



Designation: ~~D5466 – 15~~ D5466 – 21

## Standard Test Method for Determination of Volatile Organic Compounds in Atmospheres (~~Canister Sampling~~ Sampling, Mass Spectrometry Analysis 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 test method 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.

~~1.2 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 low resolution 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>~~

~~1.3 This test method is applicable to specific VOCs that have been determined to be stable when stored in ~~canisters~~ canisters (see [Table 1](#)). 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 also available for many polar compounds as well ~~(5-7)~~. This test method has been documented for the compounds listed in [Table 1](#) and performance results apply only to those compounds. A laboratory may determine other VOCs by this test method after completion of verification studies that include measurement of recovery as specified in [5.7](#) and that are as extensive as required to meet the performance needs of the customer and the given application.~~

1.4 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.

<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. Current edition approved Dec. 1, 2015 Aug. 15, 2021. Published June 2016 September 2021. Originally approved in 1993. Last previous edition approved in 2007 2015 as ~~D5466 – 01 (2007):D5466 – 15~~. DOI: 10.1520/D5466-15.10.1520/D5466-21.

<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. [Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry \(GC/MS\)](#)" January 1999.

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

1.5 The organic compounds that have been successfully measured at ~~single-digit~~ single-digit micrograms per cubic metre ( $\mu\text{g}/\text{m}^3$ ) (or ~~single digit~~ parts-per-billion by volume (~~ppbv~~) levels(ppbv)) concentration with this test method are listed in order of approximate retention time in **Table 1**. The test method is applicable to VOC concentrations ranging from the detection limit to approximately ~~300 ppbv~~ 1000  $\mu\text{g}/\text{m}^3$  (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~~ air or equivalent.

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

1.7 *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~~ safety, health, and health environmental practices and determine the applicability of regulatory limitations prior to use. Safety practices should be part of the ~~user~~ user's SOP manual.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 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 of Toxic Organic Compounds in Ambient Air, Method TO-14A Air — Second Edition TO-15**

**EPA 625/R-96/010b NATTS Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-15 Technical Assistance Document (TAD)**

## 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~~ mass spectrometer (MS) programmed to scan or detect all ions over a preset mass range repeatedly during the GC run.

<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~~ standard's Document Summary page on the ASTM website.

<sup>5</sup> Produced by Available from 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.epa.gov/ttn/amtic/airtox.html>. (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

**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)	C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub> CF <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-tert-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-tert-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
Tert-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>3</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>3</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 (α-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	

### 3.2.6.1 Discussion—

This procedure serves for both qualitative identification and quantitation of VOCs in the sample.

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

NOTE 1—See 5.7 for requirements to add to this list.

Compound (Synonym)	Formula	Molecular Weight	Vapor Pressure kPa (25°C)	Listed in the U.S. EPA TO-14A/TO-15	CAS Number
Freon 12 (Dichlorodifluoromethane)	$\text{Cl}_2\text{CF}_2$	120.91	568	X/X	75-71-8
Methyl chloride (Chloromethane)	$\text{CH}_3\text{Cl}$	50.49	506	X/X	74-87-3
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	$\text{ClCF}_2\text{CClF}_2$	170.93	4.1	X/X	76-14-2
Vinyl chloride (Chloroethylene)	$\text{CH}_2=\text{CHCl}$	62.50	344	X/X	75-01-4
1,3-Butadiene	$(\text{CH}_2=\text{CH})_2$	54.09	279	X	106-99-0
Methyl bromide (Bromomethane)	$\text{CH}_3\text{Br}$	94.94	3.6	X/X	74-83-9
Ethyl chloride (Chloroethane)	$\text{CH}_3\text{CH}_2\text{Cl}$	64.52	12.3	X/X	75-00-3
Acetonitrile	$\text{C}_2\text{H}_3\text{N}$	41.05	9.9	O/X	75-05-8
Freon 11 (Trichlorofluoromethane)	$\text{CCl}_3\text{F}$	137.38	23.7	X/X	75-69-4
Acrylonitrile	$\text{C}_3\text{H}_3\text{N}$	53.03	11.0		107-13-1
Vinylidene chloride (1,1-Dichloroethene)	$\text{C}_2\text{H}_2\text{Cl}_2$	96.95	31.7	X/X	75-35-4
Dichloromethane (Methylene chloride)	$\text{CH}_2\text{Cl}_2$	84.94	39.8	X/X	75-09-2
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	$\text{CF}_2\text{ClCCl}_2\text{F}$	187.38	47.7	X/X	76-13-1
Trans-1,2-Dichloroethylene	$\text{C}_2\text{H}_2\text{Cl}_2$	96.95	44.13	O/X	156-60-5
1,1-Dichloroethane	$\text{CH}_3\text{CHCl}_2$	98.96	57.3	X/X	74-34-3
Methyl <i>tert</i> -Butyl Ether	$(\text{CH}_3)_3\text{COCH}_3$	88.15	32.7	O/X	1634-04-4
2-Butanone Methyl Ethyl Ketone	$\text{C}_4\text{H}_8\text{O}$	77.11	13.3	O/X	78-93-3
Chloroprene	$\text{C}_4\text{H}_5\text{Cl}$	88.54	25.06	O/X	126-99-8
cis-1,2-Dichloroethylene	$\text{CHCl}=\text{CHCl}$	96.94	60.3		156-59-2
Bromochloromethane	$\text{CH}_2\text{BrCl}$	129.38	15.6	O/X	74-97-5
Chloroform (Trichloromethane)	$\text{CHCl}_3$	119.38	61.7	X/X	67-66-3
Ethyl <i>tert</i> -Butyl Ether	$\text{C}_8\text{H}_{14}\text{O}$	102.18	32.7	X/X	637-92-3
1,2-Dichloroethane (Ethylene dichloride)	$\text{ClCH}_2\text{CH}_2\text{Cl}$	98.96	83.5	X/X	107-06-2
Methyl chloroform (1,1,1,-Trichloroethane)	$\text{CH}_3\text{CCl}_3$	133.41	74.1	X/X	71-55-6
Benzene	$\text{C}_6\text{H}_6$	78.12	80.1	X/X	71-43-2
Carbon tetrachloride (Tetrachloromethane)	$\text{CCl}_4$	153.82	76.5	X/X	56-23-5
Tert-Amyl Methyl Ether	$\text{C}_8\text{H}_{14}\text{O}$	102.18	9	O/X	994-05-8
1,2-Dichloropropane (Propylene dichloride)	$\text{CH}_2\text{CHClCH}_2\text{Cl}$	112.99	96.4	X/X	78-87-5
Ethyl Acrylate	$\text{C}_6\text{H}_8\text{O}_2$	100.12	2	O/X	140-88-5
Trichloroethylene (Trichloroethene)	$\text{ClCH}=\text{CCl}_2$	131.29	87	X/X	79-01-6
Methyl Methacrylate	$\text{C}_5\text{H}_8\text{O}_2$	100.12	3.9	X/X	80-62-6
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	$\text{CH}_3\text{CC}=\text{CHCl}$	110.97	4.59	X/X	542-75-6
Methyl Isobutyl Ketone	$\text{C}_8\text{H}_{12}\text{O}$	100.16	2.13	O/X	108-10-1
trans-1,3-Dichloropropene (trans-1,3-Dichloropropylene)	$\text{ClCH}_2\text{CH}=\text{CHCl}$	110.97	3.07	X/X	542-75-6
1,1,2-Trichloroethane (Vinyl trichloride)	$\text{CH}_2\text{ClCHCl}_2$	133.41	2.53	X/X	79-00-5
Toluene (Methyl benzene)	$\text{C}_6\text{H}_5\text{CH}_3$	92.15	2.8	X/X	108-88-3
Dibromochloromethane	$\text{CHBr}_2\text{Cl}$	208.28	7.32	O/X	124-48-1
1,2-Dibromoethane (Ethylene dibromide)	$\text{BrCH}_2\text{CH}_2\text{Br}$	187.88	1.56	X/X	106-93-4
n-Octane	$\text{C}_8\text{H}_{18}$	114.23	1.47	X/X	111-65-9
Tetrachloroethylene (Perchloroethylene)	$\text{Cl}_2\text{C}=\text{CCl}_2$	165.83	1.87	X/X	127-18-4
Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	112.56	1.20	X/X	108-90-7
Ethylbenzene	$\text{C}_6\text{H}_5\text{C}_2\text{H}_5$	106.17	1.33	X/X	100-41-4
m-Xylene (1,3-Dimethylbenzene)	$1,3-(\text{CH}_3)_2\text{C}_6\text{H}_4$	106.17	1.20	X/X	108-38-3
p-Xylene (1,4-Dimethylxylene)	$1,4-(\text{CH}_3)_2\text{C}_6\text{H}_4$	106.17	1.20	X/X	106-42-3
Bromoform	$\text{CH}_2\text{Br}_3$	252.73	0.747	X/X	75-25-2
Styrene (Vinyl benzene)	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	104.16	0.67	X/X	100-42-5
1,1,2,2-Tetrachloroethane	$\text{CHCl}_2\text{CHCl}_2$	167.85	0.67	X/X	79-34-5
o-Xylene (1,2-Dimethylbenzene)	$1,2-(\text{CH}_3)_2\text{C}_6\text{H}_4$	106.17	0.93	X/X	95-47-6
4-Ethyltoluene	$\text{C}_9\text{H}_{12}$	120.19	1.38	X/O	622-96-8
1,3,5-Trimethylbenzene (Mesitylene)	$1,3,5-(\text{CH}_3)_3\text{C}_6\text{H}_6$	120.20	0.267	X/X	108-67-8
1,2,4-Trimethylbenzene	$1,2,4-(\text{CH}_3)_3\text{C}_6\text{H}_6$	120.20	0.665	X/X	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	$1,3-\text{Cl}_2\text{C}_6\text{H}_4$	147.01	0.286	X/X	541-73-1
Chloromethylbenzene	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	126.58	0.133	O/X	100-44-7
Benzyl chloride ( $\alpha$ -Chlorotoluene)	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	126.59	0.123	X/O	100-44-7
o-Dichlorobenzene (1,2-Dichlorobenzene)	$1,2-\text{Cl}_2\text{C}_6\text{H}_4$	147.01	0.181	X/X	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	$1,4-\text{Cl}_2\text{C}_6\text{H}_4$	147.01	0.232	X/X	106-46-7
1,1,2,3,4,4-Hexachloro-1,3-butadiene	$\text{Cl}_6\text{C}_4$	260.76	0.04	X/X	7-68-3
1,2,4 - Trichlorobenzene	$\text{C}_6\text{H}_3\text{Cl}_3$	181.44		0.133	O/X 120-82-1

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.

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

Compound <sup>A</sup>	m/z (Primary)	m/z Secondary (amu/% base peak)
Compound <sup>A</sup>	m/Q (Primary)	m/Q Secondary (typical mass/% 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)
Ethyl Chloride (Chloroethane)	64	66(30)
Acetonitrile	41	40(50)
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)
Trans-1,2-Dichloroethene	96	61(98)
1,1-Dichloroethane	63	27(64) and 65(33)
Trans-1,2-Dichloroethene	96	64(98)
Methyl tert-Butyl Ether	73	57(26)
2-Butanone (Methyl Ethyl Ketone)	43	72(25)
Chloroprene	53	88(63) and 90(21)
cis-1,2-Dichloroethene	61	96(60) and 98(44)
Bromochloromethane	83	85(64) and 129(14)
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)
Methyl Isobutyl Ketone	43	58(35), 100(15)
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 ( $\beta$ -Chlorotoluene)	94	126(26)
Benzyl chloride ( $\alpha$ -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)
p-Dichlorobenzene (1,4-Dichlorobenzene)	146	148(65) and 111(40)
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro- 1,3-butadiene)	225	227(66) and 223(60)
1,2,4-Trichlorobenzene	180	182(98) and 184(30)

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

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, canister is examined to verify the inlet valve is closed, there is no or insignificant damage of the sample container, the chain of custody is complete from the field, 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) detector. 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).

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~~: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~~ Non-target compound identification possible,
- (6) Quantitative determination of calibrated compounds, and
- (7) Qualitative and semiquantitative determination of compounds not on calibration list.

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#### 4.7.1.2 *GC/MS-SIM:*

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

#### 4.7.1.3 ~~GC/TOF-MS~~GC/TOFMS:

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

4.7.2 The ~~GC/MS-Scan~~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~~GC/TOFMS option uses a capillary column GC coupled to a ~~TOF-MS~~TOFMS 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~~GC/TOFMS 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 contributing to air toxics with their associated acute or chronic human-health impacts.

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

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~~available, and (9) grab sample collection for survey or screening purposes.

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~~test method, 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~~(see Table 1 mm Hg for examples).

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~~test method 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 test method and are listed in **Table 1**.

5.7 ~~Recovery and stability studies shall be conducted on compounds~~ VOCs not listed in **Table 1** before expanding the use of this test method to ~~additional compounds~~. Recovery from humidified spiked canisters shall agree with the spiked amount by  $\pm 30\%$ . The laboratory shall be responsible for verifying the relevant method performance characteristics for each compound added to the analyte list as agreed with their customer(s). The laboratory shall retain records of verification and make them available to customers upon request. Added VOCs (that is, those not listed in **Table 1**) shall be clearly identified in customer reports

## 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).~~

6.1 For those applications where a membrane dryer is used, interferences can occur in sample analysis if moisture accumulates in the dryer (see Water management can 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.

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6.1.1 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 mass spectrometric systems. Inline permeable membrane dryers have historically been used prior to preconcentration and do not produce artifacts for a number of nonpolar VOCs (19, 20).

6.1.2 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 if condensed water remains on the canister interior (21).

6.1.3 In-line permeable dryers may contribute to the loss of polar species as these species may also partition with the water vapor. For those applications where a permeable membrane dryer is used, interferences can also 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, five to ten 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.

6.2 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.

6.3 ~~If the concentrator-GC/MS~~ preconcentrator-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 together 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.

6.4 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 interferents 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.

6.4.1 Any components 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.

6.4.2 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 interferents and the target compound are the same. Reanalysis of the sample on a different chromatographic column, analysis at higher mass resolution, or use of an alternative compound selective detector 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).  
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7.2.1.1 *Inlet Line*, stainless steel or silica lined 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.

7.2.1.4 *Mass Flow Meter and Controller*, capable of maintaining a constant flow rate ( $\pm 10\%$ ) of less than 10 % change 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- $\mu$ 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.

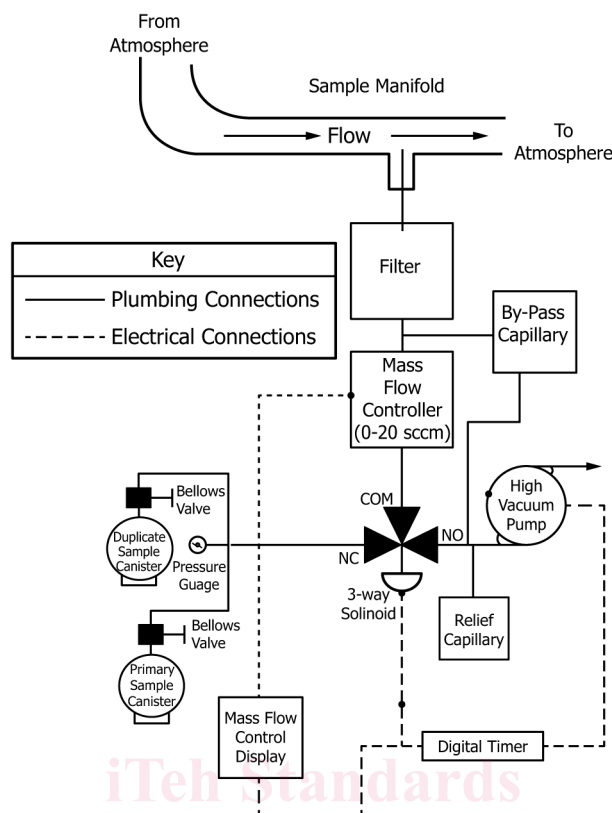


FIG. 1 Example Sampler Configuration for Subatmospheric Pressure Canister Sampling

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~~ Maximum-minimum *Thermometer*, records highest and lowest temperatures during sampling period.

7.2.1.13 ~~Shut-Off~~ 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, test method, 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.

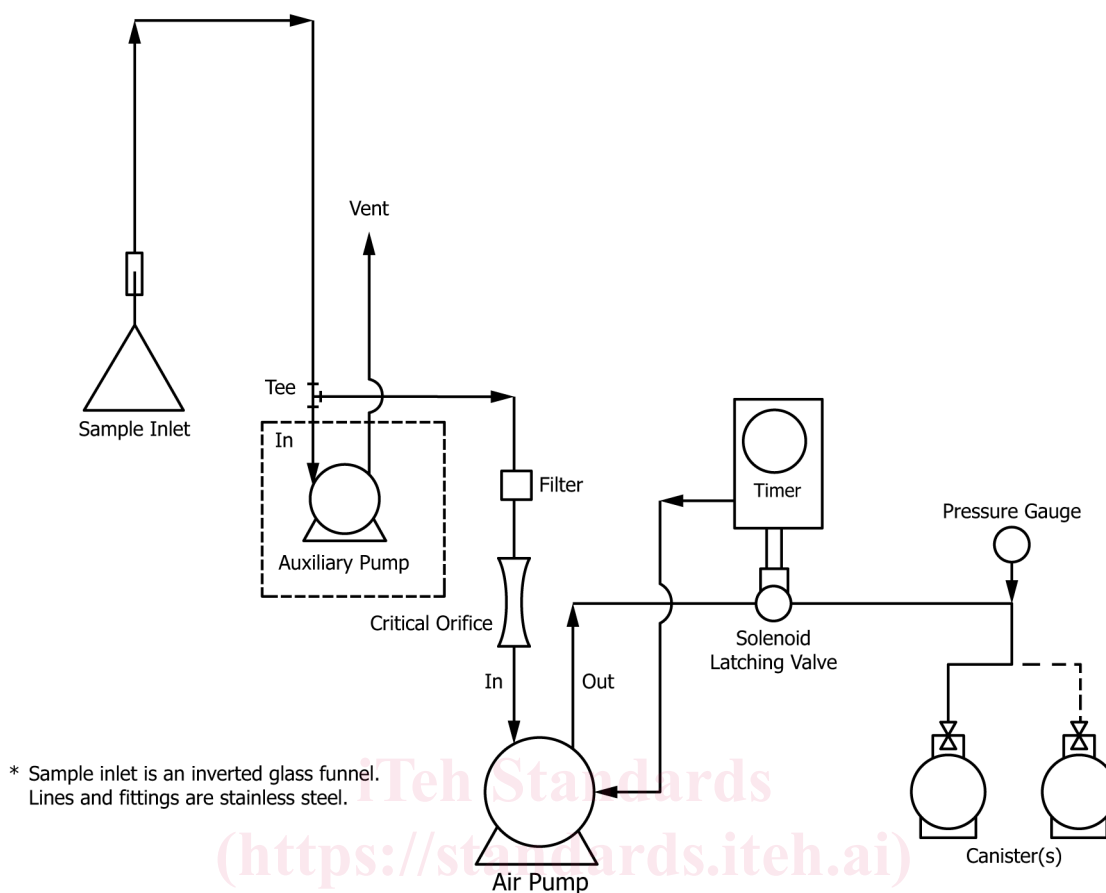


FIG. 2 Alternative Sampler Configuration for Pressurized Canister Sampling

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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~~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 ~~and~~ and ~~electronic carrier gas pressure control (EPC) are~~ optional.

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

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