



Designation: **D5466 – 01 (Reapproved 2007) D5466 – 15**

Standard Test Method for Determination of Volatile Organic Chemicals Compounds in Atmospheres (Canister Sampling Methodology)¹

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 (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method standard describes a procedure for sampling and analysis of selected volatile organic compounds (VOCs) in ambient, indoor, or 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).²

1.2 This test method is applicable to specific VOCs that have been tested and 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).³ Although not as extensive, documentation is also available demonstrating stability of VOCs in subatmospheric pressure canisters. While initial studies were concentrated on non-polar VOCs, information on storage stability has been extended to 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 and lines, air filters, flow rate regulators for obtaining time-integrated samples, and in the case of pressurized samples, an air pump. Canister-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 is may be required if the sampler is to be used outdoors. For the purposes of this test method, refer to Practice D1357 outside 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. ThisThe test method is applicable to VOC concentrations ranging from the detection limit to approximately 300 ppbv. Above this concentration, samples require dilution 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:⁴

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

¹ 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 April 1, 2007Dec. 1, 2015. Published June 2007June 2016. Originally approved in 1993. Last previous edition approved in 20042007 as D5466 – 01.D5466 – 01 (2007). DOI: 10.1520/D5466-01R07-10.1520/D5466-15.

² 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.

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

⁴ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

TABLE 2 Ion/Abundance and Expected Retention Time for Selected VOCs Analyzed by GC-MS-SIM

Compound	Ion/ Abundance (amu/% base-peak)	Expected Retention Time (min)
Freon 12 (Dichlorodifluoromethane)	-85/100	-5.01
	-87/31	
Methyl chloride (Chloromethane)	-50/100	-5.69
	-52/34	
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	-85/100	-6.55
	135/56	
	-87/33	
Vinyl chloride (Chloroethene)	-62/100	-6.71
	-27/125	
	-64/32	
Methyl bromide (Bromomethane)	-94/100	-7.83
	-96/85	
Ethyl chloride (Chloroethane)	-64/100	-8.43
	-29/140	
	-27/140	
Freon 11 (Trichlorofluoromethane)	101/100	-9.97
	103/67	
Vinylidene chloride (1,1-Dichloroethylene)	-61/100	10.93
	-96/55	
	-63/31	
Dichloromethane (Methylene chloride)	-49/100	11.21
	-84/65	
	-86/45	
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	151/100	11.60
	101/140	
	103/90	
1,1-Dichloroethane	-63/100	12.50
	-27/64	
	-65/33	
cis-1,2-Dichloroethylene	-61/100	13.40
	-96/60	
	-98/44	
Chloroform (Trichloromethane)	-83/100	13.75
	-85/65	
	-47/35	
1,2-Dichloroethane (Ethylene dichloride)	-62/100	14.39
	-27/70	
	-64/31	
Methyl chloroform (1,1,1-Trichloroethane)	-97/100	14.62
	-99/64	
	-61/61	
Benzene	-78/100	15.04
	-77/25	
	-50/35	
Carbon tetrachloride (Tetrachloromethane)	117/100	15.18
	119/97	
	-63/100	
1,2-Dichloropropane (Propylene dichloride)	-41/90	15.83
	-62/70	
	130/100	
Trichloroethylene (Trichloroethene)	132/92	16.10
	-95/87	
	-75/100	
cis-1,3-Dichloropropene	-39/70	16.96
	-77/30	
	-75/100	
trans-1,3-Dichloropropene	-39/70	17.49
	-77/30	
	-97/100	
1,1,2-Trichloroethane (Vinyl trichloride)	-83/90	17.61
	-61/82	
	-91/100	
Toluene (Methyl benzene)	-92/57	17.86
	107/100	
1,2-Dibromoethane (Ethylene dibromide)	109/96	18.48
	-27/115	
	166/100	
Tetrachloroethylene (Perchloroethylene)	164/74	19.01
	131/60	
	112/100	
Chlorobenzene	-77/62	19.73
	114/32	

TABLE 2—Continued

Compound	Ion/ Abundance (amu/% base peak)	Expected Retention Time (min)
Ethylbenzene	-91/100 106/28	20.20
m,p-Xylene (1,3/1,4-dimethylbenzene)	-91/100 106/40	20.41
Styrene (Vinyl benzene)	104/100 -78/60	20.81
1,1,2,2-Tetrachloroethane	103/49 -83/100 -85/64	20.92
o-Xylene (1,2-Dimethylbenzene)	-91/100 106/40	20.92
4-Ethyltoluene	105/100 120/29	22.53
1,3,5-Trimethylbenzene (Mesitylene)	105/100 120/42	22.65
1,2,4-Trimethylbenzene	105/100 120/42	23.18
m-Dichlorobenzene (1,3-Dichlorobenzene)	146/100 148/65 111/40	23.31
Benzyl chloride (α -Chlorotoluene)	-91/100 126/26	23.32
p-Dichlorobenzene (1,4-Dichlorobenzene)	146/100 148/65 111/40	23.41
o-Dichlorobenzene (1,2-Dichlorobenzene)	146/100 148/65 111/40	23.88
1,2,4-Trichlorobenzene	180/100 182/98 184/30	26.71
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)	225/100 227/66 223/60	27.68

TABLE 1 Typical Volatile Organic Compounds Determined by the Canister Method

Compound (Synonym)	Formula	Molecular Weight	Boiling Point (°C)	Melting Point (°C)	CAS Number
Freon-12 (Dichlorodifluoromethane)	Cl ₂ CF ₂	120.91	-29.8	-158.0	
Methyl chloride (Chloromethane)	CH ₃ Cl	50.49	-24.2	-97.1	74-87-3
Freon-114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	ClCF ₂ CClF ₂	170.93	-4.1	-94.0	
Vinyl chloride (Chloroethylene)	CH ₂ =CHCl	62.50	-13.4	-1538.0	75-01-4
Methyl bromide (Bromomethane)	CH ₃ Br	94.94	-3.6	-93.6	74-83-9
Ethyl chloride (Chloroethane)	CH ₃ CH ₂ Cl	64.52	-12.3	-136.4	75-00-3
Freon-11 (Trichlorofluoromethane)	CCl ₃ F	137.38	-23.7	-111.0	
Vinylidene chloride (1,1-Dichloroethene)	C ₂ H ₂ Cl ₂	96.95	-31.7	-122.5	75-35-4
Dichloromethane (Methylene chloride)	CH ₂ Cl ₂	84.94	-39.8	-95.1	75-09-2
Freon-113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	CF ₂ ClCClF ₂	187.38	-47.7	-36.4	
1,1-Dichloroethane	CH ₃ CHCl ₂	98.96	-57.3	-97.0	74-34-3
cis-1,2-Dichloroethylene	CHCl=CHCl	96.94	-60.3	-80.5	
Chloroform (Trichloromethane)	CHCl ₃	119.38	-61.7	-63.5	67-66-3
1,2-Dichloroethane (Ethylene dichloride)	ClCH ₂ CH ₂ Cl	98.96	-83.5	-35.3	107-06-2
Methyl chloroform (1,1,1-Trichloroethane)	CH ₃ CCl ₃	133.41	-74.1	-30.4	71-55-6
Benzene	C ₆ H ₆	78.12	80.1	-5.5	71-43-2
Carbon tetrachloride (Tetrachloromethane)	CCl ₄	153.82	-76.5	-23.0	56-23-5
1,2-Dichloropropane (Propylene dichloride)	CH ₂ CHClCH ₂ Cl	112.99	-96.4	-100.4	78-87-5
Trichloroethylene (Trichloroethene)	ClCH=CCl ₂	131.29	-87	-73.0	79-01-6
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	CH ₂ CC=CHCl	110.97	76		
trans-1,3-Dichloropropene (trans-1,3-Dichloropropylene)	ClCH ₂ CH=CHCl	110.97	112.0		
1,1,2-Trichloroethane (Vinyl trichloride)	CH ₂ ClCHCl ₂	133.41	113.8	-36.5	79-00-5
Toluene (Methyl benzene)	C ₆ H ₅ CH ₃	92.15	110.6	-95.0	108-88-3
1,2-Dibromoethane (Ethylene dibromide)	BrCH ₂ CH ₂ Br	187.88	131.3	9.8	106-93-4
Tetrachloroethylene (Perchloroethylene)	Cl ₂ C=CCl ₂	165.83	121.1	-19.0	127-18-4
Chlorobenzene	C ₆ H ₅ Cl	112.56	132.0	-45.6	108-90-7
Ethylbenzene	C ₆ H ₅ C ₂ H ₅	106.17	136.2	-95.0	100-41-4
m-Xylene (1,3-Dimethylbenzene)	1,3-(CH ₃) ₂ C ₆ H ₄	106.17	139.1	-47.9	
p-Xylene (1,4-Dimethylxylene)	1,4-(CH ₃) ₂ C ₆ H ₄	106.17	138.3	-13.3	
Styrene (Vinyl benzene)	C ₆ H ₅ CH=CH ₂	104.16	145.2	-30.6	100-42-5
1,1,2,2-Tetrachloroethane	CHCl ₂ CHCl ₂	167.85	146.2	-36.0	79-34-5
o-Xylene (1,2-Dimethylbenzene)	1,2-(CH ₃) ₂ C ₆ H ₄	106.17	144.4	-25.2	
1,3,5-Trimethylbenzene (Mesitylene)	1,3,5-(CH ₃) ₃ C ₆ H ₃	120.20	164.7	-44.7	108-67-8

Compound (Synonym)	Formula	Molecular Weight	Boiling Point (°C)	Melting Point (°C)	CAS Number
1,2,4-Trimethylbenzene	1,2,4-(CH ₃) ₃ C ₆ H ₆	120.20	169.3	-43.8	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	1,3-Cl ₂ C ₆ H ₄	147.01	173.0	-24.7	541-73-1
Benzyl chloride (α-Chlorotoluene)	C ₆ H ₅ CH ₂ Cl	126.59	179.3	-39.0	100-44-7
o-Dichlorobenzene (1,2-Dichlorobenzene)	1,2-Cl ₂ C ₆ H ₄	147.01	180.5	-17.0	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	1,4-Cl ₂ C ₆ H ₄	147.01	174.0	-53.1	106-46-7
1,1,2,3,4,4-Hexachloro-1,3-butadiene	C ₆ Cl ₆	260.76	215	-21.0	7-68-3

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

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
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TABLE 3 General GC and MS Operating Conditions

<i>Chromatography</i>						
—Column				50-m × 0.32-mm I.D. crosslinked 100% dimethylpolysiloxane (17-µm film thickness)		
—Carrier Gas				Helium (2.0 cm ³ /min at 250°C)		
—Injection Volume				Constant (1–3 µL)		
—Injection Mode				Splitless		
<i>Temperature Program</i>						
—Initial Column Temperature				–50°C		
—Initial Hold Time				2 min		
—Program				8°C/min to 150°C		
—Final Hold Time				15 min		
<i>Mass Spectrometer</i>						
—Mass Range				18 to 250 amu		
—Scan Time				1 s/scan		
—EI Condition				70 eV		
—Mass Scan				Follow manufacturer's instruction for		
				—selecting mass selective detector (MS)		
				—and selected ion monitoring (SIM) mode		
				Multiple ion detection		
—Detector Mode						
<i>FID System (Optional)</i>						
—Hydrogen Flow				30 cm ³ /min		
—Carrier Flow				30 cm ³ /min		
—Burner Air				400 cm ³ /min		

2.2 ~~Other EPA Documents.~~⁵

~~U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Method TO-14A, EPA 600/R-96/010b~~ Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Method TO-14A

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

<https://standards.iteh.ai/catalog/standards/sist/856341e3-9740-44aa-a1b2-4d1d2fcbad33/astm-d5466-15>

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, 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*—*pressure, n*— $P_g + P_a$, where P_g = gage = gauge pressure in the canister. (kPa, psi) canister; (kPa) and P_a = barometric pressure.

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

3.2.3 *certification*—the process of demonstrating with humid zero air and humid calibration gases that the sampling systems components and the canister will not change the concentrations of sampled and stored atmospheres.

3.2.3 *cryogen*—*cryogen, n*—a refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is ~~Typical cryogens are liquid argon (bp –185.7°C) or (bp –185.7°C) and liquid nitrogen (bp –195°C).~~ (bp –195°C).

3.2.4 *dynamic calibration*—*calibration, n*—calibration of an analytical system using calibration gas standard concentrations standards generated by diluting known concentration 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.

⁵ Available from the 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 or 22161, <http://www.cpa.gov/ttn/amtic/airtox.html>.

3.2.5.1 *Discussion*—

Such standards are in a form identical or very similar to the samples to be analyzed. 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 gage pressure—gauge pressure, n—~~pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero ~~gage~~gauge pressure is equal to ambient atmospheric (barometric) pressure.

~~3.2.7 megabore column—~~chromatographic column having an internal diameter (I.D.) greater than 0.50 mm.

3.2.7.1 Discussion—

The Megabore column is a trademark of the J & W Scientific Co. For purposes of this test method, Megabore refers to chromatographic columns with 0.53 mm I.D.

~~3.2.6 MS-SCAN—MS-SCAN, n—~~the GC 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—

~~As used in the current context, this procedure serves as a~~This procedure serves for both qualitative identification and ~~characterization~~quantitation of VOCs in the sample.

~~3.2.7 MS-SIM—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 ~~performed using~~termed selected ion monitoring (SIM) ~~coupled to retention time discriminators.~~The GC-SIM(MS-SIM). The MS-SIM analysis provides quantitative results for selected constituents of the sample gas as programmed VOCs that are preselected by the user.

~~3.2.8 pressurized sampling—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—accuracy, n—~~the ability of an analytical system to correctly identify compounds.

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

~~3.2.11 static calibration—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 ~~would be injecting~~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—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 described is taken from published work (1-22) and is the basis of EPA Compendium Method TO-14A. ~~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 ~~assess~~determine the ~~toxicity~~concentrations of selected VOCs in the ambient air (13, 14).

~~4.2 Both subatmospheric pressure and pressurized sampling modes use an evacuated canister. A sampling line less than 2 % of the volume of the canister or a pump-ventilated sample line are used during sample collection. Pressurized sampling requires an~~

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

Compound ^A	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)

^A In typical retention time order using a dimethylpolysiloxane-phase column

additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprising components that regulate the rate and duration of sampling into a pre-cleaned and pre-evacuated passivated canister.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 gage which will allow accurate measurement of gauge to accurately measure the final canister pressure. During analysis, water vapor may be

reduced in the gas stream by a permeable membrane dryer (if applicable), and the VOCs are then concentrated by collection on a sorbent trap or in a cryogenically-cooled trap. The temperature of the trap is raised and the VOCs originally collected in the trap are revolatilized, separated on a GC column, and then detected by a mass spectrometer. Compound identification and quantitation are performed with this test method.

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 the a flame ionization detector (FID) or an electron capture detector (ECD). ~~The analytical procedure can be automated~~Both compound identification and quantitation are (performed **15-17**) or manual with this (test **18**). A procedure for measuring total FID response to a sample method. For the purposes of this test method, refer to Practice **E355** without gas chromatographic separation is also documented for terms and practices used in gas (chromatography, **19**).

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-Full Scan and GC/MS-SIM: GC/MS Technologies:~~

4.7.1.1 ~~GC/MS-Full Scan: GC/MS-SCAN:~~

- ~~(1) Positive nontarget compound identification possible,~~
- ~~(1) Less/Lower sensitivity than GC/MS-SIM,~~
- ~~(2) Greater sample volume may be required compared to SIM, 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 compounds on calibration list, calibrated compounds, and~~
- ~~(7) Qualitative and semiquantitative determination of compounds not contained on calibration list.~~

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<https://standards.iteh.ai/catalog/standards/sist/856341e3-9740-44aa-a1b2-4d1d2fcbad33/astm-d5466-15>

4.7.1.2 GC/MS-SIM:

- (1) Can't identify non-target compounds,
- (2) Less operator interpretation, and
- (3) Higher sensitivity than ~~GC/MS—full scan~~ 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—full scan GC/MS—Scan option uses a capillary column GC coupled to a MS operated in a scanning mode and which repeatedly acquires a wide mass range of ion data; the acquired mass spectra are supported by spectral library search routines. This option offers the nearest approximation to unambiguous identification and covers~~ 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 library-libraries, with GC/TOF MS providing greater sensitivity in most cases. GC/MS-SIM mode is limited to a set of target compounds which are user defined and 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. ~~The practical limit~~ Maximum sensitivity for GC/MS-SIM is reached at about achieved when no more than 4 to 5 ions are monitored simultaneously.

5. Significance and Use

5.1 VOCs are emitted into the ambient, indoor, and workplace atmosphere ~~from air from many different sources. These VOCs are of interest for a variety of sources. In addition to the emissions from the use of various products, appliances, and building materials, fugitive or direct emissions from ambient sources such as manufacturing processes further complicate air composition. Many of these VOC compounds are reasons including participation in atmospheric chemistry and acute or chronic toxins. Therefore, their determination in air is necessary to assess human health impacts.~~

5.2 ~~The use of canisters is~~ Canisters are particularly well suited for the collection and analysis of very ~~volatile, stable~~ compounds in atmosphere (for example, vinyl chloride), ~~volatile and volatile organic compounds. This test method collects and analyzes~~ describes the collection and analysis of whole gas samples and is not subject to high volatility limitations.

5.3 ~~VOCs can be~~ 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 ~~or analysis, or both, of samples by~~ through replicate analyses of the same sample by one or several analytical systems, and (8) sample collection ~~in remote access areas using a vacuum regulator flow controller if electricity is not available.~~

5.4 Interior surfaces of the canisters ~~are~~ 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 ~~This test method can be applied to sampling and analysis of~~ For this standard, VOCs are defined as organic compounds that can be quantitatively recovered from the canisters. ~~The typical range of VOC applicable to this test method are ones having saturated vapor pressures at 25°C greater than 15 Pa (10~~ canisters having a vapor pressure greater than 10^{-1-2} mm Hg). ~~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 ~~must~~ shall be conducted on ~~any compound~~ 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~~ condensation (for example dehydration traps). The water can restrict and even stop the sample air flow, alter chromatography and GC retention times, and remove dissolved polar species and adversely affect the operation of detector systems, especially the mass spectrometric systems. In-line permeable membrane dryers ~~are frequently~~ have historically been used prior to preconcentration and do not produce artifacts for a number of compounds including nonpolar VOCs those (19, 20 that), are on the target list for this method provided certain precautions are observed. However, in-line permeable dryers may contribute to the loss of polar species as (these 20, 21) 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 (221).

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). ~~An~~ 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°C. In extreme circumstances, an automated cleanup procedure that periodically heats the dryer to about 100°C while purging with zero air ~~eliminates any or an inert gas (such as N₂ or He) can help to remove moisture buildup~~. This procedure does not degrade sample integrity.

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

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) ~~must shall~~ be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples. Instructions for cleaning the canisters and ~~certifying~~ 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 as soon as it occurs~~ contamination.

6.4 If the ~~GC/MS~~ 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 ~~moisture~~ water. Consequently, the analyst ~~must calibrate his or her~~ shall calibrate the system with the specific organic constituents under examination target VOCs. For quantitative analysis of polar compounds, analytical systems ~~may shall~~ not employ permeable membrane dryers.

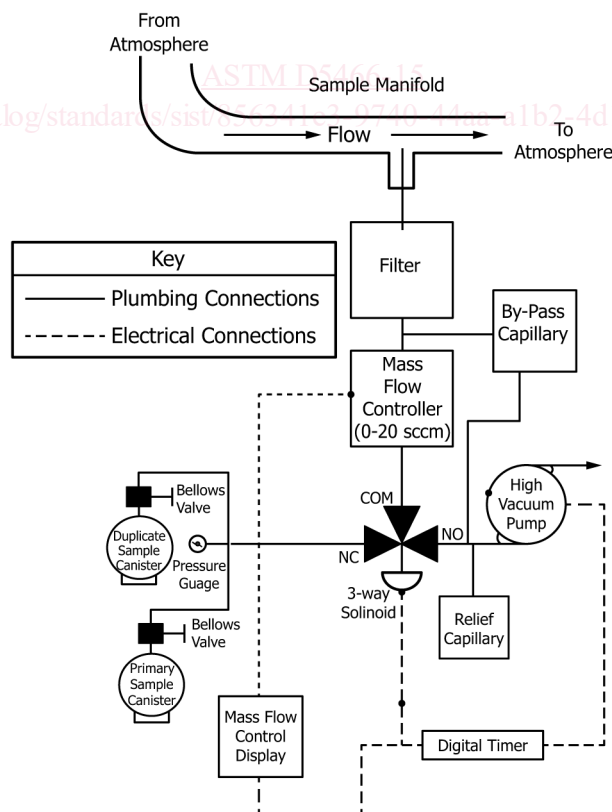


FIG. 1 Example Sampler Configuration For Subatmospheric Pressure Canister Sampling

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 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.

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, Stainlesssteel* 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 Gage, gauge*, capable of measuring vacuum (-100 to 0 kPa or 0 to 30 in-Hg) (-100 to 0 kPa) and pressure (0 to 200 kPa or 0 to 30 psig) kPa) in the sampling system. Gages/Gauges shall be tested clean and leak tight.

7.2.1.4 *Mass Flow Meter and Controller*, capable of maintaining a constant flow rate ($\pm 10\%$) ($\pm 10\%$) 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*, $7\text{-}\mu\text{m}$ $2\text{-}\mu\text{m}$ 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, that is, for example, for unattended sample collection.

7.2.1.7 *Solenoid Valve*, electrically operated, bi-stable 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 samplersampling 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 gage/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 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. Pump is not necessary if the intake manifold volume represents less than 5% 5% of the final sample 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, 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% 60% or less of the total capacity of the canister used for collection. Typically this limits the sample duration to a maximum of 824 h per 6 L canister or 2072 h per 15 L canister.

7.2.2 *Pressurized, Pressurized Sampling Apparatus*, see Fig. 1 and Fig. 2.

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

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 whichthat regulates the flow, and flow into the canisters: 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:*