Designation: D7911 – 14

Standard Guide for
Using Reference Material to Characterize Measurement Bias Associated with Volatile Organic Compound Emission Chamber Test[1]

This standard is issued under the fixed designation D7911; 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 procedures for using a reference material with a known emission rate of a volatile organic compound (VOC) to estimate the bias associated with a VOC emission chamber test.

1.2 This guide may be used to assess measurements of VOC emissions conducted in a variety of environmental chambers, such as small-scale chambers, full-scale chambers, emission cells, and micro-scale chambers.

1.3 This guide may be used to assess measurements of VOC emissions from a variety of sources including "dry" materials (for example, carpet, floor tile and particleboard) and "wet" materials (for example, paint and cleaning products).

1.4 This guide can be used to support quality control efforts by emissions testing laboratories, third party accreditation of testing laboratories participating in emissions testing programs, and quality control efforts by manufacturers of building and other materials.

1.5 This guide may be used to support the determination of precision and bias of other commonly used VOC emission standards including Guide D5116, Test Method D6007, ISO 16000-9, ANSI/BIFMA M7.1, and CDPH/EHLB/Standard Method V1.1.

1.6 This guide also describes the attributes of a suitable emission reference material and the different methods available to independently determine the reference material's VOC emission rate.

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

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres
D5116 Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products
D5197 Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)
D5466 Test Method for Determination of Volatile Organic Chemicals in Atmospheres (Canister Sampling Methodology)
D6007 Test Method for Determining Formaldehyde Concentrations in Air from Wood Products Using a Small-Scale Chamber
D6196 Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6330 Practice for Determination of Volatile Organic Compounds (Excluding Formaldehyde) Emissions from Wood-Based Panels Using Small Environmental Chambers Under Defined Test Conditions
D6617 Practice for Laboratory Bias Detection Using Single Test Result from Standard Material
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

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

Current edition approved Sept. 1, 2014. Published September 2014. DOI: 10.1520/D7911-14.

[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.

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

D7440 Practice for Characterizing Uncertainty in Air Quality Measurements

D7706 Practice for Rapid Screening of VOC Emissions from Products Using Micro-Scale Chambers

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E741 Test Method for Determining Air Change in a Single Zone by Means of a Tracer Gas Dilution

E1333 Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Using a Large Chamber

2.2 *ISO Standards:*[3]

ISO 12219-3 Interior Air of Road Vehicles—Part 3: Screening Method for the Determination of the Emissions of Volatile Organic Compounds from Vehicle Interior Parts and Materials—Micro-scale Chamber Method

ISO 16000-3 Indoor Air—Part 3: Determination of Formaldehyde and Other Carbonyl Compounds in Indoor Air and Test Change Air—Active Sampling Method

ISO 16000-6 Indoor Air—Part 6: Determination of Volatile Organic Compounds in Indoor and Test Chamber Air by Active Sampling on Tenax TA Sorbent, Thermal Desorption and Gas Chromatography Using MS or MS-FID

ISO 16000-9 Indoor Air—Part 9: Determination of the Emission of Volatile Organic Compounds from Building Products and Furnishing—Emission Test Chamber Method

ISO 16000-10 Indoor Air—Part 10: Determination of the Emission of Volatile Organic Compounds from Building Products and Furnishing—Emission Test Cell Method

ISO 16000-11 Indoor Air—Part 11: Determination of the Emission of Volatile Organic Compounds from Building Products and Furnishing—Sampling, Storage of Samples and Preparation of Test Specimens

ISO/IEC 17025 General Requirements for the Competence of Testing and Calibration Laboratories

ISO/IEC 17043 Conformity Assessment—General Requirements for Proficiency Testing

ISO/IEC Guide 98 Guide to the Expression of Uncertainty in Measurement (GUM)

ISO Guide 30 Terms and Definitions Used in Connection with Reference Materials

ISO Guide 33 Uses of Certified Reference Materials

ISO Guide 34 General Requirements for the Competence of Reference Material Producers

ISO Guide 35 Reference Materials—General and Statistical Principles for Certification

2.3 *Other Standards:*

ANSI/BIFMA M7.1 2011 Test Method for Determining VOC Emissions from Office Furniture Systems, Components, and Seating[4]

CDPH/EHLB/Standard Method V1.1 2010 Standard Method for the Testing and Evaluation of Volatile Organic Chemical Emissions from Indoor Sources Using Environmental Chambers, Version 1.1[5]

Method TO-17 1999 "Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes," Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition (EPA/625/R-96/010b)[6]

3. Terminology

3.1 *Definitions*—For definitions and terms commonly used in Commitee D22 standards, refer to Terminology D1356. For definitions and terms commonly used when testing materials and products for VOC emissions, refer to Guide D5116. For definitions and terms commonly used to describe reference materials, refer to ISO Guide 30.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *constant emission source, n*—an emission source where the concentration of the chemical at the material surface does not change with time.

3.2.2 *diffusion-controlled source, n*—an emission source that is limited by the movement of contaminants within the material boundaries.

3.2.2.1 *Discussion*—The rate of diffusion depends on the diffusivity of the VOC, the temperature, and the structure of the material.

3.2.3 *dynamic emission source, n*—an emission source where the concentration of the chemical at the material surface changes with time.

3.2.3.1 *Discussion*—A dynamic source can still generate emissions in a predictable and consistent manner.

3.2.4 *evaporative-controlled source, n*—an emission source that is limited by the ability of a contaminant to transfer from the material surface through a boundary layer to the surrounding air.

3.2.4.1 *Discussion*—The rate of mass transfer at the surface of an evaporative-controlled source is dependent on VOC volatility, air velocity, and turbulence near the material surface.

3.2.5 *primary reference measurement procedure, n*—"Reference measurement procedure used to obtain a measurement result without relation to a measurement standard for a quantity of the same kind" (**1**).[7]

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[3] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland, http://www.iso.org.

[4] Available from Business + Institutional Furniture Manufacturers Association (BIFMA), 678 Front Ave. NW, Ste. 150, Grand Rapids, Michigan 49504-5368, https://www.bifma.org.

[5] Available from California Department of Public Health (CDPH), PO Box 997377, MS 0500, Sacramento, CA 95899-7377, http://www.cdph.ca.gov.

[6] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20004, http://www.epa.gov.

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

3.2.6 *reference emission rate value, n*—the independently-determined mass of VOC emitted per unit of time from a reference emission source at specified conditions.

3.2.6.1 *Discussion*—If the reference emission rate value is "certified," the reference value and associated uncertainty will be available on the accompanying certificate for the reference material.

3.2.7 *reference material, n*—a material that is "sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process" (ISO Guide 30).

4. Summary of Guide

4.1 This guide describes procedures for using a reference material to evaluate the measurement bias associated with tests of VOC emissions from materials and products. The reference materials described in this guide have independently-determined emission rates that can be measured in an environmental test chamber according to commonly used VOC emission and analytical standards and by following the instructions in the reference material's accompanying documentation. Example instructions associated with published uses of reference materials are provided in Appendix X1.

4.2 In general, reference materials used in laboratory emission tests can provide traceability for test results determined at different times and in different laboratories using the same environmental conditions (for example, chamber airflow rate, temperature and relative humidity). Chamber air samples are collected at specific times and analyzed according to referenced standards. If no analytical standard is prescribed, samples are analyzed according to a laboratory's standard operating procedures. Chamber concentrations and source emission rates are calculated. The measured emission rates, at defined time periods, are then compared with the known value for the reference material to estimate the measurement bias of the value obtained in the emission chamber. If applicable, the value of the measurement bias can be compared with acceptance criteria for the emission testing program of interest to the user.

4.3 This guide also describes the qualities of an emission reference material, the different methods available to independently determine the VOC emission rate of a reference material, and the chamber operating parameters that potentially influence a reference material's emission results.

5. Significance and Use

5.1 Chamber testing is a globally-accepted method for measuring the emissions of VOCs from building materials and products. Chamber emission test data have a variety of uses including identification and labeling of products as low-VOC emitting for improved indoor air quality, manufacturing quality control, and development of new and improved products for reduced VOC emissions.

5.2 Currently, an inter-laboratory study (ILS) is the most frequently used method for assessing the bias of a laboratory's VOC emission test results. An ILS typically relies on a VOC source with an uncharacterized emission rate. Consequently, a large number of participants (Practice E691 recommends 30, with a minimum requirement of six) are needed to produce the data required to calculate a laboratory's performance relative to the central tendency and distribution of the results for all participants. Due to the participant size requirement and other logistical issues, an ILS involves significant planning and coordination to achieve useful results.

5.3 Inter-laboratory studies have often shown significant variations in measured VOC emission rates among participating laboratories for a given source. Variability in the emission rate from the source often is suspected to be a contributing factor, but it is difficult to be certain of the cause. Thus, better characterized sources are needed for evaluating the ability of laboratories to generate VOC emission test results with acceptable bias as discussed in 8.6.

5.4 Proficiency tests (PT) for VOC emission testing typically focus on a laboratory's analytical capabilities. For example, an analytical PT relies on a certified standard prepared by an accredited vendor as a reference. A laboratory analyzes the PT sample without knowledge of its concentration value. Acceptance of the results is judged by the deviation from the known value. Use of reference materials can expand analytical PT schemes to also include the impacts of test sample handling, test specimen preparation, chamber operation, and chamber air sampling.

5.5 Laboratories accredited under ISO/IEC 17025 are required to derive uncertainty estimates for their test results. Typically, this is done by developing an uncertainty budget and estimating an expanded uncertainty (ISO/IEC Guide 98, Practice D7440). An uncertainty budget for a VOC emission test combines relevant sources of measurement uncertainty for all steps in the testing process from test specimen preparation through air sample analysis. A more efficient approach to determining the overall bias and precision for a VOC emission test is with repeated testing of a reference material (see ISO/IEC Guide 98, ISO Guide 33). This guide addresses the estimation of bias through comparison of the measured value to the reference material value. The precision is determined through repeated testing of multiple reference materials, ideally from the same production batch (see Practices D6299 and E691).

5.6 Other uses of an emissions reference material include verifying quality control emission measurements of manufactured product batches and providing traceability for third party certification.

6. Reference Material Attributes

6.1 According to ISO Guide 30, a reference material with an "assigned quantity value" can be used to improve the accuracy of test methods and analysis, to evaluate laboratory equipment performance characteristics, and to establish metrological traceability. For material VOC emission testing, the assigned quantity value for the reference material is its emission rate of a specific VOC (see Guide D5116 for a discussion of material emission rates).

6.2 To meet ISO Guide 30 criteria, a reference material for material emission testing should consist of a known amount of

VOC that transfers to the surrounding air at a predictable rate. In addition to meeting this "homogeneous and stable" criterion, reference materials for material emission testing should have the following characteristics.

6.2.1 An ideal reference material has a similar chemical matrix to a typical indoor material (for example, building product, furniture component, paint or cleaning product) and emits VOCs in a similar manner. For the purpose of this standard, the test item is referred to as a "material" regardless of its actual composition or description. In general, mass transfer rates of VOCs from materials are controlled by evaporative mass transfer from the surface, desorption of adsorbed compounds, or diffusion within the material, or a combination thereof (Guide D5116).

6.2.1.1 The dominating mass transfer process depends upon the age and type of material. For example, VOC emission rates from so-called "dry" materials (carpets, floor tiles, and particleboard) are initially affected by evaporation, but are ultimately controlled by internal diffusion processes. The VOC emission rates from so-called "wet" materials (for example, paints and cleaning products) tend to be more dynamic than dry materials with a high initial emission rate. The initial emission rate is primarily controlled by evaporation. Once most of the solvent has evaporated from a material, the emission rate is controlled by internal diffusion processes as described for dry materials.

6.2.1.2 The reference material's VOC emission rate should respond to laboratory chamber conditions similar to the way typical test materials respond. Therefore, the emission rate should be sensitive to environmental conditions that affect mass transfer processes (for example, temperature, relative humidity, airflow rate and air velocity). Additionally, the reference material's response to these different environmental factors should be well understood.

6.2.2 For commercial distribution, the reference material should be produced in batch quantities (typically on the order of hundreds of units) that are determined to be consistent (**2**). Stratified random sampling and a null-hypothesis statistical approach is used to verify the "homogeneity" of the batch (ISO Guide 35). Additional requirements for reference material producers are discussed in ISO Guide 34.

6.2.3 The reference material should emit VOCs that are measurable by the same sampling and analytical techniques used in VOC emission testing (for example, Test Method D5197, Test Method D7339 and ISO 16000-9). Chemical emissions should result in chamber concentrations appropriate to the level for which the measurement process is intended. Thus, reference materials of different sizes or numbers may be required for different types and sizes of test chambers.

6.2.4 The reference material should be packaged and shipped to prevent physical damage and minimize loss or degradation of the material. Short-term stability tests are described in ISO Guide 35.

6.2.5 The reference material shelf life should be known. ISO Guide 35 provides further information regarding long-term stability tests. Ideally, the shelf life should be several months or longer.

6.3 The temporal emission characteristics should be known for both constant and dynamic emission sources.

6.3.1 A reference material with a constant emission rate of a VOC allows test chamber air to reach a steady-state concentration. The time to reach near steady-state conditions is roughly three times the inverse of the air change rate. Thus, sampling should not occur until at least 3 h after the start of a test operating with a 1 h^{-1} air change rate. An example of a constant emission source is a filled liquid inner-tube diffusion film emission source described in Wei et al. (**3**). One advantage of a constant emission source is that chamber samples can be collected after only a few hours, allowing results to be obtained quickly.

6.3.2 A reference material with a dynamic emission rate is representative of a dry material whose emissions change with time as the source becomes depleted. To evaluate sampling at multiple concentrations, chamber air samples should be collected at a minimum of two elapsed times (for example, 24 and 72 h) in order to generate an emission profile. An example of a dynamic emission source is a polymer film loaded to equilibrium with a VOC as described in Cox et al. (**4**). A dynamic emission source also allows for the assessment of a laboratory's ability to measure analytes at different concentration levels.

6.4 According to NIST (**5**), there are several ways to determine a reference material's emission rate value.

6.4.1 A "certified" reference value is determined using at least two independent measurement methods. The optimal approach to determine a material's reference value is with a primary reference measurement procedure. For example, gravimetric determination is a primary method to measure the chemical content of a standard gas mixture.

6.4.2 Non-certified, reference values may be determined by one or multiple laboratories using a single method. For example, an ILS may be designed to determine an average reference value for a small subset of samples from a single batch. The resulting ILS value and uncertainty are then assigned to the remaining samples from that batch.

6.5 Temporal emission profiles may be determined by modeling. For example, the emission rates of VOCs from a relatively homogeneous polyvinyl chloride (PVC) flooring product have been well-characterized by fundamental mass transfer models (**4, 6 and 7**). Although not commonly used to assign reference values, such models may provide additional information regarding the performance of a test chamber. Cox et al. (**4**) developed a mass transfer model to predict the emission rate of toluene from a dynamic emission source. And, Wei et al. (**3**) developed a mass transfer model to predict the emission rate of toluene from a constant emission source.

6.6 When a new batch of reference materials is introduced, the associated reference emission rate value and its uncertainty should be re-established through accepted methods. An expanded uncertainty for a reference emission rate value may be determined using procedures in ISO/IEC Guide 98.

7. Apparatus and Operating Parameters

7.1 The state of the art for measuring VOC emissions from indoor materials is environmental chamber testing. An environmental chamber test exposes a material or representative portion of a material of known dimension (typically the material area, but results also may be normalized to material length or mass as appropriate) to a specified temperature, relative humidity and airflow rate. At these conditions, VOCs diffuse or evaporate from the material surface to chamber air. At a specified elapsed time, the resulting concentration of a VOC in chamber air is measured to determine the material's VOC emission rate or area-specific emission rate, termed emission factor (Guide D5116). Reference materials are designed to mimic material sources that are commonly evaluated for VOC emissions by chamber testing.

7.2 The emissions of VOCs during a test primarily depend upon the physicochemical properties and application of the material sample and the environmental exposure conditions. Chamber operating parameters have the potential to affect VOC emission rates. Thus, use of a reference material whose emission rate is also impacted by these parameters provides a check of chamber performance. Chamber parameters are addressed in the documentation accompanying a reference material. Detailed descriptions of the impacts of chamber parameters on VOC emission rates from materials can be found elsewhere (Guide D5116 and Practice D6670). A brief summary is provided here.

7.2.1 Temperature affects a VOC's volatility and diffusivity properties. As such, higher material and ambient air temperatures will result in faster emission rates. A commonly used temperature setpoint for chamber testing is 23°C with an associated precision and accuracy of ±0.5°C (Guide D5116). A relatively small deviation in chamber temperature can significantly affect a material's emission rate, and some reference materials can behave similarly. For example, a chamber study of environmental factors using a diffusion bottle source (**3**) estimated that the emission rate of toluene at 23.5°C was approximately 10 % higher than the emission rate for the same source at 22.5°C.

7.2.2 Relative humidity can impact the emission rates of water-soluble compounds such as formaldehyde. Relative humidity may also affect VOC emissions from materials that are hygroscopic since the adsorbed water may change the diffusion properties of the material and how the VOC desorbs from the surface. A commonly used relative humidity setpoint for chamber testing is 50 % with an associated precision of ±5 % and accuracy of ±10 % (Guide D5116). Some existing reference materials contain hydrophobic compounds and mimic sources that don't contain significant amounts of water.

7.2.3 Air change rate determines the rate of contaminant removal from the chamber system. When describing the amount of chamber air dilution, the air change rate is often normalized by the material surface area (area specific airflow rate). By the process of dilution with clean air, VOC concentrations in the chamber air will be lower for higher air change rates. In addition, the test chamber air concentration provides resistance to the rate of VOC evaporation. Thus, the greater the difference in concentration between the material surface and the chamber air, the greater the evaporation rate. This effect will be more pronounced for materials where VOC mass transfer is more impacted by the evaporation rate rather than by the diffusion rate in the bulk material. Ideally, reference materials result in chamber air concentrations of a VOC that are similar to concentrations of interest in emission testing of indoor materials.

7.2.4 Surface air velocity and turbulence affect the mass transfer evaporation rate of a VOC by changing the resistance of the boundary layer between the material surface and the chamber air. At higher air velocities and greater turbulence, the boundary layer resistance is reduced resulting in greater emissions, especially for wet materials. This effect, however, does have a threshold such that air velocities greater than a certain value will result in similar mass transfer rates (Guide D5116). Air velocity at the surface of a material is difficult to measure and often varies substantially between chambers used in different laboratories (**8**). Thus, this parameter may be an uncontrolled source of bias when comparing chamber measurements to reference material values.

7.2.5 In general, the emission profiles of indoor materials change with time, often following a first or second order decay rate. As a result, the elapsed time at which the material emission rate is determined will have an impact on the result. The impact of elapsed time is potentially greater for sources with a faster mass transfer rate (for example, evaporative "wet" sources). Some reference materials are dynamic sources. Exposure and sampling times must be controlled carefully when using dynamic sources.

7.3 Reference materials can be applied to a broad range of chamber designs and sizes including small chambers (Guide D5116, Test Method D6007, Practice D6330, Practice D6803, ISO 16000-9, ISO 16000-11 and CDPH/EHLB/Standard Method V1.1), full-scale chambers (Practice D6670, Test Method E1333, ANSI/BIFMA M7.1), emission cells (Practice D7143, ISO 16000-10) and micro-scale chambers (Practice D7706, ISO 12219-3). More general descriptions of environmental chamber systems are provided in Guide D5116 and Practice D6670.

7.4 Descriptions of sampling and analysis of VOCs in material emission tests are found in several standards, for example, Test Method D5197, Test Method D5466, Practice D6196, Test Method D7339, ISO 16000-3, ISO 16000-6 and Method TO-17. Possible sources of error during the collection and chemical analysis of air samples that may impact material emissions and reference material test results include collection efficiency, recovery, contamination, storage losses, analytical equipment calibrations and data analysis. In general, a laboratory's analytical accuracy is assessed regularly through a PT program.

7.5 As described in Guide D5116, the chamber concentration at a specific time point for a reference material is converted to an emission factor [EF in μg/(m^{2}h)] using Eq 1, with the assumption that this steady-state approximation is applied to constant sources and to dynamic sources with relatively low decay rates.

$$EF = C_t(N/L) \quad (1)$$

where:

C_t = chamber air concentration at time t (μg⁄m^3),
N = chamber air change rate (h^{-1}), and
L = sample loading factor (m^2/m^3).

The material emission rate (ER in μg/h) is equivalent to the product of the emission factor (EF) and the sample surface area (A).

8. Procedures for Using Reference Material

8.1 *Reference Material Characteristics*—Through prior efforts, a reference material has a well-characterized emission rate and associated uncertainty at specific test conditions. This essential information is provided on an accompanying certificate or other documentation for the reference material (ISO Guide 33). The reference material's documentation also provides detailed instructions for its handling, storage and use that must be followed in order to generate valid results. The general steps for using a reference material to evaluate the quality of a laboratory's measurement of a VOC emission rate are described here with the caveat that these recommendations may be superseded by the instructions associated with the use of a specific reference material. Examples of instructions associated with existing uses of reference materials are provided in Appendix X1.

8.2 *Shipping and Storage*—Reference materials manufactured offsite must be packaged and shipped to test laboratories in a manner that prevents losses of the reference compound. Since the compounds are volatile, special packaging and shipping measures (for example, shipping on dry ice, sealing materials in chemical equilibrium conditions, etc.) may be required. All reference materials should be stored by the test laboratory according to documented requirements and for no longer than the pre-determined expiration date. For example, if the reference material documentation states the need for sub-ambient temperature storage, a laboratory's results would be invalid for room temperature storage. Important information regarding the shipping and storage of a reference material includes the date of production, the date of receipt at the test laboratory, the condition of the material upon arrival, and the laboratory storage conditions.

8.3 *Chamber Preparation*—Specified chamber parameters for testing of reference materials include, at a minimum, chamber temperature, chamber relative humidity and chamber airflow rate. These values with allowable tolerances are provided in the reference material documentation. Each environmental condition should be independently verified with a measurement device traceable to established references. Prior to each test, the test chamber should be conditioned at the specified parameters for a minimum of four times the inverse of the chamber air change rate, after which background samples are collected to verify that VOC concentrations are less than a value that would significantly impact the results (see Guide D5116 for background concentration criteria).

8.4 *Sample Preparation and Loading*—Sample preparation instructions include the process for removing the reference material from its packaging. If the sample was stored at a reduced temperature, an equilibration time to allow the sample to reach room air temperature is necessary before opening the package. For some dynamic emission sources, the timing of this process is particularly important since the initial emissions may be lost before the sample is loaded in the chamber. If required, samples are placed in an inert material holder inside the chamber. Samples are typically placed near the center of the test chamber in the least obstructed way. After loading, the chamber is immediately closed and the emission test begins. In general, the sample preparation and loading time are minimized (only one to several minutes) to reduce losses of VOC before starting the test. Time zero for the test is dictated by the reference material documentation and may be when the material is first unwrapped, when the material is placed in the chamber, or when the chamber is closed after loading.

8.5 *Chamber Air Sampling*—The number of chamber air samples and their collection times during the test are indicated in the reference material documentation. In general, the elapsed sampling times should be the same or similar to those in the material emission test being evaluated. For example, Test Method E1333 requires chamber samples to be collected 16 to 20 h after the start of the test.

8.6 *Chamber Performance Evaluation*—A reference material may be used by a single laboratory to assess its proficiency for measuring the emissions of the analyte under defined conditions. As explained in several references (ISO 33, Practice D6617, **9**), the comparison of a test result to the reference value is assessed through statistical hypothesis testing. Due to the destructive nature of most material emission tests, laboratory bias based on a single test result is described here (see Practice D6617 for mathematical equations). Practice D6299 provides more information for assessing measurement precision with multiple test results.

8.6.1 The reference material's certificate provides the reference emission rate value and how well it is known in terms of an expanded standard uncertainty. All information regarding the determination of the reference value (for example, single versus multiple laboratories), traceability to established references, and uncertainty (due to material inhomogeneity, within-lab variability, and between-lab variability) is typically listed in the accompanying documentation.

8.6.2 According to ISO Guide 33 and Practice D6617, statistical hypothesis testing is used to determine if a laboratory's measured emission rate is equivalent to the reference emission rate value. Hypothesis testing can also be used to determine significant differences between chamber test results of two laboratories using a reference material for the comparison (Appendix X1). Hypothesis testing includes a null hypothesis (the measured and reference emission rates are not statistically different), and an alternative hypothesis (the measured and reference emission rates are statistically different). Since a laboratory's test results and the reference value have associated measurement error, it is necessary to determine a "tolerance zone" when making this comparison. The tolerance zone accounts for the measurement uncertainty and a predetermined confidence interval that the correct hypothesis is selected. For example, a 95 % confidence interval indicates that the null hypothesis would be incorrectly rejected 5 % of the time when it was actually true.

8.6.3 The first step is to determine the standard deviation of the test laboratory (σ_{LAB}) through replicate reference material emission tests. To calculate a site-specific (that is, a single test laboratory) standard deviation, a minimum of three emission test results are required, each using a fresh reference material (all from the same production batch) (see Practice E691).

8.6.4 The laboratory's standard deviation determined in 8.6.3 is compared to the standard error of the reference emission rate value (SE_{RERV}) provided with the reference material documentation. According to Practice D6617, the ratio of SERERV/σ_{LAB} should be less than or equal to 0.5 to be considered "useful."

8.6.5 Next, combine the uncertainties of the measured value and the reference emission rate value using the root sums of squares method:

$$\varepsilon = \sqrt{\sigma_{LAB}^2 + SE_{RERV}^2} \qquad (2)$$

8.6.6 The reference material certificate will specify the significance level (typically $\alpha = 0.05$) for which the null hypothesis is incorrectly rejected (Type I error) and the maximum bias (Δ) that is allowable for a test laboratory to be considered proficient (for example, 20 %).

8.6.7 Calculate the standardized delta (Δ_s) with the following equation:

$$\Delta s = \Delta / \varepsilon \qquad (3)$$

8.6.8 Use Table 1 from Practice D6617 to determine the associated power of bias detection and the value of k that is multiplied by ε to determine the acceptable tolerance zone. A truncated version of Table 1 from Practice D6617 for Type I error rates of 0.05 and 0.10 is provided below. Refer to Practice D6617 for entire table contents.

8.6.8.1 *Tolerance Zone*—The acceptable tolerance zone is defined as $0 \pm k\varepsilon$. The value of k is selected from Column B in Table 1 according to the Type I Error Rate. For a user-specified Type I Error Rate of 0.05, the value of k is 1.96.

8.6.8.2 *Power of Bias Detection*—Table 1 also provides the associated probability of detecting a bias of at least Δ. For a given Δ/ε (Δ_s) and Type I error rate, there is an associated probability of correctly rejecting the null hypothesis. To determine this probability, find the cell that intersects the column with the value closest to the Δ_s calculated in 8.6.7 and the row with the Type I Error Rate. For example, a Δ_s of 2.5 and Type I Error Rate of 0.05 has an associated power of bias detection of 0.71. Practice D6617 provides further instruction on how to adjust values to increase the associated power of bias detection if the calculated value is deemed too low for a given application.

8.6.9 If the difference between the laboratory's average test result and the reference emission rate value for each specified sampling time is less than the acceptable tolerance zone, then the testing laboratory is considered proficient for quantifying emissions from the reference material without significant bias.

8.6.10 If the difference between the laboratory's average test result and the reference emission rate value for any of the required sampling times is greater than the acceptable tolerance zone, then significant measurement bias has been detected. This may necessitate the entry of a corrective action request in the laboratory's quality management system.

8.7 *Cause Analysis*—As described in earlier sections, there are several factors that may cause an emission rate value to be outside the acceptable tolerance zone. Isolating the following factors can help to identify a measurement issue.

8.7.1 *Analytical Problems*—The calibration of the analytical equipment may be inaccurate and lead to bias in the emission rate result. It is often possible to isolate this issue by performing an analytical PT as required by ISO 17025.

8.7.2 *Chamber Operation Setpoints*—Confirm temperature and relative humidity setpoints with a second measurement device traceable to a standard reference. Air change rates can be verified using electronic mass flow sensors or a tracer gas decay test (Test Method E741). Losses of chemical to chamber surfaces can be determined with mass recovery tests (Guide D5116 and Practice D6617).

9. Reporting Test Results

9.1 The laboratory reports the results of reference material chamber testing in a format that is consistent with the full reporting of emission tests results for customers. The report includes all information required to be reported by the referenced standards and all information needed for interpretation of the reference material test results. Any deviations from standards and reference material instructions are noted. Information specific to the reporting of reference material test results includes:

9.1.1 Name and address of the reference material supplier, the supplier's accreditation certificate number if applicable (see ISO 17043), the material's lot number and serial number if applicable, the material's production date, the shipping and receipt dates, and the condition of the shipped package on arrival. Attach a copy of the reference material certificate to the report.

TABLE 1 Type I Error and Associated Power of Bias Detection for Various Δ_s Values (reproduced from Practice D6617)

A	B	Power of Detecting [bias] = Δ_s[A]												
Required Type I Error Rate	k	(Δ_s) = 0.5	0.75	1	1.25	1.5	1.75	2	2.25	2.5	2.75	3	3.5	4
0.05	1.96	0.07	0.11	0.17	0.24	0.32	0.42	0.52	0.61	0.71	0.79	0.85	0.94	0.98
0.10	1.64	0.13	0.19	0.26	0.35	0.44	0.54	0.64	0.73	0.80	0.87	0.91	0.97	0.99

[A] Δ_s = Power of detecting bias.

9.1.2 Reference material storage conditions such as the temperature range during storage.

9.1.3 Chamber background air concentration of the test analyte.

9.1.4 Reference material handling and use:

9.1.4.1 Date and time reference material is removed from its packaging or was assembled.

9.1.4.2 Amount of time expended preparing the reference material for the emission test after its removal from packaging.

9.1.4.3 Position of the reference material in the chamber and description of any specialized holder. Photographic documentation is recommended.

9.1.4.4 Time reference material test begins (time zero).

9.1.5 Details of air sample collection where there are deviations from procedures used in emission testing of material specimens including sample collection start times, sampling intervals, sampling airflow rates and sample volumes.

9.1.6 Details of air sample analysis where there are deviations from procedures for normal emission test air samples.

9.2 Documentation associated with the laboratory testing of the hypothesis regarding the deviations of the test results from the defined reference material value (see 8.6).

9.2.1 Typically hypothesis testing requires calculation of the chamber concentrations of the analyte including any corrections for measured chamber background. If applicable, the analyte emission rates or emission factors also are calculated.

9.2.2 If replicate tests have been performed, report the individual values and the summary statistics.

9.2.3 Identify the significance level and the maximum allowed bias for the comparison.

9.2.4 Indicate whether the laboratory was successful at measuring the emissions from the reference material without significant bias. If not, indicate the corrective actions that are to be taken or the tracking number of the corrective action request that was generated.

10. Keywords

10.1 building materials; building products; environmental test chambers; emission rate; volatile organic compounds; reference materials; proficiency testing; indoor air quality

APPENDIX

(Nonmandatory Information)

X1. EXAMPLE REFERENCE MATERIAL PROCEDURES

X1.1 Example instructions for using a polymethyl pentene film loaded with toluene to compare the performance of micro-scale chamber emission systems in two different laboratories.

X1.1.1 *Shipping and Storage*—To retain the total mass of toluene, the reference material films are individually packaged in aluminum foil and are kept at subzero temperature. This criteria requires the films to be shipped overnight on dry ice to the test laboratory. Upon receipt, the test laboratory removes the films from the shipping container and stores them (still in original packaging) in a laboratory freezer. The date of receipt is recorded as well as the condition of the shipment and packaging (for example, complete loss of dry ice, any damage, etc.).

X1.1.2 *Chamber Preparation*—Three films are run simultaneously in three different micro-scale chambers to allow for triplicate sampling. The following parameters are used for each chamber and are verified prior to the test:

X1.1.2.1 *Inlet Airflow Rate Setpoint*—100 mL/min of air. Dry air (0 % relative humidity) is provided by high purity compressed air cylinders. Flow rates are set prior to the test with chambers at 65°C and the same number of chambers in the open flow condition as during the test. Also prior to the test, duplicate background samples are collected to ensure the inlet air and chamber air do not have detectable concentrations of toluene.

X1.1.2.2 *Temperature*—The starting condition is room temperature. The test temperature of 65°C is verified with a temperature measurement device traceable to NIST or other national reference system.

X1.1.3 *Sample Preparation and Loading in Chamber:*

X1.1.3.1 During loading, the micro-scale chamber is at room temperature with no airflow through the chamber.

X1.1.3.2 Remove packaged film from laboratory freezer.

X1.1.3.3 Place the film with its holder in the center of the bottom of the chamber (do not use any inserts). Position the film so it is perpendicular to an imaginary line between the inlet and outlet holes in the micro-scale chamber cover.

X1.1.3.4 Close the chamber lid.

X1.1.3.5 The entire loading process should take less than 30 s.

X1.1.3.6 After closing the chamber lid, raise the temperature setpoint to 65°C. As soon as the temperature reaches 65°C, turn on the air flow. Record time “zero” and the time when the temperature in the chamber reaches 65°C.

X1.1.4 *Chamber Air Sampling*—A total of 18 samples are collected consisting of two sampling times collected in triplicate from three separate chambers.

X1.1.4.1 Chamber air samples are collected from the micro-scale chamber exhaust port. Samples are collected on an appropriate sorbent for toluene and analyzed using thermal desorption gas chromatography/mass spectrometry (TD/GC/MS).

X1.1.4.2 The first sample is collected at 60 min elapsed time and the second sample is collected at 120 min.

X1.1.4.3 The sample times are 3 min in duration for the 60 min sample and 5 min in duration at 120 min.

X1.1.4.4 *Chamber Performance Evaluation*—Hypothesis testing is used to determine if the results are statistically different between the two test laboratories. The averages of triplicate samples from each time (that is, 60 min and 120 min) are tested using a null hypothesis comparison between the two laboratories with a tolerance based on a significance level (α) of 0.05 and an allowable bias of 20 %.

X1.2 Example instructions for using a toluene liquid inner-tube diffusion film emission (LIFE) reference material to compare the emission rate measured in a small chamber to that determined gravimetrically (**3**).

X1.2.1 *Shipping and Storage*—The LIFE reference source consists of a 20-mm diameter polytetrafluoroethylene tube (34-mm height) and a diffusion lid containing a hole covered with a 1-mm diameter aluminum oxide melamine-impregnated paper. When in use, the tube contains 5 mL of liquid toluene with a purity of 99.8 %. The source and toluene may be shipped separately and stored as recommended.

X1.2.2 *Chamber Preparation*—The small chamber parameters are as follows:

X1.2.2.1 Temperature: 23 ± 0.5°C.

X1.2.2.2 Relative humidity: 50 ± 5 %.

X1.2.2.3 Chamber air change rate: 1 ± 0.01 h^{-1}.

X1.2.2.4 Mixing fan is on.

X1.2.2.5 Chamber is conditioned at the above setpoints for at least 4 h prior to starting the test. After the 4 h conditioning period, duplicate background samples are collected to ensure toluene concentration in the chamber is less than 2 $\mu g/m^3$.

X1.2.3 *Sample Preparation and Loading in Chamber:*

X1.2.3.1 In a fume hood, 5 mL of liquid toluene is added to polytetrafluoroethylene tube and the tube is capped with diffusion lid.

X1.2.3.2 The source remains in the fume hood at 23°C to allow the diffusion film to become saturated with toluene. After 6 h, the source is considered to have a constant emission rate of toluene.

X1.2.4 *Chamber Air Sampling*—At least three chamber air samples are collected in duplicate after the chamber reaches steady-state conditions ($t > 3$ h). Sample times include 4, 5, and 6 h. Air samples are collected on sorbent tubes and analyzed using TD/GC/MS.

X1.2.4.1 *Comparison to Gravimetric Measurement Provided with Device (**3**)*—The average values of all samples collected after steady-state concentration is reached are converted to emission rate values and compared to the reported gravimetrically-determined emission rate with a significance level (α) of 0.05.

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