Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-15

Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)

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1   **Acknowledgements**

1 # Disclaimer

2 This Compendium has been subjected to the Agency's peer and administrative review, and it has been
3 approved for publication as an EPA document. Mention of trade names or commercial products does
4 not constitute endorsement or recommendation for use.

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1 **Contents**

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1. Scope

1.1 This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10-1 Torr at 25°C and 760 mm Hg. Table 1 is the list of the target VOCs along with their CAS number, boiling point, vapor pressure and an indication of their membership in both the list of VOCs covered by Compendium Method TO-14A (1) and the list of VOCs in EPA's Contract Laboratory Program (CLP) document titled Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites (2).

Many of these compounds have been tested for stability in concentration when stored in specially-prepared canisters (see Section 8) under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed (3). Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with co-collected ozone or other gas phase species also account for some short term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation (4) also exist. No models are currently known to be available to estimate and characterize all these potential losses, although a number of experimental observations are referenced in Section 8. Some of the VOCs listed in Title III have short atmospheric lifetimes and may not be present except near sources.

1.2 This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10-6 or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10-6 risk concentrations, the total risk may be significantly greater.

1.3 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (see Section 8).

1.4 Use of the Compendium Method TO-15 for many of the VOCs listed in Table 1 is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how to obtain an audit standard. In certain cases a chemical similarity exists between a thoroughly tested compound and others on the Title III list. In this case, what works for one is likely to work for the

1   other in terms of making standards. However, this is not always the case and some compound standards
2   will be troublesome. The reader is referred to the Section 9.2 on standards for guidance. Calibration of
3   compounds such as formaldehyde, diazomethane, and many of the others represents a challenge.

4   **1.5** Compendium Method TO-15 should be considered for use when a subset of the 97 Title III VOCs
5   constitute the target list. Typical situations involve ambient air testing associated with the permitting
6   procedures for emission sources. In this case sampling and analysis of VOCs is performed to determine
7   the impact of dispersing source emissions in the surrounding areas. Other important applications are
8   prevalence and trend monitoring for hazardous VOCs in urban areas and risk assessments downwind of
9   industrialized or source-impacted areas.

10   **1.6** Solid adsorbents can be used in lieu of canisters for sampling of VOCs, provided the solid adsorbent
11   packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria
12   specified in Compendium Method TO-17 which specifically addresses the use of multisorbent packings.
13   The two sample collection techniques are different but become the same upon movement of the sample
14   from the collection medium (canister or multisorbent tubes) onto the sample concentrator. Sample
15   collection directly from the atmosphere by automated gas chromatographs can be used in lieu of
16   collection in canisters or on solid adsorbents.

17

2. Summary of Method

19   **2.1** The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister.
20   Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A
21   pump ventilated sampling line is used during sample collection with most commercially available
22   samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample
23   canister. A sample of air is drawn through a sampling train comprised of components that regulate the
24   rate and duration of sampling into the pre-evacuated and passivated canister.

25   **2.2** After the air sample is collected, the canister valve is closed, an identification tag is attached to the
26   canister, and the canister is transported to the laboratory for analysis.

27   **2.3** Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until
28   analysis. Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

29   **2.4** To analyze the sample, a known volume of sample is directed from the canister through a solid
30   multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator
31   during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other
32   factors. Water content of the sample can be further reduced by dry purging the concentrator with helium
33   while retaining target compounds. After the concentration and drying steps are completed, the VOCs are
34   thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on
35   a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal
36   desorption and carried onto a gas chromatographic column for separation.

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

EPA
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Environmental Protection
Agency

Method TO-15
December 2015

VOCs

1   Other water management approaches are also acceptable as long as their use does not compromise the
2   attainment of the performance criteria listed in Section 11. A listing of some commercial water
3   management systems is provided in Appendix A. One of the alternative ways to dry the sample is to
4   separate VOCs from condensate on a low temperature trap by heating and purging the trap.

5   **2.5** The analytical strategy for Compendium Method TO-15 involves using a high resolution gas
6   chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole
7   system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN
8   mode) or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the mass
9   spectrometer is based on a standard ion trap design, only a scanning mode is used (note, however, that
10   the selected ion storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for
11   individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of
12   ions corresponding to various VOCs including the intensity of primary and secondary ions. The
13   fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify
14   the compound. For any given compound, the intensity of the primary fragment is compared with the
15   system response to the primary fragment for known amounts of the compound. This establishes the
16   compound concentration that exists in the sample.

17   Mass spectrometry is considered a more definitive identification technique than single specific detectors
18   such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID),
19   or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of
20   both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce
21   the chances for misidentification. If the technique is supported by a comprehensive mass spectral
22   database and a knowledgeable operator, then the correct identification and quantification of VOCs is
23   further enhanced.

24

3. Significance

26   **3.1** Compendium Method TO-15 is significant in that it extends the Compendium Method TO-14A
27   description for using canister-based sampling and gas chromatographic analysis in the following ways:

28   • Compendium Method TO-15 incorporates a multisorbent/dry purge technique or equivalent (see
29   Appendix A) for water management thereby addressing a more extensive set of compounds (the
30   VOCs mentioned in Title III of the CAAA of 1990) than addressed by Compendium Method TO-
31   14A. Compendium Method TO-14A approach to water management alters the structure or
32   reduces the sample stream concentration of some VOCs, especially water-soluble VOCs.

33   • Compendium Method TO-15 uses the GC/MS technique as the only means to identify and
34   quantitate target compounds. The GC/MS approach provides a more scientifically-defensible
35   detection scheme which is generally more desirable than the use of single or even multiple
36   specific detectors.

37   • In addition, Compendium Method TO-15 establishes method performance criteria for acceptance
38   of data, allowing the use of alternate but equivalent sampling and analytical equipment. There are
39   several new and viable commercial approaches for water management as noted in Appendix A of
40   this method on which to base a VOC monitoring technique as well as other approaches to
41   sampling (i.e., autoGCs and solid to be acceptable alternatives for monitoring ambient VOCs.

1   •   Finally, Compendium Method TO-15 includes enhanced provisions for inherent quality control.
2   The method uses internal analytical standards and frequent verification of analytical system
3   performance to assure control of the analytical system. This more formal and better documented
4   approach to quality control guarantees a higher percentage of good data.

5   **3.2** With these features, Compendium Method TO-15 is a more general yet better defined method for
6   VOCs than Compendium Method TO-14A. As such, the method can be applied with a higher confidence
7   to reduce the uncertainty in risk assessments in environments where the hazardous volatile gases listed
8   in the Title III of the Clean Air Act Amendments of 1990 are being monitored. An emphasis on risk
9   assessments for human health and effects on the ecology is a current goal for the U.S. EPA.

10

4. Applicable Documents

12   **4.1 ASTM Standards**

13   •   Method D1356 Definitions of Terms Relating to Atmospheric Sampling and Analysis.

14   •   Method E260 Recommended Practice for General Gas Chromatography Procedures.

15   •   Method E355 Practice for Gas Chromatography Terms and Relationships.

16   •   Method D5466 Standard Test Method of Determination of Volatile Organic Compounds in
17   Atmospheres (Canister Sampling Methodology).

18   **4.2 EPA Documents**

19   •   Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, U. S.
20   Environmental Protection Agency, EPA-600/R-94-038b, May 1994.

21   •   Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in
22   Ambient Air, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.

23   •   Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air:
24   Method TO-14, Second Supplement, U. S. Environmental Protection Agency, EPA-600/4-89-018,
25   March 1989.

26   •   Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites, U. S.
27   Environmental Protection Agency, Office of Solid Waste, Washington, D.C., Draft Report, June
28   1990.

29   •   Clean Air Act Amendments of 1990, U. S. Congress, Washington, D.C., November 1990.

30

5. Definitions

32   [Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs)
33   should be consistent with ASTM Methods D1356, E260, and E355. Aside from the definitions given
34   below, all pertinent abbreviations and symbols are defined within this document at point of use.]

1   **5.1 Gauge Pressure**—pressure measured with reference to the surrounding atmospheric pressure,

2   usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric)

3   pressure.

4   **5.2 Absolute Pressure**—pressure measured with reference to absolute zero pressure, usually

5   expressed in units of kPa, or psi.

6   **5.3 Cryogen**—a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on

7   front of the analytical column. Typical cryogens are liquid nitrogen (bp -195.8°C), liquid argon (bp -

8   185.7°C), and liquid CO2 (bp -79.5°C).

9   **5.4 Dynamic Calibration**—calibration of an analytical system using calibration gas standard

10   concentrations in a form identical or very similar to the samples to be analyzed and by introducing such

11   standards into the inlet of the sampling or analytical system from a manifold through which the gas

12   standards are flowing.

13   **5.5 Dynamic Dilution**—means of preparing calibration mixtures in which standard gas(es) from

14   pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing

15   stream of calibration mixture is available at the inlet of the analytical system.

16   **5.6 MS-SCAN**—mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled

17   to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

18   **5.7 MS-SIM**—mass spectrometric mode of operation in which the GC is coupled to a MS that is

19   programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

20   **5.8 Qualitative Accuracy**—the degree of measurement accuracy required to correctly identify

21   compounds with an analytical system.

22   **5.9 Quantitative Accuracy**—the degree of measurement accuracy required to correctly measure the

23   concentration of an identified compound with an analytical system with known uncertainty.

24   **5.10 Replicate Precision**—precision determined from two canisters filled from the same air mass over

25   the same time period and determined as the absolute value of the difference between the analyses of

26   canisters divided by their average value and expressed as a percentage (see Section 11 for performance

27   criteria for replicate precision).

28   **5.11 Duplicate Precision**—precision determined from the analysis of two samples taken from the same

29   canister. The duplicate precision is determined as the absolute value of the difference between the

30   canister analyses divided by their average value and expressed as a percentage.

31   **5.12 Audit Accuracy**—the difference between the analysis of a sample provided in an audit canister and

32   the nominal value as determined by the audit authority, divided by the audit value and expressed as a

33   percentage (see Section 11 for performance criteria for audit accuracy).

34

6. Interferences and Contamination

36   **6.1** Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and

37   co-elution with other species if the compounds are not delivered to the GC column in a small volume of

38   carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing

39   trap or at the head of the gas chromatographic column, mitigates this problem.

EPA
United States
Environmental Protection
Agency

Method TO-15
December 2015

VOCs

1 **6.2** Interferences in canister samples may result from improper use or from contamination of: (1) the
2 canisters due to poor manufacturing practices, (2) the canister cleaning apparatus, and (3) the sampling
3 or analytical system. Attention to the following details will help to minimize the possibility of contamination
4 of canisters.

5 *6.2.1* Canisters should be manufactured using high quality welding and cleaning techniques, and new
6 canisters should be filled with humidified zero air and then analyzed, after "aging" for 24 hours, to
7 determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be
8 assembled of clean, high quality components and each system should be shown to be free of
9 contamination.

10 *6.2.2* Canisters should be stored in a contaminant-free location and should be capped tightly during
11 shipment to prevent leakage and minimize any compromise of the sample.

12 *6.2.3* Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-
13 gassing from the system components ahead of the trap, and solvent vapors in the laboratory account
14 for the majority of contamination problems. The analytical system must be demonstrated to be free
15 from contamination under the conditions of the analysis by running humidified zero air blanks. The
16 use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow
17 controllers with Buna-N rubber components must be avoided.

18 *6.2.4* Significant contamination of the analytical equipment can occur whenever samples containing
19 high VOC concentrations are analyzed. This in turn can result in carryover contamination in
20 subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is
21 encountered, it should be followed by an analysis of humid zero air to check for carry-over
22 contamination.

23 *6.2.5* In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents
24 should be tested to identify artifact formation (see Compendium Method TO-17 for more information
25 on artifacts).

26

7. Apparatus and Reagents

28 [Note: Compendium Method To-14A list more specific requirements for sampling and analysis apparatus
29 which may be of help in identifying options. The listings below are generic.]

30 **7.1 Sampling Apparatus**

31 [Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available
32 and have been used as part of U.S. Environmental Protection Agency's Toxic Air Monitoring Stations
33 (TAMS), Urban Air Toxic Monitoring Program (UATMP), the non-methane organic compound (NMOC)
34 sampling and analysis program, and the Photochemical Assessment Monitoring Stations (PAMS).]

35 *7.1.1 Subatmospheric Pressure* (see Figure 1, without metal bellows type pump).

36 **7.1.1.1 Sampling Inlet Line.** Stainless steel tubing to connect the sampler to the sample inlet.

37 **7.1.1.2 Sample Canister.** Leak-free stainless steel pressure vessels of desired volume (e.g., 6
38 L), with valve and specially prepared interior surfaces (see Appendix B for a listing of known
39 manufacturers/resellers of canisters).

EPA
United States
Environmental Protection
Agency

Method TO-15
December 2015

VOCs

7.1.1.3 Stainless Steel Vacuum/Pressure Gauges. Two types are required, one capable of measuring vacuum (–100 to 0 kPa or 0 to - 30 in Hg) and pressure (0–206 kPa or 0–30 psig) in the sampling system and a second type (for checking the vacuum of canisters during cleaning) capable of measuring at 0.05 mm Hg (see Appendix B) within 20%. Gauges should be tested clean and leak tight.

7.1.1.4 Electronic Mass Flow Controller. Capable of maintaining a constant flow rate (± 10%) over a sampling period of up to 24 hours and under conditions of changing temperature (20–40°C) and humidity.

7.1.1.5 Particulate Matter Filter. 2-μm sintered stainless steel in-line filter.

7.1.1.6 Electronic Timer. For unattended sample collection.

7.1.1.7 Solenoid Valve. Electrically operated, bi-stable solenoid valve with Viton® seat and O-rings. A Skinner Magnelatch valve is used for purposes of illustration in the text (see Figure 2).

7.1.1.8 Chromatographic Grade Stainless Steel Tubing and Fittings. For interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel or equivalent.

7.1.1.9 Thermostatically Controlled Heater. To maintain above ambient temperature inside insulated sampler enclosure.

7.1.1.10 Heater Thermostat. Automatically regulates heater temperature.

7.1.1.11 Fan. For cooling sampling system.

7.1.1.12 Fan Thermostat. Automatically regulates fan operation.

7.1.1.13 Maximum-Minimum Thermometer. Records highest and lowest temperatures during sampling period.

7.1.1.14 Stainless Steel Shut-off Valve. Leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary Vacuum Pump. Continuously draws air through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted.

[Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.]

7.1.1.16 Elapsed Time Meter. Measures duration of sampling.

7.1.1.17 Optional Fixed Orifice, Capillary, or Adjustable Micrometering Valve. May be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (see Figure 1 with metal bellows type pump and Figure 3).

7.1.2.1 Sample Pump. Stainless steel, metal bellows type, capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

1   [Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon
2   Graduate Institute of Science and Technology, 20000 N.W. Walker Rd., Beaverton, Oregon
3   97006, 503-690-1077, and is illustrated in Figure 3. This flow system uses, in order, a pump, a
4   mechanical flow regulator, and a mechanical compensation flow restrictive device. In this
5   configuration the pump is purged with a large sample flow, thereby eliminating the need for an
6   auxiliary vacuum pump to flush the sample inlet.]

7   **7.1.2.2 Other Supporting Materials.** All other components of the pressurized sampling system
8   are similar to components discussed in Sections 7.1.1.1 through 7.1.1.17.

9   **7.2 Analytical Apparatus**

10   *7.2.1 Sampling/Concentrator System* (many commercial alternatives are available).

11   **7.2.1.1 Electronic Mass Flow Controllers.** Used to maintain constant flow (for purge gas, carrier
12   gas and sample gas) and to provide an analog output to monitor flow anomalies.

13   **7.2.1.2 Vacuum Pump.** General purpose laboratory pump, capable of reducing the downstream
14   pressure of the flow controller to provide the pressure differential necessary to maintain controlled
15   flow rates of sample air.

16   **7.2.1.3 Stainless Steel Tubing and Stainless Steel Fittings.** Coated with fused silica to
17   minimize active adsorption sites.

18   **7.2.1.4 Stainless Steel Cylinder Pressure Regulators.** Standard, two-stage cylinder regulators
19   with pressure gauges.

20   **7.2.1.5 Gas Purifiers.** Used to remove organic impurities and moisture from gas streams.

21   **7.2.1.6 Six-port Gas Chromatographic Valve.** For routing sample and carrier gas flows.

22   **7.2.1.7 Multisorbent Concentrator.** Solid adsorbent packing with various retentive properties for
23   adsorbing trace gases are commercially available from several sources. The packing contains
24   more than one type of adsorbent packed in series.

25   *7.2.1.7.1* A pre-packed adsorbent trap (Supelco 2-0321) containing 200 mg Carbopack B
26   (60/80 mesh) and 50 mg Carbosieve S-III (60/80 mesh) has been found to retain VOCs and
27   allow some water vapor to pass through (6). The addition of a dry purging step allows for
28   further water removal from the adsorbent trap. The steps constituting the dry purge technique
29   that are normally used with multisorbent traps are illustrated in Figure 4. The optimum
30   trapping and dry purging procedure for the Supelco trap consists of a sample volume of 320
31   mL and a dry nitrogen purge of 1300 mL. Sample trapping and drying is carried out at 25°C.
32   The trap is back-flushed with helium and heated to 220°C to transfer material onto the GC
33   column. A trap bake-out at 260°C for 5 minutes is conducted after each run.

34   *7.2.1.7.2* An example of the effectiveness of dry purging is shown in Figure 5. The
35   multisorbent used in this case is Tenax/Ambersorb 340/Charcoal (7). Approximately 20% of
36   the initial water content in the sample remains after sampling 500 mL of air. The detector
37   response to water vapor (hydrogen atoms detected by atomic emission detection) is plotted
38   versus purge gas volume. Additional water reduction by a factor of 8 is indicated at
39   temperatures of 45°C or higher. Still further water reduction is possible using a two-stage
40   concentration/dryer system.

1   **7.2.1.8 Cryogenic Concentrator.** Complete units are commercially available from several vendor
2   sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the
3   concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the
4   separation of compounds on the gas chromatographic column.

5   *7.2.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System.*

6   **7.2.2.1 Gas Chromatograph.** The gas chromatographic (GC) system must be capable of
7   temperature programming. The column oven can be cooled to subambient temperature (e.g., -
8   50°C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic
9   compounds. In other designs, the rate of release of compounds from the focusing trap in a two
10   stage system obviates the need for retrapping of compounds on the column. The system must
11   include or be interfaced to a concentrator and have all required accessories including analytical
12   columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper
13   tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber
14   components must not be used.

15   **7.2.2.2 Chromatographic Columns.** 100% methyl silicone or 5% phenyl, 95% methyl silicone
16   fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for
17   separation of many of the possible subsets of target compounds involving nonpolar compounds.
18   However, considering the diversity of the target list, the choice is left to the operator subject to the
19   performance standards given in Section 11.

20   **7.2.2.3 Mass Spectrometer.** Either a linear quadrupole or ion trap mass spectrometer can be
21   used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70
22   volts (nominal) electron energy in the electron impact ionization mode, and producing a mass
23   spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of
24   p-bromofluorobenzene (BFB) is analyzed.

25   *7.2.2.3.1 Linear Quadrupole Technology.* A simplified diagram of the heart of the
26   quadrupole mass spectrometer is shown in Figure 6. The quadrupole consists of a parallel
27   set of four rod electrodes mounted in a square configuration. The field within the analyzer is
28   created by coupling opposite pairs of rods together and applying radiofrequency (RF) and
29   direct current (DC) potentials between the pairs of rods. Ions created in the ion source from
30   the reaction of column eluates with electrons from the electron source are moved through the
31   parallel array of rods under the influence of the generated field. Ions which are successfully
32   transmitted through the quadrupole are said to possess stable trajectories and are
33   subsequently recorded with the detection system. When the DC potential is zero, a wide
34   band of m/z values is transmitted through the quadrupole. This "RF only" mode is referred to
35   as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens
36   analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A
37   mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio
38   and a constant drive frequency or by scanning the frequency and holding the DC and RF
39   constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion
40   source actually reach the detector.

41   *7.2.2.3.2 Ion Trap Technology.* An ion-trap mass spectrometer consists of a chamber
42   formed between two metal surfaces in the shape of a hyperboloid of one sheet (ring
43   electrode) and a hyperboloid of two sheets (the two end-cap electrodes). Ions are created

within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) are applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r, from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z, along the ion traps axis), and if the field were static the ions would eventually strike an electrode. However, in an RF field the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. A diagram of a typical ion trap is illustrated in Figure 7. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable. The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

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

7.2.2.5 Data System. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of sample spectra with reference library spectra. The National Institute of Standards and Technology (NIST) or Wiley Libraries or equivalent are recommended as reference libraries.

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

7.3 Calibration System and Manifold Apparatus (see Figure 8)

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

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

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

7.3.4 Teflon Filter(s). 47-mm Teflon® filter for particulate collection.

7.4 Reagents

7.4.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures. Best source (see Section 9).

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

7.4.3 Liquid Nitrogen or Liquid Carbon Dioxide. Used to cool secondary trap.

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

8. Collection of Samples in Canisters

8.1 Introduction

8.1.1 Canister samplers, sampling procedures, and canister cleaning procedures have not changed very much from the description given in the original Compendium Method TO-14. Much of the material in this section is therefore simply a restatement of the material given in Compendium Method TO-14, repeated here in order to have all the relevant information in one place.

8.1.2 Recent notable additions to the canister technology has been in the application of canister-based systems for example, to microenvironmental monitoring (8), the capture of breath samples (9), and sector sampling to identify emission sources of VOCs (10).

8.1.3 EPA has also sponsored the development of a mathematical model to predict the storage stability of arbitrary mixtures of trace gases in humidified air (3), and the investigation of the SilcoSteel™ process of coating the canister interior with a film of fused silica to reduce surface activity (11). A recent summary of storage stability data for VOCs in canisters is given in the open literature (5).

8.2 Sampling System Description

8.2.1 Subatmospheric Pressure Sampling [see Figure 1 (without metal bellows type pump)].

8.2.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg (see Appendix C for discussion of evacuation pressure). When the canister is opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-weighted- average (TWA) samples (duration of 1-24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

8.2.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

8.2.2 Pressurized Sampling [see Figure 1 (with metal bellows type pump)].

8.2.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 101-202 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 mL/min for 24 hours to achieve a final pressure of 144 kPa (21 psig).

8.2.2.2 In pressurized canister sampling, a metal bellows type pump draws in air from the sampling manifold to fill and pressurize the sample canister.

8.2.3 All Samplers.

8.2.3.1 A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by:

$$F = \frac{P \times V}{T \times 60}$$

where:

F = flow rate, mL/min.

P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{kPa\ gauge}{101.2} + 1$$

V = volume of the canister, mL.

T = sample period, hours.

For example, if a 6-L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = \frac{2 \times 6000}{24 \times 60} = 8.3\ mL/min$$

8.2.3.2 For automatic operation, the timer is designed to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and to close the valve when stopping the pump.

8.2.3.3 The use of the Skinner Magnelatch valve (see Figure 2) avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton® valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 2(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better

1 circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure
2 2(b).

3 **8.2.3.4** The connecting lines between the sample inlet and the canister should be as short as
4 possible to minimize their volume. The flow rate into the canister should remain relatively
5 constant over the entire sampling period.

6 **8.2.3.5** As an option, a second electronic timer may be used to start the auxiliary pump several
7 hours prior to the sampling period to flush and condition the inlet line.

8 **8.2.3.6** Prior to field use, each sampling system must pass a humid zero air certification (see
9 Section 8.4.3). All plumbing should be checked carefully for leaks. The canisters must also pass a
10 humid zero air certification before use (see Section 8.4.1).

11 **8.3 Sampling Procedure**

12 ***8.3.1*** The sample canister should be cleaned and tested according to the procedure in Section 8.4.1.

13 ***8.3.2*** A sample collection system is assembled as shown in Figures 1 and 3 and must be cleaned
14 according to the procedure outlined in Sections 8.4.2 and 8.4.4.

15 [Note: The sampling system should be contained in an appropriate enclosure.]

16 ***8.3.3*** Prior to locating the sampling system, the user may want to perform "screening analyses" using
17 a portable GC system, as outlined in Appendix B of Compendium Method TO-14A, to determine
18 potential volatile organics present and potential "hot spots." The information gathered from the
19 portable GC screening analysis would be used in developing a monitoring protocol, which includes
20 the sampling system location, based upon the "screening analysis" results.

21 ***8.3.4*** After "screening analysis," the sampling system is located. Temperatures of ambient air and
22 sampler box interior are recorded on the canister sampling field test data sheet (FTDS), as
23 documented in Figure 9.

24 [Note: The following discussion is related to Figure 1]

25 ***8.3.5*** To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system.

26 [Note: For a subatmospheric sampler, a flow meter and practice canister are needed. For the pump-
27 driven system, the practice canister is not needed, as the flow can be measured at the outlet of the
28 system.]

29 A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The
30 canister is opened. The sampler is turned on and the reading of the certified mass flow meter is
31 compared to the sampler mass flow controller. The values should agree within ±10%. If not, the
32 sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be
33 investigated and corrected.

34 [Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the
35 zero reading when reading or adjusting the sampler flow rate to compensate for any zero drift.]

36 After 2 minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the
37 certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 mL/min for 24 hr, 7.0
38 mL/min for 12 hr). Record final flow under "CANISTER FLOW RATE" on the FTDS.

39

1   *8.3.6* The sampler is turned off and the elapsed time meter is reset to 000.0.

2   [Note: Whenever the sampler is turned off, wait at least 30 seconds to turn the sampler back on.]

3   *8.3.7* The "practice" canister and certified mass flow meter are disconnected and a clean certified
4   (see Section 8.4.1) canister is attached to the system.

5   *8.3.8* The canister valve and vacuum/pressure gauge valve are opened.

6   *8.3.9* Pressure/vacuum in the canister is recorded on the canister FTDS (see Figure 9) as indicated
7   by the sampler vacuum/pressure gauge.

8   *8.3.10* The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset
9   to current temperature. Time of day and elapsed time meter readings are recorded on the canister
10   FTDS.

11   *8.3.11* The electronic timer is set to start and stop the sampling period at the appropriate times.
12   Sampling starts and stops by the programmed electronic timer.

13   *8.3.12* After the desired sampling period, the maximum, minimum, current interior temperature and
14   current ambient temperature are recorded on the FTDS. The current reading from the flow controller
15   is recorded.

16   *8.3.13* At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly
17   opened and closed and the pressure/vacuum is recorded on the FTDS. Pressure should be close to
18   desired pressure.

19   [Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the
20   field final pressure check is performed, the sampling period may be suspect. This information should
21   be noted on the sampling field data sheet.]

22   Time of day and elapsed time meter readings are also recorded.

23   *8.3.14* The canister valve is closed. The sampling line is disconnected from the canister and the
24   canister is removed from the system. For a subatmospheric system, a certified mass flow meter is
25   once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is
26   attached to the Magnelatch valve of the sampling system. The final flow rate is recorded on the
27   canister FTDS (see Figure 9).

28   [Note: For a pressurized system, the final flow may be measured directly.]

29   The sampler is turned off.

30   *8.3.15* An identification tag is attached to the canister. Canister serial number, sample number,
31   location, and date, as a minimum, are recorded on the tag. The canister is routinely transported back
32   to the analytical laboratory with other canisters in a canister shipping case.

33   **8.4 Cleaning and Certification Program**

34   *8.4.1 Canister Cleaning and Certification.*

35   **8.4.1.1** All canisters must be clean and free of any contaminants before sample collection.

36   **8.4.1.2** All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with
37   zero air.

38   [Note: The canister cleaning system in Figure 10 can be used for this task.]

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

8.4.1.3 A canister cleaning system may be assembled as illustrated in Figure 10. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to <0.05 mm Hg (see Appendix B) for at least 1 hour.

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

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

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

8.4.1.5 The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.4.1.3 through 8.4.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

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

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

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

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

Once heated, the canisters are evacuated to <0.05 mm Hg (see Appendix B) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with

humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to <0.05 mm Hg (see Appendix B) and remain in the evacuated state until used. As noted in Section 8.4.1.7, reevacuation can occur just prior to the next use.

8.4.2 Cleaning Sampling System Components.

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

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

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

8.4.3 Zero Air Certification.

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

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

8.4.3.2 The calibration system and manifold are assembled, as illustrated in Figure 8. The sampler (without an evacuated gas canister) is connected to the manifold and the zero air cylinder is activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8(b)].

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

[Note: The exit of the sampling system (without the canister) replaces the canister in Figure 11.]

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocused on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocused prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 10) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms (using an FID) of a certified sampler and contaminated sampler are illustrated in Figures 12(a) and 12(b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.4.4.

EPA
United States
Environmental Protection
Agency

Method TO-15
December 2015

VOCs

8.4.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System.

8.4.4.1 Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

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

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

8.4.4.4 For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system as illustrated in Figure 8. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

8.4.4.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(b).

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

8.4.4.7 Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system [Figure 8(a)] to provide reference concentrations of generated VOCs.

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

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

8.4.5 Sampler System Certification without Compressed Gas Cylinder Standards.

8.4.5.1 Not all the gases on the Title III list are available/compatible with compressed gas standards. In these cases sampler certification must be approached by different means.

8.4.5.2 Definitive guidance is not currently available in these cases; however, Section 9.2 lists several ways to generate gas standards. In general, Compendium Method TO-14A compounds (see Table 1) are available commercially as compressed gas standards.

9. GC/MS Analysis of Volatiles from Canisters

9.1 Introduction

9.1.1 The analysis of canister samples is accomplished with a GC/MS system. Fused silica capillary columns are used to achieve high temporal resolution of target compounds. Linear quadrupole or ion trap mass spectrometers are employed for compound detection. The heart of the system is composed of the sample inlet concentrating device that is needed to increase sample loading into a detectable range. Two examples of concentrating systems are discussed. Other approaches are

EPA
United States
Environmental Protection
Agency

Method TO-15
December 2015

VOCs

acceptable as long as they are compatible with achieving the system performance criteria given in Section 11.

9.1.2 With the first technique, a whole air sample from the canister is passed through a multisorbent packing (including single adsorbent packings) contained within a metal or glass tube maintained at or above the surrounding air temperature. Depending on the water retention properties of the packing, some or most of the water vapor passes completely through the trap during sampling. Additional drying of the sample is accomplished after the sample concentration is completed by forward purging the trap with clean, dry helium or another inert gas (air is not used). The sample is then thermally desorbed from the packing and backflushed from the trap onto a gas chromatographic column. In some systems a "refocusing" trap is placed between the primary trap and the gas chromatographic column. The specific system design downstream of the primary trap depends on technical factors such as the rate of thermal desorption and sampled volume, but the objective in most cases is to enhance chromatographic resolution of the individual sample components before detection on a mass spectrometer.

9.1.3 Sample drying strategies depend on the target list of compounds. For some target compound lists, the multisorbent packing of the concentrator can be selected from hydrophobic adsorbents which allow a high percentage of water vapor in the sample to pass through the concentrator during sampling and without significant loss of the target compounds. However, if very volatile organic compounds are on the target list, the adsorbents required for their retention may also strongly retain water vapor and a more lengthy dry purge is necessary prior to analysis.

9.1.4 With the second technique, a whole air sample is passed through a concentrator where the VOCs are condensed on a reduced temperature surface (cold trap). Subsequently, the condensed gases are thermally desorbed and backflushed from the trap with an inert gas onto a gas chromatographic column. This concentration technique is similar to that discussed in Compendium Method TO-14, although a membrane dryer is not used. The sample size is reduced in volume to limit the amount of water vapor that is also collected (100 mL or less may be necessary). The attendant reduction in sensitivity is offset by enhancing the sensitivity of detection, for example by using an ion trap detector.

9.2 Preparation of Standards

9.2.1 Introduction.

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

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

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

1   *9.2.2 Preparing Working Standards.*

2   **9.2.2.1 Instrument Performance Check Standard.** Prepare a standard solution of BFB in
3   humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the
4   optimized concentration parameters.

5   **9.2.2.2 Calibration Standards.** Prepare five working calibration standards in humidified zero air
6   at a concentration which will allow collection at the 2, 5, 10, 20, and 50 ppbv level for each
7   component under the optimized concentration parameters.

8   **9.2.2.3 Internal Standard Spiking Mixture.** Prepare an internal spiking mixture containing
9   bromo- chloromethane, chlorobenzene-d5, and 1,4-difluorobenzene at 10 ppmv each in
10   humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture
11   spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is
12   introduced into the trap during the collection time for all calibration, blank, and sample analyses
13   using the apparatus shown in Figure 13 or by equivalent means. The volume of internal standard
14   spiking mixture added for each analysis must be the same from run to run.

15   *9.2.3 Standard Preparation by Dynamic Dilution Technique.*

16   **9.2.3.1** Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s)
17   containing the gas calibration stock standards with humidified zero air using mass flow controllers
18   and a calibration manifold. The working standard may be delivered from the manifold to a clean,
19   evacuated canister using a pump and mass flow controller.

20   **9.2.3.2** Alternatively, the analytical system may be calibrated by sampling directly from the
21   manifold if the flow rates are optimized to provide the desired amount of calibration standards.
22   However, the use of the canister as a reservoir prior to introduction into the concentration system
23   resembles the procedure normally used to collect samples and is preferred. Flow rates of the
24   dilution air and cylinder standards (all expressed in the same units) are measured using a bubble
25   meter or calibrated electronic flow measuring device, and the concentrations of target compounds
26   in the manifold are then calculated using the dilution ratio and the original concentration of each
27   compound.

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

29   **9.2.3.3** Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of
30   humid air provides a nominal 10 ppbv mixture, as calculated below:

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

32   *9.2.4 Standard Preparation by Static Dilution Bottle Technique*

33   [Note: Standards may be prepared in canisters by spiking the canister with a mixture of components
34   prepared in a static dilution bottle (12). This technique is used specifically for liquid standards.]

35   **9.2.4.1** The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to
36   accept a Mininert septum cap, is determined by weighing the amount of water required to
37   completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in
38   grams is taken as the volume of the flask in milliliters.

EPA
United States
Environmental Protection
Agency

Method TO-15
December 2015

VOCs

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

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

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

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

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

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

$$\text{Concentration, mg/L} = \frac{(V_a)(d)}{V_f}$$

where:

V_a = Volume of liquid neat standard injected into the flask, μL.

d = Density of the liquid neat standard, mg/μL.

V_f = Volume of the flask, L.

9.2.4.8 To obtain concentrations in ppbv, the equation given in Section 9.2.5.7 can be used.

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

9.2.5 Standard Preparation Procedure in High Pressure Cylinders

[Note: Standards may be prepared in high pressure cylinders (13). A modified summary of the procedure is provided below.]

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

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

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

1   **9.2.5.4** The cylinder is pressurized to 1000 psig with zero nitrogen.

2   [Note: User should read all SOPs associated with generating standards in high pressure
3   cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.]

4   **9.2.5.5** The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of
5   aliquots into the GC system.

6   **9.2.5.6** If the neat standard is a gas, the cylinder concentration is determined using the following
7   equation:

8
$$\text{Concentration, ppbv} = \frac{\text{Volume}_{standard}}{\text{Volume}_{dilution\ gas}} \times 10^9$$

9   [Note: Both values must be expressed in the same units.]

10   **9.2.5.7** If the neat standard is a liquid, the gaseous concentration can be determined using the
11   following equations:

12
$$V = \frac{nRT}{P}$$

13   and

14
$$n = \frac{(mL)(d)}{MW}$$

15   where:

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

18   n = Moles.

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

20   T = 298°K (standard temperature).

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

22   mL = Volume of liquid injected, mL.

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

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

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

27   *9.2.6 Standard Preparation by Water Methods.*

28   [Note: Standards may be prepared by a water purge and trap method (14) and summarized as
29   follows].

30   **9.2.6.1** A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1
31   atm) with zero grade air.

32   **9.2.6.2** The air gauge is removed from the canister and the sparging vessel is connected to the
33   canister with the short length of 1/16 in. stainless steel tubing.

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

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

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

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

9.2.6.6 The canister is allowed to equilibrate overnight before use.

9.2.6.7 A schematic of this approach is shown in Figure 14.

9.2.7 Preparation of Standards by Permeation Tubes.

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

9.2.7.2 The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of over 250 compounds. Some commercial suppliers of permeation tube equipment are listed in Appendix D.

9.2.8 Storage of Standards.

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

9.2.8.2 It is imperative that a storage logbook be kept to document storage time.

10. GC/MS Operating Conditions

10.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. The reader is referred to Tables 1 and 2 of Compendium Method TO-17 for guidance on selection of sorbents. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature (15). Oven temperature programming starts above ambient.

1   *10.1.1 Sample Collection Conditions*

Cryogenic Trap		Adsorbent Trap	
Set point	-150°C	Set point	27°C
Sample volume	- up to 100 mL	Sample volume	- up to 1,000 mL
Carrier gas purge flow	- none	Carrier gas purge flow	- selectable

2

3   [Note: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume
4   to be used. Other preconcentration systems may be used provided performance standards (see
5   Section 11) are realized.]

6   *10.1.2 Desorption Conditions*

Cryogenic Trap		Adsorbent Trap	
Desorb Temperature	120°C	Desorb Temperature	Variable
Desorb Flow Rate	~ 3 mL/min He	Desorb Flow Rate	~ 3 mL/min He
Desorb Time	<60 sec	Desorb Time	<60 sec

7

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

10   *10.1.3 Trap Reconditioning Conditions.*

Cryogenic Trap		Adsorbent Trap	
Initial bakeout Variable (24hrs)	120°C (24 hrs)	Initial bakeout	Variable
After each run	120°C (5 min)	After each run	Variable (5 min)

11

12   **10.2 GC/MS System**

13   *10.2.1* Optimize GC conditions for compound separation and sensitivity. Baseline separation of
14   benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of
15   acceptable chromatographic performance.

16   *10.2.2* The following are the recommended gas chromatographic analytical conditions when using a
17   50-meter by 0.3-mm I.D., 1 µm film thickness fused silica column with refocusing on the column.

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

18

19

1   *10.2.3* The following are the recommended mass spectrometer conditions:

Item	Condition
Electron Energy:	70 Volts (nominal)
Mass Range:	35-300 amu [the choice of 35 amu excludes the detection of some target compounds such as methanol and formaldehyde, and the quantitation of others such as ethylene oxide, ethyl carbamate, etc. (see Table 2). Lowering the mass range and using special programming features available on modern gas chromatographs will be necessary in these cases, but are not considered here.
Scan Time:	To give at least 10 scans per peak, not to exceed 1 second per scan.

2

3   A schematic for a typical GC/MS analytical system is illustrated in Figure 15.

4   **10.3 Analytical Sequence**

5   *10.3.1 Introduction.* The recommended GC/MS analytical sequence for samples during each 24-
6   hour time period is as follows:

7   • Perform instrument performance check using bromofluorobenzene (BFB).

8   • Initiate multi-point calibration or daily calibration checks.

9   • Perform a laboratory method blank.

10   • Complete this sequence for analysis of ≤ 20 field samples.

11   **10.4 Instrument Performance Check**

12   *10.4.1 Summary.* It is necessary to establish that a given GC/MS meets tuning and standard mass
13   spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up
14   according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS
15   system are then verified by the analysis of the instrument performance check standard,
16   bromofluorobenzene (BFB).

17   *10.4.2 Frequency.* Prior to the analyses of any samples, blanks, or calibration standards, the
18   Laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for
19   the instrument performance check standard containing BFB. The instrument performance check
20   solution must be analyzed initially and once per 24-hour time period of operation.

21   The 24-hour time period for GC/MS instrument performance check and standards calibration (initial
22   calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory
23   records as documentation of a compliance tune.

24   *10.4.3 Procedure.* The analysis of the instrument performance check standard is performed by
25   trapping 50 ng of BFB under the optimized preconcentration parameters. The BFB is introduced from
26   a cylinder into the GC/MS via a sample loop valve injection system similar to that shown in Figure 13.

27   The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex
28   scan and the scans immediately preceding and following the apex) are acquired and averaged.
29   Background subtraction is conducted using a single scan prior to the elution of BFB.

30   *10.4.4 Technical Acceptance Criteria.* Prior to the analysis of any samples, blanks, or calibration
31   standards, the analyst must establish that the GC/MS system meets the mass spectral ion
32   abundance criteria for the instrument performance check standard as specified in Table 3.

1   *10.4.5 Corrective Action.* If the BFB acceptance criteria are not met, the MS must be retuned. It may
2   be necessary to clean the ion source, or quadrupoles, or take other necessary actions to achieve the
3   acceptance criteria.

4   *10.4.6 Documentation.* Results of the BFB tuning are to be recorded and maintained as part of the
5   instrumentation log.

6   **10.5 Initial Calibration**

7   *10.5.1 Summary.* Prior to the analysis of samples and blanks but after the instrument performance
8   check standard criteria have been met, each GC/MS system must be calibrated at five concentrations
9   that span the monitoring range of interest in an initial calibration sequence to determine instrument
10 sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of
11 interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv.

12 One of the calibration points from the initial calibration curve must be at the same concentration as
13 the daily calibration standard (e.g., 10 ppbv).

14 *10.5.2 Frequency.* Each GC/MS system must be recalibrated following corrective action (e.g., ion
15 source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration
16 criteria or if the daily calibration acceptance criteria have not been met.

17 If time remains in the 24-hour time period after meeting the acceptance criteria for the initial
18 calibration, samples may be analyzed.

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

22 *10.5.3 Procedure.* Verify that the GC/MS system meets the instrument performance criteria in
23 Section 10.4.

24 The GC must be operated using temperature and flow rate parameters equivalent to those in Section
25 10.2.2. Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use
26 one of the standards preparation techniques described under Section 9.2 or equivalent.

27 A minimum of five concentration levels are needed to determine the instrument sensitivity and
28 linearity. One of the calibration levels should be near the detection level for the compounds of
29 interest. The calibration range should be chosen so that linear results are obtained as defined in
30 Sections 10.5.1 and 10.5.5.

31 Quantitation ions for the target compounds are shown in Table 2. The primary ion should be used
32 unless interferences are present, in which case a secondary ion is used.

33 *10.5.4 Calculations.*

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

36   **10.5.4.1 Relative Response Factor (wherRRF).** Calculate the relative response factors for each
37   target compound relative to the appropriate internal standard (i.e., standard with the nearest
38   retention time) using the following equation:

1

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

2 where:

3   RRF = Relative response factor.

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

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

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

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

8 [Note: The equation above is valid under the condition that the volume of internal standard
9 spiking mixture added in all field and QC analyses is the same from run to run, and that the
10 volume of field and QC sample introduced into the trap is the same for each analysis. Cis and
11 Cx must be in the same units.]

12 **10.5.4.2 Mean Relative Response Factor.** Calculate the mean RRF for each compound by
13 averaging the values obtained at the five concentrations using the following equation:

14

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

15 where:

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

17   x_i = RRF of the compound at concentration i.

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

19 **10.5.4.3 Percent Relative Standard Deviation (%RSD).** Using the RRFs from the initial
20 calibration, calculate the %RSD for all target compounds using the following equations

21

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

22 and

23

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

24 where:

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

26   RRF_i = Relative response factor at a concentration level i.

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

28 **10.5.4.4 Relative Retention Times (RRT).** Calculate the RRTs for each target compound over
29 the initial calibration range using the following equation:

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

where:

RT_c = Retention time of the target compound, seconds

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

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

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

where:

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

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

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

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

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

where:

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

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

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

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

where:

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

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

10.5.5 Technical Acceptance Criteria for the Initial Calibration.

10.5.5.1 The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

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

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

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

10.5.5.4 The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

10.5.6 Corrective Action.

10.5.6.1 Criteria. If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the initial calibration technical acceptance criteria.

10.5.6.2 Schedule. Initial calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed.

10.6 Daily Calibration

10.6.1 Summary. Prior to the analysis of samples and blanks but after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a daily calibration standard to ensure that the instrument continues to remain under control. The daily calibration standard, which is the nominal 10 ppbv level calibration standard, should contain all the target compounds.

10.6.2 Frequency. A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met the tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed.

10.6.3 Procedure. The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 10.5.

10.6.4 Calculations. Perform the following calculations.

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

10.6.4.1 Relative Response Factor (RRF). Calculate a relative response factor (RRF) for each target compound using the equation in Section 10.5.4.1.

10.6.4.2 Percent Difference (%D). Calculate the percent difference in the RRF of the daily RRF (24-hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound using the following equation:

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Method TO-15
December 2015

VOCs

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

where:

RRF_C = RRF of the compound in the continuing calibration standard.

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

10.6.5 Technical Acceptance Criteria. The daily calibration standard must be analyzed at the concentration level and frequency described in this Section 10.6 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 10.4).

The %D for each target compound in a daily calibration sequence must be within ±30 percent in order to proceed with the analysis of samples and blanks. A control chart showing %D values should be maintained.

10.6.6 Corrective Action. If the daily calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the daily calibration technical acceptance criteria.

Daily calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed. If the % D criteria are not met, it will be necessary to rerun the daily calibration sample.

10.7 Blank Analyses

10.7.1 Summary. To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

10.7.2 Frequency. The laboratory method blank must be analyzed after the calibration standard(s) and before any samples are analyzed.

Whenever a high concentration sample is encountered (i.e., outside the calibration range), a blank analysis should be performed immediately after the sample is completed to check for carryover effects.

10.7.3 Procedure. Fill a cleaned and evacuated canister with humidified zero air (RH >20 percent, at 25°C). Pressurize the contents to 2 atm.

The blank sample should be analyzed using the same procedure outlined under Section 10.8.

10.7.4 Calculations. The blanks are analyzed similar to a field sample and the equations in Section 10.5.4 apply.

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Method TO-15
December 2015

VOCs

1   *10.7.5 Technical Acceptance Criteria.* A blank canister should be analyzed daily.

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

4   The retention time for each of the internal standards must be within ±0.33 minutes between the blank
5   and the most recent valid calibration.

6   The blank should not contain any target analyte at a concentration greater than its quantitation level
7   (three times the MDL as defined in Section 11.2) and should not contain additional compounds with
8   elution characteristics and mass spectral features that would interfere with identification and
9   measurement of a method analyte.

10   **10.7.6 Corrective Action.** If the blanks do not meet the technical acceptance criteria, the analyst
11   should consider the analytical system to be out of control. It is the responsibility of the analyst to
12   ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing
13   hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be
14   eliminated. If contamination is a problem, the source of the contamination must be investigated and
15   appropriate corrective measures need to be taken and documented before further sample analysis
16   proceeds.

17   If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also
18   found in associated samples, those sample results should be "flagged" as possibly contaminated.

19   **10.8 Sample Analysis**

20   *10.8.1 Summary.* An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and
21   analyzed by GC/MS under conditions stated in Sections 10.1 and 10.2. If using the multisorbent/dry
22   purge approach, adjust the dry purge volume to reduce water effects in the analytical system to
23   manageable levels.

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

28   *10.8.2 Frequency.* If time remains in the 24-hour period in which an initial calibration is performed,
29   samples may be analyzed without analysis of a daily calibration standard.

30   If time does not remain in the 24-hour period since the injection of the instrument performance check
31   standard in which an initial calibration is performed, both the instrument performance check standard
32   and the daily calibration standard should be analyzed before sample analysis may begin.

33   *10.8.3 Procedure for Instrumental Analysis.* Perform the following procedure for analysis.

34   **10.8.3.1** All canister samples should be at temperature equilibrium with the laboratory.

35   **10.8.3.2** Check and adjust the mass flow controllers to provide correct flow rates for the system.

36   **10.8.3.3** Connect the sample canister to the inlet of the GC/MS analytical system, as shown in
37   Figure 15 [Figure 16 shows an alternate two stage concentrator using multisorbent traps followed
38   by a trap cooled by a closed cycle cooler (15)]. The desired sample flow is established through
39   the six-port chromatographic valve and the preconcentrator to the downstream flow controller.
40   The absolute volume of sample being pulled through the trap must be consistent from run to run.

1   **10.8.3.4** Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a
2   six-port value is being used, as soon as the trap reaches its lower set point, the six-port
3   chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample
4   collection time which has been optimized by the analyst.

5   **10.8.3.5** Use the arrangement shown in Figure 13, (i.e., a gastight syringe or some alternate
6   method) introduce an internal standard during the sample collection period. Add sufficient internal
7   standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of
8   internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500
9   mL, will result in 10 ppbv of each internal standard in the sample.

10   **10.8.3.6** After the sample and internal standards are preconcentrated on the trap, the GC
11   sampling valve is cycled to the inject position and the trap is swept with helium and heated.
12   Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a
13   focusing trap and then onto the head of the capillary column and are separated on the column
14   using the GC oven temperature program. The canister valve is closed and the canister is
15   disconnected from the mass flow controller and capped. The trap is maintained at elevated
16   temperature until the beginning of the next analysis.

17   **10.8.3.7** Upon sample injection onto the column, the GC/MS system is operated so that the MS
18   scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic
19   peak should be acquired. Scanning also allows identification of unknown compounds in the
20   sample through searching of library spectra.

21   **10.8.3.8** Each analytical run must be checked for saturation. The level at which an individual
22   compound will saturate the detection system is a function of the overall system sensitivity and the
23   mass spectral characteristics of that compound.

24   **10.8.3.9** Secondary ion quantitation is allowed only when there are sample matrix interferences
25   with the primary ion. If secondary ion quantitation is performed, document the reasons in the
26   laboratory record book.

27   *10.8.4 Calculations.* The equation below is used for calculating concentrations.

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

29   where:

30   C_X = Compound concentration, ppbv.

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

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

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

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

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

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

4 ### 10.8.5 Technical Acceptance Criteria.

5 [Note: If the most recent valid calibration is an initial calibration, internal standard area responses and
6 RTs in the sample are evaluated against the corresponding internal standard area responses and
7 RTs in the mid level standard (10 ppbv) of the initial calibration.]

8 **10.8.5.1** The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial
9 calibration, and continuing calibration technical acceptance criteria at the frequency described in
10 Sections 10.4, 10.5 and 10.6.

11 **10.8.5.2** The field samples must be analyzed along with a laboratory method blank that met the
12 blank technical acceptance criteria.

13 **10.8.5.3** All of the target analyte peaks should be within the initial calibration range.

14 **10.8.5.4** The retention time for each internal standard must be within ±0.33 minutes of the
15 retention time of the internal standard in the most recent valid calibration.

16 ### 10.8.6 Corrective Action. If the on-column concentration of any compound in any sample exceeds
17 the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed.
18 Guidance in performing dilutions and exceptions to this requirement are given below.

19 •   Use the results of the original analysis to determine the approximate dilution factor required to
20   get the largest analyte peak within the initial calibration range.

21 •   The dilution factor chosen should keep the response of the largest analyte peak for a target
22   compound in the upper half of the initial calibration range of the instrument.

23 [Note: Analysis involving dilution should be reported with a dilution factor and nature of the dilution
24 gas.]

25 **10.8.6.1** Internal standard responses and retention times must be evaluated during or
26 immediately after data acquisition. If the retention time for any internal standard changes by more
27 than 20 sec from the latest daily (24-hour) calibration standard (or mean retention time over the
28 initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections
29 made as required.

30 **10.8.6.2** If the area response for any internal standard changes by more than ±40 percent
31 between the sample and the most recent valid calibration, the GC/MS system must be inspected
32 for malfunction and corrections made as appropriate. When corrections are made, reanalysis of
33 samples analyzed while the system was malfunctioning is necessary.

34 **10.8.6.3** If, after reanalysis, the area responses or the RTs for all internal standards are inside the
35 control limits, then the problem with the first analysis is considered to have been within the control
36 of the Laboratory. Therefore, submit only data from the analysis with SICPs within the limits. This
37 is considered the initial analysis and should be reported as such on all data deliverables.

38

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United States
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Method TO-15
December 2015

VOCs

11. Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

11.1 Introduction

11.1.1 There are three performance criteria which must be met for a system to qualify under Compendium Method TO-15. These criteria are: the method detection limit of ≤0.5 ppbv, replicate precision within 25 percent, and audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv).

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

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

11.2 Method Detection Limit

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

11.2.2 The method detection limit is defined for each system by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values). Employing this approach, the detection limits given in Table 4 were obtained for some of the VOCs of interest.

11.3 Replicate Precision

11.3.1 The measure of replicate precision used for this program is the absolute value of the difference between replicate measurements of the sample divided by the average value and expressed as a percentage as follows:

$$\text{percent difference} = \frac{|X_1 - X_2|}{\bar{x}} \times 100$$

where:

x_1 = First measurement value.

x_2 = Second measurement value.

$\bar{x}$ = Average of the two values

11.3.2 There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar

1   VOCs. A primary influence on precision is the concentration level of the compound of interest in the

2   sample, i.e., the precision degrades as the concentration approaches the detection limit. A

3   conservative measure was obtained from replicate analysis of "real world" canister samples from the

4   TAMS and UATMP networks. These data are summarized in Table 5 and suggest that a replicate

5   precision value of 25 percent can be achieved for each of the target compounds.

6   **11.4 Audit Accuracy**

7   *11.4.1* A measure of analytical accuracy is the degree of agreement with audit standards. Audit

8   accuracy is defined as the difference between the nominal concentration of the audit compound and

9   the measured value divided by the audit value and expressed as a percentage, as illustrated in the

10   following equation:

11
$$\text{Audit Accuracy (\%)} = \frac{\text{Spiked Value} - \text{Observed Value}}{\text{Spiked Value}} \times 100$$

12   *11.4.2* Audit accuracy results for TAMS and UATMP analyses are summarized in Table 6 and were

13   used to form the basis for a selection of 30 percent as the performance criterion for audit accuracy.

14

12. References

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21

22

Appendix A: Listing of Some Commercial Water Management Systems Used with AutoGC Systems

Tekmar Dohrman Company
7143 East Kemper Road
Post Office Box 429576
Cincinnati, Ohio 45242-9576
(513) 247-7000
(513) 247-7050 (Fax)
(800) 543-4461
[Moisture control module]

Entech Laboratory Automation
950 Enchanted Way No. 101
Simi Valley, California 9306
(805) 527-5939
(805) 527-5687 (Fax)
[Microscale Purge and Trap]

Dynatherm Analytical Instruments
Post Office Box 159
Kelton, Pennsylvania 19346
(215) 869-8702
(215) 869-3885 (Fax)
[Thermal Desorption System]

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380
(818) 787-4275 (Fax)
[Multi-adsorbent trap/dry purge]

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(770) 319-9999
(770) 319-0336(Fax)
(800) 241-6898
[Controlled Desorption Trap]

Varian Chromatography System
2700 Mitchell Drive
Walnut Creek, California 94898
(510) 945-2196
(510) 945-2335 (Fax)
[Variable Temperature Adsorption Trap]

Appendix B: Comment on Canister Cleaning Procedures

The canister cleaning procedures given in Section 8.4 require that canister pressure be reduced to <0.05mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (<0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2mm Hg.

Canister cleaning as described in Section 8.4 and illustrated in Figure 10 requires components with special features. The vacuum gauge shown in Figure 10 must be capable of measuring 0.05 mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components.

An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

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Agency

Method TO-15
December 2015

VOCs

Appendix C: Listing of Commercial Manufacturers and Re-Suppliers of Specially Prepared Canisters

BRC/Rasmussen
17010 NW Skyline Blvd.
Portland, Oregon 97321
(503) 621-1435

Meriter
1790 Potrero Drive
San Jose, CA 95124
(408) 265-6482

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823-8812
(814) 353-1300
(800) 356-1688

Scientific Instrumentation Specialists
P.O. Box 8941
815 Courtney Street
Moscow, ID 83843
(208) 882-3860

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(404) 319-9999
(800) 241-6898

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380

Appendix D: Listing of Commercial Suppliers of Permeation Tubes and Systems

Kin-Tek
504 Laurel St.
Lamarque, Texas 77568
(409) 938-3627
(800) 326-3627

Vici Metronics, Inc.
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

Ecology Board, Inc.
9257 Independence Ave.
Chatsworth, CA 91311
(213) 882-6795

Tracor, Inc.
6500 Tracor Land
Austin, TX
(512) 926-2800

Metronics Associates, Inc.
3201 Porter Drive
Standford Industrial
Park Palo Alto, CA 94304
(415) 493-5632

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Method TO-15
December 2015

VOCs

Table 1. Volatile Organic Compounds on the Title III Clean Air Amendment List—Membership in Compendium Method TO-14A List and the SOW-CLP List of VOCs

Compound	CAS No.	BP (°C)[1]	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl chloride (chloromethane); CH_3Cl	74-87-3	-23.7	3.8 x 10	50.5	X	X
Carbonyl sulfide; COS	463-58-1	-50.0	3.7 x 10	60.1		
Vinyl chloride (chloroethene); C_2H_3Cl	75-01-4	-14.0	3.2 x 10	62.5	X	X
Diazomethane; CH_2N_2	334-88-3	-23.0	2.8 x 10	42.1		
Formaldehyde; CH_2O	50-00-0	-19.5	2.7 x 10	30		
1,3-Butadiene; C_4H_6	106-99-0	-4.5	2.0 x 10	54		X
Methyl bromide (bromomethane); CH_3Br	74-83-9	3.6	1.8 x 10	94.9	X	X
Phosgene; CCl_2O	75-44-5	8.2	1.2 x 10	99		
Vinyl bromide (bromoethene); C_2H_3Br	593-60-2	15.8	l.l x 10	107		
Ethylene oxide; C_2H_4O	75-21-8	10.7	1.1 x 10	44		
Ethyl chloride (chloroethane); C_2H_5Cl	75-00-3	12.5	1.0 x 10	64.5	X	X
Acetaldehyde (ethanal); C_2H_4O	75-07-0	21.0	952	44		
Vinylidene chloride (1,1-dichloroethylene); $C_2H_2Cl_2$	75-35-4	31.7	500	97	X	X
Propylene oxide; C_3H_6O	75-56-9	34.2	445	58		
Methyl iodide (iodomethane); CH_3I	74-88-4	42.4	400	141.9		
Methylene chloride; CH_2Cl_2	75-09-2	40.0	349	84.9	X	X
Methyl isocyanate; C_2H_3NO	624-83-9	59.6	348	57.1		
Allyl chloride (3-chloropropene); C_3H_5Cl	107-05-1	44.5	340	76.5	X	X
Carbon disulfide; CS_2	75-15-0	46.5	260	76		
Methyl tert-butyl ether; $C_5H_{12}O$	1634-04-4	55.2	249	86		
Propionaldehyde; C_2H_5CHO	123-38-6	49.0	235	58.1		
Ethylidene dichloride (1,1-dichloroethane); $C_2H_4Cl_2$	75-34-3	57.0	230	99	X	
Chloroprene (2-chloro-1,3-butadiene); C_4H_5Cl	126-99-8	59.4	226	88.5		
Chloromethyl methyl ether; C_2H_5ClO	107-30-2	59.0	224	80.5		
Acrolein (2-propenal); C_3H_4O	107-02-8	52.5	220	56		X
1,2-Epoxybutane (1,2-butylene oxide); C_4H_8O	106-88-7	63.0	163	72		
Chloroform; $CHCl_3$	67-66-3	61.2	160	119	X	X
Ethyleneimine (aziridine); C_2H_5N	151-56-4	56	160.0	43		
1,1-Dimethylhydrazine; $C_2H_8N_2$	57-14-7	63	157.0	60.0		
Hexane; C_6H_{14}	110-54-3	69.0	120	86.2	X	
1,2-Propyleneimine (2-methylaziridine); C_3H_7N	75-55-8	66.0	112	57.1		
Acrylonitrile (2-propenenitrile); C_3H_3N	107-13-1	77.3	100	53	X	
Methyl chloroform (1,1,1-trichloroethane); $C_2H^3Cl_3$	71-55-6	74.1	100	133.4	X	X
Methanol; CH_4O	67-56-1	65.0	92.0	32		X
Carbon tetrachloride; CCl_4	56-23-5	76.7	90.0	153.8	X	X
Vinyl acetate; $C_4H_6O_2$	108-05-4	72.2	83.0	86		X
Methyl ethyl ketone (2-butanone); C_4H_8O	78-93-3	79.6	77.5	72		X
Benzene; C_6H_6	71-43-2	80.1	76.0	78	X	X
Acetonitrile (cyanomethane); C_2H_3N	75-05-8	82	74.0	41.0		X

Compound	CAS No.	BP (°C)[1]	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Ethylene dichloride (1,2-dichloroethane); $C_2H_4Cl_2$	107-06-2	83.5	61.5	99	X	X
Triethylamine; $C_6H_{15}N$	121-44-8	89.5	54.0	101.2		
Methylhydrazine; CH_6N_2	60-34-4	87. 8	49.6	46.1		
Propylene dichloride (1,2-dichloropropane); $C_3H_6Cl_2$	78-87-5	97.0	42.0	113	X	X
2,2,4-Trimethyl pentane C_8H_{18}	540-84-l	99.2	40.6	114		
1,4-Dioxane (1,4-Diethylene oxide); $C_4H_8O_2$	123-91-1	101	37.0	88		
Bis(chloromethyl) ether; $C_2H_4Cl_2O$	542-88-1	104	30.0	115		
Ethyl acrylate; $C_5H_8O_2$	140-88-5	100	29.3	100		
Methyl methacrylate; $C_5H_8O_2$	80-62-6	101	28.0	100.1		
1,3-Dichloropropene; $C_3H_4Cl_2$ (cis)	542-75-6	112	27.8	111	X	X
Toluene; C_7H_8	108-88-3	111	22.0	92	X	X
Trichloroethylene; C_2HCl_3	79-01-6	87.0	20.0	131.4	X	X
1,1,2-Trichloroethane; $C_2H_3Cl_3$	79-00-5	114	19.0	133.4	X	X
Tetrachloroethylene; C_2Cl_4	127-18-4	121	14.0	165.8	X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane); C_3H_5ClO	106-89-8	117	12.0	92.5		
Ethylene dibromide (1,2-dibromoethane); $C_2H_4Br_2$	106-93-4	132	11.0	187.9	X	X
N-Nitroso-N-methylurea; $C_2H_5N_3O_2$	684-93-5	124	10.0	103		
2-Nitropropane; $C_3H_7NO_2$	79-46-9	120	10.0	89		
Chlorobenzene; C_6H_5Cl	108-90-7	132	8.8	112.6	X	X
Ethylbenzene; C_8H_{10}	100-41-4	136	7.0	106	X	X
Xylenes (isomer & mixtures); C_8H_{10}	1330-20-7	142	6.7	106.2	X	X
Styrene; C_8H_8	100-42-5	145	6.6	104	X	X
p-Xylene; C_8H_{10}	106-42-3	138	6.5	106.2	X	X
m-Xylene; C_8H_{10}	108-38-3	139	6.0	106.2	X	X
Methyl isobutyl ketone (hexone); $C_6H_{12}O$	108-10-1	117	6.0	100.2		
Bromoform (tribromomethane); $CHBr_3$	75-25-2	149	5.6	252.8		
l,l,2,2-Tetrachloroethane; $C_2H_2Cl_4$	79-34-5	146	5.0	167.9	X	X
o-Xylene; C_8H_{10}	95-47-6	144	5.0	106.2	X	X
Dimethylcarbamyl chloride; C_3H_6ClNO	79-44-7	166	4.9	107.6		
N-Nitrosodimethylamine; $C_2H_6N_2O$	62-75-9	152	3.7	74		
Beta-Propiolactone; $C_3H_4O_2$	57-57-8	Decomposes at 162	3.4	72		
Cumene (isopropylbenzene); C_9H_{l2}	98-82-8	153	3.2	120		
Acrylic acid; $C_3H_4O_2$	79-10-7	141	3.2	72		
N,N-Dimethylformamide; C_3H_7NO	68-12-2	153	2.7	73		
1,3-Propane sultone; $C_3H_6O_3S$	1120-71-4	180/30mm	2.0	122.1		
Acetophenone; C_8H_8O	98-86-2	202	1.0	120		
Dimethyl sulfate; $C_2H_6O_4S$	77-78-1	188	1.0	126.1		
Benzyl chloride (a-chlorotoluene); C_7H_7Cl	100-44-7	179	1.0	126.6	X	X
1,2-Dibromo-3-chloropropane; $C_3H_5Br_2Cl$	96-12-8	196	0.80	236.4		
Bis(2-Chloroethyl)ether; $C_4H_8Cl_2O$	111-44-4	178	0.71	143		
Chloroacetic acid; $C_2H_3ClO_2$	79-11-8	189	0.69	94.5		
Aniline (aminobenzene); C_6H_7N	62-53-3	184	0.67	93		

Compound	CAS No.	BP (°C)[1]	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
1,4-Dichlorobenzene (p-); $C_6H_4Cl_2$	106-46-7	173	0.60	147	X	X
Ethyl carbamate (urethane); $C_3H_7NO_2$	51-79-6	183	0.54	89		
Acrylamide; C_3H_5NO	79-06-1	125/25 mm	0.53	71		
N,N-Dimethylaniline; $C_8H_{11}N$	121-69-7	192	0.50	121		
Hexachloroethane; C_2Cl_6	67-72-1	Sublimes at 186	0.40	236.7		
Hexachlorobutadiene; C_4Cl_6	87-68-3	2l5	0.40	260.8	X	X
Isophorone; $C_9H_{14}O$	78-59-1	215	0.38	138.2		
N-Nitrosomorpholine; $C_4H_8N_2O_2$	59-89-2	225	0.32	116.1		
Styrene oxide; C_8H_8O	96-09-3	194	0.30	120.2		
Diethyl sulfate; $C_4H_{10}O_4S$	64-67-5	208	0.29	154		
Cresylic acid (cresol isomer mixture);C_7H_8O	1319-77-3	202	0.26	108		
o-Cresol; C_7H_8O	95-48-7	191	0.24	108		
Catechol (o-hydroxyphenol); $C_6H_6O_2$	120-80-9	240	0.22	110		
Phenol; C_6H_6O	108-95-2	182	0.20	94		
1,2,4-Trichlorobenzene; $C_6H_3Cl_3$	120-82-1	213	0.18	181.5	X	X
Nitrobenzene; $C_6H_5NO_2$	98-95-3	211	0.15	123		

[1]Vapor pressure (v.p.), boiling point (BP) and molecularweight (MW) data from:

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Method TO-15
December 2015

VOCs

Table 2. Characteristic Masses (M/Z) Used for Quantifying the Title III Clean Air Act Amendment Compounds

Compound	CAS No.	Primary Ion	Secondary Ion
Methyl chloride (chloromethane); CH_3Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-S8-1	60	62
Vinyl chloride (chloroethene); C_2H_3Cl	7S-01-4	62	64
Diazomethane; CH_2N_2	334-88-3	42	41
Formaldehyde; CH_2O	50-00-0	29	30
1,3-Butadiene; C_4H_6	106-99-0	39	54
Methyl bromide (bromomethane); CH_3Br	74-83-9	94	96
Phosgene; CCl_2O	75-44-5	63	65
Vinyl bromide (bromoethene); C_2H_3Br	593-60-2	106	108
Ethylene oxide; $C2H4O$	75-21-8	29	44
Ethyl chloride (chloroethane); C_2H_5Cl	75-00-3	64	66
Acetaldehyde (ethanal); C_2H_4O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene); $C_2H_2Cl_2$	75-35-4	61	96
Propylene oxide; C_3H_6O	75-56-9	58	57
Methyl iodide (iodomethane); CH_3I	74-88-4	142	127
Methylene chloride; CH_2Cl_2	75-09-2	49	84, 86
Methyl isocyanate; C_2H_3NO	624-83-9	57	56
Allyl chloride (3-chloropropene); C_3H_5Cl	107-05-1	76	41, 78
Carbon disulfide; CS_2	75-15-0	76	44, 78
Methyl tert-butyl ether; $C_5H_{12}O$	1634-04-4	73	41, 53
Propionaldehyde; C_2H_5CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane); $C_2H_4Cl_2$	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene); C_4H_5Cl	126-99-8	88	53, 90
Chloromethyl methyl ether; C_2H_5ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C_3H_4O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide); C_4H_8O	106-88-7	42	41, 72
Chloroform; $CHCl_3$	67-66-3	83	85, 47
Ethyleneimine (aziridine); C_2H_5N	151-56-4	42	43
1,1-Dimethylhydrazine; $C_2H_8N_2$	57-14-7	60	45, 59
Hexane; C_6H_{14}	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylazindine); C_3H_7N	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C_3H_3N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane); $C_2H_3Cl_3$	71-55-6	97	99, 61
Methanol; CH_4O	67-56-1	31	29
Carbon tetrachloride; CCl_4	56-23-5	117	119
Vinyl acetate; $C_4H_6O_2$	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C_4H_8O	78-93-3	43	72
Benzene; C_6H_6	71-43-2	78	77,50
Acetonitrile (cyanomethane); C_2H_3N	75-05-8	41	40
Ethylene dichloride (1,2-dichloroethane); $C_2H_4Cl_2$	107-06-2	62	64, 27

Compound	CAS No.	Primary Ion	Secondary Ion
Triethylamine; $C_6H_{15}N$	121-44-8	86	58, 101
Methylhydrazine; CH_6N_2	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane); $C_3H_6Cl_2$	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C_8H_{18}	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide); $C_4H_8O_2$	123-91-1	88	58
Bis(chloromethyl) ether; $C_2H_4Cl_2O$	542-88-1	79	49, 81
Ethyl acrylate; $C_5H_8O_2$	140-88-5	55	73
Methyl methacrylate; $C_5H_8O_2$	80-62-6	41	69, 100
1,3-Dichloropropene; $C_3H_4Cl_2$ (cis)	542-75-6	75	39, 77
Toluene; C_7H_8	108-88-3	91	92
Trichloethylene; C_2HCl_3	79-01-6	130	132, 95
1,1,2-Trichloroethane; $C_2H_3Cl_3$	79-00-5	97	83, 61
Tetrachloroethylene; C_2Cl_4	127-18-4	166	164, 131
Epichlorohydrin (l-chloro-2,3-epoxy propane); C_3H_5ClO	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane); $C_2H_4Br_2$	106-93-4	107	109
N-Nitrso-N-methylurea; $C_2H_5N_3O_2$	684-93-5	60	44, 103
2-Nitropropane; $C_3H_7NO_2$	79-46-9	43	41
Chlorobenzene; C_6H_5Cl	108-90-7	112	77, 114
Ethylbenzene; C_8H_{10}	100-41-4	91	106
Xylenes (isomer & mixtures); C_8H_{10}	1330-20-7	91	106
Styrene; C_8H_8	100-42-5	104	78, 103
p-Xylene; C_8H_{10}	106-42-3	91	106
m-Xylene; C_8H_{10}	108-38-3	91	106
Methyl isobutyl ketone (hexone); $C_6H_{12}O$	108-10-1	43	58, 100
Bromoform (tribromomethane); $CHBr_3$	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; $C_2H_2Cl_4$	79-34-5	83	85
o-Xylene; C_8H_{10}	95-47-6	91	106
Dimethylcarbamyl chloride; C_3H_6ClNO	79-44-7	72	107
N-Nitrosodimethylamine; $C_2H_6N_2O$	62-75-9	74	42
Beta-Propiolactone; $C_3H_4O_2$	57-57-8	42	43
Cumene (isopropylbenzene); C_9H_{12}	98-82-8	105	120
Acrylic acid; $C_3H_4O_2$	79-10-7	72	45, 55
N,N-Dimethylformamide; C_3H_7NO	68-12-2	73	42, 44
1,3-Propane sultone; $C_3H_6O_3S$	1120-71-4	58	65, 122
Acetophenone; C_8H_8O	98-86-2	105	77,120
Dimethyl sulfate; $C_2H_6O_4S$	77-78-1	95	66,96
Benzyl chloride (a-chlorotoluene); C_7H_7Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; $C_3H_5Br_2Cl$	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; $C_4H_8Cl_2O$	111-44-4	93	63, 95
Chloroacetic acid; $C_2H_3ClO_2$	79-11-8	50	45, 60
Aniline (aminobenzene); C_6H_7N	62-53-3	93	66
1,4-Dichlorobenzene (p-); $C_6H_4Cl_2$	106-46-7	146	148, 111

Compound	CAS No.	Primary Ion	Secondary Ion
Ethyl carbamate (urethane); $C_3H_7NO_2$	51-79-6	31	44, 62
Acrylamide; C_3H_5NO	79-06-1	44	55, 71
N,N-Dimethylaniline; $C_8H_{11}N$	121-69-7	120	77, 121
Hexachloroethane; C_2Cl_6	67-72-1	201	199, 203
Hexachlorobutadiene; C_4Cl_6	87-68-3	225	227, 223
Isophorone; $C_9H_{14}O$	78-59-1	82	138
N-Nitrosomorpholine; $C_4H_8N_2O_2$	59-89-2	56	86, 116
Styrene oxide; C_8H_8O	96-09-3	91	120
Diethyl sulfate; $C_4H_{10}O_4S$	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture); C_7H_8O	1319-77-3		
o-Cresol; C_7H_8O	95-48-7	108	107
Catechol (o-hydroxyphenol); $C_6H_6O_2$	120-80-9	110	64
Phenol; C_6H_6O	108-95-2	94	66
1,2,4-Trichlorobenzene; $C_6H_3Cl_3$	120-82-1	180	182, 184
Nitrobenzene; $C_6H_5NO_2$	98-95-3	77	51, 123

Table 3. Required BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria[1]
50	8.0 to 40.0 Percent of m/e 95
75	30.0 to 66.0 Percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95 (See note)
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 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 percent that of m/z 95.	

Table 4. Method Detection Limits (MDLs)[1]

TO-14A List	Lab #1, SCAN	Lab #2, SIM
Benzene	0.34	0.29
Benzyl Chloride		
Carbon tetrachloride	0.42	0.15
Chlorobenzene	0.34	0.02
Chloroform	0.25	0.07
1,3-Dichlorobenzene	0.36	0.07
1,2-Dibromoethane		0.05
1,4-Dichlorobenzene	0.70	0.12
1,2-Dichlorobenzene	0.44	
1,1-Dichloroethane	0.27	0.05

TO-14A List	Lab #1, SCAN	Lab #2, SIM
1,2-Dichloroethane	0.24	
1,1-Dichloroethene		0.22
cis-1,2-Dichloroethene		0.06
Methylene chloride	1.38	0.84
1,2-Dichloropropane	0.21	
cis-1,3-Dichloropropene	0.36	
trans-1,3-Dichloropropene	0.22	
Ethylbenzene	0.27	0.05
Chloroethane	0.19	
Trichlorofluoromethane		
1,1,2-Trichloro-1,2,2-trifluoroethane		
1,2-Dichloro-1,1,2,2-tetrafluoroethane		
Dichlorodifluoromethane		
Hexachlorobutadiene		
Bromomethane	0.53	
Chloromethane	0.40	
Styrene	1.64	0.06
1,1,2,2-Tetrachloroethane	0.28	0.09
Tetrachloroethene	0.75	0.10
Toluene	0.99	0.20
1,2,4-Trichlorobenzene		
1,1,1-Trichloroethane	0.62	0.21
1,1,2-Trichloroethane	0.50	
Trichloroethene	0.45	0.07
1,2,4-Trimethylbenzene		
1,3,5-Trimethylbenzene		
Vinyl Chloride	0.33	0.48
m,p-Xylene	0.76	0.08
o-Xylene	0.57	0.28
[1]Method Detection Limits (MDLs) are defined as the product of the standard deviation of seven replicate analyses and the student's "t" test value for 99% confidence. For Lab #2, the MDLs represent an average over four studies. MDLs are for MS/SCAN for Lab #1 and for MS/SIM for Lab #2.		

Table 5. Summary of EPA Data on Replicate Precision (RP) from EPA Network Operations[1]

Identification	EPA's Urban Air Toxics Monitoring Program (UATMP)			EPA's Toxics Air Monitoring Stations (TAMS)		
	%RP	#	ppbv	%RP	#	ppbv
Dichlorodifluoromethane	--		--	13.9	47	0.9
Methylene chloride	16.3	07	4.3	19.4	47	0.6
1,2-Dichloroethane	36.2	31	1.6	--	--	--
1,1,1-Trichloroethane	14.1	44	1.0	10.6	47	2.0

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Method TO-15
December 2015

VOCs

Identification	EPA's Urban Air Toxics Monitoring Program (UATMP)			EPA's Toxics Air Monitoring Stations (TAMS)		
	%RP	#	ppbv	%RP	#	ppbv
Benzene	12.3	56	1.6	4.4	47	1.5
Trichloroethene	12.8	08	1.3	--	--	--
Toluene	14.7	76	3.1	3.4	47	3.1
Tetrachloroethene	36.2	12	0.8	--	--	--
Chlorobenzene	20.3	21	0.9	--	--	--
Ethylbenzene	14.6	32	0.7	5.4	47	0.5
m-Xylene	14.7	75	4.0	5.3	47	1.5
Styrene	22.8	59[2]	1.1	8.7	47	0.2[2]
o-Xylene	--		--	6.0	47	0.5
p-Xylene	--					
1,3-Dichlorobenzene	49.1	06	0.6	--	--	--
1,4-Dichlorobenzene	14.7	14	6.5	--	--	--
[1]Denotes the number of replicate or duplicate analysis used to generate the statistic. The replicate precision is defined as the mean ratio of absolute difference to the average value.						
[2]Styrene and o-xylene coelute from the GC column used in UATMP. For the TAMS entries, both values were below detection limits for 18 of 47 replicates and were not included in the calculation.						

Table 6. Audit Accuracy (AA) Values[1] for Selected Compendium Method TO-14A Compounds

| Selected Compounds From TO-14A List	FY-88 TAMS AA(%), N=30	FY-88 UATMP AA(%), N=3
Vinyl chloride	4.6	17.9
Bromomethane	--	6.4
Trichlorofluoromethane	6.4	--
Methylene chloride	8.6	31.4
Chloroform	--	4.2
1,2-Dichloroethane	6.8	11.4
1,1,1-Trichloroethane	18.6	11.3
Benzene	10.3	10.1
Carbon tetrachloride	12.4	9.4
1,2-Dichloropropane	--	6.2
Trichloroethene	8.8	5.2
Toluene	8.3	12.5
Tetrachloroethene	6.2	--
Chlorobenzene	10.5	11.7
Ethylbenzene	12.4	12.4
o-Xylene	16.2	21.2
[1]Audit accuracy is defined as the relative difference between the audit measurement result and its nominal value divided by the nominal value. N denotes the number of audits averaged to obtain the audit accuracy value. Information is not available for other TO-14A compounds because they were not present in the audit materials.		
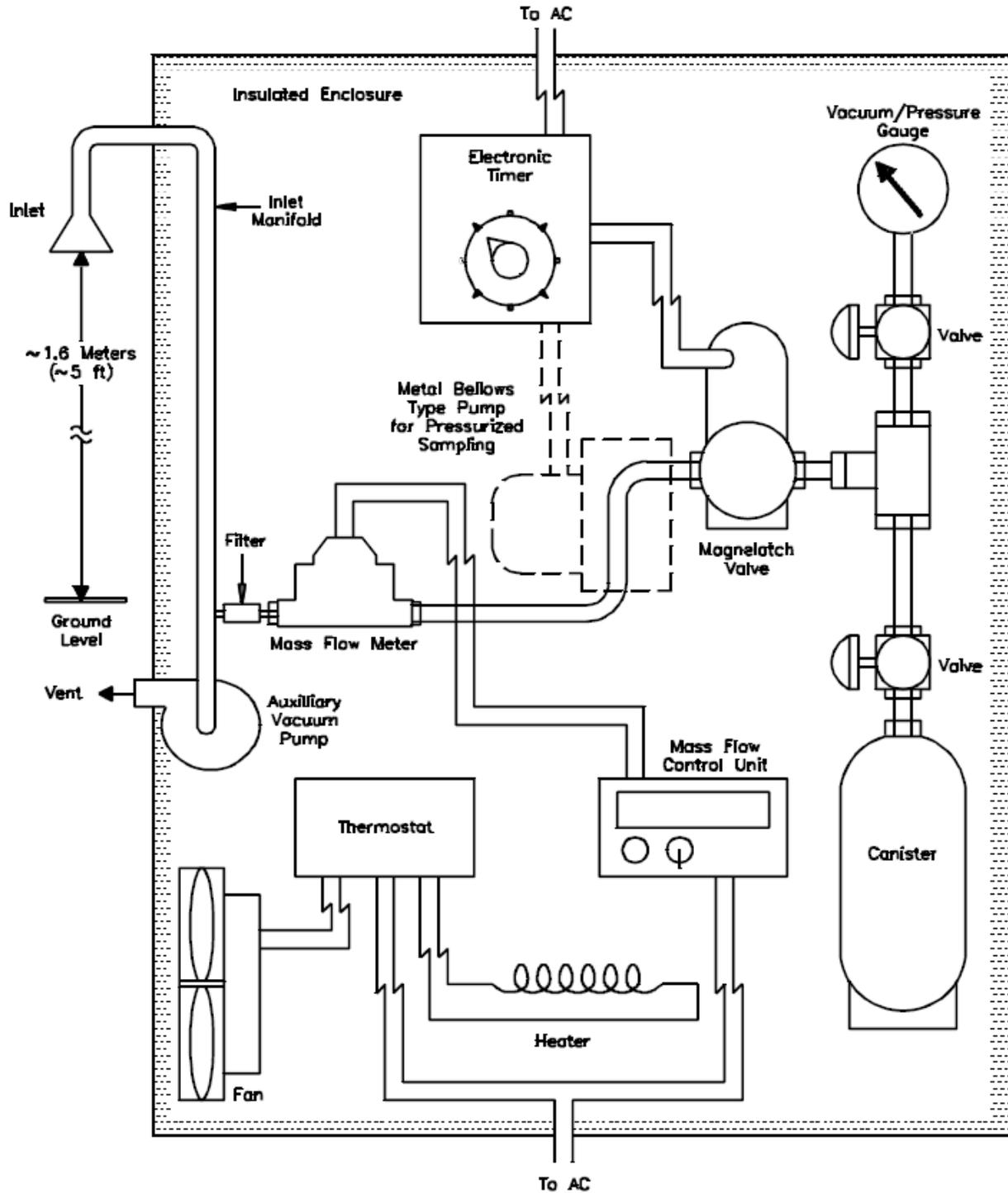
Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.
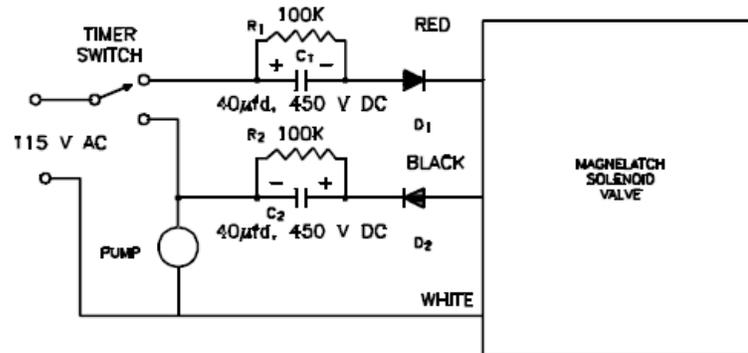
COMPONENTS

Capacitor C_1 and C_2 — 40 uf, 450 VDC (Sprague Atom TVA 1712 or equivalent)
Resistor R_1 and R_2 — 0.5 watt, 5% tolerance
Diode D_1 and D_2 — 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)

(a). Simple Circuit for Operating Magnelatch Valve
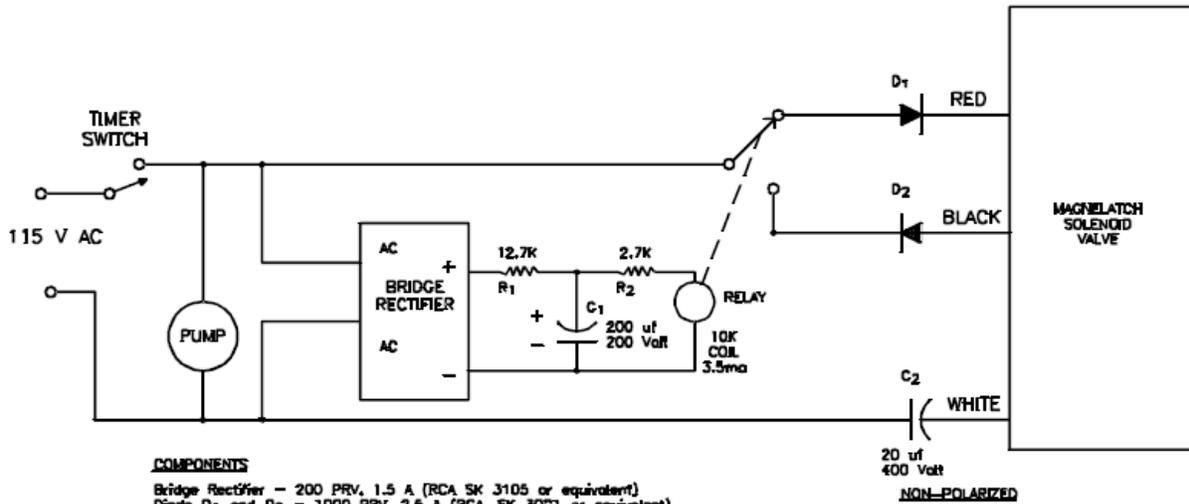
COMPONENTS

Bridge Rectifier — 200 PRV, 1.5 A (RCA SK 3105 or equivalent)
Diode D_1 and D_2 — 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)
Capacitor C_1 — 200 uf, 250 VDC (Sprague Atom TVA 1520 or equivalent)
Capacitor C_2 — 20 uf, 400 VDC Non-Polarized (Sprague Atom TVAN 1632 or equivalent)
Relay — 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
Resistor R_1 and R_2 — 0.5 watt, 5% tolerance

(b). Improved Circuit Designed to Handle Power Interruptions

Figure 2. Electrical pulse circuits for driving Skinner magnelatch solenoid valve with mechanical timer.
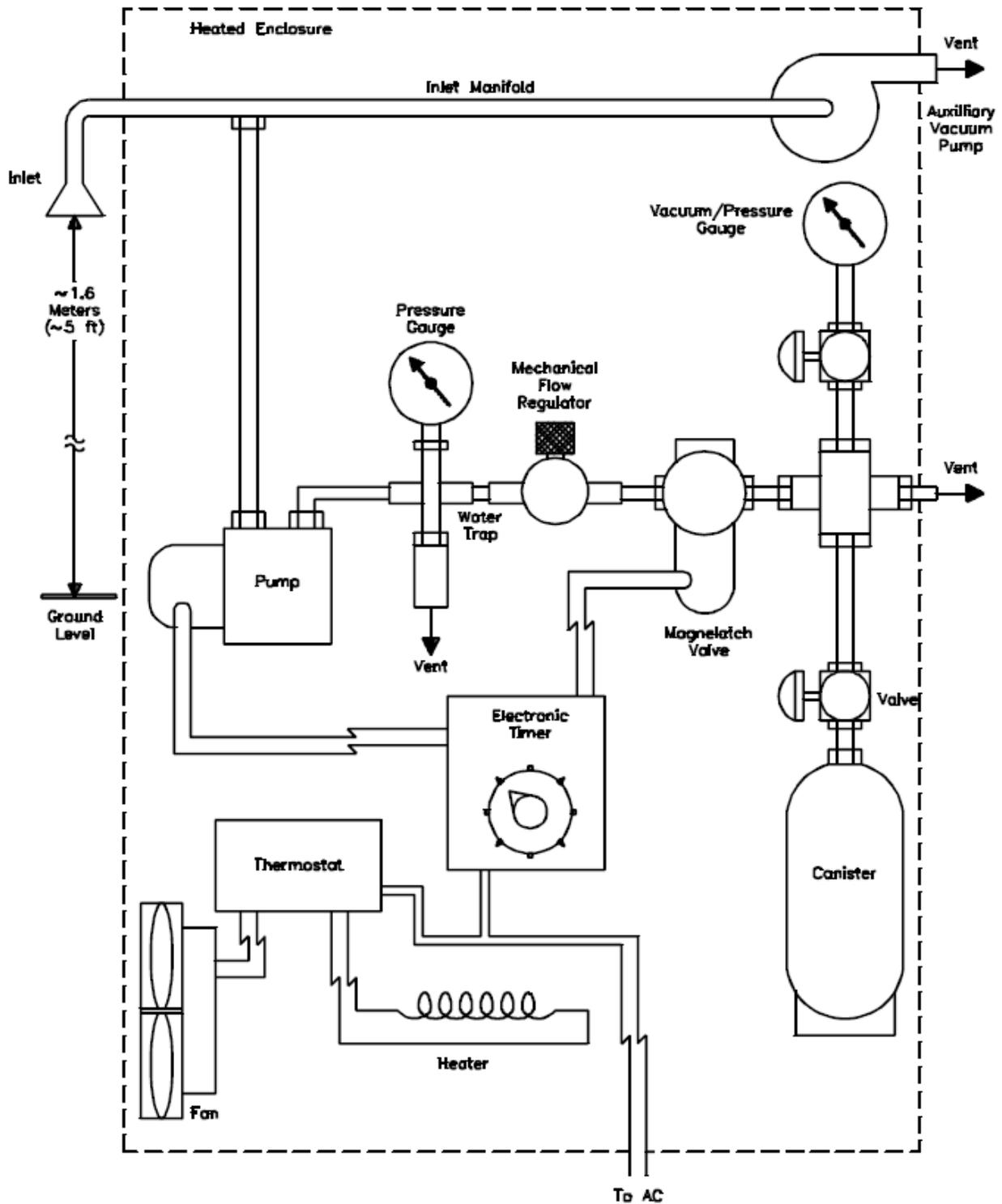
Figure 3. Alternative sampler configuration for pressurized canister sampling.

STAGE 1: SAMPLE TRANSFER TO THE PRECONCENTRATION TRAP

CANISTER

SORBENT TUBE

ADSORBENT TRAP

AT NEAR AMBIENT
TEMPERATURE

GC
COLUMN

SAMPLER INLET

AIR SAMPLE IN

SAMPLE GAS
FLOW

CARRIER
GAS IN

STAGE 2: DRY PURGING

DRY HELIUM
PURGE GAS

ADSORBENT TRAP

AT NEAR AMBIENT
TEMPERATURE

GC
COLUMN

PURGE GAS
PLUS WATER

CARRIER
GAS IN
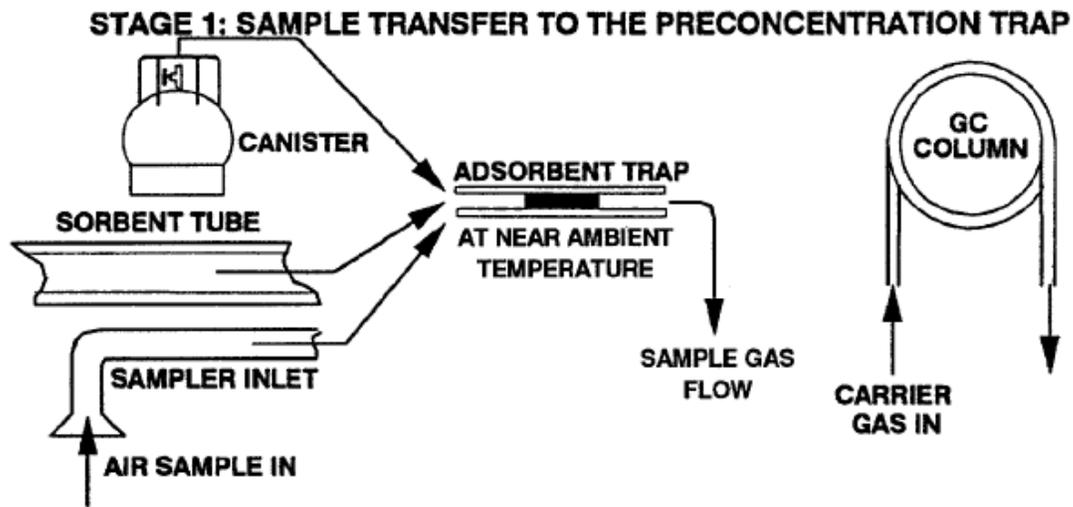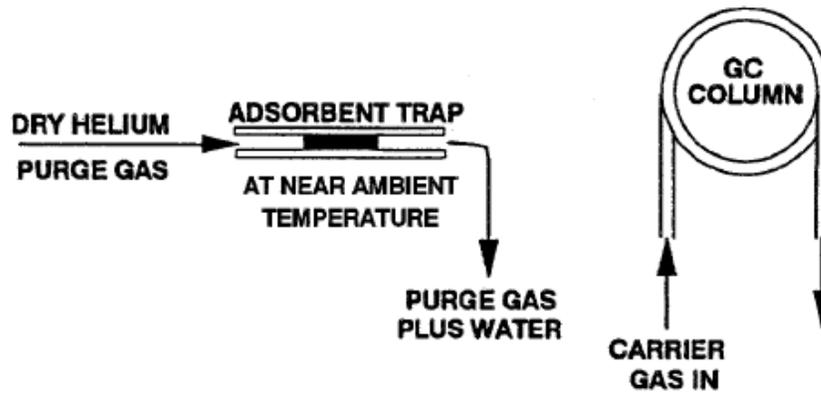
STAGE 3: TRAP DESORPTION - ANALYTE TRANSFER TO GC COLUMN

CARRIER GAS IN

ADSORBENT TRAP

(HOT)

GC
COLUMN
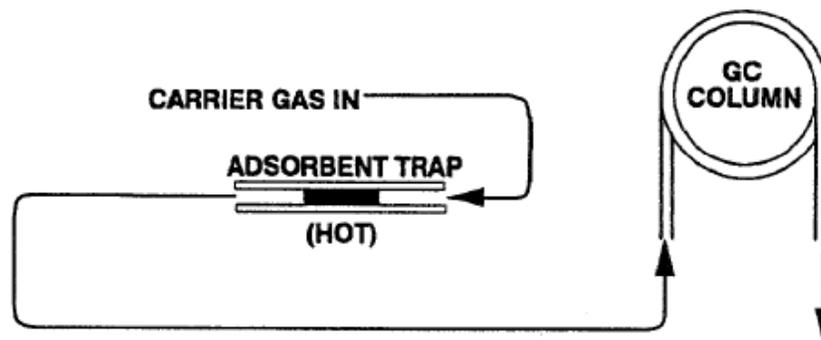
Figure 4. Illustration of three stages of dry purging of adsorbent trap.
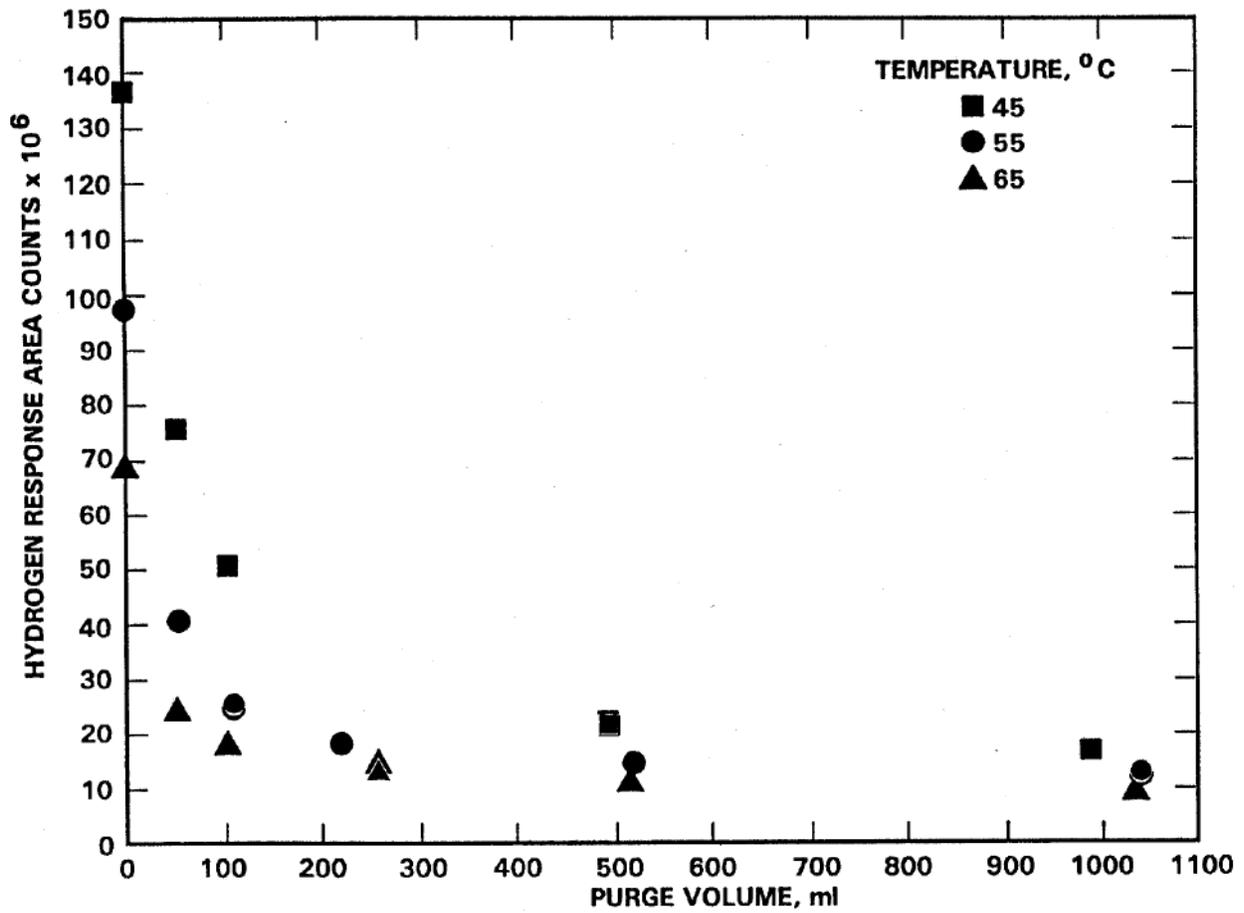
Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.
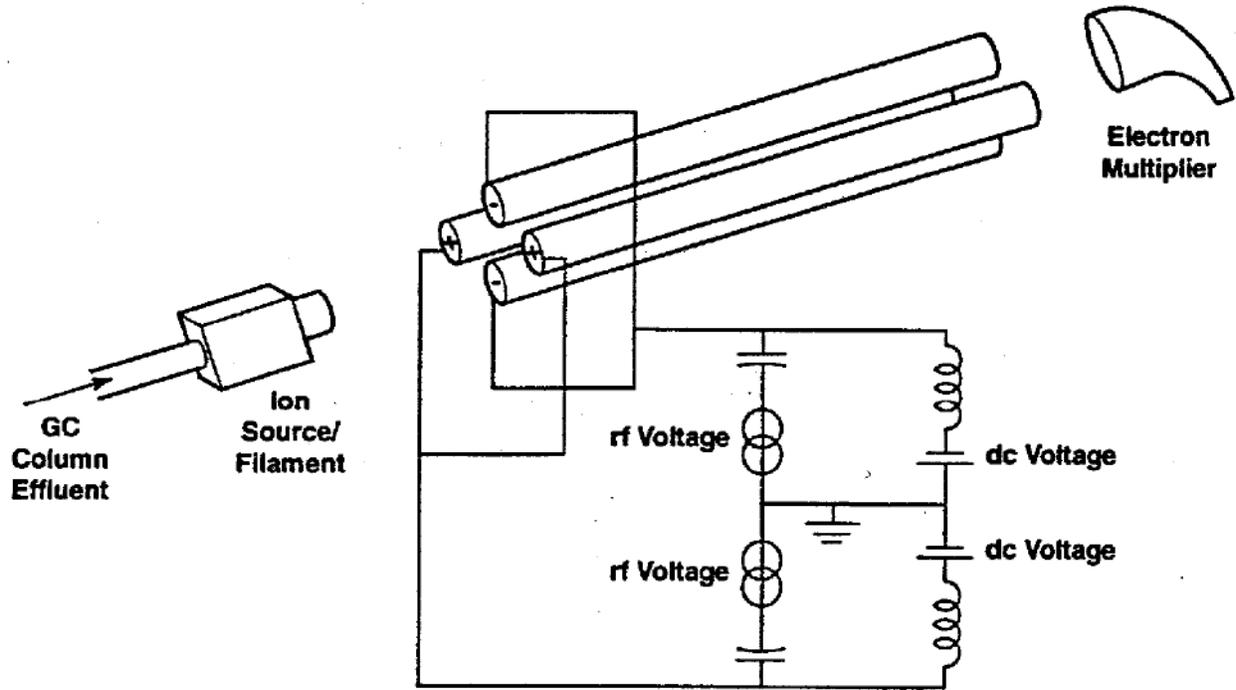
Figure 6. Simplified diagram of a quadrupole mass spectrometer.

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Filament

End Cap

Ring Electrode

Ring Electrode

Fundamental rf Voltage

Supplementary rf Voltage

GC Column Effluent

End Cap

Electron Multiplier
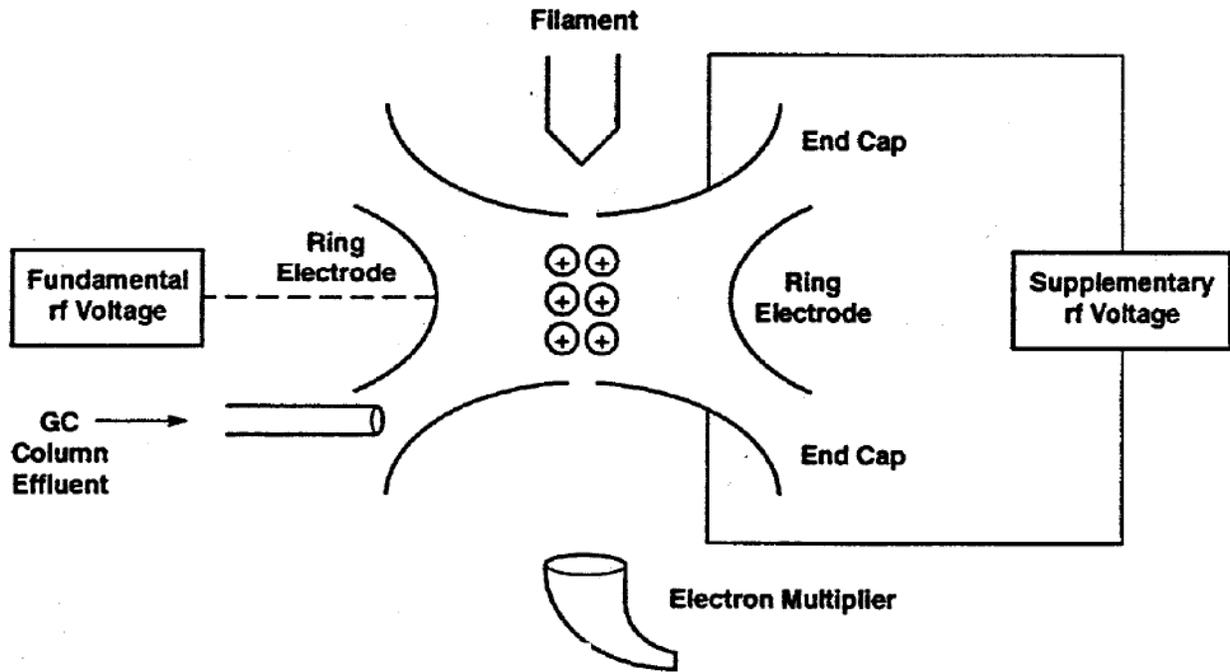
Figure 7. Simplified diagram of an ion trap mass spectrometer.
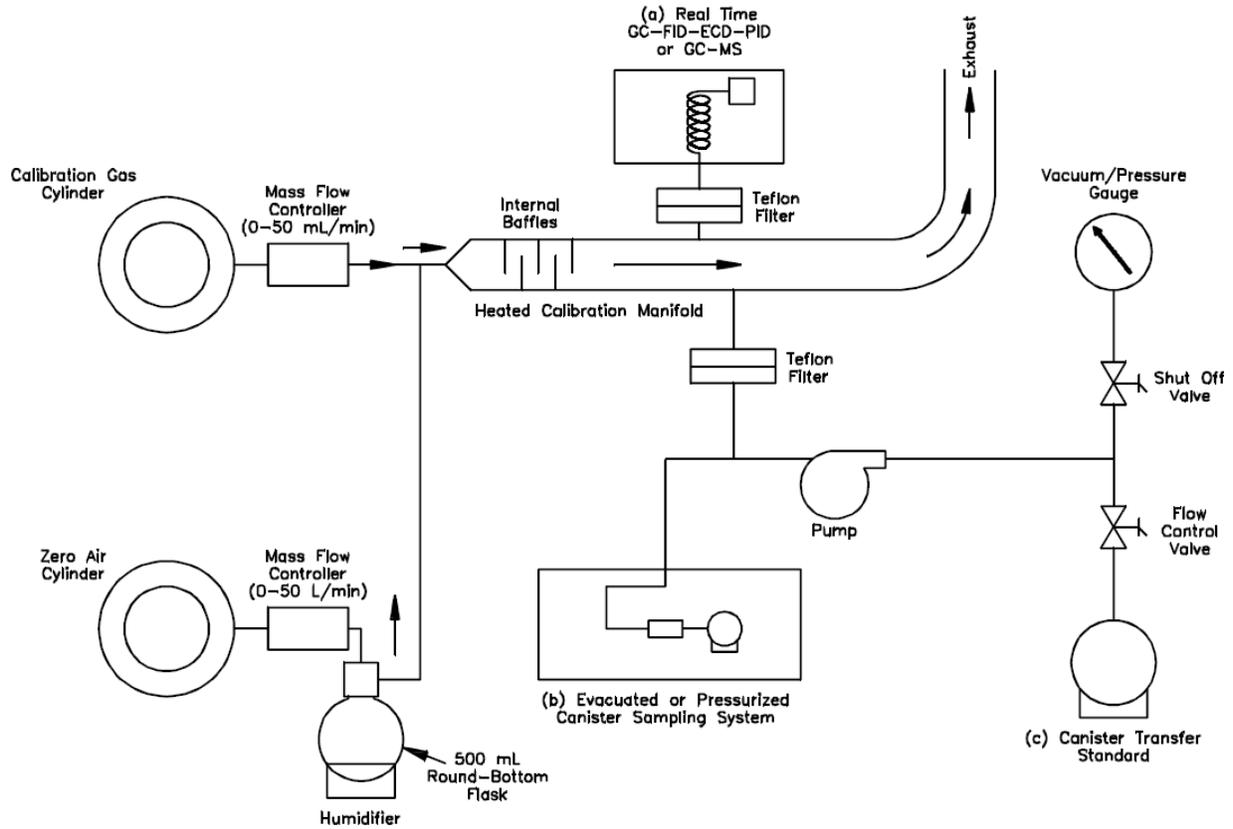
Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

COMPENDIUM METHOD TO-15
CANISTER SAMPLING FIELD TEST DATA SHEET

A.GENERAL INFORMATION

SITE LOCATION: _____

SITE ADDRESS: _____

_____

SAMPLING DATE: _____

SHIPPING DATE: _____

CANISTER SERIAL NO.: _____

SAMPLER ID: _____

  OPERATOR: _____

CANISTER LEAK

    CHECK DATE: _____

B. SAMPLING INFORMATION

TEMPERATURE

	INTERIOR	AMBIENT	MAXIMUM	MINIMUM
START				
STOP				

PRESSURE

CANISTER PRESSURE	

SAMPLING TIMES

	LOCAL TIME	ELAPSED TIME METER READING
START		
STOP		

FLOW RATES

MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT

SAMPLING SYSTEM CERTIFICATION DATE: _____

QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

DATA RECEIVED: _____

RECEIVED BY: _____

INITIAL PRESSURE: _____

FINAL PRESSURE: _____

DILUTION FACTOR: _____

ANALYSIS

  GC-FID-ECD DATE: _____

  GC-MSD-SCAN DATE: _____

  GC-MSD-SIM DATE: _____

RESULTS*: _____

_____

  GC-FID-ECD: _____

  GC-MSD-SCAN: _____

  GC-MSD-SIM: _____

_____

SIGNATURE/TITLE

Figure 9. Canister sampling field test data sheet (FTDS).
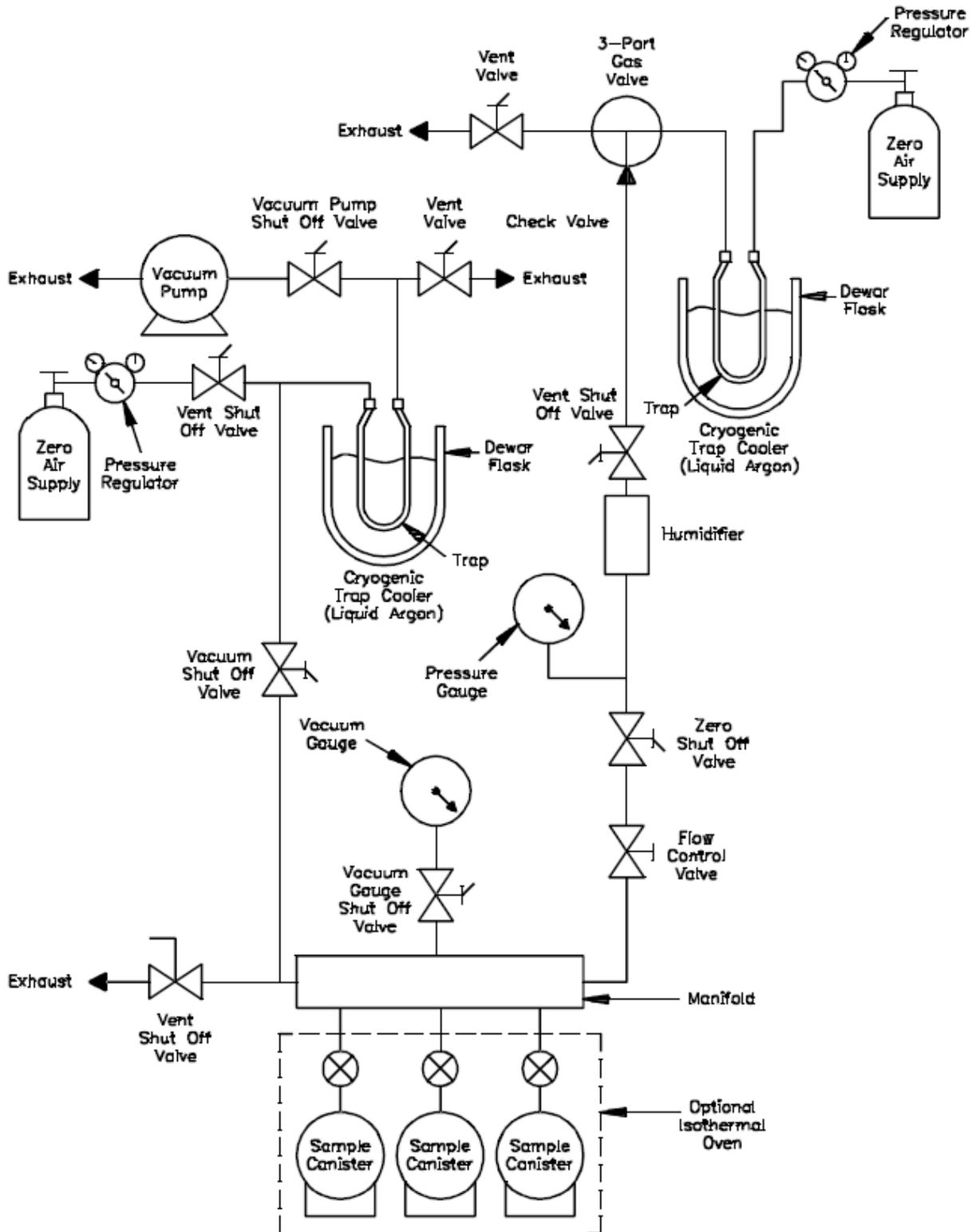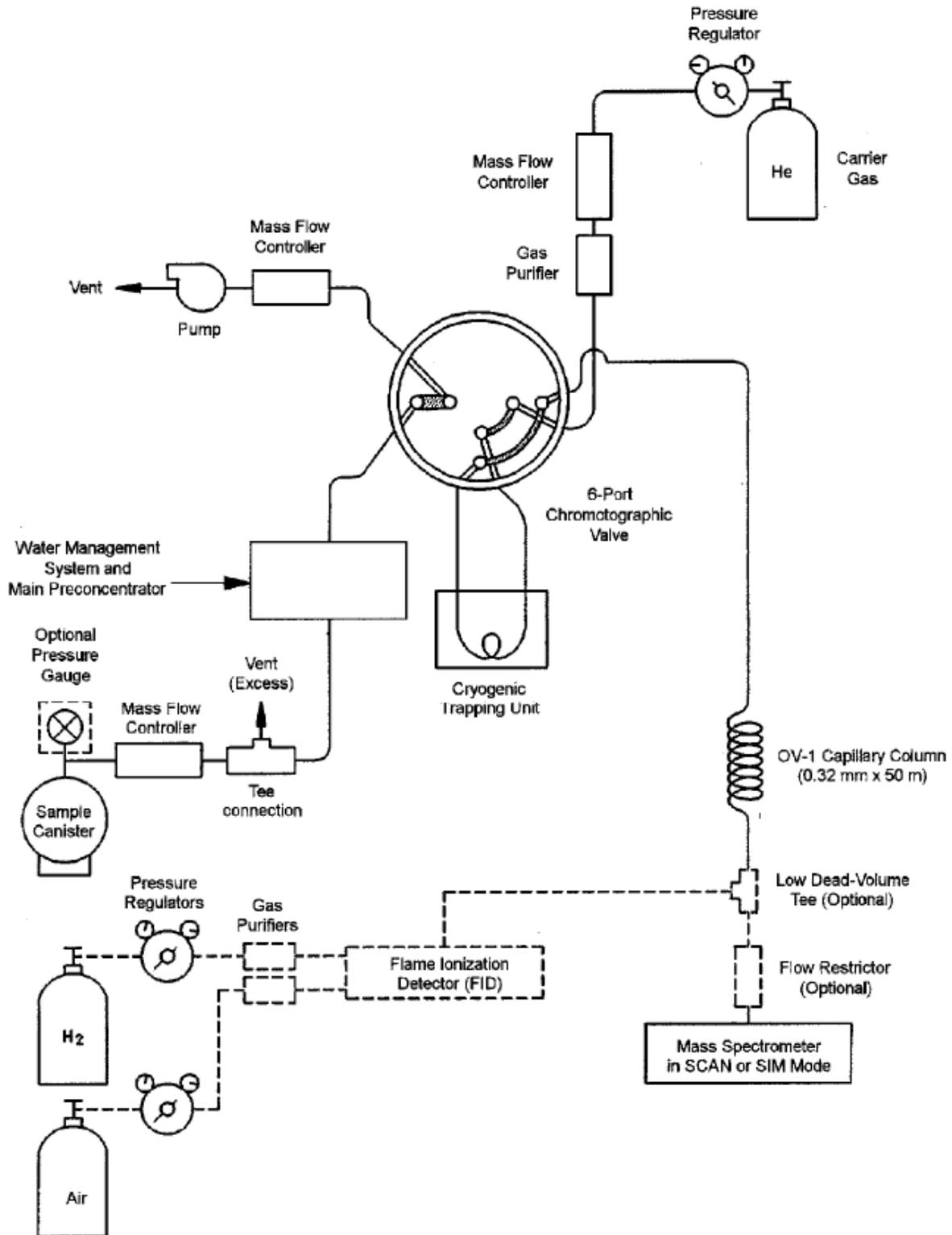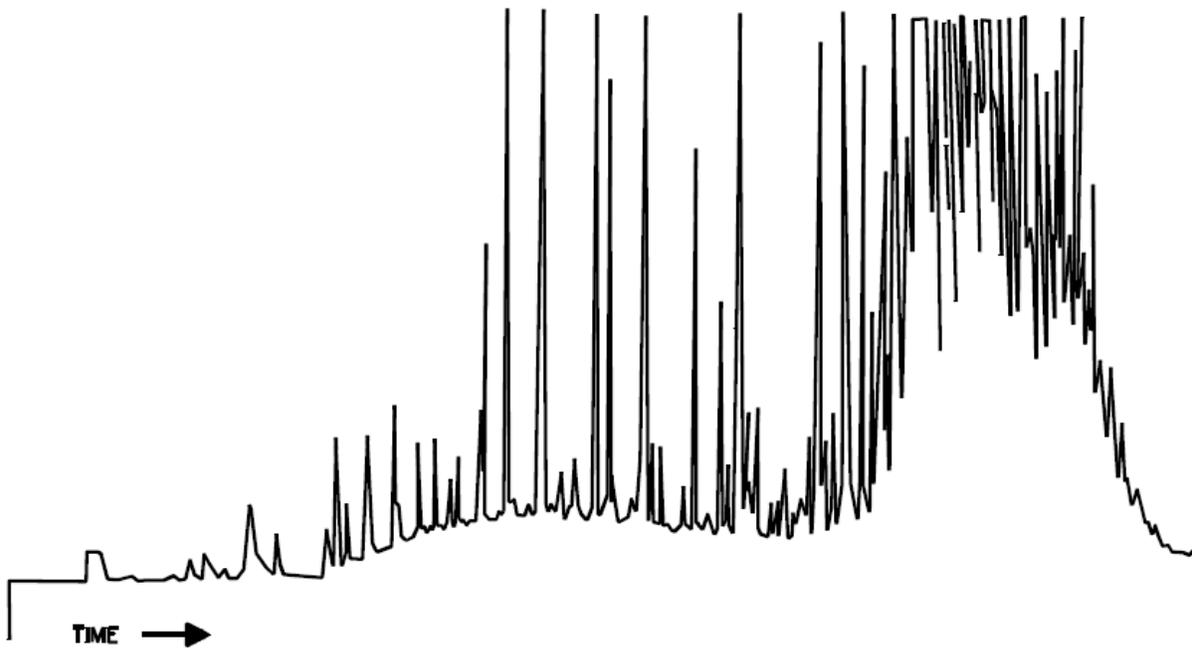
Figure 10. Canister cleaning system.

Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
[Alternative analytical system illustrated in Figure 16.]

(a). Certified Sampler

(b). Contaminated Sampler

Figure 12. Example of humid zero air test results for a clean sample canister (a) and a contaminated sample canister (b).
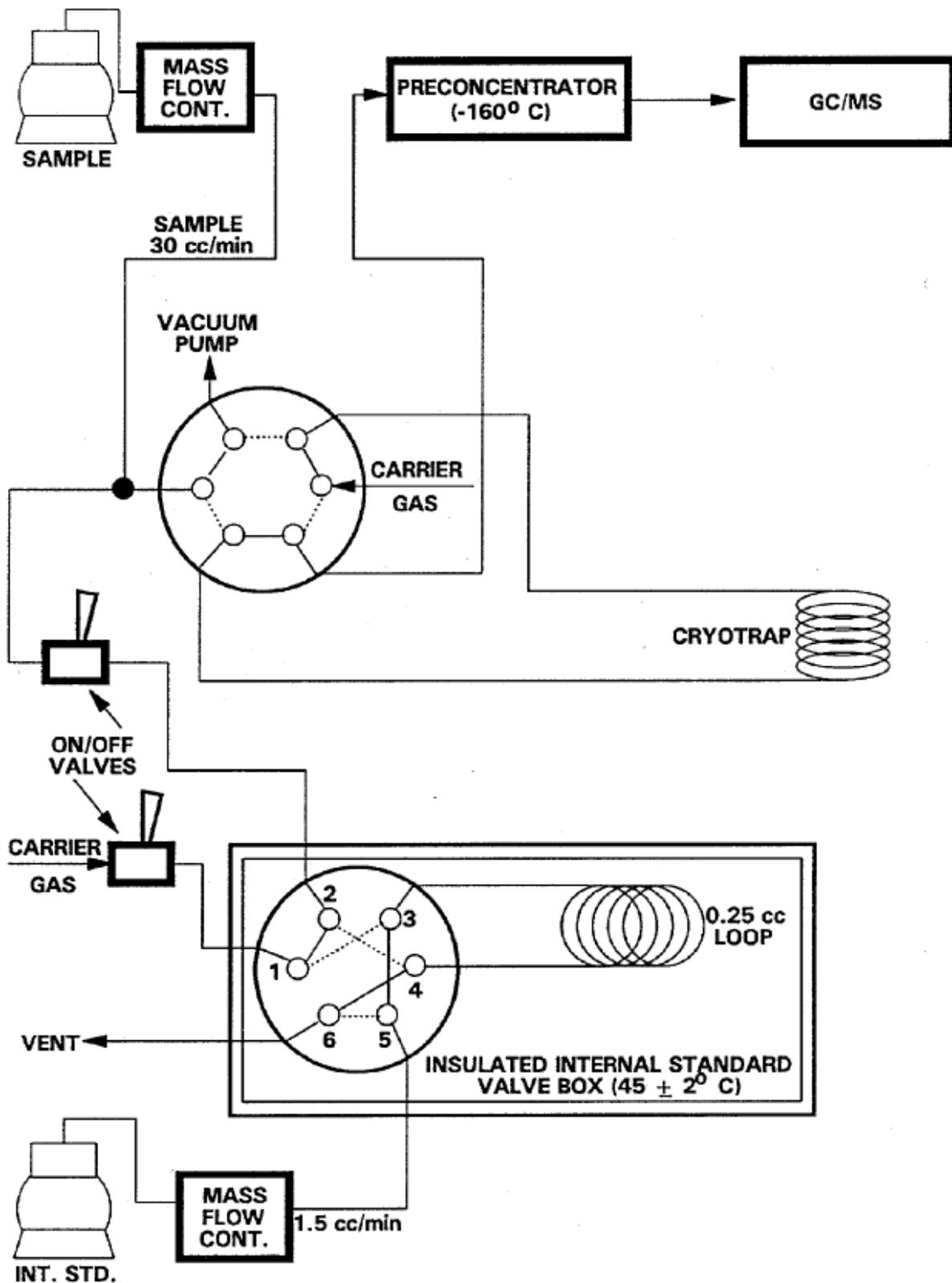
Figure 13. Diagram of design for internal standard addition.
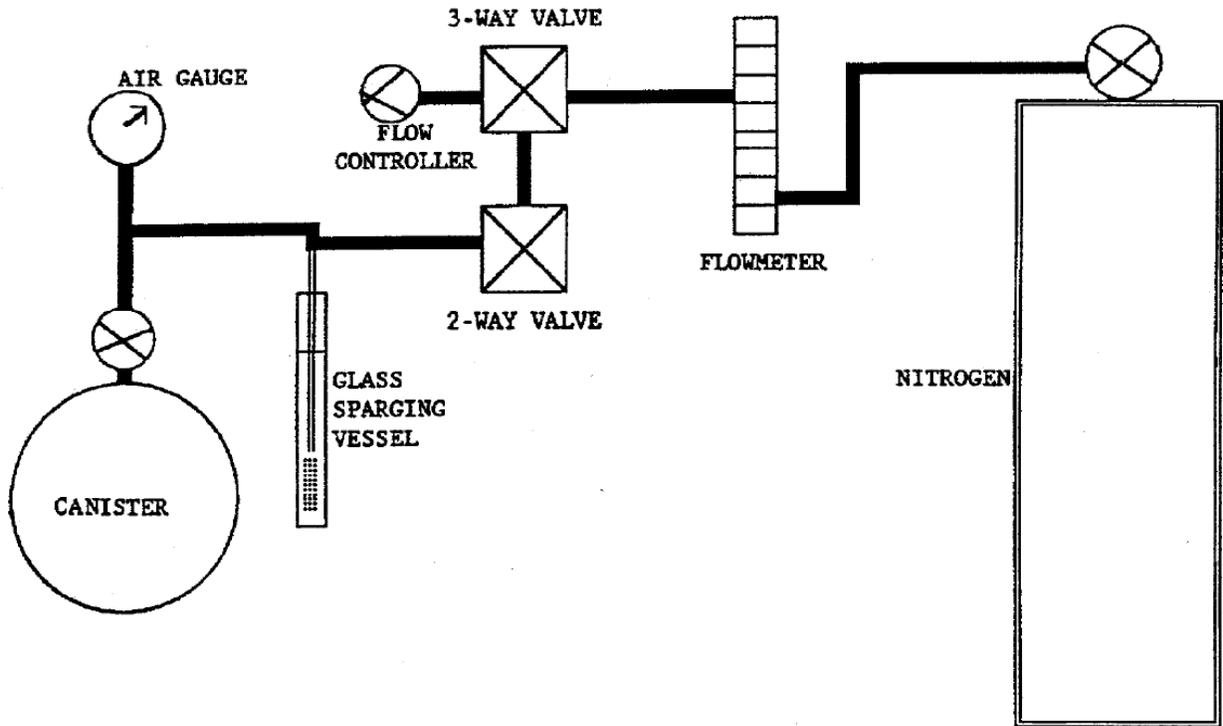
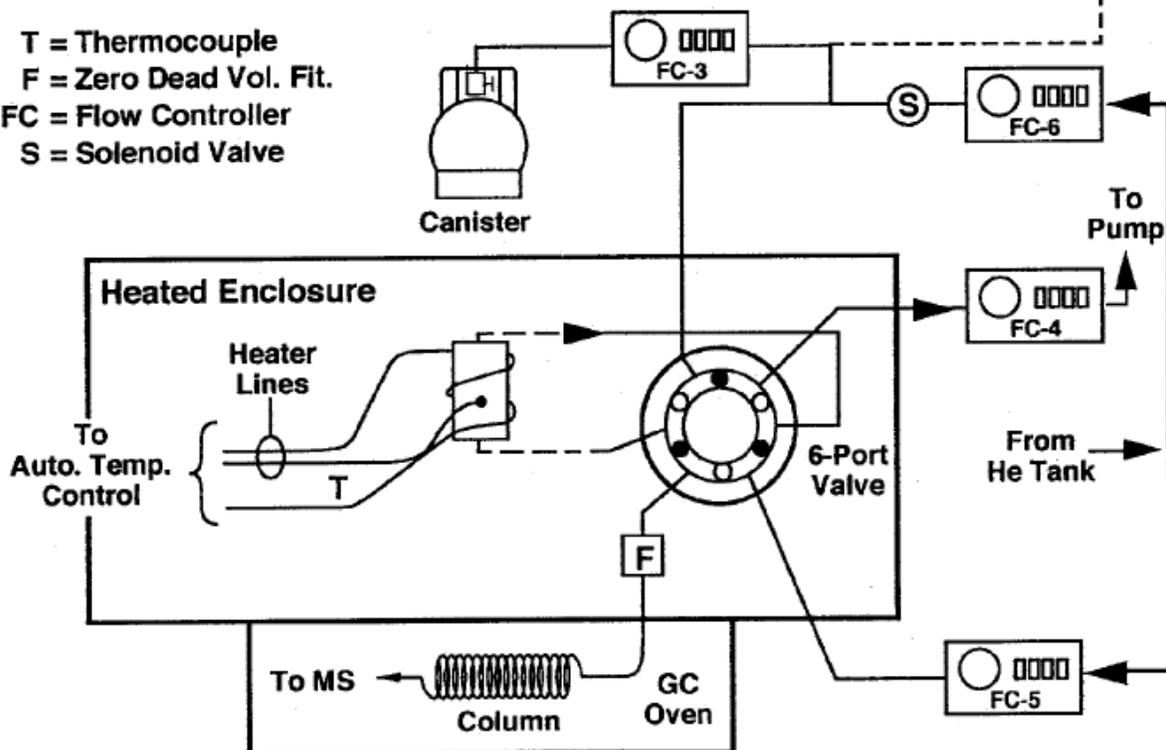**Figure 14. Water method of standard preparation in canisters.**
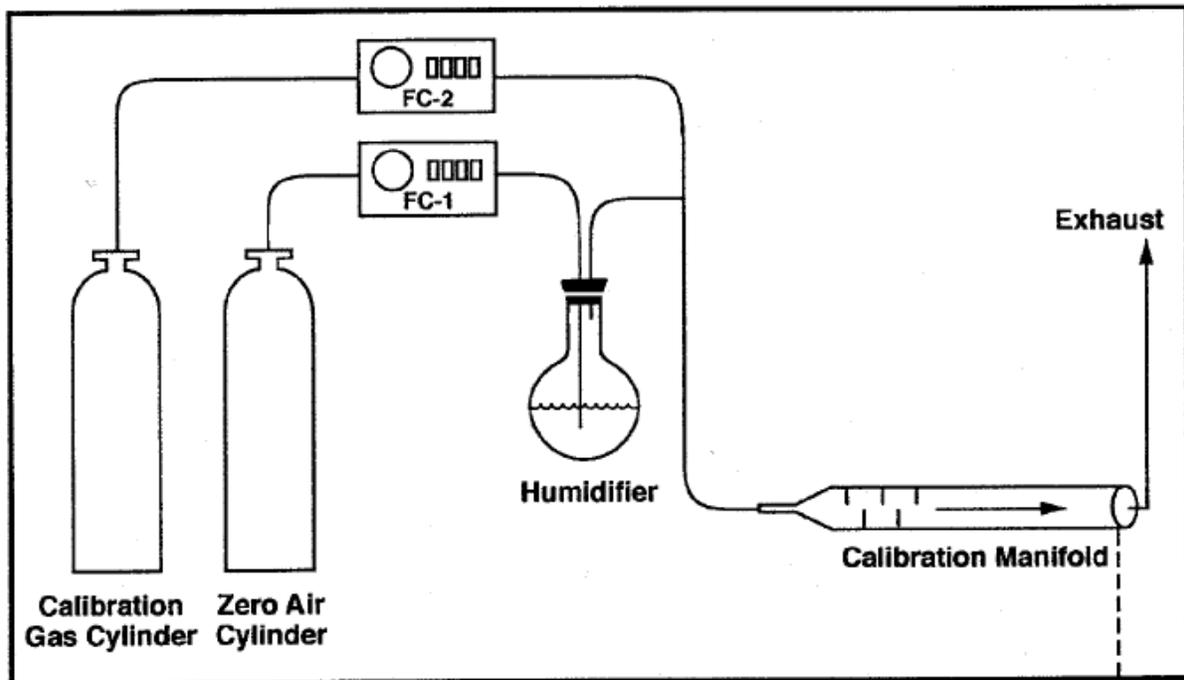
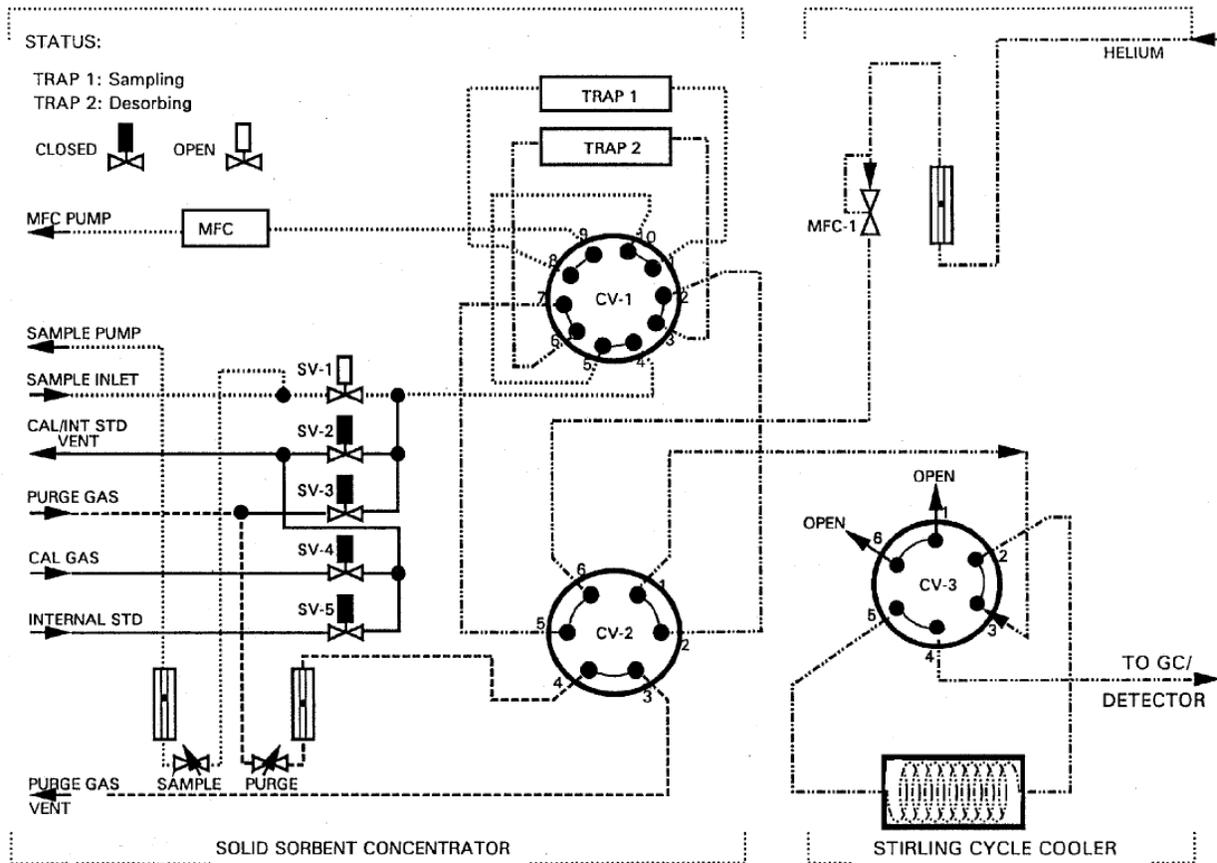**Figure 15. Diagram of the GC/MS analytical system.**

Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).