

Designation: D 6196 – 97

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

This standard is issued under the fixed designation D 6196; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice is intended to assist in the selection of sorbents and procedures for the sampling and analysis of ambient (**Ref 1**)², 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^{3,4} are appropriate for normal alkanes from n-C₆(hexane) to n-C₁₀(decane) and substances with similar volatility (v.p. 15 to 0.3 kPa at 25°C). More volatile materials should be sampled on stronger sorbents, such as sorbent Type B^{3,5}. Other sorbent types than those specified may be used, if their breakthrough capacities are adequate and their thermal desorption blanks are sufficiently small. Examples are given in Appendix X2. A broader range of VOCs may be sampled using multi-bed tubes.

1.5 This practice can be used for the measurement of airborne vapors of these volatile organic compounds in a concentration range of approximately 0.1 μ g/m³ to 1 g/m³, 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^{3.6} and carbonaceous sorbents such as graphitized carbon, carbon molecular sieves and pure charcoals; at 1 to 5 ng levels for sorbent Type D^{3.7} and at 5 to 50 ng levels for other porous polymers such as sorbent Type A and sorbent Type E^{3.8}. Method sensitivity is typically limited to 0.5 μ g/m³ 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.

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¹ 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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 $^{^{2}}$ The bold face numbers in parentheses refer to the list of references at the end of this practice.

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

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

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

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

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

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

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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. Referenced Documents

2.1 ASTM Standards:

- D 1356 Terminology Relating to Atmospheric Sampling and Analysis⁹
- D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)⁹

⁹ 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^A Sorbent Tube at 20°C

| Organic compound | Boiling Point, °C | Vapor Pressure, kPa | Retention Volume (L), 25°C | Safe Sampling Volume (SSV ^B) (L) | SSV/g (L/g) | Desorption Temperature, °C | Reference |
|-----------------------------|----------------------|------------------------|----------------------------------|---|--------------------------|----------------------------------|------------|
| | | | Hydrocarbo | ons | | | |
| Propane ^C | -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) |
| | | (https | Chlorinated Hydro | ocarbons | toh ai) | | |
| Dichloromethane | 40 | 47 | 6.9/ Stall | 3.45 | 11.5 | 130 | (9) |
| Carbon tetrachloride | 76 | 12 | 44 | 22 | 73 | 160 | (3) |
| 1,2-dichloroethane | 84 | 8.4 | 34 | 17- Drown | 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) |
| | | | Esters and Glyco | ol Ethers | | | |
| Methyl acetate | 58 | 22.8 | 14.04 ASTM | 7.02 96-97 | 23.4 | 125 | (9) |
| Ethyl acetate | 71 ards. iteh.a | 9.7 talog/standa | 39s/sist/66h88 | 208-3fle-4559 | $67_{66} - 5d21ff6$ | 615092/astm- | (3) 196-97 |
| Propyl acetate | 102 | 5.5 | 297 5157 00000 | 150-5110-4559 | 500 ⁰⁰⁻⁵⁰²¹¹⁰ | 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) |
| | | | Ketones | | | | |
| 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) |
| | | | Alcohols | | | | |
| Methanol ^C | 65 | 12.3 | 0.78 | 0.39 | 1.3 | | (9) |
| Ethanol | 78 | 5.9 | 3.18 | 1.59 | 5.3 | 120 | (9) |
| <i>n</i> -propanol | 97 | 1.9 | 17 | 8 | 27 | 125 | (3) |
| Isopropanol | 82 | 4.3 | 88 | 44 | 145 | 120 | (3) |
| <i>n</i> -butanol | 118 | 0.67 | 135 | 67.5 | 225 | 170 | (9) |
| Isobutanol | 108 | 1.6 | 60 | 30 | 100 | 150 | (3) |
| | | | Others | | | | |
| Ethylene oxide ^C | 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) |

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

^BSSV; see 11.5.1 and 11.5.2.

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

🕼 D 6196 – 97

 TABLE 2
 Extrapolated Retention Volumes and Safe Sampling

 Volumes for Organic Vapors Sampled on a 500 mg Sorbent Type

 B^A Sorbent Tube at 20°C (9)

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

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

^BSSV; see 11.5.1 and 11.5.2.

^CDesorption recovery is poor (see Table 7).

 $E\ 355\ Practice\ for\ Gas\ Chromatography\ Terms\ and\ Relationships ^{10}$

2.2 ISO Standards:¹¹

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:¹²
- 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

<u>ASTM</u>

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^{13} or mg/m³ 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 percentage, by a combination of bias and precision usually according to the formula:

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

¹⁰ Annual Book of ASTM Standards, Vol 14.02.

 $^{^{11}}$ Available from American National Standards Institute, 11 W. 42nd St., 13th floor, New York, NY 10036

¹² Available from Comité Européen de Normalisation, Brussels.

¹³ Volume fraction, $(\phi) = 10^{-9}$.

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🕼 D 6196 – 97

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

| | | 20106 | ent Tube at 20°C (3) | | | |
|---------------------------------|----------------------|--------------------------------|------------------------|--|---------------|----------------------------------|
| Organic Compound | Boiling Point, °C | Vapor Pressure, kPa 25°C | Retention Volume, L | Safe Sampling Volume SSV ^B , L | SSV/g, L/g | Desorption Temperature, °C |
| | | | Hydrocarbons | 001,2 | | |
| 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 | 143 | - | 2400 | 1200 | 6000 | 170 |
| | 107 | | rinated Hydrocarbons | 1200 | 0000 | 110 |
| Carbon tetrachloride | 76 | 12 | 12.4 | 6.2 | 31 | 120 |
| 1,2-dichloroethane | 84 | 8.4 | 12.4 | 5.4 | 27 | 120 |
| 1,1,1-trichloroethane | 84 74 | 8.4 2.7 | | 5.4 d on sorbent Type D | 21 | 120 |
| | 74 114 | 2.7 | not recommende 68 | a on sorbent Type D 34 | 170 | 120 |
| 1,1,2-trichloroethylene | | | | | | |
| 1,1,1,2-tetrachloroethane | 130 | - | 156 | 78 | 390 | 150 |
| 1,1,2,2-tetrachloroethane | 146 | 0.67 2.7 | 340 11.2 | 170 S | 850 | 150 |
| Trichloroethylene | 87 | | | | 28 | 120 |
| Tetrachloroethylene | 121 | 1.87 | 96 | 48 | 240 | 150 |
| Chlorobenzene | 131 | 1.2 | 52 | 26 - Oh | 130 | 140 |
| | | Este | ers and Glycol Ethers | u5.11011.0 | 41) | |
| Ethyl acetate | 71 | 9.7 | 7.2 | 3.6 | 18 | 120 |
| Propyl acetate | 102 | 3.3 | 36 | | 92 | 140 |
| Isopropyl acetate | 90 | 6.3 | 12 | 6 | 31 | 120 |
| Butyl acetate | 126 | 1.0 | 170 | 85 | 420 | 150 |
| Isobutyl acetate | 115 | 1.9 | 265 | 130 | 650 | 130 |
| t-butyl acetate | 98 | - | AS not recommende | d on sorbent Type D | | |
| Methyl acrylate | . 81 | / . 1 1 / . | 13 | 6.5 | 32 | 120 |
| Ethyl acrylate TDS://standards | .ite100a1/catalog | st 3.9 lards/si | st/664888598-31 | le-45 24-8b6c-50 | 1211206cd92 | /ast120d6196-9 |
| 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 |
| | | Ald | ehydes 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 |
| | - 1 | | 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 | | d on sorbent Type D | | - |
| Octanol | 180 | _ | 2800 | 1400 | 7000 | 160 |
| Phenol | 182 | 0.03 | 480 | 240 | 1200 | 190 |
| | | 0.00 | Others | _ 10 | .200 | |
| Maleic anhydride | 202 | 6.7E-6 | 176 | 88 | 440 | 180 |
| Pyridine | 116 | 0.72-0 | 16 | 8 | 40 | 150 |
| Aniline | 184 | 0.09 | 440 | o 220 | 1100 | 190 |
| Nitrobenzene | 211 | 0.09 | 28000 | 14000 | 70000 | 200 |
| | 211 | 0.02 | 20000 | 14000 | 10000 | 200 |

^AAn example of sorbent Type D known to perform as specified in this practice is Tenax TA manufactured by Enka Research Institute NV, NL. ^BSSV; see 11.5.1 and 11.5.2.

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🏭 D 6196 – 97

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

| | | | Sorbent Tube at | 20 0 (3) | | |
|---------------------|-----------------------|----------------------------------|------------------------|---|------------|----------------------------------|
| Organic Compound | Boiling Point (°C) | Vapor Pressure (kPa)(25°C) | Retension Volume, L | Safe Sampling Volume, SSV ^B , L | SSV/g, L/g | Desorption Temperature, °C |
| | | | Hydrocarbo | ons | | |
| 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 |
| n-butanol | 118 | 0.67 | 10 | 5 | 25 | 120 |
| Isobutanol | 108 | 1.6 | 5.6 | 2.8 | 14 | 120 |
| Octanol | 180 | - | 2800 | 1400 | 7000 | 160 |
| Phenol | 182 | 0.03 | 480 | 240 | 1200 | 190 |
| | | | Others | | | |
| Acetic acid | 116 | - | 97 | 50 | 97 | 180 |
| Acetonitrile | 82 | 9.9 | 7 | 3.5 | 7 | 180 |
| Acrylonitrile | 77 | 13.3 | 16 | 8 | 16 | 180 |
| Propionitrile | 97 | - | 23 | 11 | 23 | 180 |
| Pyridine | 116 | - | 390 | 200 | 390 | 180 |
| Methyl ethyl ketone | 80 | 10.3 | 95 | 50 | 95 | 180 |

^AAn example of sorbent Type H known to perform as specified in this practice is Porapak N manufactured by Waters Associates Inc., USA.³ ^BSSV; see 11.5.1 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^A Sorbent Tube at 20°C (3)

| Organic Compound | Boiling Point, ℃ | Vapor Pressure, kPa, 25°C | Retention Volume, L | Safe Sampling Volume SSV ^B L | SSV/g, L/g | Desorption Temperature, °C |
|-----------------------|---------------------|---------------------------------|------------------------|--|-----------------------------|----------------------------------|
| Butane | -0.5 | - DOC | 1640 | 1820 EVIE | 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 M D6 | 96 200 | 700 | 250 |
| 1,1,1-trichloroethane | 74 | 13.3 | 17.6k 1.00500 | 2.8k 1550 01. | 27k 1.00 (10) | 290 16106 05 |
| Methanol Mups://star | 65 as. tten.av | catalogs tandards | 264 | 5-31 <mark>130</mark> -4339-800 | - 430 ² 1100Cd92 | /a340 - d6196-97 |
| Ethanol | 78 | 5.9 | 6900 | 3500 | 12k | 370 |

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

^BSSV; 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 ^A L | SSV/g, L/g | Desorption Temperature, °C |
| Propane | -42 | _ | 10 ^{<i>B</i>} | 5 | 15 | 220 ^B |
| Butane | -0.5 | - | 900 ^B | 450 | 600 | 270 ^B |
| Pentane | 35 | 56 | 27k | 13k | 43k | 327 |
| Hexane | 69 | 16 | 1.5M | 750k | 2.5k | 388 |
| Benzene | 80 | 10.1 | 340k | 170k | 560k | 370 |

ASSV; see 11.5.1 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. ^BExtrapolated 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).

🚓 D 6196 – 97

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, $6.3 \text{ mm} (\frac{1}{4} \text{ in.}) \text{ OD}$, 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 preconditioned sorbents (8.3), so that the sorbent bed will be within the desorber heated zone, and a gap of at least 14 mm is retained at each end to minimize errors due to diffusive ingress at a very low pump flow rates. Tubes contain between 200 and 1000 mg sorbent, depending on sorbent density - typically about 250 mg sorbent Type D, 300 mg sorbent Type A or 500 mg sorbent Type B. The sorbents are retained by stainless steel gauzes or unsilanized glass wool plugs, or both. If more than one sorbent is used in a single tube, the sorbents should be arranged in order of increasing sorbent strength and separated by unsilanized glass wool, with weakest sorbent nearest to the marked sampling inlet end of the tube.

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

7.3 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 μ L liquid syringe readable to 0.1 μ L, a precision 10 μ L gas tight syringe readable to 0.1 μ L 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