



Designation: D6196 – 03(Reapproved 2009)

Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air¹

This standard is issued under the fixed designation D6196; 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 practice is intended to assist in the selection of sorbents and procedures for the sampling and analysis of ambient (1)², indoor (2) and workplace (3, 4) atmospheres for a variety of common volatile organic compounds (VOCs). It may also be used for measuring emissions from materials in small or full scale environmental chambers or for human exposure assessment.

1.2 A complete listing of VOCs for which this practice has been tested, at least over part of the measurement range (1.6), is shown in Tables 1-9. For other compounds this practice shall be tested according to EN 1076 (pumped); Practice D6246, ISO 16107, ANSI/ISEA 104, EN 838 or EN 13528-1/EN 13528-2 (diffusive); or other appropriate validation protocols (Sections 13 and 14). (5,1)

1.3 This practice is based on the sorption of VOCs from air onto selected sorbents or combinations of sorbents. Sampled air is either drawn through a tube containing one or a series of sorbents (pumped sampling) or allowed to diffuse, under controlled conditions, onto the sorbent tube or tubes (diffusive or passive sampling). The sorbed VOCs are subsequently recovered by thermal desorption and analyzed by capillary gas chromatography.

1.4 This practice applies to three basic types of samplers that are compatible with thermal desorption: (1) pumped sorbent tubes containing one or more sorbents; (2) axial diffusive samplers (typically of the same physical dimensions as standard pumped sorbent tubes and containing only one sorbent); and (3) radial diffusive samplers.

1.5 This practice recommends a number of sorbents that can be packed in sorbent tubes, for use in the sampling of a wide range of different volatile organic compounds boiling in the range 0 to 400°C (v.p. 15 to 0.01 kPa at 25°C).

1.5.1 For pumped sampling, sorbent selection is based on breakthrough capacity. Single-bed tubes containing for example sorbent Type A^{3,4} are appropriate for normal alkanes from n-C₆ (hexane) to n-C₁₀ (decane) and substances with similar volatility (v.p. 15 to 0.3 kPa at 25°C). More volatile materials should be sampled on stronger sorbents, such as sorbent Type B^{3,5}. Other sorbent types than those specified may be used, if their breakthrough capacities are adequate and their thermal desorption blanks are sufficiently small. Examples are given in Appendix X2. A broader range of VOCs may be sampled using multi-bed tubes.

1.5.2 Guidance given for the selection of sorbents for pumped monitoring tubes can be applied equally well to axial diffusive sampling tubes. The restriction to a single sampling surface (hence single sorbent), limits the target analyte range that can be monitored by a single tube. However, the unobtrusive nature and low cost of diffusive samplers usually means that two or more samplers containing different sorbents can be used in parallel without impacting study objectives.

1.5.3 The high sampling rate and associated risk of back diffusion associated with radial diffusive samplers typically restricts the use of these samplers to compounds of equal or lower volatility than benzene. It also means that stronger sorbents are generally required for these samplers when compared with either axial diffusive or pumped sorbent tubes.

1.6 This practice can be used for the measurement of airborne vapors of these volatile organic compounds over a wide concentration range.

1.6.1 With pumped sampling, this practice can be used for the measurement of airborne vapors of VOCs in a concentration range of approximately 0.1 $\mu\text{g}/\text{m}^3$ to 1 g/m^3 , for individual organic compounds in 1–10 L air samples. The method is also suitable for the measurement of the airborne concentrations of individual components of volatile organic mixtures, provided

¹ This practice 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 The bold face numbers in parentheses refer to the list of references at the end of this practice.

³ If you are aware of alternative sorbent types, please provide this information to ASTM Headquarters. Your comments will be carefully considered at a meeting of the responsible technical committee, which you may attend.

⁴ An example of sorbent Type A known to perform as specified in this practice is Chromosorb 106 manufactured by Manville Corp., USA and available from several commercial sources.

⁵ An example of sorbent Type B known to perform as specified in this practice is Carboxen 569 manufactured by Supelco, Inc., USA.

that the total loading of the mixture does not exceed the capacity of the tube. Quantitative measurements are possible when using validated procedures with appropriate quality assurance measures.

1.6.2 With axial diffusive sampling, this practice is valid for the measurement of airborne vapors of volatile organic compounds in a concentration range of approximately 2 mg/m³ to 10 mg/m³ for individual organic compounds for an exposure time of 8 h or 0.3 mg/m³ to 300 mg/m³ for individual organic compounds for an exposure time of four weeks. The method is also suitable for the measurement of the airborne concentrations of individual components of volatile organic mixtures provided that the total loading of the mixture does not exceed the capacity of the tube.

1.6.3 With radial diffusive sampling, this practice is valid for the measurement of airborne vapors of volatile organic compounds in a concentration range of approximately 0.3 mg/m³ to 300 mg/m³ for individual organic compounds for exposure times of one to six hours. The method is also suitable for the measurement of the airborne concentrations of individual components of volatile organic mixtures provided that the total loading of the mixture does not exceed the capacity of the tube.

1.6.4 The upper limit of the useful range is set by the sorptive capacity of the sorbent used, and by the linear dynamic range of the gas chromatograph, column and detector, or by the sample splitting capability of the analytical instrumentation used. The sorptive capacity is measured as a breakthrough volume of air, which determines the maximum air volume that must not be exceeded when sampling with a pump.

1.6.5 The lower limit of the useful range depends on the noise level of the detector and on blank levels of analyte or interfering artifacts, or both, on the sorbent tubes.

1.6.6 Artifacts are typically <1ng for typical sampling tubes (7.2) containing well-conditioned sorbent Type C^{3,6} and carbonaceous sorbents such as graphitized carbon, carbon molecular sieves and pure charcoals; at 1 to 5 ng levels for sorbent Type D^{3,7} and at 5 to 50 ng levels for other porous polymers such as sorbent Type A and sorbent Type E^{3,8}. Method sensitivity is typically limited to 0.5 µg/m³ for 10 L air samples with this latter group of sorbent types because of their inherent high background.

1.7 This procedure can be used for personal and fixed location sampling. It cannot be used to measure instantaneous or short-term fluctuations in concentration. Alternatives for on-site measurement include, but are not limited to gas chromatography and infrared spectrometry.

1.8 The sampling method gives a time-weighted average result.

1.9 *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.*

2. Referenced Documents

2.1 ASTM Standards:⁹

[D1356 Terminology Relating to Sampling and Analysis of Atmospheres](#)

[D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors \(Activated Charcoal Tube Adsorption Method\)](#)

[D6246 Practice for Evaluating the Performance of Diffusive Samplers](#)

[D6306 Guide for Placement and Use of Diffusion Controlled Passive Monitors for Gaseous Pollutants in Indoor Air](#)

[E355 Practice for Gas Chromatography Terms and Relationships](#)

2.2 ISO Standards:¹⁰

[ISO 5725 Precision of Test Methods](#)

[ISO 6349 Gas Analysis. Preparation of Calibration Gas Mixtures. Permeation Method](#)

[ISO 6879 Air Quality. Performance Characteristics and Related Concepts for Air Quality Measuring Methods 1983](#)

[ISO 16107 Workplace Atmospheres—Protocol for Evaluating the Performance of Diffusive Samplers](#)

2.3 CEN Standards:¹¹

[EN 482 Workplace Atmospheres: General Requirements for the Performance of Procedures for the Measurement of Chemical Agents](#)

[EN 838 Workplace Atmospheres: Requirements and Test Methods for Diffusive Samplers for the Determination of Gases and Vapours](#)

[EN 1076 Workplace Atmospheres: Pumped Sorbent Tubes for the Determination of Gases and Vapours. Requirements and Test Methods](#)

[EN 1232 Workplace Atmospheres: Pumps for Personal Sampling of Chemical Agents. Requirements and Test Methods](#)

[EN ISO-16017 \(parts 1 and 2\) Air Quality—Sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/capillary gas chromatography](#)

[EN 13528-1 Ambient Air Quality—Diffusive samplers for the determination of concentrations of gases and vapours - Requirements and test methods. Part 1: General requirements](#)

[EN 13528-2 Ambient Air Quality—Diffusive samplers for the determination of concentrations of gases and vapours](#)

⁶ An example of sorbent Type C known to perform as specified in this practice is Tenax GR manufactured by Enka Research Institute NV, NL.

⁷ An example of sorbent Type D known to perform as specified in this practice is Tenax TA manufactured by Enka Research Institute NV, NL.

⁸ An example of sorbent Type E known to perform as specified in this practice is Porapak Q manufactured by Waters Associates Inc., USA.

⁹ 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.

¹⁰ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

¹¹ Available from European Committee for Standardization (CEN), 36 rue de Stassart, B-1050, Brussels, Belgium, <http://www.cenorm.be>.

TABLE 1 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a 300 mg Sorbent Type A^A Sorbent Tube at 20°C

Organic compound	Boiling Point, °C	Vapor Pressure, kPa	Retention Volume (L), 25°C	Safe Sampling Volume (SSV ^B) (L)	SSV/g (L/g)	Desorption Temperature, °C	Reference
Hydrocarbons							
Propane ^C	-42	–	0.17	0.09	0.29		(10)
Pentane	35	56	23.4	11.7	39	130	(10)
Hexane	69	16	73.8	36.9	123	160	(10)
Heptane	98	4.7	325	160	530	180	(3)
Octane	125	1.4	2076	1000	3300	200	(3)
Nonane	151	–	14k	7k	23k	220	(3)
Decane	174	–	62k	31k	104k	250	(10)
Benzene	80	10.1	57	28.5	95	160	(10)
Toluene	111	2.9	165	80	270	200	(3)
Xylene	138-144	0.67–0.87	1554	770	2600	250	(3)
Ethylbenzene	136	0.93	730	360	1200	250	(3)
Trimethylbenzene	165-176	–	5650	2800	9300	250	(3)
α Pinene	53	0.51	6600	3300	11k	200	(10)
Chlorinated Hydrocarbons							
Dichloromethane	40	47	6.9	3.45	11.5	130	(10)
Carbon Tetrachloride	76	12	44	22	73	160	(3)
1,2-Dichloroethane	84	8.4	34	17	67	150	(3)
Trichloroethylene		2.7	80	40	140	170	(3)
1,1,1-Trichloroethane	74	13.3	42.6	21.3	71	140	(10)
Esters and Glycol Ethers							
Methyl Acetate	58	22.8	14.04	7.02	23.4	125	(10)
Ethyl Acetate	71	9.7	39	20	67	150	(3)
Propyl Acetate	102	3.3	297	150	500	170	(3)
Isopropyl Acetate	90	6.3	147	75	250	165	(3)
Butyl Acetate	126	1.0	1460	730	2400	95	(3)
Isobutyl Acetate	115	1.9	880	440	1500	90	(3)
t-Butyl Acetate	98	–	327	160	530	185	(3)
Methoxyethanol	125	0.8	45	22.5	75	140	(10)
Ethoxyethanol	136	0.51	150	75	200	250	(3)
Methoxyethyl Acetate	145	0.27	1720	860	2900	250	(3)
Ethoxyethyl Acetate	156	0.16	8100	4000	13k	250	(3)
Ketones							
Acetone	56	24.6	2.9	1.5	5	120	(3)
Methyl Ethyl Ketone	80	10.3	21	10.5	35	145	(10)
Methyl Isobutyl Ketone	118	0.8	490	250	830	190	(3)
Alcohols							
Methanol ^C	65	12.3	0.78	0.39	1.3		(10)
Ethanol	78	5.9	3.18	1.59	5.3	120	(10)
n-Propanol	97	1.9	17	8	27	125	(3)
Isopropanol	82	4.3	88	44	145	120	(3)
n-Butanol	118	0.67	135	67.5	225	170	(10)
Isobutanol	108	1.6	60	30	100	150	(3)
Others							
Ethylene Oxide ^C	11	147	0.84	0.42	1.4	100	(10)
Propylene Oxide	34	59	2.04	1.02	3.4	120	(10)
Hexanal	131	–	1680	840	2800	220	(10)

^AAn example of sorbent Type A known to perform as specified in this practice is Chromosorb 106 manufactured by Marville Corp., USA.

^BSSV; see 11.1.5.1 and 11.1.5.2.

^CSSV below recommended 1L. sorbent Type B is preferred (Table 2).

TABLE 2 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a 500 mg Sorbent Type B^A Sorbent Tube at 20°C (10)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume, SSV ^B , L	SSV/g, L/g	Desorption Temperature, °C
Propane	-42	–	7.2	3.6	7.2	200
Methanol ^C	65	12.3	4	2	4	200
Ethylene Oxide	11	147	140	70	140	250

^AAn example of sorbent Type B known to perform as specified in this practice is Carboxen 569 manufactured by Supelco, Inc., USA.

^BSSV; see 11.1.5.1 and 11.1.5.2.

^CDesorption recovery is poor (see Table 10).

- Requirements and test methods. Part 2: Specific requirements and test methods

EN 13528-3 Ambient Air Quality—Diffusive samplers for the determination of concentrations of gases and vapours
Part 3: Guide to selection, use and maintenance

2.4 The Safety Equipment Association / American National Standards Institute Standards¹⁰

ANSI/ISEA 104 American National Standard for Air Sampling Devices—Diffusive Type for Gases and Vapors in Working Environments

3. Terminology

3.1 Definitions—Refer to Terminology D1356 and Practice E355 for definitions of terms used in this practice.

TABLE 3 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a 200 mg Sorbent Type D^A Sorbent Tube at 20°C (3)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV ^B , L	SSV/g, L/g	Desorption Temperature, °C
Hydrocarbons						
Hexane	69	16	6.4	3.2	16	110
Heptane	98	4.7	34	17	85	130
Octane	125	1.4	160	80	390	140
Nonane	151	—	1400	700	3500	150
Decane	174	—	4200	2100	10k	160
Undecane	196	—	25k	12k	60k	170
Dodecane	216	—	126k	63k	300k	180
Benzene	80	10.1	12.5	6.2	31	120
Toluene	111	2.9	76	38	90	140
Xylene	138–144	0.67–0.87	600	300	1500	140
Ethylbenzene	136	0.93	360	180	900	145
Propylbenzene	159	—	1700	850	4000	160
Isopropylbenzene	152	—	960	480	2400	160
Ethyltoluene	162	—	2000	1000	5000	160
Trimethylbenzene	165–176	—	3600	1800	8900	170
Styrene	145	0.88	600	300	1500	160
Methylstyrene	167	—	2400	1200	6000	170
Chlorinated Hydrocarbons						
Carbon tetrachloride	76	12	12.4	6.2	31	120
1,2-Dichloroethane	84	8.4	10.8	5.4	27	120
1,1,1-Trichloroethane	74	2.7	not recommended on sorbent Type D			
1,1,2-Trichloroethylene	114	—	68	34	170	120
1,1,1,2-Tetrachloroethane	130	—	156	78	390	150
1,1,2,2-Tetrachloroethane	146	0.67	340	170	850	150
Trichloroethylene	87	2.7	11.2	5.6	28	120
Tetrachloroethylene	121	1.87	96	48	240	150
Chlorobenzene	131	1.2	52	26	130	140
Esters and Glycol Ethers						
Ethyl Acetate	71	9.7	7.2	3.6	18	120
Propyl Acetate	102	3.3	36	18	92	140
Isopropyl Acetate	90	6.3	12	6	31	120
Butyl Acetate	126	1.0	170	85	420	150
Isobutyl Acetate	115	1.9	265	130	650	130
t-butyl Acetate	98	—	not recommended on sorbent Type D			
Methyl Acrylate	81	—	13	6.5	32	120
Ethyl Acrylate	100	3.9	48	24	120	120
Methyl Methacrylate	100	3.7	55	27	130	120
Methoxyethanol	125	0.8	3	3	15	120
Ethoxyethanol	136	0.51	10	5	25	130
Butoxyethanol	170	0.1	70	35	170	140
Methoxypropanol	118	—	27	13	65	115
Methoxyethyl Acetate	145	0.27	16	8	40	120
Ethoxyethyl Acetate	156	0.16	30	15	75	140
Butoxyethyl Acetate	192	0.04	300	150	750	160
Aldehydes and Ketones						
Methyl Ethyl Ketone	80	10.3	6.4	3.2	16	120
Methyl Isobutyl Ketone	118	0.8	52	26	130	140
Cyclohexanone	155	0.45	340	170	850	150
3,5,5-Trimethylcyclohex-2-enone	214	0.05	11200	5600	28000	90
Furfural	162	0.15	600	300	1500	200
Alcohols						
n-Butanol	118	0.67	10	5	25	120
Isobutanol	108	1.6	5.6	2.8	14	120
t-Butanol	83	1.17	not recommended on sorbent Type D			
Octanol	180	—	2800	1400	7000	160
Phenol	182	0.03	480	240	1200	190
Others						
Maleic Anhydride	202	6.7E-6	176	88	440	180
Pyridine	116	—	16	8	40	150
Aniline	184	0.09	440	220	1100	190
Nitrobenzene	211	0.02	28000	14000	70000	200

^AAn example of sorbent Type D known to perform as specified in this practice is Tenax TA manufactured by Enka Research Institute NV, NL.

^BSSV; see 11.1.5.1 and 11.1.5.2.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *bias*—consistent deviation of the results of a measurement process from the true value of the air quality characteristic itself (ISO 6879).

3.2.2 *breakthrough volume*—the volume of a known atmosphere that can be passed through the tube before the concentration of the vapor eluting from the tube reaches 5 % of the applied test concentration.

TABLE 4 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a 500 mg Sorbent Type H^A Sorbent Tube at 20°C (3)

Organic Compound	Boiling Point (°C)	Vapor Pressure (kPa)(25°C)	Retention Volume, L	Safe Sampling Volume, SSV ^B , L	SSV/g, L/g	Desorption Temperature, °C
Hydrocarbons						
Pentane	35	56	8.2	12	8.2	180
Hexane	69	16	32	16	32	180
Heptane	98	4.7	90	95	90	180
Benzene	80	10.1	52	26	52	180
Alcohols						
Ethanol	78	5.9	7.5	3.7	7.5	120
n-Propanol	97	1.9	40	20	40	120
n-Butanol	118	0.67	10	5	25	120
Isobutanol	108	1.6	5.6	2.8	14	120
Octanol	180	–	2800	1400	7000	160
Phenol	182	0.03	480	240	1200	190
Others						
Acetic Acid	116	–	97	50	97	180
Acetonitrile	82	9.9	7	3.5	7	180
Acrylonitrile	77	13.3	16	8	16	180
Propionitrile	97	–	23	11	23	180
Pyridine	116	–	390	200	390	180
Methyl Ethyl Ketone	80	10.3	95	50	95	180

^AAn example of sorbent Type H known to perform as specified in this practice is Porapak N manufactured by Waters Associates Inc., USA.³

^BSSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by factor of 2 if sampling at high humidity.

TABLE 5 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on Tubes Packed with 300 mg Sorbent Type I^A or Sorbent Type U^B at 20°C (3)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa, 25°C	Sorbent Type	Retention Volume, L	Safe Sampling Volume SSV, ^C L	SSV/g, L/g	Desorption Temperature, °C
Butane	–0.5	–	I	1640	820	2700	270
Pentane	35	56	I	63k	30k	100k	335
Hexane	69	16	I	3.9k	2M	7M	390
Benzene	80	10.1	I	1M	500k	1700k	375
Dichloromethane	40	47	I	395	200	700	250
1,1,1-Trichloroethane	74	13.3	I	17.6k	8k	27k	290
Methanol	65	12.3	I	264	130	430	340
Ethanol	78	5.9	I	6900	3500	12k	370
Benzene	80	10.1	U	3240	1620	5400 ± 740	400

^AAn example of sorbent Type I known to perform as specified in this practice is Spherocarb manufactured by Analabs Inc., USA.

^BAn example of sorbent Type U known to perform as specified in this practice is 40–60 mesh Carboxpack X manufactured by Supelco, Inc., USA.

^CSSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 10 if sampling at high humidity; reduce SSV by a factor of 2 if sampling at high concentration.

TABLE 6 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a 300 mg Charcoal Sorbent Tube at 20°C (3)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa, 25°C	Retention Volume, L	Safe Sampling Volume, SSV ^A L	SSV/g, L/g	Desorption Temperature, °C
Propane	–42	–	10 ^B	5	15	220 ^B
Butane	–0.5	–	900 ^B	450	600	270 ^B
Pentane	35	56	27k	13k	43k	327
Hexane	69	16	1.5M	750k	2.5k	388
Benzene	80	10.1	340k	170k	560k	370

^ASSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 10 if sampling at high humidity; reduce SSV by a factor of 2 if sampling at high concentration.

^BExtrapolated from data on pentane, hexane, and benzene.

3.2.3 *desorption efficiency*—the ratio of the mass of analyte desorbed from a sampling device to that applied.

3.2.4 *loading*—the product of concentration expressed in ppb¹² or mg/m³ and the sampled atmosphere volume (flow rate × sampling time).

3.2.5 *overall uncertainty (OU)*—quantity used to characterize, as a whole, the uncertainty of the result given by an apparatus or measuring procedure. It is expressed, as a percentage, by a combination of bias and precision usually according to the formula:

$$OU = \frac{|\bar{x} - x_{ref}| + 2s}{x_{ref}} \times 100 \quad (1)$$

where:

\bar{x} = mean value of results of a number (n) of repeated measurements

x_{ref} = true or accepted reference value of concentration, and

s = standard deviation of measurements.

NOTE 1—In strict mathematical terms there is no way to combine precision (a variance) and bias (an absolute number). However, by occupational hygiene precedent and time honored convention they have been combined according to the above formula (Clause 3.7 of EN 482:1994).

3.2.6 *precision*—the closeness of agreement between the results obtained by applying the method several times under prescribed conditions (ISO 6879). Precision may be expressed either as repeatability or reproducibility (ISO 5725)

3.2.7 *pumped sampler*—a device which is capable of taking samples of gases and vapors from the atmosphere and consisting of a sampling medium, such as a sorbent tube, and an air sampling pump. Air is passed through the sorbent tube at a rate controlled by the sampling pump. The sampling pump shall conform to the specifications in 18.3.

3.2.8 *safe sampling volume*—70 % of breakthrough volume (3.2.2) or 50 % of the chromatographically-determined retention volume.

3.2.9 *sorbent strength*—term to describe the affinity of sorbents for VOCs; a stronger sorbent is one which offers greater safe sampling volumes for VOCs relative to another, weaker, sorbent.

3.2.10 *sorbent tube*—a tube, usually made of metal or glass, containing an active sorbent or a reagent-impregnated support which may be used to collect vapor-phase organic chemicals either by passing air through the tube at a rate controlled by an air sampling pump (pumped sampling) or by allowing controlled diffusion of gases or vapors onto the sorbent sampling surface (diffusive or passive sampling).

3.2.11 *diffusive sampler*—a device that is capable of collecting gases and vapors from an atmosphere at rates controlled by gaseous diffusion through a static air layer (boundary layer) or permeation through a membrane, but which does not involve the active movement of air through the sampler. Provided the concentration of analyte or analytes at the sampling surface remains at or close to zero, and provided the concentration of analyte at the surface of the sampler remains at ambient levels, components migrate into the sampler by diffusion at a rate proportional to their atmospheric concentrations and are retained by the sorbent.

3.2.11.1 *axial diffusive sampler*—a tube-form device with precisely controlled dimensions that samples gaseous organic chemicals in air diffusively through one end of the tube onto the sorbent surface held inside the tube at a fixed distance from the sampling end. The diffusion-controlling mechanism is typically the air gap at the end of the tube; that is, the static layer of air, inside the tube separating the external atmosphere from the sorbent sampling surface.

3.2.11.2 *radial diffusive sampler*—a tube form device which allows controlled diffusive sampling around the walls of the sampler; that is, parallel to the radius. The sampling center of a radial diffusive sampler for thermal desorption, typically comprises sorbent contained in a fine (for example, 400-mesh) gauze cylinder. For sampling, the cylindrical sorbent core is held inside a diffusion barrier typically consisting of an external tube or membrane comprised of porous polymeric or other permeable material. The ends of a radial sampler are sealed.

3.2.12 *diffusive uptake rate*—the rate at which the diffusive sampler collects a particular gas or vapor from the atmosphere, expressed in nanograms per parts per million (volume/volume) per minute (ng.ppm⁻¹ (V/V) min⁻¹), picograms per parts per billion (volume/volume) per minute (pg.ppb⁻¹ (V/V) min⁻¹), or cubic centimetres per minute (cm³/min).

4. Summary of Practice

4.1 For active (pumped) sampling, a suitable sorbent type or series of sorbents should be selected for the compound or mixture to be sampled. The sorbents selected should be arranged in order of increasing sorbent strength by linking tubes containing the individual sorbents together in series. Alternatively, a single tube containing several sorbents in series may be used. Provided suitable sorbents are chosen, volatile organic components are retained by the sorbent tube(s) and thus are removed from the flowing air stream. The use of weaker sorbents in front of stronger sorbents during sampling prevents irreversible adsorption of higher boiling compounds on the stronger sorbents.

4.2 For axial diffusive sampling, a suitable sorbent should be selected for the compound or mixture to be sampled. If more than one sorbent is required, two or more diffusive sampling tubes, packed with different sorbents, should be used in parallel. The diffusive sampler or samplers are exposed to the atmosphere for a measured time period. Provided suitable sorbents are chosen, volatile organic components migrate into the tube by diffusion at a rate proportional to the atmospheric concentration and are retained by the sorbent.

4.3 For radial diffusive sampling, a suitable sorbent should be selected for the compound or mixture to be sampled. If more than one sorbent is required, two or more samplers, packed with different sorbents, should be used in parallel. The diffusive sampler or samplers are exposed to the atmosphere for a measured time period. Provided suitable sorbents are chosen, volatile organic components migrate into the tube by diffusion at a rate proportional to the atmospheric concentration and are retained by the sorbent. Once the sampling period is over, the radial sorbent core, is immediately removed and placed in a

¹² Volume fraction, (ϕ) = 10⁻⁹.

sealable transportation container - typically a modified empty sample tube (compatible with the thermal desorption system) - and sealed with sorbent tube end caps. (7.6)

4.4 The collected vapor (on each tube or cartridge) is desorbed by heat and is transferred under inert carrier gas into a gas chromatograph (GC) equipped with a capillary column and either a conventional detector (such as the flame ionization or electron capture detector (ECD)) or a mass spectrometric detector, where it is analyzed. A sample focusing trap between the sampling tube and the gas chromatograph is commonly employed to ensure injection of the analytes in as small a volume of carrier gas as possible, providing better peak resolution than is normally achievable with single stage desorption. Where the sample to be analyzed contains unknown components (indoor/ambient air applications), preliminary analysis of typical samples by mass spectrometry should be undertaken.

5. Significance and Use

5.1 This practice is recommended for use in measuring the concentration of VOCs in ambient, indoor, and workplace atmospheres. It may also be used for measuring emissions from materials in small or full scale environmental chambers for material emission testing or human exposure assessment.

5.2 Such measurements in ambient air are of importance because of the known role of VOCs as ozone precursors, and in some cases (for example, benzene), as toxic pollutants in their own right.

5.3 Such measurements in indoor air are of importance because of the association of VOCs with air quality problems in indoor environments, particularly in relation to sick building syndrome and emissions from building materials. Many volatile organic compounds have the potential to contribute to air quality problems in indoor environments and in some cases toxic VOCs may be present at such elevated concentrations in home or workplace atmospheres as to prompt serious concerns over human exposure and adverse health effects (6).

5.4 Such measurements in workplace air are of importance because of the known toxic effects of many such compounds.

5.5 In all three environments, in order to protect the environment as a whole and human health in particular, it is necessary to take measurements of air quality as part of an overall assessment in relation to mandatory requirements.

5.6 The choices of sorbents, sampling method, and analytical methodology affect the efficiency of sorption, recovery, and quantification of individual VOCs. This practice is potentially effective for a wide range of volatile organic compounds found in air, over a wide range of volatilities and concentration levels. However, it is the responsibility of the user to ensure that the sampling, recovery, analysis, and quality control for the measurement of a specific VOC of interest are within acceptable limits. Guidance for this evaluation is part of the scope of this practice.

6. Interferences

6.1 Organic components, that have the same or nearly the same retention time as the analyte of interest, will interfere

during the gas chromatographic analysis. Analytes and artifacts can be generated during sampling and analysis (7,8). Interferences can be minimized by proper selection of gas chromatographic columns and conditions, and by stringent conditioning of both the sorbent tubes or radial sorbent cores and the analytical system before use. The use of capillary or microbore columns with superior resolution or columns of different polarity will frequently eliminate these problems. Artifacts may be formed during storage of blank sorbent tubes/cores. This is minimized by correctly sealing and storing blank and sampled tubes (see 9.1, 11.1.8, 11.1.9 and 16.3). Such artifact formation is generally at low to sub-nanogram levels. It is typically lower for carbon type sorbents and the more stable (sorbent Type D) porous polymers, than for other, less stable, porous polymers (9,10).

6.2 Selectivity may be further enhanced by the use of selective GC detectors such as the ECD for certain compounds or by using a mass spectrometer in the selected ion monitoring (SIM) mode as a GC detector. In this mode, co-eluting compounds can usually be determined.

6.3 Competitive sorption between VOCs, although unlikely at normal sampling levels, is possible and shall be taken into consideration during method development.

6.4 The method is suitable for use in atmospheres of up to 95 % relative humidity for all hydrophobic sorbents such as porous polymers and graphitized carbon. When less hydrophobic, strong sorbents such as pure charcoals or carbonized molecular sieves are used in atmospheres with humidity in excess of 65 % RH, exercise care to prevent water interfering with the analytical process. Suitable water elimination or reduction procedures include sample splitting; *dry purging* moisture from the sorbent tube or secondary focusing trap prior to analysis, reducing the air volume sampled to 0.5 L (pumped sampling), use of a membrane that excludes water in the diffusion barrier (diffusive sampling), and reducing the time of sampling (diffusive sampling).

7. Apparatus

7.1 Use ordinary laboratory apparatus in addition to the following.

7.2 *Sorbent tubes for pumped sampling*, compatible with the thermal desorption apparatus to be used (7.5). Typically, but not exclusively, they are constructed of stainless steel tubing, 6.4 mm [$\frac{1}{4}$ in.] OD, 5 mm ID and 89 mm long and contain up to 60 mm total length of sorbent or sorbents, held in place with stainless steel gauzes. Tubes of other dimensions may be used but the safe sampling volumes (SSV) given in Tables 1-6 are based on these tube dimensions. For labile analytes, such as sulfur-containing compounds, fused-silica-coated steel or glass tubes (typically 4 mm ID) should be used (in glass-lined or glass tubes the sorbent is typically held in place using plugs of unsilanized glass wool). One end of the tube is marked, for example by a scored ring about 10 mm from the sampling inlet end to represent the end open to the atmosphere during sampling, otherwise the direction of sampling flow may be marked with an arrow. The tubes are packed with one or more preconditioned sorbents (8.3), so that the sorbent bed will be

within the desorber heated zone, and a gap of at least 14 mm is retained at each end to minimize errors due to diffusive ingress at a very low pump flow rates. Tubes contain between 200 and 1000 mg sorbent, depending on sorbent density — typically about 250 mg sorbent Type D, 300 mg sorbent Type A or 500 mg sorbent Type B. The sorbents are retained by stainless steel gauzes or unsilanized glass wool plugs, or both. If more than one sorbent is used in a single tube, the sorbents should be arranged in order of increasing sorbent strength and separated by unsilanized glass wool, with weakest sorbent nearest to the marked sampling inlet end of the tube.

7.2.1 Sorbents with widely different (> 50°C) maximum desorption temperatures such as sorbent Type A and graphitized carbon, must NOT be packed into a single tube or it will be impossible to condition or desorb the more stable sorbent(s) sufficiently thoroughly without causing degradation of the least stable sorbent(s).

7.3 *Sorbent tubes for axial diffusive sampling*, compatible with the thermal desorption apparatus to be used (7.5) and with the sampling surface of the sorbent retained by a metal (typically stainless steel) gauze to give a precisely defined air gap (7.3.1). Typically, but not exclusively, they are constructed of stainless steel tubing, 6.4 mm [¼ in.] OD, 5 mm ID and 89 mm long and with the sorbent held in place 14.3 mm from the sampling end using a stainless steel gauze. (Fig. 1) Tubes of other dimensions may be used but the uptake rates given in Tables 7 and 8 are based on these tube dimensions. For labile analytes, such as sulfur-containing compounds, fused silica-coated steel should be used for both the tube and sorbent-retaining gauze. One end of the tube is marked, for example by a scored ring about 14 mm from the sampling inlet end. The tubes are packed with sorbents (8.3) such that the sorbent bed will be within the desorber heated zone and a consistent inner

air gap of about 14.3 mm is retained between the end of the tube and the surface of the sorbent-retaining gauze at the sampling marked (diffusive) end of the tube. Tubes contain between 200 and 1000 mg sorbent, depending on sorbent density - typically about 250 mg sorbent Type D, 300 mg sorbent Type A or 500 mg sorbent Type B. Label the tubes uniquely prior to conditioning. Do not use solvent-containing paints and markers or adhesive labels to label the tubes. Tubes may be obtained, pre-marked with suitable identifiers such as unique serial numbers.

7.3.1 *Uptake rates* in Tables 7 and 8 are given for tubes with a nominal total air gap (between the sampling surface of the sorbent bed and sampling surface of the diffusive end cap (7.3.2) of 15 mm. In practice packed tube dimensions will vary slightly (13) and tubes should be rejected where the inner air gap (between stainless steel screen retaining the sorbent bed and the end of the tube) is outside the range 14.0 and 14.6 mm (See Fig. 1).

7.3.2 *Diffusive End Caps*, typically push-on, “O”-ring seal caps fitted with a metal gauze allowing the diffusive ingress of vapor. The size of the gauze covered opening in the sampling cap should be the same as the cross section of the tube (Fig. 1). Some versions of the diffusive end cap incorporate a silicon membrane next to the gauze to minimize ingress of water.

7.4 *Sorbent cores for radial diffusive sampling*, compatible with the thermal desorption apparatus to be used (7.5). Typically, but not exclusively, they are constructed of a fine (400 mesh), stainless steel gauze tube, 4.8 mm OD and 55 mm long such that they are a snug fit inside a 5.0 mm ID desorption tube. Sorbent cores of other dimensions may be used but the uptake rates given in Table 9 are based on these dimensions. For labile analytes, such as sulfur-containing compounds, fused silica-coated steel should be used for the gauze tube. The

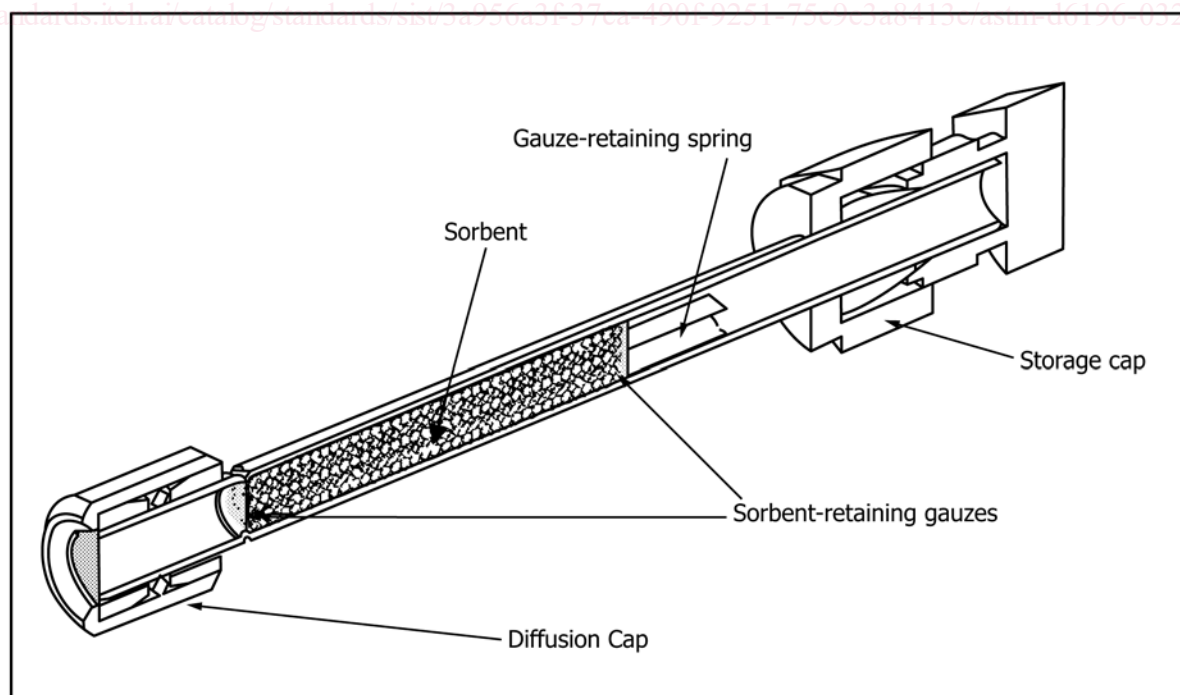


FIG. 1 Schematic of a Typical Axial Diffusive Sampler

TABLE 7 Diffusive Sampling Rates on Axial Diffusion Tubes^A at 20°C^B (11)

Compound	Sorbent	Level	Uptake Rate ng.ppm ⁻¹ .min ⁻¹
Hydrocarbons			
1,3-Butadiene	Molecular Sieve ^C	A	1.30
n-Pentane	Type A	A	1.46
	Type F	B	1.77
n-Hexane	Type A	A	1.77
Cyclohexane	Type A	D	1.60
	Type D	D	1.32
Benzene	Type E	A	1.37
	Type C	B	1.81
	Type A	B	1.72
n-Heptane	Type A	A	1.95
	Type D	A	1.77
	Type F	B	1.94
2-Methylhexane	Type A	D	1.79
	Type D	D	1.48
3-Methylhexane	Type A	D	1.80
	Type D	D	1.48
Methylcyclohexane	Type A	D	1.88
	Type D	D	1.55
Toluene	Type D	B	1.67
	Type C	B	2.12
	Type A	B	1.94
	Type F	B	2.06
2-Methylheptane	Type A	D	2.33
	Type D	D	1.95
n-Octane	Type A	A	2.13
	Type D	A	2.00
Xylene	Type D	B	1.82
	Type A	B	2.10
	Type C	B	2.48
Ethyl Benzene	Type D	B	2.00
	Type C	B	2.43
	Type A	B	1.90
	Type E	D	2.38
Styrene	Type D	A	2.00
	Type A	B	2.15
n-Nonane	Type A	A	2.40
	Type D	A	2.12
n-Propylbenzene	Type A	D	2.45
	Type D	D	2.28
Iso-propyl Benzene	Type A	D	2.38
	Type D	D	2.28
1,2,3-Trimethylbenzene	Type A	D	2.45
	Type D	D	2.34
1,2,4-Trimethylbenzene	Type A	D	2.26
	Type D	D	2.16
1,3,5-Trimethylbenzene	Type A	D	2.33
	Type D	D	2.23
1,3-Dimethyl-4-Ethylbenzene	Type D	D	2.45
1,4-Diethylbenzene	Type D	D	2.56
m-Ethyltoluene	Type A	D	2.43
	Type D	D	2.25
o-Ethyltoluene	Type A	D	2.57
	Type D	D	2.44
p-Ethyltoluene	Type A	D	2.35
	Type D	D	2.21
n-Decane	Type D	A	2.30
	Type A	A	2.47
Cumene	Type E	D	2.50
a-Pinene	Type D	D	2.35
	Type A	A	2.56
Naphthalene	Type D	A	2.55
Chlorinated hydrocarbons			
Methyl Chloride	Type I ^D	B	1.30
Vinyl Chloride	Type I	B	2.00
1,1-Dichloro-Ethene	Type I	B	2.50
Trichloro Trifluoroethane	Type O	B	3.50
Chloro Trifluoromethane	Type O	B	1.80
Dichloro Methane	Type A	B	1.56
	Type O	B	1.56
1,2-Dichloroethane	Type O	B	1.90
	Type A	B	2.03
	Type C	B	1.72

TABLE 7 *Continued*

Halothane	Type O	B	3.60
	Type D	B	2.59
Enflurane	Type D	B	2.29
	Type A	D	2.80
Isoflurane	Type D	B	2.20
	Type A	D	2.51
Bromoethane	Type A	A	2.55
Bromobenzene	Type A	D	3.59
	Type D	D	3.31
Trichloromethane (Chloroform)	Type C	B	1.97
	Type O	B	2.35
	Type A	B	2.47
Tetrachloromethane (Carbon Tetrachloride)	Type C	B	3.72
	Type O	B	2.87
Trichloroethene	Type A	B	2.64
	Type O	B	2.30
1,1,1-Trichloroethane	Type A	B	2.30
	Type O	B	2.30
	Type C	B	2.92
Tetrachloroethene	Type A	B	3.19
	Type D	B	2.80
	Type O	B	2.60
	Type C	B	2.90
Epichlorohydrin	Type A	E	2.45
Allyl Chloride	Type A	D	1.75
Benzyl Chloride	Type ^E	D	2.72
Perfluorodimethyl Cyclobutane	Type G ^E	B	15 mL/h
Perfluoromethyl- Cyclopentane	Type G ^E	B	15 mL/h
Perfluoromethyl- Cyclohexane	Type G ^E	B	15 mL/h
Esters and Glycol Ethers			
Methyl Acetate	Type A	A	1.74
Ethyl Acetate	Type A	B	1.98
	Type D	B	1.65
n-Butyl Acetate	Type D	B	1.93
	Type A	A	2.60
	Type C	B	1.93
Isobutyl Acetate	Type A	D	2.17
	Type D	D	1.91
Sec-butyl Acetate	Type A	D	2.29
	Type D	D	1.90
Tert-butyl Acetate	Type A	D	2.26
	Type D	D	1.79
Vinyl Acetate	Type A	D	1.93
Methyl Methacrylate	Type E	B	2.00
	Type A	D	2.14
	Type D	D	1.77
Methyl Acrylate	Type A	D	1.96
	Type D	D	1.50
Butyl Acrylate	Type D	D	2.00
	Type A	D	2.11
Ethylhexyl Acrylate	Type D	D	2.99
2-Methoxyethanol	Type E	A	1.50
	Type A	A	2.10
2-Ethoxyethanol	Type D	A	1.80
2-Methoxyethyl Acetate	Type E	A	2.80
	Type A	B	2.08
	Type C	B	1.81
	Type D	B	1.64
2-Ethoxyethyl Acetate	Type A	B	2.25
	Type D	B	2.05
	Type C	B	2.08
Butoxyethanol	Type A	B	2.06
	Type D	B	1.77
1-Methoxy-2-Propanol	Type A	B	1.88
	Type D	B	1.56
	Type C	B	1.55
Methoxypropyl Acetate	Type A	A	2.50
	Type D	B	2.21
	Type C	B	2.23
1-Ethoxy-2-Propanol	Type A	B	1.94
	Type C	B	1.64