Designation: D6345 – 10

Standard Guide for
Selection of Methods for Active, Integrative Sampling of Volatile Organic Compounds in Air[1]

This standard is issued under the fixed designation D6345; 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 guide provides assistance in the selection of active integrative sampling methods, in which the volatile organic analytes are collected from air over a period of time by drawing the air into the sampling device, with subsequent recovery for analysis. Where available, specific ASTM test methods and practices are referenced.

1.2 Guidance is provided for the selection of active sampling methods based either on collection of an untreated air sample (whole air samples) or selective sampling using sorbent concentration techniques that selectively concentrate components in air. Advantages and disadvantages of specific collection vehicles are presented.

1.3 This guide does not cover the use of cryogenically cooled field sampling devices used in some automated analysis systems. Detailed instructions for cryogenic recovery of compounds captured as whole air samples or thermally desorbed from sorbents are typically covered in standard methods for sample analysis and are beyond the scope of this guide.

1.4 Both thermal and solvent desorption techniques for sample recovery are discussed.

1.5 Organic compounds are classified on the basis of vapor pressure as very volatile, volatile, semivolatile and nonvolatile. Physical characteristics of many volatile organic compounds (VOCs) are provided to aid in selection of sampling techniques for VOC measurement. Semivolatile and nonvolatile organic compounds are defined in the guide to help guide users avoid misidentifying compounds that are not covered in this guide.

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

1.7 *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:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

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

D3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method

D5197 Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)

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

D5953M Test Method for Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection Method

D6196 Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide refer to Terminology D1356.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *cryofocus*—the process of concentrating compounds from an air sample for subsequent analysis by collection on a trap cooled with a cryogen to very low temperatures (for example, -186°C).

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

Current edition approved April 1, 2010. Published June 2010. Originally approved in 1998. Last previous edition approved in 2004 as D6345 - 98(2004)$^{\varepsilon1}$. DOI: 10.1520/D6345-10.

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

3.2.1.1 *Discussion*—Cryogenic traps used for cryofocusing are typically U-shaped stainless steel tubes filled with glass beads or other inert material. An example of such a cryofocusing trap is given in Test Method D5953M. Compounds are typically released from cryogenic traps into the analytical system by rapid heating to elevated temperatures. Sorbent-filled tubes cooled to sub-ambient temperatures (for example, -30°C) have also been used for this purpose.

3.2.2 *very volatile organic compounds (VVOCs)*—Low molecular weight organic compounds that possess vapor pressures greater than 15 kPa at 25°C and boiling points typically below 30°C.

4. Significance and Use

4.1 This guide provides a broad perspective on techniques that can be used by environmental managers for selecting VOC air monitoring methods. It summarizes various methods for measurement of VOC in air derived from a variety of sources and experiences and incorporates them into condensed guidelines. This guide provides a common basis for selecting methods for VOC measurement as well a discussion of the limitations of typical methods.

4.2 This guide should be used during the planning stages of an air monitoring program along with other applicable guides and practices (for example, D1357) to select ASTM or other appropriate methods.

5. Characteristics of Organic Compounds

5.1 Physical and chemical characteristics of VOCs are available from numerous references (**1**, **2**, **3**, **4**).[3] The properties of the VOCs listed under the Clean Air Act of 1990 (**5**) are presented in Table 1 and Table 2.

TABLE 1 Properties of Clean Air Act Very Volatile Organic HAPs[A,B]

Compound	CAS No.	Vapor Pressure (kPa at 25°C)	Boiling Point (°C)	Water Solubility (g/L at °C)	Customary Classification	Reactivity in Air
Acetaldehyde	75-07-0	127	21	33.0 / 25	Polar	
Acrolein	107-02-8	29	53	>100 /21	Polar	Reactive
Allyl chloride	107-05-1	45	45	19.5 / 20	Non-Polar	
1.3-Butadiene	106-99-0	267	-5	Insoluble	Non-Polar	Reactive (?)
Carbon disulfide	75-15-0	35	47	<1 / 20	Non-polar	
Carbonyl sulfide	463-58-1	493	-50	>100 / 20	Polar	
Chloroform	67-66-3	21	61	0.85 / 20-24	Non-Polar	
Chloromethyl methyl ether	107-30-2	30	59	Reacts	Polar	Reactive
Chloroprene	126-99-8	30	59	Slightly soluble	Non-Polar	
Diazomethane	334-88-3	373	-23	Reacts	Polar	Highly reactive
1,1-Dimethylhydrazine	57-14-7	21	63	Reacts	Non-Polar	Reactive (?)
1,2-Epoxybutane	106-88-7	22	63	>100 / 17	Polar	Reactive
Ethyl chloride	75-00-3	133	13	>100 / 20	Non-Polar	
Ethyleneimine	151-56-4	21	56	Miscible	Polar	Reactive (?)
Ethylene oxide	75-21-8	147	11	Miscible	Polar	Reactive
Ethylidene dichloride	75-34-3	31	57	<1 / 20	Non-Polar	
Formaldehyde	50-00-0	360	-20	>100 / 20.5	Polar	
Hexane	110-54-3	16	69	<1 / 16.5	Non-Polar	
Methyl bromide	74-83-9	240	4	Slightly soluble	Non-Polar	Pesticide
Methyl chloride	74-87-3	507	-24	Slightly soluble	Non-Polar	
Methyl iodide	74-88-4	53	42	10-50 / 18	Non-Polar	
Methyl isocyanate	624-83-9	46	60	Reacts	Polar	Highly reactive
Methyl *tert*-butyl ether	1634-04-4	33	55	Soluble	Polar	
Methylene chloride	75-09-2	47	40	10-50 / 21	Non-Polar	
Phosgene	75-44-5	160	8	Slightly soluble	Polar	Reactive (?)
Propionaldehyde	123-38-6	31	49	50-100 / 18	Polar	Reactive
Propylene oxide	75-56-9	59	34	400 / 20	Polar	Reactive
1,2-Propyleneimine	75-55-8	15	66	>100 / 19	Polar	Highly reactive (?)
Vinyl bromide	593-60-2	147	16	Insoluble	Non-Polar	
Vinyl chloride	75-01-4	427	-14	Slightly soluble	Non-Polar	
Vinylidene chloride	75-35-4	67	32	5-10 / 21	Non-Polar	

[A] Compounds with vapor pressures > 15 kPa.

[B] Data taken from Ref. (**3**).

TABLE 2 Properties of Clean Air Act Volatile Organic HAP[A,B]

Compound	CAS No.	Vapor Pressure (kPa at 25°C)	Boiling Point (°C)	Water Solubility (g/L at °C)	Customary Classification	Reactivity in Air
Acetonitrile	75-05-8	9.86	82	>100 / 22	Polar	
Acetophenone	98-86-2	0.13	202	6.3 / 25	Polar	
Acrylamide	79-06-1	0.07	125/25 mm	>100 / 22	Polar	Reactive
Acrylic acid	79-10-7	0.43	141	>100 / 17	Polar	
Acrylonitrile	107-13-1	13.33	77	716.0 / 254	Polar	
Aniline	62-53-3	0.09	184	1.0 / 254	Polar	
o-Anisidine	90-04-0	0.01	224.0	<0.1 / 19	Polar	Reactive

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[3] The boldface numbers in parentheses refer to the list of references at the end of this standard.

TABLE 2 *Continued*

Compound	CAS No.	Vapor Pressure (kPa at 25°C)	Boiling Point (°C)	Water Solubility (g/L at °C)	Customary Classification	Reactivity in Air
Benzene	71-43-2	10.13	80	1-5 / 18	Non-Polar	
Benzyl chloride	100-44-7	0.13	179	Reacts	Non-polar	Reactive(?)
Bis (chloromethyl) ether	542-88-1	4.00	104	Reacts	Polar	Reactive
Bromoform	75-25-2	0.75	149	<0.1 / 22.5	Non-Polar	
Carbon tetrachloride	56-23-5	12.00	77	<1 / 21	Non-Polar	
Catechol	120-80-9	0.03	240	>100 / 21.5	Polar	
Chloroacetic acid	79-11-8	0.09	189	>100 / 20	Polar	
Chlorobenzene	108-90-7	1.17	132	<1 / 20	Non-Polar	
o-Cresol	95-48-7	0.03	191	25.9 / 25	Polar	
Cumene	98-82-8	0.43	153	Insoluble	Non-Polar	
1,2-Dibromo-3-chloropropane	96-12-8	0.11	196	<0.1 / 18	Non-Polar	
1,4-Dichlorobenzene	106-46-7	0.08	173	<1 / 23	Non-Polar	
Dichloroethyl ether	111-44-4	0.09	178	Reacts	Polar	Reactive(?)
1,3-Dichloropropene	542-75-6	3.71	112	<0.1 / 16.5	Non-Polar	
Diethyl sulfate	64-67-5	0.04	208	Reacts	Polar	Reactive(?)
N,N-Dimethylaniline	121-69-7	0.07	192	<1 / 21	Polar	
Dimethylcarbamyl chloride	79-44-7	0.65	166	Reacts	Polar	Highly reactive
N,N-Dimethyformamide	68-12-2	0.36	153	>100 / 22	Polar	
Dimethyl sulfate	77-78-1	0.13	188	>100 / 20	Polar	Reactive(?)
1,4-Dioxane	123-91-1	4.93	101	>100 / 20	Polar	
Epichlorohydrin	106-89-8	1.60	117	50-100- / 22	Polar	Highly reactive
Ethyl acrylate	140-88-5	3.91	100	4.2 / 204	Polar	
Ethylbenzene	100-41-4	0.93	136	<1 / 23	Non-Polar	
Ethyl carbamate	51-79-6	0.07	183	>100 / 22	Polar	
Ethyl dibromide	106-93-4	1.47	132	<1 / 21	Non-Polar	Pesticide
Ethylene dichloride	107-06-2	8.20	84	5-10 / 19	Non-Polar	Pesticide
Hexachlorobutadiene	87-68-3	0.05	215	<0.1 / 22	Non-Polar	
Hexachloroethane	67-72-1	0.05	Sublimes at 186	<1 / 21	Non-Polar	
Hexamethylphosphoramide	680-31-9	0.01	233	>100 / 18	Polar	
Isophorone	78-59-1	0.05	215	0.1-1 / 18	Polar	
Methanol	67-56-1	12.26	65	>100 / 21	Polar	
Methyl chloroform	71-55-6	13.33	74	<1 / 20	Non-Polar	
Methyl ethyl ketone	78-93-3	10.33	80	>100 / 19	Polar	
Methylhydrazine	60-34-3	6.61	88	<1 / 24	Non-Polar	Highly reactive
Methyl isobutyl ketone	108-10-1	0.80	117	1-5 / 21	Polar	
Methyl methacrylate	80-62-6	3.73	101	15.9 / 20	Polar	
Nitrobenzene	98-95-3	0.02	211	1.9 / 25	Polar	
2-Nitropropane	79-46-9	1.33	120	1.7 / 20	Polar	
N-Nitroso-N-methylurea	684-93-5	1.33	124	<1 / 18	Polar	Reactive
N-Nitrosodimethylamine	62-75-9	0.49	152	>100 / 19	Polar	Reactive
N-Nitrosomorpholine	59-89-2	0.04	225	>100 / 19	Polar	
Phenol	108-95-2	0.03	182	50-100- / 19	Polar	
1,3-Propane sultone	1120-71-4	0.27	180/30 mm	0.1	Polar	Reactive(?)
Beta-Propiolactone	57-57-8	0.45	Decomposes at 162	37.0 / 20	Polar	
Propylene dichloride	78-87-5	5.60	97	<0.1 / 21.5	Non-Polar	Pesticide
Quinoline	91-25-5	0.01	238	<0.1 / 22.5	Polar	
Styrene	100-42-5	0.88	145	<1 / 19	Non-Polar	
Styrene oxide	96-09-3	0.04	194	<1 / 19.5	Polar	Highly reactive
1,1,2,2-Tetrachloroethane	79-34-5	0.67	146	<0.1 / 22	Non-Polar	
Tetrachloroethylene	127-18-4	1.87	121	<0.1 / 17	Non-Polar	
Toluene	108-88-3	2.93	111	<1 / 18	Non-Polar	
o-Toluidine	95-53-4	0.01	200	5-10 / 15	Polar	
1,2,4-Trichlorobenzene	120-82-1	0.02	213	<1 / 21	Non-Polar	
1,1,2-Trichloroethane	79-00-5	2.53	114	1-5 / 20	Non-Polar	
Trichloroethylene	79-01-6	2.67	87	<1 / 21	Non-Polar	
Triethylamine	121-44-8	7.20	90	Soluble	Polar	Reactive (?) ; strong base
2,2,4-Trimethyl pentane	540-84-1	5.41	99	Insoluble	Non-polar	
Vinyl acetate	108-05-4	11.06	72	Insoluble	Polar	
o-Xylene	95-47-6	0.67	144	Insoluble	Non-Polar	
m-Xylene	108-38-3	0.80	139	Insoluble	Non-Polar	
p-Xylene	106-42-3	0.87	138	Insoluble	Non-Polar	

[A] Compounds with vapor pressures between 10^2 and 15 kPa.

[B] Data taken from Ref. **(4)**.

5.2 Organic compounds can be divided into four groups based on volatility (**1**).

5.2.1 VOCs with vapor pressures above 15 kPa at 25°C (boiling points typically below 30°C) are sometimes referred to as very volatile organic compounds (VVOCs). At room temperature and atmospheric pressure, VVOCs are present in the gas phase in air. Due to their high vapor pressures, VVOCs are generally more difficult to collect and retain on sorbents than other VOCs.

5.2.2 Volatile organic compounds typically have vapor pressures above 10^{-2} kPa at 25°C (typical boiling points from about 30 to 180°C). VOCs with boiling points at the upper end of the range still have a significant vapor pressure at room temperature and atmospheric pressure. At room temperature and atmospheric pressure VOCs are present in the gas phase in air.

5.2.3 Semivolatile organic compounds (SVOCs) typically have vapor pressures between 10^{-2} and 10^{-8} kPa at 25°C (typical boiling points from 180 to 350°C). SVOCs may be present in both the vapor and particulate phases (**1**).

5.2.4 Nonvolatile organic compounds have vapor pressures below 10^{-8} kPa at 25°C (boiling points typically above 300°C). Nonvolatile organic compounds occur primarily in the particulate phase.

NOTE 1—Boiling points are not reliable predictors of volatility. Some compounds that boil above 300°C are volatile at room temperature.

5.3 The polarity, water solubility, and reactivity of a VOC are critical in the choice of the sampling and analytical methods.

5.3.1 VOCs range in polarity from nonpolar (for example, propane) to very polar (for example, acetic acid). Polar organic compounds typically contain oxygen, nitrogen, sulfur, or other heteroatoms and may be categorized as either ionizable or polarizable. The former category includes alcohols, phenols, amines, and carboxylic acids; the latter includes ketones, ethers, nitro-compounds, nitriles, and isocyanates.

5.3.2 VOCs also range in reactivity from stable (for example, benzene) to highly reactive (for example, diazomethane). Polar compounds are often also reactive compounds and are generally more difficult to recover from sampling devices and present special analytical problems because of their chemical reactivities, affinities for metal and other surfaces, and water solubilities. These problems are more severe with ionizable compounds.

5.4 The sampling location and concentration of VOCs are also important in selecting a monitoring method. VOCs are typically found in indoor air in residences, offices, and public access buildings at concentrations ranging from 0.1 to 100 $\mu g/m^3$. VOC data may also be reported in parts per billion by volume (ppbv). The conversion between these reporting units is shown in Eq 1 and requires the molecular weight and the standard molar volume at standard temperature (273.15 K, 0°C) and pressure (101.3 kPa, 760 mm Hg):

$$C(ppbv) = C(\mu g/m^3) \times 22.4/molecular\ weight \quad (1)$$

NOTE 2—Indoor sampling is usually performed at temperature near 293 K (20°C). The standard molar volume at this temperature is 24.1 L/mol.

6. Selection of Sampling Methods for VOCs

6.1 The first criteria for selection of an appropriate method for sampling are the physical and chemical characteristics of the compounds to be monitored. Once the analyte has been characterized as a volatile compound, the appropriate measurement method (sampling and analysis) is chosen. Sampling methods can be active or passive.

6.1.1 Active methods employ some means of setting and controlling the air sampling rate (for example pump, syringe, or other vacuum source with a flow-controller).

6.1.2 Passive/diffusive sampling methods have sampling rates that depend on the molecular diffusion rate, sampling temperature, length and area of the diffusive path, and other conditions.

6.1.3 Active sampling methods can be divided into three broad types: whole air methods which use canisters, bags, or syringes; sorbent collection methods; and specialized sampling methods for reactive compounds.

6.1.4 Sampling can also be integrative (accumulative) or continuous (real-time).

6.2 *Whole Air Sampling:*

6.2.1 If the VOC of interest is relatively stable, and volatile enough to be recovered from an inert container, then whole air sampling may be a valid choice. The major advantage of whole air sampling is the ability to trap the most volatile compounds, since the entire air sample is collected and retained for subsequent analysis. A fraction of this sample is then concentrated under controlled conditions in the laboratory immediately prior to analysis.

6.2.2 Bags made from polyfluorinated polymer, polyester, or polyvinylidene plastics have been used for whole air sampling, but have the disadvantage of limited (24 to 48 h) useful sample holding times and should be used only when analyses can be performed within that time limit (**6, 7**). Shipping of bags is usually restricted to ground transport since changing pressures in aircraft shipping cause sample loss or contamination. Bags also have the disadvantage of being bulky and are inconvenient for personal monitoring.

6.2.3 Passivated stainless steel canisters are superior to bags for collection of whole air samples. Two ASTM test methods are available for use of this technique–Test Methods D5466 and D5953M. The canisters are treated with a proprietary electropolishing process to remove or cover reactive metal sites on the interior surface of the vessel (**8**). Another type of passivated stainless steel canister has the interior walls deactivated by a proprietary fused silica coating process (**9**).

6.2.3.1 Canister sampling is carried out by allowing the air to enter a pre-evacuated container either by way of a critical orifice or mass flow controller, or by using a pump to fill the canister to a pressure of a few atmospheres (**8**). For analysis, an aliquot (100 to 500 mL) of air is withdrawn from the canister and cryofocused into a GC attached to a mass selective detector, ion trap detector, or flame ionization detector. Detection limits are generally below 1 $\mu g/m^3$.

6.2.3.2 Various sizes are available from a number of commercial vendors that can be used to collect air volumes ranging from fractions of a litre to hundreds of litres.

6.2.3.3 Canisters have advantages over plastic bags for whole-air sampling. They display relatively good stabilities for VOCs (including some polar compounds) with vapor pressures above 10^{-2} kPa, greatly reduced problems due to contamination and artifact formation, the absence of breakthrough effects, and the ability to permit multiple analyses (**8**, **10**, **11**). Typical sample holding time before significant wall losses occurs is on the order of 35 days for most nonpolar VOCs of interest. Recovery of many polar VOCs from canisters is poor, however.

6.2.3.4 Whole air samples can be collected in canisters over a short period of time (grab samples) or integrated over a preselected period to time-weighted average concentrations.

6.2.3.5 Major disadvantages associated with the use of canisters include their high cost and bulkiness, the limited air volumes that can be sampled, difficulties experienced in recovering less volatile and more polar VOCs, and the co-collection of water.

6.2.3.6 Water is present in relatively large amounts in air samples and cause serious problems, such as ice formation that can clog the cryogenic trap. In the analysis of nonpolar compounds, the sample aliquot is normally passed through a dryer membrane tubing to remove the water (see Test Method D5466). This process also effectively removes many of the polar VOCs, however.

6.2.3.7 Water management techniques may be employed to selectively remove water, so that many polar VOCs can be determined with canister sampling (see Section 8).

6.3 *Air Sampling with Sorbents:*

6.3.1 Sorbents selectively accumulate VOCs during sampling. This is accomplished by removal of the VOC from the air matrix and retention of the VOC for subsequent analysis.

6.3.2 Collection of organic chemicals from air onto solid sorbents is a widely used air sampling methodology for both area or personal respiratory sample collection (**1**). Practices D3686 and D6196 describe the use of this technique for VOCs. Sorbents collect VOCs based on the physical and chemical characteristics of the VOC and sorbent. Retention mechanisms for sample collection on sorbents may be adsorption, absorption, chemisorption, or a combination of these. The efficiency of a sorbent for air sampling depends primarily on its capacity (usually defined by the *breakthrough* volumes of the analytes sought) and its ease of desorption. Other properties that affect overall performance are resistance to air flow (pressure drop), ability to trap particles, tendency toward artifact formation, and degree of water collection.

6.3.3 *Types of Sorbents for Air Sampling:*

6.3.3.1 Sorbents for air sampling can be classified into four types–inorganic, elemental carbon, carbonized (or graphitized) materials, and organic polymeric sorbents. There is a variety of sorbents to choose from and no one sorbent will efficiently collect and then release the entire range of VOCs. For sorbent sampling, great care should be taken to ensure that the sorbent adequately captures and releases compounds of interest. Sorbents typically have very limited capacities for VVOCs. Fig. 1 gives examples of sorbents and indicates their advantages and disadvantages.

6.3.3.2 Inorganic sorbents (for example, silica gel, alumina, magnesium silicate) are usually the most hydrophilic and are generally more effective at collecting very polar organic compounds (**1**). Compounds collected onto inorganic sorbents are typically desorbed with a solvent. Because of their high hydrophilicities, inorganic sorbents tend to collect water from the air, eventually being deactivated (that is, all of the sorptive sites become occupied with water) and cease to retain analytes effectively. In addition, there are often difficulties with separating co-collected water from the analytes during gas chromatographic separations. Method sensitivity may also be reduced due to the effects of water on the analytical detector.

6.3.3.3 Activated carbon sorbents are limited by the fact that it is difficult to desorb many organic compounds from them after sampling (for example, Practices D3686 and D3687) (**1**). This strong sorbate bonding, referred to as irreversible sorption, requires the use of polar solvents, such as carbon disulfide, for desorption. Compounds with a high degree of aromaticity or chemical functionality may be impossible to recover from activated charcoal.

6.3.3.4 Organic polymeric sorbents vary widely in their ability to trap VOCs from air and permit their desorption for analysis. 2,6-Diphenyl-*p*-phenylene oxide polymers, cross-linked polystyrene beads, porous styrene-divinylbenzene copolymers, and ethylvinylbenzene/divinylbenzene copolymers are hydrophobic and collect nonpolar VOCs more efficiently than polar VOCs (**1**). Vinylpryrrolidone polymers are hydrophilic and best suited for sampling for polar VOCs. Both are less likely to exhibit problems associated with atmospheric moisture than activated carbon sorbents.

6.3.3.5 Graphitized carbon and carbon molecular sieve sorbents are specially designed to bridge the gap between activated carbon and organic polymeric sorbents. Graphitized carbons are non-porous sorbents with relatively low surface areas (for example, 5 to 250 m^2/g). They are hydrophobic and have high thermal stabilities, but have lower capacities than most organic polymer resins. They are used alone or in a combination with other sorbents. Carbon molecular sieves are highly porous, with high surface areas (for example, 400 to 1200 m^2/g) and small pore sizes (for example, 1.5 to 4 nm), and are normally used in combination with other sorbents to collect VVOCs. They are somewhat hydrophilic. Both types of sorbents are more suitable for thermal desorption than activated charcoal.

6.3.3.6 Combinations of sorbents of differing types offer the advantages of extending the range of sampling capability. These combinations are often referred to as multisorbent beds (**12**, **13**). Typically, three sorbents of increasing retentivity are used (for example, polymeric, graphitized carbon, and carbon molecular seive). Air is drawn first through the weakest sorbent to trap less volatile compounds and last through the strongest sorbent to trap the more volatile compounds. Thermal desorption at temperatures up to 350°C are typically employed to desorb the VOCs. The desorption gas flow must be in the reverse direction from air sampling in order for components to be released efficiently from multisorbent tubes. While multisorbent tube sampling offers significant advantages over single sorbent sampling, there is always the risk that irreversible sorption (with resultant loss of analyte recovery) will occur due to break-through of less volatile VOCs to the stronger sorbent

Generic Sorbent Type	Example Sorbent Materials	Typical Target Analytes	Advantages and Comments	Limitations
Carbon	Petroleum-Based, Coconut- Based, Beaded Activated Charcoal	Very volatile compounds (VVOCs)	Thermal or Solvent sample recovery. Beaded activated carbon has the additional advantage of uniform mesh size, and more uniform recovery characteristics.	Irreversible adsorption of the less volatile VOC. Tend to be friable. Solvent desorption causes higher detection limits. Thermal desorption usually not feasible and/or shows artifacts and worse precision. Hydrophilic.
Carbonized Materials	Graphitized carbons	Intermediate volatility or specialized applications	Highly thermally stable. Thermal or solvent sample recovery depending on sorbent. Lower background, better recovery precision.	Low surface area, non-porous. Limited capacity. Thermally desorbable. Hydrophobic.
	Carbon molecular sieves	VVOCs	Same as above.	High surface area. Small pore size. Thermally desorbable. Somewhat hydrophilic. Normally used in combination with other sorbents.
Thermally-stable Polymers	2,6-diphenyl-*p*-phenylene oxide polymers	Intermediate volatility	May be thermally desorbed. Hydrophobic.	Benzene and other artifacts may occur.
Porous Polymers	Polystyrene, Styrene/divinylbenzene.	High-to-intermediate volatility	Limited thermal stability. Most commonly solvent desorbed. Hydrophobic.	Largely limited by solvent desorption to occupational concentrations.
	Vinylpyrrolidone polymers	Polar VOCs	Same as above except hydrophilic.	Same as above.
Multibed or Combination Sorbent Tubes	Combinations of sorbent materials from lesser to greater adsorption strength.	Multiple analytes over wider range of volatility.	Applicable to a wide range of VOC, including many VVOCs.	Less volatile VOCs may be irreversibly sorbed if sampling volume too large. Must be desorbed in reverse direction of sample collection.
Mineral	Silica Gel, Alumina, Magnesium silicate	Polar compounds	Can be coated with reactive matrix for special applications.	Low capacity, highly specific use, hydrophilic.
Special Sorbents for Reactive Compounds	DNPH on Silica Gel	Carbonyl compounds	Highly specific	Ozone interference. Scrubber may be required.
	HBr on carbon molecular sieve	Ethylene oxide.	Highly specific	Solvent desorption raises detection limit.
	Ion exchange resins	Organic acids or bases	Specific affinity for a limited class of VOC (e.g., amines, phenols).	Limited affinity for selected classes of compounds.

FIG. 1 Sorbents for VOC

beds. Therefore, extra care is required to fully evaluate the performance of the samplers for the target analytes.

6.4 *Sample Recovery from Sorbents:*

6.4.1 *Thermal Desorption:*

6.4.1.1 Thermal desorption has the advantage of providing maximum sensitivity, since all of the collected analyte is typically transferred quantitatively into the analytical system. Another advantage to thermal desorption is the lack of a solvent interference in chromatographic analysis.

6.4.1.2 Thermal desorption is generally limited to compounds with vapor pressures above 10^{-2} kPa (**1**). Some sorbents have such high affinities for certain VOCs that these compounds may be irreversibly sorbed (**1**). Charcoal sorbents in particular show this trend for the less volatile VOCs. Thermal decomposition of compounds that are thermally labile can occur (**14**).

6.4.1.3 If the concentrations of some or all of the compounds collected on the sorbent are higher than can be tolerated by the analytical instrument, the data for these compounds (or, in the worst case, for the entire sample) can be lost. Specialized equipment is required to split and perform replicate analysis on thermally-desorbed samples. In many cases, analytical equipment uses the entire sample during analysis. In these cases multiple, simultaneous samples must be taken if a measure of precision is required.

6.4.2 *Solvent Elution or Extraction:*

6.4.2.1 Solvent desorption offers the advantage that is permits recovery from the sorbent of organic compounds with lower volatility, polar compounds, and those that are thermally unstable or potentially reactive.

6.4.2.2 Solvent extracts generally can not be concentrated for VOC analysis due to the high probability for loss of analytes during this procedure, especially for compounds that have volatilities close to that of the desorption solvent. Therefore, the major disadvantage of solvent desorption is the loss of analytical sensitivity caused by dilution of the sample. On the other hand, solvent desorption offers the advantage of permitting replicate analyses since the entire solvent extract is not typically analyzed. It also permits derivatization prior to analysis, which can improve sensitivity. Improving analytical sensitivity by sample concentration may be possible in some cases with the use of isotopically-labeled internal standards to monitor and correct for evaporative losses during concentration.

6.4.2.3 The desorption solvent can also cause interferences in gas chromatographic separation or overwhelm the analytical instrument during the course of the analyses. Unless special precautions are taken (for example, chemical derivatization, ultrasensitive analysis techniques, special concentration techniques), solvent desorption generally limits detectability of VOC to the mg/m^3 (or ppmv) level because samples are diluted with solvents and typically are not concentrated after solvent elution.

6.5 *Reactive VOC Sampling Techniques:*

6.5.1 Reactive sampling differs from sorbent sampling only in that collection medium contains a reagent or reagents to react with the compounds of interest to produce products that can be more easily determined or that may be more efficiently retained by the sampler. Such collectors are usually designed for specific individual compounds or classes of compounds.

6.5.2 Examples of reactive sampling methods are Test Method D5197 for formaldehyde and other carbonyl compounds, octanoic acid on an organic polymeric resin for diazomethane (**15**), and hydrobromic acid on a carbon molecular sieve for ethylene and propylene oxides (**16**).

7. Sensitivity or Detection Limit as a Method Selection Criteria

7.1 Once the physical and chemical characteristics have been considered, and the sampling options have been reviewed, and next criterion for method selection is sensitivity. The analysis techniques associated with a sampling method have a bearing on the method sensitivity and certain sampling method choices affect analysis sensitivity. For example, concentration of samples before introduction in the analytical system (for example, by cryogenic or sorbent collection techniques) will increase method sensitivity, while use of an insensitive analytical detector, such as a thermal conductivity detector, may decrease overall method sensitivity.

7.2 Sensitivity for VOC monitoring techniques ranges from µg/m^3 (or parts per billion by volume) to ng/m^3 (or parts per trillion by volume). Sensitivities are typically better for techniques that concentrate samples during collection or analysis.

7.2.1 Whole air sampling techniques concentrate samples during analysis and typically have sensitivities down to 1 µg/m ^{3} (for example, canister sampling and GC/MS analysis).

7.2.2 Sensitivities in the ng/m^3 range are often possible with sorbent sampling followed by thermal desorption and cryogenic concentration.

7.3 Thermal desorption of appropriate sorbents usually provides the highest sensitivity. Solvent desorption will dilute samples and reduce the sensitivity of the method.

8. Water Management in VOC Sampling and Analysis

8.1 All air samples taken in real-world atmospheres contain water vapor, which may be collected along with the targeted VOCs to greater or lesser extent depending on the sampling method used.

8.2 If thermal desorption or cryogenic focusing is used, air samples may require special water management procedures in order to maintain sample integrity and allow analytical instruments to function properly. Potential problems include ice accumulation with possible plugging in the thermal desorption cryofocusing device and adverse effects on the chromatographic separation process.

8.3 Drying apparatuses, such as that used in Practice D5466, can effectively remove water vapor, but also remove most polar VOCs in the process.

8.4 Alternative methods for removing moisture from air samples prior to GC analysis include use of a multisorbent bed in a combined preconcentration and water management system. An example of a commercially-available two-stage trap based on a combination of graphized carbon and carbon molecular sieve sorbents is described in References **10** and **17**.

8.4.1 With this approach, the sorbent bed trap is typically used in lieu of a cryotrap to concentrate the VOCs from air collected by means of a canister. Since atmospheric moisture may be collected by the sorbent trap, it is then subjected to a dry purge at or near room temperature. In this process dry nitrogen is passed through it in the forward direction; that is, by fore-flushing. Water vapor is preferentially lost during the dry purge, after which the trap is heated and back-flushed with helium to thermally desorb the volatile compounds onto the GC column for analysis. Over 90 % of the water present is removed by this procedure.

NOTE 3—Several commerically-available purge and trap devices have an automated dry purge cycle that can be included in the analysis sequence.

8.4.2 Tests of the effectiveness of the two-stage trap for transferring polar VOCs to the GC have been conducted using humidified air samples containing the compounds of interest at levels below 5 $\mu g/m^3$ (**9**) These tests indicated that, for the most part, the transfer efficiency of the target compounds from the humidified sample to the GC by way of the trap was 70 to 100 %. A notable exception was vinyl acetate, for which the recovery efficiency was only 10 %.

8.5 When polar volatile organic compounds are sought, it may be necessary to reduce the sample volume, which increases the detection limit, so that the analytical equipment can function with the water still in the sample.

8.6 Instead of eliminating the water vapor prior to analysis as a means of dealing with the moisture problem, another method explicitly incorporates the water vapor into the analytical scheme (**18**). This approach is based on the capability of the quadrupole ion trap mass spectrometer for operating in the chemical ionization mode using the water vapor in the sample along with water from a separate vial as the reagent gas. While the potential of this technique has been clearly demonstrated, the water vapor present in the air sample passing through the GC degrades chromatographic performance to such an extent that special techniques, such as those described above, must still be incorporated into the analysis to remove the moisture.

9. Noise, Obtrusiveness, Security, and Safety

9.1 Several non-chemical factors should be considered in planning a VOC monitoring program. Indoor residential sampling can be restricted because of available space or by homeowner objections. Non-industrial workplace monitoring is often more flexible to space and noise restrictions. All sampling plans must consider the security of the monitoring equipment and samples, the security of the equipment in the monitoring environment, and the utility requirements of the equipment.

9.2 Equipment noise can be an issue depending on the size of the space being monitored, the acoustics of the area, and the presence of occupants. Noise from sampling equipment used in residences, schools, offices, and other relatively noise-free areas should be limited to 35 db (sones).

9.3 Space requirements for residential sampling often make larger ambient sampler use impractical or impossible. Personal monitoring pumps or small “suitcase” samplers are the preferred samplers. Devices with sampling rates higher than 20 to 25 L/min have limited indoor use since they may disturb the normal ventilation rate and lower the normal concentration of analytes in the room or building.

9.4 Security of sampling equipment should be considered in the plan. Typically, samplers that cannot easily be tampered with or changed by the homeowner or office worker are preferable to those with exposed sampling elements or controls. (For example the possibility of electrical power disruption or contamination by onlookers or passersby should be considered in the sampling plan for any effort). Samplers should also be secured against theft as necessary.

9.5 The safe use of the sampling equipment in the environment chosen for the monitoring should include at least two considerations–special safety requirements for sampler operation (exposure safety, radio frequency shielding or explosion potentials) and potential safety hazards to residents or workers present when they are near the sampling equipment.

10. Keywords

10.1 canisters; polarity; reactivity; sampling; semivolatile organic compounds; sorbents; SVOC; VOC; volatile organic compounds; volatility; VVOC; whole air

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