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# Standard Guide for Selecting Volatile Organic Compounds (VOCs) and Semi- Volatile Organic Compounds (SVOCs) Emission Testing Methods to Determine Emission Parameters for Modeling of Indoor Environments<sup>1</sup>

This standard is issued under the fixed designation D8141; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 This guide is intended to serve as a foundation for understanding when to use emission testing methods designed for volatile organic compounds (VOCs) to determine area-specific emission rates that are typically used in modeling indoor air VOC concentrations and when to use emission testing methods designed for semi-volatile organic compounds (SVOCs) to determine mass transfer emission parameters that are typically used to model indoor air, dust, and surface SVOC concentrations.

1.2 This guide discusses how organic chemicals are conventionally categorized with respect to volatility.

1.3 This guide presents a simplified mass-transfer model describing organic chemical emissions from a material to bulk air. The values of the model parameters are shown to be specific to material/chemical/chamber combinations.

1.4 This guide shows how to use a mass-transfer model to estimate whether diffusion of the chemical within the material or convective mass transfer of the chemical from the surface of the material to the overlying air limits chemical emissions from the material surface.

1.5 This guide describes the range of different chambers that are available for emission testing. The chambers are classified as either dynamic or static and either conventional or sandwich. The chambers are categorized as being optimal to determine either the area-specific emission rate or mass-transfer emission parameters.

1.6 This guide discusses the roles sorption and convective mass-transfer coefficients play in selecting the appropriate emission chamber and analysis method to accurately and efficiently characterize emissions from indoor materials for use in modeling indoor chemical concentrations.

1.7 This guide recommends when to choose an emission test method that is optimized to determine either the area-specific emission rate or mass-transfer emission parameters. For chemicals where the controlling mass-transfer process is unknown, the guide outlines a procedure to determine if the chemical emission is controlled by convective mass transfer of the chemical from the material.

1.8 This guide does not provide specific guidance for measuring emission parameters or conducting indoor exposure modeling.

1.9 Mechanisms controlling emissions from wet and dry materials and products are different. This guide considers the emission of chemicals from dry materials and products. Examples of functional uses of VOCs and SVOCs that this guide applies to include blowing agents, flame retardants, adhesives, plasticizers, solvents, antioxidants, preservatives, and coalescing agents **(1)**.<sup>2</sup> Emission estimations for other VOC and SVOC classes including those generated by incomplete combustion, spray application, or application as a powder (pesticides, termiticides, herbicides, stain repellents, sealants, water repellants) **(1)** may require different approaches than outlined in this guide because these processes can increase short-term concentrations of chemicals in the air independent of the volatility of the chemical and its categorization as a VVOC (very volatile organic compounds), VOC, SVOC, or NVOC (non-volatile organic compounds).

1.10 The effects of the emissions (for example, exposure, and health effects on occupants) are not addressed and are beyond the scope of this guide.

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

1.12 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the*

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<sup>2</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

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.

1.13 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:<sup>3</sup>

**D1356** Terminology Relating to Sampling and Analysis of Atmospheres

**D5116** Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products

**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

**D6330** Practice for Determination of Volatile Organic Compounds (Excluding Formaldehyde) Emissions from Wood-Based Panels Using Small Environmental Chambers Under Defined Test Conditions

**D6345** Guide for Selection of Methods for Active, Integrative Sampling of Volatile Organic Compounds in Air (Withdrawn 2018)<sup>4</sup>

**D6670** Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/Products

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

**D8142** Test Method for Determining Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation using Micro-Scale Environmental Test Chambers

**D8345** Test Method for Determination of an Emission Parameter for Phthalate Esters and Other Non-Phthalate Plasticizers from Planar Polyvinyl Chloride Indoor Materials for Use in Mass Transfer Modeling Calculations

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

### 2.2 Other Documents:

**Directive 2004/42/CE** of the European Parliament and of the Council on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products and amending Directive 1999/13/EC<sup>5</sup>

**Emission Testing Method for CDPH Standard Method V1.2.,**

**2017 Standard Method for the Testing and Evaluation of Volatile Organic Chemical Emissions from Indoor Sources using Environmental Chambers, Indoor Air Quality Section, Environmental Health Laboratory Branch, Division of Environmental and Occupational Disease Control, California Department of Public Health<sup>6</sup>**

**I.S. EN 16402:2013** Paints and Varnishes—Assessment of Emissions of Substances from Coatings into Indoor Air—Sampling, Conditioning, and Testing<sup>7</sup>

**ISO 16000-6:2011** 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<sup>8</sup>

**ISO 12219-1** Interior Air of Road Vehicles—Part 1: Whole Vehicle Test Chamber—Specification and Method for the Determination of volatile Organic Compounds in Cabin Interiors<sup>8</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definitions of terms commonly used for sampling and analysis of atmospheres, refer to Terminology **D1356**. For definitions and terms commonly used when testing materials and products for emissions, refer to Guide **D5116** and Practices **D6670** and **D7706**.

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *conventional chamber, n*—a chamber with test materials on one surface only.

3.2.2 *dynamic chamber, n*—a chamber with input and output airflow.

3.2.3 *sandwich chamber, n*—a chamber with test materials on opposite surfaces (typically top and bottom); typically used to reduce the surface-to-volume ratio to mitigate wall sorption effects; sometimes these chambers are referred to as material-air-material chambers.

3.2.4 *static chamber, n*—a sealed chamber with no airflow.

## 4. Significance and Use

4.1 Emissions of VOCs are typically controlled by internal mass-transfer limitations (for example, diffusion through the material), while emissions of SVOCs are typically controlled by external mass-transfer limitations (migration through the air immediately above the material). The emission of some chemicals may be controlled by both internal and external mass-transfer limitations. In addition, due to their lower vapor pressure, SVOCs generally adsorb to different media (chamber walls, building materials, particles, and other surfaces) at greater rates than VOCs. This sorption can increase the amount

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>4</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>5</sup> Available at <https://www.legislation.gov.uk/>.

<sup>6</sup> Available from Underwriters Laboratories (UL), UL Headquarters, 333 Pfingsten Road, Northbrook, IL, 60062, <http://www.ul.com>.

<sup>7</sup> Available from European Committee for Standardization (CEN), Avenue Marnix 17, B-1000, Brussels, Belgium, <http://www.cen.eu>.

<sup>8</sup> Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <https://www.iso.org>.

of time required to reach steady-state SVOC concentrations using conventional VOC emission test methods to months for a single test (2).

4.2 Thus, existing methods for characterizing emissions of VOCs may not be appropriate or practical to properly characterize emission rates of SVOCs for use in modeling SVOC concentrations in indoor environments. A mass-transfer framework is needed to accurately assess emission rates of SVOCs when predicting the SVOC indoor air concentrations in indoor environments. The SVOC mass-transfer framework includes SVOC emission characteristics and its partition to multimedia including sorption to indoor surfaces, airborne particles, and settled dust. Once the SVOC emission parameters and partitioning coefficients have been determined, these values can be used to modeling SVOC indoor concentrations.

## 5. Overview of Concepts Related to Organic Chemical Emissions in Indoor Environments

5.1 *Semi-Volatile Organic Compound (SVOC)*—There are many physical property based definitions used to describe the difference between a VVOC, a VOC, an SVOC, and a NVOC. The definitions typically are based on the chemicals' vapor pressure at 25 °C, the chemical boiling point, or the relative position (time) a chemical is observed on a chromatograph. These definitions are useful to differentiate between chemicals in laboratory settings and experiments. Table 1 lists the different physical property-based definitions from ten different

references. The data in Table 1 are not provided as authoritative definitions for VOC and SVOCs, but rather to inform the reader to the extent of variation in accepted definitions for these terms. As an example, the chemical properties used to differentiate between a VOC and an SVOC are listed in the row between the VOC and SVOC rows. There are five different boiling points spanning a 107 °C range that have been used to define the cut off between a VOC and an SVOC. The delineation between VOC and SVOC is further complicated by the fact that some chemicals do not have an accurately measured boiling point or decompose prior to boiling. Likewise, there are no universally accepted vapor pressure or chromatographic retention time delineations between VOCs and SVOCs. The use of chromatographic retention time as a delineator is further complicated because retention times are strongly influenced by chromatographic conditions such as the choice of the column stationary phase polarity.

5.1.1 Labeling chemicals as VVOCs, VOCs, SVOCs, or NVOCs using chemical properties such as vapor pressure and boiling point may have limited value when trying to describe how chemicals emit from materials in indoor environments. This is especially true for chemicals close to the edge of these physical property definitions.

5.1.2 When modeling material emissions into an indoor environment, the classification (VOC, SVOC) is not as important as defining the rate limiting step for the emission of the chemical. The rate limiting step is the slowest step in the

**TABLE 1 Chemical Classification Definition Ranges for VVOC, VOC, SVOC, and NVOC**

NOTE 1—The chemical properties used to differentiate between different classifications are listed in the row between the classification rows. Some values listed are illustrative examples given in the references listed below the table. The maximum chromatogram retention time describes how the chemical elutes from a non-polar or slightly polar gas chromatographic separation column compared to n-alkane.

	Maximum Vapor Pressure at 25 °C	Maximum Boiling Point at 101.3 kPa	Maximum Chromatogram Retention Time
<b>VVOC</b>			
VVOC / VOC Delineation	15 kPa <sup>A</sup> 500 kPa <sup>C</sup>	30 °C <sup>A</sup> 68 °C <sup>D</sup> 50–100 °C <sup>F</sup>	C <sub>5</sub> <sup>B</sup> C <sub>6</sub> <sup>E,D</sup>
<b>VOC</b>			
VOC / SVOC Delineation	10 <sup>-2</sup> kPa <sup>G,H,I,J,C</sup>  10 <sup>-4</sup> kPa <sup>L</sup>	180 °C <sup>A</sup> 250 °C <sup>K</sup> 240–260 °C <sup>F,H</sup> 287 °C <sup>E,D</sup>	C <sub>16</sub> <sup>E,D</sup> C <sub>17</sub> <sup>B</sup>
<b>SVOC</b>			
SVOC / NVOC Delineation	10 <sup>-8</sup> kPa <sup>G,H,J</sup> 10 <sup>-12</sup> kPa <sup>I</sup> 10 <sup>-11</sup> kPa <sup>L</sup>	>300–350 °C <sup>A</sup> 380–400 °C <sup>F,H</sup>	C <sub>22</sub> <sup>D</sup>
<b>NVOC</b>			

<sup>A</sup> Guide D6345

<sup>B</sup> Emission Testing Method for CDPH Standard Method V1.2., 2017 (also known as California Specification 01350)

<sup>C</sup> Practice D6330

<sup>D</sup> I.S. EN 16402:2013

<sup>E</sup> ISO 16000-6:2011

<sup>F</sup> WHO (3)

<sup>G</sup> Terminology D1356

<sup>H</sup> ISO 12219-1

<sup>I</sup> Little, Weschler (1)

<sup>J</sup> Practice D6177

<sup>K</sup> Directive 2004/42/CE

<sup>L</sup> Donahue, et al. 2006 (4)

migration of a chemical from the interior of the material to the bulk air and is a function of the chemical, material, and environment combination. Chemicals emitting from materials can be broadly classified into three groups: (1) chemicals where the rate limiting step is the migration of the chemical to the material's surface (internal mass transfer, typical of chemicals classified as VOCs), (2) chemical where the rate limiting step is the migration of the chemical from the materials surface to the bulk air (external mass transfer, typical of chemicals classified as SVOCs), or (3) chemicals where the rate of migration of the chemical to the material surface and migration of the chemical from the material surface into the bulk air are similar for a given environment.

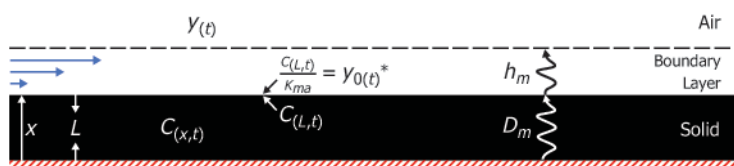
5.1.3 In addition, the emission of a chemical might be limited by internal diffusion in one material, but limited by external mass transfer in another material depending upon the material composition and physical structure. These cases illustrate that there is no definitive delineation between a VOC or an SVOC from either a chemical characteristic definition or from a mass transfer framework. However, if applicable, common assumptions for SVOCs will be stated explicitly for context.

5.2 Mass-Transfer Parameters—To understand how VOC and SVOC emissions differ, it is important to understand a mathematical model of mass transfer for a chemical moving from the solid material phase to the air phase. Fig. 1 illustrates a simplified, one-dimensional mass-transfer model for a chemical emitting from a material. This model is applicable to the emission of both VOCs and SVOCs from a material. However, several simplifications of the model are often made if the model is applied to SVOCs. In this model, the following parameters are defined as:

- $C_{(x,t)}$  = the chemical concentration in the solid material at a depth  $x$  at time  $t$  ( $\mu\text{g}/\text{m}^3$ ). For SVOCs, this parameter is often assumed to be constant over time (no depletion) and throughout the material (6). Then,  $C_{(x,t)}$  is replaced by  $C_0$  for  $0 \leq x \leq L$  and  $t > 0$ .
- $C_{(L,t)}$  = the chemical concentration on the surface of the solid material ( $x = L$ ) at time  $t$  ( $\mu\text{g}/\text{m}^3$ ). For SVOCs, this parameter is often assumed to equal  $C_0$  (6).
- $y(t)$  = the chemical concentration in the bulk air at time  $t$  ( $\mu\text{g}/\text{m}^3$ ).
- $y_{o(t)}$  = the chemical concentration in the air phase immediate above the material surface at time  $t$  ( $\mu\text{g}/\text{m}^3$ ).
- $L$  = the thickness of the solid material (m).
- $K_{ma}$  = the material-air partition coefficient, that is, the ratio of the chemical concentrations in the solid and air phases when the chemical is in equilibrium across the interface between the two phases (dimensionless or  $\text{m}^3 \text{air} / \text{m}^3 \text{material}$ ).
- $D_m$  = the diffusion constant for the chemical in the solid material (resistance to movement through the material) ( $\text{m}^2/\text{s}$ ). For SVOCs, emission from solid materials is often assumed to be controlled only by external mass transfer (that is, by  $h_m$ ) and further it is often assumed that  $C_{(x,t)} = C_0$ , the influence of  $D_m$  becomes negligible for SVOCs (6, 7).
- $h_m$  = the convective mass-transfer coefficient (resistance to movement through the gaseous boundary layer, (m/s).

5.2.1 Other parameters used in this guide include:

- $A$  = the surface area of the solid material of interest ( $\text{m}^2$ ),
- $Bi_m$  = Biot number for mass transfer,  $Bi_m = \left( \frac{h_m L}{D_m} \right)$  (dimensionless), and



\*Simplification for SVOCs. Assumptions discussed in Section 6.10

FIG. 1 Mass Transfer from a One-Dimensional Material to Bulk Air (adapted from Xu and Zhang (5) and Liu et al. (6))



$Fo_m$  = Fourier number for mass transfer,  $Fo_m = \frac{D_m t}{L^2}$   
(dimensionless).

## 6. Choosing between VOC and SVOC Emission Test Methods using a Mass Transfer Framework

6.1 Choosing the correct emission test method to determine emission parameter values requires knowledge of how the emission parameters are going to be used in a model. Many mass-transfer models have been used to describe dry (diffusional) sources of VOCs and SVOCs (6, 8 and 9). The models differ in their assumptions and how they are solved (analytically, numerically, ordinary differential equations or partial differential equations). However, all the mass-transfer models require the surface area of the material of interest ( $A$ ), the thickness of the material ( $L$ ), the chemical partition coefficient ( $K_{ma}$ ), and the diffusion constant in the bulk material ( $D_m$ ). Some of the models also require the initial chemical concentration in the material of interest ( $C_{(L,0)}$ ), and the convective mass-transfer coefficient ( $h_m$ ). The values of these parameters can be used to determine which type of emission test method is appropriate for the chemical and material of interest.

6.2 Typically, the diffusion coefficient,  $D_m$ , varies from  $10^{-13}$  m<sup>2</sup>/s to  $10^{-11}$  m<sup>2</sup>/s. Approaches to estimate  $D_m$  are readily available (10). The convective mass-transfer coefficient,  $h_m$ , typically varies from  $10^{-4}$  m/s to  $10^{-2}$  m/s and estimation approaches are readily available (11). The material-air partition coefficient,  $K_{ma}$ , varies from  $10^1$  to  $10^{13}$ . While estimation approaches are available (12), material- and chemical-specific experimental data are recommended to reduce uncertainty. Hence, the partition coefficient value can play an important role in determining the rate limiting step controlling emissions from materials for VOCs and SVOCs.

6.3 The partition coefficient,  $K_{ma}$ , describes the ratio of chemical concentrations in the solid and air phases when the chemical is in equilibrium across the interface between the two phases. Most models assume that equilibrium partitioning across the interface is instantaneous.

$$K_{ma} = \frac{C_{(eq)}}{y_{(eq)}} \quad (1)$$

where:

$C_{(eq)}$  = the equilibrium chemical concentration in the solid material ( $\mu\text{g}/\text{m}^3$ ), and

$y_{(eq)}$  = the equilibrium chemical concentration in the air phase ( $\mu\text{g}/\text{m}^3$ ).

6.4 The dimensionless Biot number for mass transfer ( $Bi_m$ ) divided by the partition coefficient ( $K_{ma}$ ) can be used to determine whether chemical emissions are controlled by the migration of the chemical to the materials surface (internal mass transfer) or by the migration of the chemical from the materials surface to the bulk air (external mass transfer) (5).

$$\frac{Bi_m}{K_{ma}} = \left( \frac{h_m L}{D_m} \right) = \left( \frac{L}{D_m} \right) \left( \frac{h_m}{K_{ma}} \right) \quad (2)$$

6.5  $Bi_m/K_{ma}$  relates the two fundamental processes that control the rate of emissions of organic chemicals from indoor materials: diffusion within the material (represented by  $L/D_m$  above), and convective mass transfer from the surface of the material to the overlying air (represented by  $h_m/K_{ma}$  above). For any given chemical/material/chamber combination, one of these two processes will typically be the rate limiting step controlling the rate of chemical emissions from the material. However, in some cases the emission rate is controlled by both processes.

6.6 If  $Bi_m/K_{ma}$  is greater than 35, then the rate of migration of the chemical from the surface to the bulk air is twenty times greater than the rate of migration of the chemical to the materials surface (valid for cases when the Fourier number for mass transfer,  $Fo_m = \frac{D_m t}{L^2}$  is equal to  $10^{-4}$ ) (5, 6). Hence, the emission of the chemical in these cases will be controlled by the rate limiting diffusion of the chemical to the material's surface and not dependent on the airflow above the material. In these cases, the modeled emission rate in an indoor environment can be directly represented by a constant determined in a conventional emission test chamber study. This emission rate for modeling indoor environments is often referred to as the area-specific emission rate ( $E_{AS}$ ,  $\mu\text{g}/(\text{m}^2 \text{ h})$ ) and is calculated from conventional emission chamber studies as follows:

$$E_{AS} = \frac{Q_{(Chamber)} y_{(SS-Chamber)}}{A_{(Chamber)}} \quad (3)$$

where:

$Q_{(Chamber)}$  = the flow into the chamber ( $\text{m}^3/\text{h}$ ),

$y_{(SS-Chamber)}$  = the steady-state chemical concentration in the air phase ( $\mu\text{g}/\text{m}^3$ ), and

$A_{(Chamber)}$  = the area of the source material ( $\text{m}^2$ ).

6.7 Calculating the area-specific emission rate by means of Eq 3 assumes that (1) there is no chemical concentration in the inflow to the chamber, (2) the chemical has reached a steady-state concentration, and (3) sorption to chamber walls is minimal or has reached a steady-state condition. In summary, when  $Bi_m/K_{ma}$  is greater than 35, the chamber determined area-specific emission rate ( $E_{AS}$ ) can be used to estimate emissions when modeling chemical concentrations in indoor environments.

6.8 If  $Bi_m/K_{ma}$  is less than 1, then the rate of migration of the chemical from the surface to the bulk air is the primary limiting mass-transfer process (6). The chemical's emission will be controlled by the migration from the surface to the bulk air. In these cases, internal diffusion becomes negligible and the chemical emission rate in an indoor environment can be modeled using a mass-transfer approach ( $E_{MT}$ ,  $\mu\text{g}/(\text{m}^2 \text{ h})$ ). This approach is usually chosen for SVOCs. The modeled emission rate ( $E_{MT}$ ) can be represented by the product of the convective mass-transfer coefficient ( $h_m$ ), and the difference between the gaseous concentration near the material surface ( $y_{o(t)}$ ) and the bulk air ( $y_{(t)}$ ):

$$E_{MT} = h_m (y_{o(t)} - y_{(t)}) \quad (4)$$

6.9 While the gaseous concentration near the material surface ( $y_{o(t)}$ ) and the bulk air ( $y_{(t)}$ ) are the same in a chamber and

the indoor environment (assuming the same temperature and relative humidity), the convective mass-transfer coefficient ( $h_m$ ), can be different for chamber systems and indoor environments. Hence, when the chemical emission is limited by the migration of the chemical from the materials surface to the bulk air, the emission rate calculated in Eq 4 may be different in the chamber and in an indoor environment.

6.10 For chemicals in dynamic flow environments (chambers and indoor environments) with emission rates that are limited by external mass transfer (diffusion through the air boundary layer), the bulk air concentration,  $y(t)$ , will not be equal to the equilibrium concentration,  $y_{(eq)}$ . In these cases, the chemical concentration in the air phase immediately above the material surface,  $y_{0(t)}$ , is often assumed to be in equilibrium with solid phase  $y_0 = \frac{C_{(L,0)}}{K_{ma}}$ , Fig. 1) and constant (5, 9, 13). The assumption of a constant  $y_0$  value is typically valid for materials with large partition coefficients (for example,  $K > 10^8$ ) and large initial concentrations (for example,  $>10\%$ ) (9). Further, for SVOCs it is often assumed that the chemical concentration in the material is uniform and then  $C_{(L,0)}$  is replaced by  $C_0$ .

6.11 In summary, when  $Bi_m K_{ma}$  is less than 1, the mass-transfer parameters ( $K_{ma}$ ,  $h_m$ ,  $y_0$ ,  $C_{(L,0)}$ ) should be used to estimate the emission rate ( $E_{MT}$ ) when modeling indoor chemical concentrations.

6.12 For situations where  $1 < Bi_m/K_{ma} < 35$ , the rates of the chemical's migration from the surface to the bulk air and its rate of migration to the material's surface will be similar. An experimental approach like that outlined in 8.4 should be used to determine how to best estimate emissions when modeling indoor chemical concentrations.

## 7. Chambers for Emission Testing to Determine Emission Modeling Parameters

7.1 Once the best approach for estimating emissions in modeling of chemical concentrations in indoor environments (chamber area-specific emission rate or mass-transfer parameters) is determined, the optimal experimental chamber method should be selected. There are wide variety of chambers and methods used to measure chemical emissions from materials in the literature (14). Chambers used for emission testing are summarized in Table 2. Literature examples of products, materials, and chemical groups used for emission testing are summarized in Table 3. Emission test chambers can be described by two major characteristics.

7.1.1 First, chambers can be dynamic or static. Dynamic chambers have airflow through the chamber. Chemical concentrations are typically measured at the exhaust of the chamber. Static chambers have no airflow through them. Chemical concentrations are measured by sampling in the chamber.

**TABLE 2 Example Chamber Types Used to Measure Emissions from Materials**

Chamber Description	Type	Typical Volume	Typical Use for Emission Modeling <sup>A</sup>	Possible Limitations in Using Chamber for Determining Emission Modeling Parameters of Typical SVOCs	Examples
Large chamber	Dynamic, Conventional	20 m <sup>3</sup> to 50 m <sup>3</sup>	$E_{AS}$	Sorption to chamber walls and sampling line Time to reach steady-state	Practice D6670 Test Method E1333 Practice D6177
Small chamber	Dynamic, Conventional	0.02 m <sup>3</sup> to 1.0 m <sup>3</sup>	$E_{AS}$	Sorption to chamber walls and sampling line Time to reach steady-state Uncertainty in convective mass transfer coefficient measurement or estimation	Guide D5116 Test Method D6007 Practice D6330
Microchamber	Dynamic, Conventional	4.0 × 10 <sup>-5</sup> m <sup>3</sup> to 1.0 × 10 <sup>-3</sup> m <sup>3</sup>	$E_{AS}$	Sorption to chamber walls and sampling line  Uncertainty in convective mass transfer coefficient estimation	Practice D7706
Microchamber	Dynamic, Sandwich	1.5 × 10 <sup>-4</sup> m <sup>3</sup>	$E_{MT}$	Uncertainty related to convective mass transfer coefficient estimation methods Assumes air diffusion coefficient Sorption to (minimized) chamber walls	Test Method D8142
Small chamber	Static, Sandwich	2.0 × 10 <sup>-4</sup> m <sup>3</sup> to 3.0 × 10 <sup>-4</sup> m <sup>3</sup>	$E_{MT}$	Calibration of Solid Phase Micro Extraction (SPME) sampling methods Requires curve fit to determine parameters Assumes air diffusion coefficient	<sup>B</sup>
Diffusion chamber	Static, Conventional	1.0 × 10 <sup>-7</sup> m <sup>3</sup> to 6.0 × 10 <sup>-7</sup> m <sup>3</sup>	$E_{MT}$	Requires curve fit to determine two parameters Sorption to chamber walls assumed linear for thermal desorption tubes Sorption to chamber walls has been assumed to be negligible for chambers with surface-to-volume ratios greater than 3.9.	<sup>B</sup>

<sup>A</sup> Area-specific emission rate ( $E_{AS}$ ). Mass transfer parameters ( $E_{MT}$ ).

<sup>B</sup> No ASTM methods for these approaches have been developed. Examples can be found in Table 3.

**TABLE 3 Example Products and Materials for Chambers Used to Measure Emissions**

Chamber Description	Type	Example Product/Material, Chemical Group	Literature Examples
Large chamber	Dynamic,	Sealant, Lacquer, coated particleboard (VOCs)	(15)
	Conventional	Furniture (VOCs)	(16, 17)
Small chamber	Dynamic,	Polymer-based Children's Toys (VOCs)	(18)
		Spray Polyurethane Foam (VOCs and SVOCs)	(19)
	Conventional	Gypsum Board and Latex Paint (VOCs)	(20, 21)
Microchamber	Dynamic,	Polymer-based Children's Toys (VOCs)	(18)
		Spray Polyurethane Foam (VOCs and SVOCs)	(19)
	Conventional	Polyisocyanurate rigid foam (SVOCs)	(22)
Microchamber	Dynamic,	Vinyl Flooring (SVOCs)	(23)
		Sandwich	Polyisocyanurate rigid foam (SVOCs)
Small chamber	Static,	Vinyl Flooring (SVOCs)	(14)
	Sandwich	Vinyl Flooring (source) and Clothing (Sink)	(25)
Diffusion Chamber	Static,	Vinyl Flooring (SVOCs)	(26)
		Polymer-based Children's Toys (SVOCs)	(27, 28)
	Conventional	PVC-based products (SVOCs)	

7.1.2 Second, chambers can be classified by the ratio of exposed chamber wall surface area of the sample material. For conventional chambers the material is placed at the bottom of the chamber. The ratio of the sample material area to exposed chamber wall area is typically less than 1. “Sandwich” chambers are designed with the top and bottom of the chamber consisting of the emission material and with minimal wall height (heights are typically less than 10 % of the chamber diameter). For “sandwich” chambers the ratio of the sample material area to exposed chamber wall area is typically greater than 1. For example, the surface-to-volume ratio for a dynamic sandwich microchamber used by Xu et. al. was 1.8 (29).

7.2 Most emission chambers can theoretically be used to measure the area-specific emission rate ( $E_{AS}$ ) and many of the mass transfer parameters required for emission modeling ( $D_m$ ,  $K_{ma}$ ,  $h_m$ ,  $y_0$ ). However, some chambers are better suited to determine area-specific emission rates that can be directly used for modeling indoor environments (Eq 3) and some are better suited to determine the mass-transfer parameters used for modeling emission rates in indoor environments (Eq 4). The two main reasons that chambers are suited for one type of measurement or the other are the importance of sorption of the chemical to exposed chamber walls and if the rate limiting step for emission is the diffusion of the chemical from the material surface to the bulk air ( $Bi_m/K_{ma} < 1$ ,  $Fo_m = 10^{-4}$ ).

7.2.1 *Sorption*—In conventional emission test chambers (for example, Guide D5116 or Test Method D6007) sorption of VOCs to chamber walls is considered minimal enough to not impact results. However, at ambient temperatures (20 °C to 25 °C), SVOCs typically partition to adjoining surfaces prolonging the time for the system to reach steady-state. In their supplementary information, Cao et al. (14) provide an overview of modeling SVOC emissions accounting for sorption to chamber walls. Clausen, Hansen (2) showed it took over 150 days for di-2-ethylhexyl phthalate (DEHP) to reach steady-state concentrations in a 50 L glass chamber that contained vinyl flooring. Liang, Liu (22) demonstrated that tris(1-chloro-2-propyl) phosphate (TCPP) was still measurable in a small, stainless-steel chamber (53 L) over 433 days after the source was removed from the chamber. These studies demonstrate that sorption to chamber walls can serve as significant sinks for

SVOC emissions in chamber studies. The prolonged time to reach steady-state SVOC concentrations in dynamic conventional emission chambers at ambient temperatures indicates that chambers with large exposed surface areas relative to the sample area are not well suited for practical SVOC emission characterization. Most methods that seek to measure SVOC emissions in practical time frames minimize the exposed chamber surface area relative to the sample area. The sandwich chamber design minimizes the exposed surface area, shortening the time required for the chemical partitioning to the chamber wall to saturate the chamber surface. Although dynamic, conventional chambers can be used to determine emission mass transfer parameters, the time required for these methods due to sorption typically make them less practical than dynamic, sandwich chamber or static chamber systems.

7.2.2 *Convective Mass Transfer*—When the emission of the chemical is limited by the rate of chemical migration from the material surface to the bulk air ( $Bi_m/K_{ma} < 1$ , typically chemicals classified as SVOCs) the emission rate will be flow and chamber dependent. In these cases (6.8), the emission rate in a chamber will likely differ from an emission rate in a full-scale environment due to different mass transfer coefficients. This becomes more of an issue the smaller the ratio of  $Bi_m/K_{ma}$ . When the convective mass-transfer coefficient ( $h_m$ ) of the chamber is significantly different than the convective mass-transfer coefficient ( $h_m$ ) of the modeled environment, mass transfer parameters ( $K_{ma}$ ,  $h_m$ ,  $y_0$ ,  $C_{(L,0)}$ ) should be determined for accurate emission characterization in an indoor environment. Emission methods designed for measuring emissions of chemicals that are externally mass-transfer limited address the varying mass-transfer condition issue by two techniques. For dynamic, sandwich chambers, the chamber convective mass-transfer coefficient is either measured or estimated from previous measurements allowing the determination of the remaining mass-transfer coefficients for the material/chemical combination. When emission rates in an indoor environment are modeled, the convective mass-transfer coefficient for the indoor environment is estimated or measured and the remaining chamber determined mass-transfer parameter values are used. For static chambers, it is assumed that there is no convective mass transfer allowing the determination