Designation: D6196 – 15

Standard Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air[1]

This standard is issued under the fixed designation D6196; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

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

1.2 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 surface at the sampling end of the tube (diffusive or passive sampling). The sorbed VOCs are subsequently recovered by thermal desorption and analyzed by capillary gas chromatography.

1.3 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 passive (diffusive) samplers (typically of the same physical dimensions as standard pumped sorbent tubes and containing only one sorbent); and (*3*) radial passive (diffusive) samplers.

1.4 This practice recommends a number of sorbents that can be packed in sorbent tubes for use in the sampling of vapor-phase organic chemicals; including volatile and semi-volatile organic compounds which, generally speaking, boil in the range 0 to 400°C (v.p. 15 to 0.01 kPa at 25°C).

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

1.5.1 With pumped sampling, this practice can be used for the speciated 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. Quantitative measurements are possible when using validated procedures with appropriate quality control measures.

1.5.2 With axial diffusive sampling, this practice is valid for the speciated measurement of airborne vapors of volatile organic compounds in a concentration range of approximately 100 μg/m^3 to 100 mg/m^3 for individual organic compounds for an exposure time of 8 h or 1 μg/m^3 to 1 mg/m^3 for individual organic compounds for an exposure time of four weeks.

1.5.3 With radial diffusive sampling, this practice is valid for the measurement of airborne vapors of volatile organic compounds in a concentration range of approximately 5 μg/m^3 to 5 mg/m^3 for individual organic compounds for exposure times of one to six hours.

1.5.4 The upper limit of the useful range is almost always set by the linear dynamic range of the gas chromatograph column and detector, or by the sample splitting capability of the analytical instrumentation used.

1.5.5 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 This procedure can be used for personal and fixed location sampling. It cannot be used to measure instantaneous or short-term fluctuations in concentration. Alternative 'grab sampling' procedures using canister air samplers (for example, Test Method D5466) may be suitable for monitoring instantaneous or short term fluctuations in air concentration. Alternatives for on-site measurement include, but are not limited to, gas chromatography, real-time mass spectrometry detectors and infrared spectrometry.

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

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

[1] This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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[2] The bold face numbers in parentheses refer to the list of references at the end of this practice.

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:*[3]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3670 Guide for Determination of Precision and Bias of Methods of Committee D22

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

D5466 Test Method for Determination of Volatile Organic Chemicals in Atmospheres (Canister Sampling Methodology)

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *ISO Standards:*[4]

ISO 5725 Accuracy (Trueness and Precision) of Measurement Methods and Results

ISO 6145-10 Gas Analysis. Preparation of Calibration Gas Mixtures. Permeation Method

ISO 13137 Workplace Atmospheres: Pumps for Personal Sampling of Chemical and Biological Agents. Requirements and Test Methods

ISO 16017-1 Indoor, Ambient, and Workplace Air – Sampling and Analysis of Volatile Organic Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography — Part 1: Pumped Sampling

ISO 16017-2 Indoor, Ambient, and Workplace Air – Sampling and Analysis of Volatile Organic Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography — Part 2: Diffusive Sampling

ISO 16107 Workplace Atmospheres—Protocol for Evaluating the Performance of Diffusive Samplers

ISO GUM Guide to the Expression of Uncertainty in Measurement

2.3 *CEN Standards:*[5]

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

EN 14662-1 Ambient air quality – standard method for measurement of benzene concentrations – Part 1: Pumped sampling followed by thermal desorption and gas chromatography

EN 14662-4 Ambient air quality – standard method for measurement of benzene concentrations – Part 4: Diffusive sampling followed by thermal desorption and gas chromatography

2.4 *EPA Method:*[6]

EPA Method TO-17 Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

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

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

3.2.3 *diffusive (passive) 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 (diffusion gap), permeation through a membrane or some other diffusion-barrier, but which does not involve the active movement of air through the sampler.

3.2.4 *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.

3.2.5 *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 ends of a radial sampler are sealed.

3.2.6 *diffusive uptake rate or diffusive sampling rate (U)*—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).

3.2.7 *loading*—the mass of analyte collected or introduced on the sampler.

3.2.8 *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

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

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

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

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

sampling pump. Air is passed through the sorbent tube at a rate controlled by the sampling pump.

3.2.9 *safe sampling volume*—70 % of breakthrough volume (3.2.1) or 50 % of the chromatographically-determined retention volume.

3.2.10 *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.

3.2.11 *sorbent tube*—a tube, usually made of metal or glass, containing one or more sorbents 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).

3.3 *Definitions of Acronyms Used in This Standard to Denote Specific Types or Classes of Sorbent (See Also for Details and Examples):*

3.3.1 *PDMS*—Polydimethyl siloxane-based sorbent (GC column packing material), typically comprising polydimethyl siloxane gum coated on particles of inert support at a specified loading levels: for example, 3 % or 10 %.

3.3.2 *VW-GCB*—Very weak graphitized carbon black sorbent.

3.3.3 *W-PP*—Weak porous polymer sorbent.

3.3.4 *WM-GCB*—Weak to medium strength graphitized carbon black sorbent.

3.3.5 *M-PP*—Medium strength porous polymer sorbent.

3.3.6 *MS-GCB*—Medium to strong graphitized carbon black sorbent.

3.3.7 *CMS*—Carbonized molecular sieve sorbent.

4. Summary of Practice

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

4.2 For axial diffusive sampling, a suitable sorbent is 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, are used in parallel. The diffusive sampler or samplers are exposed to the atmosphere for a measured time period. Provided the sorbents chosen are strong enough to maintain a zero (or negligible) analyte concentration at the sampling surface (that is, to minimize back diffusion), Fick's law of diffusion will apply. The uptake rate of each volatile organic component, in terms of mass retained per unit of ambient air concentration per unit exposure time, will be a constant U – See 3.2.4. This means that, while Fick's law applies and back-diffusion remains negligible, the analyte mass collected by the sampler is directly proportional to the time weighted average atmospheric concentration over a given exposure period.

4.3 For radial diffusive sampling, a suitable sorbent is selected for the compound or mixture to be sampled. If more than one sorbent is required, two or more samplers, packed with different sorbents, are used in parallel. The diffusive sampler or samplers are exposed to the atmosphere for a measured time period. Provided the sorbents chosen are strong enough to maintain a zero (or negligible) analyte concentration at the sampling surface (that is, to minimize back diffusion), Fick's law of diffusion will apply and the uptake rate of each volatile organic component, in terms of mass retained per unit exposure time, is directly proportional to the atmospheric concentration.

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 and sensitivity 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 GC-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 (**5**).

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

NOTE 1—While workplace air monitoring has traditionally been carried

out using disposable sorbent tubes, typically packed with charcoal and extracted using chemical desorption (solvent extraction) prior to GC analysis – for example following NIOSH and OSHA reference methods – routine thermal desorption (TD) technology was originally developed specifically for this application area. TD overcomes the inherent analyte dilution limitation of solvent extraction improving method detection limits by 2 or 3 orders of magnitude and making methods easier to automate. Relevant international standard methods include ISO 16017-1 and ISO 16017-2. For a detailed history of the development of analytical thermal desorption and a comparison with solvent extraction methods see Ref (**6**).

5.5 In order to protect the environment as a whole and human health in particular, it is often necessary to take measurements of air quality and assess them 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 any GC-compatible vapor-phase organic compound 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 overall quality control of each measurement are within acceptable limits for each specific VOC of interest. 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 nanogram levels on well conditioned tubes desorbed at moderate temperatures – See 8.3 and Refs (**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 extracted- or selected ion monitoring (SIM) mode as a GC detector. In this mode, co-eluting compounds can usually be determined. Spectral deconvolution is also useful for distinguishing and identifying co-eluting GCMS peaks.

6.3 Competitive sorption between VOCs, although unlikely at normal sampling levels, is possible at high concentrations (for example, >100 ppm) and shall be taken into consideration if necessary 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 blacks – See Appendix X1. When less hydrophobic, strong sorbents such as 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 and selectively dry purging moisture from the sorbent tube or secondary focusing trap, or both, prior to analysis. Other useful approaches to minimizing water interference include reducing the air volume sampled, for example, to 0.5 L (pumped 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 glass or stainless steel tubing, 6.4 mm 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 or glass wool, or both. Tubes of other dimensions may be used but the safe sampling volumes (SSV) given in Appendix X2 are based on these tube dimensions. For labile analytes, such as sulfur-containing compounds, fused-silica-coated steel (typically 5 mm ID) or glass tubes (typically 4 mm ID) should be used. (See Note 2.) 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), taking care to ensure that the entire sorbent bed will be within the desorber heated zone during thermal desorption, and that an air gap of at least 14 mm is retained at each end of the tube to minimize errors due to diffusive ingress at a very low pump flow rates. The tubes described above typically contain between 100 and 1000 mg sorbent, depending on sorbent density, and the number of adsorbent beds. If more than one sorbent is used in a single tube, the sorbents should be arranged in discrete beds in order of increasing sorbent strength with the weakest sorbent nearest to the sampling (inlet) end of the tube. Tubes should be labelled uniquely prior to conditioning. Do not use solvent-containing paints and markers or adhesive labels to label the tubes as high levels of solvent might contaminate the tubes and adhesive labels might jam the thermal desorption mechanism. Tubes may be obtained commercially which are already permanently marked (for example, etched) with suitable identifiers such as unique serial numbers in alphanumeric or barcode format, or both.

NOTE 2—With glass tubes the sorbent is typically held in place using a glass frit, or plugs of quartz or unsilanized glass wool.

7.2.1 Sorbents with widely different (>100°C) maximum desorption temperatures such as medium strength porous polymers and graphitized carbon blacks, or carbon molecular sieve when packed in the same tube, or both, must be conditioned and desorbed at temperatures below the maximum of the least stable adsorbent in the tube.

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 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 Appendix X3 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. Glass tubes are not usually considered suitable for passive sampling because it is more difficult to define the diffusive air gap sufficiently accurately and reproducibly.

NOTE 3—Tubes packed with more than one sorbent may be used for diffusive monitoring, but only the first sorbent, nearest the sampling end, plays any role in the sampling process.

7.3.1 *Uptake rates* in Appendix X3 are given for stainless steel or fused silica-coated stainless steel 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 (see Fig. 1) and an inner air gap of 14.3 mm (between the outer surface of the sorbent retaining gauze and the end of the tube). In practice packed tube dimensions will vary slightly **(11)** and tubes should be rejected where the inner air gap is outside the range 14.0 and 14.6 mm.

7.3.2 *Diffusive End Caps,* typically push-on, "O"-ring seal caps fitted with a metal gauze allowing the diffusive ingress of vapor. The size of the gauze covered opening in the sampling cap should being the same as the cross section of the tube (Fig. 1). The diffusive endcap maintains the diffusive air gap between the inlet of the tube and the sorbent. The use of the diffusive endcap also minimizes air movement within the diffusive air gap if sampling in windy conditions.

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 Appendix X4 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 of weak porous polymer sorbent, or 400 mg of medium to strong graphitized carbon black sorbent.

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 OD, 5 mm ID and 89 mm long, capable of retaining the sorbent core approximately 14 mm from the desorption end of the carrier tube. The sorbent core

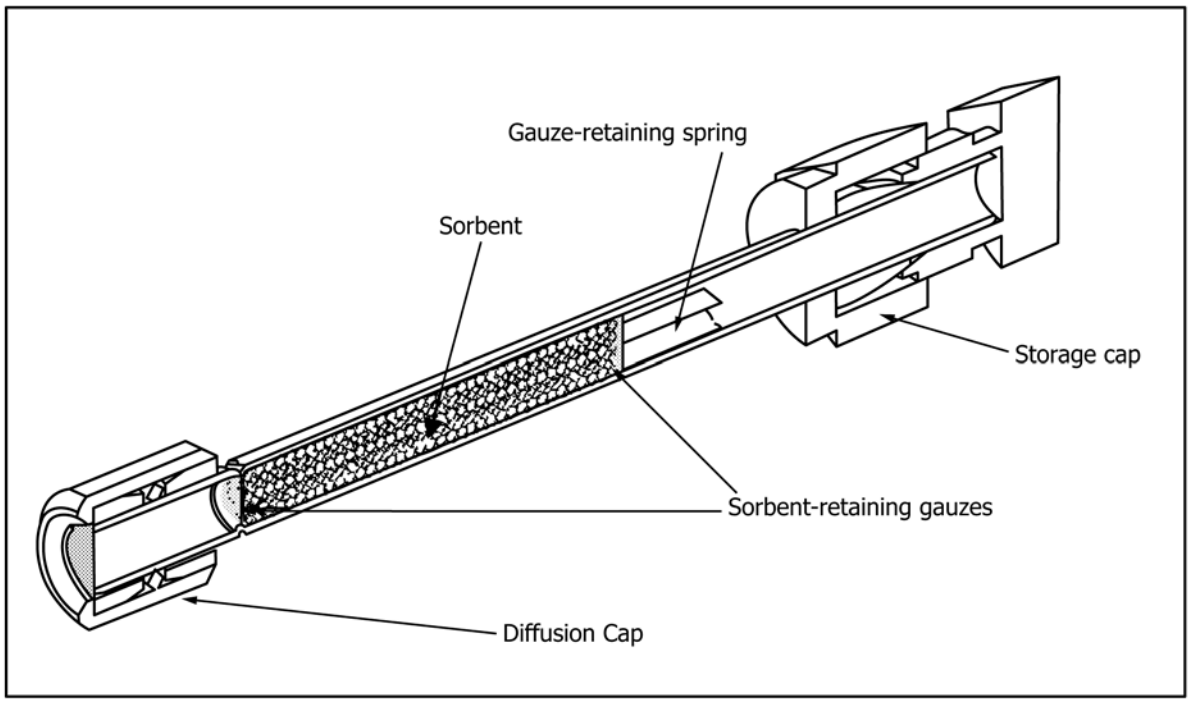

FIG. 1 Schematic of a Typical Axial Diffusive Sampler

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. It should be possible to seal the carrier tubes with long-term sorbent tube storage caps (7.6). Carrier tubes should be labelled uniquely prior to conditioning. Do not use solvent-containing paints and markers or adhesive labels to label the tubes. Carrier tubes may be obtained commercially which are already permanently marked (for example, etched) with suitable identifiers such as unique serial numbers in alphanumeric or barcode format, or both.

7.5 *Thermal Desorption Apparatus,* for two-stage thermal desorption of 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 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. Contaminants from the outer surfaces of tubes should be excluded from the sample flow path. If the design of the given TD means contaminants cannot be completely excluded, care should be taken to minimize contamination of the outer surfaces of tubes (for example, from finger oils, grease, etc.) for example, by wearing clean white cotton gloves when handling the tubes in the field and laboratory.

NOTE 4—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.

NOTE 5—Internal standard addition to the sampling end of every sample tube can be used as an additional or alternative check on sample integrity, however, without a pre-desorption leak test (Note 4) results from leaking samples will be lost.

7.6 *Sorbent Tube End Caps,* to combine two or more tubes together in series during pumped sampling. They typically comprise 6.4 mm OD stainless steel couplings fitted with combined (one-piece) PTFE ferrule seals.

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 1 or 5 µL liquid syringe readable to 0.01 or 0.05 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 8.3.1.

7.10 *Connecting Tubing (pumped sampling only),* if tubing is required upstream (for example, for connecting between the sampling point and the sample tube when sampling in a remote location), inert PTFE tubing should be used and should be replaced regularly. Any tubing used downstream of the sampler (that is, for connecting the non-sampling end of 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 typically needs to be about 90-cm long. All connections should be leak proof.

7.11 *Soap Bubble Flow Meter or Electronic Flow Meter,* 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. Typical dimensions are 50 or 60 m long fused silica capillary columns, 0.25 mm ID or 0.32 mm ID with a 0.5 to 5 micron film of an appropriate stationary phase.

7.13 *Injection Facility for Preparing Standards,* comprising a conventional packed column GC injection port may be used for preparing sample tube standards. Ready-made injection systems for loading liquid or gas-phase standards onto the sampling end of sorbent tubes are also available commercially. Essential components include a fitting for the sampling end of the tube, a controllable flow of inert (carrier) gas through the injector body and a septum cap such that the liquid or gas standard can be injected into the stream of gas at or near the sampling surface of the sorbent tube.

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.[7] 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 acetate, 2-methoxyethanol, methyl ethyl ketone, acetonitrile, *n*-butyl acetate, ∝-pinene, decane, ethylene oxide, propylene oxide, and hexanal.

8.2.2 *Solvent,* of chromatographic quality, free from compounds co-eluting with the compound or compounds of interest

[7] 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.

(8.2.1). Methanol is most commonly used because it can often be selectively purged from tubes packed with weaker sorbents prior to standard analysis. However, 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, typically 35–60 mesh. Medium strength porous polymer sorbents (Appendix X1) which are prone to shrinkage should be 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. If tubes are packed with unconditioned sorbent, they should be stringently conditioned 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. The lowest effective analytical desorption temperature shall be used (13.4) to minimize artifact levels. Temperatures shall be kept below those used for conditioning. Sorbent tubes prepacked by the manufacturer are also available with or without preconditioning.

8.3.1 Sorbent selection is determined by sorbent strength, typically assessed in terms of retention of the compound of interest (See Annex A2) – or breakthrough volume (that is, the volume of air that can be sampled before the concentration of analyte breaking through the sorbent and exiting from the far end of the tube becomes significant – typically >5 %) – See Annex A1. In essence, the sorbent or sorbents selected must be strong enough for complete retention of all the compounds of interest during sampling and weak enough for effective release of all the compounds of interest (under reasonable analytical conditions) during subsequent thermal desorption.

NOTE 6—Analyte breakthrough (loss) from the far end of a sorbent tube during pumped sampling is not a function of sampler 'capacity' in the normal sense of the word – that is, it does not indicate that the sorbent tube is 'full' or 'saturated' with that analyte under the given conditions. It is, more accurately, a chromatographic function, relating to the affinity of the analyte (sorbate) for the sorbent. Breakthrough, to a large extent, will be unaffected by analyte concentration or loading in the same way that chromatographic retention times are constant for a given analyte however big or small the peak. Studies have shown that the breakthrough volume of a given analyte on a given sorbent tube remains constant for air concentrations up to 100 ppm (**12**).

8.3.1.1 In the case of pumped sampling, single-bed tubes containing a weak porous polymer (W-PP) sorbent are appropriate for normal alkanes ranging in volatility from n-C_6 (hexane) or n-C_7 (depending on required air sample volume) up to n-C_{22} or n-C_{30} (depending on analytical thermal desorption capabilities and conditions). More volatile materials should be sampled on stronger sorbents, such as medium to strong graphitized carbon blacks (MS-GCB) or carbon molecular sieves (CMS). Example sorbents and their respective applications are given in Appendix X1. A broader range of VOCs may be sampled using multi-bed tubes, that is, sampling tubes packed with two or more sorbents, arranged in discrete layers in order of increasing sorbent strength from the sampling end.

8.3.1.2 Guidance given for the selection of sorbents for pumped monitoring tubes can be applied equally well to axial passive sampling tubes because, in this case, sufficient sorbent strength (breakthrough volume) equates to low back diffusion and stable uptake rates. The restriction to a single sampling surface (hence single sorbent) limits the target analyte range that can be monitored by any one passive sampling tube. However, the unobtrusive nature and low cost of passive samplers usually means that two or more samplers containing different sorbents can be used in parallel without impacting study objectives.

8.3.1.3 The high sampling rate and associated increased risk of back diffusion associated with radial diffusion typically limits these samplers to compounds of equal or lower volatility than benzene. It also means that stronger sorbents are generally required when compared with sampling the same compounds using either axial passive or pumped sorbent tubes.

8.3.1.4 A guide for selection of sorbents for pumped and axial diffusive sampling is given in Appendix X1. Equivalent sorbents may be used. Information on sorbent conditioning and analytical desorption parameters is given in Appendix X1 and is also available from manufacturers.

8.3.2 Apparent sorbent strength (breakthrough volumes) may be reduced when air concentrations exceed 100 ppm (in the same way that retention times may fall slightly when a packed GC column is overloaded), but pumped sampling volumes or diffusive sampling times are invariably minimized when sampling under such extreme conditions so this effect is rarely a significant limiting factor.

8.3.3 Sorbent tube artifacts are <1ng for typical sampling tubes (7.2) containing well-conditioned carbonaceous sorbents such as graphitized carbon blacks (GCBs) and carbon molecular sieves (CMSs); at 1 to 5 ng levels for thermally stable weak porous polymer (W-PP) sorbents and at 5 to 50 ng levels for the range of medium strength porous polymer (M-PP) sorbents.

NOTE 7—Use of M-PP sorbents is in decline due to their inherent high and variable background levels. Data relating to M-PP sorbents is designated using gray font in this standard to indicate these sorbents should be used with caution.

NOTE 8—Inherent artifact levels will increase significantly with desorption temperature. The lowest effective desorption temperature should always be used.

8.4 *Calibration Standards:*

8.4.1 Gas standards suitable for introducing target compounds to the sampling end of conditioned sorbent tubes at the levels of interest provide an optimum calibration option for air monitoring methods because they allow analytes to be introduced to the sorbent in a way which is closely analogous to air sampling and which introduces no potential interferences – for example, solvent. However, certified gas standards are difficult and expensive to obtain at trace (ppb) levels and stable gas standards are not available for all compounds – for example; higher boiling VOCs, polar compounds, reactive species and semi-volatile organics.

8.4.2 *Calibration Solutions for Ambient and Indoor Air:*

8.4.2.1 *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 solvent (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 10 µg/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 solvent, stopper and shake to mix.

8.4.2.4 *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 solvent to enter the syringe. The action of the gas dissolving 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.

8.4.3 *Calibration Solutions for Workplace Air:*

8.4.3.1 *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 solvent (8.2.2), stopper and shake to mix.

8.4.3.2 *Solutions Containing Approximately 1 mg/mL of Liquid Components*—Introduce 50 mL of solvent into a 100 mL volumetric flask. Add 10 mL of solution (8.4.3.1) Make up to 100 mL with solvent, stopper and shake to mix.

8.4.3.3 *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 solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the solvent. Open the valve and withdraw the plunger slightly to allow the solvent to enter the syringe. The action of the gas dissolving 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 litres.

8.4.4 *Loading Sorbent Tubes with Calibration Standards*—Prepare fresh liquid 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 all 3 sorbent-based monitoring methods described in this standard; axial and radial passive samplers and pumped sorbent tubes. Prepare loaded sorbent tubes by connecting the sampling end of blank, conditioned sorbent tubes to a metered source of gas-phase standard (8.4.1) using inert tubing and connections. A fixed and measured volume of standard gas at known pressure, for example, in a gas sample loop, can be introduced onto the sampling end of the tube in a stream of pure carrier gas. Alternatively, a controlled flow of standard gas can be passed through a blank sorbent tube for a specific length of time. Aliquots of liquid standard solutions can be injected 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 2 µL aliquot of an appropriate standard solution injected through the septum. After 5 min, disconnect the tube and seal it. If calibration tubes are to be prepared using multiple standards (gas-phase or liquid solutions, or both), introduce those containing the least volatile compounds of interest first and the most volatile compounds of interest (typically the gas phase standards) last. Load fresh blank tubes with appropriate calibration standards for each batch of samples. When using liquid standards to calibrate typical ambient and indoor air monitoring methods, load sorbent tubes with 1 to 2 µL (at least 3 levels) of solutions 8.4.2.1, 8.4.2.2, or 8.4.2.3. When using liquid standards to calibrate typical workplace air monitoring methods, load sorbent tubes with 1 to 2 µL (at least 3 levels) of solutions 8.4.3.1, 8.4.3.2, or 8.4.3.3.

8.5.1 If it is not possible to selectively purge the solvent from the tubes during the standard loading process, for example when using tubes packed with stronger sorbents, the liquid standard volume should be limited to 1 µL. High levels of unpurged solvent can cause chromatographic interferences, split discrimination, detector quenching and column overload and make standards behave significantly differently to than real samples. Use a syringe with sufficient precision to deliver the low volume accurately (7.8).

9. Sampling Tubes and Radial Sorbent Cores

9.1 Prior to use, re-condition pre-conditioned or desorbed sorbent tubes and radial sorbent cores in their carrier tubes by desorbing them at a temperature above the analytical desorption temperature (see Appendix X1) 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, it may be possible to reuse the desorbed tubes 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 envisioned.

9.2 Seal the sorbent and carrier tubes with appropriate long term storage caps (7.6) and store 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 low level 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 D3686, Annexes on Methods for Calibration of Small Volume Air Pumps.

10.2 The uptake rates given in Appendix X3 (axial) and Appendix X4 (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 relevant protocols referenced in Section 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 X1.

11.1.2 If more than one tube is to be used in series, prepare a tube assembly by joining the non-sampling end of the front tube to the sampling end of the second (back-up) tube with a union (7.7).

11.1.3 Attach the pump to the non-sampling end of the sorbent tube or tube assembly with flexible tubing (7.10), so that the tube or section of tube containing the stronger sorbent is nearest the pump (7.2).

11.1.4 When used for personal sampling, to minimize risk of channeling, mount the tube vertically in the worker's breathing zone, for example on his/her lapel. Attach the pump to the worker as appropriate to minimize inconvenience. When used for fixed location sampling, choose a representative sampling site not immediately adjacent to a local emission or contamination source.

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 the analytical system may be overloaded. Safe sampling volumes decrease with increasing temperature and are typically quoted at 20°C. Monitoring temperatures should be considered when selecting sampling volumes. 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 close to 100 %, provided there is no channeling (11.1.4) and provided the breakthrough volume of the least well retained analyte is not exceeded on the sorbent tube selected under the given monitoring conditions. Sampling efficiency can be tested on individual samplers and under actual monitoring conditions using distributed volume pairs (11.1.5) and by checking for significant (>10 %) breakthrough (18.2.1) on the back up tubes used in each monitoring exercise (11.1.6). The breakthrough volume may be measured directly by sampling from a standard vapor atmosphere, while monitoring the effluent air with a flame ionization or equivalent detector (a suitable 'direct' method is described in Annex A1). Alternatively, the breakthrough volume can be determined indirectly from the mathematically related retention volume. The retention volume is determined chromatographically at elevated temperatures and subsequent extrapolation to room temperature. A suitable 'indirect' 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. A study of breakthrough volumes **(13)** using weak porous polymer sorbents has reported indirect breakthrough volumes values between twice and twenty times smaller than direct values indicating that the indirect method is a conservative estimate. However, similar studies using weak to medium strength graphitized carbon black sorbents **(12)** have reported indirect values between four times smaller and ten times larger than the direct 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 field air monitoring conditions as possible. Alternatively, use a second (back-up) tube in series (11.1.6) during field sampling as a check on breakthrough.

NOTE 9—The concept of safe sampling volume (SSV) has been adopted (Appendix X2) 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. The tables in Appendix X2 give typical values for retention volumes and safe sampling volumes.

11.1.5.4 The safe sampling volumes in Appendix X2 have been determined by the chromatographic method (Annex A2) which did not take account of humidity **(13)**. 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 respective low humidity values. If high concentrations (>100 ppm, 300 mg/m^3) are also anticipated, breakthrough volumes 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 field 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 (10 %) of the sampling tubes in each field monitoring exercise.

11.1.7 Note and record the identification numbers of each tube, the sampling location, the times, temperature, the sampling flow rate and the barometric pressure when the pump was turned on. At the end of the sampling period, note and record the flow rate, turn the pump off, and note and record the time, temperature, and unadjusted barometric pressure.

NOTE 10—The barometric pressure reported by most weather sources has been (reduced) or adjusted to sea-level and is not appropriate for higher altitudes.

11.1.8 Disconnect the sample tube assembly and seal both ends of each tube with long term storage caps (7.6). Tighten these seals securely.

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 (14.1.1.2).

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 Appendix X1 and Appendix X3.

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 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 securely 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 pointing down. The diffusion end cap should have unrestricted access to the sampled atmosphere, that is, it 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 air 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 (1.5.2) will be effected accordingly. For example, for a four hour sampling period, the working range is approximately 200 µg/m^3 to 200 mg/m^3.

11.2.6 Note and record the identification number of each tube, the sampling location 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 the sampling end of each tube with long-term storage seals. Tighten these seals securely and recheck the tightness of the seals at the non-sampling ends of the tubes.

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 (14.2.1.2).

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 Appendix X1 and Appendix X4.

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, it 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 (1.5.3) 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, the sampling location 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 long term storage caps (7.6). 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 (14.2.1.2).

11.3.10 *Field Banks*—Prepare field blanks by using carrier tubes and radial sorbent cores 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. As each tube in turn is sealed into the analytical flow path, system integrity should be checked to ensure there are no leaks which could lead to sample losses. Purge the air from each tube before heat is applied to avoid chromatographic artifacts arising from oxidation of the sorbent or damage to the chromatographic system. 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 sampling 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, larger volumes of carrier gas may be required to completely purge air and water from the strongest sorbents (see 6.4).

12.2 The desorbed sample occupies a volume of several millilitres 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 by the capillary column. 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 to 1 will typically be required for operation with high resolution capillary columns. Single stage thermal desorption may thus significantly 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 (sorbent packed traps) Or down to -150°C (Using capillary cryofocusing or cryofocusing on glass beads)
Flow rate through trap for desorption	2 to 50 mL/min
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 11—The desorption temperature depends on the analyte and the sorbent used. Recommendations are given in Appendix X1 but the lowest effective desorption temperature should always be used (13.4) and maximum temperatures for each sorbent should be respected.

NOTE 12—If the secondary focusing trap contains multiple sorbents arranged in order of increasing strength (see 7.2), the direction of the gas flow during desorption must be reversed in order to efficiently release the analytes to the capillary column (see 12.1). If the secondary trap contains a single adsorbent or glass beads, reversing the flow during desorption of the trap may not be required.

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.. 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, a length of uncoated, deactivated fused silica, should be threaded back through the transfer line from the gas chromatograph to the thermal desorption apparatus 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. All internal tubing in the thermal desorber must be inert and dead volumes must be minimized. A split valve(s) is conveniently placed at the inlet or outlet of the secondary focusing trap, or both. 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 3:2 to 100 000:1. Lower split ratios are suitable for ambient and indoor air measurements; higher split ratios for workplace air measurements, contaminated soil gas and high concentration emissions.

NOTE 13—Correspondence of retention time on a single column should not be regarded as proof of analyte identity.

13. 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).

where:

$$\text{mass of analyte}(\mu l) = \text{concentration in solution} \times \text{volume injected}(\mu l;\ 8.5) \quad (1)$$

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 %, attempt to resolve the discrepancy by modifying the desorption parameters.

13.4.1 Some types 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 using flame ionization detection (**15**). If the ratio of the slopes of the calibration graphs do not agree with the relative response factor within 10 %, attempt to resolve the discrepancy by modifying the desorption parameters.

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) ideally with the inclusion of one or more compounds well validated under the analytical conditions selected (Appendix X2 to Appendix X4). 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 response of that compound relative to others in the mix or relative to the actual split ratio, or both.

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:

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

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:

$$\rho(VOC)\text{corr} = \rho(VOC) \times \frac{101}{P} \times \frac{T+273}{298} \quad (3)$$

where:

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

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:

$$\rho(VOC) = \frac{F - B}{U' \times t} \times 10^6 \quad (4)$$

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 Appendix X3), and
t = exposure time in min.

14.2.1.1 If F and B are expressed in mg the resultant concentration, $\rho(VOC)$, 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:

$$\rho(VOC)_{corr} = \rho(VOC) \times \frac{101}{P} \times \frac{T+273}{298} \quad (5)$$

where:

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

$$U'' = U' \times 101/P \times ((T+273)/298)^{1.5} \quad (6)$$

U" is then inserted into Eq 6 in place of U to give the volume fraction in air in 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:

$$U = U' \times \frac{24.45}{M} \times \frac{101}{P} \times \frac{T+273}{298} \quad (7)$$

where:

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

15. Published Precision and Bias

15.1 Laboratory tests of the procedure with pumped sampling (**13**), 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 a percentage combining bias and precision ('overall uncertainty'); for porous polymer sorbents (mean of five determinations), 8.9 %; and for weak to medium strength graphitized carbon black sorbents (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 Appendix X3. 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 uptake (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 (**13**) on sorbent tubes spiked with the many of the compounds specified in 8.2.1 at a load level of approximately 1.0 µg 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**) on tubes packed with weak porous polymer sorbent, liquid spiked with a broader range of compounds at a single load level of approximately 10 µg are summarized in Table 1. Excluding hexane, for which this type of sorbent has a low Safe Sampling Volume, 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 1.1 % to 5.6 %.

15.5 Laboratory tests (ISO ISO 16017-1 and (**18**)) on tubes liquid spiked with 11 model compounds including benzene, toluene, xylene, and isopropylbenzene on a medium strength porous polymer sorbent at load levels between 0.5 µg and 250 µg are shown in ISO 16017-1. The precision, expressed as repeatability (ISO 5725) was found to be between 7.2 % and 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 (**13**) on medium-strength porous polymer tubes spiked with the compounds specified in 8.2.1 at a loading level of approximately 1.0 µg and stored at room temperature for two weeks showed a mean recovery (relative to unstored tubes) of 105.6 %.

16.2 Laboratory tests (**3**) on tubes liquid spiked with a broader range of compounds on weak porous polymer sorbent at a single loading level of approximately 10 µg and stored at room temperature for 5 months are summarized in Table 1. Excluding hexane and methoxyethanol (neither of which should be sampled using weak porous polymer sorbent), 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 many possible sorbent combinations. However, a recent study of 9 VOCs on 2 example multi-sorbent tubes has shown no difference in analyte recovery (relative to single sorbent tubes) for at least 4 week storage (**19**). A proposed recommendation is to store for not more than 30 days 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.

16.4 Storage data on single bed tubes is available ((**3**) and Table 1) and shows nearly 100 % recovery over many months at room temperature.

16.5 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. Estimating Expanded Uncertainty

17.1 Factors to be considered when estimating the expanded uncertainty of the type of pumped and diffusive air monitoring procedures covered by this practice are outlined Determination D3670 and ISO GUM.

17.2 An example of how the contribution of these factors can be assessed for pumped air monitoring is given in EN 14662-1. The respective factors include: sample volume (sampling time and pump flow rate), deviation of monitoring conditions from standard temperature and pressure, sampling efficiency, sample stability, calibration performance (standard stability, non-linearity, drift, interferences, blank values) and desorption efficiency.

TABLE 1 Precision and Storage Recovery of Solvents on Tubes Packed with Weak Porous Polymer (W-PP / 1&2 – See Appendix X1)

Organic Compound	Loading level as measured at time = 0 (µg)	Time = 0 % CV[A]	Time = 5 mo. Mean Recovery (%)[B] + % 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] Six replicates.
[B] Normalized to toluene = 100. The stability of toluene has been established in a BCR intercomparison (17).

17.2.1 An example calculation of expanded uncertainty for pumped monitoring of ambient air is given in EN 14662-1 and is reported as 16.6 %.

17.3 An example of how the contribution of these factors can be assessed for diffusive (passive) monitoring is given in EN 14662-4. The respective factors include: uptake rate (impact of environmental factors, onset of back diffusion), sampling time, deviation of monitoring conditions from standard temperature and pressure, sample stability, calibration performance (standard stability, non-linearity, drift, interferences, blank values) and desorption efficiency.

17.3.1 An example calculation of expanded uncertainty for diffusive (passive) monitoring of ambient air is given in EN 14662-4 and is reported as 18.6 %.

18. Quality Control

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 weak porous polymer sorbents as described in Appendix X1. 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 Use of back up tubes (11.1.6) allows breakthrough (SSVs) to be tested under actual field monitoring conditions. If the level of one or more analytes is detected on the back up tube at >10 % of the sampled tube levels, the sampled tube data for affected compounds are invalid.

18.2.2 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.

18.2.3 Unless damaged, tubes should last for many (>100) thermal cycles. At the end of a tube's life, when the SSV falls significantly below the normal air sample collection volume for the analytes in question, the tube should be discarded or 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 ISO 13137 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. 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 ≤2.5µg/m^3. In general, over a concentration range of 0.1µg/m^3 to 1g/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.

$$\%\ \text{difference} = \left(\frac{(X\ 1\ -\ X\ 2)}{X} \right) \times 100 \qquad (8)$$

where:

X1 = conc. (for example, µg/m^3) for the smaller sample volume,
X2 = conc. (for example, µg/m^3) for the larger sample volume), and
X = average conc. (for example, µg/m^3) of both sample volumes.

NOTE 14—The concentration units must be in mass per volume units.

19.1.4 The 'audit accuracy' or degree of agreement with audit standards (that is, tubes pre-loaded with certified masses of specific compounds of interest) should be within 30 % for concentrations normally expected in contaminated ambient air (2.5 to 125 µg/m^3).

20. Keywords

20.1 ambient air; diffusive sampling; indoor air; pumped sampling; volatile organic compounds; workplace air

ANNEXES

(Mandatory Information)

A1. DETERMINATION OF BREAKTHROUGH VOLUMES

A1.1 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 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 (20) 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)

These appendixes provide supporting information for this standard practice. The information they contain is as follows:

• Appendix X1 (Table X1.1) provides a summary of example sorbents, their key characteristics and the various vapor-phase organic compounds they are suitable for sampling in air when packed into sorbent tubes or radial sampling cores as described in this method.

• Appendix X2 (Tables X2.1 through X2.8) highlights safe sampling volumes for illustrative chemicals using pumped sampling with standard tubes packed with various strength sorbents.

• Appendix X3 (Table X3.1) lists diffusive uptake rates for illustrative chemicals using axial passive sampling onto standard tubes packed with various sorbents.

• Appendix X4 (Table X4.1) lists diffusive uptake rates for illustrative chemicals using radial passive samplers packed with specified sorbents.

X1. TABULATED SUMMARY OF SORBENT TYPES, EXAMPLES, FEATURES, AND APPLICATIONS

TABLE X1.1 Tabulated Summary of Sorbent Types, Examples, Features, and Applications

NOTE 1—The values italicized are to be used with caution.

Sorbent type code	Commercial examples	Approx analyte range	Notes	Example analytes and applications
Polydimethyl-siloxane PDMS	1. 3 % OV-101 2. 10 % OV-101 Various suppliers	Semi-volatiles – Compounds less volatile than n-C_{16}	Working on gas-liquid chromatographic principles, this absorbent is more commonly used as a GC stationary phase, but has been found suitable for very high boiling air pollutants	PAH PCBs phthalates
Very weak graphitized carbon black VW-GCB	1. Carbopack C[A] 2. Carbotrap C[A] 3. Carbograph 2 TD[B] 4. Anasorb GCB1[C] 5. Carbopack F[A] 6. Carbotrap F[A] 7. Carbopack Y[A] 8. Carbotrap Y[A]	n-C_8 to n-C_{20}	Conditioning temp up to 400°C Desorb temp up to 360°C Hydrophobic Artifacts per tube: individual VOCs <1 ng Friable Recommended mesh size: 40/60 Some activity for labile compounds Desorption efficiency: medium (some band broadening) Typical surface area: 10 m^2/g	Higher boiling aliphatics and aromatics for example middle distillate fuels (jet fuel, kerosene, diesel, etc.)
Weak porous polymer W-PP	1. Tenax TATM[D] 2. Tenax TA[E] 3. Tenax GR[E]	n-C_6 to n-C_{30}	Conditioning temp: 320°C Desorption temp: 280°C Very hydrophobic Artifacts per tube: 1–2 ng of some VOCs (incl. benzene) Very inert Desorption efficiency good (narrow peaks) Typical surface area: 30 m^2/g Recommended mesh size: 35/60	Indoor air, outdoor air, personal exposure studies and material emission tests for compounds ranging from n-hexane incl. reactive species, for example, monoterpenes

TABLE X1.1 *Continued*

Sorbent type code	Commercial examples	Approx analyte range	Notes	Example analytes and applications
Weak to medium graphitized carbon black WM-GCB	1. Carbopack B[A] 2. Carbotrap[A] 3. Carbograph 1 TD[B] 4. Carbograph 4 TD[B] 5. Anasorb GCB2[C]	n-C_5 to n-C_{14}	Conditioning temp up to 400°C Desorb temp up to 360°C Hydrophobic Artifacts per tube: individual VOCs <1 ng Friable Recommended mesh size: 40/60 Some activity for labile compounds Desorption efficiency medium (some band broadening) Typical surface area: 100 m^2/g	Wide range of stable polar and apolar VOCs including aldehydes boiling above 75°C
Various medium strength porous polymer sorbents *M-PP*	*Chromosorb Century series:[F]* *1. 102* *2. 106* *Porapaks:[G]* *3. Porapak Q* *4. Porapak N*	*Varies within range n-C_5 to n-C_{14}. Some of these sorbents are very specific for a given polarity or compound group*	*Low desorb temps (Range: 180–200°C) – preclude use in multi-bed tubes* *Hydrophobic* *Artifacts per tube: individual VOCs >10 ng* *Use of these sorbents is reducing due to supply issues, high background and high batch-to-batch variability*	*Historically, Chromosorb 102 was often used for volatile haloforms, Chromosorb 106 for hydrocarbons from n-C_5 to n-C_{12} and Porapak N for volatile nitriles; now largely superseded*
Medium to strong graphitized carbon black MS-GCB	1. Carbopack X[A] 2. Carbograph 5 TD[B] 3. Carbograph 4 TD[B]	1,3-butadiene to benzene	Conditioning temp up to 400°C Desorb temp up to 360°C Hydrophobic Artifacts <1 ng per tube Friable Recommended mesh size: 40/60 Some activity for labile compounds Desorption efficiency poor (band broadening) Typical surface area: 240 m^2/g	Validated for 1,3-butadiene and benzene.
Carbon molecular sieves[I] CMS	1. Carboxen 1003[A] 2. Carboxen 569[A] 3. Sulficarb[H] (formerly Unicarb or Spherocarb) 4. Carbosieve SIII[A] 5. Anasorb CMS[C] 6. Carboxen 1000[A] 7. Carboxen-56[D]	n-$C_{2/3}$ to n-$C_{5/6}$	Condition slowly up to 350°C Desorb temp up to 330°C Hydrophobic Artifacts <1 ng per tube Recommended mesh size: 40/60 Desorption efficiency poor (band broadening) Typical surface area: 400–1000 m^2/g Retention volumes reduced significantly when % RH > 80 %	Ultra volatile compounds such as vinyl chloride, Freons, and C_3, C_4 hydrocarbons

[A] Carbopack, Carbotrap, Carboxen, Carbosieve are all trademarks of Supelco/Sigma- Aldrich CO., LLC, USA.
[B] Carbograph is a trademark of LARA S.r.l. Formello, Rome, Italy.
[C] Anasorb is a trademark of SKC Inc., USA.
[D] Tenax TA is a trademark of Enka Research Institute NV, NL.
[E] Tenax is a trademark of Buchem B.V., Netherlands.
[F] *Chromosorb is a trademark of Imerys Minerals California, Inc., USA.*
[G] *Porapak is a trademark of Waters Associates Inc., USA.*
[H] Sulficarb is a trademark of Markes International Ltd., Llantrisant, UK.
[I] These sorbents exhibit some water retention. Safe sampling volumes should be reduced by a factor of 10 if sampling a high (>80 %) relative humidity – See 11.1.5.4.

X2. TABULATED RETENTION VOLUME AND SAFE SAMPLING VOLUME DATA FOR SAMPLING TUBES DESCRIBED IN 7.2 PACKED WITH VARIOUS TYPES OF SORBENT

TABLE X2.1 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 200 mg of Weak Porous Polymer Sorbent at 20°C (W-PP / 1 and 2 – See Appendix X1)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, 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 this sorbent			
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 this sorbent			
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 this sorbent			
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] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.2 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 250 mg of a Very Weak Graphitized Carbon Black Sorbent 20°C (VW-GCB / 5 and 6 – See Appendix X1) (21)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
Decane	174	0.19	.013	1.6	6.3	400
Decanol	231	0.0011	6.45	3.2	12.9	400
Ethylbenzene	136	1.3	18.7	9.4	37.4	400
Biphenyl	256	0.0012	21.1	10.6	42.2	400
Dodecane	216	0.018	21.3	10.7	42.6	400
Tetradecane	253	0.00015	12 500	6 250	25 000	400

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.3 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 250 mg of a Very Weak Graphitized Carbon Black Sorbent 20°C (VW-GCB / 1 and 2 – See Appendix X1) (21)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
Decane	174	0.19	3.25	1.63	6.50	400
Biphenyl	256	0.0012	28	14	57	400
Dodecane	216	0.018	825	413	1650	400

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.4 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 250 mg of a Very Weak Graphitized Carbon Black Sorbent 20°C (VW-GCB / 1 and 2 – See Appendix X1) (22)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
p-Xylene	138	1.18	19	9	38	400
Benzylamine	185	0.09	27	13	54	400
p-Cresol	202	0.015	64	32	127	400
n-Pentanoic Acid	186	0.02	86	43	171	400
Decane	174	0.19	149	74	297	400

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.5 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 500 mg of a Weak to Medium Graphitized Carbon Black Sorbent 20°C (WM-GCB / 1 and 2 – See Appendix X1) (23)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
Benzene	80	10.1	5.85	2.9	5.9	400
1,1,2-Trichloroethylene	87	9.2	6.35	3.2	6.4	400
n-Butanol	118	0.67	12.4	6.2	12.4	400
1,1,2-Trichloroethane	114	3.1	12.4	6.2	12.4	400
p-Xylene	138	1.18	21	11	21	400
Hexane	69	16	40	20	40	400
Cyclohexanone	155	0.45	55	28	55	400
n-Pentanoic Acid	186	0.02	216	108	216	400
Phenol	182	0.03	308	154	308	400
Toluene	111	2.9	325	163	325	400
Chlorobenzene	131	1.2	790	395	790	400
Butylamine	78	12.4	1 040	520	1 040	400
4-Heptanone	144	0.7	1 220	610	1 220	400
1,4-Dichlorobenzene	174	0.23	6 700	3 350	6 700	400
Octane	125	1.9	8 050	4 025	8 050	400
Ethylbenzene	136	0.93	10 150	5 075	10 150	400
p-Cresol	202	0.015	10 300	5 150	10 300	400
Benzylamine	185	0.09	11 150	5 575	11 150	400
o-Xylene	144	0.88	21 350	10 675	21 350	400
Acetophenone	202	0.053	32 00	16 000	32 000	400
Isopropylbenzene	152	0.6	85 000	42 500	85 000	400
n-Propylbenzene	159.2	0.45	8.60E+05	4.30E+05	8.60E+05	400
Decane	174	0.19	2.40E+06	1.20E+06	2.40E+06	400
n-Butylbenzene	183.3	0.14	2.92E+06	1.46E+06	2.92E+06	400
Biphenyl	256	0.0012	1.87E+09	9.35E+08	1.87E+09	400

TABLE X2.5 *Continued*

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
n-Hexylbenzene	226	–	3.50E+09	1.75E+09	3.50E+09	400
Dodecane	216	0.018	8.15E+10	4.08E+10	8.15E+10	400
n-Octylbenzene	264	–	6.55E+11	3.28E+11	6.55E+11	400

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.6 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 500 mg of Weak to Medium Graphitized Carbon Black Sorbent at 20°C (WM-GCB / 3 – See Appendix X1) (24-26)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
n-Hexane	69	16		>11	>21	250
1-Hexene	63			>11	>21	250
n-Heptane	98	4.7		>11	>21	250
Benzene	80	10.1		>11	>21	250
Methyl Ethyl Ketone	80	10.3	8.9	4.4	8.9	300
1,1,1-Trichloroethane	74	2.7	5.3	2.6	5.3	300

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.7 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 500 mg of Medium to Strong Graphitized Carbon Black Sorbent at 20°C (MS-GCB / 1 – See Appendix X1) (27)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
1,3-Butadiene	–4	280	80	40.0	80.0	400
Benzene	80	10.1	3240	1620	5400 ± 740	400

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.8 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 500 mg of Medium to Strong Graphitized Carbon Black Sorbent at 20°C (MS-GCB / 2 – See Appendix X1) (24-26

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
Aromatic and Aliphatic Hydrocarbons						
iso-Butane	–11			>11	>22	250
n-Butane	–0.5			>11	>22	250
trans-2-Butene	0.9			>11	>22	250
1-Butene	–6.5			>11	>22	250
cis-2-Butene	3.7			>11	>22	250
iso-Pentane	28	77		>22	>43	250
n-Pentane	35	56		>22	>43	250
trans-2-Pentene	36			>22	>43	250
1-Pentene	30			>22	>43	250
cis-2-Pentene	37			>22	>43	250
n-Hexane	69	16		>22	>43	250
1-Hexene	63			>22	>43	250
n-Heptane	98	4.7		>22	>43	250
Benzene	80	10.1		>22	>43	250
Ethylbenzene	136	0.93	600 000	300 000	600 000	300
Styrene			1 500 000	750 000	1 500 000	300
o-Xylene			3 250 000	1 625 000	3 250 000	300
1,2,3-Trimethylbenzene			450M	225M	450M	300
Halogenated Hydrocarbons						
Chlorobromomethane			2 750	1 375	2 750	300
1,2-Dichloropropane			1 825	913	1 825	300
1,1,2,2-Tetrachloroethane			67 500	33 750	67 500	300
1,1-Dichloroethane			425	213	425	300
1,1,2-Trichloroethane			8 250	4 125	8 250	300
Chlorobenzene			225 000	111 250	600 000	300
Oxygenates						
Ethanol			5.0	2.5	5.0	300
Acetone			35	18	35	300

TABLE X2.8 *Continued*

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
Methyl Ethyl Ketone			825	413	825	300
Methoxyethanol			825	413	825	300
Ethyl Acetate			2 025	1 013	2025	300
Cyclohexanone			30 000	15 000	30 000	300
Methyl-i-butyl Ketone			122 500	61 250	122 500	300
i-Butyl Acetate			2 225 000	1 112 500	2 225 000	300
2-Ethoxyethyl Acetate			5 000 000	2 500 000	5 000 000	300
2-Butoxyethyl Acetate			10 000 000	5 000 000	10 000 000	300

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.9 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 300 mg of Carbon Molecular Sieve Sorbent at 20°C (CMS / 3 – See Appendix X1) (3)

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

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.10 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 250 mg of various Carbon Molecular Sieves Sorbent 20°C (CMS – See Appendix X1) (28)

Organic Compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C
CMS / 7 (400m^2/g)						
Dichloromethane	40	58	31.5	15.8	63.0	400
CMS / 2 (485m^2/g)						
Vinyl Chloride	–13	397	4.13	2.1	8.3	400
Dichloromethane	40	58	43.3	21.7	86.6	400
CMS / 4 (820m^2/g)						
Vinyl Chloride	–13	397	17.5	8.8	35.0	400
Dichloromethane	40	58	66.2	33.1	132.4	400
CMS / 6 (1000m^2/g)						
Vinyl Chloride	–13	397	4.13	2.1	8.3	400
Dichloromethane	40	58	43.3	21.7	86.6	400

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.11 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 500 mg of an Example Carbon Molecular Sieve Sorbent at 20°C (CMS / 2 – See Appendix X1) (9)

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

[A] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.12 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 300 mg of a Medium Porous Polymer Sorbent Tube at 20°C (M-PP / 2 – See Appendix X1)

NOTE 1—This table is related to medium strength porous polymer sorbents that are not widely used because of high and variable artifact levels. The data is retained for historical purpose. The values italicized are to be used with caution.

Organic compound	Boiling Point, °C	Vapor Pressure, kPa 25°C	Retention Volume, L	Safe Sampling Volume, SSV,[A, B] L	SSV/g, L/g	Desorption Temperature, °C	Reference
			Hydrocarbons				
Propane	*–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	*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	*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] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

TABLE X2.13 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a Tube Packed with 500 mg of a Medium Porous Polymer Sorbent Tube at 20°C (M-PP / 4 – See Appendix X1) (3)

NOTE 1—This table is related to medium strength porous polymer sorbents that are not widely used because of high and variable artifact levels. The data is retained for historical purpose. The values italicized are to be used with caution.

Organic Compound	Boiling Point °C	Vapor Pressure kPa 25°C	Retension Volume, L	Safe Sampling Volume SSV,[A, 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] SSV; see 11.1.5.1 and 11.1.5.2. Reduce SSV by a factor of 2 if sampling at high concentration (>100 ppm) – see 11.1.5.4.
[B] Reduce SSV by a factor of 2 if sampling at high humidity (>80 % RH) – see 11.1.5.4.

X3. DIFFUSIVE UPTAKE (SAMPLING) RATES[8] FOR THE AXIAL PASSIVE (DIFFUSIVE) SAMPLING TUBES DESCRIBED IN 7.3 PACKED WITH VARIOUS TYPES OF SORBENT AT 20°C[9]

NOTE X3.1—The uptake rates quoted in Table X3.1 and Table X3.1 have been assigned levels of confidence as follows:

A = Full validation according to CEN protocols.
B = Partial validation according to CEN protocols.
C = Calculated – ideal value.
D = Calculated from dynamic breakthrough volume.
E = Calculated from sorption isotherm.
F = Experimental observation.

TABLE X3.1 Short Term Diffusive Uptake (Sampling) Rates for Workplace and Other Air Monitoring Applications

NOTE 1—Quoted as ng adsorbed or collected on the tube per ppm analyte concentration in the atmosphere per minute of exposure.

NOTE 2—Rates measured at 8 hours unless otherwise stated (**15**, **29**).

NOTE 3—These published uptake rates were generated using 6.4 mm OD × 5 mm ID × 89 mm stainless steel tubes using a diffusive end cap attached to the sampling end.

NOTE 4—The values italicized are to be used with caution.

Compound	Sorbent	Level of confidence	Uptake Rate $ng.ppm^{-1}.min^{-1}$
		Hydrocarbons	
1,3-Butadiene	MS-GCB / 1	B	1.64
n-Pentane	*M-PP / 2*	A	1.46
	WM-GCB / 1	B	1.77
n-Hexane	*M-PP / 2*	A	1.77
Cyclohexane	*M-PP / 2*	D	1.60
	W-PP / 1&2	D	1.32
Benzene	*M-PP / 3*	A	1.37
	W-PP / 3	B	1.81
	M-PP / 2	B	1.72
n-Heptane	*M-PP / 2*	A	1.95
	W-PP / 1&2	A	1.77
	WM-GCB / 1	B	1.94
2-Methylhexane	*M-PP / 2*	D	1.79
	W-PP / 1&2	D	1.48
3-Methylhexane	*M-PP / 2*	D	1.80
	W-PP / 1&2	D	1.48
Methylcyclohexane	*M-PP / 2*	D	1.88
	W-PP / 1&2	D	1.55
Toluene	W-PP / 1&2	B	1.67
	W-PP / 3	B	2.12
	M-PP / 2	B	1.94
	WM-GCB / 1	B	2.06
2-Methylheptane	*M-PP / 2*	D	2.33
	W-PP / 1&2	D	1.95
n-Octane	*M-PP / 2*	A	2.13
	W-PP / 1&2	A	2.0
Xylene	W-PP / 1&2	B	1.82
	M-PP / 2	B	2.10
	W-PP / 3	B	2.48
Ethylbenzene	W-PP / 1&2	B	2.00
	W-PP / 3	B	2.43
	M-PP / 2	B	1.90
	M-PP / 3	D	2.38
Styrene	W-PP / 1&2	A	2.00
	M-PP / 2	B	2.15
n-Nonane	*M-PP / 2*	A	2.40
	W-PP / 1&2	A	2.12
n-Propylbenzene	*M-PP / 2*	D	2.45
	W-PP / 1&2	D	2.28
Iso-propyl Benzene (Cumene)	*M-PP / 2*	D	2.38
	W-PP / 1&2	D	2.28
1,2,3-Trimethylbenzene	*M-PP / 2*	D	2.45
	W-PP / 1&2	D	2.34
1,2,4-Trimethylbenzene	*M-PP / 2*	D	2.26
	W-PP / 1&2	D	2.16
1,3,5-Trimethylbenzene	*M-PP / 2*	D	2.33
	W-PP / 1&2	D	2.23
1,3-Dimethyl-4-Ethylbenzene	W-PP / 1&2	D	2.45
1,4-Diethylbenzene	W-PP / 1&2	D	2.56
m-Ethyltoluene	*M-PP / 2*	D	2.43
	W-PP / 1&2	D	2.25
o-Ethyltoluene	*M-PP / 2*	D	2.57

TABLE X3.1 *Continued*

Compound	Sorbent	Level of confidence	Uptake Rate ng.ppm^{-1}.min^{-1}
	W-PP / 1&2	D	2.44
p-Ethyltoluene	*M-PP / 2*	D	2.35
	W-PP / 1&2	D	2.21
n-Decane	W-PP / 1&2	A	2.30
	M-PP / 2	A	2.47
a-Pinene	W-PP / 1&2	D	2.35
	M-PP / 2	A	2.56
Naphthalene	W-PP / 1&2	A	2.55
n-Undecane (n-C_{11})	W-PP / 1&2	F	1.97
n-Dodecane (n-C_{12})	W-PP / 1&2	F	2.08
n-Tridecane (n-C_{13})	W-PP / 1&2	F	2.33
n-Tetradecane (n-C_{14})	W-PP / 1&2	F	2.41
n-Pentadecane (n-C_{15})	W-PP / 1&2	F	2.19
n-Hexadecane (n-C_{16})	W-PP / 1&2	F	2.36
		Chlorinated Hydrocarbons	
Methyl Chloride	CMS / 2	B	1.30
Vinyl Chloride	CMS / 2	B	2.00
1,1-Dichloro-Ethene	CMS / 2	B	2.50
Trichlorotrifluoroethane (Freon 113)	*M-PP / 1*	B	3.50
Chlorotrifluoromethane	*M-PP / 1*	B	1.80
Dichloromethane	*M-PP / 2*	B	1.56
	M-PP / 1	B	1.56
1,2-Dichloroethane	*M-PP / 1*	B	1.90
	M-PP / 2	B	2.03
	W-PP / 3	B	1.72
Halothane	*M-PP / 1*	B	3.60
	W-PP / 1&2	B	2.59
Enflurane	W-PP / 1&2	B	2.29
	M-PP / 2	D	2.80
Sevoflurane	*M-PP / 2*	B	2.09
Isoflurane	W-PP / 1&2	B	2.20
	M-PP / 2	D	2.50
Bromoethane	*M-PP / 2*	A	2.55
Bromobenzene	*M-PP / 2*	D	3.59
	W-PP / 1&2	D	3.31
Trichloromethane (Chloroform)	W-PP / 3	B	1.97
	M-PP / 1	B	2.35
	M-PP / 2	B	2.47
Tetrachloromethane (Carbon Tetrachloride)	W-PP / 3	B	3.72
	M-PP / 1	B	2.87
Trichloroethene	*M-PP / 2*	B	2.64
	M-PP / 1	B	2.30
1,1,1-Trichloroethane	*M-PP / 2*	B	2.30
	M-PP / 1	B	2.30
	W-PP / 3	B	2.92
Tetrachloroethene	*M-PP / 2*	B	3.19
	W-PP / 1&2	B	2.80
	M-PP / 1	B	2.60
	W-PP / 3	B	2.90
Epichlorohydrin	*M-PP / 2*	E	2.45
Allyl Chloride	*M-PP / 2*	D	1.75
Benzyl Chloride	W-PP / 1&2	D	2.72
Perfluorodimethyl Cyclobutane	WM-GCB / 2[A]	B	15 mL/h
Perfluoromethyl-Cyclopentane	WM-GCB / 2[A]	B	15 mL/h
Perfluoromethyl-Cyclohexane	WM-GCB / 2[A]	B	15 mL/h
p-Dichlorobenzene	W-PP / 1&2	C	3.23
		Esters and Glycol Ethers	
Methyl Acetate	*M-PP / 2*	A	1.74
Ethyl Acetate	*M-PP / 2*	B	1.98
	W-PP / 1&2	B	1.65
n-Butyl Acetate	W-PP / 1&2	B	1.93
	M-PP / 2	A	2.60
	W-PP / 3	B	1.93
Isobutyl Acetate	*M-PP / 2*	D	2.17
	W-PP / 1&2	D	1.91
Sec-butyl Acetate	*M-PP / 2*	D	2.29
	W-PP / 1&2	D	1.90
Tert-butyl Acetate	M-PP / 2	D	2.26

TABLE X3.1 *Continued*

Compound	Sorbent	Level of confidence	Uptake Rate ng.ppm^{-1}.min^{-1}
	W-PP / 1&2	D	1.79
Vinyl Acetate	*M-PP / 2*	D	1.93
Methyl Methacrylate	*M-PP / 3*	B	2.00
	M-PP / 2	D	2.14
	W-PP / 1&2	D	1.77
Methyl Acrylate	*M-PP / 2*	D	1.96
	W-PP / 1&2	D	1.50
Butyl Acrylate	W-PP / 1&2	D	2.00
	M-PP / 2	D	2.11
Ethylhexyl Acrylate	W-PP / 1&2	D	2.99
2-Methoxyethanol	*M-PP / 3*	A	1.50
	M-PP / 2	A	2.10
2-Ethoxyethanol	W-PP / 1&2	A	1.80
2-Methoxyethyl Acetate	*M-PP / 3*	A	2.80
	M-PP / 2	B	2.08
	W-PP / 3	B	1.81
	W-PP / 1&2	B	1.64
2-Ethoxyethyl Acetate	*M-PP / 2*	B	2.25
	W-PP / 1&2	B	2.05
	W-PP / 3	B	2.08
2-Butoxyethanol	*M-PP / 2*	B	2.06
	W-PP / 1&2	B	1.77
1-Methoxy-2-Propanol	*M-PP / 2*	B	1.88
	W-PP / 1&2	B	1.56
	W-PP / 3	B	1.55
Methoxypropyl Acetate	*M-PP / 2*	A	2.50
	W-PP / 1&2	B	2.21
	W-PP / 3	B	2.23
1-Ethoxy-2-Propanol	*M-PP / 2*	B	1.94
	W-PP / 3	B	1.64
	W-PP / 1&2	B	1.65
2-Butoxyethyl Acetate	*M-PP / 2*	B	2.79
	W-PP / 3	B	2.19
	W-PP / 1&2	B	2.25
Propoxyethanol	*M-PP / 2*	D	1.94
	W-PP / 1&2	D	1.65
Dipropylene Glycol Methyl Ether	*M-PP / 2*	A	2.70
		Ketones and Aldehydes	
2-Butanone	*M-PP / 2*	B	1.72
	W-PP / 3	B	1.37
	W-PP / 1&2	B	1.34
Methyl Isobutyl Ketone (2-Methyl-4-Pentanone)	W-PP / 1&2	B	1.71
	W-PP / 3	B	1.69
	M-PP / 2	B	2.01
Cyclohexanone	W-PP / 1&2	B	1.78
	M-PP / 2	B	1.96
	W-PP / 3	B	1.78
2-Methylcyclohexanone	W-PP / 1&2	D	2.31
3-Methylcyclohexanone	W-PP / 1&2	D	2.22
4-Methylcyclohexanone	W-PP / 1&2	D	2.14
Furfural	W-PP / 1&2	A	2.50
Hexanal	W-PP / 1&2	D	1.64
	M-PP / 2	A	2.06
Decanal	W-PP / 1&2	D	2.32
		Alcohols	
Ethanol	*M-PP / 2*	A	1.30
Propan-1-ol	*M-PP / 2*	D	1.47
Propan-2-ol (Isopropanol)	CMS / 2	C	2.00
	M-PP / 2	A	1.52
n-Butanol	*M-PP / 2*	A	1.74
	W-PP / 1&2	D	1.33
Isobutanol	*M-PP / 2*	B	1.61
	W-PP / 3	B	1.26
		B	1.26
Furfuryl Alcohol	W-PP / 1&2	D	2.50
Tetrahydrofurfuryl Alcohol	*M-PP / 2*	D	2.39
	W-PP / 1&2	D	1.90
		Miscellaneous	
Acrylonitrile	*M-PP / 4*	A	1.35
	M-PP / 2	C	1.48

TABLE X3.1 *Continued*

Compound	Sorbent	Level of confidence	Uptake Rate ng.ppm^{-1}.min^{-1}
Acetonitrile	*M-PP / 4*[B]	A	1.00 (2 h)
	M-PP / 4	A	0.80 (8 h)
	M-PP / 2	A	1.48
Propionitrile	*M-PP / 4*[B]	A	1.40 (2 h)
	M-PP / 4	A	1.30 (3 h)
Carbon Disulphide	CMS / 2	A	2.60
Nitrous Oxide	Zeolite Molecular Sieve[C]	B	1.25
Ethylene Oxide	CMS / 2	B	1.60
Propylene Oxide	*M-PP / 2*	A	1.24
1,4-Dioxane	CMS / 2	C	3.00
Allyl Glycidyl Ether	*M-PP / 2*	D	2.40
	W-PP / 1&2	D	1.83
Butyl Glycidyl Ether	*M-PP / 2*	D	2.61
	W-PP / 1&2	D	2.36
Tetrahydrofuran	*M-PP / 2*	D	1.64
n-Methyl Pyrrolidone	W-PP / 1&2	C	1.83
	M-PP / 2	A	2.41
n-Vinyl Pyrrolidone	W-PP / 1&2	A	2.51

[A] 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 steel gauze is used.
[B] Two-hour exposure period
[C] 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 X3.2 Longer-Term Diffusive Uptake (Sampling) Rates for Environmental Air Monitoring Applications (16, 30-35)

NOTE 1—The values italicized are to be used with caution.

Compound	Sorbent	Level	Uptake Rate ng.ppm^{-1}.min^{-1}
		24-h Exposures	
1,3-butadiene	MS-GCB / 1	F	1.35
Benzene	MS-GCB / 1	F	2.14
Toluene	MS-GCB / 1	F	1.96
Xylene	MS-GCB / 1	F	1.99
Styrene	MS-GCB / 1	F	2.13
1,3,5-Trimethylebenzene	MS-GCB / 1	F	2.01
p-Ethyltoluene	MS-GCB / 1	F	2.01
Chlorobenzene	MS-GCB / 1	F	2.11
3-Chloropropene	MS-GCB / 1	F	1.59
Dichlorobenzene	MS-GCB / 1	F	2.7
1,1-Dichloroethane	MS-GCB / 1	F	2.3
1,2-Dichloroethane	MS-GCB / 1	F	2.3
cis-1,2-Dichloroethene	MS-GCB / 1	F	2.3
1,1-Dichloroethene	MS-GCB / 1	F	2.3
1,2-Dichloropropane	MS-GCB / 1	F	2.4
1,2-Dichlorotetrafluoroethane	MS-GCB / 1	F	3.07
Tetrachloroethene	MS-GCB / 1	F	3.25
Tetrachloromethane (Carbon tetrachloride)	MS-GCB / 1	F	3.2
1,1,2-Trichloroethane	MS-GCB / 1	F	2.67
1,1,1-Trichloroethane	MS-GCB / 1	F	2.78
Trichloroethene	MS-GCB / 1	F	2.68
Trichlorofluoromethane	MS-GCB / 1	F	2.86
1,1,2-Trichloro-1,2,2-trifluoroethane	MS-GCB / 1	F	3.52
		One-Week Exposures	
1,3-butadiene	MS-GCB / 1	B	1.2
Cyclohexane	W-PP / 1&2	F	0.86
Methylcyclohexane	W-PP / 1&2	F	0.8
n-Heptane	W-PP / 1&2	F	1.06
n-Octane	W-PP / 1&2	F	1.26
n-Nonane	W-PP / 1&2	F	1.78
n-Dodecane	W-PP / 1&2	F	1.81
Benzene	W-PP / 1&2	A	1.45
	WM-GCB / 1&2	A	2.14
	M-PP / 2	*A*	*1.52*
Toluene	WM-GCB / 1&2	A	2.16
	M-PP / 2	*A*	*2.05*
Xylene	WM-GCB / 1&2	A	2.37
	M-PP / 2	*A*	*2.42*

TABLE X3.2 *Continued*

Compound	Sorbent	Level	Uptake Rate ng.ppm^{-1}.min^{-1}
Ethylbenzene	WM-GCB / 1	A	2.04
	W-PP / 1&2	A	1.52
Propylbenzene	W-PP / 1&2	A	1.77
Styrene	W-PP / 1&2	A	1.53
Tetrachloroethane	W-PP / 1&2	A	1.90
Benzaldehyde	W-PP / 1&2	A	1.78
Ethyl Acetate	W-PP / 1&2	A	0.83
Limonene	W-PP / 1&2	A	1.50
Phenol	W-PP / 1&2	A	1.65
a-Pinene	W-PP / 1&2	A	1.11
		Two-Week Exposures	
1,3-Butadiene	MS-GCB / 1	B	1.02
n-Butane	MS-GCB / 1	F	1.3
Isobutane	MS-GCB / 1	F	0.8
n-Pentane	WM-GCB / 1	F	1.34
	MS-GCB / 1	F	1.8
Isopentane	MS-GCB / 1	F	1.6
n-hexane	WM-GCB / 1	F	1.75
	MS-GCB / 1	F	2.0
Benzene	WM-GCB / 1&2	A	2.02
	MS-GCB / 1	A	1.99
	M-PP / 2	*A*	*1.47*
	W-PP / 1&2	A	1.03
Toluene	W-PP / 1&2	A	1.22
	WM-GCB / 1&2	A	2.13
	M-PP / 2	*A*	*1.91*
Xylene	W-PP / 1&2	A	1.49
	WM-GCB / 1&2	A	2.07
	M-PP / 2	*A*	*2.09*
Ethylbenzene	WM-GCB / 1	A	2.19
	M-PP / 2	*A*	*2.31*
Trimethylbenzene	WM-GCB / 1	A	2.30
		Hydrocarbons – Four-Week Exposures	
Benzene	W-PP / 1&2	A	0.70
	WM-GCB / 1&2	A	1.85
	M-PP / 2	*A*	*1.28*
Toluene	W-PP / 1&2	B	1.03
	WM-GCB / 1&2	A	2.07
	M-PP / 2	*A*	*1.82*
Xylene	W-PP / 1&2	A	1.46
	WM-GCB / 1&2	A	1.94
	M-PP / 2	*A*	*1.91*
Ethylbenzene	WM-GCB / 1&2	A	2.03
	M-PP / 2	*A*	*2.24*
Trimethylbenzene	W-PP / 1&2	A	2.67
	WM-GCB / 1&2	A	2.20
n-Decane	W-PP / 1&2	A	2.93
n-Undecane	W-PP / 1&2	A	3.34
n-Dodecane	W-PP / 1&2	C	3.75
Tetrachlorobutadiene	W-PP / 1&2	B	3.0
Pentachlorobutadiene	W-PP / 1&2	B	3.4
Hexachlorobutadiene	W-PP / 1&2	B	3.5
Hexachloroethane	W-PP / 1&2	F	2.4

X4. DIFFUSIVE UPTAKE (SAMPLING) RATES[10] (36) ON RADIAL PASSIVE (DIFFUSIVE) SAMPLERS AT 25°C

TABLE X4.1 Environmental Applications – One-Week Exposure

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

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