



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)	C ₂ H ₄ Cl ₂	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	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)	C ₂ HCl=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)	C ₃ H ₃ Cl ₂	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](#)

2.2 *EPA Documents*:⁵

EPA 600/R-96/010b Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air — Second Edition TO-15

NATTS 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°C) and liquid nitrogen (bp -195°C).

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

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

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

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

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

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

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

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

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

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

3.2.11.1 *Discussion*—An example of a static calibration is injection of a small volume of a high concentration standard directly onto a GC column, bypassing the sample extraction and preconcentration portion of the analytical system.

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

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

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

4. Summary of Test Method

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

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

4.2.1 Procedures are provided for canister cleaning and performance evaluation.

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

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

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

4.4 Upon receipt at the laboratory, the 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

⁵ Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.