



Designation: D5466 – 15

# Standard Test Method for Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology)<sup>1</sup>

This standard is issued under the fixed designation D5466; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This standard describes a procedure for sampling and analysis of selected volatile organic compounds (VOCs) in ambient, indoor, and workplace atmospheres. The test method is based on the collection of whole air samples in stainless steel canisters with specially treated (passivated) interior surfaces. For sample analysis, a portion of the sample is subsequently removed from the canister and the collected VOCs are selectively concentrated by adsorption or condensation onto a trap, subsequently released by thermal desorption, separated by gas chromatography, and measured by a mass spectrometric detector or other detector(s). This test method describes procedures for sampling into canisters to final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).<sup>2</sup>

1.2 This test method is applicable to specific VOCs that have been determined to be stable when stored in canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters (1-4).<sup>3</sup> Documentation is also available demonstrating stability of VOCs in subatmospheric pressure canisters. Information on storage stability is available for many polar compounds as well (5-7).

1.3 The procedure for collecting the sample involves the use of inlet lines, air filters, flow rate regulators for obtaining time-integrated samples, and in the case of pressurized samples, an air pump. Typical long-term fixed location canister samplers have been designed to automatically start and stop the sample collection process using electronically actuated valves and timers (8-10). Temporary or short-term canister samplers may require the user to manually start and stop sample

collection. A weatherproof shelter may be required if the sampler is used outdoors. For the purposes of this test method, refer to Practice D1357 for practices and planning ambient sampling events.

1.4 The organic compounds that have been successfully measured at single-digit parts-per-billion by volume (ppbv) levels with this test method are listed in Table 1. The test method is applicable to VOC concentrations ranging from the detection limit to approximately 300 ppbv. Above this concentration, smaller sample aliquots of sample gas may be analyzed or samples can be diluted with dry ultra-high-purity nitrogen or air.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Safety practices should be part of the user's SOP manual.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>4</sup>

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

E355 Practice for Gas Chromatography Terms and Relationships

### 2.2 EPA Documents:<sup>5</sup>

EPA 600/R-96/010b Compendium of Methods for the Determination to Toxic Organic Compounds in Ambient Air, Method TO-14A

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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<sup>2</sup> This test method is based on EPA Compendium Method TO-14, "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA Passivated Canister Sampling and Gas Chromatographic Analysis," May 1988.

<sup>3</sup> The boldface numbers in parentheses refer to the list of references at the end of the standard.

<sup>4</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>5</sup> Produced by United States Environmental Protection Agency (EPA). Available from U.S. Dept. of Commerce, National Technical Information Service, Port Royal Road, Springfield, VA 22161, <http://www.cpa.gov/ttn/amtic/airtox.html>.

**TABLE 1 Typical Volatile Organic Compounds Determined by the Canister Method**

Compound (Synonym)	Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure kPa at 25°C	Listed in the U.S. EPA TO-14A/TO-15	CAS Number
Acetylene						
Propylene						
Freon 12 (Dichlorodifluoromethane)	Cl <sub>2</sub> CF <sub>2</sub>	120.91	-29.8		X/X	
Methyl chloride (Chloromethane)	CH <sub>3</sub> Cl	50.49	-24.2		X/X	74-87-3
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	ClCF <sub>2</sub> CClF <sub>2</sub>	170.93	4.1		X/X	
Vinyl chloride (Chloroethylene)	CH <sub>2</sub> =CHCl	62.50	-13.4		X/X	75-01-4
1,3-Butadiene					/X	
Methyl bromide (Bromomethane)	CH <sub>3</sub> Br	94.94	3.6		X/X	74-83-9
Ethyl chloride (Chloroethane)	CH <sub>3</sub> CH <sub>2</sub> Cl	64.52	12.3		X/X	75-00-3
Acetonitrile					/X	
Freon 11 (Trichlorofluoromethane)	CCl <sub>3</sub> F	137.38	23.7		X/X	
Acrylonitrile						
Vinylidene chloride (1,1-Dichloroethene)	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	96.95	31.7		X/X	75-35-4
Dichloromethane (Methylene chloride)	CH <sub>2</sub> Cl <sub>2</sub>	84.94	39.8		X/X	75-09-2
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	CF <sub>2</sub> ClCCl <sub>2</sub> F	187.38	47.7		X/X	
Trans-1,2-Dichloroethylene					/X	
1,1-Dichloroethane	CH <sub>3</sub> CHCl <sub>2</sub>	98.96	57.3		X/X	74-34-3
Methyl <i>tert</i> -Butyl Ether					/X	
2-Butanone Methyl Ethyl Ketone					/X	
Chloroprene					/X	
cis-1,2-Dichloroethylene	CHCl=CHCl	96.94	60.3		X/X	
Bromochloromethane					/X	
Chloroform (Trichloromethane)	CHCl <sub>3</sub>	119.38	61.7		X/X	67-66-3
Ethyl <i>tert</i> -Butyl Ether					X/X	
1,2-Dichloroethane (Ethylene dichloride)	ClCH <sub>2</sub> CH <sub>2</sub> Cl	98.96	83.5		X/X	107-06-2
Methyl chloroform (1,1,1-Trichloroethane)	CH <sub>3</sub> CCl <sub>3</sub>	133.41	74.1		X/X	71-55-6
Benzene	C <sub>6</sub> H <sub>6</sub>	78.12	80.1		X/X	71-43-2
Carbon tetrachloride (Tetrachloromethane)	CCl <sub>4</sub>	153.82	76.5		X/X	56-23-5
<i>Tert</i> -Amyl Methyl Ether					/X	
1,2-Dichloropropane (Propylene dichloride)	CH <sub>3</sub> CHClCH <sub>2</sub> Cl	112.99	96.4		X/X	78-87-5
Ethyl Acrylate					/X	
Trichloroethylene (Trichloroethene)	ClCH=CCl <sub>2</sub>	131.29	87		X/X	79-01-6
Methyl Methacrylate					X/X	
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	CH <sub>3</sub> CC=CHCl	110.97	76		X/X	
Methyl Methacrylate					/X	
trans-1,3-Dichloropropene (trans-1,3-Dichloropropylene)	ClCH <sub>2</sub> CH=CHCl	110.97	112.0		X/X	
1,1,2-Trichloroethane (Vinyl trichloride)	CH <sub>2</sub> ClCHCl <sub>2</sub>	133.41	113.8		X/X	79-00-5
Toluene (Methyl benzene)	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	92.15	110.6		X/X	108-88-3
Dibromochloromethane					/X	
1,2-Dibromoethane (Ethylene dibromide)	BrCH <sub>2</sub> CH <sub>2</sub> Br	187.88	131.3		X/X	106-93-4
n-Octane					X/X	
Tetrachloroethylene (Perchloroethylene)	Cl <sub>2</sub> C=CCl <sub>2</sub>	165.83	121.1		X/X	127-18-4
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	112.56	132.0		X/X	108-90-7
Ethylbenzene	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	106.17	136.2		X/X	100-41-4
m-Xylene (1,3-Dimethylbenzene)	1,3-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	106.17	139.1		X/X	
p-Xylene (1,4-Dimethylxylene)	1,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	106.17	138.3		X/X	
Styrene (Vinyl benzene)	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	104.16	145.2		X/X	100-42-5
1,1,2,2-Tetrachloroethane	CHCl <sub>2</sub> CHCl <sub>2</sub>	167.85	146.2		X/X	79-34-5
o-Xylene (1,2-Dimethylbenzene)	1,2-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	106.17	144.4		X/X	
4-Ethyltoluene	C <sub>9</sub> H <sub>12</sub>	120.19	162	3 mm Hg	X	622-96-8
1,3,5-Trimethylbenzene (Mesitylene)	1,3,5-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>6</sub>	120.20	164.7		X/X	108-67-8
1,2,4-Trimethylbenzene	1,2,4-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>6</sub>	120.20	169.3		X/X	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	1,3-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.01	173.0		X/X	541-73-1
Chloromethylbenzene					/X	
Benzyl chloride ( <i>α</i> -Chlorotoluene)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	126.59	179.3		X	100-44-7
o-Dichlorobenzene (1,2-Dichlorobenzene)	1,2-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.01	180.5		X/X	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	1,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.01	174.0		X/X	106-46-7
1,1,2,3,4,4-Hexachloro-1,3-butadiene	Cl <sub>6</sub> C <sub>4</sub>	260.76	215		X	7-68-3
1,2,4 - Trichlorobenzene					/X	

**EPA 625/R-96/010b** Compendium of Methods for the Determination to Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-15

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this standard, refer to Terminology **D1356**. Other pertinent abbreviations and symbols are defined within this practice at point of use.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *absolute canister pressure, n*— $P_g + P_a$ , where  $P_g$  = gauge pressure in the canister; (kPa) and  $P_a$  = barometric pressure.

3.2.2 *absolute pressure, n*—pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), expressed as kPa.

3.2.3 *cryogen, n*—a refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. Typical cryogenes are liquid argon (bp  $-185.7^\circ\text{C}$ ) and liquid nitrogen (bp  $-195^\circ\text{C}$ ).

3.2.4 *dynamic calibration, n*—calibration of an analytical system using calibration gas standards generated by diluting compressed gas standards of known concentration with purified, humidified inert gas. Calibration standards are introduced into the inlet of the sampling or analytical system in the same manner as authentic field samples.

3.2.4.1 *Discussion*—An example is dilution of compressed gas standards into canisters followed by analysis of these canisters.

3.2.5 *gauge pressure, n*—pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

3.2.6 *MS-SCAN, n*—the gas chromatograph (GC) is coupled to a Mass Spectrometer (MS) programmed to scan all ions over a preset range repeatedly during the GC run.

3.2.6.1 *Discussion*—This procedure serves for both qualitative identification and quantitation of VOCs in the sample.

3.2.7 *MS-SIM, n*—the GC is coupled to a MS programmed to acquire data for only specified ions (for example, **Table 2**) and to disregard all others. This is termed selected ion monitoring (MS-SIM). The MS-SIM analysis provides quantitative results for VOCs that are preselected by the user.

3.2.8 *pressurized sampling, n*—collection of an air sample in a canister with a (final) canister pressure above atmospheric pressure, using a sample pump.

3.2.9 *qualitative accuracy, n*—the ability of an analytical system to correctly identify compounds.

3.2.10 *quantitative accuracy, n*—the ability of an analytical system to correctly measure the concentration of an identified compound.

3.2.11 *static calibration, n*—calibration of an analytical system using standards in a form that is different than the form of the samples to be analyzed.

3.2.11.1 *Discussion*—An example of a static calibration is injection of a small volume of a high concentration standard

directly onto a GC column, bypassing the sample extraction and preconcentration portion of the analytical system.

3.2.12 *subatmospheric sampling, n*—collection of an air sample in an evacuated canister to a (final) canister pressure below atmospheric pressure, with or without the assistance of a sampling pump.

3.2.12.1 *Discussion*—The canister is filled as the internal canister pressure increases to ambient or near ambient pressure. An auxiliary vacuum pump may be used as part of the sampling system to flush the inlet tubing prior to or during sample collection.

3.2.13 *verification, n*—the process of demonstrating with humid zero air and humid calibration gases that the sampling system components and the canister do not contribute positive or negative bias to the analysis results.

### 4. Summary of Test Method

4.1 The method is taken from published work (**1-22**) and is the basis of EPA Compendium Methods TO-14A and TO-15. It has been used since the early 1980s in studies to establish long term trends in certain atmospheric gases (**11**), to determine the prevalence and extent of VOC contributions to ozone production (**12**), and to determine the concentrations of selected VOCs in ambient air (**13, 14**).

4.2 Both subatmospheric pressure and pressurized sampling modes using a passivated, evacuated canister are described.

4.2.1 Procedures are provided for canister cleaning and performance evaluation.

4.2.2 A sampling line less than 2 % of the volume of the canister, or a pump-ventilated sample line, is used during sample collection. A sample of air is drawn through a sampling train consisting of components that regulate the rate and duration of sampling into a pre-cleaned and pre-evacuated canister.

4.2.3 Pressurized sampling requires an additional pump to provide positive pressure to the canister.

4.3 After the air sample is collected, the canister isolation valve is closed, the canister is removed from the sampler, an identification tag is attached to the canister, and the canister is transported to a laboratory for analysis.

4.4 Upon receipt at the laboratory, the data on the canister tag are recorded and the canister is attached to a pressure gauge to accurately measure the final canister pressure.

4.5 For analysis, VOCs are concentrated by collection in a trap with or without cryogenic cooling. The VOCs are thermally desorbed from the trap into a small volume of carrier gas, separated by gas chromatography, and measured by a mass spectrometric detector or other detector(s) such as a flame ionization detector (FID) or an electron capture detector (ECD). Both compound identification and quantitation are performed with this test method. For the purposes of this test method, refer to Practice **E355** for terms and practices used in gas chromatography.

4.6 The analytical procedure can be automated (**15-17**) or manual (**18**).

**TABLE 2 Primary and Secondary Ions for Selected VOCs Analyzed by GC-MS**

Compound <sup>A</sup>	m/z (Primary)	m/z Secondary (amu/% base peak)
Freon 12 (Dichlorodifluoromethane)	85	87(31)
Methyl chloride (Chloromethane)	50	52(34)
Freon 114 (1,2-Dichloro-1,1,2,2- tetrafluoroethane)	85	135(56) and 87(33)
Vinyl chloride (Chloroethene)	62	27(125) and 64(32)
1,3-Butadiene	54	39(89)
Methyl bromide (Bromomethane)	94	96(85)
Ethyl chloride (Chloroethane)	64	29(140) and 27(140)
Freon 11 (Trichlorofluoromethane)	101	103(67)
Acrylonitrile	53	52(85)
Vinylidene chloride (1,1-Dichloroethylene)	61	96(55) and 63(31)
Dichloromethane (Methylene chloride)	49	84(65) and 86(45)
Freon 113 (1,1,2-Trichloro-1,2,2- trifluoroethane)	151	101(140) and 103(90)
1,1-Dichloroethane	63	27(64) and 65(33)
Trans-1,2-Dichloroethene	96	61(98)
Methyl tert-Butyl Ether	73	57(26)
Chloroprene	53	88(63) and 90(21)
cis-1,2-Dichloroethene	61	96(60) and 98(44)
Chloroform (Trichloromethane)	83	85(65) and 47(35)
Ethyl tert-Butyl Ether	59	87(44) and 57(33)
1,2-Dichloroethane (Ethylene dichloride)	62	27(70) and 64(31)
Methyl chloroform (1,1,1-Trichloroethane)	97	99(64) and 61(61)
Benzene	78	77(25) and 50(35)
Carbon tetrachloride (Tetrachloromethane)	117	119(97)
Tert-Amyl Methyl Ether	73	87(27)
1,2-Dichloropropane (Propylene dichloride)	63	41(90) and 62(70)
Ethyl Acrylate	55	99(8)
Bromodichloromethane	83	85(64) and 129(14)
Trichloroethylene (Trichloroethene)	130	132(92) and 95(87)
Methyl Methacrylate	41	69(26) and 100(8)
cis-1,3-Dichloropropene	75	39(70) and 77(30)
Methyl Isobutyl Ketone	75	39(70) and 77(30)
trans-1,3-Dichloropropene	75	39(70) and 77(30)
1,1,2-Trichloroethane (Vinyl trichloride)	97	83(90) and 61(82)
Toluene (Methyl benzene)	91	92(57)
Dibromochloromethane	129	127(19) and 131(6)
1,2-Dibromoethane (Ethylene dibromide)	107	109/96 and 27(115)
Octane	43	85(51) and 114(4)
Tetrachloroethylene (Perchloroethylene)	166	164(74) and 131(60)
Chlorobenzene	112	77(62) and 114(32)
Ethylbenzene	91	106(28)
m,p-Xylene (1,3/1,4-dimethylbenzene)	91	106(40)
Bromoform	173	171(51) and 175(49)
Styrene (Vinyl benzene)	104	78/60 and 103/49
1,1,2,2-Tetrachloroethane	83	85(64)
o-Xylene (1,2-Dimethylbenzene)	91	106(40)
4-Ethyltoluene	105	120(29)
1,3,5-Trimethylbenzene (Mesitylene)	105	120(42)
1,2,4-Trimethylbenzene	105	120(42)
m-Dichlorobenzene (1,3-Dichlorobenzene)	146	148(65) and 111(40)
Benzyl chloride (-Chlorotoluene)	91	126(26)
p-Dichlorobenzene (1,4-Dichlorobenzene)	146	148(65) and 111(40)
o-Dichlorobenzene (1,2-Dichlorobenzene)	146	148(65) and 111(40)
1,2,4-Trichlorobenzene	180	182(98) and 184(30)
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro- 1,3-butadiene)	225	227(66) and 223(60)

<sup>A</sup> In typical retention time order using a dimethylpolysiloxane-phase column

4.7 A mass spectrometric detector (MS coupled to a GC) is the principal analytical tool used for qualitative and quantitative analysis because it allows positive compound identification. MS detectors include, but are not limited to, magnetic sector mass analyzers, quadrupole mass filters, combined magnetic sector-electrostatic sector mass analyzers, time-of-flight mass analyzers and ion trap mass spectrometers.

#### 4.7.1 Comparison of GC/MS Technologies:

##### 4.7.1.1 GC/MS–SCAN:

(1) Lower sensitivity than GC/MS-SIM,

(2) Greater sample volume may be required compared to GC/MS-SIM,

(3) Resolution of co-eluting interfering ions is possible,

(4) Positive target compound identification,

(5) Positive non-target compound identification possible,

(6) Quantitative determination of calibrated compounds, and

(7) Qualitative and semiquantitative determination of compounds not on calibration list.



#### 4.7.1.2 GC/MS-SIM:

- (1) Can't identify non-target compounds,
- (2) Less operator interpretation,
- (3) Higher sensitivity than GC/MS-SCAN,
- (4) Less sample volume required to obtain same MDLs compared to GC/MS-Scan, and
- (5) Quantitative determination of calibrated compounds.

#### 4.7.1.3 GC/TOF MS:

- (1) Positive target compound identification,
- (2) Positive non-target compound identification possible,
- (3) Resolution of co-eluting interfering ions is possible and superior to GC-MS-Scan,
- (4) Sensitivity is equal to GC/MS-SIM mode, or better,
- (5) Less sample volume required to obtain same MDLs compared to GC/MS-Scan,
- (6) Quantitative determination of calibrated compounds, and
- (7) Qualitative determination of compounds not contained on calibration list.

4.7.2 The GC/MS-Scan option uses a capillary column GC coupled to a MS operated in a scanning mode which repeatedly acquires a wide mass range of ion data; the acquired mass spectra are supported by spectral library search routines. The GC/TOF MS option uses a capillary column GC coupled to a TOF MS which acquires wide mass range of ion fragment data continuously; the mass spectra are supported by library search routines. These options allow unambiguous compound identification and cover a wide range of compounds as defined by the completeness of the spectral libraries, with GC/TOF MS providing greater sensitivity in most cases. GC/MS-SIM mode is limited to a set of user-selected target compounds; this mode is more sensitive than GC/MS-SCAN by virtue of the longer dwell times at the restricted number of  $m/z$  values. As the number of ions monitored simultaneously in a GC/MS-SIM analysis increases, the sensitivity of this technique approaches GC/MS-SCAN. Maximum sensitivity for GC/MS-SIM is achieved when no more than 4 to 5 ions are monitored simultaneously.

## 5. Significance and Use

5.1 VOCs are emitted into ambient, indoor, and workplace air from many different sources. These VOCs are of interest for a variety of reasons including participation in atmospheric chemistry and acute or chronic human health impacts.

5.2 Canisters are particularly well suited for the collection and analysis of very volatile and volatile organic compounds. This test method describes the collection and analysis of whole gas samples and is not subject to high volatility limitations.

5.3 Chemically stable selected VOCs have been successfully collected in passivated stainless steel canisters. Collection of atmospheric samples in canisters provides for: (1) convenient integration of air samples over a specific time period (for example, 8 to 24 h), (2) remote sampling and central laboratory analysis, (3) ease of storing and shipping samples, (4) unattended sample collection, (5) analysis of samples from multiple sites with one analytical system, (6) dilution or additional sample concentration to keep the sample size introduced into the analytical instrument within the calibration range, (7)

collection of sufficient sample volume to allow assessment of measurement precision through replicate analyses of the same sample by one or several analytical systems, and (8) sample collection using a vacuum regulator flow controller if electricity is not available.

5.4 Interior surfaces of the canisters may be treated by any of several proprietary passivation processes including an electropolishing process to remove or cover reactive metal sites on the interior surface of the vessel and a fused silica coating process.

5.5 For this standard, VOCs are defined as organic compounds that can be quantitatively recovered from the canisters having a vapor pressure greater than  $10^{-2}$  kPa at 25°C and 760 mm Hg.

5.6 Target compound polarity is also a factor in compound recovery. Aliphatic and aromatic hydrocarbons from C1 to C13 have been successfully measured with this standard but are not listed in **Table 1 (21)**. Higher polarity target compounds may interact with the canister surface or humidity on the canister surface causing their apparent vapor pressure to decrease. Polar VOCs such as ethers and esters have been successfully measured by this method and are listed in **Table 1**.

5.7 Recovery and stability studies shall be conducted on compounds not listed in **Table 1** before expanding the use of this test method to additional compounds.

## 6. Interferences and Limitations

6.1 Water management is a significant analytical problem because VOC preconcentrators typically accumulate water vapor as well as VOCs, especially those preconcentrators that use reduced temperature condensation (for example dehydration traps). The water can restrict and even stop the sample air flow, alter chromatography and GC retention times, remove dissolved polar species and adversely affect the operation of detector systems, especially mass spectrometric systems. In-line permeable membrane dryers have historically been used prior to preconcentration and do not produce artifacts for a number of nonpolar VOCs (**19, 20**). However, in-line permeable dryers may contribute to the loss of polar species as these species may also partition with the water vapor. Release of an air sample from a pressurized canister that contains humid air will result in a systematic increase in the humidity of the released sample air as long as condensed water remains on the canister interior (**21**).

6.2 For those applications where a membrane dryer is used, interferences can occur in sample analysis if moisture accumulates in the dryer (see **10.1.1.3**). This can be avoided by ensuring flow rates of the drying gas are high (for example 5 to 10 times the sample flow rate) and the drying gas has a dew point  $<-50^{\circ}\text{C}$ . In extreme circumstances, an automated cleanup procedure that periodically heats the dryer to about  $100^{\circ}\text{C}$  while purging with zero air or an inert gas (such as  $\text{N}_2$  or He) can help to remove moisture buildup. This procedure does not degrade sample integrity.

NOTE 1—Removing moisture from samples may not be necessary with GC/MS systems that are differentially pumped and that do not employ a membrane drying apparatus.

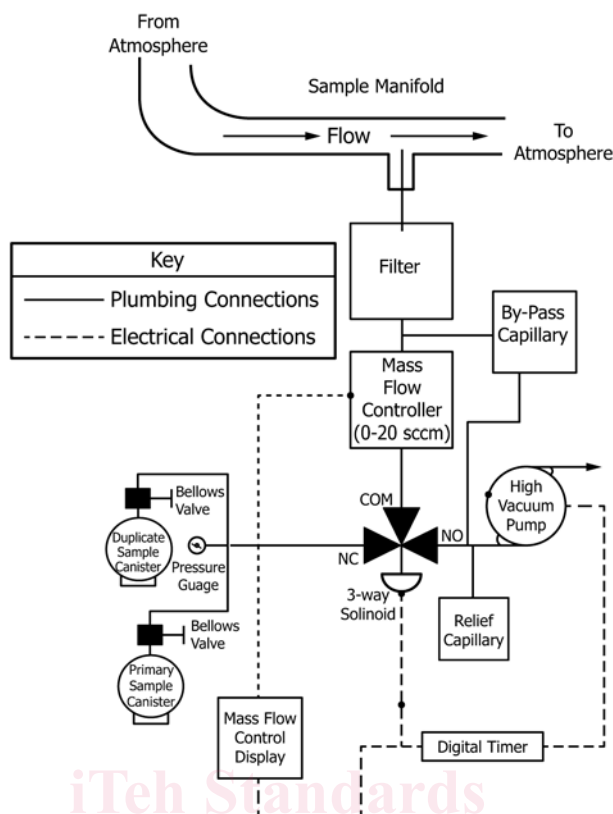


FIG. 1 Example Sampler Configuration for Subatmospheric Pressure Canister Sampling

6.3 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (for example, pump and flow controllers) shall be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples. Instructions for cleaning the canisters and the field sampling system are described in 11.1 and 11.2, respectively. In addition, sufficient system and field blank samples shall be analyzed to detect contamination.

6.4 If the concentrator-GC/MS analytical system employs a permeable membrane dryer or equivalent to remove water vapor selectively from the sample stream, polar organic compounds will permeate this membrane concurrently with the water. Consequently, the analyst shall calibrate the system with the target VOCs. For quantitative analysis of polar compounds, analytical systems shall not employ permeable membrane dryers.

6.5 The analysis methodology is based upon the identification of a VOC by comparison of its chromatographic retention time and mass spectrum to the retention time and mass spectrum of a pure standard run on the same system using the same analytical conditions. Quantitation is based on pure standard calibrations. Any elements of the air matrix that interfere with the ability to identify the mass spectrum, obtain accurate peak areas, or obtain an accurate retention time of a VOC will affect the performance of the analysis. High concentration interfering compounds generate distorted chromatographic peaks and may affect detector response. Dilution or smaller sample injection size may resolve retention time

uncertainty but may adversely affect the method sensitivity. If a co-eluting compound is encountered, the mass spectrum may allow deconvolution of compounds unless the co-eluting compound is an isomer of the compound of interest or the characteristic masses of the interferences and the target compound are the same. Reanalysis of the sample on a different chromatographic column may aid in measurement of target and interfering VOC.

## 7. Apparatus

7.1 Stainless steel canisters with interior surfaces passivated by either electropolishing or silica coating, available from various commercial sources.

7.2 Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been evaluated for VOC testing in air (8-10). Several configurations of standard hardware can be used successfully as canister sampling units.

7.2.1 *Subatmospheric Pressure* (see Fig. 1).

7.2.1.1 *Inlet Line*, stainless steel tubing to connect the sampler to the sample inlet.

7.2.1.2 *Canister*, leak-free stainless steel pressure vessels of desired volume (for example, 6 L), with valve and passivated interior surfaces.

7.2.1.3 *Vacuum/Pressure gauge*, capable of measuring vacuum (-100 to 0 kPa) and pressure (0 to 200 kPa) in the sampling system. Gauges shall be tested clean and leak tight.

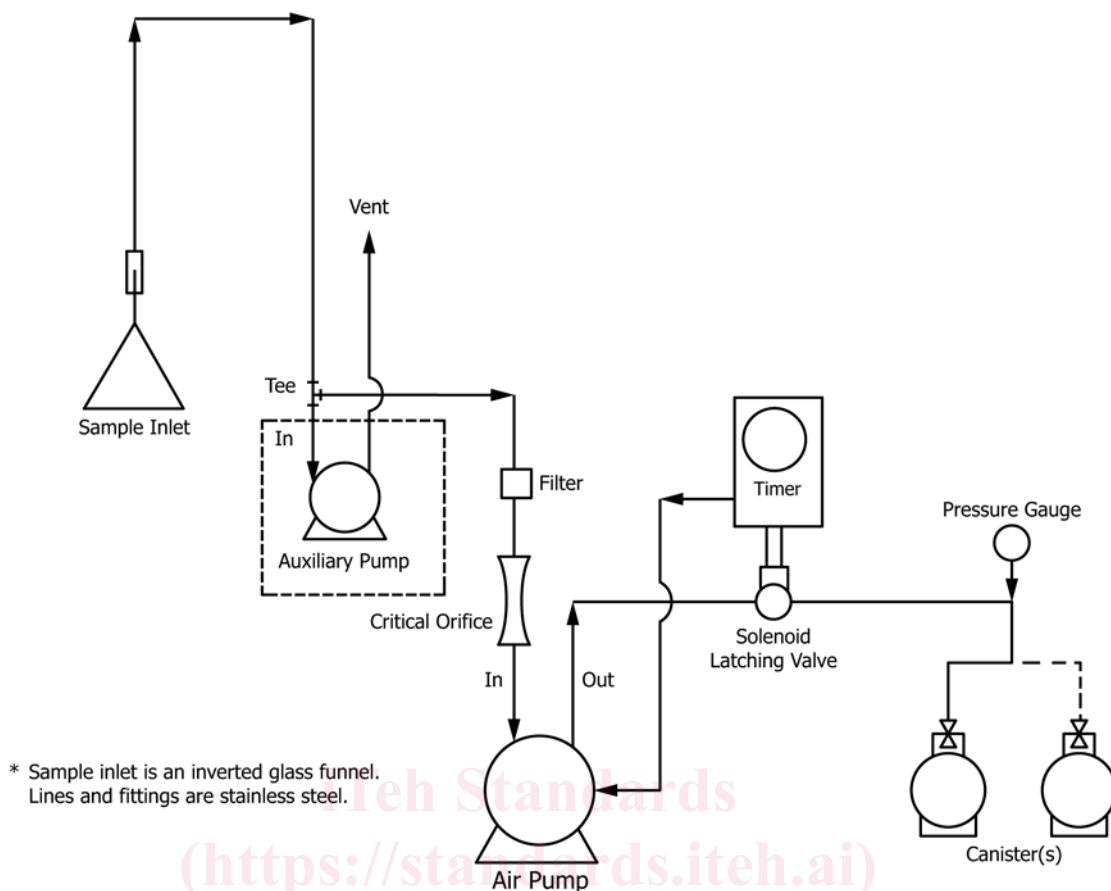


FIG. 2 Alternative Sampler Configuration for Pressurized Canister Sampling

7.2.1.4 *Mass Flow Meter and Controller*, capable of maintaining a constant flow rate ( $\pm 10\%$ ) over a sampling period of up to 24 h and under conditions of changing temperature (20 to 40°C) and humidity.

7.2.1.5 *Filter*, 2- $\mu\text{m}$  sintered stainless-steel in-line filter.

7.2.1.6 *Electronic Timer*, capable of activating a solenoid valve (see 7.2.1.7) to start and stop flow entering a canister, for example, for unattended sample collection.

7.2.1.7 *Solenoid Valve*, electrically operated, latching solenoid valve with fluoroelastomer seat and o-rings, or low temperature solenoid valve with fluoroelastomer seat and o-rings

7.2.1.8 *Tubing and Fittings*, chromatographic grade stainless steel tubing and fittings for interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis shall be chromatographic grade stainless steel.

7.2.1.9 *Heater*, thermostatically controlled to maintain temperature inside insulated sampling enclosure above ambient temperature if needed.

7.2.1.10 *Fan*, for cooling sampling system, if needed.

7.2.1.11 *Thermostat*, automatically regulates fan operation, if needed.

7.2.1.12 *Maximum-Minimum Thermometer*, records highest and lowest temperatures during sampling period.

7.2.1.13 *Shut-Off Valve*, stainless steel—leak free, for vacuum/pressure gauge.

7.2.1.14 *Auxiliary Vacuum Pump (optional)*, continuously draws air to be sampled 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. The use of higher inlet flow rates dilutes contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls. Pump is not necessary if the intake manifold volume represents less than 5 % of the final sample volume.

7.2.1.15 *Elapsed Time Meter*, capable of measuring the duration of sampling to the nearest second.

7.2.1.16 *Optional Fixed Orifice, Capillary, Adjustable Micrometering Valve, or Vacuum Regulator Manual Flow Controllers*, may be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Such systems require manual activation and deactivation. In this standard, application of a pumpless simple orifice sampler is appropriate only in situations where samples consume 60 % or less of the total capacity of the canister used for collection. Typically this limits the sample duration to a maximum of 24 h per 6 L canister or 72 h per 15 L canister.

7.2.2 *Pressurized Sampling Apparatus*, see Fig. 2.

7.2.2.1 *Sample Pump*, stainless steel pump head, metal bellows type capable of 200 kPa output pressure. Pump shall be free of leaks, clean, and uncontaminated by oil or organic compounds.

**TABLE 3 Preconcentration, GC, and MS Operating Condition Guidelines**

System Component		Alternative System Description	
Preconcentrator		Electrically cooled/Non Cryogen systems	Cryogen systems
	Focusing trap packing	Multibed trap (for example, porous polymer/graphitized carbon black/carbon molecular sieve)	
	Trap low temperature	–40 to 25°C	–150 to –178°C
	Trap high temperature	280°C	200°C
	Flow path temperature	160°C	
Chromatography Column		60-m × 0.32-mm I.D. (1 to 1.8 μm film thickness) cyanopropylphenyl-dimethylpropylsiloxane	50-m × 0.32-mm I.D. (17 μm film thickness) crosslinked 100 % dimethylpolysiloxane
Carrier Gas		Constant pressure 68.9 kPa	Helium (2.0 cm <sup>3</sup> /min at 250°C)
GC Oven Temperature Program			
	Initial Column Temperature	35 to 40°C	–50°C
	Initial Hold Time	5 mins	2 min
	Program	5 to 8°C/min to 220°C	8°C/min to 220°C
	Final Hold Time	5 min	5 min
Mass Spectrometer			
	Mass Range		
	Scan Time		
	EI Condition	70 eV	
	Mass Scan	Follow manufacturer's instruction for selecting	
	Detector Mode	mass selective detector (MS) and selected ion	
	Scan Time	monitoring (MS-SIM) mode	
	EI Condition	Multiple ion detection	

NOTE 2—Several sampling systems have been developed that result in pressurizing a canister with sample air. The system illustrated in Fig. 2 uses an auxiliary vacuum pump to flush the sample inlet. A non-contaminating air pump pulls air from the inlet tubing, through a critical orifice that regulates the flow into the canister.

7.2.2.2 *Other Supporting Materials*, all other components of the pressurized sampling system are similar to components discussed in 7.2.1.1 – 7.2.1.16.

### 7.3 Sample Analysis Equipment:

7.3.1 *GC/MS-Analytical System (Full Mass Range Data Acquisition and MS-SIM)*:

7.3.1.1 The GC/MS-SCAN analytical system shall be capable of acquiring and processing data in the MS-SCAN mode. The GC/MS-SIM analytical system shall be capable of acquiring and processing data in the MS-SIM mode.

7.3.1.2 *Gas Chromatograph*, including standard features such as gas flow regulators, automatic control of valves and oven parameters, etc. Sub ambient temperature programming is optional.

7.3.1.3 *Chromatographic Detector*, mass spectrometric detector equipped with computer and appropriate software. The GC/MS is set in the SCAN mode, where the MS screens the sample for identification and quantitation of VOC species.

7.3.1.4 *Thermal Desorber/Preconcentrator*, refer to 10.1.1.4 for complete description of the system. Thermal desorbers/preconcentration devices may be added to the GC/MS system or built into the GC by the manufacturer.

7.3.1.5 Complete cryogenic concentrator units are commercially available from several vendors. The characteristics of current concentrators include rapid, “ballistic” heating of the concentrator to release trapped VOC’s into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

7.3.1.6 *Electronic Mass Flow Controllers*, to maintain constant flow for carrier gas and sample gas and to continuously monitor flow rates.

7.3.1.7 *Vacuum Pump*, general purpose laboratory pump, capable of drawing the desired sample volume through the thermal desorber/preconcentrator.

7.3.1.8 *Chromatographic Grade Stainless Steel Tubing and Stainless Steel Plumbing Fittings*, Refer to 7.2.1.8 for description.

7.3.1.9 *Chromatographic Column* (see Table 3), to provide compound separation.

NOTE 3—Columns other than those in Table 3 (for example, 6 % cyanopropylphenyl/94 % dimethylpolysiloxane) can be used as long as the system meets user needs. Wider megabore columns (that is, greater than 0.530 mm I.D.) are less susceptible to plugging as a result of trapped water, thus potentially eliminating the need for a permeable membrane dryer or other water management procedures in the analytical system. These columns have sample capacity approaching that of a packed column, while retaining much of the peak resolution traits of narrower columns (that is, 0.32 mm I.D.). Multibed sorbent traps, cold trap dehydration or microscale purge and trap techniques for moisture management in conjunction with 0.32 mm I.D. columns have also been used with no plugging from water.

7.3.1.10 *Stainless Steel Vacuum/Pressure Gauge (optional)*, capable of measuring vacuum (–100 to 0 kPa) and pressure (0–200 kPa) in the sampling system. Gauges shall be tested clean and leak tight.

7.3.1.11 *Cylinder Pressure Stainless Steel Regulators*, two-stage cylinder regulators with pressure gauges for helium, zero air, nitrogen, and hydrogen gas cylinders as needed.

7.3.1.12 *Gas Purifiers (4)*, molecular sieve or carbon used to remove organic impurities and moisture from gas streams.

7.3.1.13 *Low Dead-Volume Tee or Press Fit Splitter (optional)*, used to split the exit flow from the GC column.

7.3.1.14 *Dryer (optional)*, consisting of permeable membrane tubing coaxially mounted within larger tubing, available commercially. Refer to 10.1.1.3 for description.

7.3.1.15 *Six-Port Gas Chromatographic Valve*.

7.4 *Canister Cleaning System (see Fig. 3)*:

7.4.1 *Vacuum Pump*, capable of evacuating sample canister(s) to an absolute pressure of less than 0.0064 kPa.

7.4.2 *Manifold*, made of stainless steel with connections for simultaneously cleaning several canisters.

7.4.3 *Shut-Off Valve(s)*, on-off toggle valves.



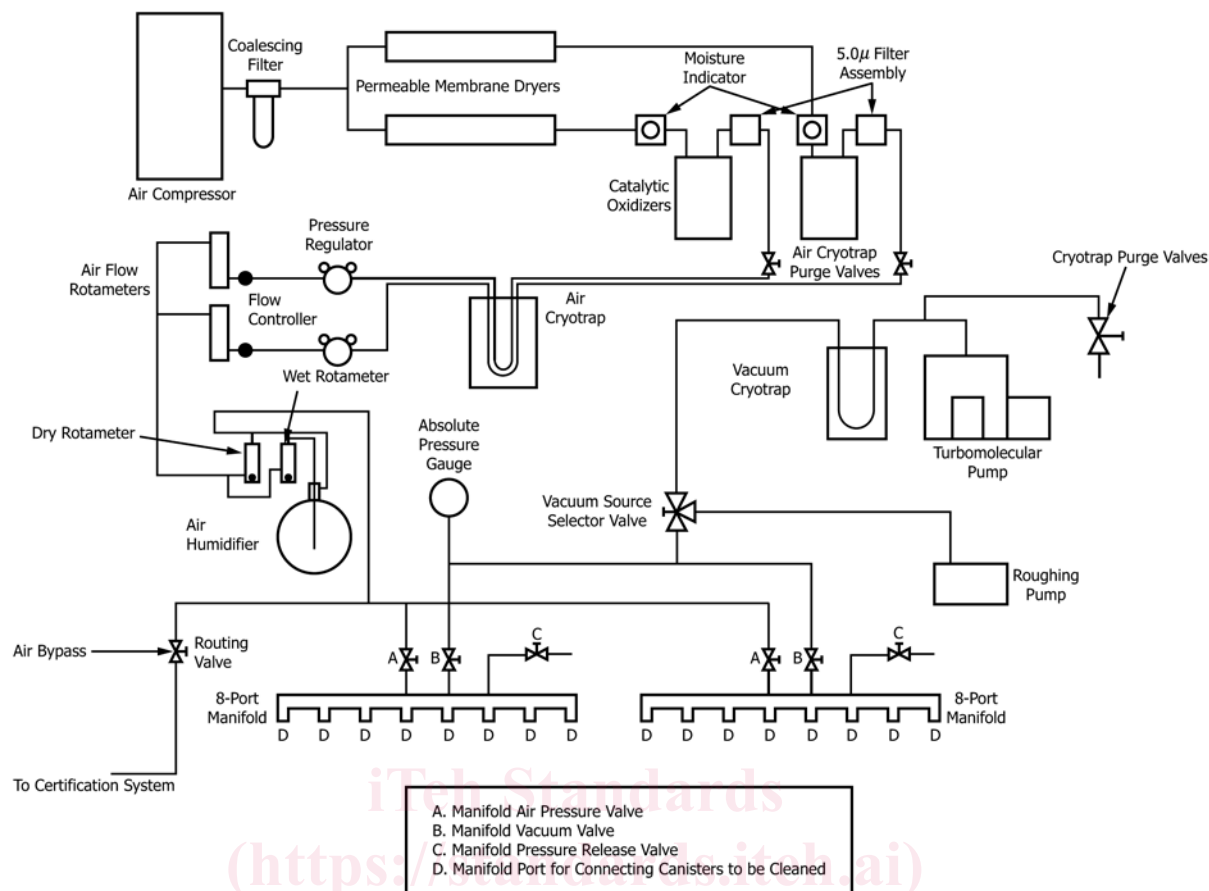


FIG. 3 Canister Cleanup Apparatus

7.4.4 *Stainless Steel Vacuum Gauge*, capable of measuring vacuum in the manifold to an absolute pressure of 0.0064 kPa, or less.

7.4.5 *Cryogenic Trap* required only for those system using oil-based vacuum pumps or gases that are not sufficient to meet blank criteria), made of stainless steel U-shaped open tubular trap cooled with liquid nitrogen for air purification purposes to prevent contamination from back diffusion of oil from vacuum pump and to provide clean, zero air to sample canister(s).

7.4.6 *Stainless Steel Pressure Gauges* (2), 0 to 350 kPa to monitor zero air pressure.

7.4.7 *Stainless Steel Flow Control Valve*, to regulate flow of zero air into canister(s).

7.4.8 *Humidifier*, consisting of pressurizable water bubbler, (typically a passivated canister with or without a dip tube and dual valves). Humidifier contains high performance liquid chromatography (HPLC) grade deionized water.

7.4.9 *Isothermal Oven (optional)*, for heating canisters.

NOTE 4—Oven temperature shall not exceed the manufacturer’s recommendation during cleaning to avoid degradation of the passivated canister surface on repeated cleaning.

7.5 *Calibration System and Manifold (see Fig. 4):*

7.5.1 *Calibration Manifold*, chromatographic grade stainless steel or glass manifold (125 mm I.D. by 660 mm), with sampling ports and internal mixing for flow disturbance to ensure proper mixing.

7.5.2 *Humidifier*, 500-mL impinger flask containing HPLC grade deionized water or equivalent.

7.5.3 *Electronic Mass Flow Controllers*, to control flow of standard/diluent gas with acceptable flow ranges (for example, one 0 to 5 L/min, one 0 to 50 mL/min).

7.5.4 *PTFE–Fluorocarbon Filter(s)*, 47-mm TFE–Fluorocarbon filter or sintered stainless steel filter capable of removing particulate matter greater than 2 µm in diameter.

## 8. Reagents and Materials

8.1 Gas cylinders of helium, hydrogen, nitrogen, and zero air ultrahigh purity grade, as required.

8.2 *Gas Calibration Standards*—cylinder(s) containing approximately 100 ppb to 1.0 ppm of each of the target VOCs. Candidate VOCs are shown in Table 2. Gas calibration standards shall be diluted with sufficient accuracy and precision to meet the performance requirements in this standard at concentrations down to five times the required method detection limit (MDL).

8.2.1 The gas calibration cylinder(s) shall be traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). The components may be purchased in one cylinder or may be separated into different cylinders. Refer to manufacturer’s specification for guidance on purchasing and mixing VOCs in gas cylinders.

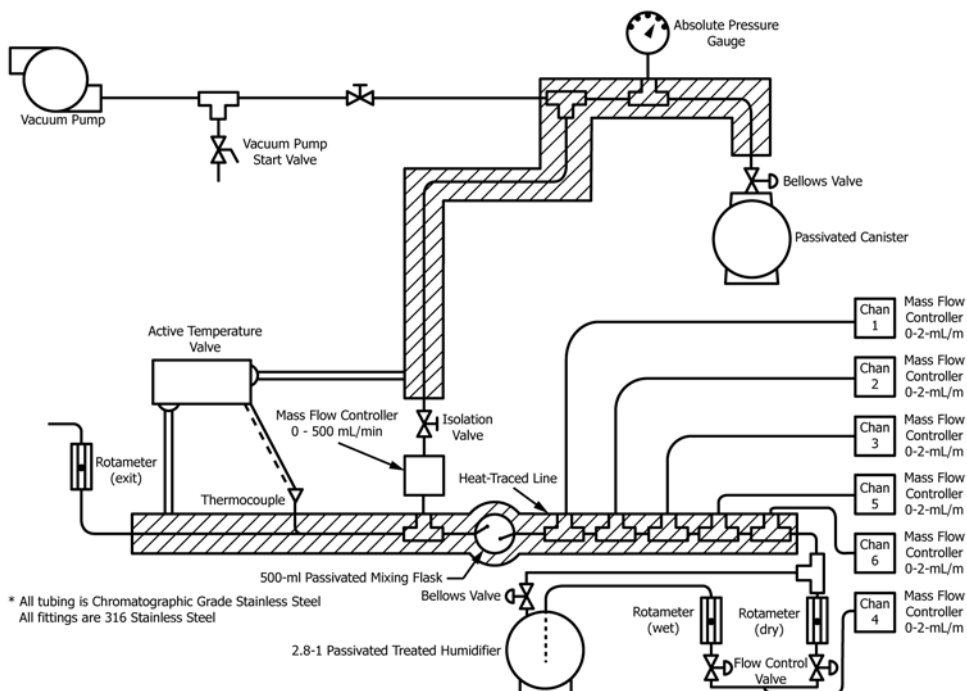


FIG. 4 Schematic of Calibration System and Manifold for (a) Analytical System Calibration, (b) Testing Canister Sampling System and (c) Preparing Canister Transfer Standards

8.3 *Liquid Nitrogen* ( $bp -195.8^{\circ}C$ ), used only for clean air traps and GC oven coolant, and for sample concentration traps requiring active control to maintain  $-185.7^{\circ}C$ .

8.4 *Liquid Argon* ( $bp -185.7^{\circ}C$ ), for sample traps that are not actively controlled to  $-185.7^{\circ}C$ .

8.5 *Gas Purifiers*, molecular sieve or carbon, connected in-line between hydrogen, nitrogen, and zero air gas cylinders and system inlet line, to remove moisture and organic impurities from gas streams.

8.6 *Deionized Water*, high performance liquid chromatography (HPLC) grade, ultrahigh purity (for humidifier).

8.7 *4-4-Bromofluorobenzene*, used to check GC/MS tuning.

8.8 *Methanol*, for cleaning sampling system components, reagent grade.

## 9. Sampling System

### 9.1 System Description:

#### 9.1.1 Subatmospheric Pressure Sampling—See Fig. 1.

9.1.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.0064 kPa, or less. When opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. Manual initiation and termination of canister sampling can be conducted using a filter, vacuum gauge, and mass flow controller or vacuum regulator connected directly to the canister inlet. The canister valve is manually opened to initiate sampling and closed after the duration is complete and canister is filled to approximately 88.1 kPa. This technique may be used to collect grab samples (duration of 10 to 30 s) or time-integrated samples (duration of 12 to 24 h) taken through a flow-restrictive inlet.

9.1.1.2 With a critical orifice flow restrictor, the flow rate decreases as the canister pressure approaches atmospheric pressure. With a mass flow controller, the flow rate varies to compensate for reduced canister vacuum. For example, an electronic flow controller with a flow rate range of 0 to 50 cc/min can maintain a constant (less than 5 % change) flow rate of 5 cc/min from full vacuum to within 7 kPa below ambient pressure.

#### 9.1.2 Pressurized Sampling—See Fig. 2.

9.1.2.1 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 100–200 kPa final canister pressure. For example, a 6-L evacuated canister can be filled at 7.1 mL/min for 24 h to achieve a final pressure of about 67 kPa.

NOTE 5—Collection of pressurized samples in humid environments may result in condensation of water in canisters. The presence of condensed water may decrease the recovery of polar compounds from the canister and adversely impact chromatography.

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

#### 9.1.3 All Samplers:

9.1.3.1 A flow control device is used to maintain a relatively 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:

$$F = \frac{(P \times V)}{(t \times 60)} \quad (1)$$