



Designation: D5466 – 21

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

1.3 This test method is applicable to specific VOCs that have been determined to be stable when stored in canisters (see [Table 1](#)). Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters ([1-4](#)).³ Information on storage stability is also available for polar compounds ([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 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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² This test method is based on EPA Compendium Method TO-15, “Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)” January 1999.

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

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.

1.5 The organic compounds that have been successfully measured single-digit micrograms per cubic metre ($\mu\text{g}/\text{m}^3$) (or single digit parts-per-billion by volume (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 $1000 \mu\text{g}/\text{m}^3$ (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 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Safety practices should be part of the 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.*

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)	Cl ₂ CF ₂	120.91	568	X/X	75-71-8
Methyl chloride (Chloromethane)	CH ₃ Cl	50.49	506	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	76-14-2
Vinyl chloride (Chloroethylene)	CH ₂ =CHCl	62.50	344	X/X	75-01-4
1,3-Butadiene	(CH ₂ =CH) ₂	54.09	279	/X	106-99-0
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	C ₂ H ₃ N	41.05	9.9	O/X	75-05-8
Freon 11 (Trichlorofluoromethane)	CCl ₃ F	137.38	23.7	X/X	75-69-4
Acrylonitrile	C ₂ H ₃ N	53.03	11.0		107-13-1
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 CClCF ₂	187.38	47.7	X/X	76-13-1
Trans-1,2-Dichloroethylene	C ₂ H ₂ Cl ₂	96.95	44.13	O/X	156-60-5
1,1-Dichloroethane	CH ₃ CHCl ₂	98.96	57.3	X/X	74-34-3
Methyl <i>tert</i> -Butyl Ether	(CH ₃) ₃ COCH ₃	88.15	32.7	O/X	1634-04-4
2-Butanone Methyl Ethyl Ketone	C ₄ H ₈ O	77.11	13.3	O/X	78-93-3
Chloroprene	C ₄ H ₅ Cl	88.54	25.06	O/X	126-99-8
cis-1,2-Dichloroethylene	CHCl=CHCl	96.94	60.3		156-59-2
Bromochloromethane	CH ₂ BrCl	129.38	15.6	O/X	74-97-5
Chloroform (Trichloromethane)	CHCl ₃	119.38	61.7	X/X	67-66-3
Ethyl <i>tert</i> -Butyl Ether	C ₆ H ₁₄ O	102.18	32.7	X/X	637-92-3
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
<i>Tert</i> -Amyl Methyl Ether	C ₆ H ₁₄ O	102.18	9	O/X	994-05-8
1,2-Dichloropropane (Propylene dichloride)	CH ₃ CHClCH ₂ Cl	112.99	96.4	X/X	78-87-5
Ethyl Acrylate	C ₅ H ₈ O ₂	100.12	2	O/X	140-88-5
Trichloroethylene (Trichloroethene)	ClCH=CCl ₂	131.29	87	X/X	79-01-6
Methyl Methacrylate	C ₅ H ₈ O ₂	100.12	3.9	X/X	80-62-6
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	CH ₃ CC=CHCl	110.97	4.59	X/X	542-75-6
Methyl Isobutyl Ketone	C ₆ H ₁₂ O	100.16	2.13	O/X	108-10-1
trans-1,3-Dichloropropene (trans-1,3-Dichloropropylene)	ClCH ₂ CH=CHCl	110.97	3.07	X/X	542-75-6
1,1,2-Trichloroethane (Vinyl trichloride)	CH ₂ ClCHCl ₂	133.41	2.53	X/X	79-00-5
Toluene (Methyl benzene)	C ₆ H ₅ CH ₃	92.15	2.8	X/X	108-88-3
Dibromochloromethane	CHBr ₂ Cl	208.28	7.32	O/X	124-48-1
1,2-Dibromoethane (Ethylene dibromide)	BrCH ₂ CH ₂ Br	187.88	1.56	X/X	106-93-4
n-Octane	C ₈ H ₁₈	114.23	1.47	X/X	111-65-9
Tetrachloroethylene (Perchloroethylene)	Cl ₂ C=CCl ₂	165.83	1.87	X/X	127-18-4
Chlorobenzene	C ₆ H ₅ Cl	112.56	1.20	X/X	108-90-7
Ethylbenzene	C ₆ H ₅ C ₂ H ₅	106.17	1.33	X/X	100-41-4
m-Xylene (1,3-Dimethylbenzene)	1,3-(CH ₃) ₂ C ₆ H ₄	106.17	1.20	X/X	108-38-3
p-Xylene (1,4-Dimethylxylene)	1,4-(CH ₃) ₂ C ₆ H ₄	106.17	1.20	X/X	106-42-3
Bromoform	CH ₂ Br ₃	252.73	0.747	X/X	75-25-2
Styrene (Vinyl benzene)	C ₆ H ₅ CH=CH ₂	104.16	0.67	X/X	100-42-5
1,1,2,2-Tetrachloroethane	CHCl ₂ CHCl ₂	167.85	0.67	X/X	79-34-5
o-Xylene (1,2-Dimethylbenzene)	1,2-(CH ₃) ₂ C ₆ H ₄	106.17	0.93	X/X	95-47-6
4-Ethyltoluene	C ₉ H ₁₂	120.19	1.38	X/O	622-96-8
1,3,5-Trimethylbenzene (Mesitylene)	1,3,5-(CH ₃) ₃ C ₆ H ₃	120.20	0.267	X/X	108-67-8
1,2,4-Trimethylbenzene	1,2,4-(CH ₃) ₃ C ₆ H ₃	120.20	0.665	X/X	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	1,3-Cl ₂ C ₆ H ₄	147.01	0.286	X/X	541-73-1
Chloromethylbenzene	C ₆ H ₅ CH ₂ Cl	126.58	0.133	O/X	100-44-7
Benzyl chloride (α-Chlorotoluene)	C ₆ H ₅ CH ₂ Cl	126.59	0.123	X/O	100-44-7
o-Dichlorobenzene (1,2-Dichlorobenzene)	1,2-Cl ₂ C ₆ H ₄	147.01	0.181	X/X	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	1,4-Cl ₂ C ₆ H ₄	147.01	0.232	X/X	106-46-7
1,1,2,3,4,4-Hexachloro-1,3-butadiene	Cl ₆ C ₄	260.76	0.04	X/X	7-68-3
1,2,4 - Trichlorobenzene	C ₆ H ₃ Cl ₃	181.44	0.133	O/X	120-82-1

2. Referenced Documents

2.1 ASTM Standards:⁴

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.

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