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Standard Practice for ~~Selection of Sorbents, Sampling,~~ Choosing Sorbents, Sampling Parameters and Thermal Desorption ~~Analysis Procedures~~Analytical Conditions for Monitoring Volatile Organic ~~Compounds~~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 A complete listing of VOCs for which this practice has been tested, at least over part of the measurement range (1.6), is shown in Tables 1-9. For other compounds this practice shall be tested according to EN 1076 (pumped); Practice D6246, ISO 16107, ANSI/ISEA 104, EN 838 or EN 13528-1/EN 13528-2 (diffusive); or other appropriate validation protocols (Sections 13 and 14). (5,1)~~

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

1.4 This practice recommends a number of sorbents that can be packed in sorbent ~~tubes,~~tubes for use in the sampling of ~~a wide range of different volatile organic compounds boiling~~ 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).

~~1.5.1 For pumped sampling, sorbent selection is based on breakthrough capacity. Single-bed tubes containing for example sorbent Type A[3,4] are appropriate for normal alkanes from n-C_6 (hexane) to n-C_{10} (decane) and substances with similar volatility (v.p. 15 to 0.3 kPa at 25°C). More volatile materials should be sampled on stronger sorbents, such as sorbent Type B[3,5]. Other sorbent types than those specified may be used, if their breakthrough capacities are adequate and their thermal desorption blanks are sufficiently small. Examples are given in Appendix X2. A broader range of VOCs may be sampled using multi-bed tubes.~~

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

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

1.5 This practice can be used for the measurement of airborne vapors of these ~~volatile~~ 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. ~~The method~~

[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.

~~is also suitable for the measurement of the airborne concentrations of individual components of volatile organic mixtures, provided that the total loading of the mixture does not exceed the capacity of the tube.~~ Quantitative measurements are possible when using validated procedures with appropriate quality ~~assurance~~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 ~~2 mg/m~~100 µg/m^3 to ~~10~~100 mg/m^3 for individual organic compounds for an exposure time of 8 h or ~~0.3 mg/m~~1 µg/m^3 to ~~300~~1 mg/m^3 for individual organic compounds for an exposure time of four weeks. ~~The method is also suitable for the measurement of the airborne concentrations of individual components of volatile organic mixtures provided that the total loading of the mixture does not exceed the capacity of the tube.~~

1.5.3 With radial diffusive sampling, this practice is valid for the measurement of airborne vapors of volatile organic compounds in a concentration range of approximately ~~0.3 mg/m~~5 µg/m^3 to ~~300~~5 mg/m^3 for individual organic compounds for exposure times of one to six hours. ~~The method is also suitable for the measurement of the airborne concentrations of individual components of volatile organic mixtures provided that the total loading of the mixture does not exceed the capacity of the tube.~~

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

1.5.5 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,~~artifacts (or both) on the sorbent tubes.

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

1.6 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~~ 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.

1.9 *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)

~~D6246~~D5466 ~~Practice for Evaluating the Performance of Diffusive Samplers~~Test Method for Determination of Volatile Organic Chemicals in Atmospheres (Canister Sampling Methodology)

~~D6306 Guide for Placement and Use of Diffusion Controlled Passive Monitors for Gaseous Pollutants in Indoor Air~~

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *ISO Standards:*[4]

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

~~ISO 6349~~ISO 6145-10 Gas Analysis. Preparation of Calibration Gas Mixtures. Permeation Method

~~ISO 6879~~ISO 13137 ~~Air Quality. Performance Characteristics and Related Concepts for Air Quality Measuring Methods 1983~~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

[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.

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 1232 Workplace Atmospheres: Pumps for Personal Sampling of Chemical Agents. Requirements and Test Methods~~

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

~~EN 13528-1~~EN 13528-3 Ambient Air Quality—Diffusive samplers for the determination of concentrations of gases and vapours ~~- Requirements and test methods. Part 1: General requirements~~– Part 3: Guide to selection, use and maintenance

~~EN 13528-2~~EN 14662-1 Ambient ~~Air Quality—Diffusive samplers for the determination of concentrations of gases and vapours - Requirements and test methods. Part 2: Specific requirements and test methods~~air quality – standard method for measurement of benzene concentrations – Part 1: Pumped sampling followed by thermal desorption and gas chromatography

~~EN 13528-3~~EN 14662-4 Ambient ~~Air Quality—Diffusive samplers for the determination of concentrations of gases and vapours Part 3: Guide to selection, use and maintenance~~air quality – standard method for measurement of benzene concentrations – Part 4: Diffusive sampling followed by thermal desorption and gas chromatography

2.4 ~~*The Safety Equipment Association / American National Standards Institute Standards*~~*EPA Method:*[6]

~~ANSI/ISEA 104~~EPA Method TO-17 ~~American National Standard for Air Sampling Devices—Diffusive Type for Gases and Vapors in Working Environments~~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 *bias*—consistent deviation of the results of a measurement process from the true value of the air quality characteristic itself (ISO 6879).~~

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 ~~*loading—diffusive (passive) sampler—*~~the ~~product of concentration expressed in ppb~~a device that is capable of collecting gases and vapors ~~or mg/m~~from an atmosphere at rates controlled by gaseous diffusion through a static air layer (diffusion gap), permeation through a membrane or some[3] ~~and the sampled atmosphere volume (flow rate × sampling time).~~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 ~~*overall uncertainty (OU)—*~~*radial diffusive sampler*—~~quantity used to characterize, as a whole, the uncertainty of the result given by an apparatus or measuring procedure. It is expressed, as a percentage, by a combination of bias and precision usually according to the formula:~~ 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.

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

~~where:~~

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

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

~~s = standard deviation of measurements.~~

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

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

[6] ~~Volume fraction, (φ) = 10~~Available from United States Environmental~~[-9]~~ Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

3.2.6 ~~*precision—diffusive uptake rate or diffusive sampling rate (U)—*~~the ~~closeness of agreement between the results obtained by applying the method several times under prescribed conditions (ISO 6879). Precision may be expressed either~~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} ~~as repeatability~~(V/V) min^{-1}), picograms per parts per billion (volume/volume) per minute (pg.ppb^{-1} (V/V) min^{-1}~~or reproducibility (ISO 5725)~~), 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 sampling pump. Air is passed through the sorbent tube at a rate controlled by the sampling pump. ~~The sampling pump shall conform to the specifications in 18.3.~~

3.2.9 *safe sampling volume*—70 % of breakthrough volume (~~3.2.2~~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 ~~an active sorbent or~~ 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).

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

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

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

~~3.2.12 *diffusive uptake rate*—the rate at which the diffusive sampler collects a particular gas or vapor from the atmosphere, expressed in nanograms per parts per million (volume/volume) per minute (ng.ppm^{-1} (V/V) min^{-1}), picograms per parts per billion (volume/volume) per minute (pg.ppb^{-1} (V/V) min^{-1}), or cubic centimetres per minute (cm^3/min).~~

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 ~~type~~ or series of sorbents ~~should be~~ is selected for the compound or mixture to be sampled. The sorbents selected ~~should be~~ are arranged in series, in order of increasing sorbent strength ~~by linking~~ from the sampling end. This can be done by linking together tubes containing the individual sorbents ~~together in series. Alternatively,~~ or by packing a single tube ~~containing several sorbents in series may be used.~~ 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 ~~should be~~ 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, ~~should be~~ are used in parallel. The diffusive sampler or samplers are exposed to the atmosphere for a measured time period. Provided ~~suitable~~the sorbents ~~are chosen, volatile organic components migrate into~~ 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~~the tube by diffusion at a rate~~. 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 ~~atmospheric concentration and are retained by the sorbent.~~time weighted average atmospheric concentration over a given exposure period.

4.3 For radial diffusive sampling, a suitable sorbent ~~should be~~ 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, ~~should be~~ are used in parallel. The diffusive sampler or samplers are exposed to the atmosphere for a measured time period. Provided ~~suitable~~the sorbents ~~are chosen, volatile organic components migrate into the tube by diffusion at a rate proportional to the atmospheric concentration and are retained by the sorbent. Once the sampling period is over, the radial sorbent core, is immediately removed and placed in a sealable transportation container - typically a modified empty sample tube (compatible with the thermal desorption system) - and sealed with sorbent tube end caps.~~ (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. ~~7.6~~)

4.4 The collected vapor (on each tube or cartridge) is desorbed by heat and is transferred under inert carrier gas into a gas chromatograph (GC) equipped with a capillary column and either a conventional detector (such as the flame ionization or electron capture detector (ECD)) or a mass spectrometric detector, where it is analyzed. A sample focusing trap between the sampling tube and the gas chromatograph is commonly employed to ensure injection of the analytes in as small a volume of carrier gas as possible, providing better peak resolution 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 ~~mass~~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 ~~((~~**6**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 ~~all three environments, in~~ order to protect the environment as a whole and human health in particular, it is often necessary to take measurements of air quality ~~as part of an overall assessment~~ 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 ~~a wide range of volatile organic compounds~~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 ~~for the measurement of a specific VOC of interest~~ of each measurement are within acceptable ~~limits.~~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 ~~to sub-nanogram levels. It is typically lower for carbon type sorbents~~ nanogram levels on well conditioned tubes desorbed at moderate temperatures – See 8.3 and ~~the more stable (sorbent Type D) porous polymers, than for other, less stable, porous polymers (~~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 ~~the~~ 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.~~ carbon blacks – See Appendix X1. When less hydrophobic, strong sorbents such as ~~pure charcoals or~~ carbonized molecular sieves are used in atmospheres with humidity in excess of 65 % RH, exercise care to prevent water interfering with the analytical process. Suitable water elimination or reduction procedures include sample ~~splitting;~~splitting and selectively dry purging moisture from the sorbent tube or secondary focusing ~~trap prior to analysis,~~ trap, or both, prior to analysis. Other useful approaches to minimizing water interference include reducing the air volume ~~sampled~~ sampled, for example, to 0.5 L (pumped sampling), ~~use of a membrane that excludes water in the diffusion barrier (diffusive sampling),~~ and reducing the time of sampling (diffusive sampling).

7. Apparatus

7.1 Use ordinary laboratory apparatus in addition to the following.

7.2 *Sorbent tubes for pumped sampling,* compatible with the thermal desorption apparatus to be used (7.5). Typically, but not exclusively, they are constructed of glass or stainless steel tubing, 6.4 mm ~~[¼ in.]~~ OD, 5 mm ID and 89 mm long and contain up to 60 mm total length of sorbent or sorbents, held in place with stainless steel ~~gauzes.~~ gauzes or glass wool, or both. Tubes of other dimensions may be used but the safe sampling volumes (SSV) given in ~~Tables 1-6~~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 (in~~used. (See Note 2~~glass-lined or glass tubes the sorbent is typically held in place using plugs of unsilanized glass wool).~~ .) One end of the tube is marked, for example by a scored ring about 10 mm from the sampling inlet end to represent the end open to the atmosphere during sampling, otherwise the direction of sampling flow may be marked with an arrow. The tubes are packed with one or more preconditioned sorbents (8.3), ~~so~~ taking care to ensure that the entire sorbent bed will be within the desorber heated ~~zone, and a~~ 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. ~~Tubes~~ The tubes described above typically contain between ~~200~~100 and 1000 mg sorbent, depending on sorbent ~~density — typically about 250 mg sorbent Type D, 300 mg sorbent Type A or 500 mg sorbent Type B. The sorbents are retained by stainless steel gauzes or unsilanized glass wool plugs, or both.~~ 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 ~~and separated by unsilanized glass wool, with~~ with the weakest sorbent nearest to the ~~marked~~ sampling ~~inlet~~(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 ~~(> 50°C)~~ (>100°C) maximum desorption temperatures such as ~~sorbent Type A and graphitized carbon, must NOT be packed into a single tube or it will be impossible to condition or desorb the more stable sorbent(s) sufficiently thoroughly without causing degradation~~ 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 ~~sorbent(s).~~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 ~~[¼ in.]~~ OD, 5 mm ID and 89 mm long and with the sorbent held in place 14.3 mm from the sampling end using a stainless steel ~~gauze.~~gauze (Fig. 1) Tubes of other dimensions may be used but the uptake rates given in ~~Tables 7 and 8~~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 and a consistent inner air gap of about 14.3~~

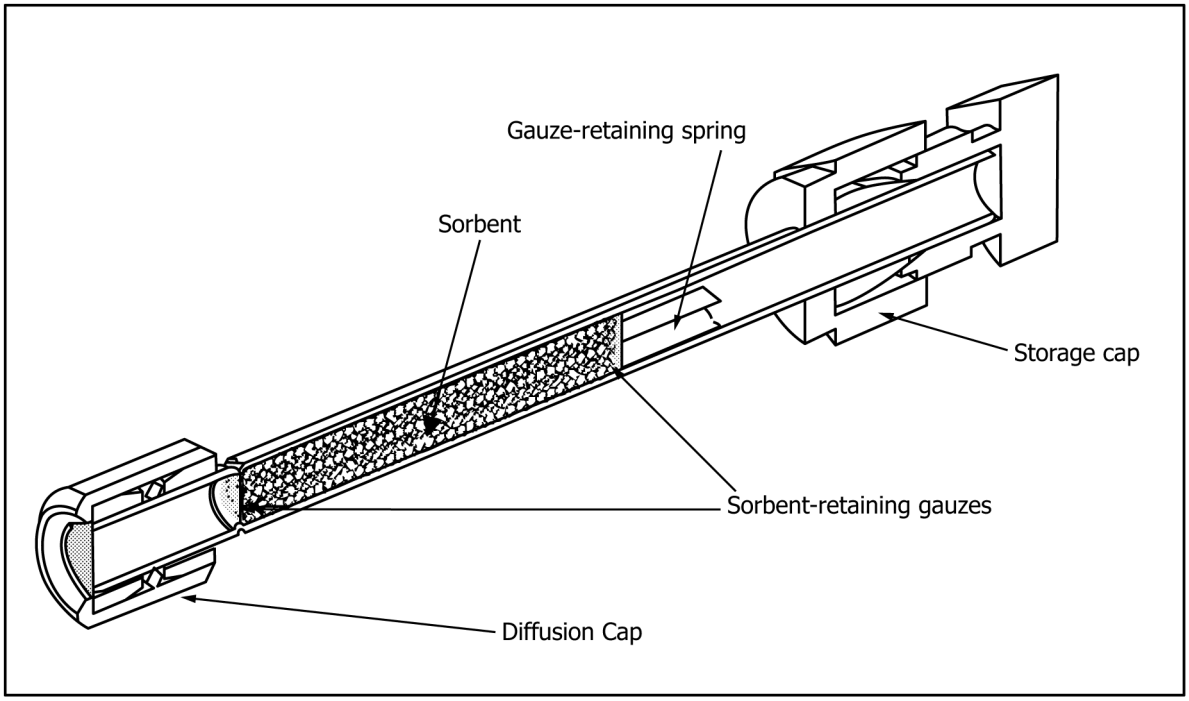

FIG. 1 Schematic of a Typical Axial Diffusive Sampler

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

7.3.1 *Uptake rates* in ~~Tables 7 and 8~~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.~~ 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 ~~((13~~11~~))~~ and tubes should be rejected where the inner air gap ~~(between stainless steel screen retaining the sorbent bed and the end of the tube)~~ is outside the range 14.0 and 14.6 ~~mm (See~~ mm.~~Fig. 1).~~

7.3.2 *Diffusive End Caps,* typically push-on, "O"-ring seal caps fitted with a metal gauze allowing the diffusive ingress of vapor. The size of the gauze covered opening in the sampling cap should being the same as the cross section of the tube (Fig. 1). ~~Some versions of the diffusive end cap incorporate a silicon membrane next to the gauze to minimize ingress of water.~~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 ~~Table 9~~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~~ density—typically about 200 mg ~~sorbent Type D, 250 mg sorbent Type A~~ of weak porous polymer sorbent, or 400 mg ~~sorbent Type B.~~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 ~~[¼ in.]~~ OD, 5 mm ID and 89 mm ~~long and with a~~ long, capable of retaining the sorbent core ~~retaining~~

~~gauze~~ approximately 14 mm from the desorption ~~end.~~ end of the carrier tube. The sorbent core should be a relatively snug fit inside the carrier tube such that it can be easily inserted and removed but that gas flow passes through the sorbent core (rather than around the outside) during thermal desorption. ~~The other end of the carrier tube is typically machined to have a wider OD and~~It should be possible to seal the carrier tubes with long-term sorbent tube storage caps (7.6 ~~slight cone-shape leading into the tube such that insertion and removal of the sorbent core can be readily achieved without handling. It should be possible to seal the carrier tubes with sorbent tube end caps~~ (). 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,~~7.6~~). etched) with suitable identifiers such as unique serial numbers in alphanumeric or barcode format, or both.

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

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

7.6 *Sorbent Tube End Caps,* ~~sealed with metal screw-cap fittings with combined (one-piece) PTFE ferrules to seal both sorbent tubes and the carrier tubes for radial samplers.~~ 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 ~~10~~ 1 or 5 µL liquid syringe readable to ~~0.1~~ 0.01 or 0.05 µL, a precision ~~10 µL~~ 10-µL gas tight syringe readable to 0.1 µL and a precision ~~10 mL~~ 10-mL gas tight syringe readable to 0.1 mL.

7.9 *Sampling Pump,* conforming to the performance requirements of ~~18.3~~8.3.1.

7.10 *Connecting Tubing (pumped sampling only),* ~~PTFE,~~ if tubing is required upstream (for example, for connecting between the sampling point and the sample tube when sampling in a remote ~~location. Tubing~~ 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 ~~will need~~typically needs to be about ~~90 cm~~ 90-cm long. All connections should be leak proof. ~~Sampling tubes shall not be used with plastic or rubber tubing upstream of the sorbent. Interferences from the tubing may introduce sampling errors. Such errors may be reduced by replacing the tubing regularly.~~

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

7.12 *Gas Chromatographic Apparatus:*

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

7.12.2 *Gas Chromatographic Column,* capable of separating the analytes of interest from other components. ~~A 50 m dimethylsiloxane or a 50 m 7 % cyanopropyl, 7 % phenyl, 86 % methyl siloxane~~ Typical dimensions are 50 or 60 m long fused silica capillary ~~column has been found suitable~~ (columns, 0.25 mm ID or 0.32 ~~3~~).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 ~~gas chromatographic~~ packed column GC injection port may be used for preparing sample tube standards. ~~This can be used~~Ready-made injection systems for ~~in situ,~~loading liquid or ~~it can be mounted separately. The carrier gas line to the injector should be retained. The back of the injection port should be adapted if necessary to fit the sample tube. This can be done conveniently by means of a compression coupling with a PTFE ring seal.~~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 ~~acetage,~~acetate, 2-methoxyethanol, methyl ethyl ketone, acetonitrile, *n*-butyl acetate, ∝-pinene, decane, ethylene oxide, propylene oxide, and hexanal.

8.2.2 ~~*Methanol,*~~*Solvent,* of chromatographic quality, free from compounds co-eluting with the compound or compounds of interest (8.2.1). ~~Alternative~~ 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. ~~To prevent recontamination of the sorbents, keep them in a clean atmosphere during cooling to room temperature, storage, and loading into the tubes.~~ If tubes are packed with unconditioned sorbent, ~~stringently condition them~~ 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. ~~Wherever possible, keep analytical desorption temperatures~~ 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 ~~for most sorbents and as such only require conditioning.~~with or without pre-conditioning.

8.3.1 ~~A guide for selection of sorbents for pumped and axial diffusive sampling~~Sorbent selection is determined by sorbent strength, typically assessed in terms of retention of the compound of interest (See Annex A2~~is given in~~) – or ~~Appendix X2. Equivalent sorbents may be used. A guide to sorbent conditioning and analytical desorption parameters is given in~~ 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 ~~Appendix X3~~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.

[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.

8.3.1.4 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 ~~Solutions:~~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 ~~methanol~~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 (~~8.4.1.1~~8.4.2.1). Make up to 100 mL with ~~methanol,~~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~~ 10-µL gas-tight syringe with 10 µL of the pure gas and close the valve of the syringe. Using a ~~2 mL~~ 2-mL septum vial, add ~~2 mL~~ 2-mL methanol and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the methanol. Open the valve and withdraw the plunger slightly to allow the ~~methanol~~solvent to enter the syringe. The action of the gas dissolving ~~in the methanol~~ creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws; that is, 1 mol of gas at STP occupies 22.4 L.

8.4.3 *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 ~~methanol~~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 ~~methanol~~solvent into a 100 mL volumetric flask. Add 10 mL of solution (~~8.4.2.1~~8.4.3.1) Make up to 100 mL with ~~methanol,~~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 ~~methanol~~solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the ~~methanol.~~solvent. Open the valve and withdraw the plunger slightly to allow the ~~methanol~~solvent to enter the syringe. The action of the gas dissolving ~~in the methanol~~ creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws, that is, 1 mol of gas at STP occupies 22.4 ~~liters.~~litres.

8.4.4 *~~Stability of Calibration Blend Solutions~~—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 ~~monitoring methods using radial diffusive sampling as well as those using pumped and axial diffusive sampling.~~all 3 sorbent-based monitoring methods described in this standard; axial and radial passive samplers and pumped sorbent tubes. Prepare loaded sorbent tubes by ~~injecting aliquots of standard~~ connecting the sampling end of blank, conditioned sorbent tubes to a metered source of gas-phase standard (8.4.1~~solutions~~) 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 ~~4~~2 µL aliquot of an appropriate standard solution injected through the septum. After 5 min, disconnect the tube and seal it. ~~Prepare fresh standards with~~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. ~~For~~ When using liquid standards to calibrate typical ambient and indoor ~~air,~~ air monitoring methods, load sorbent tubes with 1 to ~~5~~2 µL (at least 3 levels) of solutions ~~8.4.1.1~~8.4.2.1, ~~8.4.1.2~~8.4.2.2, or ~~8.4.1.3~~8.4.2.3. ~~For workplace air,~~ When using liquid standards to calibrate typical workplace air monitoring methods, load sorbent tubes with 1 to ~~5~~2 µL (at least 3 levels) of solutions ~~8.4.2.1~~8.4.3.1, ~~8.4.2.2~~8.4.3.2, or ~~8.4.2.3~~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 ~~Label sorbent tubes (and carrier tubes for radial sorbent cores) uniquely prior to conditioning. Do not use solvent-containing paints and markers or adhesive labels to label the tubes.~~ Prior to use, ~~condition~~ re-condition pre-conditioned or desorbed sorbent tubes and radial sorbent cores in their carrier tubes by desorbing them at a temperature ~~just~~ above the analytical desorption temperature (see Appendix ~~X3~~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, ~~the tubes~~ it may be ~~reused to~~ 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 ~~envisaged. Seal the sorbent and carrier tubes with metal screw caps with combined PTFE ferrule fittings and stored in an airtight container when not sampling or being conditioned. The sorbent tube blank level is acceptable if artifact peaks are no greater than 10 % of the typical areas of the analytes of interest.~~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.

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

10.2 The uptake rates given in ~~Tables 7 and 8~~Appendix X3 (axial) and ~~Table 9~~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 ~~listed~~referenced in Section ~~1.2~~2 to determine and validate the uptake rate.

11. Sampling Procedures

11.1 *Active (Pumped)* ~~*Sampling*~~*Sampling:*

11.1.1 Select a sorbent tube (or tube combination) appropriate for the compound or mixture to be sampled. Guidance on suitable sorbents is given in Appendix ~~X2~~X1.

11.1.2 If more than one tube is to be ~~used,~~ used in series, prepare a tube assembly by joining the ~~tubes~~ 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 ~~plastic or rubber~~flexible tubing (7.10 ~~tubing,~~), so that the tube or section of tube containing the stronger sorbent is nearest the ~~pump.~~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~~his/her lapel. Attach the pump to the worker as appropriate to minimize inconvenience. When used for fixed location sampling, choose a ~~sampling site.~~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 ~~electrometer overload may occur. At temperatures above 20°C, reduce the sample volume by a factor of two for each 10°C rise in temperature.~~ 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~~the sampling capacity of the sorbents is not exceeded. If this capacity is exceeded,~~) 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~~breakthrough of~~) and by checking for significant (>10 %) breakthrough (18.2.1 ~~vapor from the tube assembly will occur.~~) 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, ~~instead of determining~~ the breakthrough volume ~~directly,~~ can be determined indirectly from the mathematically related retention ~~volume may be determined.~~ 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 for sorbent Type D. This is confirmed by the European study~~ (results. A study of breakthrough volumes (~~15~~13)~~), where for sorbent Type D and sorbent Type C, direct values were~~ using weak porous polymer sorbents has reported indirect breakthrough volumes values between twice and twenty times ~~the indirect; that is,~~ smaller than direct values indicating that the indirect method is a ~~safe~~conservative estimate. However, ~~for sobent Type A~~ (similar studies using weak to~~16), sorbent Type F~~ medium strength graphitized~~: and sorbent Type~~carbon black sorbents ~~G~~(12)~~:, direct values were~~ have reported indirect values between four times ~~and one tenth of the indirect~~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 ~~sampled~~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 (~~Tables 1-6~~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. ~~Tables 1-6~~The tables in Appendix X2 give typical values for retention volumes and safe sampling volumes. ~~These values have been determined by the chromatographic method (Annex A2). Use of back-up tubes (11.1.6) during field monitoring will help confirm quantitative retention under actual monitoring conditions.~~

11.1.5.4 The safe sampling volumes in ~~Tables 1-6~~Appendix X2 have been determined by the chromatographic method (Annex A2) which did not take account of humidity ~~((~~(~~15~~13)~~).)~~. Measurements by the direct method ~~((~~(~~17~~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 ~~value.~~values. If high concentrations (>100 ppm, 300 mg/m^3) are also anticipated, ~~the~~ breakthrough volumes ~~for carbonaceous sorbents~~ should be further reduced by a factor of two. Use of back-up tubes (11.1.6) during field monitoring will help confirm quantitative retention under actual 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 ~~(5 or 10 %)~~ (10 %) of the sampling tubes ~~used~~ in each field monitoring exercise.

11.1.7 Note and record the ~~times, temperature, flow rate or register reading, if appropriate,~~ 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 or register reading,~~ 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 ~~screw caps and~~long term storage caps (7.6 ~~PTFE ferrule seals.~~). Tighten these seals securely. ~~Label the tubes uniquely prior to conditioning. Do not use solvent-containing paints and markers or adhesive labels to label the tubes.~~