



## Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions From Indoor Materials/Products<sup>1</sup>

This standard is issued under the fixed designation D 5116; 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 reappraisal. A superscript epsilon (ε) indicates an editorial change since the last revision or reappraisal.

### 1. Scope

1.1 The use of small environmental test chambers to characterize the organic emissions of indoor materials and products is still evolving. Modifications and variations in equipment, testing procedures, and data analysis are made as the work in the area progresses. Until the interested parties agree upon standard testing protocols, differences in approach will occur. This guide will provide assistance by describing equipment and techniques suitable for determining organic emissions from indoor materials. Specific examples are provided to illustrate existing approaches; these examples are not intended to inhibit alternative approaches or techniques that will produce equivalent or superior results.

1.2 Small chambers have obvious limitations. Normally, only samples of larger materials (for example, carpet) are tested. Small chambers are not applicable for testing complete assemblages (for example, furniture). Small chambers are also inappropriate for testing combustion devices (for example, kerosene heaters) or activities (for example, use of aerosol spray products). For some products, small chamber testing may provide only a portion of the emission profile of interest. For example, the rate of emissions from the application of high solvent materials (for example, paints and waxes) via brushing, spraying, rolling, etc. are generally higher than the rate during the drying process. Small chamber testing can not be used to evaluate the application phase of the coating process.

1.3 The guide does not provide specific guidance for determining emissions of formaldehyde from pressed wood products, since large chamber testing methods for such emissions are well developed and widely used. For more information refer to Test Method E 1333. It is possible, however, that the guide could be used to support alternative testing methods.

1.4 The guide is applicable to the determination of emissions from products and materials that may be used indoors. The effects of the emissions (for example, toxicity) are not addressed and are beyond the scope of the guide.

1.5 As an ASTM guide, options are described, but specific courses of action are not recommended. The purpose of this guide is to increase the awareness of the user to available techniques for evaluating organic emissions from indoor materials/products via small chamber testing and to provide information from which subsequent evaluation and standardization can be derived.

1.6 Within the context of the limitations discussed in this section, the purpose of this guide is to describe the methods and procedures for determining organic emission rates from indoor materials/products using small environmental test chambers. The techniques described are useful for both routine product testing by manufacturers and testing laboratories and for more rigorous evaluation by indoor air quality (IAQ) researchers. Appendix XI provides additional references for readers wishing to supplement the information contained in this guide.

1.7 The values stated in SI units are to be regarded as standard.

1.8 *This standard does not purport to address 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 1193 Specification for Reagent Water<sup>2</sup>

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres<sup>3</sup>

D 1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres<sup>3</sup>

D 3195 Practice for Rotameter Calibration<sup>3</sup>

D 3609 Practice for Calibration Techniques Using Permeation Tubes<sup>3</sup>

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)<sup>3</sup>

<sup>1</sup> 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.

Current edition approved December 10, 1997. Published February 1998. Originally published as D 5116 – 90. Last previous edition D 5116 – 90.

<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.03.

D 3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method<sup>3</sup>

E 355 Practice for Gas Chromatography Terms and Relationships<sup>4</sup>

E 1333 Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Using a Large Test Chamber<sup>5</sup>

### 3. Terminology

3.1 *Definitions*—For definitions and terms used in this guide, refer to Terminology D 1356. For an explanation of units, symbols, and conversion factors, refer to Practice D 1914.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *air change rate*—the flow rate of clean, conditioned air into the chamber divided by the chamber volume; usually expressed in units of h<sup>-1</sup>.

3.2.2 *product loading*—the ratio of the test specimen area to the chamber volume.

### 4. Significance and Use

4.1 *Objectives*—The use of small chambers to evaluate organic emissions from indoor materials has several objectives:

4.1.1 Develop techniques for screening of products for organic emissions;

4.1.2 Determine the effect of environmental variables (that is, temperature, humidity, air exchange) on emission rates;

4.1.3 Rank various products and product types with respect to their emissions profiles (for example, emission factors, specific organic compounds emitted);

4.1.4 Provide compound-specific data on various organic sources to guide field studies and assist in evaluating indoor air quality in buildings;

4.1.5 Provide emissions data for the development and verification of models used to predict indoor concentrations of organic compounds; and

4.1.6 Develop data useful to manufacturers and builders for assessing product emissions and developing control options or improved products.

4.2 *Mass Transfer Considerations*—Small chamber evaluation of emissions from indoor materials requires consideration of the relevant mass transfer processes. Three fundamental processes control the rate of emissions of organic vapors from indoor materials; evaporative mass transfer from the surface of the material to the overlying air, desorption of adsorbed compounds, and diffusion within the material. For more information, refer to Bird, Stewart, and Lightfoot (1960) and Bennett and Myers (1962) in X1.1.

4.2.1 The evaporative mass transfer of a given organic compound from the surface of the material to the overlying air can be expressed as:

$$E = km(VP_s - VP_a) \quad (1)$$

where:

$E$  = emission rate,

$km$  = mass transfer coefficient,

$VP_s$  = vapor pressure at the surface of the material, and

$VP_a$  = vapor pressure in the air above the surface.

Thus, the emission rate is proportional to the difference in vapor pressure between the surface and the overlying air. Since the vapor pressure is directly related to the concentration, the emission rate is proportional to the difference in concentration between the surface and the overlying air. The mass transfer coefficient is a function of the diffusion coefficient (in air) for the specific compound of interest, the level of turbulence in the bulk flow.

4.2.2 The desorption rate of compounds adsorbed on materials can be determined by the retention time (or average residence time) of an adsorbed molecule:

$$\tau = \tau_o e^{Q/RT} \quad (2)$$

where:

$\tau$  = retention time, s,

$\tau_o$  = constant with a typical value from 10<sup>-12</sup> to 10<sup>-15</sup> s,

$Q$  = molar enthalpy change for adsorption (or adsorption energy), J/mol,

$R$  = gas constant, 8.314 J/mol-K, and

$T$  = temperature, K.

The larger the retention time, the slower the rate of desorption.

4.2.3 The diffusion mass transfer within the material is a function of the diffusion coefficient (or diffusivity) of the specific compound. The diffusion coefficient of a given compound within a given material is a function of the compound's physical and chemical properties (for example, molecular weight, size, and polarity), temperature, and the structure of the material within which the diffusion is occurring. The diffusivity of an individual compound in a mixture is also affected by the composition of the mixture.

4.2.4 *Variables Affecting Mass Transfer*—While a detailed discussion of mass transfer theory is beyond the scope of this guide, it is necessary to examine the critical variables affecting mass transfer within the context of small chamber testing:

4.2.4.1 Temperature affects the vapor pressure, desorption rate, and the diffusion coefficients of the organic compounds. Thus, temperature impacts both the mass transfer from the surface (whether by evaporation or desorption) and the diffusion mass transfer within the material. Increases in temperature cause increases in the emissions due to all three mass transfer processes.

4.2.4.2 Air change rate is flow of outdoor air entering the indoor environment divided by the volume of the indoor space, usually expressed in units of h<sup>-1</sup>. The air exchange rate indicates the amount of dilution and flushing that occurs in indoor environments. The higher the air change rate the greater the dilution, assuming the indoor air is cleaner, and the lower the concentration. If the concentration at the surface is unchanged, a lower concentration in the air increases the evaporative mass transfer by increasing the difference in concentration between the surface and the overlying air.

4.2.4.3 *Air Velocity*—The mass transfer coefficient ( $km$ ) is affected by the velocity in the boundary layer above the surface and the level of turbulence. Generally, the higher the velocity

<sup>4</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>5</sup> Annual Book of ASTM Standards, Vol 04.10.

and the higher the level of turbulence, the greater the mass transfer coefficient. In a practical sense, above a certain velocity and level of turbulence, the resistance to mass transfer through the boundary layer is minimized (that is, the mass transfer coefficient reaches its maximum value). In chamber testing, some investigators prefer to use velocities high enough to minimize the mass transfer resistance at the surface. For example, air velocities of 0.3 to 0.5 m/s have been used in evaluating formaldehyde emissions from wood products. Such velocities are higher than those observed in normal residential environments by Matthews et al.,<sup>6</sup> where in six houses they observed velocities with a mean of 0.07 m/s and a median of 0.05 m/s. Thus, other investigators prefer to keep the velocities in the range normally found indoors. In either case, an understanding of the effect of velocity on the emission rate is needed in interpreting small chamber emissions data.

**4.3 Other Factors Affecting Emissions**—Most organic compounds emitted from indoor materials and products are non-reactive, and chambers are designed to reduce or eliminate reactions and adsorption on the chamber surfaces (see 5.2.1). In some cases, however, surface adsorption can occur. Some relatively high molecular weight, high boiling compounds can react (that is, with ozone) after being deposited on the surface. In such cases, the simultaneous degradation and buildup on and the ultimate re-emission from the chamber walls can affect the final chamber concentration and the time history of the emission profile. Unless such factors are properly accounted for, incorrect values for the emission rates will be calculated (see 9.4). The magnitude of chamber adsorption and reaction effects can be evaluated by way of mass balance calculations (see 9.5). For further information on these processes see Jaycock, et al. (X1.1).

**4.4 Use of the Results**—It is emphasized that small chamber evaluations are used to determine source emission rates. These rates are then used in IAQ models to predict indoor concentration of the compounds emitted from the tested material. Consultation with IAQ modelers may be required to ensure that the small chamber test regime is consistent with the IAQ model assumptions. The concentrations observed in the chambers themselves should not be used as a substitute for concentrations expected in full-scale indoor environments.

## 5. Facilities and Equipment

**5.1** A facility designed and operated to determine organic emission rates from building materials and consumer products found indoors should contain the following: test chambers, clean air generation system, monitoring and control systems, sample collection and analysis equipment, and standards generation and calibration systems. Fig. 1 is a schematic showing an example system with two test chambers.

**5.2 Environmental Test Chambers**—Small environmental test chambers are designed to permit the testing of samples of various types of building materials and consumer products.

<sup>6</sup> Matthews, T. J., Thompson, C. V., Wilson, D. L., Hawthorne, A. R., and Mage, D. T. "Air Velocities Inside Domestic Environments: An Important Parameter for Passive Monitoring," *Indoor Air '87—Proceedings of the 4th International Conference on Indoor Air Quality and Climate*, Institute for Water, Soil and Air Hygiene, West Berlin, Vol 1, August 1987, pp. 154-158.

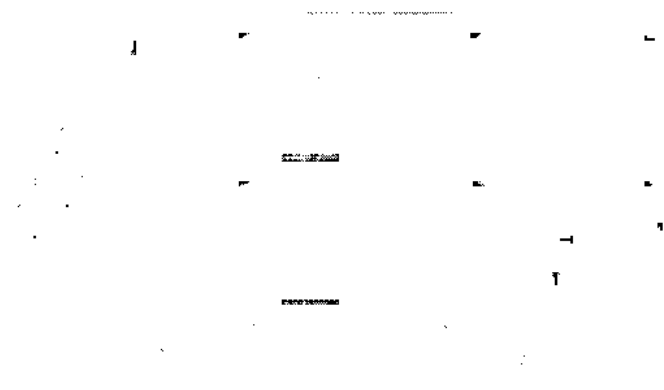


FIG. 1 Small Chamber Test Facility Schematic

They can range in size from a few litres to 5 m<sup>3</sup>. Generally, chambers of more than 5 m<sup>3</sup> are considered "large." Large chambers permit the testing of complete assemblages (for example, furniture); they may also be used to evaluate activities (for example, spray painting). For the purpose of this guide, small chambers are assumed to be used to test samples of larger materials and products, as opposed to full scale materials or processes.

**5.2.1 Construction**—Small environmental test chambers should have non-adsorbent, chemically inert, smooth interior surfaces so as not to adsorb or react with compounds of interest. Care must be taken in their construction to avoid the use of caulks and adhesives that emit or adsorb volatile organic compounds. Electropolished stainless steel and glass are common interior surfaces. The chamber must have an access door with air tight, non-adsorbent seals. The chambers must be fitted with inlet and outlet ports for air flow. Ports for temperature and humidity probes may also be required. Ports for sample collection are needed only if the sampling is not conducted in the outlet air (see 6.2).

**5.2.2 Mixing**—The chamber and its air moving components need to be designed to ensure good mixing of the incoming air with the chamber air. While contaminant concentration gradients are expected to exist in the chamber, particularly near the emissions source, the mixing issue concerns only the uniformity of the distribution of the air entering the chamber. Mixing fans and multi-port inlet and outlets are two techniques that have been used successfully to ensure adequate mixing of air in the chamber.

**5.2.2.1 Assessment of Air Mixing**—The adequacy of mixing in the chamber can be assessed using a tracer gas decay test, but other approaches may also be useful. Tests to determine the adequacy of mixing should be conducted not only in an empty chamber, but also with inert substrates of the types of samples to be tested to ensure that placement of the samples in the chamber will not result in inadequate mixing.

**5.2.2.2 Decay Test for Quantifying Mixing**—The decay approach involves establishing a uniform tracer gas concentration within the chamber and monitoring the tracer gas concentration decay in the outlet air over time. A uniform concentration can be established by injecting tracer at a constant rate and waiting until the outlet air concentration has reached equilibrium. The monitoring of the decay should start as soon as the

tracer gas injection is stopped and continue for at least one time constant  $t_n$ , where  $t_n$  equals the inverse of the chamber air change rate. In this analysis, the tracer gas concentration is assumed to equal zero in the inlet air during the decay. The degree of mixing is assessed by determining a mixing level  $\eta$  defined as follows:

$$n = \left\{ 1 - \frac{\sum_{i=1}^n [C_m(t_i) - C(t_i)](t_i - t_{i-1})}{\sum_{i=1}^n [C(t_i) (t_i - t_{i-1})]} \right\} \times 100 \% \quad (3)$$

where:

- $\eta$  = mixing level,
- $N$  = chamber air change rate in units of inverse time,
- $t_n$  = time constant of chamber =  $N^{-1}$ ,
- $C_m(t_i)$  = tracer gas concentration in chamber exhaust,
- $C(t_i)$  = concentration for perfectly mixed system, calculated by  $C(t) = C_{oa} e^{-Nt}$ ,
- $n$  = number of discrete concentration measurements, and
- $t_i$  = time of  $i$ th concentration measurement, and
- $C_{oa}$  = tracer gas concentration at  $t=0$ .

If the mixing level  $\eta$ , as determined using Eq 3, is above 80 %, then the air mixing within the chamber can be considered adequate.

**5.2.3 Surface Velocity**—As discussed in 4.2.4.3, the velocity near the surface of the material being tested can affect the mass transfer coefficient. Thus, sources with evaporative (gas-phase limited) emissions should be tested under typical indoor velocities (for example, 5 - 10 cm/s). A small fan can be used to achieve such velocities. Some investigators have had success with DC voltage computer fans (the ones used to cool the chips). The fan can be suspended above the source with wire. A diffuser should be used to eliminate the calm spot downstream of the fan hub. If the air stream is directed upward, the air will circulate and flow across the source. Velocity measurements can be made with hot wire or hot film anemometers. These devices typically have lower detection limits of 3 to 5 cm/s. Velocities should be measured close to the source; for example, a height of 1 cm above the surface of a horizontal source. An average velocity can be based on measurements at several locations. For example, a source area could be divided into grid sectors (for example, 2 by 3, 3 by 4, and so forth) and measurements made at the sector mid-points. Without a fan, velocities near the source surface will be below the detection limit of the anemometer. If the emissions from the source being tested are limited by diffusion within the source, a fan is not necessary. For example, multisorbent traps containing glass beads, Tenax, Amborsorb, and charcoal have been used for quantitative collection and thermal desorption of compounds with boiling points from 36 to 253°C. Multisorbent traps containing graphitized carbons and carbon molecular sieve are also useful for collection and thermal desorption of a broad range of analytes. Recoveries of analytes may vary dramatically from one medium to another as well as with desorption temperature or other factors.

**5.2.4 Temperature Control**—Temperature control can be achieved by placing the test chambers in incubator cabinets or other controllable constant temperature environments. The temperature of the inlet air can be controlled by using conditioning coils.

**5.2.5 Lights**—Small chambers are normally operated without lights. If the effect of lighting on emissions is to be determined, appropriate interior illumination should be provided. If lighting is used, care should be taken to avoid heating of the chamber interior.

**5.3 Clean Air Generation System**—Clean air must be generated and delivered to the chambers. A typical clean air system might use an oilless compressor drawing in ambient air followed by removal of moisture (for example, using a membrane dryer) and trace organics (for example, by catalytic oxidation units). Other options include gas cylinders or charcoal filtered outside or laboratory air. If granular media (for example, charcoal) are used for control of organics, a filter should be used downstream to remove particulate matter. Calculations should be conducted on the amount of air flow required before a decision is reached on the supply system. For most sources to be tested, extremely clean air is needed. Inlet concentrations should not exceed 2  $\mu\text{g}/\text{m}^3$  for any single compound or 10  $\mu\text{g}/\text{m}^3$  for the sum of all VOCs. The purity of the air should be verified by routine analysis of background air samples from a clean chamber.

**5.3.1 Humidity Control**—Humidity control of the chamber air is achieved by adding deionized water (see Specification D 1193) or HPLC grade distilled water to the air stream. Injection by syringe pumps followed by heating to vaporize the water can achieve desired humidity levels, although syringe pumps are prone to breakdown during prolonged, continuous use. Other types of pumps (for example, HPLC) might also provide sufficient accuracy. Humidification can also be accomplished by bubbling a portion of the airstream through deionized water at a controlled temperature (for example, in a water bath). The saturated air is then mixed with dry air to achieve the desired humidity. Steam humidification can also be used. Coiled lines inside the constant temperature environment can be used for inlet temperature equilibration before delivery to the test chambers.

**5.4 Environmental Measurement and Control Systems**—Measurement and control are required for air flow, temperature, and humidity. Air flow can be automatically monitored and controlled by electronic mass flow controllers, or manual flow control (for example, needle valve, orifice plate) and measurement (for example, bubble meter, rotameter) (see Practice D 3195) can be used. Some investigators recommend that the chamber be operated slightly above atmospheric pressure and that measurements be made of both atmospheric and chamber pressure. Temperature control is discussed in 5.2.4. Temperature measurement can be accomplished automatically via thermocouples or thermistors; manual dial or stem thermometers can also be used. Control of humidity depends on the humidification system employed. If liquid injection is used, water flow is controlled by the pump setting.

Control of humidity by saturated air requires temperature control of the water and flow control of the saturated air stream. Humidity measurement can be done by several types of sensors, including dew point detectors and thin-film capacitors. Temperature and humidity sensors should be located inside the chamber at least 5 cm from the inside wall and near the midpoint between the air inlet and outlet ports.

5.4.1 *Automatic Systems*—Microcomputer based measurement and control systems can be used to set air flow rates and monitor temperature, relative humidity and air flow during the course of experiments. Analog signals from temperature, relative humidity, and flow sensors are converted to digital units that can be stored by a microcomputer-based system, then processed to engineering units using appropriate calibration factors. In this way, chamber environmental data can be continuously monitored, then compiled and reduced for archival storage or display with minimal operator effort. Automatic systems are also capable of certain control functions. Digital signals can be output to control valves or converted to analog signals and sent out as set point signals to mass flow controllers. A graphics overlay program can be used to show current setpoints and measured values on a system schematic displayed on the microcomputer's monitor.

5.4.2 *Manual Systems*—While automatic systems provide enhanced data collection and control, they are also expensive and complex. The simplicity and low cost of manual systems may be preferable under many circumstances.

## 6. Sample Collection and Analysis

6.1 Indoor sources of organic emissions vary widely in both the strength of their emissions and the type and number of compounds emitted. Differences in emissions rates of several orders of magnitude among sources is not unusual. To characterize organic emissions fully, the sample collection/analysis system must be capable of quantitative collection and analysis of volatile, semivolatile, polar, and non-polar compounds. Any small chamber sampling and analysis technique or strategy developed must consider the emission characteristics of the specific source being evaluated. The design and operation of sample collection and analysis systems must be appropriate for the organic compounds (and their concentrations) being sampled. Such systems generally include sampling devices (for example, syringes, pumps), sample collectors (for example, syringes, adsorbent media, evacuated canisters), and instruments to analyze organic emissions (for example, gas chromatographs [GC], see Practice E 355). The remainder of this section provides a discussion of the alternatives available for small chamber sampling and analysis of organic emissions; technical details of specific systems are not included.

6.2 *Sampling Devices*—The exhaust flow (for example, chamber outlet) is normally used as the sampling point, although separate sampling ports in the chamber can be used. A multipoint sampling manifold can provide flexibility for duplicate samples. A mixing chamber between the test chamber and the manifold can be used to permit addition and mixing of internal standard gases with the chamber air stream. Sampling ports with septums are needed if syringe sampling is to be conducted. The sampling system should be constructed of inert material (for example, glass, stainless steel), and the system

should be maintained at the same temperature as the test chambers. The exhaust from the sampling system should be ducted into a fume hood, ensuring that any hazardous chemicals emitted by the test materials are isolated from the laboratory environment.

6.2.1 Samples can be drawn into gas tight syringes, GC sampling loops, evacuated canisters, or through sorbent cartridges using sampling pumps. Gas tight syringes and closed-loops are frequently used when chamber concentrations are high and sample volumes must be small to prevent overloading of the analytical instrument. Larger volume samples can be pulled through sorbent cartridges using sampling pumps. Flow rate can be controlled by an electronic mass flow controller or other means. The sampling flow rate should be regulated to prevent instabilities in the chamber system flow. Generally, this will require that the sampling flow rate be limited to <50 % of the chamber flow rate. Valves and a vacuum gage may be incorporated into the system to permit verification of system integrity before samples are drawn. The entire system can be connected to a programmable electronic timer to permit unattended sample collection.

6.3 *Sample Collection Media*—Selection of appropriate sample collection technique(s) will depend upon factors such as boiling point, polarity, and concentration ranges of the compounds of interest, as well as the amount of water vapor in the sample airstream. No single sample collection, concentration, and delivery system will be adequate for all analytes of interest, and the user must understand the limitations of any system used to characterize source emissions. If the sample is collected by way of syringe or closed-loop sampling, it is injected directly into a GC or other instrument for analysis. Collection in a sampling bag (for example, Tedlar<sup>7</sup>) or vessel (for example, glass, stainless steel) allows for larger samples. For many small chamber evaluations of indoor materials, low concentrations of the compounds of interest require large volume samples, and collection on an appropriate adsorbent medium is required. Several sorbent materials are available for use, singly or in combination, including activated carbon (see Practice D 3686), glass beads, Amborsorb,<sup>8</sup> Tenax<sup>9</sup> (polyphenylene oxide), graphitized carbon, and XAD-2.<sup>10</sup> The selection of the sorbent (or sorbent combination) depends on the compound(s) to be collected. XAD-2<sup>10</sup> resin can be used to collect compounds considered to be semi- or non-volatile (for example, boiling points above 180°C). If sorbent collection is used, the laboratory must be equipped with appropriate storage capabilities. Air tight glass tubes or chemically inert bags are both appropriate. Flushing the storage containers with high purity nitrogen prior to use will help assure their cleanliness. Samples should be stored in a freezer at -20°C. If possible, sorbent samples should be desorbed and analyzed within 48 h of collection.

6.3.1 When sorbents are used for sample collection, desorption and concentration is necessary (see Practice D 3687). For

<sup>7</sup> Tedlar is a registered trademark of Dupont.

<sup>8</sup> Amborsorb is a registered trademark of Rohm and Haas.

<sup>9</sup> Tenax is a registered trademark of Tmka Research Institute.

<sup>10</sup> XAD-2 is a registered trademark of Rohm and Haas.

example, a clamshell oven can be used to thermally desorb sorbent cartridges with the vapors fed to the concentrator column of a purge and trap concentrator that thermally desorbs the organic compounds to the GC column. Supercritical fluid or solvent extraction and liquid injection to the GC can also be employed. Other concentration techniques are also available, including cryotrapping.

**6.4 Organic Analysis Instrumentation**—A variety of analytical instruments is available for determining the concentration of the organics sampled from the chamber, with GCs being the most commonly used. GCs have a wide variety of columns available for separating organic compounds. Capillary columns are generally preferred. Several detectors can be used depending on the purpose of the test and the compounds of interest. Mass spectrometers (MS) are the most versatile and can be used in the scan mode to identify unknown compounds. When used in the scan mode, a conventional MS has a sensitivity of about  $10^{-9}$  g. An ion trap may have a sensitivity approaching  $10^{-12}$  g in the scan mode. If conventional MS is being used to analyze for known compounds, it is operated in the selected ion mode where its sensitivity increases to  $10^{-12}$  g. MS can be made even more sensitive via negative ionization. Flame ionization detectors (FID) are also widely used. They respond to a wide variety of organic compounds and have a sensitivity of  $10^{-11}$  g. Electron capture detectors (ECD) are used for analyzing electronegative compounds (for example, halogenated organics) and have a sensitivity of  $10^{-13}$  g. Some compounds are not easily measured with GCs; for example, low molecular weight aldehydes require other instrumentation (for example, HPLC or wet chemical colorimetric).

**6.5 Standards Generation and System Calibration**—Calibration gas may be added to the test chamber or sampling manifold from permeation ovens (see Practice D 3609), gas cylinders, or dilution bottles. Calibration (or tracer) gas is added through the test chamber in tests to determine chamber mixing, check for leaks, or to evaluate chamber “sink” effects. Internal standards for quality control may be added at the head of the sampling system. The internal standard should not be added to the chamber due to the potential for adsorption on the material being tested. Quality control can also be achieved by spiked samples.

## 7. Experimental Design

**7.1 Test Objectives**—The first step in designing an experiment for chamber tests of indoor materials/products is to determine the test objectives. For example, a builder or architect would be interested in emissions from a variety of materials to be used under a given set of conditions for a specific building. In this case, the experiment would be designed to handle many materials with one set of environmental conditions. A manufacturer might want to know the emissions characteristics of a single product under both normal and extreme conditions and would design a test to cover the appropriate range of environmental variables. IAQ researchers interested in the interactions among variables would use a more complex design involving ranges of several variables.

**7.2 Critical Parameters**—A basic experimental design for small chamber tests should include consideration of the effects of various parameters on the emission characteristics of the

materials to be tested. Six variables are generally considered to be critical parameters: temperature [ $T$ ], humidity [ $H$ ], air exchange rate [ $N$ ], product loading [ $L$ ], time [ $t$ ], and air velocity [ $v$ ].

**7.2.1 Temperature** ( $^{\circ}\text{C}$ ), [ $T$ ] affects the vapor pressure, diffusion coefficient (diffusivity), and desorption rates of the organic compounds in the materials/products and can have a major impact on emission rates.

**7.2.2 Humidity**, [ $H$ ] has been shown to affect the emission rate of formaldehyde from particleboard and may have similar effects for other water-soluble gases. Humidity can be expressed in relative (% of saturation) or absolute (g water/ $\text{m}^3$  air) terms.

**7.2.3 Air Exchange Rate** ( $\text{h}^{-1}$ ), [ $N$ ] is determined by the flow rate of clean air to the chamber divided by the chamber volume. The air exchange rate indicates the amount of dilution and flushing that occurs in indoor environments and can have a major impact on chamber concentrations.

**7.2.4 Product Loading** ( $\text{m}^2/\text{m}^3$ ), [ $L$ ] is the ratio of the test specimen area to the chamber volume. This variable allows product usage in the test chambers to correspond to normal use patterns for the same product in “full scale” environments. Studies of formaldehyde emissions have shown that the ratio of air change rate ( $N$ ) to product loading ( $L$ ) is proportional to the emission rate. Thus, ( $N/L$ ) is often selected as a parameter in designing chamber experiments. In some cases, the configuration of the source makes product loading an inappropriate parameter. For example, studies of sealants often employ elongated beads. In this case, the configuration and length of the bead are appropriate experimental design parameters.

**7.2.5 Age** (hours, days, etc.), [ $t$ ] is a critical parameter, since most materials have emission rates that vary with time. Fresh, wet solvent-containing products can have emission rates that vary several orders of magnitude in a few hours; other materials such as pressed wood products may have emission rates that take several years to decay.

**7.2.6 Air Velocity** (cm/s or m/s), [ $v$ ] is a critical parameter, because the air velocity over the surface of the emitting source can affect the emission rate, especially for wet, evaporative sources (see 4.2.4.3 and 5.2.3).

**7.3 Product History**—Information on the history of the material/product to be tested is useful in designing the testing program. Details of manufacture, production, or assembly may be useful in determining compounds to be emitted. Information on product age, treatment (for example, coatings, cleaning), storage conditions (that is, time, temperature, humidity, ventilation), and handling/transportation may provide additional insight. For example, older materials may emit at a lower rate than new materials; materials stored at high temperatures may also have lower emission rates when tested; storage or transportation with other materials may cause adsorption of organics that will be emitted during the chamber tests.

**7.4 Selection of Sample to be Tested**—The method used to select samples of materials for evaluation in small chambers depends on the purpose of the proposed testing.

**7.4.1** If the purpose is to develop emission rates that are representative of a given product or material (or class of products or materials), a statistically based sampling strategy

(for example, random, stratified, systematic) should be developed and implemented. The sampling strategy may be applied to the selection of multiple items (for example, cans of paint) or multiple sub-samples of a complete piece of material (for example, carpet). A statistical consultant should be used to assist in the design of such a strategy. Also, ASTM standards for sampling are available for many types of materials, and they should be reviewed.

7.4.2 If, on the other hand, the purpose of the testing is to investigate the effect of environmental variables on the emission rates of a type of indoor source, a simple “off the shelf” retail purchase of one or more “brand names” of the product may be adequate. However, if the emission mechanisms, the VOCs emitted, or the magnitude of the emissions differ significantly between materials apparently of the same “type”, the observed effects of the environmental variables may differ with different choices of test material. It may be that the magnitude of the effects of environmental variables applies only to the particular test material evaluated. This same technique may also be used to compare emissions among various manufacturers of the same product. Because of the effect of product history (see 7.3) on the emission characteristics of materials, when making such comparisons it is important to assure that the histories of the products being compared are the same. It is also important that the products are, in fact, the same; for example, products made for residential or commercial use can have widely varying emission characteristics.

7.4.3 A detailed discussion of sampling strategies is beyond the scope of this guide. The reader should consult appropriate statistical references for further information.

7.5 *Test Matrix*—For each material tested, a test matrix is developed to allow the variables of interest to be investigated. As is normal in experimental programs of this type, the desire to collect data over an extensive parameter range is limited by cost and time constraints. To maximize the information production within available resources, a statistical consultant can be used to provide guidance on appropriate experimental designs. Table 1 is an example of a test matrix developed to evaluate the effect of several variables on emission factors.

## 8. Experimental Procedures

8.1 *Emissions Composition*—A preliminary evaluation of the product/material is performed to guide selection of appropriate test strategies and analytical techniques. This evaluation is conducted to obtain information on the specific compounds to be quantified. If only a single compound is to be quantified, selection of the appropriate sampling and analysis strategy is straightforward, and no further screening is needed. When a more complete characterization is desired, more information is required. An initial evaluation of the composition of the emissions expected from a source can be conducted by surveying available information, including: reports or papers on previous studies of the source, ingredients listed on the product label, material safety data sheets (MSDS), and information obtained from the manufacturer or appropriate trade organizations. Such information is usually insufficient to identify the compounds of interest, but it does provide some guidance in what compounds to look for. Analysis of the

**TABLE 1 Example Test Matrix**

NOTE 1 This test matrix covers five experimental conditions, each with two replicates (A and B). The test matrix was designed to evaluate the effect of specific parameters as follows:

*Effect of Temperature (T)*—Tests 1 and 5;

*Effect of Air Exchange Rate (N)*—Tests 1, 2, and 3;

*Effect of Product Loading (L)*—Tests 2 and 4; and

*Evaluation of Constant N/L*—Tests 1 and 4.

The effect of humidity was not examined during this set of experiments. The effect of age was investigated by collecting multiple samples over the drying time of the product.

| Test Number | Temperature (°C) | RH (%) | N (h <sup>-1</sup> ) | L (m <sup>2</sup> /m <sup>3</sup> ) | N/L (m/h) |
|-------------|------------------|--------|----------------------|-------------------------------------|-----------|
| 1A          | 23               | 50     | 0.5                  | 0.2                                 | 2.5       |
| 1B          | 23               | 50     | 0.5                  | 0.2                                 | 2.5       |
| 2A          | 23               | 50     | 1.0                  | 0.2                                 | 5.0       |
| 2B          | 23               | 50     | 1.0                  | 0.2                                 | 5.0       |
| 3A          | 23               | 50     | 2.0                  | 0.2                                 | 10.0      |
| 3B          | 23               | 50     | 2.0                  | 0.2                                 | 10.0      |
| 4A          | 23               | 50     | 1.0                  | 0.4                                 | 2.5       |
| 4B          | 23               | 50     | 1.0                  | 0.4                                 | 2.5       |
| 5A          | 35               | 50     | 0.5                  | 0.2                                 | 2.5       |
| 5B          | 35               | 50     | 0.5                  | 0.2                                 | 2.5       |

formulation or composition of liquid products (for example, paints) provides information on the maximum VOCs that could be emitted. This is useful for calculating a mass balance of the emissions over time (see 9.5). Such formulation analyses can be difficult depending on the matrix. Investigators should try to identify existing methods and validate them on the specific product. Even if the composition of the product is known, the emissions could include compounds formed during the use of the product or compounds not identified as ingredients by the manufacturer or the formulation analysis. Therefore, further analyses are required, and testing must be conducted to determine the actual compounds being emitted. One technique involves headspace analysis of the source emissions.

8.2 *Headspace Analysis*—The process of identifying the organic compounds present in the “headspace” or air above the material is termed “headspace analysis.” Both static (that is, closed container) and flow-through headspace analyses are used.

8.2.1 One method of conducting a headspace analysis is to place a sample of material in a small (for example, one litre or less) container lined with inert material. For materials with high emission rates of organic compounds, the quantity of volatile organic material in the sealed (for example, static) headspace over a 0.1 to 0.25 g sample may be more than enough to meet the detection limit requirements of an MS operated in the scan mode or other detectors. Low emission materials, such as carpet, may require a different approach. A purge gas (for example, nitrogen) can be pulled over the material (for example, flow-through) and collected on a sorbent trap. Sufficient material and sampling time must be used to accumulate components to a level adequate for detection by the MS or other detector. While headspace analyses are normally conducted at ambient temperature (for example, 23°C) and pressure, it may be necessary to increase the temperature (and thus the emissions) or collect a larger sample if insufficient material is collected for the detector being used.

8.2.2 Identification of the headspace components is usually accomplished by gas chromatography coupled with a mass spectrometer (GC/MS) operated in the scan mode, although other detectors can be used if sufficient information is available on the retention times for all compounds of interest for a given GC column, gas flow, and temperature program. Use of several sampling and analytical approaches may be necessary to characterize the spectrum of compounds present in the headspace of a material. Techniques applied depend upon such factors as polarity, solubility, and boiling points of the compounds emitted. A variety of sorbent materials are available (see 6.3). Once the sample is collected, appropriate techniques (for example, thermal desorption or solvent extraction) are used to remove the organics from the sorbent. Methods for injecting the sample into the GC will depend on the sample phase (vapor or liquid) and on the specific equipment available.

8.2.3 If different instruments are used for the headspace analysis and chamber testing, the GC column, gas flow, and temperature program used in both instruments should be the same so the retention times for the compounds selected for quantification will be known.

8.2.4 Based on the study objectives, some (or all) of the compounds identified in the headspace analysis are selected for measurement and quantification in subsequent chamber tests. Criteria for selection of compounds may include: major peaks in the gas chromatograph; known carcinogen, toxicant, or irritant; low odor threshold; etc.

8.2.5 While the headspace analysis provides useful information on the direct emissions from the material or product of interest, it does not ensure that all emissions will be identified. Sampling and analysis techniques may be insufficient, or compounds not found in the headspace may be emitted later due to being formed in the drying process or by interactions with the substrate.

8.3 *Chamber Testing*—Chamber testing requires a preparation phase as well as a testing phase. The preparation stage begins with development of the test plan that specifies environmental conditions for each test (see Section 7 on Experimental Design), method of application of the material, conditioning period, and methods of sample collection and analysis. The conditioning period is the time the test specimen is held in a conditioned environment, usually at the same temperature and humidity as the test conditions, prior to placement in the test chamber. Development of the test plan is followed by calibration of environmental control and measurement systems, sample collection and concentration devices, and analytical systems as specified in the quality assurance plan. At this stage the information from the GC/MS headspace analysis is evaluated to provide guidance in selection of analytical columns and detectors and sample collection media and an appropriate internal standard.

8.3.1 *Internal Standard*—The internal standard, an organic compound added at a known rate to the chamber exhaust, must meet the following criteria:

8.3.1.1 It must be a readily available material (that is, suitable for use in a permeation tube or available in a gas cylinder);

8.3.1.2 It must have a retention time on the analytical column that does not overlap other compounds emitted by the material;

8.3.1.3 It must be able to be quantitatively collected and recovered from the sample collection media used during the testing.

8.3.1.4 Also, it is desirable that the internal standard be inexpensive and have low toxicity.

8.3.2 *Chamber Preparation*—Prior to actual testing, chambers are cleaned by scrubbing the inner surfaces with an alkaline detergent followed by thorough rinsing with tap water. Deionized water is used as a final rinse. Chambers are then dried, placed in position in the temperature controlled environment and purged at test conditions. Chamber background is monitored to insure that background contamination is within quality assurance (QA) limits. At this point, the chamber conditions are at test setpoints of flow and relative humidity, all analytical systems have been calibrated, the quality control system has been developed, and the internal standard has been selected. A chamber background sample is then taken to quantify any contribution of organic compounds from the clean air system or the empty chamber, or both. In addition, any substrate materials, such as wood, that will be used during the tests must be included to account for actual background. Once all the preparatory steps have been completed, testing of the selected material/product can commence.

8.3.3 *Specimen Preparation*—The types of test specimens used in the chambers vary according to the material or product being tested. Solid materials are tested “as is.” If emissions from edges may differ from the normally exposed surface, the edges should be sealed. For example, particleboard specimens can have their edges sealed with sodium silicate to eliminate excessively high edge emissions. Wet products (for example, paint, stain, polyurethane, wax) may be applied with a brush, roller, spray, sponge, or other typical method. Such products may also be applied using slit applicators or other devices designed to provide uniform and repeatable coating thicknesses. The type of applicator depends on the objectives of the testing program. For example, if the objective is to compare emission from a large number of products, a slit applicator will provide accurate and repeatable coating thickness on the substrate. Liquid products may be applied to a number of different substrates, including glass, stainless steel, wood, plastic, and so forth. The selection of substrate is important, because the substrate can affect the emissions from the product. For example, VOC emissions from latex paint on gypsumboard are quite different than those from stainless steel. Some of the VOCs are adsorbed into the gypsumboard, and the emissions occur over long time periods. In this case, using a non-adsorbent substrate (that is, stainless steel) would not provide a useful emission regime. Therefore, if the test results are to be used to predict exposures, realistic substrates should be used. For example, a wood stain would be applied to a board; a vinyl floor wax to floor tile, etc. As noted above, the uncoated substrate should be placed in the chamber during background tests to determine the magnitude of its organic emissions. Also edge effects should be eliminated by edge sealing. Wet materials are applied to the substrate outside the chamber and



placed in the chamber shortly thereafter. The start of the test (time = 0) is set when the door to the chamber is closed. As discussed in the scope, small chambers are not suitable for evaluating the application phase of wet material use. Thus, emissions from the earliest portion of the drying cycle (that is, from application until placement in the chamber) will not be measured. The time between application and the start of the test should be less than 10 min; the time of application and the test start time should both be recorded.

**8.3.4 Specimen Conditioning**—In some cases, emissions data are desired on later stages of a material/product lifecycle (for example, several months after a coating has been applied). In these cases, the specimen must be conditioned prior to testing. Conditioning should occur under the same environmental parameters (temperature, humidity, air change rate, and product loading) as those used for chamber tests. If this is not possible, the conditioning environmental parameters should be well documented. Ideally, the sample should be conditioned over its complete life-cycle up to the time of testing. If this is not possible, conditioning should be conducted for a period of time sufficient to allow the emissions to equilibrate to the test conditions (for example, one to two weeks).

**8.3.5 Specimen Contamination**—Care should be taken in testing materials that have been used or stored with other materials. In such cases, the material of interest could have acted as a “sink” and adsorbed organics from the other materials. Subsequent testing could provide emissions data that represent the re-emission of the adsorbed compounds rather than emissions from the original material.

**8.4 Sampling**—Collection of a representative sample of chamber effluent requires the use of a sampling strategy that is appropriate to the ranges of volatilities of the compounds present. The information gained from a GC/MS headspace analysis should be used with caution for selection of appropriate sample collection and concentration media, since the headspace sample may be dominated by the most volatile compounds rather than the compounds that will be emitted as the product or material ages. As discussed above, the sampling method can range from syringe/pump sampling to adsorption on various sorbent media.

**8.4.1 Sampling techniques and sampling times** must also be appropriate to the concentrations of compounds in the chamber air stream over time.

**8.4.2** For constant emission rate sources, the sampling times are not critical since the chamber concentration will reach a constant equilibrium value. A minimum of three samples should be taken after the time required to reach 99.9 % of the equilibrium value. Eq 3 can be rearranged and used to calculate this time, based on the air change rate,  $N$  (that is,  $0.999 = 1 - e^{-Nt}$ ;  $e^{-Nt} = 0.001$ ;  $Nt = 6.9$ ;  $t = 6.9/N$ ). Thus, at an air change rate ( $N$ ) of  $1 \text{ h}^{-1}$ , it takes 6.9 h for the chamber concentration to reach 99.9 % of its equilibrium value when a constant emission source is placed in the chamber at time = 0; for  $N = 0.5$ , it would take 13.8 h, etc.

**8.4.3** When testing wet materials such as glues, waxes, and wood finishes, chamber concentrations may change by orders of magnitude over a period of minutes. Note that glues and adhesives are open to the air until they are covered by a barrier

(for example, carpet, tile, wall covering) that will inhibit emissions. The effect of this barrier can also be tested in the test chamber; however, the emissions from the barrier itself must also be considered. Accurate description of chamber concentration with time may require sampling very frequently or use of a continuous or semicontinuous monitor. A combination of both techniques is the most effective way to characterize rapidly changing emissions. The concentration of individual compounds varies as the material ages. In some cases, compounds not detected in the headspace or in the first few hours of testing may become the major emission component. Therefore, a total hydrocarbon monitor can be effective in tracking rapidly changing concentrations but may provide an incomplete qualitative picture.

**8.4.4** It is important, therefore, to monitor changes in the emission profile as the material dries. The sampling strategy should provide a means to collect approximately the same mass in each sample. Thus, the sample volume is an important consideration. When chamber concentrations are high, sample volume must be kept low to avoid breakthrough in the collection trap or overloading of the concentrator column of a purge-and-trap device. Sample volumes less than 1 L can be drawn directly by gas tight syringes, then injected through a heated port to a clean air stream flowing through sampling cartridges. Gas tight syringes should be used with care, since adsorption of higher molecular weight compounds can occur on the surface (for example, glass) and cause poor accuracy and precision. Much smaller samples (for example, 1 ml.) can be injected directly into the GC. Larger volume samples are taken by pulling chamber air stream through sample cartridges as described. Since the flow through the cartridges is constant, increasing the sampling time will increase the sample volume. It may be necessary to conduct trial runs to develop a sampling strategy.

**8.4.5** Extreme care must be employed in handling the sample cartridges to avoid contamination. One technique is to immediately place the cartridge in a sealed inert (for example, TFB-fluorocarbon bag that has been purged with nitrogen). Glass tubes with air tight fittings are also used.

**8.5 Analysis**—The analysis technique depends on the sampling strategy and adsorbent media employed. Methods of introducing the sample to the GC include direct injection, thermal desorption followed by purge-and-trap concentration, and solvent extraction followed by liquid injection.

## 9. Data Analysis

**9.1** Data reduction and analysis is a multistep process. Electronic spreadsheets can be used to reduce and compile the environmental and chemical analysis data with minimal data entry steps. Chamber concentration data are used in various models to produce estimates of material/product emission rates.

**9.2 Environmental Data**—Environmental data (that is, temperature, relative humidity, flow rate, air velocity) can be recorded manually or automatically stored by a PC based system. Summary statistics that describe the environmental condition “setpoints” and the actual values achieved (including variability) can be computed, and a data summary sheet prepared (see Table 2).

TABLE 2 Example Environmental Data Summary

| Test ID Number: PWF10                                     |            |          |                    |                 |
|---|------------|----------|--------------------|-----------------|
| Material: Polyurethane Wood Finish                        |            |          |                    |                 |
| Sample Size: Weight = 2.39 g Area = 347 cm <sup>2</sup>   |            |          |                    |                 |
| Chamber ID: #1U Chamber Volume: 0.166 m <sup>3</sup>      |            |          |                    |                 |
| Material Loading (L): 0.21 m <sup>2</sup> /m <sup>3</sup> |            |          |                    |                 |
| Start Date  | Start Time | End Date | End Time           |                 |
| 6/16/87   | 11:05      | 6/19/87  | 13:00              |                 |
| Chamber Environmental Parameters                          |            |          |                    |                 |
| Parameter   | Setpoint   | Average  | Standard Deviation | Maximum/Minimum |
| Temp (°C)   | 35.0       | 34.91    | 0.18               | 35.4/34.5       |
| RH (%)  | 50.0       | 54.25    | 1.57               | 60.4/45.2       |
| Flow (L/min)  | 2.6        | 2.72     | 0.01               | 2.66/2.67       |

9.3 Gas Chromatography Data—GCs (including GC/MS) are interfaced to computing integrators (or PC-based chromatographic data analysis systems) for plotting of the chromatograms and computation of the areas of peaks obtained. The data output is printed on paper as an analog chromatogram plus a summary report. The data can also be stored on magnetic media for future review or reprocessing.

9.3.1 The environmental information and the GC analysis results are combined to give chamber concentrations for individual compounds and total organics. In calculating concentrations, the following factors are considered:

9.3.1.1 Gas chromatographic system background (includes sorbent blank for sampling cartridge and purge-and-trap concentrator);

9.3.1.2 Chamber background (determined from analysis of sample of chamber background, including substrate; the sample volume will be dependent on the sampling media and analytical system);

9.3.1.3 Elapsed time (period of time in minutes or hours from start of test to midpoint of sampling period);

9.3.1.4 Flow rate of the airstream carrying the internal standard;

9.3.1.5 Mass of internal standard added and mass observed providing percent recovery;

9.3.1.6 Mass observed for individual selected organic compounds;

9.3.1.7 An estimate of the total organics reported as a given compound (for example, toluene);

9.3.1.8 Sampling duration and flow rate; and

9.3.1.9 Test chamber flow rate.

9.3.2 Chamber concentrations for total organics and individual compounds for each sample are calculated via a multistep process:<sup>11</sup>

9.3.2.1 Data may be normalized to the recovery of the internal standard by multiplying the measured mass by the reciprocal of percent recovery of the internal standard. For example, if the percent recovery was 95 %, the multiplier would be 1/0.95 = 1.053. If data are not normalized, the percent recoveries should be reported.

9.3.2.2 Normalized mass is adjusted for system background and chamber background.

9.3.2.3 The adjusted mass is divided by sample volume to generate sampling manifold concentration data.

9.3.2.4 Finally, chamber concentration is calculated by multiplying the sampling manifold concentration data by the ratio of flow out of the chamber plus standard addition flow divided by flow out:

$$\text{chamber concentration} = \text{sample concentration} \times \frac{(\text{chamber flow} + \text{internal standard flow})}{(\text{chamber flow})} \quad (4)$$

This compensates for dilution of the chamber effluent with the internal standard flow.

9.3.3 Chamber concentration data coupled with sample size and chamber air exchange rate are then used to estimate emission factors, as discussed in the following sections.

9.4 Emission Factors—Two technical terms are commonly used to describe the rate of emissions from indoor materials: emission factor (EF) and emission rate (ER), related as follows:

$$ER = A(EF) \quad (5)$$

where:

ER = emission rate, mg h<sup>-1</sup>,

A = source area, m<sup>2</sup>, and

EF = emission factor, mg m<sup>-2</sup> h<sup>-1</sup>.

Thus, the emission rate can be applied to both area sources and non-area sources, whereas the emission factor can only be applied to area sources. In some cases, emission factors are reported as mass/mass/time, or in the case of caulk beads, mass/length/time, when a standard bead diameter is used. In the remainder of this section, only the emission factor is used in the examples.

9.4.1 Emission Factor Calculation Methods—Once the chamber concentration data are obtained, the emission factor can be calculated by four methods: (1) direct calculation from individual data points, (2) direct calculation from the time-concentration profile, (3) using an explicit chamber model, and (4) using advanced techniques. Selection of the most suitable method or methods depends on several factors such as the type of source, data quality, and sampling frequency.

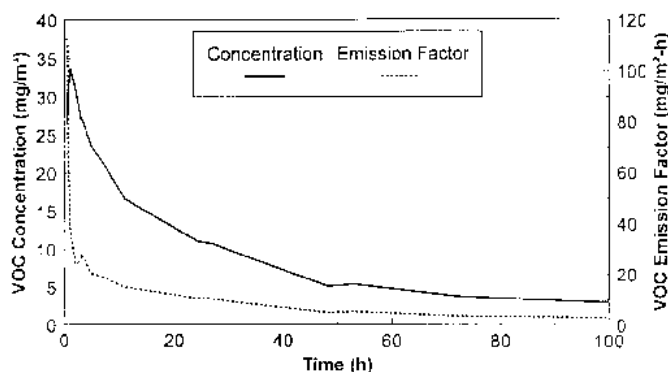


FIG. 2 Direct Calculation of Emission Factor from the Time-Concentration Profile (Latex Paint Test)

<sup>11</sup> Tichenor, B. A., Sparks, L. E., and Jackson, M. D., "Evaluation of Perchloroethylene Emissions from Dry Cleaned Fabrics," U.S. Environmental Protection Agency, EPA-600/2-88-061, Research Triangle Park, NC, October 1988.

9.4.1.1 *Direct Calculation of Emission Factor from Individual Concentration Data Points*—If the emissions rate is nearly constant and the chamber has reached steady-state, the emission factor can be calculated from a single data point:

$$EF = C_s(N/L) \quad (6)$$

where:

- $C_s$  = steady state chamber concentration,  $\text{mg m}^{-3}$ ,
- $N$  = air change rate,  $\text{h}^{-1}$ , and
- $L$  = loading factor,  $\text{m}^2 \text{m}^{-3}$ .

It should be pointed out that this method may have significant error if the emission rate is not constant and/or the chamber has not reached steady-state.

9.4.1.2 *Direct Calculation of Emission Factor from the Time-Concentration Profile*—If there are enough chamber concentration vs. time data points (for example, 10 or more) and the data are relatively smooth, a time-dependent emission factor profile can be obtained directly from the concentration data:

$$EF(t_i) = (\Delta C_i / \Delta t_i - NC_0) / L \quad (7)$$

where:

- $EF(t_i)$  = emission factor at time  $t_i$ ,
- $C_i$  = chamber concentration at time  $t_i$ , and
- $\Delta C / \Delta t_i$  = the slope of the time-concentration curve at time  $t_i$ .

The slope is approximated by the average of the slopes of two adjacent intervals:

$$\Delta C_i / \Delta t_i = [(C_i - C_{i-1}) / (t_i - t_{i-1}) + (C_{i+1} - C_i) / (t_{i+1} - t_i)] / 2 \quad (8)$$

Thus, if there are  $n + 1$  data points for concentration,  $n - 1$  emission factor values can be obtained by this method. Such calculations can be easily carried out in an electronic worksheet. Before making the calculations, make sure that replicate samples are replaced by the average values to avoid dividing by zero. This method has broader usage than the one described in 9.4.1.1 because it does not require that the emission rate be constant nor does it require steady state conditions. The results from this method are independent of any source emission models. The benefits of direct calculations are two-fold: the results can be used to check the validity of a chosen model (see below), and they can help select the most appropriate model for further data analysis. Note that differential methods such as this have the potential for high levels of uncertainty. If there are sufficient data points but the random error is significant, a data smoothing process can be considered before using this method. Figure 3 is an example of this method using VOC emissions from latex paint.

9.4.1.3 *Estimation of Emission Factor Based on an Explicit Chamber Model*—If the emission pattern for a source can be approximated by a mathematical expression (that is, a source model), the emission factor can be estimated by fitting a proper chamber model (not the source model itself) to the time-concentration data by means of non-linear regression. Many indoor source models can be found in the literature; two simple examples are provided below. Note that choosing the right model is as important as collecting quality data from the

chamber. One way to assess the appropriateness of the model is to estimate by way of statistical methods the uncertainty in the estimates of the model parameters (for example,  $EF_0$  and  $k$  in the first-order decay model [see *b*]). Large errors in the estimates may indicate that the wrong model was selected. Unfortunately, large errors in parameter estimates can also result from rough chamber data even when the appropriate model is selected. One can also compare the fitted curve to the data (see Fig. 4) visually or by calculating the goodness of fit, for example, by way of the sum of the squares of the deviation of the data from the predicted value,  $SS_{\text{res}}$ . Assuming the same number of data points, the lower the  $SS_{\text{res}}$ , the better the fit.

(a) *Example 1: Constant Source*—For a constant source with emission factor  $EF$  the following mass balance equation holds:

$$dC/dt = L(EF) - NC \quad (9)$$

Given the initial conditions:  $t = 0$  and  $C = 0$ , the solution to  $C$  is:

$$C = L(EF)(1 - e^{-Nt})/N \quad (10)$$

The unknown parameter  $EF$  can be estimated by fitting Eq 10 to the chamber concentration data. Note that at large values of  $t$ , Eq 10 approaches Eq 6.

(b) *Example 2: First-Order Decay Source*—The first-order decay source model is one of the most commonly used empirical models for decaying emissions:

$$EF = (EF_0)e^{-kt} \quad (11)$$

where:

- $EF_0$  = initial emissions factor,  $\text{mg m}^{-2} \text{h}^{-1}$ , and
- $k$  = first-order decay rate constant,  $\text{h}^{-1}$ .

The corresponding chamber model is

$$dC/dt = L(EF_0)e^{-kt} - NC \quad (12)$$

which has the following solution under the condition of  $t = 0$  and  $C = 0$ :

$$C = L(EF_0)(e^{-kt} - e^{-Nt}) / (N - k) \quad (13)$$

Eq 13 is the model to be used to fit the chamber concentration data using non-linear regression techniques. Figure 4 is an example of the data-fitting results. Using a curve-fitting program implemented on a computer requires the user to provide initial values for the parameters to be estimated (that is,  $EF_0$  in Eq 10 or  $EF_0$  and  $k$  in Eq 13). If the initial estimates are too far from the real values, the non-linear regression may fail. A good initial estimate for  $k$  in Eq 13 is:

$$k = (N)e^{(k - N)t_{max}} \quad (14)$$

where:

- $t_{max}$  = the time of maximum concentration,  $C_{max}$ .

NOTE 1—Eq 14 has two roots, one of which is  $k = N$ . The other root should be selected.

9.4.1.4 *Estimation of Emission Factor Based on Advanced Techniques*—If a source model does not have an explicit

solution for chamber concentration, or the solution is too complicated to handle, the emission factor can be estimated with the chamber model in its ordinary differential equation form. Some commercial software packages have the capability to estimate model parameters while solving the differential equations numerically. Source models based on mass transfer theory, including evaporation, diffusion, and adsorption, have been developed for several products and materials. Chamber data are fit with such models using numerical techniques. Readers interested in these methods are encouraged to review the references in the Appendix.

**9.5 Mass Balance Calculations**—Calculating a mass balance for a test chamber can be useful for several reasons: (1) determine the total pollutant mass emitted from the source being tested, (2) check on the performance of the chamber testing method with a known source, and (3) evaluate the sink effect of the chamber walls.

**9.5.1 General Mass Balance Equation for Source Testing**—If the air pollutant of interest does not participate in any gas-phase chemical reactions inside the test chamber or on the chamber walls, the mass balance equation is

$$W_E = (W_{a,t} - W_{a,0}) + (W_{s,t} - W_{s,0}) - W_x \quad (15)$$

where:

- $W_E$  = total mass emitted by the source during the test period 0 to  $t$ ,
- $W_{a,t}$  = total mass in the chamber air at the end of test,
- $W_{a,0}$  = total mass in the chamber air at the beginning of the test,
- $W_{s,t}$  = total mass adsorbed by the chamber walls at the beginning of the test,
- $W_{s,0}$  = total mass adsorbed by the chamber walls at the end of test, and
- $W_x$  = total mass leaving the chamber through the air change flow.

When the test starts with a clean chamber (that is,  $W_{a,0} = 0$  and  $W_{s,0} = 0$ ), the mass balance equation can then be simplified to

$$W_E = W_{a,t} + W_{s,t} + W_x \quad (16)$$

Further simplification can be made if the adsorption by the chamber walls can be ignored:

$$W_E = W_{a,t} + W_x \quad (17)$$

Thus, the total mass emitted from the source is the sum of the mass remaining in the chamber plus the mass that is carried out by the air change flow. Determination of  $W_x$  is described in the following section and  $W_{a,t}$  can be calculated from

$$W_{a,t} = C_{a,t}V \quad (18)$$

where:

- $C_{a,t}$  = chamber concentration at time  $t$ , and
- $V$  = chamber volume.

**9.5.2 Calculate the Total Mass Leaving the Chamber**—The total mass carried out by the air change flow can be estimated by integrating the time-concentration data by the trapezoid

rule. Suppose there are  $n + 1$  data points:  $(t_0, C_0)$ ,  $(t_1, C_1)$ ,  $(t_2, C_2)$ , ...,  $(t_n, C_n)$ ; the total area under the concentration curve,  $S_C$ , can be approximated by the sum of  $n$  trapezoids:

$$S_C = \sum [(C_i + C_{i-1})(t_i - t_{i-1})/2] \quad (i = 0, 1, 2, \dots, n) \quad (19)$$

This calculation can be easily made in an electronic worksheet. The total amount of a given pollutant leaving the chamber,  $W_x$ , is:

$$W_x = S_C Q \quad (20)$$

where:

$Q$  = chamber flow rate.

**9.5.3 Using a Mass Balance to Determine the Total Pollutant Mass Emitted from the Source**—If there are no gas-phase reactions in the chamber and the adsorption by chamber walls at the end of test can be ignored, the total amount of pollutant emitted from the source can be calculated from Eq 17.

**9.5.4 Using a Mass Balance to Check the Performance of the Chamber System**—A simple way to check the performance of the chamber system is to introduce a certain amount of a non-adsorbing test compound by pulse injection (for gas) or flash vaporization (for liquid), then purge the chamber with clean air while monitoring the concentration over time. Continue the monitoring until the chamber concentrations are below the quantification limit. A significant difference between the amount of the compound introduced and that calculated from Eq 17 is an indicator of problems with either the chamber system or the sampling/analytical method.

**9.5.5 Using a Mass Balance to Determine Chamber Wall Sink Effects**—If the adsorption of a compound by chamber walls is reversible, as in most cases, one way to determine the adsorption by chamber walls is to introduce the test compound into the chamber through pulse injection or flash vaporization. After steady-state is reached, take air samples to determine the initial chamber concentration,  $C_0$ . Then flush the chamber with clean air and keep monitoring the concentration decay until the chamber concentration is much lower than  $C_0$  or below method quantification limit. The total amount of test compound adsorbed by the chamber walls,  $M_s$ , can be estimated from:

$$M_s = QS_C - [(C_0 - C_n)V] \quad (21)$$

## 10. Quality Assurance/Quality Control

**10.1 Small chamber testing of organic emissions from indoor materials/products** should be conducted within the framework of a quality assurance project plan (QAPP). The QAPP should contain the following:

**10.2 Project Description**—A brief description of what materials are to be tested; how the testing is to be conducted; who is responsible for various project activities. The project experimental design (see Section 7) should contain the necessary information for this portion of the QAPP.

**10.3 Data Quality Objectives/Acceptance Criteria**—This section of the QAPP defines the precision, accuracy, and completeness desired for each parameter being measured.

Table 3 provides an example. These criteria need to be developed to meet the specific needs of the measurement program.

10.4 *QA/QC Approaches/Activities*—The types of QA/QC activities that might be specified in the QAPP include establishment of a system of records/notebooks to ensure proper operation of equipment and recording of data, such as the following:

10.4.1 Sample log book to record receipt, storage, and disposition of materials;

10.4.2 GC standards preparation log to document preparation of all organic compound standards;

10.4.3 Permeation tube log to record weight loss data for all permeation tubes;

10.4.4 Calibration logs to contain environmental systems calibration data;

10.4.5 Instrument maintenance logs to document maintenance and repairs of all equipment;

10.4.6 Materials testing log books in which to record all pertinent information for each test, including sample details, sample identification (ID) number, and GC run ID number;

10.4.7 Sorbent cartridge cleanup/desorption log detailing thermal cleanup and QC validation of sorbent cartridges;

10.4.8 Floppy disk or lab notebook storage log to document location and content of electronically stored data; and

10.4.9 Maintenance of manuals governing operation of all equipment used by the project.

10.5 Quality control activities are carried out by project staff in a routine, consistent manner to provide necessary feedback in operation of all measurement systems. Such activities might include the following:

10.5.1 Routine maintenance and calibration of systems;

10.5.2 Daily recording of GC calibration accuracy and precision (that is, control charting);

10.5.3 Timely monitoring of percent recovery of the internal standard that was added to all samples;

10.5.4 Collection and analysis of duplicate samples;

10.5.5 QC checking of organic collection sorbent tubes; and

**TABLE 3 Example Data Quality Objectives/Acceptance Criteria**

NOTE 1— Precision and accuracy are normally reported as  $\pm$  one standard deviation unless otherwise noted. Completeness refers to the percentage of planned measurements actually conducted. For example, if 100 measurements were planned and 92 were conducted, the completeness would be 92 %.

| Parameter                  | Precision                 | Accuracy                  | Completeness |
|----------------------------|---------------------------|---------------------------|--------------|
| Temperature                | $\pm 0.5^{\circ}\text{C}$ | $\pm 0.5^{\circ}\text{C}$ | >90 %        |
| Relative Humidity          | +5.0 %                    | -10.0 %                   | >90 %        |
| Air Flow Rate              | +1.0 %                    | -2.0 %                    | >90 %        |
| Substrate Area             | $\pm 1.0$ %               | ...                       | >90 %        |
| Sample Weight <sup>a</sup> | +10.0 %                   | ...                       | >90 %        |
| Organic Concentration      | +20 % RSD <sup>b</sup>    | ...                       | >90 %        |
| Emission Rate              | $\pm 20$ % RSD            | ...                       | >90 %        |

<sup>a</sup>For wet samples.

<sup>b</sup>RSD = relative standard deviation =  $(s/m) 100$  %, where,  $s$  = estimate of the standard deviation, and  $m$  = mean.

10.5.6 Periodic analysis of audit gases supplied by an independent source.

10.6 *QA/QC Audits*—Finally, the QA/QC program should include periodic audits by QA personnel to evaluate compliance with QAPP protocols.

## 11. Reporting Test Results

11.1 The report of the test results should contain the following sections:

11.2 *Test Objectives*—Provide a clear description of the purpose of the test program.

11.3 *Facilities and Equipment*—Give a description of the test chambers, clean air systems, environmental measurement and control, sample collection (including adsorbents if used), analytical instrumentation (that is, GC, GC/MS), and standards generation and calibration.

11.4 *Experimental Design*—Describe the test conditions, including temperature, humidity, air exchange rate, and material loading; include a test matrix if appropriate.

11.5 *Sample Descriptions*—Provide a complete description of the sample(s) tested, including type of material/product, size or amount of material tested, product history, brand name (if appropriate), and sample selection process (for example, random). For wet samples, describe the sample substrate. Also, provide information on sample conditioning, including duration and environmental conditions.

11.6 *Experimental Procedures*—Describe the experimental procedures used during the testing, including details of the sampling and analysis techniques. For wet samples provide information on the application method.

11.7 *Data Analysis*—Show the methods, including appropriate models or equations, used to analyze the chamber data to produce emission factors.

11.8 *Results*—Provide emission factors for each type of sample tested and for each environmental condition evaluated. Emission factors can be provided for individual organic compounds or total organics, or both. For sources with variable emission rates provide appropriate rate constants.

11.9 *Discussion and Conclusions*—Discuss the relevance of the findings and provide conclusions. For example, describe the effect of temperature or air exchange rate, or both, on the emission factor.

11.10 *Quality Assurance/Quality Control*—Describe the data quality objectives and discuss adherence to the acceptance criteria. This should be done for both the environmental variables and the chemical results. Provide the results of duplicate and replicate sampling, and discuss the outcome of any audits.

## 12. Keywords

12.1 indoor air quality; indoor sources; indoor materials; indoor products; small chamber testing; environmental test chambers; organic emissions; emission factor; emission rate; mass transfer.

**APPENDIX**
**(Nonmandatory Information)**
**X1. SUPPLEMENTAL MATERIAL**

X1.1 The scientific and technical literature contains numerous references that report on the use of small environmental test chambers for determining emissions of organic compounds from indoor materials and products. The following references give information on approaches to small chamber testing taken by several investigators. These references are provided as suggested reading for those who wish to supplement the information contained in this guide. Further references are cited in each of these publications.

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