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Standard Guide for Selection of Methods for Active, Integrative Sampling of Volatile Organic Compounds in Air¹

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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 *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.*

¹ This guide is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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2. Referenced Documents

2.1 *ASTM Standards:*²

- D 1356 Terminology Relating to Sampling and Analysis of Atmospheres
- D 1357 Practice for Planning the Sampling of the Ambient Atmosphere
- D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)
- D 3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method
- D 5197 Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)
- D 5466 Test Method for Determination of Volatile Organic Chemicals in Atmospheres (Canister Sampling Methodology)
- D 5953M Test Method for Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection Method (Metric)
- D 6196 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 D 1356.

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).

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 D 5933M. 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, D 1357) 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.

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

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 <i>tert</i> -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	

^ACompounds with vapor pressures > 15 kPa.

^BData 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	

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
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
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	
Dimethylcarbonyl chloride	79-44-7	0.65	166	Reacts	Polar	Highly reactive
N,N-Dimethylformamide	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-Trimethylpentane	540-84-1	5.41	99	Insoluble	Non-polar	
Vinyl acetate	108-05-4	11.06	72	Insoluble	Polar	

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
<i>o</i> -Xylene	95-47-6	0.67	144	Insoluble	Non-Polar	
<i>m</i> -Xylene	108-38-3	0.80	139	Insoluble	Non-Polar	
<i>p</i> -Xylene	106-42-3	0.87	138	Insoluble	Non-Polar	

^ACompounds with vapor pressures between 10² and 15 kPa.

^BData 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 µg/m³. 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):

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

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