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A Proposed Standard Practice for Determination of Volatile Organic Compounds Emissions from Surface Coatings Using Small Environmental Chambers Under Defined Test Conditions

by

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1. Scope

1.1 The practice measures the volatile organic compounds (VOCs) emitted from surface coating materials such as wood stains, paints, floor wax and polyurethane. A pre-screening analysis is used to identify the VOCs emitted from the panel. Emission factors (i.e., emission rates per unit surface area) for the VOCs of interest are then determined by measuring the concentrations in a small environmental test chamber containing a specimen and being ventilated at a constant air change rate under the standard environmental conditions.

1.2 This practice describes a method that is specific to the measurement of VOC emissions from coating materials stored in an unopened original container for the purpose of comparing the emission characteristics of different surface coating products under the standard test condition. For general guide of conducting small environmental chamber tests see Guide D 5116 "Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products".

1.3 VOC concentrations in the environmental test chamber are determined by adsorption on an appropriate single adsorbent tube or multi-adsorbent tube, followed by thermal desorption and combined gas chromatograph/mass spectrometry (GC/MS) or gas chromatograph/flame ionization detection (GC/FID). Air sampling and analytical method recommended in this practice is generally valid for the identification and quantification of VOCs with saturation vapor pressure between 500 and 0.01 kPa at 25 °C, depending on the selection of adsorbent(s). The analytical method described in this practice can not be applied to the measurement of formaldehyde and other aldehydes with low molecule weight (C1 to C3 aldehydes).

Note 1 – VOCs being captured by an adsorbent tube depend on the adsorbent(s) and sampling procedure selected. The user should have a thorough understanding of the limitations of each adsorbent used.

1.4 The emission factors determined using the above procedure describe the emission characteristics of the specimen under the standard test condition. These data can be used directly to compare the emissions of different products. The data can also be used to analyze the impact of surface coating materials on the VOC concentrations in buildings by using an appropriate indoor air quality model, which is beyond the scope of this practice.

1.5 Values stated in SI units are to be regarded as the standard (see SI E 380).

1.6 This practice does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of the standard to establish practices for appropriate safety and health, and to determine the applicability of regulatory limitations prior to use. For specified hazard statements see Section 6.

2. Reference Documents

2.1 ASTM Standards

D 1356 Standard Terminology Relating to Sampling and Analysis of Atmospheres
D 1914 Recommended Practice for Conversion Units and Factors Related to Atmospheric Analysis
D 5116 Standard Guide for Small Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products
E 355 Recommended Practice for Gas Chromatography Terms and Relationships
E 380 SI Standard
E 741 Standard Test Method for Determining Air Leakage Rate by Tracer Dilution
Z 6685Z (*temporary number, needs to be designated for proper ASTM document number*) Standard Practice for Selection of Sorbents and Pumped Sampling / Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air

2.2 Other Standards

EPA TO-17 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

3. Terminology

3.1 Definitions - For definitions and terms that are commonly used, refer to Terminology D1356 and Practice E 355. For definitions and terms related to test methods using small-scale environmental chamber, refer to Guide D 5116. For an explanation of units, symbols, and conversion factors, refer to Practice D1914.

3.2 Descriptions of terms specific to this Standard:

3.2.1 Environmental enclosure - a chamber or other container in which the environmental test chamber(s) is placed.

3.2.2 Loading ratio (m^2/m^3) - the total exposed surface area of each test specimen divided by the net air volume of the environmental test chamber.

3.2.3 Nominal time constant (t_n) – the time required to obtain 1 air change in the environmental test chamber, which is equal to the inverse of the air change rate

3.2.4 Pre-screening analysis - a procedure for identifying the VOCs emitted from a test specimen. The results are used to determine the appropriate GC/MS or GC/FID analytical method for the separation and quantification of VOCs of interest, and air sampling volume for subsequent dynamic chamber tests.

3.2.5 Standard environmental test chamber condition - a test condition of 23 ± 0.5 °C in temperature, $50\% \pm 5\%$ RH in relative humidity, 1 ± 0.03 /h in chamber air change rate, 0.40 ± 0.01 m^2/m^3 in chamber loading ratio, and <0.03 m/s in surface air velocity over the test specimen (see section 3.2.8).

3.2.6 Substrate - a rigid material on which a coating material can be applied for the purpose of testing emissions from coated material.

3.2.7 Surface coatings - materials that are applied on the surface of another building material such as a substrate (see section 3.2.6) to modify its surface characters. Common surface coatings include stains, paints, floor wax and polyurethane.

3.2.8 Test specimen - a specimen of a coating material applied on a rigid panel (such as oak wood panel or maple wood panel) for testing.

3.2.9 Tracer gas - a gaseous compound that is neither emitted by the wood-based panel, nor present in the supply air to the chamber, and that can be used to determine the mixing characteristics of the environmental test chamber and provide a cross-check of the air change rate measurements.

3.2.10 TVOC – sum of measured mass of all individual volatile organic compounds (VOCs) that are captured by a given adsorbent, or a combination of several given adsorbents, in an adsorbent tube, and are thermally desorbed and measured by an analytical system. For VOC definition, see Terminology D1356.

Note 2 – TVOC value is measurement method dependent. When reporting TVOC values, the user of this practice shall indicate the measurement method used, such as adsorbents, sampling volume, instruments and analytical conditions. One way to report TVOC values is recommended in section 8.2.7.6.

4. Significance and Use

4.1 The effects of VOC sources on the indoor air quality in buildings have not been well established. One basic requirement that has emerged from indoor air quality studies is the need for well-characterized test data on the emission factors of VOCs from materials used in the building. Standard test method and procedure are essential for the comparison of emission factor data from different materials.

4.2 This practice describes a procedure of using a small environmental test chamber to determine the emission factors of VOCs surface coating materials, which are applied onto a substrate, over the initial (first several hours) and long (up to several days) period of time. A pre-screening analysis procedure is also provided to identify the VOCs emitted from the products, to determine the appropriate GC/MS or GC/FID analytical procedure, and to estimate sampling volume for the subsequent environmental chamber testing.

4.3 Test results obtained using this practice provide a basis for comparing the short term (within 12 hours) and long term (up to 10 days) VOC emission characters among different surface coating materials. They can be used to assist manufacturers in reducing VOC emissions from their products. They can also be used in selecting surface coating materials with minimum VOC emissions.

4.4 While emission factors can be used to compare different products, the concentrations measured in the chamber shall not be considered as the resultant concentrations in an actual indoor environment.

5. Apparatus

5.1 This practice requires the use of an environmental chamber test system, an air sample collection system and a chemical analysis system. A general guide for conducting small environmental chamber tests is provided in Guide D 5116. The following sections describe the requirements that are specific to this practice:

5.2 Environmental Chamber Testing System – The system shall include an environmental test chamber, an environmental enclosure, equipment for supplying clean and conditioned air to the chamber, and outlet fitting for sampling the air exhausted from the chamber. Figure 1 illustrates an example of such systems. All materials and components in contact with panel specimen or air stream from the chamber inlet to sample collection point shall be chemically inert and accessible for cleaning. Suitable materials include stainless steel and glass. All gaskets and flexible components shall be made from chemically inert materials.

5.2.1 The Environmental Test Chamber – The chamber shall have a volume of 0.05 m³ with the interior dimensions of 0.5 m by 0.4 m by 0.25 m high. A chamber with a different size and shape may also be used if the same standard environmental test chamber condition (see section 3.2.6) can be maintained. The chamber shall include a supply air system having an inlet port with distributed openings to assist mixing between the supply

air and chamber air, and an outlet port with distributed exhaust openings to ensure that concentration measured at the chamber exhaust is the average concentration in the chamber. The chamber criteria are as follows:

5.2.1.1 Air-tightness of the chamber: The nominal air leakage rate of the chamber shall be less than 1% of the air change rate used for the emission test at 10 Pa. Air-tightness is measured as follows: (1) seal the outlet of the chamber; (2) supply air to the chamber through the inlet and adjust the airflow rate so that the pressure difference between the inside and outside of the chamber is maintained at 10 ± 1 Pa, which is measured by a pressure transducer with a minimum specified accuracy of ± 1 Pa; and (3) measure the airflow rate. The rate is the nominal leakage rate of the chamber.

5.2.1.2 Air mixing in the chamber: Adequate air mixing in the chamber shall be achieved to ensure that concentrations measured at the chamber exhaust are representative of those in the chamber. This may be determined by using the following tracer gas decay method: (1) place a small mixing fan (e.g., a cooling fan for a personal computer) in the chamber; (2) operate the chamber under the standard test condition and turn on the mixing fan; (3) inject a small amount (a pulse) of an inert tracer gas (e.g., SF_6) into the chamber directly or via the supply air; (4) allow 5 minutes for the gas to mix with the chamber air; (5) turn off the mixing fan and record the time as $t = 0$; and (6) measure the concentrations of the tracer gas at the exhaust of the chamber at the following time points: $t = 0, 0.25 t_n, 0.5 t_n, 1.0 t_n, 1.5 t_n$, and $2.0 t_n$, where t_n is the nominal time constant and is equal to 1.0 h for the standard test condition. The measured concentrations are compared to the values given by the following theoretical equation under the perfect mixing condition (in which the concentrations measured at the exhaust are the same as those in the chamber):

$$C(t) = C_0 e^{-Nt}$$

where,

- C_0 = initial concentration at $t=0$, $\mu\text{g}/\text{m}^3$;
- $C(t)$ = concentration at time t , $\mu\text{g}/\text{m}^3$;
- N = air change rate, 1/h;
- t = time from the start of the air purging, h.

The maximum difference between the measured and calculated theoretical values shall be within $\pm 5\%$ of the theoretical value. The above mixing test shall be conducted with a simulated test specimen placed in the chamber.

Note 3 – The above method is a simplified version of the decay method described in Guide D5116. Alternatively, the method of determining adequate air mixing described in Guide D5116 may also be used to check the mixing condition in the chamber.

5.2.1.3 Surface air velocity above test specimen: Surface air velocity shall be measured at a minimum of five locations (one in the center and four at each edge) at 1 cm above the specimen surface should be <0.03 m/s, using hot wire or film anemometers. Low

air velocity can be achieved by mixing chamber air with distributed openings on inlet and outlet ports (also called manifold) rather than with mixing fans (see section 5.2.1). The test specimen shall be placed between the two ports with a support of stainless steel plate (250 mm by 150 mm) in the middle bottom of the chamber. For air velocity and its measurement also see Guide D 5116.

Note 4 – Low surface air velocity (for example <0.05 m/s) is more representative of real indoor air movement. To increase the data comparability among testing laboratories, surface air velocity range is narrowed down to <0.03 m/s, from <0.05 m/s in Guide D 5116. Surface velocity of <0.03 m/s can be achieved when proposed chamber settings are followed. However, the user should conduct surface air velocity test for each chamber setting to make sure velocity is <0.03 m/s.

5.2.1.4 Sink effect: The chamber and specimen holder shall have minimum sink effect. The recovery factor determined by the following procedure shall be higher than 95% for decane: (1) seal the supply inlet and exhaust of the chamber; (2) inject 5 µg of vaporized decane into the chamber; (3) take an air sample from the chamber exhaust at 5 minutes after the injection, and record this concentration as the initial concentration C_0 and the time as $t = 0$; (4) at $t = 0$, begin purging the air through the chamber at $t = 0$ under standard test conditions; (5) take air samples from the chamber exhaust at the following times after the start of purging: $t_1 = 0.25 t_n$, $t_2 = 0.5 t_n$, $t_3 = 1.0 t_n$, $t_4 = 1.5 t_n$, $t_5 = 2.0 t_n$, $t_6 = 3.0 t_n$, $t_7 = 4.5 t_n$, $t_8 = 6 t_n$, $t_9 = 8 t_n$, and $t_{10} = 10 t_n$, where t_n is the nominal time constant and is equal to 1.0 h for the standard test condition; and (6) calculate the recovery factor (RF) as follows:

$$RF = \frac{N}{2C_0} \sum_{i=0}^{n-1} [C(t_i) + C(t_{i+1})](t_{i+1} - t_i) 100\%$$

where,

- RF = recovery factor, %;
- N = air change rate, 1/h;
- C_0 = initial concentration at $t=0$, µg/m³;
- $C(t_i)$ = concentration at time t_i , µg/m³ ($i=0, 1, 2, \dots, 10$);
- t_i = time from the start of the air purging, h.

The above sink effect test should be conducted after the mixing condition in the chamber has been verified (see section 5.2.1.2).

Note 5 – The concentration decay is usually close to the first-order exponential decay curve (i.e., $C(t)/C_0 = e^{-Nt}$). The above sampling time intervals are chosen such that the amount of concentration decrease during each sampling interval will be similar.

Note 6 – The above sink effect test is to check if the chamber system has significant non-reversible sinks. Non-reversible sink effect would result in underestimation of the emission rates in environmental chamber tests (see section 8.2). The chamber may also have reversible sink effect (i.e., compounds adsorbed at one time may re-emit in a later time). But such effect on the results of the environmental chamber tests is expected to be minimal

because the procedure adopted for the environmental chamber tests (for example, the chamber is ventilated continuously during the test, see section 8.2) as well as stainless steel materials used in the chamber construction.

5.2.1.5 The environmental test chamber shall be contained in an environmental enclosure (see section 5.2.2).

5.2.1.6 The background concentration of the environmental test chamber is measured at the chamber exhaust. The background concentration shall meet the following criteria: (1) $20 \mu\text{g}/\text{m}^3$ or $1/6$ of the lowest concentration to be measured, whichever is lower, for TVOC, and (2) $1 \mu\text{g}/\text{m}^3$ or $1/6$ of the lowest concentrations to be measured, whichever is lower, for individual VOCs.

Note 7 – Conventionally, the minimum quantifiable concentration is determined by:

$$C_{\min} = c + 10 s$$

where, C_{\min} is the minimum quantifiable concentration; c is the mean background concentration; s is the standard deviation of the background concentration during the test period. For simplicity, it may be assumed that $s = 0.5 c$. As a result, $C_{\min} = 6 c$.

Note 8 – The $20 \mu\text{g}/\text{m}^3$ limit set for TVOC in chamber air is the minimum level of cleanness that a test chamber system shall have.

5.2.2 Environmental Enclosure – The enclosure shall have sufficient size to accommodate the test chamber, and shall be capable of maintaining the temperature at $23.0 \pm 0.5^\circ\text{C}$ and relative humidity at $50\% \pm 5\%$ RH during the period of loading the test specimen, and maintaining the temperature at $23.0 \pm 0.5^\circ\text{C}$ in the chamber during the entire testing period. Once the chamber door is closed, the relative humidity in the chamber is maintained with the air supplied to the chamber.

5.2.3 Clean Air Supply System – The system shall be capable of supplying a controlled flow of clean air into the test chamber. Concentrations measured at the chamber inlet shall meet the following criteria, at an airflow rate equal to or greater than 1.0 chamber volume per hour:

TVOC (as defined in 5.4.5.4) concentration $\leq 10 \mu\text{g}/\text{m}^3$,
concentration of any individual VOC $\leq 0.5 \mu\text{g}/\text{m}^3$,
particulate concentration $\leq 100 \text{ particles}/\text{m}^3$ of $0.5 \mu\text{m}$ diameter or larger,

and

ozone concentration $\leq 20 \mu\text{g}/\text{m}^3$.

A typical clean air supply system should include the following components (Figure 1):

5.2.3.1 An air pump(s) or an oil-free compressor capable of supplying air at a rate of 1.0 chamber volume per hour. A particulate filter shall be installed for the air intake.

5.2.3.2 A dehumidifier (e.g., a desiccant drier) capable of keeping the relative humidity below 45% RH.

5.2.3.3 A catalytic oxidizer or equivalent air purifier (e.g., activated carbon filter) capable of removing organic compounds so that the concentrations of TVOC and any individual VOCs are below $10 \mu\text{g}/\text{m}^3$ and $0.5 \mu\text{g}/\text{m}^3$, respectively.

5.2.3.4 An air conditioning device and an airflow controller capable of controlling the airflow rate, temperature and relative humidity of the supply air at 1.0 ± 0.03 ACH, 23.0 ± 0.5 °C and 50 ± 5 % RH, respectively. Deionized water (or equivalent) shall be used in the humidification.

5.2.3.5 An exhaust air pump and an airflow controller for controlling the pressure in the chamber. The airflow controller shall be adjusted so that the air pressure in the chamber will be positive relative to air pressure outside the chamber despite of the fluctuations in the ambient air pressure. A typical pressure to be maintained in the chamber is 10 ± 5 Pa relative to the outside of the chamber.

5.2.3.6 Sensors and a recording system for monitoring airflow rate, temperature, relative humidity, and pressure in the environmental test chamber.

5.3 Air Sampling System – The system shall include an adsorbent tube, a mechanic pump and an airflow controller, which can measure and control the airflow rate through the sampling system to within $\pm 5\%$ of a specified value. All system components between the chamber and the adsorbent tube shall be constructed of chemically inert materials.

5.3.1 The adsorbent tube should be connected as close to the chamber exhaust as possible by using a short (< 0.15 m from the environmental enclosure) stainless steel or PTFE tube/connector. The pump shall be operated in suction mode downstream of the adsorbent tube to avoid contamination of air samples by the pump.

5.3.2 For effective collections of VOCs in the exhaust air of the test chamber, an appropriate single or multi-layered adsorbent tube should be used depending on the VOCs to be measured.

5.3.3 Sampling of the exhaust air shall not affect the control of airflow rate to the test chamber. The airflow controller for the exhaust air pump shall be adjusted before air sampling so that the air pressure in the chamber will remain positive during the sample collection period. A sampling flow rate of less than $1/3$ of the total supply airflow rate to the test chamber is recommended to avoid excessive depressurization in the chamber during the sampling period. Recommendations on the use of adsorbent tubes from manufacturer or supplier, or both, shall be followed in selecting the sampling airflow rate and sampling

period to avoid breakthrough of VOCs through the adsorbent tube. Air sampling volume (i.e., sampling flow rate times the sampling period) should be determined by the safe sampling volume (SSV, see Practice Z6685Z) of the least retained VOC, concentrations to be measured, and detection limits of the analytical method. A proper air sampling volume should be determined through the pre-screening analysis (section 8.1).

5.4 Chemical Analysis System - The chemical analysis system shall include a thermal desorption unit connected to a GC/MS system or a GC/FID system. EPA TO-17 may be consulted for general procedures of determining VOCs in air sample. Chemical analysis system that is specific to this practice is as follows:

5.4.1 A single or multi-tube thermal desorption (TD) unit shall have desorption efficiency of greater than 90% for VOCs of interest in general, and $100 \pm 5\%$ for toluene, decane, and dodecane, at 50 ng per compound per tube. Desorption efficiency should be determined by comparing results from thermal desorption with direct GC injection.

5.4.2 GC/MS system can be used for both identification of VOCs in the pre-screening analysis and quantification of the VOCs in the environmental chamber tests.

5.4.2.1 For identification of VOCs, the GC/MS is operated in a full scan mode, and shall be capable of scanning mass range from 15 to 350 amu (atomic mass unit). The measured mass spectrum shall be compared to those in a standard mass spectrum library to identify the individual VOCs detected. Selected VOCs of interest shall be confirmed by spiking with the corresponding standards (see section 8.1).

5.4.2.2 For quantification of individual VOCs of interest, the GC/MS system shall be operated under either full scale or selected ion monitoring (SIM) modes. If SIM mode is selected, at least three ions shall be monitored for each VOC of interest. Other conditions used in section 5.4.2.1 shall be maintained.

5.4.3 GC/FID system can be used for quantification of VOCs of interest as an alternative to GC/MS. The identification of the VOCs of interest in a GC/FID chromatogram shall be confirmed by GC/MS analysis and by spiking with the corresponding standards (see section 8.1).

5.4.4 Optimal operating conditions (GC column and temperature program) shall be selected for GC/MS and GC/FID system based on the pre-screening analysis (section 8.1).

5.4.5 Chemical analytical system shall be properly calibrated for quantitative analysis. Initial calibration of GC/MS or GC/FID system shall be conducted before testing each type of product material. Initial calibration is conducted by analyzing standards of selected VOCs (or toluene for TVOC, see 5.4.5.4) at different concentrations. At least five different concentrations covering anticipated VOC concentration range in the test are needed for such calibration. User of this practice shall demonstrate that the analytical system has a linear response in the anticipated VOC concentration range.

5.4.5.1 If GC/FID system is used for the quantification, single point calibration checking shall be conducted on each day the system is used. If the result of such single point checking deviates less than $\pm 10\%$ from the initial calibration line, the initial calibration line shall be used to calculate the mass concentrations. Otherwise, problem shall be identified and the system fully re-calibrated as in the initial calibration (section 5.4.5).

5.4.5.2 If GC/MS system is used for the quantification, daily calibration shall be conducted at two concentration levels (i.e., a two-point calibration) as a minimum. The low point should be where the linearity of the calibration curve starts or 10 times the method detection limit, whichever is higher. The high point should be where the linearity of the calibration curve ends or the anticipated highest concentration in the samples, whichever is lower. Results of this daily calibration shall be used to calculate the concentrations if they deviate less than 10% from the previous day and less than 25% from the initial calibration. Otherwise, problem shall be identified and the system fully re-calibrated as in the initial calibration (section 5.4.5).

Note 9 – Different calibration practices are specified for GC/FID (section 5.4.5.1) and GC/MS (section 5.4.5.2) system because a GC/MS system is usually subject to more day to day variations than a GC/FID system.

5.4.5.3 If the testing objective is to measure the emission factors of target individual compound, the TD-GC/MS or TD-GC/FID system shall be calibrated for each individual compound with standards of the same compound.

5.4.5.4 If the testing objective is to measure TVOC concentration, the TD-GC/FID system or TD-GC/MS system shall be calibrated by using toluene as the reference standard. The result shall be reported as the concentration of toluene equivalent TVOC-by-GC/FID or TVOC-by-GC/MS, depending on which system is used. GC/MS system in this case shall be operated in full scan mode (20 to 350 amu) and peak areas of the total ion currency must be used.

5.4.5.5 If the testing objective is to measure both the concentrations of TVOC and individual target compounds, the TD-GC/FID system or TD-GC/MS system shall be calibrated for both toluene and individual target compounds.

5.5 The method detection limit of the system shall be less than 1/3 of the lowest concentration to be measured.

6. Hazards

6.1 The transportation, handling, cutting, testing and clean-up of wood-based panel involve a number of chemical and physical hazards.

6.2 Proper workplace health and safety procedures and good laboratory practice shall be developed and implemented.

6.3 Chemicals - Appropriate procedures shall be developed and implemented for using and disposing chemicals for cleaning and calibration.

7. Material Sampling, Storage, Preparation of a Test Specimen and its Placement in the Environmental Test Chamber

7.1 Material Collection - A testing laboratory shall secure the testing materials in an unbiased manner. Surface coating materials may be collected at local retail stores provided that the material is in its original, unopened container within shelf-life time. At least two containers shall be collected: one for pre-screening analysis and the other for dynamic chamber test.

7.2 Sample Storage - Coating materials shall be kept in a clean and dark space at the room temperature for at least 48 hours to allow equalization of the sample temperature with the room temperature. The materials shall be tested within one month after being received or within manufacturer specified shelf-life time, whichever is short.

7.3 Preparation of Test Specimens

7.3.1 Preparation of substrate - The standard size of the substrate shall be 200x110 mm with a thickness of between 10 and 20 mm. Substrate shall be prepared as follows:

7.3.1.1 Cut the substrate into standard size using a clean saw. Clean the saw by wiping with methanol soaked lab tissue paper, rinsing thoroughly with deionized water, and wiping with a dry lab tissue paper before use.

7.3.1.2 Plane and sand the surface of the substrate if it is rough and not flat. The surface of the substrate shall be flat.

7.3.1.3 Condition the substrate in section 7.3.1.2 in a clean ventilated area with a minimum of 0.1 air change per hour for at least 10 days. Further condition the substrate at room temperature ($23 \pm 2^{\circ}\text{C}$) for at least 24 hours under ventilation to allow equalization of the sample temperature with the room temperature.

7.3.2 Application of surface coating material - Test specimen with exact 200 mm by 100 mm exposure surface shall be prepared using the following procedures:

7.3.2.1 Put the conditioned substrate on an electronic balance and measure the weight of the substrate (W_1).

7.3.2.2 Invert the container several times to ensure that the material in the container is well mixed. Do not shake the container as it will result in air being trapped in the material.

7.3.2.3 Pour 10 ml of coating material into a xx-ml wide-mouth jar. Soak a xxx mm wide paint brush by dipping it in the jar. Cover the jar mouth with an aluminum sheet to minimize the loss of VOCs.

7.3.2.4 Use a suction tube to apply certain amount of the material, depending on the nature of the material and manufacturer recommended amount per unit surface, onto the substrate and immediately afterwards distribute the coating material evenly among the surface of the substrate using a pre-soaked new brush.

7.3.2.5 Measure the weight of the substrate applied with the coating material (W_2).

7.3.3 The amount applied onto the substrate surface W is calculated by $W = W_2 - W_1$. The test specimen shall be rejected and a new specimen shall be prepared according to 7.3.2 if the applied amount W is not within 10 % of the pre-determined amount.

7.3.4 Manage the total time of preparing the test specimen (i.e., from opening the material container to placing the specimen in the chamber) within five minutes, and step 7.3.2.4 within 2 minutes.

7.4 Placement of the Test Specimen – Place the test specimen, immediate after the completion of section 7.3.2, at the center of the chamber bottom so that air circulation in the chamber is not affected by the specimen.

8. Test Procedure

8.1 Pre-Screening Analysis Procedure

8.1.1 A pre-screening analysis shall be conducted to identify VOCs emitted by the product, to find optimal operating conditions for the GC/MS and/or GC/FID system, to select model VOCs, and to estimate proper air sampling volumes for subsequent environmental chamber tests.

8.1.1.1 Place the test material in a headspace (static) vial. Close the vial and leave it at room temperature for 24 hours, allowing VOCs to reach the equilibrium in the headspace.

8.1.1.2 Draw 1 to 5 ml of headspace air into a gas-tight syringe. Transfer the air in the syringe into analytical system by (a) directly injecting the air sample through GC injection port; or (b) loading to a thermal desorption tube and afterwards thermally desorbing the VOCs from the tube to GC/MS.

Note 10 – To avoid overloading GC/MS system, it is advisable to collect and analyze a small volume (e.g. 1 ml) of head space air, and increase the sample size accordingly if the first sample volume is too small.

8.1.1.4 Analyze the air samples by using the TD-GC/MS (preferably in the order of low to high volume samples to avoid possible over loading of the analytical system). Different GC operating parameters (columns and temperature program) may be tested to obtain a good separation of emitted VOCs. The results will be used to determine a proper set of operating parameters of the analytical system for subsequent environmental chamber testing. More samples may be taken from the environmental test chamber if necessary.

8.1.2 Identify GC peaks based on the results of GC/MS analysis (see section 5.4.2). The selection of VOCs for subsequent environmental chamber testing depends on the objective of the testing. Confirm the identification of each selected VOCs by spiking with a corresponding VOC standard.

8.1.3 Quantify and record equilibrium concentrations of TVOC in the headspace. Analytical system shall be calibrated with toluene standards and section 8.2.7.6 shall be followed for calculating and reporting TVOC concentrations.

8.1.4 Estimate the proper air sample volumes for the subsequent environmental chamber tests according to TVOC concentrations in the headspace. The air sample in the environmental chamber tests should contain VOC mass at least 3 times, preferably 10 times, higher than the detection limit of the analytical system. For example, if the detection limit of a TD-GC/MS system is $0.001\ \mu\text{g}$ per sample tube for a VOC of interest, and the concentration of that VOC in chamber air is $1.0\ \mu\text{g}/\text{m}^3$, a minimum air sample volume of $0.003\ \text{m}^3$ should be collected ($0.001\ \mu\text{g} \times 3 / 1.0\ \mu\text{g}/\text{m}^3 = 0.003\ \text{m}^3$).

8.2 Environmental Chamber Testing Procedure

8.2.1 Place the environmental test chamber in the environmental enclosure. Prior to testing, clean the environmental test chamber, and all internal hardware and equipment by wiping the interior surfaces with an alkaline detergent, followed by a thorough rinsing with tap water, wiping with methanol, rinsing thoroughly with deionized water, and drying with clean laboratory tissue paper.

Note 11 – The cleaning procedure described here is recommended if the chamber has not been used for long time, or previous sample contained high VOC concentrations. For normal operation wiping and rinsing with deionized water may be sufficient after each test. Check the chamber air after cleaning for acceptable background level.

8.2.2 Operate the environmental test chamber under the standard environmental test condition (i.e., $23\ ^\circ\text{C}$, 50% RH and 1 /h ACH). Operate the chamber in a way that positive chamber pressure is maintained at $10\ \text{Pa} \pm 5\ \text{Pa}$ during test including air sample collection (see section 8.2.6).

8.2.3 Take a 10-L air sample after a minimum of six hours to check the background concentration in the chamber. The background VOC concentration (C_{bk}), shall meet the criteria specified in sections 5.2.1.6. Otherwise check the testing system for the cause of the excessive background contamination and take actions to eliminate contamination.

8.2.4 Prepare the test specimen and place it in the specimen holder according to section 7.3.

8.2.5 Open the door of environmental test chamber, load the test specimen into the chamber, position the specimen at the center of the chamber bottom, and close the chamber. Keep supply air flowing through the chamber during specimen loading. Record the time when the chamber door is closed, which is defined as the *time zero* for the environmental chamber testing.

8.2.6 Sampling

8.2.6.1 Select adsorbent tubes packed with adsorbent(s) according to Practice Z6685Z.

8.2.6.2 Clean and condition the adsorbent tubes within 72 hours prior to air sampling.

8.2.6.3 Configure the exhaust system to have part of the exhaust going through sampling port/line.

8.2.6.4 Take air samples at $t = 0.1$ h, 0.3 h, 0.6 h, 1.0 h, 1.5 h, 2.0 h, 3.0 h, 4.0 h, 6.0 h, 9.0 h, 12 h, 24 h, 36 h, 48 h, 72 h, and 96 h from the time zero (see section 8.2.5) to determine the concentrations of TVOC and individual VOCs of interest in the chamber air.

Note 12 – Number of air samples specified in 8.2.6.4 is the minimum. Additional air samples may be taken if more detailed characterization of the VOC emissions is of interest, depending on the objectives of the testing.

Note 13 – Because of the initial high and fast decaying emission rate of surface coating materials VOC concentration in the chamber is generally characterized by fast increase to a maximum and then decrease to low levels within first few hours. Sampling volumes should be adjusted accordingly to avoid overloaded samples.

8.2.6.5 Seal both end of the tube upon completion of sampling, and keep the tube in a clean environment at room temperature till analysis. The tubes shall be analyzed within 10 days after the sampling time.

8.2.6.6 If duplicate air samples are collected, use separate flow controllers for each adsorbent tube and record exact flow rate for each tube.

8.2.6.7 Remove the specimen from the chamber after the last air sample has been taken. Take an air sample from the air supply tube/line immediately upstream of the chamber to verify the background concentration of the supply air. If the background concentration exceeds the criteria specified in section 5.2.3, identify and correct the problems and repeat the test.

8.2.7 Chemical analysis

8.2.7.1 Prepare calibration standard solutions in methanol or other proper solvents using the following procedure: (1) take 1 to 5 μL of standard solution using a syringe; (2) transfer the liquid in the syringe onto the tube under a clean air flow, and (3) purge the tube with a proper volume of clean air to remove methanol or other solvents from the tube. The volume of purge air will depend upon adsorbent(s) selected. A small volume (less than 0.5 μL) of solution shall be loaded onto adsorbent tubes if solvents can not be removed from the adsorbent tube.

8.2.7.2 Check the instrument performance before analysis. If GC/MS system is used, tune the instrument using manufacturers predefined autotune procedure. The system shall pass manufacturer's autotune criteria. If GC/FID is used, make sure the detector is turned on and is stabilized before sample analysis.

8.2.7.3 Calibrate the analytical system according to section 5.4.5.

8.2.7.4 Analyze sample tubes within 7 days after sample collection.

8.2.7.5 Calculate VOC concentrations using method in section 5.4.5.1 for GC/FID system and section 5.4.5.2 for GC/MS system.

8.2.7.6 Calculate TVOC defined in section 5.4.5.4, if required, using the following procedures: (1) convert the area count of each peak to the equivalent toluene mass by using the calibration curve for toluene; and (2) sum all the equivalent toluene mass. The result of the total mass is the TVOC-by-GC/FID mass if GC/FID is used, and TVOC-by-GC/MS if GC/MS is used.

Note 14 – The total mass of VOCs determined also depends on the adsorbent(s) used for the collection of air samples. TVOC should be reported with information on the range of VOCs that can be effectively captured and measured by a given analytical system. It is recommended that the VOC range, expressed as vapor pressure (v.p.) at 25 °C, of a given method be reported in parentheses with TVOC results, for example, TVOC-by-GC/MS (v.p. 150 to 0.3 kPa) = 10 mg/m^3 .

9. Data Analysis and Interpretation

9.1 Emissions from surface coating materials can be, in general, divided into two periods with high and fast decaying emission rate in the first and low and slow decaying emission rate in the second period (see Note 12). While other appropriate methods may be used for calculating the emission factors such as those described in Guide D 5116, this practice recommends the following method for data analysis.

9.2 The emission factor of VOCs from surface coating materials in the first decay period (EF_1), which is defined from zero to 12 hours for the purpose of this practice, may be described using the following equations based on the VB model¹:

$$EF_1(t) = \frac{C_v \times K}{r_1 - r_2} \times [(r_1 + N) \times \exp(-r_1 t) - (r_2 + N) \times \exp(-r_2 t)] \quad (9.1)$$

Where,

$$r_{1,2} = 0.5 \times \left\{ -[N + L \times K + \frac{C_v \times K}{M_{01}}] \pm [(N + L \times K + \frac{C_v \times K}{M_{01}})^2 - \frac{4N \times C_v \times K}{M_{01}}]^{0.5} \right\}$$

C_v = VOC vapor pressure on freshly applied surface in concentration unit, mg/m³;

K = mass transfer coefficient, m/h;

M_{01} = total VOC mass per unit area emitted during the first period, mg/m²;

L = loading ratio of specimen to chamber volume, m²/m³;

N = air change per hour, /h.

9.2.1 Equation (9.1) for the emission factor $EF_1(t)$ would result in equation (9.2) for describing VOC concentrations $C(t)$ in the small environmental chamber, where a , b , and c in the equation are determined experimentally by conducting non-linear regression analysis using equation (9.2).

$$C(t) = a \times [\exp(-bt) - \exp(-ct)] \quad (9.2)$$

9.2.2 C_v , K and M_{01} can then be calculated using equations (9.3) through (9.5):

$$C_v = [a \times N \times (c - b)] / [(N - b) \times (c - N)] \quad (9.3)$$

$$K = [(N - b) \times (c - N)] / N \times L \quad (9.4)$$

$$M_{01} = [a \times N \times (N - b) \times (c - b)] / \{b \times [(N - b) \times (c - N) + N^2]\} \quad (9.5)$$

9.3 The emission factor of surface coating materials during the second decay period may be described using the following power law equation. It is realized that the second

¹ Guo, Z, Tichenor, B.A. (1992) "Fundamental Mass Transfer Model Applied to Evaluating the Emissions of Vapor-Phase Organics from Interior Architectural Coatings". EPA/AWMA Symposium, Durham, NC, USA.

period may last for weeks, months, or even years. However, for the purpose of this practice, the second period is limited from 12 hours to 10 days for the application of power law equation.

$$EF_2(t) = A_2 \times t^{(-k)} \quad (9.6)$$

where,

k = decay constant, /h;

A_2 = initial value of the equation, $mg/(m^2 \times h)$.

Note 15 – EF_2 becomes infinite (∞) when $t = 0$. By definition, the power law equation used for the second period can not be applied to $t < 12$ h. In addition, there would be a discontinuity at $t = 12$ h since equations (9.1) and (9.6) do not result in the same EF value at $t = 12$ h. Introducing a transition period between the first and second period may be overcome this problem. However, such a method is not recommended in this practice because it would require more complicated procedures. We propose to introduce a nominal emission factor $EF_{2(24h)}$ for the second decay period at $t = 24$ for the purpose of comparing emission factors of the second decay period among surface coating materials.

9.3.1 Determine the VOC concentrations in the air samples and correct the concentrations for chamber background using the following equation:

$$C_{corr.}(t_i) = C(t_i) - C_{bk}, \quad t_i > 12 \text{ h} \quad (9.7)$$

where,

$C(t_i)$ = measured concentration in the chamber at t_i ;

C_{bk} = background concentration of the chamber determined prior to chamber tests (see section 8.2.3).

9.3.2 Calculate the emission factor at time t_i , $EF(t_i)$, using the following equations, assuming the concentrations in the chamber reached quasi-equilibrium in the second decay period:

$$EF(t_i) = C_{corr.}(t_i) \times N/L, \quad t_i > 12 \text{ h} \quad (9.8)$$

9.3.3 Conduct non-linear regression analysis using equation (9.6) to determine A_2 and k .

9.4 The emission factors determined using the above procedure describe the emission characteristics of the specimen under the standard test condition. These data can be used directly to compare the performance of different surface coating materials, and for estimating the emission rates up to 10 days after the application. They shall not be used to predict the emission rates over longer period of time (i.e., more than 10 days) or under different environmental conditions, unless validated extrapolation methods are available.

10. Report

10.1 The report shall include the following information:

10.1.1 Testing objectives - the purpose of the testing project and intended use of the results shall be stated.

10.1.2 Testing laboratory identification - the name, address, phone/fax numbers and contact person.

10.1.3 Product identification - the name, specific identifiers from the manufacturer and a brief description of the product, its application, and history shall be provided.

10.1.4 Collection and handling of sample materials – Date of sample receiving date, storage time and conditions, specimen preparation.

10.1.5 Facility and equipment identification - A general description of the facilities and equipment, including chemical sampling and analysis.

10.1.6 Test conditions - including temperature, humidity, air change rate, and dimensions of the test specimen.

10.1.7 Results - (1) names of VOCs identified in the pre-screening analysis; (2) basis of selecting the individual VOCs for environmental chamber testing; (3) initial emission factors, EF_0 , and the exponential decay constants, k , calculated for TVOC and the selected individual VOCs according to the procedure in section 9.

10.1.8 Reference - Reference to this practice and state any variations in the test procedure from this practice.

10.2 All values shall be reported in SI units unless specified otherwise.

11. Quality Control and Quality Assurance

11.1 A quality assurance and quality control (QA/QC) plan shall be designed and implemented to ensure the integrity of the measured and reported data obtained during product evaluation studies. This plan shall encompass all facets of the measurement program from sample receipt to final review and issuance of reports.

11.2 Data Quality Objectives and Acceptance Criteria - The QA/QC plan shall be based on established data quality objectives and acceptance criteria which will depend on the purpose of the testing and the capability of the laboratory (equipment and personnel) to conduct the test procedures. Data quality objectives shall be established for the following parameters prior to initiating the testing program:

11.2.1 Test sample transfer time and environmental conditions - Tolerance limits shall be established for the duration time from sample production to testing under an acceptable range of specified environmental conditions.

11.2.2 Test chamber conditions and test results - Precision and accuracy limits should be met for each of the parameters in Table 1. Accuracy certifications are supplied by the manufactures of the sensors who calibrate them against NIST-traceable primary sources. Precision measurements are obtained within the laboratory by continuous recording of the parameters. Non-compliance requires immediate correction or replacement of sensors, or both. Calibrated replacements shall be retained in the laboratory. Experience shows that routine calibration and tracking of precision can prevent noncompliance.

11.2.3 Record keeping and logs - Various documentation requirements shall be implemented for all test parameters including environmental test chamber and analytical performance. Many of these are identified in ASTM D5116. Additionally, the identity of persons conducting each procedure shall be recorded. All devices used, date and time of tests, and the test data shall be part of QA/QC recording process. Completeness of records demonstrates the care and attention given to the quality control process.

11.3 Calibration - Calibration shall be conducted frequently enough to assure performance of the system within the specified parameters. Frequency of calibration shall be determined prior to the test and periodic equipment checks shall verify the maintenance of acceptable performance. All calibration and verification measurements shall be recorded including the time, equipment description, and measurement data.

11.4 Accuracy of test results - Accuracy determinations require measurements of a known emission source (e.g. permeation tubes, spiked samples) or test gas. These measurements shall be made prior to establishing the project data quality objectives, and shall be consistent with the overall testing objectives. The procedures and materials used for establishing accuracy of the measurement system shall be recorded.

11.5 Precision of test results - Precision determinations require replications sufficient to establish statistically validated variations associated with all measurements. When multiple chambers are used as part of an experiment, duplicate samples shall be used for this determination. Variation in test data from a single chamber and among chambers can be established by use of standardized sources such as permeation tubes for determining organic concentrations and calculated emission rates.

11.6 Duplicate Analysis - No less than 30% of duplicate air samples shall be collected and analyzed. The results of such analyses shall be recorded and assessed to determine the adequacy of the total system performance relative to the testing objectives.

11.7 Charting - Charting quality control data will allow analysis of system performance and observation of anomalous or unacceptable deviations.

12. Keywords

Chemical analysis, emission factors, small environmental test chamber, standard dynamic chamber test condition, volatile organic compounds, surface coating materials.

Table 1: Precision and accuracy limits for test chamber conditions and test results

Parameter	Precision	Accuracy
Chamber temperature	±0.5 °C	±0.5 °C
Chamber relative humidity	±5.0 %	±5.0 %
Air flow rate	±5.0 %	±5.0 %
Area of the testing surface of the specimen	±1.0 %	±1.0 %
Time measurement	±1.0 %	±1.0 %
Organic concentration	±10.0 % RSD*	±10.0 % RSD*
Emission factor	±20.0 % RSD*	±20.0 % RSD*

* RSD = Relative standard deviation, = $(s/m) \times 100\%$, where, s = standard deviation; and m = mean value. The RSD should be determined at the medium of the chamber concentrations observed during the test period.

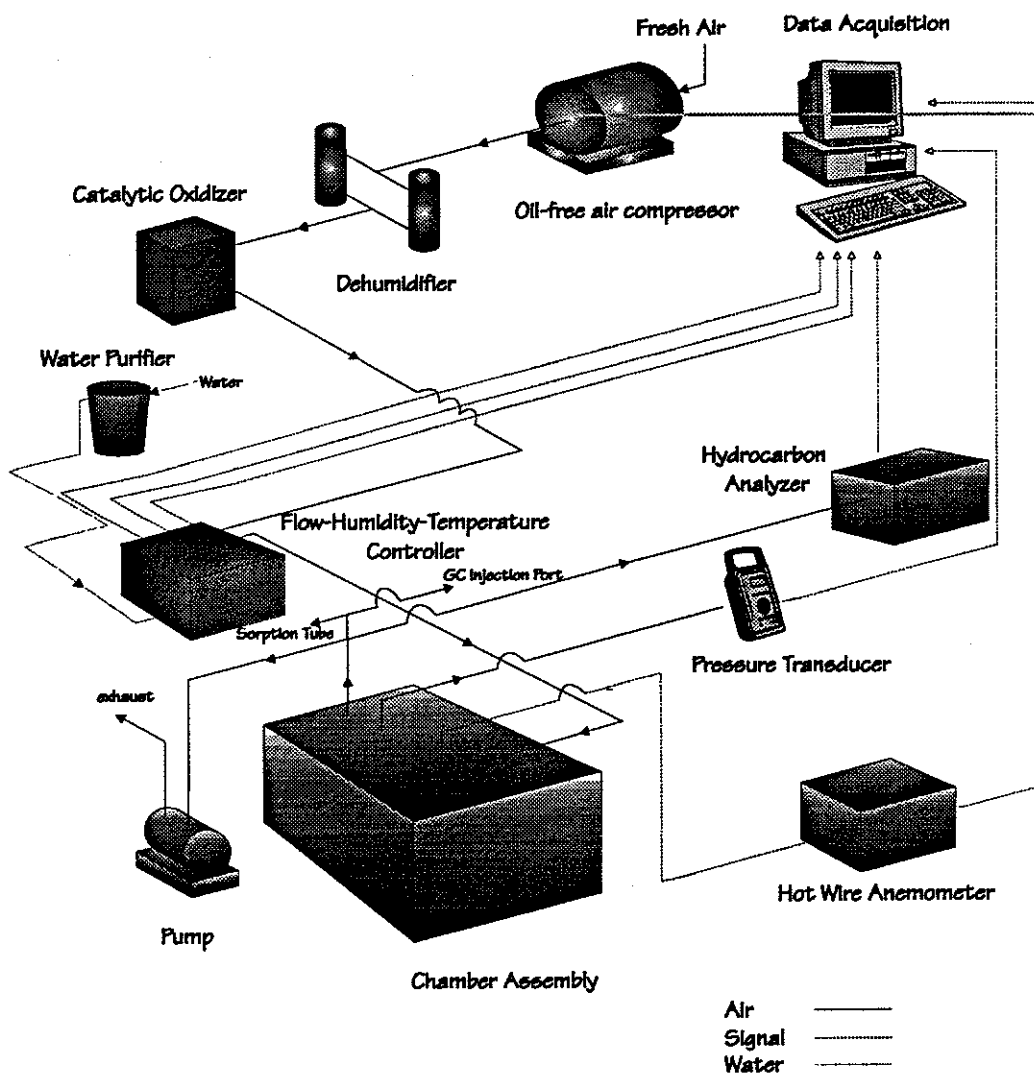


Figure 1: Schematic of an example small chamber test system
 (The chamber assembly should be contained in an environmental enclosure to maintain the required temperature)