	0.0125	0.0125	0.202	0.037	0.605
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether (E1)	3330-15-2	0.0125	0.014	0.165	0.042	0.495
1H-Perfluorohexane	355-37-3	0.0125	0.016	0.206	0.048	0.618
1H-Perfluoroheptane	375-83-7	0.0125	0.011	0.163	0.033	0.489
2H-Perfluoro-5-methyl-3,6-dioxanonane (E2)[2]	3330-14-1	0.0125	0.0125	0.235	0.037	0.705
1H-Perfluorooctane[2]	335-65-9	0.0125	0.0125	0.218	0.037	0.655
Octadecafluorooctane[2]	307-34-6	0.0125	0.0125	0.228	0.037	0.683
1H-Nonafluorobutane[3]	375-17-7	0.0125	0.011	0.097	0.033	0.291
1H-Heptafluoropropane	2252-84-8	0.0125	0.014	0.098	0.042	0.294
1,1,1,2-Tetrafluoroethane (HFC-134a)	811-97-2	0.0125	0.016	0.066	0.048	0.198
1,1,1-Trifluoroethane (HFC-143a)	420-46-2	0.050	0.032	0.111	0.096	0.333
Chlorodifluoromethane (HCFC-22)	75-45-6	0.0125	0.011	0.038	0.033	0.114
Chlorotrifluoromethane (CFC-13)[2]	75-72-9	0.0125	0.0125	0.054	0.037	0.163
Octafluorocyclobutane (FC-C 318)[2]	115-25-3	0.0125	0.0125	0.104	0.037	0.311
Octafluorocyclopentene (FC-C1418)[2]	559-40-0	0.0125	0.0125	0.110	0.037	0.331
Trichloromonofluoromethane (CFC-11)	75-69-4	0.0125	0.014	0.079	0.042	0.237

[1]The concentration of the canister used for MDL determination. MDLs were determined using the standard deviation of eight injections from four canisters prepared at 0.0125, 0.025, 0.050, and 0.125 ppbv (CF_4 only) multiplied by the student's t-test for 99% confidence with n-1 degrees of freedom (2.998). MDLs were determined using the 0.0125 ppbv canister unless the target compound could not be detected at that concentration.

[2]No standard deviation between replicate injections. MDL estimated at spiking level (3-5:1 signal-to-noise visual).

[3]Some, but not all, of the LBs had numerical results for the target analyte. The MDL was set to the highest LB concentration result.

[4]All LBs had numerical results for the target analyte. The MDL was calculated using the standard deviation of the LB concentrations multiplied by the student's t-test for 99% confidence with n-1 degrees of freedom (2.998) and added to the average concentration of the LB.

Table OTM-50-3. Quantifying and Qualifying Ions for Target Compounds[1]

Target Compound	CAS #	Quantifying Ion (m/z)	Qualifying Ions (m/z)
Carbon tetrafluoride	75-73-0	69	50
Hexafluoroethane (FC-116)	76-16-4	119	69
Tetrafluoroethene	116-14-3	81	100, 50
Trifluoromethane (HFC-23)	75-46-7	69	51, 31
Octafluoropropane	76-19-7	169	69, 119, 100
Difluoromethane (HFC-32)	75-10-5	51	52
Fluoromethane (HFC-41)	593-53-3	33	34
Pentafluoroethane (HFC-125)	354-33-6	51	101, 69
Hexafluoropropene	116-15-4	131	100, 150
Hexafluoropropene oxide (HFPO)	428-59-1	69	50, 81, 100
Decafluorobutane	355-25-9	119	150, 219
Dodecafluoropentane	678-26-2	69	119, 169, 131
Tetradecafluorohexane	355-42-0	69	119, 131, 169
1H-Perfluoropentane	375-61-1	69	101, 119
Hexadecafluoroheptane	335-57-9	69	119, 131, 169
Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether (E1)	3330-15-2	101	69, 169, 51
1H-Perfluorohexane	355-37-3	51	69, 101, 131
1H-Perfluoroheptane	375-83-7	51	69, 101, 131
2H-Perfluoro-5-methyl-3,6-dioxanonane (E2)	3330-14-1	169	101, 69
1H-Perfluorooctane	335-65-9	51	69, 119, 131
Octadecafluorooctane	307-34-6	69	119, 131, 219
1H-Nonafluorobutane	375-17-7	51	69, 119, 131
1H-Heptafluoropropane	2252-84-8	51	69, 100, 151
1,1,1,2-Tetrafluoroethane (HFC-134a)	811-97-2	33	83, 51
1,1,1-Trifluoroethane (HFC-143a)	420-46-2	64	84
Chlorodifluoromethane (HCFC-22)	75-45-6	51	67
Chlorotrifluoromethane (CFC-13)	75-72-9	85	87, 69
Octafluorocyclobutane (FC-C318)	115-25-3	100	131, 69
Octafluorocyclopentene (FC-C1418)	559-40-0	93	162, 143, 193
Trichloromonofluoromethane (CFC-11)	75-69-4	101	103, 105

[1.] These ions have been used previously during method development. Ions should be selected based on ion abundance, uniqueness, and lack of interference with other target compounds and internal standards.

Table OTM-50-4. Quality Control Parameters and Performance Specifications

Section	Requirement	Specification and Frequency	Acceptance Criteria	Consequences and Corrective Actions
8.6.1	Sample Train Leak Check	Before and after each test run	Zero flow from the outlet of the bypass pump.	Inspect/tighten train components/connections and retry leak check. Void any test run that doesn't pass post leak-check.
8.6.10	Sample Holding Time	Every Sample	30 days from sample collection.	Flag sample data for possible rejection.
Sampling Quality Controls (Section 9.1)				
9.1.1	Determine Sampling System Background	Represents the sampling system associated with field sample collection. One per source.	Analysis must show that any detected target compounds in the zero-air challenge sample are at response levels that are expected to be < 3 x MDL or preferably not detected.	Failure to meet these levels does not invalidate the sampling run. If > MDL, flag data. The measured target compound mass in each fraction will need to be reported and used to assess the impact on results. .
9.1.2	Field Integrity Check of Collected Samples	After each test run	Actual volume collected should be within 20% RPD of the theoretical volume.	• If the actual volume collected is >20%RPD of the theoretica1 check for leaks and void the sample. • If the actual volume is >20% RPD check the critical orifice for plugging and replace or clean as needed. Ensure sufficient volume is collected to achieve the project specific detection limits and flag the sample on the COC.
9.1.3	Laboratory Integrity Check of Collected Samples	Measure the pressure of each canister upon receipt and compare the volume collected as received to the field post-test volume.	The canister as received should be within 5% RPD of the field volume.	• If the volume as received is >5% RPD, flag the sample for potential exclusion from the data set.
Analysis Quality Control Requirements (Section 9.2)				
9.2.1	Gas Dilution Systems	Verified annually	Measured values +/-3% of calculated values based on certified concentrations.	

Section	Requirement	Specification and Frequency	Acceptance Criteria	Consequences and Corrective Actions
9.2.1.4	Dynamic Gas Dilution Systems	Calibrated annually	Calibrated against NIST traceable primary flow standards with uncertainties <=0.25%.	
9.2.1.5	Static Gas Dilution Systems	Calibrated annually	Pressure transducer(s) must have an accuracy of ± 0.1 % full scale or 0.13 kPa, whichever is smaller.	
9.2.3.1	ICAL	Analysis of a minimum of five calibration levels before sample analysis, annually or, after a failing CCV, or when changes/maintenance to the instrument affect calibration response.	Each calibration level must be calculated to be within ±20% of its true value. If using average RRF calibration, average RRF ≤ 20% RSD; Relative Retention Times (RRTs) for target peaks within 0.06 units from mean RRT.	• Check for leaks, perform maintenance, and reanalyze. • Prepare fresh standards and reanalyze ICAL. • Flag any target analytes that are manually integrated in the calibration curve.
9.2.3.2, 9.3.1	Laboratory Blank (LB)	A canister filled with humidified (50% RH) clean diluent gas. After high ICAL standard and at the beginning of each analytical sequence.	Sample analytes <3 x MDL or <50% of project-required reporting limit, whichever is higher.	• Check for instrument leaks and reanalyze. • Check instrument for contamination and reanalyze. • Prepare a fresh LB and reanalyze.
9.2.3.4	MDL Confirmation	A canister of all target VFC prepared at the MDL. Analyze after each MDL study (Annually or after significant instrument	Verify that the primary quantitation ion is detected at 3 times signal to noise and the retention time is within ±5 seconds of the initial calibration standard.	• Reprepare the MDL Confirmation standard. • Reanalyze the MDL study and repeat confirmation.

Section	Requirement	Specification and Frequency	Acceptance Criteria	Consequences and Corrective Actions
		maintenance/repair).		
9.2.3.5	Demonstration of Precision	At startup, annually, and after significant instrument maintenance/repair. Analyze seven replicate injections of a canister spiked at a midpoint of the calibration curve.	% RSD of seven replicate injections must be less than 25%.	• Check for leaks in the analytical system, repair and reanalyze. • Check for leaks in the standard preparation system.
9.2.3.6	Demonstration of Accuracy	At startup, annually, and after significant instrument maintenance/repair. Analyze seven replicate injections of a canister spiked at a midpoint of the calibration curve.	Average % recovery of seven replicates must be within ±30% of the concentration prepared in 9.2.3.5.	• Check for leaks in the analytical system, repair and reanalyze. • Check for leaks in the standard preparation system.
9.2.3.7	Lowest Calibration Concentration Confirmation	At startup, annually, or during ICAL.	The lowest calibration concentration must be ≥3x MDL. Must be within ±30% of each target compound spike concentration.	• Check for instrument leaks and reanalyze. • Prepare fresh standard and reanalyze.
9.2.2.3, 11.2.3	Internal Standard (IS) Retention Times	For each ICAL, LB, CCV, and sample	Retention time must be within +/-5 seconds of the most recent calibration.	• Check for leaks in the chromatographic system, repair and reanalyze. • Flag any sample data that does not meet IS retention time criteria.
9.3.2.4, 11.2.6	Internal Standard (IS) Responses	Certified concentrations of representative	All IS responses must be within ±40% of the average response of the ICAL or most recent calibration	• Check for leaks in the analytical system, perform maintenance and reanalyze.

Section	Requirement	Specification and Frequency	Acceptance Criteria	Consequences and Corrective Actions
		standard compounds added to each sample and standard at the same amount prior to analysis. IS compounds may be labeled but are not required to be.	check, whichever is more appropriate.	• Retune and recalibrate instrument and reanalyze. • Flag any sample results with failing IS responses.
9.3.3	Continuing Calibration Verification (CCV)	Standard in lower third of calibration range. Analyzed at the beginning of each sequence, after ten samples, and at the end of the sequence. Prepare new CCV at least every 30 days.	Recovery within ±20% of theoretical concentrations.	• Reanalyze all samples after the last passing CCV. • Check instrument for leaks and reanalyze. • Re-prep and reanalyze CCV. • Perform instrument maintenance and reanalyze. • Clean the MS source and rerun the ICAL. • Flag target analytes that do not meet ending CCV criteria.
9.3.4	Replicate Field Sample	One duplicate field sample analysis must be run in each sample sequence.	If concentrations are >3x MDL, they must be within ±25% of one another.	Flag the field sample and target analytes that did not meet acceptance criteria.
9.3.5	Canister Cleaning Batch Blank	Analyze one or more cleaned canister as an LB from a given batch of clean canisters.	Sample analytes <3 x MDL or <50% of project-required reporting limit, whichever is higher.	• Analyze other cans in batch as LBs. • Check canister cleaning system for contamination. • Reclean failed canisters.
10.8	CO_2 Bias Check	At setup and before analysis of field samples, verify that the amount of CO_2	Each target compound of interest must be recovered within ±30% of the actual standard value to be reported.	• Optimize the analytical system to reduce/eliminate bias, recalibrate, and reanalyze. • Flag any sample results generated using a system that

Section	Requirement	Specification and Frequency	Acceptance Criteria	Consequences and Corrective Actions
		present in the samples does not bias the analytical results.		exceeds the ±30 percent bias threshold.

Table OTM-50-5. Water Saturation Density at Various Temperatures

Temperature (°C)	Water Saturation Vapor Density (mg/L)[1]
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

[1]Values are generated according to the following formula (Nave, 2017): vapor density (mg/L) = 5.018 + 0.32321 * T + 8.1847×10^{-3} * T^2 + 3.1243×10^{-4} * T^3, where: T = temperature in °C.
Nave, C. R. (2017). Relative Humidity. HyperPhysics website, Department of Physics and Astronomy, Georgia State University, Atlanta, GA. Available at http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/relhum.html#c3 (accessed November 27, 2023).

Table OTM-50-6. Calibration Bias Assessment for a Seven-Point VFC Calibration[1]

Target Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
	% bias	% bias	% bias	% bias	% bias	% bias	% bias
	0.5 ppbv/ 50 ppbv CF_4	1.0 ppbv/ 100 ppbv CF_4	1.5 ppbv/ 150 ppbv CF_4	2.0 ppbv/ 200 ppbv CF_4	5.0 ppbv/ CF_4 NA	10.0 ppbv/ CF_4 NA	20.0 ppbv/ CF_4 NA
Carbon tetrafluoride	15.0%	-6.8%	-19.5%	-11.6%	NA	NA	NA
Hexafluoroethane (FC-116)	-1.9%	-11.1%	-7.4%	-1.9%	-14.0%	6.1%	-0.6%
Tetrafluoroethene	19.3%	8.2%	7.2%	9.2%	-8.4%	1.1%	-0.6%
Trifluoromethane (HFC-23)	9.8%	-13.6%	-7.9%	-6.5%	-12.2%	5.4%	-0.2%
Octafluoropropane	-31.0%	-19.9%	-10.1%	-3.7%	-8.9%	2.6%	-0.9%
Difluoromethane (HFC-32)	0.1%	-18.3%	-15.6%	-9.1%	-14.0%	5.0%	-1.2%
Fluoromethane (HFC-41)	2.7%	-5.5%	-4.2%	0.6%	3.9%	1.2%	NA
Pentafluoroethane (HFC-125)	-15.6%	-6.4%	-4.7%	0.3%	-6.2%	4.7%	1.5%
Hexafluoropropene	-25.2%	-21.1%	-11.7%	-5.0%	-9.6%	2.1%	-1.4%
Hexafluoropropene Oxide	-4.5%	-11.6%	-1.8%	-15.7%	-7.9%	3.4%	7.2%
Decafluorobutane	-15.8%	-13.8%	-17.9%	-14.3%	-5.7%	3.6%	-0.3%
Dodecafluoropentane	11.6%	14.6%	-5.3%	-3.7%	-5.1%	1.7%	-0.1%
Tetradecafluorohexane	7.8%	11.9%	-18.6%	4.8%	NA	NA	NA
1H-Perfluoropentane	21.2%	8.1%	-8.4%	5.6%	0.8%	-1.4%	0.2%
Hexadecafluoroheptane	22.4%	20.4%	5.4%	6.1%	-0.4%	0.2%	0.9%
Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether (E1)	13.9%	9.9%	-0.3%	4.3%	-1.7%	-4.7%	-0.7%
1H-Perfluorohexane	28.4%	21.3%	3.3%	5.0%	-0.7%	0.0%	0.6%
1H-Perfluoroheptane	17.4%	12.3%	-0.1%	2.7%	-0.2%	-0.4%	0.1%
2H-Pefluoro-5-methyl-3,6-dioxanonane (E2)	-12.3%	-6.2%	-9.6%	-2.1%	1.5%	1.1%	0.7%
1H-Perfluorooctane	-2.8%	0.2%	-8.2%	0.7%	0.2%	-0.8%	-0.7%
Octadecafluorooctane	23.7%	14.6%	2.8%	5.5%	0.4%	-1.7%	-0.4%
1H-Nonafluorobutane	13.0%	14.0%	-4.5%	-3.6%	-5.3%	1.8%	-0.1%

1H-Heptafluoropropane	-10.6%	0.6%	-16.7%	-12.1%	-5.9%	3.4%	-0.3%
1,1,1,2-tetrafluoroethane (HFC-134a)	-12.0%	-8.9%	-5.8%	-4.8%	-1.7%	1.2%	-0.1%
1,1,1-Trifluoroethane (HFC-143a)	29.0%	7.5%	9.2%	10.5%	-6.9%	0.6%	-0.4%
Chlorodifluoromethane (HCFC-22)	-7.4%	-3.3%	-1.9%	0.3%	-2.7%	3.4%	1.6%
Chlorotrifluoromethane (CFC-13)	22.0%	11.8%	10.4%	12.8%	-8.5%	1.4%	-0.1%
Octafluorocyclobutane (FC-C318)	-11.0%	-12.0%	-11.0%	-6.5%	-1.5%	-1.1%	-1.8%
Octafluorocyclopentene (FC-C1418)	7.5%	10.5%	-6.7%	-7.2%	-6.9%	0.8%	-1.4%
Trichloromonofluoromethane (CFC-11)	-11.7%	-5.5%	-16.5%	-12.7%	-4.7%	4.4%	1.0%

[1]Calibration bias was assessed using variable volume injections from a 20 ppbv VFC calibration standard (200 ppbv CF_4) with a single injection per calibration point. The calibration curve was fit using a quadratic equation forced through 0.

Table OTM-50-7. Relative Percent Difference (RPD) for Duplicate Analysis of VFC Standards[1]

Target Compound	0.5 ppbv/50 ppbv CF_4				1.0 ppbv/100 ppbv CF_4			
	Run 1	Run 2			Run 1	Run 2		
	ppbv	ppbv	AVG	% RPD	ppbv	ppbv	AVG	% RPD
Carbon tetrafluoride	56.57	54.77	55.67	3.2%	80.43	79.05	79.74	1.7%
Hexafluoroethane (FC-116)	0.48	0.46	0.47	4.3%	0.85	0.9	0.875	-5.7%
Tetrafluoroethene	0.59	0.57	0.58	3.4%	0.98	1.07	1.025	-8.8%
Trifluoromethane (HFC-23)	0.54	0.45	0.495	18.2%	0.87	0.88	0.875	-1.1%
Octafluoropropane	0.34	0.34	0.34	0.0%	0.83	0.91	0.87	-9.2%
Difluoromethane (HFC-32)	0.49	0.45	0.47	8.5%	0.84	0.94	0.89	-11.2%
Fluoromethane (HFC-41)	0.5	0.42	0.46	17.4%	0.9	1.03	0.965	-13.5%
Pentafluoroethane	0.41	0.42	0.415	-2.4%	0.88	0.96	0.92	-8.7%
Hexafluoropropene	0.37	0.38	0.375	-2.7%	0.82	0.90	0.86	-9.3%
Hexafluoropropene oxide	0.47	0.43	0.45	8.9%	0.85	0.99	0.92	-15.2%
Decafluorobutane	0.41	0.43	0.42	-4.8%	0.78	0.85	0.815	-8.6%
Dodecafluoropentane	0.55	0.56	0.555	-1.8%	0.96	0.98	0.97	-2.1%
Tetradecafluorohexane	0.53	0.54	0.535	-1.9%	0.82	0.79	0.805	3.7%
1H-Perfluoropentane	0.60	0.58	0.59	3.4%	1.07	1.08	1.075	-0.9%
Hexadecafluoroheptane	0.60	0.62	0.61	-3.3%	1.05	1.11	1.08	-5.6%
Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether (E1)	0.56	0.55	0.555	1.8%	0.98	0.97	0.975	1.0%
1H-Perfluorohexane	0.63	0.63	0.63	0.0%	1.05	1.09	1.07	-3.7%
1H-Perfluoroheptane	0.58	0.59	0.585	-1.7%	1.02	1.03	1.025	-1.0%
2H-Pefluoro-5-methyl-3,6-dioxanonane (E2)	0.43	0.45	0.44	-4.5%	0.86	0.97	0.915	-12.0%
1H-Perfluorooctane	0.48	0.51	0.495	-6.1%	0.93	1.04	0.985	-11.2%
Octadecafluorooctane	0.61	0.62	0.615	-1.6%	1.04	1.08	1.06	-3.8%
1H-Nonafluorobutane	0.56	0.57	0.565	-1.8%	0.97	1.00	0.985	-3.0%

Target Compound	0.5 ppbv/50 ppbv CF_4				1.0 ppbv/100 ppbv CF_4			
	Run 1	Run 2			Run 1	Run 2		
	ppbv	ppbv	AVG	% RPD	ppbv	ppbv	AVG	% RPD
1H-Heptafluoropropane	0.44	0.46	0.45	-4.4%	0.84	0.88	0.86	-4.7%
1,1,1,2-Tetrafluoroethane (HFC-134a)	0.43	0.42	0.425	2.4%	0.87	1.00	0.935	-13.9%
1,1,1-Trifluoroethane (HFC-143a)	0.63	0.59	0.61	6.6%	1.06	1.09	1.075	-2.8%
Chlorodifluoromethane (HCFC-22)	0.45	0.46	0.455	-2.2%	0.92	0.97	0.945	-5.3%
Chlorotrifluoromethane (CFC-13)	0.60	0.58	0.59	3.4%	1.05	1.11	1.08	-5.6%
Octafluorocyclobutane (FC-C318)	0.44	0.46	0.45	-4.4%	0.87	0.97	0.92	-10.9%
Octafluorocyclopentene (FC-C1418)	0.53	0.54	0.535	-1.9%	0.92	0.96	0.94	-4.3%
Trichloromonofluoromethane (CFC-11)	0.43	0.44	0.435	-2.3%	0.81	0.85	0.83	-4.8%

[1] RPDs for CF_4 were evaluated based on 20 mL injection volumes of the VFC standard while all other compounds were evaluated using 200 mL injection volumes. A lower injection volume was utilized for CF_4 due to its low breakthrough volume. Since CF_4 is present at a 10-fold higher concentration than the remaining compounds in the standard and was injected at a lower volume, the CF_4 concentration is 100-fold higher in this evaluation.

Table OTM-50-8. Volatile VFC Stability Data for the Targeted Analytes – 30 VFC Standard Mix[1]

Target Compound	Duration (weeks)							
	0	3	5	7	11	13	17	23
Carbon tetrafluoride	100%	89%	87%	105%	85%	97%	57%	54%
Hexafluoroethane (FC-116)	100%	102%	95%	88%	93%	81%	76%	78%
Tetrafluoroethene	100%	125%	116%	111%	113%	131%	93%	96%
Trifluoromethane (HFC-23)	100%	112%	109%	103%	111%	100%	98%	100%
Octafluoropropane	100%	117%	108%	108%	105%	94%	90%	94%
Difluoromethane (HFC-32)	100%	107%	103%	96%	101%	95%	89%	90%
Fluoromethane (HFC-41)	100%	103%	101%	97%	103%	95%	89%	87%
Pentafluoroethane	100%	110%	99%	99%	97%	90%	83%	86%
Hexafluoropropene	100%	113%	107%	104%	103%	170%	88%	91%
Hexafluoropropene oxide	100%	113%	113%	110%	90%	89%	78%	69%
Decafluorobutane	100%	93%	97%	98%	110%	108%	107%	104%
Dodecafluoropentane	100%	92%	99%	93%	104%	103%	99%	97%
Tetradecafluorohexane	100%	17%[2]	101%	95%	102%	99%	91%	89%
1H-Perfluoropentane	100%	21%[2]	105%	96%	116%	114%	113%	108%
Hexadecafluoroheptane	100%	92%	105%	99%	104%	100%	94%	95%
Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether (E1)	100%	104%	110%	105%	119%	116%	116%	105%
1H-Perfluorohexane	100%	103%	100%	96%	101%	96%	93%	89%
1H-Perfluoroheptane	100%	108%	101%	97%	99%	90%	89%	91%
2H-Pefluoro-5-methyl-3,6-dioxanonane (E2)	100%	101%	102%	98%	103%	101%	100%	103%
1H-Perfluorooctane	100%	96%	97%	92%	96%	97%	93%	95%
Octadecafluorooctane	100%	113%	110%	105%	106%	96%	95%	97%
1H-Nonafluorobutane	100%	100%	102%	97%	109%	111%	107%	103%
1H-Heptafluoropropane	100%	94%	105%	96%	115%	112%	109%	105%

1,1,1,2-Tetrafluoroethane (HFC-134a)	100%	113%	104%	104%	103%	96%	88%	92%
1,1,1-Trifluoroethane (HFC-143a)	100%	114%	113%	111%	108%	110%	92%	92%
Chlorodifluoromethane (HCFC-22)	100%	116%	108%	108%	105%	98%	91%	92%
Chlorotrifluoromethane (CFC-13)	100%	123%	117%	112%	112%	110%	93%	98%
Octafluorocyclobutane (FC-C 318)	100%	98%	99%	98%	105%	100%	99%	100%
Octafluorocyclopentene (FC-C 1418)	100%	100%	108%	100%	113%	115%	109%	103%
Trichloromonofluoromethane (CFC-11)	100%	90%	103%	97%	114%	115%	114%	109%

[1]The stability of the 30 components in a canister containing the VFC calibration standard was assessed over a period of 23 weeks. All compounds were present in the standard at 20 ppbv except for CF_4 (200 ppbv).

[2] Time of flight Mass Spectrometer Electronics Error.

Table OTM-50-9. BFB Tuning Check Key Ions and Abundance Criteria

Mass (*m/z*)	Ion Abundance Criteria[1]
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

[1]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.

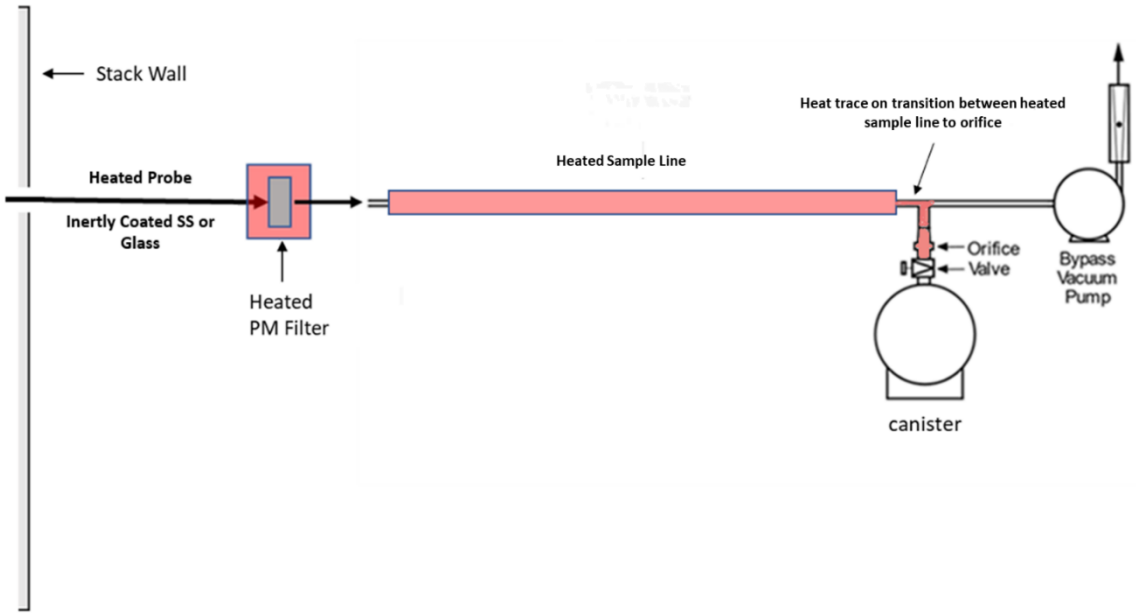

Figure OTM-50-1. Direct VFC Sampling System

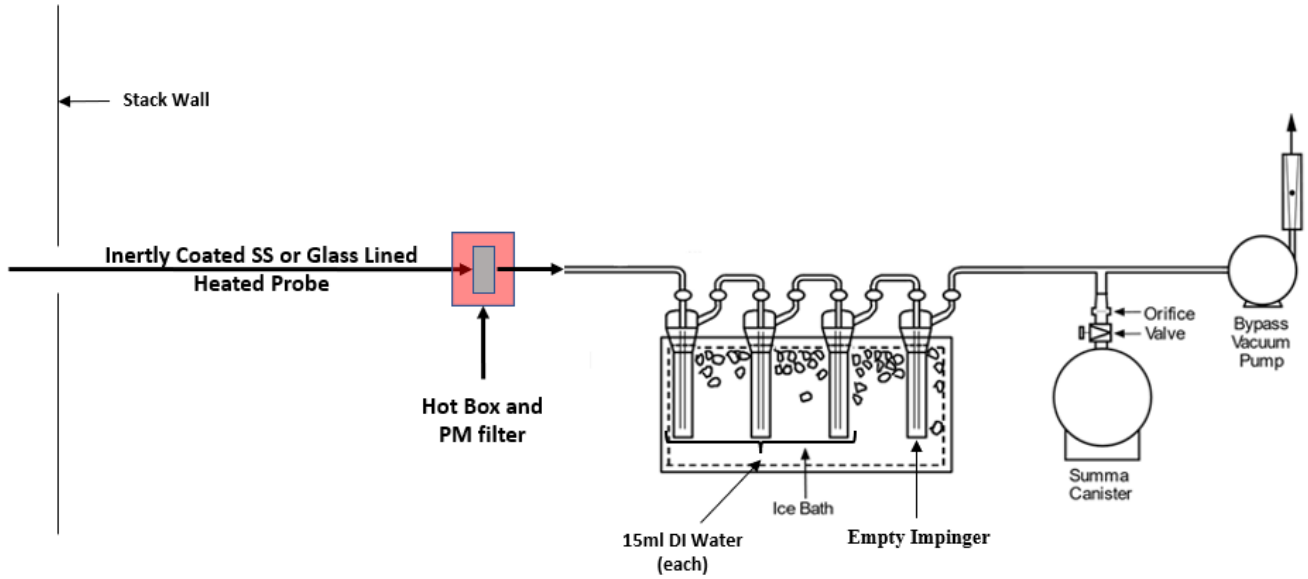

Figure OTM-50-2. VFC Canister Sampling System with Water/Acid Gas Management

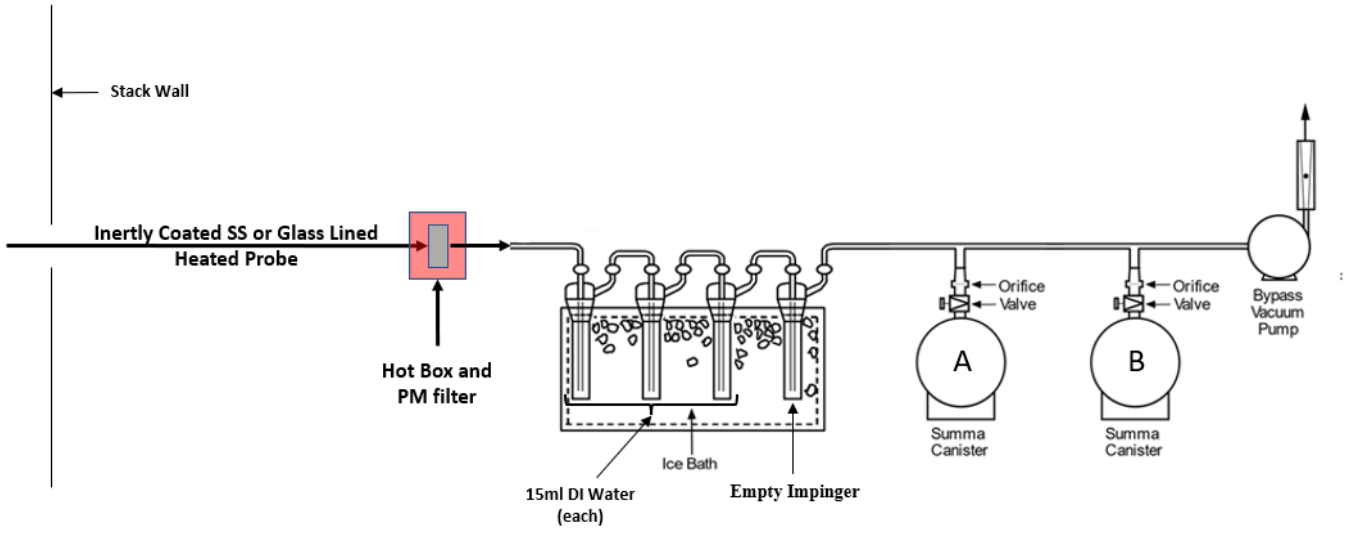

Figure OTM-50-3. VFC Canister Sampling System with Multiple Canisters

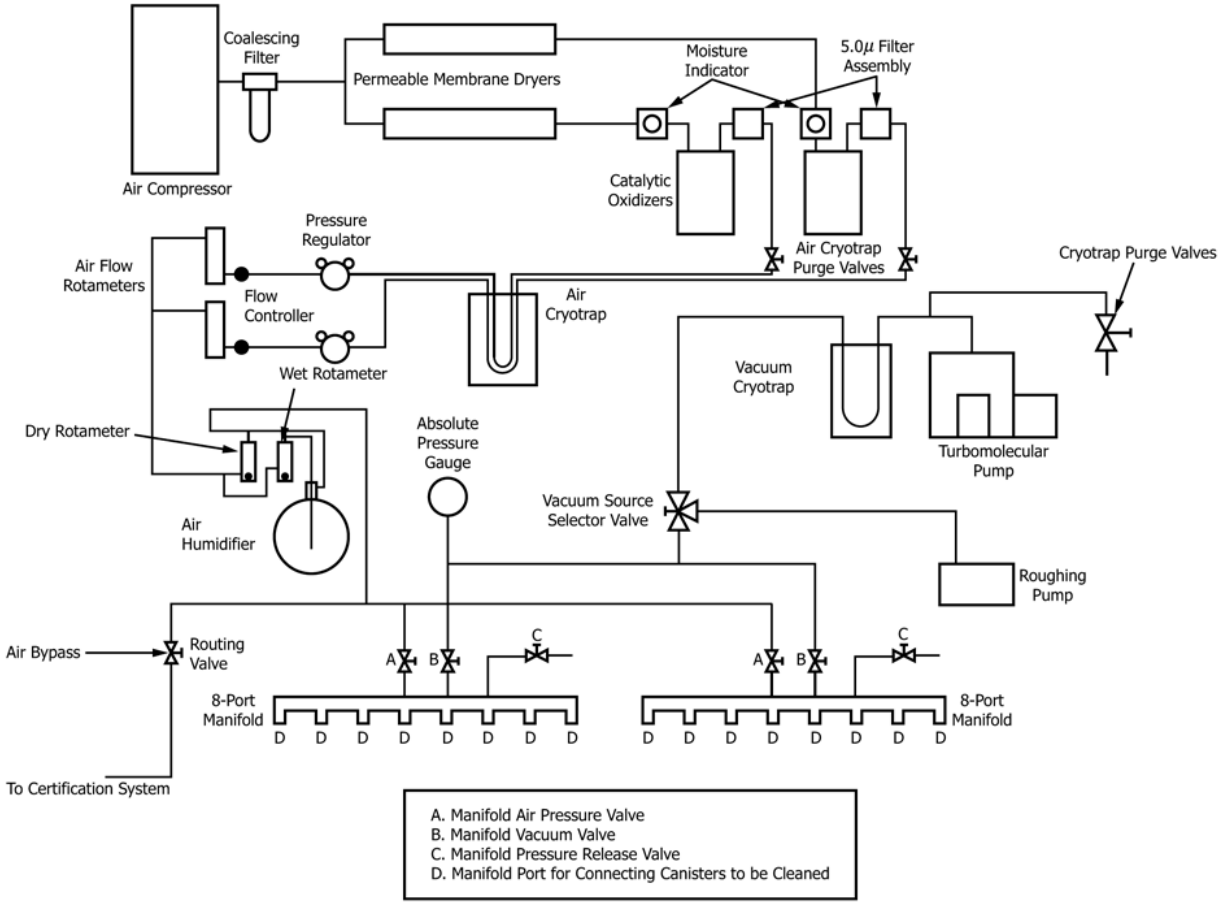

Figure OTM-50-4. Example Canister Cleaning Apparatus

PROJECT ID:

Date:

Sample Location Description:

Barometric Pressure:

Operator:

Run ID	Can ID	Sampling Date	Initial Can Pressure (in Hg)	Orifice Sampling Rate (cc/min)	Stack Temp (°C)	Probe Temp (°C)	Pre-Test Leak Check (Pass/Fail)	Pre-Test Leak Check Vacuum (in Hg)	Bypass Pump Flow (lpm)	Start Time	Stop Time	Post-Test Leak Check (Pass/Fail)	Post-Test Leak Check Vacuum (in Hg)	Final Can Pressure (in Hg)	CO_2 (%)	Volume Sampled[1] (L)	Volume Sampled[2] (L)
Traverse Pt 1																	
Traverse Pt 2																	
Traverse Pt 3																	
Run Notes:																	
Traverse Pt 1																	
Traverse Pt 2																	
Traverse Pt 3																	
Run Notes:																	
Traverse Pt 1																	
Traverse Pt 2																	
Traverse Pt 3																	
Run Notes:																	

[1] Volume sampled calculated from intial and final canister pressures

[2] Volume sampled calculated from orifice flow rate and sample duration

Figure OTM-50-5. Field Sample Data Sheet

Sampling Information						Laboratory Information				
Project:										
Location:										
Operator:										
Canister ID	**Date Sampled**	**Final Pressure**	**Volume Sampled[1]**	**Barometric Pressure***	**CO_2 Concentration**	**Date Received**	**Received Pressure**	**Volume Sampled[2]**	**Barometric Pressure***	**Date Analyzed**
Field Notes:						**Laboratory Notes:**				
Field Notes:						**Laboratory Notes:**				
Field Notes:						**Laboratory Notes:**				
Field Notes						**Laboratory Notes:**				

[1] Report sample volume determined from orifice flow rate and sample duration.

[2] Report sample volume determined from can vacuum pressures.

*** Report barometric pressure as station/absolute pressure.**

Note: Complete all fields. Please provide any other information that may aid in analysis, including estimations of elevated concentrations, potential interferences, other supporting information.

Samples relinquished by: _____ Signature and Date: _____

Samples received by: _____ Signature and Date: _____

Samples relinquished by: _____ Signature and Date: _____

Samples received by: _____ Signature and Date: _____

Figure OTM-50-6. Chain of Custody Sheet