Designation: D 6196 – 03

Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air[1]

This standard is issued under the fixed designation D 6196; 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 D 6246, 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-C$_6$(hexane) to n-C$_{10}$(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 µg/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

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[1] This practice is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres 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.

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individual components of volatile organic mixtures, provided 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/m^3 to 10 mg/m^3 for individual organic compounds for an exposure time of 8 h or 0.3 mg/m^3 to 300 mg/m^3 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/m^3 to 300 mg/m^3 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/m^3 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:*

D 1356 Terminology Relating to Atmospheric Sampling and Analysis[9]

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)[9]

D 6246 Practice for Evaluating the Performance of Diffusive Samplers[9]

D 6306 Guide for Placement and Use of Diffusion Controlled Passive Samplers for Gaseous Pollutants in Indoor Air[9]

E 355 Practice for Gas Chromatography Terms and Relationships[10]

2.2 *ISO Standards:*[11]

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:*[12]

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

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[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] *Annual Book of ASTM Standards*, Vol 11.03.

[10] *Annual Book of ASTM Standards,* Vol 14.02.

[11] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

[12] Available from Comité Européen de Normalisation, Brussels.

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)**

[A] An example of sorbent Type A known to perform as specified in this practice is Chromosorb 106 manufactured by Manville Corp., USA.
[B] SSV; see 11.1.5.1 and 11.1.5.2.
[C] SSV below recommended 1L. sorbent Type B is preferred (Table 2).

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 Standards*[11]

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 D 1356 and Practice E 355 for definitions of terms used in this practice.

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).

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

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

^{B}SSV; see 11.1.5.1 and 11.1.5.2.

^{C}Desorption recovery is poor (see Table 10).

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.

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 ppb[13] or mg/m^3 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:

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

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 (cm^3/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

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[13] Volume fraction, (ϕ) = 10^{-9}.

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	6	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

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

[B] SSV; see 11.1.5.1 and 11.1.5.2.

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)	Retension 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

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

[B] SSV; 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

[A] An example of sorbent Type I known to perform as specified in this practice is Spherocarb manufactured by Analabs Inc., USA.

[B] An example of sorbent Type U known to perform as specified in this practice is 40–60 mesh Carbopack X manufactured by Supelco, Inc., USA.

[C] SSV; 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

[A] SSV; 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.

[B] Extrapolated from data on pentane, hexane, and benzene.

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 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 [¼ 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 (**11**) 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

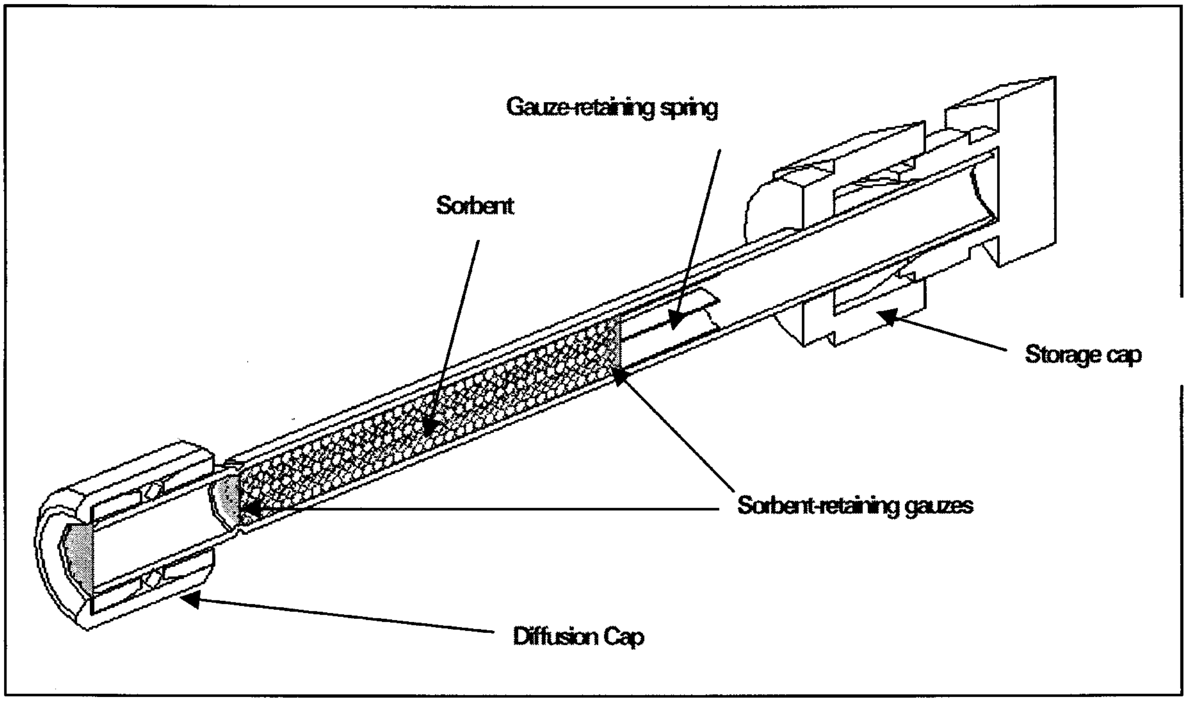

FIG. 1 Schematic of a Typical Axial Diffusive Sampler

cap should being 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.

TABLE 7 Diffusive Sampling Rates on Axial Diffusion Tubes[A] at 20°C[B] (15)

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

TABLE 7 *Continued*

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
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

TABLE 7 *Continued*

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
	Type D	B	1.65
2-Butoxyethyl Acetate	Type A	B	2.79
	Type C	B	2.19
	Type D	B	2.25
Propoxyethanol	Type A	D	1.94
	Type D	D	1.65
Dipropylene Glycol Methyl Ether	Type A	A	2.70
Ketones			
2-Butanone	Type A	B	1.72
	Type C	B	1.37
	Type D	B	1.34
Methyl Isobutyl Ketone (2-Methyl-4-Pentanone)	Type D	B	1.71
	Type C	B	1.69
	Type A	B	2.01
Cyclohexanone	Type D	B	1.78
	Type A	B	1.96
	Type C	B	1.78
2-Methylcyclohexanone	Type D	D	2.31
3-Methylcyclohexanone	Type D	D	2.22
4-Methylcyclohexanone	Type D	D	2.14
Furfural	Type D	A	2.50
Hexanal	Type D	D	1.64
	Type A	A	2.06
Decanal	Type D	D	2.32
Alcohols			
Ethanol	Type A	A	1.30
Propan-1-ol	Type A	D	1.47
Propan-2-ol (Isopropanol)	Type I[D]	C	2.00
	Type A	A	1.52
n-Butanol	Type A	A	1.74
	Type D	D	1.33
Isobutanol	Type A	B	1.61
	Type C	B	1.26
	Type D	B	1.26
Furfuryl Alcohol	Type D	D	2.50
Tetrahydrofurfuryl Alcohol	Type A	D	2.39
	Type D	D	1.90
Miscellaneous			
Acrylonitrile	Type H	A	1.35
	Type A	D	1.48
Acetonitrile	Type H[F]	A	1.00 (2 h)
	Type H	A	0.80 (8 h)
	Type A	A	1.48
Propionitrile	Type H[F]	A	1.40 (2 h)
	Type H	A	1.30 (8 h)
Carbon Disulphide	Type I[D]	A	2.60
Nitrous Oxide	Molecular Sieve[G]	B	1.25
Ethylene Oxide	Type I[D]	B	1.60
Propylene Oxide	Type A	A	1.24
1,4-Dioxane	Type I	C	3.00
Allyl Glycidyl Ether	Type A	D	2.40
	Type D	D	1.83
Butyl Glycidyl Ether	Type A	D	2.61
	Type D	D	2.36
Tetrahydrofuran	Type A	D	1.64
n-Methyl Pyrrolidone	Type D	C	1.83
	Type A	A	2.41
n-Vinyl Pyrrolidone	Type D	A	2.51

[A] This list has been complied from sources available to ASTM. It is not complete. Unless otherwise stated, rates refer to eight hour exposure using samplers without a membrane in the diffusion cap. Users of the data are strongly advised to consult the original source material to determine the level of confidence and the range of applicability of the values.

[B] The source material does not always give the applicable temperature. See EN 13528-3 for the relationship between diffusive sampling rate and temperature.

[C] Sampler with membrane: An example of the zeolite molecular sieve known to perform as specified in this practice is molecular sieve 13×.

[D] Sorbent no longer available.

[E] A nickel disk, rather than the conventional stainless steel gauze, was used to support the sorbent during method validations. The uptake rates may not be applicable if the steel gauzes are used.

[F] Two-hour exposure period

[G] Variable diffusive sampling rate - varies predictably with sample dose. An example of the zeolite molecular sieve known to perform as specified in this practice is Molecular Sieve 5A.

TABLE 8 Diffusive Sampling Rates on Axial Diffusion Tubes[A] at 20°C[B] (15,22)

Compound	Sorbent	Level	Uptake Rate ng.ppm^{-1}.min^{-1}
	Hydrocarbons - Two week exposures		
Benzene	Type A[C]	B	1.52 ± 0.14
	Type A	B	1.43 ± 0.15
	Type S[D]	B	2.00 ± 0.19
	Type U[A,E]	B	1.99 ± 0.18
Toluene	Type A	B	2.09 ± 0.13
	Type A	B	1.94 ± 0.18
	Type S[D]	B	2.09 ± 0.22
	Type U[A]	B	2.23 ± 0.52
m-Xylene	Type A	B	2.37 ± 0.17
	Type A	B	2.22 ± 0.24
	Type S[D]	B	2.16 ± 0.11
o-Xylene	Type A	B	2.59 ± 0.26
	Type U[A]	B	1.79 ± 0.41
Ethylbenzene	Type A	B	2.36 ± 0.20
	Hydrocarbons - Four week exposures		
Benzene	Type D[F,G]	B	0.86
	Type C	B	0.80
	Type A	B	1.47 ± 0.36
	Type A	B	1.32 ± 0.28
	Type S[D]	B	1.83 ± 0.12
Toluene	Type D	B	1.20
	Type A	B	2.10 ± 0.03
	Type A	B	1.93 ± 0.12
	Type A	B	1.85 ± 0.18
	Type S[D]	B	2.05 ± 0.21
Xylene	Type D	B	1.91
m-Xylene	Type A	B	2.26 ± 0.12
	Type A	B	2.09 ± 0.29
	Type S[D]	B	2.04 ± 0.26
o-Xylene	Type A	B	2.41 ± 0.18
Ethylbenzene	Type A	B	2.24 ± 0.18
Trimethylbenzene	Type D	B	2.65
Decane	Type D	B	2.96
Undecane	Type D	B	3.38

[A] This list has been complied from sources available to ASTM. It is not complete. Unless otherwise stated, rates refer to samplers without a membrane in the diffusion cap. Users of the data are strongly advised to consult the original source material to determine the level of confidence and the range of applicability of the values.

[B] The source material does not always give the applicable temperature. See EN 13528-3 for the relationship between diffusive sampling rate and temperature.

[C] An example of sorbent Type A known to perform as specified in this practice is Chromosorb 106 manufactured by Manville Corp, USA.

[D] An example of sorbent Type S known to perform as specified in this practice is Carbograph 1 manufactured by Carbochimica Romana, I. Equivalent to Type F.

[E] An example of sorbent Type U known to perform as specified in this practice is Carbopack X manufactured by Supelco, Inc., USA.

[F] Sampler with membrane.

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

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 cores are completely packed with sorbent. The mass of sorbent required will vary depending on sorbent density - typically about 200 mg sorbent Type D, 250 mg sorbent Type A or 400 mg sorbent Type B.

7.4.1 *Sampler bodies for radial diffusive sampling*, compatible with the sorbent cores to be used. Typically, but not exclusively, they are constructed of high density, non-emitting/absorbing porous polymer with one permanently sealed end and the other end sealed with a screw thread fitting such that the sorbent core can readily be inserted and removed. It should not be necessary to handle the sorbent core when transferring to and from the sampler body.

7.4.2 *Storage and desorption carrier tubes for radial diffusive sampling*, compatible with the sorbent cores and thermal desorption apparatus to be used. Typically, but not exclusively, these are constructed of stainless steel or fused silica-coated stainless steel tubing, 6.4 mm [¼ in.] OD, 5 mm ID and 89 mm

TABLE 9 Diffusive Sampling Rates on Radial Diffusion Samplers[A] (21) at 25°C Environmental Applications - One-Week Exposure

Compound	Sorbent	Level	Uptake Rate cm^3/min	Uncertainty
VOCs—One Week Exposure				
Benzene	Type T[B]	A	27.8	8.3
Toluene	Type T	A	30.0	8.3
Ethylbenzene	Type T	A	25.7	9.1
m-Xylene and p-Xylene	Type T	A	26.6	11.3
o-Xylene	Type T	A	24.6	9.1
1,2,4- Trimethylbenzene	Type T	A	21.9	9.6
n-Hexane	Type T	A	25.5	10.9
Cyclohexane	Type T	A	27.6	14.7
n-Heptane	Type T	A	25.3	7.6
n-Octane	Type T	A	24.1	13.4
n-Nonane	Type T	A	21.0	11.8
1-Methoxy-2-propanol	Type T	A	26.6	11.6
2-Ethoxyethanol	Type T	A	26.0	7.7
2-Butoxyethanol	Type T	A	19.4	9.7
Isopropyl Acetate	Type T	A	25.8	9.6
n-Butyl Acetate	Type T	A	24.5	8.2
2-Ethoxyethyl Acetate	Type T	A	20.9	8.0
1,1,1-Ttrichloroethane	Type T	A	20.0	13.0
Trichloroethylene	Type T	A	27.1	9.5
Tetrachloroethylene	Type T	A	25.4	8.9
1,4-Dichlorobenzene	Type T	A	22.0	9.5
Dimethyldisulfide	Type T	A	23.7	9.1

[A] This list has been complied from sources available to ASTM. It is not complete. Users of the data are strongly advised to consult the original source material to determine the level of confidence and the range of applicability of the values.

[B] An example of sorbent Type T known to perform as specified in this practice is Carbograph 4 manufactured by Carbochimica Romana, I. Equivalent to Type F.

long and with a sorbent core retaining gauze approximately 14 mm from the desorption end. The sorbent core should be a relatively snug fit inside the carrier tube such that it can be easily inserted and removed but that gas flow passes through the sorbent core (rather than around the outside) during thermal desorption. The other end of the carrier tube is typically machined to have a wider OD and slight cone-shape leading into the tube such that insertion and removal of the sorbent core can be readily achieved without handling. It should be possible to seal the carrier tubes with sorbent tube end caps (7.6).

7.5 *Thermal Desorption Apparatus*, for the two-stage thermal desorption of the sorbent tubes (or carrier tubes for radial sorbent cores) and transfer of the desorbed vapors by an inert gas flow into a gas chromatograph. A typical apparatus contains a mechanism for holding the tubes to be desorbed while they are heated and purged simultaneously with inert carrier gas. The desorption temperature and time is adjustable, as is the carrier gas flow rate. Air must be purged from the sample tube and analytical system before heat is applied to prevent sorbent and analyte oxidation. The apparatus should also incorporate additional features, such as automatic sample tube loading, leak-testing, and a focusing (cold) trap in the transfer line to concentrate the desorbed sample (Section 12). The desorbed sample, contained in the purge gas, is routed to the gas chromatograph and capillary column by way of a heated transfer line.

NOTE 2—Leak testing should be carried out under no-flow conditions, at low temperature, and at column head pressure such that it is suitably stringent, but does not compromise sample integrity. Tubes that fail the leak test should not be analyzed but resealed to await user intervention.

7.6 *Sorbent Tube End Caps*, sealed with metal screw-cap fittings with combined (one-piece) PTFE ferrules to seal both sorbent tubes and the carrier tubes for radial samplers.

7.7 *Sorbent Tube Unions (pumped sampling only)*, to combine two or more tubes in series during pumped sampling constructed of stainless steel couplings with combined (one-piece) PTFE ferrule seals.

7.8 *Syringes*, a precision 10 µL liquid syringe readable to 0.1 µL, a precision 10 µL gas tight syringe readable to 0.1 µL and a precision 10 mL gas tight syringe readable to 0.1 mL.

7.9 *Sampling Pump*, conforming to the performance requirements of 18.3.

7.10 *Connecting Tubing (pumped sampling only)*, PTFE, for connecting between the sampling point and the sample tube when sampling in a remote location. Tubing downstream of the sampler (that is, for connecting the tube to the pump) does not need to be inert and can be of any suitable material. For personal monitoring, the tube is typically worn as close as possible to the breathing zone (for example, on the lapel of clothing), and the pump carried on a belt. In this case, clips should be provided to hold the sample tube and connecting tubing to the wearer's lapel area. This connecting tubing will need to be about 90 cm long. All connections should be leak proof. Sampling tubes shall not be used with plastic or rubber tubing upstream of the sorbent. Interferences from the tubing may introduce sampling errors. Such errors may be reduced by replacing the tubing regularly.

7.11 *Soap Bubble Meter*, or other suitable device for calibrating pump, desorb, and split flows.

7.12 *Gas Chromatographic Apparatus*:

7.12.1 *Gas Chromatograph*, fitted with a flame ionization, photo ionization, mass spectrometric, or other suitable detector. The detector selected should be capable of detecting an injection of 0.5 ng toluene with a signal-to-noise ratio of at least 5 + 1.

7.12.2 *Gas Chromatographic Column*, capable of separating the analytes of interest from other components. A 50 m dimethylsiloxane or a 50 m 7 % cyanopropyl, 7 % phenyl, 86 % methyl siloxane fused silica capillary column has been found suitable (**3**).

7.13 *Injection Facility for Preparing Standards*, comprising a conventional gas chromatographic injection port may be used for preparing sample tube standards. This can be used *in situ*, or it can be mounted separately. The carrier gas line to the injector should be retained. The back of the injection port should be adapted if necessary to fit the sample tube. This can be done conveniently by means of a compression coupling with a PTFE ring seal.

8. Reagents and Materials

8.1 Unless otherwise stated, all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[14] Other grades may be used, provided that it is ascertained that use of the reagent does not lessen the accuracy of the practice.

8.2 *Reagents*:

8.2.1 *Volatile Organic Compounds*, for calibration. These should reflect the compounds of interest. Typical components are: propane, pentane, hexane, benzene, dichloromethane, 111-trichloroethane, methanol, ethanol, *n*-butanol, methyl acetage, 2-methoxyethanol, methyl ethyl ketone, acetonitrile, *n*-butyl acetate, ∝-pinene, decane, ethylene oxide, propylene oxide, and hexanal.

8.2.2 *Methanol*, of chromatographic quality, free from compounds co-eluting with the compound or compounds of interest (8.2.1). Alternative dilution solvents, for example, ethyl acetate or cyclohexane can be used, particularly if there is a possibility of reaction or chromatographic co-elution.

8.3 *Sorbents*, particle size, in the range 20 to 80 mesh, preconditioned under a flow of inert gas by heating, at a temperature at least 25°C below the published maximum for that sorbent, for 16 h, before packing the tubes. To prevent recontamination of the sorbents, keep them in a clean atmosphere during cooling to room temperature, storage, and loading into the tubes. If tubes are packed with unconditioned sorbent, stringently condition them at a temperature just below (10 to 25°C) the maximum recommended temperature of the least stable sorbent in the tube for not less than 2 h, with a flow of at least 100 mL/min pure, inert carrier gas. The flow direction shall be opposite to that used during sampling. Wherever possible, keep analytical desorption temperatures below those used for conditioning. Sorbent tubes prepacked by the manufacturer are also available for most sorbents and as such only require conditioning.

8.3.1 A guide for selection of sorbents for pumped and axial diffusive sampling is given in Appendix X2. Equivalent sorbents may be used. A guide to sorbent conditioning and analytical desorption parameters is given in Appendix X3.

8.4 *Calibration Solutions:*

8.4.1 *Calibration Solutions for Ambient and Indoor Air*:

8.4.1.1 *Solution Containing Approximately 100 µg/mL of Each Liquid Component*—Accurately weigh approximately 10 mg of substance or substances of interest into a 100 mL volumetric flask, starting with the least volatile substance. Make up to 100 mL with methanol (8.2.2), stopper and shake to mix.

8.4.1.2 *Solution Containing Approximately 10 µg/mL of Liquid Components*—Introduce 50 mL of methanol into a 100 mL volumetric flask. Add 10 mL of solution (8.4.1.1). Make up to 100 mL with methanol, stopper and shake to mix.

8.4.1.3 *Solution Containing Approximately 10 µg/mL of Gas Components*—For gases, for example, ethylene oxide, prepare a low level calibration solution as follows. Obtain pure gas at atmospheric pressure by filling a small plastic gas bag from a gas cylinder. Fill a 10 µL gas-tight syringe with 10 µL of the pure gas and close the valve of the syringe. Using a 2 mL septum vial, add 2 mL methanol and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the methanol. Open the valve and withdraw the plunger slightly to allow the methanol to enter the syringe. The action of the gas dissolving in the methanol creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws; that is, 1 mol of gas at STP occupies 22.4 L.

8.4.2 *Calibration Solutions for Workplace Air*:

8.4.2.1 *Solution Containing Approximately 10 mg/mL of Each Liquid Component*—Accurately weigh approximately 1 g of substance or substances of interest into a 100 mL volumetric flask, starting with the least volatile substance. Make up to 100 mL with methanol (8.2.2), stopper and shake to mix.

8.4.2.2 *Solutions Containing Approximately 1 mg/mL of Liquid Components*—Introduce 50 mL of methanol into a 100 mL volumetric flask. Add 10 mL of solution (8.4.2.1) Make up to 100 mL with methanol, stopper and shake to mix.

8.4.2.3 *Solution Containing Approximately 1 mg/mL of Gas Components*—For gases, for example, ethylene oxide, prepare a low level calibration solution as follows. Obtain pure gas at atmospheric pressure by filling a small plastic gas bag from a gas cylinder. Fill a 1 mL gas-tight syringe with 1 mL of the pure gas and close the valve of the syringe. Using a 2 mL septum vial, add 2 mL methanol and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the methanol. Open the valve and withdraw the plunger slightly to allow the methanol to enter the syringe. The action of the gas dissolving in the methanol creates a vacuum, and the

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[14] Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Analar Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K. and the United States Pharmacopeia and National Formulary, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws, that is, 1 mol of gas at STP occupies 22.4 liters.

8.4.3 *Stability of Calibration Blend Solutions*—Prepare fresh standard solutions weekly, or more frequently if evidence is noted of deterioration, for example, condensation reactions between alcohols and ketones.

8.5 *Loaded Sorbent Tubes*—Loaded sorbent tubes may be prepared and used for the calibration of monitoring methods using radial diffusive sampling as well as those using pumped and axial diffusive sampling. Prepare loaded sorbent tubes by injecting aliquots of standard solutions onto clean sorbent tubes as follows: Fit the sampling end of the clean sorbent tube into the injection unit (7.13) through which inert purge gas is passing at 100 mL/min and introduce a 1 to 4 µL aliquot of an appropriate standard solution injected through the septum. After 5 min, disconnect the tube and seal it. Prepare fresh standards with each batch of samples. For ambient and indoor air, load sorbent tubes with 1 to 5 µL (at least 3 levels) of solutions 8.4.1.1, 8.4.1.2, or 8.4.1.3. For workplace air, load sorbent tubes with 1 to 5 µL (at least 3 levels) of solutions 8.4.2.1, 8.4.2.2, or 8.4.2.3.

9. Sampling Tubes and Radial Sorbent Cores

9.1 Label sorbent tubes (and carrier tubes for radial sorbent cores) uniquely prior to conditioning. Do not use solvent-containing paints and markers or adhesive labels to label the tubes. Prior to use, condition sorbent tubes and radial sorbent cores in their carrier tubes by desorbing them at a temperature just above the analytical desorption temperature (see Appendix X3) for 10 min with a carrier gas flow of at least 100 mL/min. Analyze a representative proportion of the sorbent tubes using routine analytical parameters, to ensure that the thermal desorption blank is sufficiently small. If the blank is unacceptable, recondition the tubes by repeating this procedure. Once a sample has been analyzed, the tubes may be reused to collect another sample immediately. Check the thermal desorption blank if the sorbent tubes are left for an extended period before reuse, or if sampling for a different analyte is envisaged. Seal the sorbent and carrier tubes with metal screw caps with combined PTFE ferrule fittings and stored in an airtight container when not sampling or being conditioned. The sorbent tube blank level is acceptable if artifact peaks are no greater than 10 % of the typical areas of the analytes of interest.

10. Calibration of Pump or Diffusive Sampler Uptake Rate

10.1 Calibrate the pump with a representative sorbent tube assembly in line, using an appropriate external calibrated meter. Refer to Practice D 3686, Annexes on Methods for Calibration of Small Volume Air Pumps.

NOTE 3—The sampling pump shall comply with local safety regulations.

10.2 The uptake rates given in Tables 7 and 8 (axial) and Table 9 (radial) are for tubes and radial cylindrical sorbent cores with the dimensions in 7.3 and 7.4, respectively, and (for axial diffusive sampling) without a membrane in the diffusion end cap 7.3.2. For other specifications of tubes/cores and for other analytes, it may be necessary to follow one of the protocols listed in 1.2 to determine and validate the uptake rate.

11. Sampling Procedures

11.1 *Active (Pumped) Sampling*

11.1.1 Select a sorbent tube (or tube combination) appropriate for the compound or mixture to be sampled. Guidance on suitable sorbents is given in Appendix X2.

11.1.2 If more than one tube is to be used, prepare a tube assembly by joining the tubes with a union (7.7).

11.1.3 Attach the pump to the sorbent tube or tube assembly with plastic or rubber tubing, so that the tube or section of tube containing the stronger sorbent is nearest the pump.

11.1.4 When used for personal sampling, to minimize channeling, mount the tube vertically in the worker's breathing zone, for example on his lapel. Attach the pump to the worker as appropriate to minimize inconvenience. When used for fixed location sampling, choose a sampling site.

11.1.5 Turn the pump on and adjust the flow rate so that the recommended sample volume is taken in the available time. The recommended air sample volume for the volatile organic compounds covered by this method is 1 to 10 L and the equivalent 2 h sampling rate range is 8 to 80 mL/min. For sampling over shorter periods, the flow rate may be increased in proportion, but should not exceed 200 mL/min. Thus, a 2 L sample may be collected in 10-min at 200 mL/min. For sampling over longer periods the flow rate may be decreased in proportion, but should not be less than 5 mL/min. If the total sample is likely to exceed 1 mg (that is, 1 mg on each tube), the sample volume should be reduced accordingly, or electrometer overload may occur. At temperatures above 20°C, reduce the sample volume by a factor of two for each 10°C rise in temperature. Distributed volume pairs, that is two parallel sorbent tubes or tube assemblies used for the collection of different volumes of the same atmosphere at the same time, can provide a useful tool for validation of the overall monitoring method (19.1.3).

11.1.5.1 Sampling efficiency will be 100 %, provided the sampling capacity of the sorbents is not exceeded. If this capacity is exceeded, breakthrough of vapor from the tube assembly will occur. The breakthrough volume may be measured by sampling from a standard vapor atmosphere, while monitoring the effluent air with a flame ionization or equivalent detector (a suitable method is described in Annex A1). Alternatively, instead of determining the breakthrough volume directly, the mathematically related retention volume may be determined. The retention volume is determined chromatographically at elevated temperatures and subsequent extrapolation to room temperature. A suitable method is described in Annex A2.

11.1.5.2 The direct (vapor sampling) and the indirect (chromatographic) methods of determining breakthrough volumes have been shown to give broadly equivalent results for sorbent Type D. This is confirmed by the European study (**12**), where for sorbent Type D and sorbent Type C, direct values were between twice and twenty times the indirect; that is, the indirect method is a safe estimate. However, for sobent Type A

(**13**), sorbent Type F[3,15] and sorbent Type G[3,16], direct values were between four times and one tenth of the indirect values. The indirect method is, therefore, less reliable for these sorbents, and by implication for other highly microporous sorbents. Both the direct and indirect methods are subject to large errors, so that if sampling volumes close to the recommended breakthrough volume are contemplated, the actual breakthrough volumes should be confirmed by the direct method, using conditions of concentration and relative humidity as close to the anticipated sampled air as possible. Alternatively, use a second (back-up) tube in series (11.1.6) during field sampling as a check on breakthrough.

NOTE 4—The concept of safe sampling volume (SSV) has been adopted (Tables 1-6) to help compensate for any errors involved in determining breakthrough volumes. The SSV is derived either as 70 % of a directly determined breakthrough volume or 50 % of the indirectly determined retention volume.

11.1.5.3 The breakthrough volume of porous polymers varies with ambient air temperature, reducing by a factor of about two for each 10°C rise in temperature. It also varies with sampling flow rate, being reduced substantially at flow rates below 5 mL/min or above 500 mL/min. The breakthrough volumes of carbon molecular sieves are less affected by temperature and flow rate, but are substantially reduced at high concentrations of volatile organic vapor or high relative humidity. To allow a suitable margin of safety, it is recommended that safe sample volumes not be exceeded. Tables 1-6 give typical values for retention volumes and safe sampling volumes. These values have been determined by the chromatographic method (Annex A2). Use of back-up tubes (11.1.6) during field monitoring will help confirm quantitative retention under actual monitoring conditions.

11.1.5.4 The safe sampling volumes in Tables 1-6 have been determined by the chromatographic method (Annex A2) which did not take account of humidity (**12**). Measurements by the direct method (**14**) indicate that breakthrough volumes at high (80 %) humidity are about a factor of two lower for porous polymers and graphitized carbon type sorbents and a factor of ten lower for pure charcoals and carbon molecular sieves than the low humidity value. If high concentrations (>100 ppm, 300 mg/m^3) are also anticipated, the breakthrough volumes for carbonaceous sorbents should be further reduced by a factor of two. Use of back-up tubes (11.1.6) during field monitoring will help confirm quantitative retention under actual monitoring conditions.

11.1.6 A second, identical (back-up) tube, connected in series to the primary sample tube using an appropriate metal union (7.7), should be used on a representative proportion (5 or 10 %) of the sampling tubes used in each field monitoring exercise.

11.1.7 Note and record the times, temperature, flow rate or register reading, if appropriate, and the barometric pressure when the pump was turned on. At the end of the sampling period, note and record the flow rate or register reading, turn the pump off, and note and record the time, temperature, and barometric pressure.

11.1.8 Disconnect the sample tube assembly and seal both ends of each tube with screw caps and PTFE ferrule seals. Tighten these seals securely. Label the tubes uniquely prior to conditioning. Do not use solvent-containing paints and markers or adhesive labels to label the tubes.

11.1.9 If samples are not to be analyzed within 8 h, they are to be placed in a clean, uncoated, sealed metal or glass container.

11.1.10 Record air temperature and barometric pressure periodically during sampling if it is desired to express concentrations reduced to specific conditions (14.1.2).

11.1.11 *Field Blanks*—Prepare field blanks from tubes identical to those used for sampling and subject them to the same handling procedure as that of the sample tubes except that the blank tubes are kept sealed during the actual period of sampling. The identification numbers of the blank tubes should be noted.

11.2 *Axial Diffusive sampling,*

11.2.1 Select a sorbent tube appropriate for the compound or mixture to be sampled. Guidance on suitable sorbents is given in Tables 8 and 9 and Appendix X2.

11.2.2 If more than one axial diffusive sample tube is to be used, they should be exposed simultaneously side by side.

11.2.3 Immediately before sampling, remove the storage end cap from the sampling end of the sample tube and replace it with a diffusion end cap. Make sure the diffusion cap is properly seated and that the sealing end cap at the other end of the tube is left in place.

11.2.4 When used for personal sampling, mount the tube(s) in the person's breathing zone, for example on the lapel of a jacket. When used for fixed location sampling, select an unimpeded, representative sampling site away from obvious emission sources. In either case, mount the tube(s) vertically with the sampling end at the bottom. The diffusion end cap should have unrestricted access to the sampled atmosphere, that is, should not be obscured by the wearer's clothing or other objects.

11.2.5 The recommended exposure time for the volatile organic compounds covered by this method is eight hours for workplace monitoring and one to four weeks for ambient and indoor air monitoring. Sampling over shorter periods is possible, down to 30 minutes for workplace monitoring and one day for ambient and indoor air monitoring, but the working concentration range (1.6.2) will be effected accordingly. For example, for a four hour sampling period, the working range is approximately 0.004 mg/m^3 to 20 mg/m^3.

11.2.6 Note and record the identification number of each tube and the times and temperature at the beginning and end of sampling. At the end of the sampling period, again note and record the time and temperature.

11.2.7 At the end of the sampling period, remove the diffusive sampling caps and seal both ends of each tube with screw caps and PTFE ferrule seals. Tighten these seals securely and recheck the tightness of the seals at the non-sampling ends of the tubes.

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[15] An example of sorbent Type F known to perform as specified in this practice is Carbopack B manufactured by Supelco Inc., USA.

[16] An example of sorbent Type G known to perform as specified in this practice is Carbotrap manufactured by Supelco Inc., USA.

11.2.8 If samples are not to be analyzed within eight hours, they are to be placed in a clean, uncoated, sealed metal or glass container.

11.2.9 Record the air temperature periodically during sampling if it is desired to express concentrations reduced to specific conditions (14.2).

11.2.10 *Field blanks*—Prepare field blanks by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the sample tubes except for the actual period of sampling.

11.3 *Radial diffusive sampling*

11.3.1 Select a sorbent core appropriate for the compound or mixture to be sampled. Guidance on suitable sorbents is given in Table 9 and 1.5.3.

11.3.2 If more than one radial diffusive sampler is to be used, they should be exposed simultaneously side by side.

11.3.3 Immediately prior to sampling, remove the sorbent core from the carrier tube and slide it into the sampling body without touching the sorbent core. Seal the end of the sampler body.

11.3.4 When used for personal sampling, mount the sampler(s) in the person's breathing zone, for example on the lapel of a jacket. When used for fixed location sampling, a suitable sampling site is chosen. In either case, the diffusive sampling body should have unrestricted access to the sampled atmosphere, that is, should not be obscured by the wearer's clothing or other objects.

11.3.5 The recommended exposure time for the volatile organic compounds covered by this method is up to six hours for ambient and indoor air monitoring. Sampling over shorter periods is possible, down to 30 minutes for ambient and indoor air monitoring, but the working concentration range (1.6.3) will be affected accordingly. Sampling over longer periods is also possible provided the sorbent selected is sufficiently strong to prevent back diffusion.

11.3.6 Note and record the identification number of each carrier tube and the times and temperature at the beginning and end of sampling. At the end of the sampling period, again note and record the time and temperature.

11.3.7 At the end of the sampling period, undo the removable seal on the diffusve sampling body and slide the sorbent core back into its original carrier tube without touching it. Seal both ends of each carrier tube with screw caps and PTFE ferrule seals. Tighten these seals securely and recheck the tightness of the seals.

11.3.8 If samples are not to be analyzed within eight hours, they are to be placed in a clean, uncoated, sealed metal or glass container.

11.3.9 Record air temperature periodically during sampling if it is desired to express concentrations reduced to specific conditions (14.2).

11.3.10 *Field blanks*—Prepare field blanks by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the sample tubes except for the actual period of sampling.

12. Desorption and Analysis

12.1 Place the sorbent or carrier tube in a compatible thermal desorption apparatus. Purge the air from the tube before heat is applied to avoid chromatographic artifacts arising from the terminal oxidation of the sorbent or gas chromatographic packing. Heat the tube to displace the organic vapors which are passed (usually by means of a focusing (cold) trap (7.5)) to the gas chromatograph by means of a carrier gas stream. The gas flow at this stage shall be the reverse of that used during sampling, that is, the marked end of the tube should be nearest the gas chromatograph column inlet. The gas flow through the tube should be in the order of 30 to 50 mL/min for optimum desorption efficiency. For the initial air purge, it is usually necessary to use 10× the tube volume (that is, 20 to 30 mL) of inert gas to completely displace the volume of air (2 to 3 mL) in the tube. However, if strongly hydrophilic sorbents are needed, it may be necessary to employ a larger purge to reduce sorbed air and water (see 6.4).

12.2 The desorbed sample occupies a volume of several milliliters of gas, so that pre-concentration is essential prior to capillary GC analysis. This is usually achieved using a small, cooled, secondary (focusing) sorbent trap, which can be desorbed sufficiently rapidly at a low flow rates (< 5 mL/min) to minimize band broadening and produce capillary compatible peaks. Alternatively, the desorbed sample can be passed directly to the gas chromatograph (single stage desorption) where it must be refocused. This typically requires a high phase ratio column (for example, 5 µm film thickness, 0.2 to 0.32 mm ID) and a sub-ambient starting temperature.

12.2.1 If a secondary sorbent focusing (cold) trap is not available and if sub-zero capillary cryofocusing temperatures are used to preconcentrate the analytes, water must be completely eliminated from the sample tube prior to desorption in order to prevent ice formation blocking the capillary tubing and stopping the thermal desorption process.

12.2.2 If a secondary focusing (cold) trap is not available and optimum sample tube desorption flows of 30 to 50 mL/min are used, a minimum split ratio of 30 to 50 + 1 will typically be required for operation with high resolution capillary columns. Single stage thermal desorption may thus limit method sensitivity.

12.3 Desorption conditions should be chosen such that desorption from the sample tube is complete, and no sample loss occurs in the secondary trap, if used. Typical parameters are, as follows:

Desorption temperature	250 to 325°C
Desorption time	5 to 15 min
Desorption flow rate	30 to 50 mL/min in the reverse direction to that used for sampling
Cold trap low	Between –30°C and +30°C
Flow rate through trap for desorption	2 to 50 mL/min in the reverse direction to that used for focusing
Cold trap high	250 to 350°C
Cold trap sorbent	Typically same as tubes, 10 to 100 mg,
Carrier gas	Helium
Split ratios	Split ratios between the sample tube and secondary trap, and between the secondary trap and analytical column (if applicable) should be selected dependent on expected atmospheric concentration. (See guidance from respective manufacturers of the thermal desorption apparatus)

NOTE 5—The desorption temperature depends on the analyte and the sorbent used. Recommendations are given in Table 6 but the maximum desorption temperatures given in Appendix X2 and Appendix X3 for particular sorbents should be respected.

12.4 Set the sample flow path temperature (transfer line temperature) high enough to prevent analyte condensation but not so high as to cause degradation. Analytes sufficiently volatile to be present in the vapor phase in air at ambient temperature, do not usually require flow path temperatures above 150°C.

12.5 Set up the gas chromatograph for the analysis of volatile organic compounds. A variety of chromatographic columns may be used for the analysis of these compounds. The choice will depend largely on which compounds, if any, are present that might interfere in the chromatographic analysis. Suitable choices are 50 m × 0.22 mm fused-silica columns with thick-film (1 to 5 µm), dimethylsiloxane or a 50 m 7 % cyanopropyl, 7 % phenyl, 86 % methyl siloxane stationary phase. Typical operating conditions for these columns are a temperature program from 50 to 250 at 5°C/min, with an initial hold time of 10 min at 50°C.

12.6 The capillary column or, preferably, length of uncoated, deactivated fused silica, should be threaded back through the transfer line from the thermal desorption apparatus to the gas chromatograph such that it reaches as close as possible to the sorbent in the focusing (cold) trap or as near as possible to the tube in a single stage desorber. Internal tubing must be inert and dead volumes must be minimized. A split valve(s) is conveniently placed at the inlet or outlet, or both, of the secondary focusing trap. The split valve on the outlet of the secondary trap may be located either at the inlet or the outlet of the transfer line. Typical split ratios are from 5 + 1 to 1000 + 1. Lower split ratios are suitable for ambient and indoor air measurements; higher split ratios for workplace air measurements.

12.7 Correspondence of retention time on a single column should not be regarded as proof of analyte identity.

13. Method Calibration

13.1 Analyze each sorbent tube standard (8.5) by thermal desorption and gas chromatography.

13.2 Prepare a multiple level calibration graph by plotting the $\log_{10}$ of the areas of the analyte peaks corrected for blank levels on the vertical scale against the $\log_{10}$ of the mass of the analyte, in µg, on the sorbent tube standard (8.5) corresponding to the solutions 8.4.1 or 8.4.2.

where:
mass of analyte (µg) = Concentration in solution 8.4.1 or 8.4.2 × volume injected (µl; 8.5).

13.3 *Determination of Sample Concentration*—Analyze the samples and sample blanks as described for the calibration standards in 13.1. Determine the peak response and read from the calibration graph the mass of the analyte in the desorbed sample.

13.4 *Determination of Desorption Efficiency*—Check the efficiency of desorption by injecting aliquots of the standard solutions directly into the gas chromatograph set up with a measured, matching split ratio. Prepare a second calibration graph of peak area against mass of analyte as in 13.2. This calibration should be the same or nearly the same as that in 13.2. The desorption efficiency is the response of a tube standard divided by that of the corresponding liquid standard injected directly. If the desorption efficiency is less than 95 % change the desorption parameters accordingly.

13.4.1 Some makes of thermal desorber do not have a direct liquid injection facility. In these cases, desorption efficiency should be checked by comparing the calibration graph of the substance of interest with that of n-hexane. The ratio of the slope of the calibration graph of the substance of interest relative to that of n-hexane should be the same as the relative response factor for that compound. Response factors for other compounds may be calculated approximately from effective carbon numbers (**15**). If the ratio of the slopes of the calibration graphs do not agree with the relative response factor within 10 %, change the desorption parameters accordingly.

13.4.2 Some types of thermal desorber offer a facility for quantitative re-collection of the split effluent onto a conditioned sorbent tube for repeat analysis and method development/validation. If using such apparatus, standards of untested / unvalidated compounds should be prepared (8.5) with the addition of one or more compounds well validated under the analytical conditions selected (Tables 1-9). A sequence of desorption, split, re-collection and repeat analyses can then be carried out on a single original standard. Poor desorption efficiency of any of the unvalidated compounds (if it occurs) will quickly become apparent from a change in the relative response of that compound to the well-validated component as the sequence of repeat analyses proceeds.

14. Calculations

14.1 *Pumped Sampling of a Known Volume of Air*

14.1.1 *Mass Concentration of Analyte*—Calculate the concentration of the analyte in the sampled air, in µg/m^3, by means of the following equation:

$$\rho\,(VOC) = \frac{F - B}{V} \times 1000 \tag{2}$$

where:
$\rho(VOC)$ = concentration of analyte in the air sampled, in µg/m^3,
F = mass of analyte present in the actual sample as found in 13.3, µg (sum of tubes if more than one used),
B = mass of analyte present in the blank tube, µg (sum of tubes if more than one used), and
V = volume of sample taken, L.

14.1.1.1 If F and B are expressed in mg the resultant concentration, $\rho(VOC)$, will be in mg/m^3.

14.1.1.2 If it is desired to express concentrations reduced to specified conditions, (for example, 25°C and 101 kPa) then:

$$\rho(VOC)\mathrm{corr} = \rho(VOC) \times \frac{101}{P} \times \frac{T+273}{298}, \tag{3}$$

where:
P = actual pressure of the air sampled, kPa, and
T = actual temperature of the air sampled, °C.

14.1.2 *Volume Concentration of Analyte*—Calculate the volume fraction of the analyte in air, in µL/m^3 by means of the following equation:

$$\phi(VOC) = \rho(VOC) \times \frac{24.45}{M} \times \frac{101}{P} \times \frac{T + 273}{298} \tag{4}$$

where:

$\phi(VOC)$ = volume fraction of the analyte in air, µL/m^3, and

M = molecular mass of the analyte of interest, g/mol.

14.1.2.1 If F and B are expressed in mg the resultant concentration, $\phi(VOC)$, will be in mL/m^3.

NOTE 6—If it is desired to express the volume concentrations reduced to specified conditions, use the appropriate values for P and T in Eq. 4. For the specific situation of 25°C and 101 kPa, the pressure and temperature terms cancel out. This is the procedure to be followed when comparing volume concentrations, obtained for occupational hygiene monitoring, to standards and limit values published by the American Conference of Governmental Industrial Hygienists, the US National Institute for Occupational Safety and Health, the US Occupational Safety and Health Administration and stated as volume concentrations.

14.2 *Diffusive Sampling*

14.2.1 *Mass concentration of analyte*. Calculate the concentration of the analyte in the sampled air, in µg/m^3, by means of the following equation:

$$\rho(VOC) = \frac{F - B}{U' \times t} \times 10^6 \tag{5}$$

where:

$\rho(VOC)$ = concentration of analyte in the air sampled, in µg/m^3

F = mass of analyte present in the actual sample as found in 13.3, in µg

B = mass of analyte present in the blank tube, in µg

U' = diffusive uptake in cm^3/min (10.2 or Tables 7-9), and

t = exposure time in min

14.2.1.1 If F and B are expressed in mg the resultant concentration, ρ(VOC), will be in mg/m^3.

14.2.1.2 If it is desired to express mass concentrations reduced to specified conditions, (for example, 25°C and 101 kPa) then:

$$\rho(VOC)_{corr} = \rho(VOC) \times \frac{101}{P} \times \frac{T + 273}{298} \tag{6}$$

where:

P = the actual pressure of the air sampled, in kPa

T = the actual temperature of the air sampled, in °C

14.2.2 *Volume concentration of analyte*. Calculate the volume fraction of the analyte in air, in µL/m^3 by means of the following equation:

$$\phi(VOC) = \frac{F - B}{U \times t} \times 10^6 \tag{7}$$

where:

$\phi(VOC)$ = volume fraction of the analyte in air, in µL/m^3, and

U = diffusive uptake in ng.ppm^{-1} (V/V).min^{-1}(Section 10 or Table 1)

14.2.2.1 If F and B are expressed in mg the resultant concentration, ϕ(VOC), will be in mL/m^3.

NOTE 7—If it is desired to express the volume concentrations reduced to specified conditions (for example, 25°C and 101 kPa), the sampling rate in cm^3/min provided by the manufacturer must first be adjusted for the effects of pressure and temperature in acordance with equation 8.

$$U'' = U' \times 101/P \times ((T + 273)/298)^{1.5} \tag{8}$$

U″ is then inserted into Eq. 7 in place of U to give the volume fraction in air in µL/m^3(or ppm) at normal temperature and pressure (NTP, 25°C and 101 kPa). This is the procedure to be followed when comparing volume concentrations, obtained for occupational hygiene monitoring, to standards and limit values published by the American Conference of Governmental Industrial Hygienists, the US National Institute for Occupational Safety and Health, the US Occupational Safety and Health Administration and stated as volume concentrations.

14.3 *Uptake rates*. Uptake rates in cm^3/min and ng.ppm^{-1} (V/V).min^{-1} are related by:

$$U = U' \times \frac{24.45}{M} \times \frac{101}{P} \times \frac{T + 273}{298} \tag{9}$$

where:

M = molecular mass of the analyte of interest, in g/mol.

15. Precision and Bias

15.1 Laboratory tests of the procedure with pumped sampling (**12**), following in part EN 1076 using tubes spiked from a standard atmosphere of hexane at 1.0 mg/m^3 and 50 % RH. at 20°C and using a pump in conformity with EN 1232, yielded results expressed as overall uncertainty (3.2.5); sorbent Type D, sorbent Type C and sorbent Type A (mean of five determinations), 8.9 %; sorbent Type F[15] and sorbent Type G[16] (mean of three determinations), 16.8 %.

15.2 Laboratory tests of the procedure with diffusive sampling, following in part EN 838 and using standard axial diffusive tubes (Fig. 1) containing an appropriate sorbent yielded diffusive sampling rates for individual organic compounds as given in Tables 7 and 8. This table also specifies the level of conformity with EN 482, that is, an overall uncertainty of better than 25 % at the limit value, for each listed compound and sorbent combination. In many cases, a slightly different diffusive sampling rate value applies to workplace monitoring over short periods to that used for ambient and indoor measurements. The results of this evaluation are from a variety of sources which are identified in (**16**). Different uptake rates and uncertainties may be given by other makes of diffusive tube, or if a membrane is employed, or if a different sorbent is used, but the general performance of other systems is expected to be similar to that described here (10.2).

15.3 Laboratory tests (**12**) on sorbent tubes spiked with the compounds specified in 8.2.1 on sorbent Type A or sorbent Type B at a load level of approximately 1.0 µg are summarized in Table 10. The precision expressed as a coefficient of variation, was between 1.3 % and 5.9 %, depending on analyte. Expressed as repeatability (ISO 5725) the range is equivalent to 3.7 % to 16.7 %.

15.4 Laboratory tests (**3**) or sorbent Type D tubes, liquid spiked with a broader range of compounds at a single load level of approximately 10 µg are summarized in Table 11. Excluding hexane, for which sorbent Type D is unsuitable, the precision expressed as a coefficient of variation, was between 0.4 % and 2.8 %, depending on analyte. Expressed as repeatability (ISO 5725) the range is equivalent to 11 % to 5.6 %.

15.5 Laboratory tests (**17**) on tubes liquid spiked with 11 model compounds including benzene, toluene, xylene, and isopropylbenzene on sorbent Type A at load levels between 0.5 µg and 250 µg are summarized in Table 12. The precision, expressed as repeatability (ISO 5725) was between 7.2 % and

TABLE 10 Precision of Analysis and Storage of Test Compounds on Sorbent Type A[A] and Sorbent Type B[B] (10), (Load Level 1 µg)

Organic Compound	Precision of Analysis (CV %)		Storage Recovery (%)	
	Sorbent Type A	Sorbent Type B	Sorbent Type A	Sorbent Type B
Propane		1.8		115
Pentane	1.7		112	
Hexane	2.1; 3.6		104	
Benzene	2.9		100	
Dichloromethane	1.9		114	
1,1,1-Trichloroethane	2.4		101	
Methanol		1.7		64
Ethanol	5.9		96	
Butanol	1.3		101	
Methyl acetate	1.8		113	
Methoxyethanol	5.7		121	
Methyl ethyl ketone	2.2		103	
Acetonitrile	4.1		112	
Butyl acetate	3.4		104	
A-Pinene	4.2; 2.5		104	
Decane	4.2		104	
Ethylene Oxide		not determined		not determined
Propylene Oxide	3.6		103	
Hexanal	3.5		98	

[A] An example of sorbent Type A known to perform as specified in this practice is Chromosorb 106 manufactured by Manville Corp., USA.

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

21.6 %, depending on loading level. The precision, expressed as reproducibility (ISO 5725) was between 25.9 % and 43.2 %, depending on loading level.

16. Storage

16.1 Laboratory tests (**12**) on tubes spiked with the compounds specified in 8.2.1 on sorbent Type A and sorbent Type B at a load level of approximately 1.0 µg and stored at room temperature for two weeks are summarized in Table 10. The mean recovery (relative to unstored tubes) for sorbent Type A was 105.6 %.

16.2 Laboratory tests (**3**) on tubes liquid spiked with a broader range of compounds on sorbent Type D at a single load level of approximately 10 µg and stored at room temperature for 5 months are summarized in Table 11. Excluding hexane and methoxyethanol (neither of which should be sampled using sorbent Type D), the mean recovery (relative to unstored tubes) was 99.7 % and the mean coefficient of variation was 2 %. Similar results were obtained after storage for 11 months; excluding hexane and methoxyethanol, the mean recovery (relative to unstored tubes) was 99.4 % and the mean coefficient of variation was 0.9 %.

16.3 Storage data on multi-bed sorbents tubes is not presently available for every possible sorbent combination. A proposed recommendation is to store for not more than 30 days at 4°C before analysis. Ambient conditions are normally adequate for sampling and transportation, but if the conditions exceed 40°C refrigerated transportation is advisable to reduce migration. Storage data on single bed tubes is available (**3**) and shows 100 % recovery over several months at room temperature. Ensure that the seals remain tight at refrigeration temperatures. Also ensure that tubes are allowed to re-equilibrate at room temperature after refrigerated storage, before they are opened to begin analysis. This prevents condensation within the cold tube.

17. Report

17.1 The test report shall contain at least the following information:

17.1.1 complete identification of the sample,

17.1.2 reference to this practice,

17.1.3 the sampling location, sampling time period, and volume of air pumped,

17.1.4 the barometric pressure and temperature,

17.1.5 the test result,

17.1.6 any unusual features noted during the determination

17.1.7 any operation not included in this practice or in the International Standard to which reference is made or regarded as optional.

18. Quality Assurance

18.1 *Validating the Sample Collection Procedure*:

18.1.1 *Blanks*—Artifacts on laboratory and field blanks should be at the low or sub nanogram level for carbonaceous sorbents and sorbent Type D, and the double digit nanogram level for other porous polymer sorbents as described in Appendix X1.[17] If artifact levels are considerably above this, careful attention must be paid to the tube conditioning and storage procedures described in Section 9. Artifact peaks which comprise 10 % or more of the area of the average component peaks should be marked as artifacts in the final data report.

18.1.2 If the same profile/pattern of VOCs is observed in the field blanks as on the sample tubes, and if the levels of these components is 5 % or more of the sampled VOCs, careful attention must be paid to methods of sealing the tubes and other storage procedures in any future studies. If the profile of the VOCs on the field blanks matches that of the sampled tubes and if the area of the peaks on the field blanks are 10 % or more of the sampled tube levels, the sampled tube data are invalid.

18.2 *Sampling Volumes (SSVs) (pumped sampling)*:

18.2.1 The SSVs of sorbent tubes should be retested annually or once every twenty uses (whichever comes first) using one of the procedures described in Annex A1 or Annex A2.

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[17] For typical blank levels see Note 3.

TABLE 11 Precision and Storage Recovery of Solvents on Sorbent Type D[A] Sorbent Tubes

Organic Compound	Loading, µg	Time = 0 % CV[B]	Time = 5 mo. Mean Recovery[C] +% CV		Time = 11 mo. Mean Recovery +% CV	
Hydrocarbons						
Hexane	7.8	10.7	93.6	17.9	100.8	26.1
Heptane	8.4	2.4	99.5	2.1	100.0	1.3
Octane	8.6	2.4	100.1	1.8	100.0	0.5
Nonane	12.0	0.8	nd	nd	101.0	0.4
Decane	9.2	2.2	100.4	1.5	100.2	0.5
Undecane	9.1	2.3	100.7	1.5	100.2	0.2
Dodecane	9.9	2.8	101.8	1.5	101.5	0.4
Benzene	11.0	2.5	98.7	2.0	98.6	0.8
Toluene	10.9	2.6	(100.0)	1.8	(100.0)	0.6
p-Xylene	5.3	2.5	99.9	1.7	99.8	0.7
o-Xylene	11.0	2.4	100.0	1.7	98.8	0.7
Ethylbenzene	10.0	0.5	99.6	0.4	97.9	1.3
Propylbenzene	10.5	2.3	99.7	1.5	98.5	0.7
Isopropylbenzene	10.9	2.3	98.9	1.8	97.2	1.3
m + p-Ethyltoluene	10.5	2.3	98.8	1.7	96.9	1.2
o-Ethyltoluene	5.4	2.2	100.1	1.6	98.9	0.7
1,2,4-Trimethylbenzene	10.8	2.2	100.1	1.3	99.1	0.5
1,3,5–Trimethylbenzene	10.7	2.2	100.0	1.5	99.1	0.5
Trimethylbenzene	10.2	1.7	101.6	0.5	101.3	0.8
Esters and glycol ethers						
Ethyl Acetate	10.3	0.6	97.6	1.0	100.0	2.5
Propyl Acetate	10.9	2.4	100.5	1.7	99.1	0.8
Isopropyl Acetate	9.4	1.0	97.0	0.4	100.0	1.4
Butyl Acetate	10.8	2.4	100.3	1.6	99.9	0.6
Isobutyl Acetate	10.7	2.3	100.2	1.4	99.8	0.7
Methoxyethanol	8.9	5.4	87.3	5.7	93.1	1.6
Ethoxyethanol	10.4	4.2	97.6	2.5	97.2	3.3
Butoxyethanol	10.0	2.6	100.6	4.1	100.1	3.0
Methoxypropanol	10.4	2.4	95.3	3.6	99.0	1.2
Methoxyethyl Acetate	12.5	2.1	100.6	1.4	98.9	1.4
Ethoxyethyl Acetate	11.4	0.9	99.8	2.2	98.7	2.6
Butoxyethyl Acetate	11.5	2.3	101.3	1.3	99.9	1.1
Aldehydes and ketones						
Methyl Ethyl Ketone	9.2	0.9	97.4	0.8	99.1	0.6
Methyl Isobutyl Ketone	9.3	0.6	100.7	0.6	100.7	0.5
Cyclohexanone	10.9	0.8	102.4	1.2	100.7	0.6
2-Methylcyclohexanone	10.7	0.7	101.1	0.5	101.1	1.3
3-Methylcyclohexanone	10.5	0.8	103.6	1.0	103.0	0.7
4-Methylcyclohexanone	10.6	0.9	103.6	1.4	102.7	0.6
3,5,5-Trimethylcyclohex-2-enone	10.6	2.3	101.4	0.9	97.7	1.2
Alcohols						
Butanol	9.0	1.1	94.8	3.0	96.9	1.2
Isobutanol	8.9	1.0	93.6	3.5	96.4	1.0

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

[B] Six replicates.

[C] Normalized to toluene = 100. The stability of toluene has been established in a BCR intercomparison **(19).**

TABLE 12 Precision (Repeatability and Reproducibility) on Sorbent Type A[A]

Loading level, µg	Recovery, %	ISO Repeatability, %	ISO Reproducibility, %
0.5	95.4	21.6	39.1
2.5	91.5	11.2	43.2
12.5	97.6	7.2	43.0
50	102.3	11.9	25.9
250	104.5	9.7	31.6
Overall	98.3	12.3	36.6

[A] An example of sorbent type A known to perform as specified in this practice is Chromosorb 106 manufactured by Manville Corp., USA.

18.2.2 If the SSV of a tube falls below the normal air sample collection volume for the analytes in question, the tube should be repacked with fresh sorbent and reconditioned.

18.3 *Performance Criteria for the Sampling Pump*—The pump flow rate shall be stable to within ±5 % (±2 CV) and the total volume of air sampled by the pump over the sampling period shall be within ±10 % (±2 CV) of the calculated volume. A pump conforming to EN 1232 or equivalent may be expected to be within these limits.

18.4 *Routine checking of diffusive uptake rates*

18.4.1 The uptake rates of axial or radial diffusive samplers should be retested annually or once every fifty uses (whichever comes first) using EN 838 or equivalent.

18.4.2 As an alternative, since a change in the diffusive uptake rate will be reflected in the dynamic sorption capacity (axial diffusive sampling only), check the breakthrough volume of the tube using one of the procedures described in Annex A1 or Annex A2. In addition check the dimensions of the air gap (see 7.3).

19. Performance Criteria for the Solid Sorbent Sampling of VOCs in Air

19.1 There are four performance criteria which must be met for a system to qualify under EPA Method TO-17 for pumped sampling of ambient air (**1**). Similar criteria will be appropriate for workplace air, for example, EN 1076, and for indoor air. See also EPA Method 301 (**18**). The following criteria defined in TO-17 should be adapted, where necessary, for a particular application or regulatory requirement.

19.1.1 The method detection limit shall be $\leq 2.5 \mu g/m^3$. In general, over a concentration range of $0.1 \mu g/m^3$ to $1 g/m^3$ the method shall have a dynamic range of at least 3 orders of magnitude.

19.1.2 Duplicate analytical precision shall be within 20 % on synthetic samples of a given target VOC in typical target VOC mixtures in humidified zero air.

19.1.3 Agreement within 25 % for distributed volume pairs taken in each sample set; that is, agreement within 25 % for two pumped samplers used to collect different volumes of the same atmosphere over the same time. The equivalent test for diffusive sampling is either to expose two identical samplers for different time periods in a constant atmosphere or expose two samplers with different uptake rates for the same time.

19.1.4 Audit accuracy within 30 % for concentrations normally expected in contaminated ambient air (2.5 to 125 $\mu g/m^3$).

20. Keywords

20.1 air; ambient air; diffusive sampling; indoor air; gas chromatographic analysis; passive sampling; pumped sampling; volatile organic compounds; workplace air

ANNEXES

(Mandatory Information)

A1. DETERMINATION OF BREAKTHROUGH VOLUMES

A1.1 *Definition*—The breakthrough volume for a sorbent tube is the volume of an organic vapor in air that can be passed through the tube before the concentration of eluting vapor reaches 5 % of the applied test concentration. The breakthrough volume varies with the vapor and the sorbent type.

A1.2 *Apparatus*:

A1.2.1 Use ordinary laboratory apparatus and the following.
A1.2.2 *Sorbent Tubes*, as in 7.2.
A1.2.3 *Flow Meter*, range 20 to 200 mL/min.
A1.2.4 *Flame Ionization Detector*, or similar.

A1.3 *Reagents*:

A1.3.1 *Dynamic Standard Concentration of Organic Vapor in Air*—Prepare by dilution of a measured amount of organic vapor with a metered flow of air. Generate the organic vapor by permeation tube (ISO 6349) or by syringe injection (**20**) methods. Other methods of generating atmospheres are suitable.

A1.4 *Determination*:

A1.4.1 Assemble a gas train consisting of a dynamic standard atmosphere generator delivering a concentration equivalent to a current exposure limit for the analyte of interest, a sorbent tube, a flow meter and a flame ionization detector. Pass the gas through the train at a known rate between 20 and 200 mL/min. Use a value in this range appropriate for the sampling rate intended. Note the time that the flow was initiated. When the vapor begins to emerge, the detector will show a response. Continue the measurement until a plateau corresponding to the input is reached. Determine the time at which 5 % of the plateau value had been reached.

A1.4.2 If the dead volume of the system is significant in comparison with the breakthrough volume, determine the dead volume by repeating the determination with an empty tube in the gas train and make a suitable correction.

A1.4.3 Determine the effect of moisture on the breakthrough volume by humidifying the gas stream to approximately 80 % RH. Do this by diluting a primary gas stream with air at 100 % RH. obtained by passing air through a series of water bubblers. Do not pass the organic vapor atmosphere through the water.

A1.5 *Expression of Results*—Calculate the breakthrough volume by multiplying the flow rate expressed in L/min by the elapsed time in minutes, taking the elapsed time from the point of flow initiation to the point where 5 % of the plateau value was reached.

A1.6 *Calculation of Safe Sampling Volume*—The safe sampling volume is taken as 70 % of the breakthrough volume.

A2. DETERMINATION OF SAFE SAMPLE VOLUME FROM THE EXTRAPOLATED RETENTION VOLUME

A2.1 *Definition*—The retention volume for a sorbent tube is the elution volume at peak maximum of a small aliquot of an organic vapor eluted from the tube by air or chromatographic carrier gas.

A2.2 *Apparatus*:

A2.2.1 *Ordinary Laboratory Apparatus:*

A2.2.2 *Sorbent Tubes*, as in 7.1

A2.2.3 *Gas Chromatograph*, fitted with a flame ionization detector, capable of detecting an injection of 0.5 ng toluene with a signal-to-noise ratio of at least 5 + 1.

A2.2.4 *Flow Meter*, range from 20 to 200 mL/min.

A2.2.5 *Thermocouple*.

A2.3 *Reagents*:

A2.3.1 *Dynamic Standard Concentration of Organic Vapor in Air*—Prepare by dilution of a measured amount of organic vapor with a metered flow of air. Generate the organic vapor by permeation tube (ISO 6349) or by syringe injection **(19)** methods. Other methods of generating atmospheres are suitable.

A2.4 *Determination*. Connect a sorbent tube (A2.2.2) to the injection and detection ports of a gas chromatograph (A2.2.3) in place of the normal chromatography column by means of narrow bore PTFE tubing. Determine the retention volume of a 1 mL aliquot of standard atmosphere (A2.3; approximately 100 ppm at 20°C) at least five settings of the chromatograph oven temperature such that the retention time is convenient (between 2 and 20 min). Calculate the retention volume by multiplying the retention time by the column volumetric flow rate. Repeat the determination five times at each temperature.

A2.5 *Expression of Results*—Plot the mean values of the determinations of retention volume at each temperature against reciprocal absolute temperature and extrapolate to 20°C (3.413×10^{-3}°Kelvin^{-1}).

A2.6 *Calculation of Safe Sampling Volume*—The safe sampling volume is taken as 50 % of the extrapolated retention volume.

APPENDIXES

(Nonmandatory Information)

X1. DESCRIPTION OF SORBENT TYPES

X1.1 Sorbent types are described as follows:

Sorbent[A]	**Composition**
Type G	graphitized carbon
Type J	graphitized carbon
Type F	graphitized carbon
Type K	graphitized carbon
Type P	graphitized carbon
Type Q	graphitized carbon
Type L	carbon molecular sieve
Type B	carbon molecular sieve
Type M	carbon molecular sieve
Type R	carbon molecular sieve
Type O	styrene/divinylbenzene
Type A	polystyrene
Type H	vinylpyrrolidone
Type E	ethylvinylbenzene/divinylbenzene
Type I	carbon molecular sieve
Type D	poly(diphenyl-*p*-phenylene oxide)
Type C	graphitized poly(diphenyl-*p*-phenylene oxide)
Type S	graphitized carbon
Type T	graphitized carbon
Type U	intermediate composition between graphitized carbon and carbon molecular sieve

[A] See Note X1.1 for sorbent availability.

NOTE X1.1—An example of sorbent Type G known to perform as specified in this practice is Carbotrap manufactured by Supelco Inc., USA.

An example of sorbent Type J known to perform as specified in this practice is Carbotrap C manufactured by Supelco Inc., USA.

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

An example of sorbent Type K known to perform as specified in this practice is Carbopack C manufactured by Supelco Inc., USA.

An example of sorbent Type P known to perform as specified in this practice is Anasorb GCB1 manufactured by SKC Inc., USA.

An example of sorbent Type Q known to perform as specified in this practice is Anasorb GCB2 manufactured by SKC Inc., USA.

An example of sorbent Type L known to perform as specified in this practice is Carbosieve S-III manufactured by Supelco Inc., USA.

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

An example of sorbent Type M known to perform as specified in this practice is Carboxen 1000 manufactured by Supelco Inc., USA.

An example of sorbent Type R known to perform as specified in this practice is Anasorb CMS manufactured by SKC Inc., USA.

An example of sorbent Type O known to perform as specified in this practice is Chromosorb 102 manufactured by Manville Corp, USA.

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

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

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

An example of sorbent Type I known to perform as specified in this practice is Unicarb (formerly Spherocarb) supplied by Markes International, UK.

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

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

An example of sorbent Type S known to perform as specified in this practice is Carbograph 1 manufactured by Carbochimica Romana, I.

An example of sorbent Type T known to perform as specified in this practice is Carbograph 4 manufactured by Carbochimica Romana, I.

An example of sorbent Type U known to perform as specified in this practice is Carbopack X manufactured by Supelco Inc., USA.

X2. GUIDANCE ON SORBENT SELECTION

X2.1 Table X2.1 provides guidance on sorbent selection.

TABLE X2.1 Guidance on Sorbent Selection

NOTE 1—See Note X1.1 for sorbent availability.

Sample Tube Sorbent	Approximate Analyte Volatility Range	Temperature °C, max	Specific Surface Area, m^2/g	Example Analytes
Type J Type K Type P	n-C_8- n-C_{20}	>400°C	12	Alkyl benzenes and aliphatics ranging in volatility from n-C8 to n-C16
Type D	bp 100 - 400°C n-C_7 - n-C_{26}	350°C	35	Aromatics, apolar components (bp>100°C) and less volatile polar components (bp>150°C)
Type C	bp 100 - 450°C n-C_7 to n-C_{30}	350°C	35	Alkyl benzenes, vapor phase PAHs and PCBs and as above for Type D.
Type G Type F Type Q	(n-C_4) n-C_5- n-C_{14}	>400°C	100	Wide range of VOCs Inc., ketones, alcohols, and aldehydes (bp>75°C) and all apolar compounds within the volatility range specified, plus perfluorocarbon tracer gases
Type O	bp 50 - 200°C	250°C	350	Suits a wide range of VOCs including oxygenated cpds and haloforms less volatile than methylene chloride
Type A	bp 50 - 200°C	250°C	750	Suits a wide range of VOCs including hydrocarbons from n-C_5 to n-C_{12}. Also good for volatile oxygenated cpds.
Type E	bp 50 - 200°C n-C_5- n-C_{12}	250°C	550	Suits a wide range of VOCs including oxygenated compounds
Type H	bp 50 - 150°C b-C_5- n-C_8	180°C	300	Specifically selected for volatile nitriles; acrylonitrile, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from EtOH, MEK, and so forth.
Type I[A]	-30 - 150°C C_3- n-C_8	>400°C	1200	Good for very volatile compounds such as VCM, ethylene oxide, CS_2 and CH_2Cl_2. Also good for volatile polars for example, MeOH, EtOH and acetone.
Type L[A] Type B[A] Type M[A] Type R[A]	-60 - 80°C	400°C	c 800	Good for ultra volatile compounds such as C_3, C_4 hydrocarbons, volatile haloforms and freons
Zeolite molecular Sieve[B]	-60 - 80°C	350°C		Used specifically for 1,3-butadiene and nitrous oxide.
Type U	80–145°C	400°C	240	Validated for benzene and partly for toluene and xylene.

[A] These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high (>90 %) relative humidity.

[B] Significantly hydrophilic. Do not use in high humidity atmospheres unless special precautions are taken. See 6.4.

X3. GUIDANCE ON SORBENT USE

X3.1 Table X3.1 provides guidance on sorbent use.

TABLE X3.1 Guidance on Sorbent Use

NOTE 1—See Note X1.1 for sorbent availability.

Sample Tube Sorbent	Temperature, max	Hydrophobic	Temperature and Gas Flow for Conditioning	Temperature and Minimum Gas Flow for Desorption	Recommended Cold Trap Packing
Type J Type K Type P	>400°C	Yes	350°C and 100 mL/min	325°C and 30 mL/min	Type D Type J, Type K or Type P
Type D	350°C	Yes	330°C and 100 mL/min	300°C and 30 mL/min	Type D
Type C	350°C	Yes	330°C and 100 mL/min	300°C and 30 mL/min	Type D
Type F Type G Type Q	>400°C	Yes	350°C and 100 mL/min	325°C and 30 mL/min	Type D, Type F Type G, or Type Q
Type O	250°C	Yes	250°C and 100 mL/min	225°C and 30 mL/min	Type O or dual bed graphitised carbon and carbon molecular sieve
Type A	250°C	Yes	250°C and 100 mL/min	250°C and 30 mL/min	Type A or dual bed graphitised carbon and carbon molecular sieve
Type E	250°C	Yes	250°C and 100 mL/min	225°C and 30 mL./min	Type E or dual bed graphitised carbon and carbon molecular sieve
Type H	180°C	Yes	180°C and 100 mL/min	180°C and 30 mL/min	Type H or dual bed graphitized carbon and carbon molecular sieve
Type I[A]	>400°C	No	400°C and 100 mL/min	390°C and 30 mL/min	Type I or dual bed graphitized carbon and carbon molecular sieve
Type B[A] Type L[A] Type M[A] or Type R[A]	400°C	No	350°C and 100 mL/min	325°C and 30 mL/min	carbon molecular sieve or dual bed graphitised carbon and carbon molecular sieve
Zeolite molecular Sieve[B]	350°C	No	330°C and 100 mL/min	300°C and 30 mL/min	carbon molecular sieve or dual bed graphitised carbon and carbon molecular sieve
Type D/ Type F combination tube	350°C	Yes	330°C and 100 mL/min	300°C and 30 mL/min	Type D
Type F/ carbon molecular sieve combination tube	400°C	No	350°C and 100 mL/min	325°C and 30 mL/min	dual bed graphitized carbon and carbon molecular sieve
Type K Type F and Type L combination tube	400°C	No	350°C and 100 mL/min	325°C and 30 mL/min	dual bed graphitized carbon and carbon molecular sieve
Type U	400°C	Yes	400°C and 100 mL/min	400°C and mL/min	Type A, Type D or dual bed graphitized carbon and carbon molecular sieve

[A] These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high (>90 %5) relative humidity.

[B] Significantly hydrophilic. Do not use in high humidity atmospheres unless special precautions are taken. See 6.4.

REFERENCES

(**1**) US Environmental Protection Agency,“ Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling on Sorbent Tubes,” Compendium Method TO-17, January 1997.

(**2**) Wolkoff, P., “Volatile Organic Compounds – Sources, Measurements, Emissions, and Impact on Indoor Air Quality,” *Indoor Air,* Suppl., No. 3/95 1995, Chapter 3.

(**3**) UK Health and Safety Executive (HSE). “Methods for the Determination of Hazardous Substances. Volatile organic compounds in air. Laboratory method using pumped solid sorbent tubes, thermal desorption and gas chromatography,” Report MDHS 72, 1993.

(**4**) UK Health and Safety Executive (HSE). “Methods for the Determination of Hazardous Substances. Volatile organic compounds in air. Laboratory method using diffusive samplers, thermal desorption and gas chromatography,” Report MDHS 80, 1995.

(**5**) Kennedy, E.R., Fischbein, T.J., Song, R., Eller, P.M. and Shulman, S.A., “Guidelines for Air Sampling and Analytical Method Development and Evaluation,” USDHHS CDC/NIOSH, Cincinnati, OH, May 1995.

(**6**) Wolkoff, P., Clausen, P.A., Jensen, B., Nielsen, G.D. and Wilkins, C.K., “Are We Measuring the Relevant Indoor Pollutants?,” *Indoor Air,* 7, 1997, pp 92-106.

(**7**) Clausen, P.A. and Wolkoff, P., “Degradation Products of Tenax TA Formed During Sampling and Thermal Desorption Analysis: Indicators of Reactive species Indoors,” *Atmospheric Environment* 31, 1997, pp 715-725.

(**8**) Ciccioli, P., et al., “GC Evaluation of Organic Components Present in the Atmosphere at Trace Levels with the Aid of Carbopack B for Preconcentration of the Sample, *J. of Chrom.,* Vol 351, 1986, pp 433-449.

(**9**) De Bortoli, M., et al., “Comparison Tenax and Carbotrap for VOC Sampling of Indoor Air” *Indoor Air,* Vol 2, 1992, pp 214-216.

(**10**) Helmig, D.,“ Artifact-free Preparation, Storage and Analysis of Solid Adsorbent Sampling Cartridges in the Analysis of Volatile Organic Compounds in Air,” *J of Chrom.,* Vol 732, 1996, pp 414–417.

(**11**) Wright, M.D, “The Perkin Elmer Tube Revisited,” Diffusive Monitor, 5, 1992, pp 5.

(**12**) UK Health and Safety Executive (HSE). “Study of Sorbing Agents for the Sampling of Volatile Compounds from Air,” EC Contract MATI-CT92-0038. Final Report, 1995.

(**13**) Harper, M., “Evaluation of Solid Sorbent Sampling Methods by Breakthrough Volume Studies,” *Ann Occup. Hyg.,* Vol 37, 1993, pp 65-88.

(**14**) Brown, R. H. and Purnell, C. J., Collection and Analysis of Trace Organic Vapor Pollutants in Ambient Atmospheres. The Performance of Tenax-GC Adsorbent Tube,” *J Chrom.,* Vol 178, 1979, pp 79-90.

(**15**) Sternberg, J. C. et al, “The Mechanism of Response of Flame Ionization Detectors,” 3rd Intern, *Symp. Gas Chrom.,* 1960, pp 231-267.

(**16**) UK Health and Safety Executive (HSE). “Diffusive Uptake Rates on Perkin Elmer Sorbent Tubes,” Diffusive Monitor, 12, 2001, pp 6-9.

(**17**) Coker, D.T. et al, “A Monitoring Method for Gasoline Vapor Giving Detailed Composition,” *Ann. Occup. Hyg.* Vol 33, 1989, pp 15-26.

(**18**) US Environmental Protection Agency, “Field Validation of Pollutant Measurement Methods from Various Waste Media,” Method 301 (40 CFR Part 57 Appendix A).

(**19**) Vandendriessche, S., Griepink, B, Hollander, J. C. Th., Gielen, J. W. J., Langelaan, F. G. G. M., Saunders, K. J. and Brown, R. H., “Certification of a Reference Material for Aromatic Hydrocarbons in Tenax Samplers,” *Analyst,* Vol 116, 1991, pp 437-441.

(**20**) UK Health and Safety Executive (HSE), “Methods for the Determination of Hazardous Substances. Generation of Standard Atmospheres– Syringe Injection Method,” Report MDHS 3, 1990.

(**21**) Fondazione Salvatore Maugeri-IRCCS, Centro di Ricerche Ambientali. Via Svizzera 16, I-35127, Padova, Italy. Internal Report, 2002 (Available from ASTM International).

(**22**) Martin, N.A., Marlow, D.J., Henderson, M.H., Goody, B.A., 2002. Determination of the bensene uptake rate for the sorbent Carbopack X employed in Perkin Elmer type samplers. The Diffusive Monitor, Issue 13, 9-1.

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