

Designation: D5116 - 17

Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products¹

This standard is issued under the fixed designation D5116; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

- 1.1 This guide provides direction on the measurement of the emissions of volatile organic compounds (VOCs) from indoor materials and products using small-scale environmental test chambers.
- 1.2 This guide pertains to chambers that fully enclose a material specimen to be tested and does not address other emission chamber designs such as emission cells (see instead Practice D7143).
- 1.3 As an ASTM standard, this guide describes options, but does not recommend specific courses of action. This guide is not a standard test method and must not be construed as such.
- 1.4 The use of small environmental test chambers to characterize the emissions of VOCs from 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. For several indoor materials, more detailed ASTM standards for emissions testing have now been developed. Where more detailed ASTM standard practices or methods exist, they supersede this guide and should be used in its place. Until the interested parties agree upon standard testing protocols, differences in approach will occur. This guide will continue to 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.
- 1.5 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) by means of brushing, spraying, rolling, etc. are generally higher than the rate during the drying process. Small chamber testing cannot be used to evaluate the application phase of the coating process. Large (or full-scale) chambers may be more appropriate for many of these applications. For guidance on full-scale chamber testing of emissions from indoor materials refer to Practice D6670.

- 1.6 This guide does not provide specific directions for the selection of sampling media or for the analysis of VOCs. This information is provided in Practice D6196.
- 1.7 This guide does not provide specific directions for determining emissions of formaldehyde from composite wood products, since chamber testing methods for such emissions are well developed and widely used. For more information refer to Test Methods E1333 and D6007. It is possible, however, that the guide can be used to support alternative testing methods.
- 1.8 This guide is not applicable to the determination of emissions of semi-volatile organic compounds (SVOCs) from materials/products largely due to adsorption of these compounds on materials commonly used for construction of chambers suitable for VOC emissions testing. Alternate procedures are required for SVOCs. For example, it may be possible to screen materials for emissions of SVOCs using micro-scale chambers operated at temperatures above normal indoor conditions (see Practice D7706).
- 1.9 This 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. Guide D6485 provides an example of the assessment of acute and irritant effects of VOC emissions for a given material. Specification of "target" organic species of concern is similarly beyond the scope of this guide. As guideline levels for specific indoor contaminants develop, so too will emission test protocols to provide relevant information. Emissions databases and material labeling schemes will also be expected to adjust to reflect the current state of knowledge.

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

Current edition approved Nov. 1, 2017. Published November 2017. Originally approved in 1990. Last previous edition approved in 2010 as D5116 – 10. DOI: 10.1520/D5116-17.



- 1.10 Specifics related to the acquisition, handling, conditioning, preparation, and testing of individual test specimens may vary depending on particular study objectives. Guidelines for these aspects of emissions testing are provided here, specific direction is not mandated. The purpose of this guide is to increase the awareness of the user to available techniques for evaluating organic emissions from indoor materials/products by means of small chamber testing, to identify the essential aspects of emissions testing that must be controlled and documented, and therefore to provide information, which may lead to further evaluation and standardization.
- 1.11 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 X1 provides references to standards that are widely employed to measure emissions of VOCs from materials and products used in the interiors of buildings. Some of these standards directly reference this guide.
- 1.12 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.
- 1.13 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.
- 1.14 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

- 2.1 ASTM Standards:²
- D1193 Specification for Reagent Water
- D1356 Terminology Relating to Sampling and Analysis of Atmospheres
- D1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres
- D3195 Practice for Rotameter Calibration
- D3609 Practice for Calibration Techniques Using Permeation Tubes
- D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)
- D3687 Practice for Analysis of Organic Compound Vapors
- 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.

- Collected by the Activated Charcoal Tube Adsorption Method
- D6007 Test Method for Determining Formaldehyde Concentrations in Air from Wood Products Using a Small-Scale Chamber
- D6177 Practice for Determining Emission Profiles of Volatile Organic Chemicals Emitted from Bedding Sets
- D6196 Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air
- D6330 Practice for Determination of Volatile Organic Compounds (Excluding Formaldehyde) Emissions from Wood-Based Panels Using Small Environmental Chambers Under Defined Test Conditions
- D6485 Guide for Risk Characterization of Acute and Irritant Effects of Short-Term Exposure to Volatile Organic Chemicals Emitted from Bedding Sets
- D6670 Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/ Products
- D6803 Practice for Testing and Sampling of Volatile Organic Compounds (Including Carbonyl Compounds) Emitted from Paint Using Small Environmental Chambers
- D7143 Practice for Emission Cells for the Determination of Volatile Organic Emissions from Indoor Materials/
 Products
- D7339 Test Method for Determination of Volatile Organic Compounds Emitted from Carpet using a Specific Sorbent Tube and Thermal Desorption / Gas Chromatography
- D7706 Practice for Rapid Screening of VOC Emissions from Products Using Micro-Scale Chambers
- D7911 Guide for Using Reference Material to Characterize Measurement Bias Associated with Volatile Organic Compound Emission Chamber Test
- E355 Practice for Gas Chromatography Terms and Relationships
- E1333 Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Using a Large Chamber

3. Terminology

- 3.1 *Definitions*—For definitions and terms used in this guide, refer to Terminology D1356. For an explanation of units, symbols, and conversion factors, refer to Practice D1914.
 - 3.2 Definitions of Terms Specific to This Standard:
- 3.2.1 *air change rate, n*—the flow rate of clean, conditioned air into the chamber divided by the net chamber volume; usually expressed in units of 1/h.
- 3.2.2 *chamber loading ratio*, *n*—the total amount of test specimen exposed in the chamber divided by the net or corrected internal air volume of the chamber.
- 3.2.2.1 *Discussion*—Net internal air volume of the chamber is calculated as the internal volume of the chamber enclosure minus the volume internally displaced by test specimen, holder, inlet/exhaust manifolds, etc. The chamber loading ratio is typically expressed as the ratio of the exposed specimen surface area, *A*, to net chamber volume (1/m) but depending on the nature of the test specimen, can also be expressed as 1/m³,

m/m³, and unitless for unit, line, and volume emission sources, respectively. Chamber loading also can be expressed in terms of area-specific airflow rate calculated as the ratio of the chamber's volumetric inlet airflow rate, Q, divided by the specimen surface area, A, that is Q/A (m/h).

- 3.2.3 *test chamber*; *n*—an enclosed test volume constructed of chemically inert materials with a clean air supply and exhaust.
- 3.2.3.1 *Discussion*—These chambers are designed to permit testing of emissions from samples of building materials and consumer products. The internal volume of small-scale chambers usually ranges from a few litres to a few cubic metres. Micro-scale chambers are typically less than one litre in volume and further differ from small-scale chambers in that the entire airflow rate at the chamber exhaust is sampled (see Practice D7706).

4. Significance and Use

- 4.1 *Objectives*—The use of small chambers to evaluate VOC emissions from indoor materials has several objectives:
- 4.1.1 Develop techniques for screening of products for VOC emissions;
- 4.1.2 Determine the effect of environmental variables (that is, temperature, humidity, air speed, and air change rate) 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 stakeholders and other interested parties 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.
- 4.2.1 The evaporative mass transfer of a given VOC from the surface of the material to the overlying air can be expressed as:

$$ER = A k_m (VP_s - VP_a) MW/RT$$
 (1)

where:

ER = emission rate, mg/h,

 $A = \text{source area, m}^2,$

 k_m = mass transfer coefficient, m/h,

 \overrightarrow{VP}_s = vapor pressure at the surface of the material, Pa, VP_a = vapor pressure in the air above the surface, Pa,

MW = molecular weight, mg/mol,

R = gas constant, 8.314 J/mol-K or Pa m³/mol-K, and

T = temperature, K.

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 and 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:

$$\tau = \tau_{o} e^{-Q/RT} \tag{2}$$

where:

 τ = retention time, s,

 τ_o = constant with a typical value from 10^{-12} to 10^{-15} s, and Q = molar enthalpy change for adsorption (or adsorption energy), J/mol.

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 The air change rate indicates the amount of dilution and flushing that occurs in indoor environments. The higher the air change rate the greater the dilution, and assuming the outdoor air is cleaner, the lower the indoor 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 Speed—Surface air speed is a critical parameter for evaporative-controlled sources as the mass transfer coefficient (k_m) is affected by the air speed and turbulence at the air-side of the boundary layer. Generally, the higher the air speed and turbulence, the greater the mass transfer coefficient. In a practical sense for most VOCs, above a certain air speed and 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 air speeds high enough to minimize



the mass transfer resistance at the surface. For example, air speeds of 0.3 to 0.5 m/s have been used in evaluating formaldehyde emissions from wood products. Such air speeds are higher than those observed in normal residential environments by Matthews et al., where in six houses they measured air speeds using an omni-directional heated sphere anemometer with a mean of 0.07 m/s and a median of 0.05 m/s. Thus, other investigators prefer to keep the air speeds in the range normally found indoors. In either case, an understanding of the effect of air speed 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 5.3.1). 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).

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 specimen conditioning environment, 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 Specimen Conditioning Environment—Acclimatization of test specimens to stable environmental conditions of temperature, relative humidity, and clean air change rate prior to emissions testing is commonly required by standardized test protocols. Care must be taken to ensure that the conditioning environment meets all specifications intended to prevent cross-

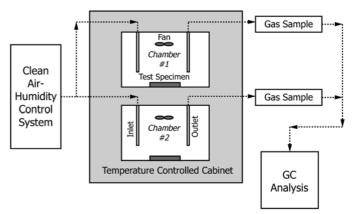


FIG. 1 Small Chamber Test Facility Schematic

contamination of test specimens and to stabilize specimens in terms of both temperature and moisture content.

5.3 Design and Operation of Small-Scale Chambers— Small-scale test chambers are designed to permit the testing of samples of various types of building materials and consumer products. They can range in size from a few litres to a few cubic metres. Other chambers, such as full-scale chambers (see Practice D6670), 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. Micro-scale chambers are typically less than one litre in volume and differ from small-scale chambers in that the entire airflow rate at the chamber exhaust is sampled (see Practice D7706). Micro-scale chambers are typically used to screen homogeneous materials that can be represented by very small specimens for emissions of VOCs.

5.3.1 Construction—Small-scale 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 exhaust 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 exhaust air (see 6.2).

5.3.1.1 Measure or calculate the internal volume of the chamber enclosure. Additionally, measure or calculate the volumes of the internal components of the chamber such as specimen holders, racks or supports, temperature/humidity probes, inlet/exhaust manifolds, etc.

5.3.1.2 The sizes, surface areas, and volumes of internal components of the chamber should be minimized to the extent practical. Also as practical, internal components should have similar surface characteristics as the interior surface of the chamber to minimize losses of compounds of interest due to adsorption or reactions.

³ 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.

5.3.2 Mixing—The chamber and its air moving components should 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 exhaust manifolds are two techniques that have been used successfully to ensure adequate mixing of air in the chamber. Refer to 5.4 for procedures for assessing the mixing characteristics of the chamber.

5.3.3 Surface Air Speed—As discussed in 4.2.4.3, the air speed 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). Chambers designed specifically to provide stable air speeds over the specimen surface independent of air change rate may be used. Alternatively, a small fan can be used to achieve such air speeds. Some investigators have had success with DC voltage computer fans. 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. Air speed measurements can be made with omni-directional heated sphere anemometers. These devices typically have lower detection limits of 3 to 5 cm/s. Air speeds should be measured close to the source; for example, a height of 1 cm above the surface of a horizontal source. An average air speed 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, air speeds near the source surface can 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 provided the chamber has been shown to be well mixed. Whenever a fan is employed, its potential contribution to the chamber temperature, VOC background, and its sink characteristics must be carefully considered. If evaporative sources are tested using either material supports/substrates (for example, wallboard used as substrate for investigation of emissions from paint) or specimen holders, then the surface air speed above the specimen should be characterized with the substrate or holder in place.

5.3.4 *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.

5.3.5 Pressure Control—Operate the chamber in such a manner that a slight positive pressure is maintained at all times relative to the surrounding environment. This is particularly important while collecting air samples from the chamber exhaust air. Transient pressure fluctuations may result from normal operation of the lab environment (door and HVAC system operation, etc.). A positive pressurization of the chamber of approximately 10 Pa should provide sufficient margin to protect the chamber from becoming negative relative to its surroundings. Continuous monitoring of chamber pressure has

the additional advantage during sample collection of ensuring that pumped flow through the sample tube is continuous and that seals for the tube are intact (by observing a maintained slight dip in the chamber pressure). Minimize any void volumes associated with the pressure sensor and use inert materials for all exposed surfaces.

5.3.6 *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 either heating of the chamber interior or radiant heating of the test specimen. The possible impact of lighting fixtures on chamber VOC background and sink characteristics must be carefully considered.

5.3.7 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 regarding the required airflow rate 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 µg/m³ for any single compound or 10 µg/m³ 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.

5.3.8 Humidity Control—Humidity control of the chamber air is achieved by adding deionized water (see Specification D1193) 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.

5.3.9 Environmental Measurement and Control Systems—Measurement and control are required for airflow rate, temperature (see 5.3.4), humidity (see 5.3.8), and differential pressure (see 5.3.5). Airflow rate 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 D3195) can be used. Temperature control is discussed in 5.3.4. Temperature measurement can be accomplished automatically by means of 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 (see 5.3.8) 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 exhaust manifolds.

5.3.10 Automatic Systems—Computer-based data acquisition and control (DAC) systems can be used to set airflow rates and monitor temperature, relative humidity, and airflow rate during the course of experiments. Analog signals from temperature, relative humidity, pressure, and flow sensors are converted to digital units that can be stored electronically, 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. DAC 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 display current set points and measured values on a system schematic.

5.3.11 *Manual Systems*—While DAC systems provide enhanced data collection and control, they also may be relatively expensive and complex. The simplicity and low cost of manual systems may be preferable in some circumstances.

5.4 Characterization of Chamber Performance—Before a chamber is used for emissions testing, its mixing and sink characteristics should be evaluated and compared to minimum performance criteria. In addition to the guidance provided below, Guide D7911 describes the use of reference materials for characterizing the performance of chambers.

5.4.1 Assessment of Air Mixing—The adequacy of air 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 determined not only in an empty chamber, but also with substrates and samples of the types used in actual tests to determine if the placement of substrates and samples in the chamber will negatively impact mixing.

5.4.2 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 exhaust air and the inlet air over time. A uniform concentration can be established by injecting tracer at a constant rate and waiting until the exhaust 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. The tracer gas concentration should be measured concurrently in the exhaust air and the inlet air at relatively high frequency, for example, not less than one sample per minute, if the inlet air concentration is >1 % of the initial chamber concentration. The degree of mixing is assessed by determining a mixing level, η , is described in Eq 3-5. If the

inlet air tracer gas concentration is <1 % of the initial chamber concentration, C_m may be calculated with Eq 6 rather than Eq 5.

$$\eta = \left\{ 1 - \frac{\sum_{i=0}^{n} [|C(t_i) - C_m(t_i)|(t_i - t_{i-1})]}{\sum_{i=0}^{n} [C_m(t_i)(t_i - t_{i-1})]} \right\} 100\%$$
 (3)

$$C_m(t_0) = C(t_0) \tag{4}$$

$$C_m(t_i) = \left[(C_m(t_i)) - C_{in}(t_{i-1}) \right] e(-N(t_i - t_{i-1})) + C_{in}(t_{i-1})$$
 (5)

$$C_m(t_i) = C_m(t_{i-1})e(-N(t_i - t_{i-1}))$$
 (6)

if maximum $C_{in}(t) < 0.01 C(t_0)$

where:

 η = mixing level,

C(i) = exhaust air concentration at ith concentration measurement, mg/m³,

C(0) = exhaust air concentration measurement at t = 0, mg/m³.

 $C_m(i)$ = calculated perfectly mixed concentration at i^{th} concentration measurement, mg/m³,

 $C_{in}(i)$ = inlet air concentration measurement at i^{th} concentration measurement, mg/m³,

n = number of discreet measurements,

 t_i = time of i^{th} concentration measurement (h),

N = chamber air change rate, ventilation rate (m³/h¹) divided by net chamber volume (m³), 1/h, and

 t_n = time constant of chamber = 1/N.

If the mixing level, η , as determined using Eq 3, is above 90 %, then the air mixing within the chamber may be considered adequate.

5.4.3 Sink Effect—While the selection of materials used in the construction of the chamber should help to minimize the adsorption of VOCs on its interior surfaces, this "sink" effect is likely to occur to some extent, and will affect the accuracy of emission testing results. Sink effect evaluation should be performed after the chamber's mixing performance has been confirmed. Sink effect is a compound-specific phenomenon, so ideally, the magnitude of this effect should be determined for each of the specific compounds to be measured under the chamber operating conditions for which an emission test is to be conducted. Refer to Practice D6670, Section 8.6, for a detailed procedure for characterizing reversible and irreversible sink effects in emissions chambers.

5.4.4 Using a Mass Balance to Determine Chamber Wall Sink Effects—If the adsorption of a compound by chamber walls and internal chamber components is reversible, as in most cases, one way to determine the adsorption by chamber walls and components 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 exhaust air concentration, C_0 . Then flush the chamber with clean air and keep monitoring the concentration decay until the exhaust air concentration reaches the method quantification limit. The total mass of test compound adsorbed by the chamber walls and internal components can be estimated from:

$$M_s = QS_c - \left[\left(C_0 - C_i \right) V \right] \tag{7}$$