



Designation: D 6196 – 97

## Standard Practice for Selection of Sorbents and Pumped Sampling/Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air<sup>1</sup>

This standard is issued under the fixed designation D 6196; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) 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 (**Ref 1**)<sup>2</sup>, indoor (**2**) and workplace (**3**) 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 (1.5), is shown in Tables 1-6. For other compounds this practice shall be tested according to EN 1076 or other appropriate validation protocols (Sections 13 and 14). (**4, 1**)

1.3 This practice is based on the sorption of VOCs from air onto selected sorbents or combinations of sorbents. Sampled air is pulled through a tube containing these sorbents. The sorbed VOCs are subsequently recovered by thermal desorption and analyzed by capillary gas chromatography.

1.4 This practice recommends a number of sorbents that can be packed in sorbent tubes, for use in the sampling of a wide range of different volatile organic compounds, in the range 0 to 400°C (v.p. 15 to 0.01 kPa at 25°C). Single-bed tubes containing for example sorbent Type A<sup>3,4</sup> are appropriate for normal alkanes from n-C<sub>6</sub>(hexane) to n-C<sub>10</sub>(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<sup>3,5</sup>. Other sorbent types than those specified may be used, if their breakthrough capacities are adequate and their thermal desorption blanks are sufficiently small. Ex-

amples are given in Appendix X2. A broader range of VOCs may be sampled using multi-bed tubes.

1.5 This practice can be used for the measurement of airborne vapors of these volatile organic compounds in a concentration range of approximately 0.1  $\mu\text{g}/\text{m}^3$  to 1  $\text{g}/\text{m}^3$ , for individual organic compounds in 1–10 L air samples. The method is also suitable for the measurement of the airborne concentrations of individual components of volatile organic mixtures, provided that the total loading of the mixture does not exceed the capacity of the tube. Quantitative measurements are possible when using validated procedures with appropriate quality assurance measures.

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

1.5.2 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.

1.5.3 Artifacts are typically <1ng for well conditioned sorbent Type C<sup>3,6</sup> and carbonaceous sorbents such as graphitized carbon, carbon molecular sieves and pure charcoals; at 1 to 5 ng levels for sorbent Type D<sup>3,7</sup> and at 5 to 50 ng levels for other porous polymers such as sorbent Type A and sorbent Type E<sup>3,8</sup>. Method sensitivity is typically limited to 0.5  $\mu\text{g}/\text{m}^3$  for 10 L air samples with this latter group of sorbent types because of their inherent high background.

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

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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<sup>2</sup> The bold face numbers in parentheses refer to the list of references at the end of this practice.

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

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

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

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

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

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

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

1.8 *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.*

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Atmospheric Sampling and Analysis<sup>9</sup>

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)<sup>9</sup>

**2. Referenced Documents**

<sup>9</sup> *Annual Book of ASTM Standards*, Vol 11.03.

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

| Organic compound                | Boiling Point, °C | Vapor Pressure, kPa | Retention Volume (L), 25°C | Safe Sampling Volume (SSV <sup>B</sup> ) (L) | SSV/g (L/g) | Desorption Temperature, °C | Reference |
|---------------------------------|-------------------|---------------------|----------------------------|--|-------------|----------------------------|-----------|
| <b>Hydrocarbons</b>             |                   |                     |                            |  |             |                            |           |
| Propane <sup>C</sup>            | -42               | –                   | 0.17                       | 0.09   | 0.29        |                            | (9)       |
| Pentane                         | 35                | 56                  | 23.4                       | 11.7   | 39          | 130                        | (9)       |
| Hexane                          | 69                | 16                  | 73.8                       | 36.9   | 123         | 160                        | (9)       |
| 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                        | (9)       |
| Benzene                         | 80                | 10.1                | 57                         | 28.5   | 95          | 160                        | (9)       |
| 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                        | (9)       |
| <b>Chlorinated Hydrocarbons</b> |                   |                     |                            |  |             |                            |           |
| Dichloromethane                 | 40                | 47                  | 6.9                        | 3.45   | 11.5        | 130                        | (9)       |
| 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                        | (9)       |
| <b>Esters and Glycol Ethers</b> |                   |                     |                            |  |             |                            |           |
| Methyl acetate                  | 58                | 22.8                | 14.04                      | 7.02   | 23.4        | 125                        | (9)       |
| 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                        | (9)       |
| 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)       |
| <b>Ketones</b>                  |                   |                     |                            |  |             |                            |           |
| Acetone                         | 56                | 24.6                | 2.9                        | 1.5  | 5           | 120                        | (3)       |
| Methyl ethyl ketone             | 80                | 10.3                | 21                         | 10.5   | 35          | 145                        | (9)       |
| Methyl isobutyl ketone          | 118               | 0.8                 | 490                        | 250  | 830         | 190                        | (3)       |
| <b>Alcohols</b>                 |                   |                     |                            |  |             |                            |           |
| Methanol <sup>C</sup>           | 65                | 12.3                | 0.78                       | 0.39   | 1.3         |                            | (9)       |
| Ethanol                         | 78                | 5.9                 | 3.18                       | 1.59   | 5.3         | 120                        | (9)       |
| 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                        | (9)       |
| Isobutanol                      | 108               | 1.6                 | 60                         | 30   | 100         | 150                        | (3)       |
| <b>Others</b>                   |                   |                     |                            |  |             |                            |           |
| Ethylene oxide <sup>C</sup>     | 11                | 147                 | 0.84                       | 0.42   | 1.4         | 100                        | (9)       |
| Propylene oxide                 | 34                | 59                  | 2.04                       | 1.02   | 3.4         | 120                        | (9)       |
| Hexanal                         | 131               | –                   | 1680                       | 840  | 2800        | 220                        | (9)       |

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

<sup>B</sup>SSV; see 11.5.1 and 11.5.2.

<sup>C</sup>SSV below recommended 1L. sorbent Type B is preferred (Table 2).

**TABLE 2 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a 500 mg Sorbent Type B<sup>A</sup> Sorbent Tube at 20°C (9)**

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

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

<sup>B</sup>SSV; see 11.5.1 and 11.5.2.

<sup>C</sup>Desorption recovery is poor (see Table 7).

E 355 Practice for Gas Chromatography Terms and Relationships<sup>10</sup>

2.2 ISO Standards:<sup>11</sup>

ISO 5725 Precision of Test Methods

ISO 6249 Gas Analysis. Preparation of Calibration Gas Mixtures. Permeation Method

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

2.3 CEN Standards:<sup>12</sup>

EN 482 Workplace Atmospheres. General Requirements for the Performance of Procedures for the Measurement of Chemical Agents.

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.

### 3. Terminology

3.1 *Definitions*—Refer to Terminology D 1356 and Practice E 355 for definitions of terms used in this practice.

3.2 *Definitions of Terms Specific to This Standard:*

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

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

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

3.2.4 *loading*—the product of concentration expressed in ppb<sup>13</sup> or mg/m<sup>3</sup> and the sampled atmosphere volume (flow rate x sampling time).

3.2.5 *overall uncertainty (OU)*—quantity used to characterize, as a whole, the uncertainty of the result given by an apparatus or measuring procedure. It is expressed, as a per-

centage, by a combination of bias and precision usually according to the formula:

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

where:

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

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

$s$  = standard deviation of measurements.

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

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

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

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

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

3.2.10 *sorbent tube*—a tube, usually made of metal or glass, containing an active sorbent or a reagent-impregnated support, through which sampled atmosphere is passed at a rate controlled by an air sampling pump.

### 4. Summary of Practice

4.1 A suitable sorbent type or series of sorbents should be selected for the compound or mixture to be sampled. The sorbents selected should be arranged in order of increasing sorbent strength by linking tubes containing the individual sorbents together in series. Alternatively, a single tube containing several sorbents in series may be used. Provided suitable sorbents are chosen, volatile organic components are retained by the sorbent tube(s) and thus are removed from the flowing air stream. The collected vapor (on each tube) 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. Where the sample to be analyzed contains unknown components (indoor/ambient air applications), preliminary analysis of typical samples using 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

<sup>10</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>11</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th floor, New York, NY 10036

<sup>12</sup> Available from Comité Européen de Normalisation, Brussels.

<sup>13</sup> Volume fraction, ( $\phi$ ) = 10<sup>-9</sup>.

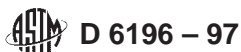


**TABLE 3 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a 200 mg Sorbent Type D<sup>A</sup> Sorbent Tube at 20°C (3)**

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

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

<sup>B</sup>SSV; see 11.5.1 and 11.5.2.



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

| Organic Compound    | Boiling Point (°C) | Vapor Pressure (kPa)(25°C) | Retention Volume, L | Safe Sampling Volume, SSV <sup>B</sup> , 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                        |
| <i>n</i> -propanol  | 97                 | 1.9                        | 40                  | 20   | 40         | 120                        |
| <i>n</i> -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                        |

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

<sup>B</sup>SSV; see 11.5.1 and 11.5.2. Reduce SSV by factor of 2 if sampling at high humidity.

**TABLE 5 Extrapolated Retention Volumes and Safe Sampling Volumes for Organic Vapors Sampled on a 300 mg Sorbent Type I<sup>A</sup> Sorbent Tube at 20°C (3)**

| Organic Compound      | Boiling Point, °C | Vapor Pressure, kPa, 25°C | Retention Volume, L | Safe Sampling Volume SSV <sup>B</sup> 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                        |

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

<sup>B</sup>SSV; see 11.5.1 and 11.5.2. Reduce SSV by a factor of 10 if sampling at high humidity; reduce SSV by a factor of 2 if sampling at high concentration.

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

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

<sup>A</sup>SSV; see 11.5.1 and 11.5.2. Reduce SSV by a factor of 10 if sampling at high humidity; reduce SSV by a factor of 2 if sampling at high concentration.

<sup>B</sup>Extrapolated from data on pentane, hexane, and benzene.

atmospheres. It may also be used for measuring emissions from materials in small or full scale environmental chambers for material emission testing or 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. However, with the possible exception of formaldehyde and acrolein, no causal relation has ever been proven between the concentration of specific VOCs in indoor air and human health, although VOCs are generally thought to contribute to air quality problems in indoor environments (5).



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

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

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

## 6. Interferences

6.1 Organic components, that have the same or nearly the same retention time as the analyte of interest, will interfere during the gas chromatographic analysis. Analytes and artifacts can be generated during sampling and analysis (6, 7). Interferences can be minimized by proper selection of gas chromatographic columns and conditions, and by stringent conditioning of both the sorbent tubes and 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 tubes. This is minimized by correctly sealing and storing blank and sampled tubes (see 9.1, 11.7, 11.8 and 16.3). Such artifact formation is generally at low to sub-nanogram levels. It is typically lower for carbon type sorbents and the more stable (sorbent Type D) porous polymers, than for other, less stable, porous polymers (8,9).

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

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

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

## 7. Apparatus

7.1 Use ordinary laboratory apparatus in addition to the following.

7.2 *Sorbent Tubes*, compatible with the thermal desorption apparatus to be used (7.3). Typically, but not exclusively, they are constructed of stainless steel tubing, 6.3 mm (¼ in.) OD, 5

mm ID and 90 mm long. Tubes of other dimensions may be used but the safe sampling volumes (SSV) given in Tables 1-6 are based on these tube dimensions. For labile analytes, such as sulfur containing compounds, glass-lined or glass tubes (typically 4 mm ID) should be used. One end of the tube is marked, for example by a scored ring about 10 mm from the sampling inlet end. The tubes are packed with one or more pre-conditioned sorbents (8.3), so that the sorbent bed will be within the desorber heated zone, and a gap of at least 14 mm is retained at each end to minimize errors due to diffusive ingress at a very low pump flow rates. Tubes contain between 200 and 1000 mg sorbent, depending on sorbent density — typically about 250 mg sorbent Type D, 300 mg sorbent Type A or 500 mg sorbent Type B. The sorbents are retained by stainless steel gauzes or unsilanized glass wool plugs, or both. If more than one sorbent is used in a single tube, the sorbents should be arranged in order of increasing sorbent strength and separated by unsilanized glass wool, with weakest sorbent nearest to the marked sampling inlet end of the tube.

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

7.3 *Thermal Desorption Apparatus*, for the two-stage thermal desorption of the sorbent tubes 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 may also incorporate additional features, such as automatic sample tube loading, leak-testing, and a 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.

7.4 *Sorbent Tube End Caps*, sealed with metal screw-cap fittings with combined (one-piece) PTFE ferrule seals.

7.5 *Sorbent Tube Unions*, constructed of metal couplings with combined (one-piece) PTFE ferrule seals.

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

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

7.8 *Connecting Tubing*, PTFE, for connecting between the sampling point and the sample tube when sampling in a remote location. Tubing downstream of the sampler (that is, for connecting the tube to the pump) does not need to be inert and can be of any suitable material. For personal monitoring, the tube is typically worn as close as possible to the breathing zone (for example, on the lapel of clothing), and the pump carried on a belt. In this case, clips should be provided to hold the sample tube and connecting tubing to the wearer's lapel area. This

connecting tubing will need to be about 90 cm long. All connections should be leak proof. Sampling tubes shall not be used with plastic or rubber tubing upstream of the sorbent. Interferences from the tubing may introduce sampling errors. Such errors may be reduced by replacing the tubing regularly.

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

7.10 *Gas Chromatographic Apparatus*:

7.10.1 *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.

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

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

## 8. Reagents and Materials

8.1 Unless otherwise stated, all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>14</sup> 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. Typical components are: propane, pentane, hexane, benzene, dichloromethane, 1,1,1-trichloroethane, methanol, ethanol, *n*-butanol, methyl acetate, 2-methoxyethanol, methyl ethyl ketone, acetonitrile, *n*-butyl acetate,  $\alpha$ -pinene, decane, ethylene oxide, propylene oxide, and hexanal.

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

8.3 *Sorbents*, particle size, in the range 20 to 80 mesh, preconditioned under a flow of inert gas by heating, at a temperature at least 25°C below the published maximum for that sorbent, for 16 h, before packing the tubes. To prevent recontamination of the sorbents, keep them in a clean atmosphere during cooling to room temperature, storage, and loading into the tubes. If tubes are packed with unconditioned

sorbent, stringently condition them at a temperature just below (10 to 25°C) the maximum recommended temperature of the least stable sorbent in the tube for not less than 2 h, with a flow of at least 100 mL/min pure, inert carrier gas. The flow direction shall be opposite to that used during sampling. Wherever possible, keep analytical desorption temperatures below those used for conditioning. Tubes prepacked by the manufacturer are also available for most sorbents and as such only require conditioning.

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

8.4 *Calibration Solutions*:

8.4.1 *Calibration Solutions for Ambient and Indoor Air*:

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

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

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

8.4.2 *Calibration Solutions for Workplace Air*:

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

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

8.4.2.3 *Solution Containing Approximately 1 mg/mL of Gas Components*—For gases, for example, ethylene oxide, prepare a low level calibration solution as follows. Obtain pure gas at atmospheric pressure by filling a small plastic gas bag from a gas cylinder. Fill a 1 mL gas-tight syringe with 1 mL of the pure gas and close the valve of the syringe. Using a 2 mL septum vial, add 2 mL methanol and close with the septum cap.

<sup>14</sup> 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.

Insert the tip of the syringe needle through the septum cap into the methanol. Open the valve and withdraw the plunger slightly to allow the methanol to enter the syringe. The action of the gas dissolving in the methanol creates a vacuum, and the syringe fills with solvent. Return the solution to the flask. Flush the syringe twice with the solution and return the washings to the flask. Calculate the mass of gas added using the gas laws, that is, 1 mol of gas at STP occupies 22.4 liters.

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

**8.5 Standard Loaded Sorbent Tubes**—Prepare loaded sorbent tubes by injecting aliquots of standard solutions onto clean sorbent tubes as follows. For a sorbent tube into the injection unit (7.11) through which inert purge gas is passed at 100 mL/min and a 1 to 4  $\mu\text{L}$  aliquot of an appropriate standard solution injected through the septum. After 5 min, disconnect the tube and seal it. Prepare fresh standards with each batch of samples. For ambient and indoor air, load sorbent tubes with 1 to 5  $\mu\text{L}$  (at least 3 levels) of solutions 8.4.1.1, 8.4.1.2, or 8.4.1.3. For workplace air, load sorbent tubes with 1 to 5  $\mu\text{L}$  (at least 3 levels) of solutions 8.4.2.1, 8.4.2.2, or 8.4.2.3.

## 9. Sample Tube Conditioning

9.1 Prior to use, condition tubes by desorbing them at a temperature just above the analytical desorption temperature (see Appendix X3) for 10 min with a carrier gas flow of at least 100 mL/min. Analyze the 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 tube may be reused to collect a further sample immediately. Check the thermal desorption blank if the tubes are left for an extended period before reuse, or if sampling for a different analyte is envisaged. Seal the tubes with metal screw caps with combined PTFE ferrule fittings and stored in an airtight container when not sampling or being conditioned. The sorbent tube blank level is acceptable if artifact peaks are no greater than 10 % of the typical areas of the analytes of interest.

## 10. Calibration of Pump

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

NOTE 2—The sampling pump shall comply with local safety regulations.

## 11. Sampling Procedure

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

11.2 If more than one tube is to be used, prepare a tube assembly by joining the tubes with a union (7.5).

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

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

11.5 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 2 for each 10°C rise in temperature.

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

11.5.2 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 (10), where for sorbent Type D sorbent Type C, direct values were between twice and twenty times the indirect; that is, the indirect method is a safe estimate. However, for sorbent Type A (11), sorbent Type F<sup>3,15</sup> and sorbent Type G<sup>3,16</sup>, direct values were between four times and one tenth of the indirect values. The indirect method is, therefore, less reliable for these sorbents, and by implication for other highly microporous sorbents. Both the direct and indirect methods are subject to large errors, so that if sampling volumes close to the recommended SSV are contemplated, the actual breakthrough volumes should be confirmed by the direct method, using conditions of concentration and relative humidity as close to the anticipated sampled air as possible. Alternatively, use a second tube in series as a check on breakthrough.

11.5.3 The breakthrough volume of porous polymers varies with ambient air temperature, reducing by a factor of about 2 for each 10°C rise in temperature. It also varies with sampling

<sup>15</sup> An example of sorbent Type F known to perform as specified in this practice is Carbo-pack B manufactured by Supelco Inc., USA.

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



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 sample volumes of not more than 70 % of the breakthrough volume be taken. Tables 1-6 give typical values for retention volumes and safe sampling volumes. These values have been determined by the chromatographic method (Annex A2).

11.5.4 The safe sampling volumes in have been determined by the chromatographic method (Annex A2) which did not take account of humidity (10). Measurements by the direct method (12) indicate that breakthrough volumes at high (80 %) humidity are about a factor of two lower for porous polymers and graphitized carbon type sorbents and a factor of ten lower for pure charcoals and carbon molecular sieves than the low humidity value. If high concentrations (>100 ppm, 300 mg/m<sup>3</sup>) are also anticipated, the breakthrough volumes for carbonaceous sorbents should be further reduced by a factor of two.

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

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

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

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

11.10 *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. Label these as blanks.

## 12. Desorption and Analysis

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

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

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

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

|                        |  |
|------------------------|--|
| Desorption Temperature | 250 to 325°C   |
| Desorption time        | 5 to 15 min  |
| Desorption flow rate   | 30 to 50 mL/min  |
| Cold trap low          | -30°C  |
| Cold trap high         | 250 to 350°C   |
| Cold trap sorbent      | typically same as tubes, 40 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 3—The desorption temperature depends on the analyte and the sorbent used. Recommendations are given in Table 6 but the maximum desorption temperatures given in Appendix X2 and Appendix X3 for particular sorbents should be respected.

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

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

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

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

### 13. Method Calibration

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

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

where:

mass of analyte ( $\mu\text{g}$ ) = Concentration in solution 8.4.1 or 8.4.2 x volume injected ( $\mu\text{l}$ ; 8.5).

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

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

13.4.1 Some makes of thermal desorber do not have a direct liquid injection facility. In these cases, desorption efficiency should be checked by comparing the calibration graph of the substance of interest with that of n-hexane. The ratio of the slope of the calibration graph of the substance of interest relative to that of n-hexane should be the same as the relative response factor for that compound. Response factors for other compounds may be calculated approximately from effective carbon numbers (13). If the ratio of the slopes of the calibration graphs do not agree with the relative response factor within 10 %, change the desorption parameters accordingly.

### 14. Calculations

14.1 *Mass Concentration of Analyte*—Calculate the concentration of the analyte in the sampled air, in  $\mu\text{g}/\text{m}^3$ , by means of the following equation:

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

where:

$\rho(\text{VOC})$  = concentration of analyte in the air sampled, in  $\mu\text{g}/\text{m}^3$ ,

$F$  = mass of analyte present in the actual sample as found in 13.3,  $\mu\text{g}$  (sum of tubes if more than one used),

$B$  = mass of analyte present in the blank tube,  $\mu\text{g}$  (sum of tubes if more than one used), and

$V$  = volume of sample taken, L.

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

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

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

where:

$P$  = actual pressure of the air sampled, kPa, and

$T$  = actual temperature of the air sampled, °C.

14.2 *Volume Concentration of Analyte*—Calculate the volume fraction of the analyte in air, in  $\mu\text{L}/\text{m}^3$  by means of the following equation:

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

where:

$\phi(\text{VOC})$  = volume fraction of the analyte in air,  $\mu\text{L}/\text{m}^3$ , and

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

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

### 15. Precision and Bias

15.1 Laboratory tests of the procedure (10), following in part EN 1076 using tubes spiked from a standard atmosphere of hexane at 1.0  $\text{mg}/\text{m}^3$  and 50 % RH. at 20°C and using a pump in conformity with EN 1232, yielded results expressed as overall uncertainty (3.2.5); sorbent Type D, sorbent Type C and sorbent Type A (mean of five determinations), 8.9 %; sorbent Type F<sup>15</sup> and sorbent Type G<sup>16</sup> (mean of three determinations), 16.8 %.

15.2 Laboratory tests (10) on tubes spiked with the compounds specified in 8.2.1 on sorbent Type A or sorbent Type B at a load level of approximately 1.0  $\mu\text{g}$  are summarized in Table 7. The precision expressed as a coefficient of variation, was between 1.3 % and 5.9 %, depending on analyte. Expressed as repeatability (ISO 5725) the range is equivalent to 3.7 % to 16.7 %.

15.3 Laboratory tests (3) or sorbent Type D tubes, liquid spiked with a broader range of compounds at a single load level of approximately 10  $\mu\text{g}$  are summarized in Table 8. Excluding hexane, for which sorbent Type D is unsuitable, the precision expressed as a coefficient of variation, was between 0.4 % and 2.8 %, depending on analyte. Expressed as repeatability (ISO 5725) the range is equivalent to 11 % to 5.6 %.

15.4 Laboratory tests (14) on tubes liquid spiked with 11 model compounds including benzene, toluene, xylene, and isopropylbenzene on sorbent Type A at load levels between 0.5

**TABLE 7 Precision of Analysis and Storage of Test Compounds on Sorbent Type A<sup>A</sup> and Sorbent Type B<sup>B</sup> (9), (Load Level 1 µg)**

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

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

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

µg and 250 µg are summarized in Table 9. The precision, expressed as repeatability (ISO 5725) was 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 (10) on tubes spiked with the compounds specified in 8.2.1 on sorbent Type A and sorbent Type B at a load level of approximately 1.0 µg and stored at room temperature for two weeks are summarized in Table 7. The mean recovery (relative to unstored tubes) for sorbent Type A was 105.6 %.

16.2 Laboratory tests (3) on tubes liquid spiked with a broader range of compounds on sorbent Type D at a single load level of approximately 10 µg and stored at room temperature for 5 months are summarized in Table 8. Excluding hexane and methoxyethanol (neither of which should be sampled using sorbent Type D), the mean recovery (relative to unstored tubes) was 99.7 % and the mean coefficient of variation was 2 %. Similar results were obtained after storage for 11 months; excluding hexane and methoxyethanol, the mean recovery (relative to unstored tubes) was 99.4 % and the mean coefficient of variation was 0.9 %.

16.3 Storage data on multi-bed sorbents tubes is not presently available. A proposed recommendation is to store for not more than 30 days at 4°C before analysis. Ambient conditions are normally adequate for sampling and transportation, but if the conditions exceed 40°C refrigerated transportation is advisable to reduce migration. Storage data on single bed tubes is available (3) and shows 100 % recovery over several months at room temperature. Ensure that the seals remain tight at refrigeration temperatures.

## 17. Report

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

17.1.1 Complete identification of the sample,

17.1.2 Reference to this practice,

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

17.1.4 The barometric pressure and temperature,

17.1.5 the test result,

17.1.6 any unusual features noted during the determination

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

## 18. Quality Assurance

18.1 *Validating the Sample Collection Procedure:*

18.1.1 *Blanks*—Artifacts on laboratory and field blanks should be at the low or sub nanogram level for carbonaceous sorbents and sorbent Type D, and the double digit nanogram level for other porous polymer sorbents as described in Appendix X1.<sup>17</sup> 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 *Routine Checking of Sorbent Tube Safe Sampling Volumes (SSVs):*

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

18.2.2 If the SSV of a tube falls below the normal air sample collection volume for the analytes in question, the tube should

<sup>17</sup> For typical blank levels see Note 2.



**TABLE 8 Precision and Storage Recovery of Solvents on Sorbent Type D<sup>A</sup> Sorbent Tubes**

| Organic Compound                | Loading,<br>µg | Time = 0<br>% CV <sup>B</sup> | Time = 5 mo.<br>Mean Recovery <sup>C</sup><br>+ % CV | Time = 11 mo.<br>Mean Recovery<br>+ % CV |
|---------------------------------|----------------|-------------------------------|--|--|
| Hydrocarbons                    |                |                               |  |  |
| Hexane                          | 7.8            | 10.7                          | 93.6   | 17.9                                     |
| Heptane                         | 8.4            | 2.4                           | 99.5   | 2.1                                      |
| Octane                          | 8.6            | 2.4                           | 100.1  | 1.8                                      |
| Nonane                          | 12.0           | 0.8                           | nd   | nd                                       |
| Decane                          | 9.2            | 2.2                           | 100.4  | 1.5                                      |
| Undecane                        | 9.1            | 2.3                           | 100.7  | 1.5                                      |
| Dodecane                        | 9.9            | 2.8                           | 101.8  | 1.5                                      |
| Benzene                         | 11.0           | 2.5                           | 98.7   | 2.0                                      |
| Toluene                         | 10.9           | 2.6                           | (100.0)  | 1.8                                      |
| p-xylene                        | 5.3            | 2.5                           | 99.9   | 1.7                                      |
| o-xylene                        | 11.0           | 2.4                           | 100.0  | 1.7                                      |
| Ethylbenzene                    | 10.0           | 0.5                           | 99.6   | 0.4                                      |
| Propylbenzene                   | 10.5           | 2.3                           | 99.7   | 1.5                                      |
| Isopropylbenzene                | 10.9           | 2.3                           | 98.9   | 1.8                                      |
| M + p-ethyltoluene              | 10.5           | 2.3                           | 98.8   | 1.7                                      |
| O-ethyltoluene                  | 5.4            | 2.2                           | 100.1  | 1.6                                      |
| 1,2,4-trimethylbenzene          | 10.8           | 2.2                           | 100.1  | 1.3                                      |
| 1,3,5-trimethylbenzene          | 10.7           | 2.2                           | 100.0  | 1.5                                      |
| Trimethylbenzene                | 10.2           | 1.7                           | 101.6  | 0.5                                      |
| Esters and glycol ethers        |                |                               |  |  |
| Ethyl acetate                   | 10.3           | 0.6                           | 97.6   | 1.0                                      |
| Propyl acetate                  | 10.9           | 2.4                           | 100.5  | 1.7                                      |
| Isopropyl acetate               | 9.4            | 1.0                           | 97.0   | 0.4                                      |
| Butyl acetate                   | 10.8           | 2.4                           | 100.3  | 1.6                                      |
| Isobutyl acetate                | 10.7           | 2.3                           | 100.2  | 1.4                                      |
| Methoxyethanol                  | 8.9            | 5.4                           | 87.3   | 5.7                                      |
| Ethoxyethanol                   | 10.4           | 4.2                           | 97.6   | 2.5                                      |
| Butoxyethanol                   | 10.0           | 2.6                           | 100.6  | 4.1                                      |
| Methoxypropanol                 | 10.4           | 2.4                           | 95.3   | 3.6                                      |
| Methoxyethyl acetate            | 12.5           | 2.1                           | 100.6  | 1.4                                      |
| Ethoxyethyl acetate             | 11.4           | 0.9                           | 99.8   | 2.2                                      |
| Butoxyethyl acetate             | 11.5           | 2.3                           | 101.3  | 1.3                                      |
| Aldehydes and ketones           |                |                               |  |  |
| Methyl ethyl ketone             | 9.2            | 0.9                           | 97.4   | 0.8                                      |
| Methyl isobutyl ketone          | 9.3            | 0.6                           | 100.7  | 0.6                                      |
| Cyclohexanone                   | 10.9           | 0.8                           | 102.4  | 1.2                                      |
| 2-methylcyclohexanone           | 10.7           | 0.7                           | 101.1  | 0.5                                      |
| 3-methylcyclohexanone           | 10.5           | 0.8                           | 103.6  | 1.0                                      |
| 4-methylcyclohexanone           | 10.6           | 0.9                           | 103.6  | 1.4                                      |
| 3,5,5-trimethylcyclohex-2-enone | 10.6           | 2.3                           | 101.4  | 0.9                                      |
| Alcohols                        |                |                               |  |  |
| Butanol                         | 9.0            | 1.1                           | 94.8   | 3.0                                      |
| Isobutanol                      | 8.9            | 1.0                           | 93.6   | 3.5                                      |

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

<sup>B</sup>Six replicates.

<sup>C</sup>Normalized to toluene = 100. The stability of toluene has been established in a BCR intercomparison (16).

**TABLE 9 Precision (Repeatability and Reproducibility) on Sorbent Type A<sup>A</sup>**

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

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

be repacked with fresh sorbent and reconditioned.

18.3 *Performance Criteria for the Sampling Pump*—The pump flow rate shall be stable to within  $\pm 5\%$  ( $\pm 2$  CV) and

the total volume of air sampled by the pump over the sampling period shall be within  $\pm 10\%$  ( $\pm 2$  CV) of the calculated volume. A pump conforming to EN 1232 or equivalent may be expected to be within these limits.

### 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 (1). Similar criteria will be appropriate for workplace air, for example, EN 1076, and for indoor air. See also EPA Method 301 (15). The following criteria defined in TO-17 should be adapted, where necessary, for a particular application or regulatory requirement.

19.1.1 The method detection limit shall be  $\leq 2.5\mu\text{g}/\text{m}^3$ . In general, over a concentration range of  $0.1\mu\text{g}/\text{m}^3$  to  $1\text{g}/\text{m}^3$  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.

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

## 20. Keywords

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

## ANNEXES

### (Mandatory Information)

#### A1. DETERMINATION OF BREAKTHROUGH VOLUMES

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

##### A1.2 Apparatus:

A1.2.1 Use ordinary laboratory apparatus and the following.

A1.2.2 *Sorbent Tubes*, as in 7.2.

A1.2.3 *Flow Meter*, range 20 to 200 mL/min.

A1.2.4 *Flame Ionization Detector*, or similar.

##### A1.3 Reagents:

A1.3.1 *Dynamic Standard Concentration of Organic Vapor in Air*—Prepare by dilution of a measured amount of organic vapor with a metered flow of air. Generate the organic vapor by permeation tube (ISO 6349) or by syringe injection (17) 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 % r.h. Do this by diluting a primary gas stream with air at 100 % r.h. obtained by passing air through a series of water bubblers. Do not pass the organic vapor atmosphere through the water.

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

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

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

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

##### A2.2 Apparatus:

A2.2.1 *Ordinary Laboratory Apparatus*:

A2.2.2 *Sorbent Tubes*, as in 7.1

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

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

A2.2.5 *Thermocouple*.

##### A2.3 Reagents:

A2.3.1 *Dynamic Standard Concentration of Organic Vapor in Air*—Prepare by dilution of a measured amount of organic vapor with a metered flow of air. Generate the organic vapor by permeation tube (ISO 6349) or by syringe injection (16) 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 ( $3.413 \times 10^{-3} \text{°Kelvin}^{-1}$ ).

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

## APPENDIXES

### (Nonmandatory Information)

#### X1. DESCRIPTION OF SORBENT TYPES

X1.1 Sorbent types are described as follows:

| Sorbent <sup>A</sup> | Composition   |
|----------------------|---|
| Type G               | graphitized carbon                                    |
| Type J               | graphitized carbon                                    |
| Type F               | graphitized carbon                                    |
| Type K               | graphitized carbon                                    |
| Type P               | graphitized carbon                                    |
| Type Q               | graphitized carbon                                    |
| Type L               | carbon molecular sieve                                |
| Type B               | carbon molecular sieve                                |
| Type M               | carbon molecular sieve                                |
| Type R               | carbon molecular sieve                                |
| Type O               | styrene/divinylbenzene                                |
| Type A               | polystyrene   |
| Type H               | vinylpyrrolidone                                      |
| Type E               | ethylvinylbenzene/divinylbenzene                      |
| Type I               | carbon molecular sieve                                |
| Type D               | poly(diphenyl- <i>p</i> -phenylene oxide)             |
| Type C               | graphitized poly(diphenyl- <i>p</i> -phenylene oxide) |

<sup>A</sup>See Note X1.1 for sorbent availability.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

#### X2. GUIDANCE ON SORBENT SELECTION

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



**TABLE X2.1 Guidance on Sorbent Selection**

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

| Sample Tube Sorbent  | Approximate Analyte Volatility Range                     | Temperature °C, max | Specific Surface Area, m <sup>2</sup> /g | Example Analytes   |
|--|--|---------------------|--|--|
| Type J<br>Type K<br>Type P   | n-C <sub>8</sub> - n-C <sub>20</sub>                     | >400°C              | 12                                       | Alkyl benzenes and aliphatics ranging in volatility from n-C <sub>8</sub> to n-C <sub>16</sub>   |
| Type D   | bp 100 - 400°C<br>n-C <sub>7</sub> - n-C <sub>26</sub>   | 350°C               | 35                                       | Aromatics, apolar components (bp>100°C) and less volatile polar components (bp>150°C)  |
| Type C   | bp 100 - 450°C<br>n-C <sub>7</sub> to n-C <sub>30</sub>  | 350°C               | 35                                       | Alkyl benzenes, vapor phase PAHs and PCBs and as above for Type D.   |
| Type G<br>Type F<br>Type Q   | (n-C <sub>4</sub> ) n-C <sub>5</sub> - n-C <sub>14</sub> | >400°C              | 100                                      | Wide range of VOCs Inc., ketones, alcohols, and aldehydes (bp>75°C) and all apolar compounds within the volatility range specified, plus perfluorocarbon tracer gases          |
| Type O   | bp 50 - 200°C  | 250°C               | 350                                      | Suits a wide range of VOCs including oxygenated cpds and haloforms less volatile than methylene chloride   |
| Type A   | bp 50 - 200°C  | 250°C               | 750                                      | Suits a wide range of VOCs including hydrocarbons from n-C <sub>5</sub> to n-C <sub>12</sub> . Also good for volatile oxygenated cpds.   |
| Type E   | bp 50 - 200°C<br>n-C <sub>5</sub> - n-C <sub>12</sub>    | 250°C               | 550                                      | Suits a wide range of VOCs including oxygenated compounds  |
| Type H   | bp 50 - 150°C<br>b-C <sub>5</sub> - n-C <sub>8</sub>     | 180°C               | 300                                      | Specifically selected for volatile nitriles; acrylonitrile, acetonitrile and propionitrile. Also good for pyridine, volatile alcohols from EtOH, MEK, and so forth.            |
| Type I <sup>A</sup>  | -30 - 150°C<br>C <sub>3</sub> - n-C <sub>8</sub>         | >400°C              | 1200                                     | Good for very volatile compounds such as VCM, ethylene oxide, CS <sub>2</sub> and CH <sub>2</sub> Cl <sub>2</sub> . Also good for volatile polars e.g. MeOH, EtOH and acetone. |
| Type L <sup>A</sup><br>Type B <sup>A</sup><br>Type M <sup>A</sup><br>Type R <sup>A</sup> | -60 - 80°C   | 400°C               | c 800                                    | Good for ultra volatile compounds such as C <sub>3</sub> , C <sub>4</sub> hydrocarbons, volatile haloforms and freons  |
| Zeolite molecular Sieve <sup>B</sup>   | -60 - 80°C   | 350°C               |  | Used specifically for 1,3-butadiene and nitrous oxide.   |

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

<sup>B</sup>Significantly hydrophilic. Do not use in high humidity atmospheres unless special precautions are taken. See 6.4.

### X3. GUIDANCE ON SORBENT USE

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



**TABLE X3.1 Guidance on Sorbent Use**

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

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

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

<sup>B</sup>Significantly hydrophilic. Do not use in high humidity atmospheres unless special precautions are taken. See 6.4.

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