



Designation: D7339 – 18

# Standard Test Method for Determination of Volatile Organic Compounds Emitted from Carpet using a Specific Sorbent Tube and Thermal Desorption / Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D7339; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method describes an analytical procedure for identifying and quantifying the masses of individual volatile organic compounds (individual VOCs or IVOCs) that are emitted into a flow of air from carpet specimens and collected on sorbent sampling tubes during emissions testing.

1.2 This test method will be used in conjunction with a standard practice for sampling and preparing carpet specimens for emissions testing. If a specific chamber practice is not available for the carpet specimens, this test method should be used in conjunction with approved standard practices for emissions testing and sample preparation.

1.3 When used in conjunction with standard practices for carpet specimen preparation and collection of vapor-phase emissions, this test method will provide a standardized means of determining the levels of IVOC in the exhaust stream of the emissions test chamber/cell. If this test method is used with a reliable practice for emissions testing, these IVOC levels can be used to determine the emission rate from a unit quantity (usually surface area) of the sample material under test.

1.4 VOCs in the exhaust stream of an emissions test device are collected on thermal desorption tubes packed with a specific combination of sorbents using active (pumped) sampling. (See Practice D6196 for a more general description of vapor collection using pumped sampling onto sorbent tubes.) The samples are analyzed by thermal desorption (TD) with gas chromatography and mass spectrometry detection (GC/MS) and/or flame ionization detection (FID) depending upon the requirements of the specific materials emissions testing/certification protocol.

1.5 This test method can be used for the measurement of most GC-compatible organic vapors ranging from the approximate volatility from *n*-hexane to *n*-hexadecane (that is, compounds with vapor pressures ranging from 16 kPa to  $4 \times 10^{-4}$

kPa at 25°C). Properties other than a compound's vapor pressure such as affinity for the sorbent may need to be taken into account. Compounds with vapor pressures outside this range may or may not be quantifiable by this test method. However, qualitative data concerning the identity of a compound(s), outside the stated volatility range for quantitation, may still be useful to the user. This test method can be applied to analytes over a wide concentration range—typically  $1 \mu\text{g}/\text{m}^3$  to  $1 \text{mg}/\text{m}^3$  concentration of vapor in the exhaust air from the emission cell or chamber.

1.6 *This test method is not capable of quantifying all compounds which are emitted from carpets. See the appropriate test practices/methods for determining other compounds that are not amenable to analysis by gas chromatography (that is, Test Method D5197 for the determination of aldehydes).*

1.7 *Units*—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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.9 *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>2</sup>

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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<sup>2</sup> 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.

- D3686** Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)
- 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)
- D5337** Practice for Flow Rate Adjustment of Personal Sampling Pumps
- D6196** Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air
- D6670** Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/Products
- D7143** Practice for Emission Cells for the Determination of Volatile Organic Emissions from Indoor Materials/Products
- D7706** Practice for Rapid Screening of VOC Emissions from Products Using Micro-Scale Chambers
- E355** Practice for Gas Chromatography Terms and Relationships

## 2.2 ISO Standards:<sup>3</sup>

- ISO 10580** Resilient, textile and laminate floor coverings—Test method for volatile organic compound (VOC) emissions
- ISO 16000-6** 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/FID
- ISO 16000-9** Indoor Air—Part 9: Determination of the emission of volatile organic compounds from building products and furnishings—Emission test chamber method
- ISO 16000-10** Indoor Air—Part 10: Determination of the emission of volatile organic compounds from building products and furnishings—Emission test cell method
- ISO 16000-11** Indoor Air—Part 11: Determination of the emission of volatile organic compounds from building products and furnishings—Sampling, storage of samples and preparation of test specimens

## 2.3 US EPA Methods:<sup>4</sup>

- TO-15** Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)
- TO-17** —Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes

## 3. Terminology

3.1 *Definitions*—Refer to Terminology **D1356** and Practice **E355** for definitions of terms used in this test method.

## 4. Summary of Test Method

4.1 A sample of the VOCs emitted from a carpet specimen is collected following the preparation and collection guidelines provided in ISO 10580 or the appropriate chamber/emission cell practices/guides. See, for example, Guide **D5116** (small chamber), Practice **D6670** (full-scale chamber), Practice **D7706** (micro-scale chamber), Practice **D7143** (emission cells), ISO 16000-9 (small chambers), ISO 16000-10 (emission cells), and ISO 16000-11 (sample preparation).

4.2 Organic vapors in the exhaust stream of an emission test chamber or cell are pumped onto standard thermal desorption tubes (see Practice **D6196**) containing ~200 mg of a polyphenylene oxide resin-based W-PP (weak porous polymer sorbent) with a short bed (1–2 mm) of quartz wool, a glass frit, or stainless steel screen (singly or combined) at each end of the ~200 mg of W-PP sorbent. The pump flow rate and sampling time must be controlled (see Practice **D6196**). The sorbent tubes are then thermally desorbed, in a reverse flow of carrier gas, using an appropriate two-stage desorption apparatus (see Practice **D6196**), such that volatile organic compounds are transferred (injected) efficiently into the capillary GC column for analysis.

4.3 GC-compatible organic compounds which are retained by the W-PP sorbent or quartz/W-PP sorbent tube during vapor collection and which elute between  $n\text{-C}_6$  and  $n\text{-C}_{16}$  on a 100 %, polydimethylsiloxane (PDMS) fused silica capillary column are identified and quantified by gas chromatography/mass spectrometry (see Section 11). Selective ion monitoring, ion extraction or spectral de-convolution shall be used to quantify specific volatile organic compounds. Individual components of interest are quantified using authentic standards of that particular compound. Other compounds are quantified using toluene as the surrogate standard reference material (see 11.7.2).

NOTE 1—The procedure is similar to that outlined in ISO 16000-6.

## 5. Significance and Use

5.1 Manufacturers of carpet need to monitor emissions of VOCs to assess the environmental impact of their products indoors. These results are also used to demonstrate compliance with VOC emission limits for individual VOCs.

5.2 These data are also used to understand which VOCs are emitted from a product or material and to measure the magnitude of those emissions.

5.3 Emission data may be used to compare different lots of carpet of the same materials of construction, or carpets composed of different materials of construction, in order to develop products with lower emissions and lower potential environmental impact.

5.4 This test method should be used in conjunction with practices/guidelines for emissions testing such as Guide **D5116**, Practice **D7143**, Practice **D7706**, ISO 16000-9, and ISO 16000-10. These detail how to select and prepare samples and how and when to carry out emissions tests such that the

<sup>3</sup> Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

<sup>4</sup> Found in “Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,” 2nd Ed., 1999, US. Environmental Protection Agency/625/R-96/010b. Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

concentration and profile of vapors in the exhaust air of the emission chamber/cell are representative of the product under test. This test method covers the sampling and analysis of volatile organic compounds in the exhaust gas from the chamber/cell using thermal desorption—compatible sorbent tubes and will provide the necessary analytical consistency to ensure that reproducible data is obtained for the analysis of identical vapor samples by different laboratories.

## 6. Interferences

6.1 Organic compounds that have the same or nearly the same retention times as the analyte of interest can interfere during gas chromatographic analysis. High resolution capillary columns are required to minimize these issues. Artifacts can be generated during sampling and analysis. Interferences can be minimized by proper selection of gas chromatographic columns and conditions, and by stringent conditioning of both the sorbent tubes and the analytical system before use. Artifacts may be formed during storage of blank sorbent tubes. This is minimized by correctly sealing and storing blank and sampled tubes (see 7.3 and 10.1). The effectiveness of these methods for controlling the potential interferences can be demonstrated by proper quality assurance procedures including the use of blanks and spiked sampling tubes.

NOTE 2—The inherent artifact levels will vary from sorbent to sorbent but are generally at sub-nanogram levels for quartz wool, W-PP and for MS-GCB (medium to strong graphitized carbon black) type sorbent (see Practice D6196).

6.2 Compounds of interest that co-elute chromatographically, are not distinguishable when using an FID. Identification and quantification shall be done using a mass spectrometer in the selected ion monitoring (SIM) mode, or in SCAN mode in combination with post-run processing using spectral deconvolution, or ion extraction, or both.

6.3 Even if mass spectroscopy is employed, it may not be possible to uniquely identify individual compounds when similar compounds co-elute exactly (co-maximize) under the analytical conditions selected.

6.4 This test method is suitable for sampling and analyzing vapor samples ranging up to 95 % relative humidity for all hydrophobic sorbents such as quartz wool, W-PP and MS-GCB. When less hydrophobic, strong sorbents such as CMS (carbonized molecular sieves) are used in a secondary (back-up) tube (see Note 3 and Note 7), care should be taken to reduce the mass of water retained from humid samples (see Practice D6196).

## 7. Apparatus

7.1 *Sorbent Tubes for Pumped Sampling*—Sample tubes (see Practice D6196) packed with 200 mg of W-PP sorbent or with a combination of 1 or 2 mm of loosely packed quartz wool, glass frit, or stainless steel screens bracketing 200 mg of W-PP sorbent should be used for collection of the volatile organic vapors in the exhaust gas from the emission chamber/cell. Analyses of glass or stainless steel spiked tubes indicates that similar results are obtained using either glass wool, or stainless steel frits, as long as the sorbent is in the heated zone of the thermal desorber (see 12.2).

NOTE 3—The use of a secondary back-up tube can serve as a useful check on the breakthrough volume of the primary W-PP or quartz/W-PP tubes. Breakthrough should be determined using two sorbent tubes containing the same sorbent and placed in series. Tube performance should be addressed by individual laboratory QC programs, see EPA Method TO-17 for guidance.

7.2 *Sorbent Tube End Caps for Long-Term Storage*—Blank and sampled tubes should be sealed with metal screw-cap fittings with combined (one-piece) PTFE ferrules for storage and transportation. If alternate fittings are used, the laboratory should determine that they meet storage and transportation stability requirements.

NOTE 4—As a quick test that long term storage caps have been fitted correctly, check the length of the capped tube to make sure the seals are seated as far down the tube as possible and check that the caps cannot be pulled off the tubes by hand using reasonable force.

7.3 *Syringes*—A precision 10- $\mu$ L liquid syringe readable to 0.1  $\mu$ L.

7.4 *Soap Bubble Meter*—A soap bubble flow meter or another suitable calibrated device is required for calibrating pump, desorption, and split flows. Follow the manufacturer's recommended procedure and or the participating laboratory QC program. See Practice D3686 for further guidance.

7.5 *Thermal Desorption Apparatus*—A two-stage apparatus is required for thermally desorbing VOCs retained on the sorbent tubes and transferring/injecting them into a gas chromatograph (GC) in a flow of inert carrier gas. A typical apparatus contains a mechanism for holding the tubes to be desorbed while they are heated and purged simultaneously with inert carrier gas. The sample flow path through the thermal desorber must be constructed entirely of inert materials (that is, quartz, fused silica, silica-coated steel, PTFE, etc.), including all valve components which may come into contact with sample vapors. The desorption temperature and time should be adjustable, as should the carrier gas flow rate. Air must be purged from the sample tube and analytical system before heat is applied to prevent sorbent and analyte oxidation. None of the purged air should be allowed to reach the GC column or detector. The apparatus should incorporate a stringent leak test of every sample (see Note 5) to check flow path integrity before sample desorption/analysis. The secondary focusing (cold) trap should contain appropriate sorbents and be of sufficient internal diameter to prevent ice from blocking the flow path during the focusing of humid samples. It should be desorbed in back-flush direction (that is, with carrier gas flowing in the reverse direction to that used during the trapping stage) to ensure compatibility with components over the widest possible volatility range. The option for sample splitting should be available during primary (tube) desorption, secondary (trap) desorption or both. Tubes on automated thermal desorption systems must be sealed, both before and after desorption, to protect the integrity of sampled and desorbed (blank) tubes. The sample should be desorbed rapidly from the secondary focusing trap to ensure efficient transfer to the capillary GC column and optimum sensitivity. The sample is routed to the gas chromatograph by way of a heated capillary-lined, or silica-lined stainless steel, transfer line. The option of internal standard addition, whereby gas phase internal standard is

automatically introduced onto the sampling end of sorbent tubes post leak test and before analytical desorption, should also be considered as a tool for checking system stability/performance over time (see 11.7.3).

NOTE 5—Leak testing should be carried out under no-flow conditions, at low temperature, and at carrier gas column head pressure such that it is suitably stringent, but does not compromise sample integrity. Tubes that fail the leak test should not be analyzed but resealed to await user intervention.

### 7.6 Gas Chromatographic (GC) Apparatus:

7.6.1 *Gas Chromatograph*—Fitted with a mass spectrometric (MS) detector and with a flame ionization detector (FID) if the latter is required (see 4.3). The gas chromatograph should be capable of split/splitless injections. The MS detector should be capable of scanning between mass ion 25 and 450.

7.6.2 *Gas Chromatographic Column*—A100 % polydimethylsiloxane (PDMS) fused silica capillary column should be used. Typical dimensions: 50 – 60-m long with 0.32-mm I.D. and a 1.0- $\mu$ m film thickness. Higher speed alternatives with similar phase ratio (narrower I.D. and thinner film) can also be used. If a more polar column (for example, cyanopropyl-phenyl-polymethylsiloxane) is used for these analyses, the testing laboratory must demonstrate that they obtain recoveries and precision that meet the guidelines outlined in 12.1 and 12.2.

7.6.3 *Effluent Splitting*—If both FID and MS detection are required by the relevant emissions test protocol, the outlet of the capillary column should be connected to both the FID and MS detector using a conventional, zero or low-dead-volume, capillary effluent splitting device. Connections from each respective detector to the capillary effluent splitter should ensure that sufficient effluent from the capillary analytical column is directed to the FID and to the MS detector to achieve the desired detection limits, taking into account the fact that the MS detector operates at vacuum.

7.7 *Injection Facility for Preparing Standards Purpose-Built*—Injection ports are available for introducing standards to the sampling end of sorbent tubes in the vapor-phase in a stream of carrier gas. A conventional gas chromatographic injection port may also be used. Injection port temperatures between 75°C and 140°C have been shown to give reliable results in preparing samples (see 12.2 and Table 1). This can be left in-situ, or it can be mounted separately. The carrier gas line to the injector should be retained. The back of the injection port should be adapted if necessary to fit the sampling end of a sorbent tube. This can be done conveniently by means of a 1/4-in. compression coupling with a PTFE or graphitized vespel ferrule. Alternatively, commercially prepared standards may be used.

7.8 Use ordinary laboratory apparatus (for example, volumetric flasks for preparing standard solutions) as needed.

## 8. Reagents and Materials

8.1 Unless otherwise stated, all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided that it is ascertained that use of the reagent does not lessen the accuracy of the practice.

### 8.2 Reagents:

8.2.1 *Volatile Organic Compounds*—To be prepared as liquid standards for calibration. These would ideally be within the volatility range of *n*-hexane to *n*-hexadecane (see 1.5) and should reflect the compounds of interest. Toluene must be included.

8.2.2 *Methanol Dilution Solvent*—To be used as the solvent for preparation of liquid standards of toluene and the volatile organic compounds of interest. The methanol used should be of chromatographic quality, free from compounds co-eluting with the compound or compounds of interest (see 8.2.1). Alternative dilution solvents, for example, ethyl acetate or cyclohexane can be used, particularly if there is a possibility of reaction or chromatographic co-elution.

8.3 *Sorbents*—Sorbent tubes, pre-packed with weighed amounts of sorbent, are available commercially. Empty industry-standard sized tubes can also be packed by the user. In this case 200 mg of W-PP sorbent ranging in particle-size from 35 to 80 mesh should be weighed into standard sample tubes that are either empty or contain 1-2 mm of loosely packed, clean and non-friable quartz wool, glass frits, or stainless steel screens at the sampling end. New commercial or self-packed W-PP sorbent or quartz-W-PP sorbent tubes should be stringently conditioned before initial use. Example conditions for cleaning the sorbent tubes are as follows: 320°C under a flow of >100 mL/min of pure inert gas (helium or nitrogen) for >2 hours, followed by a further 30 minutes at 335°C (see Practice D6196). Cleaning procedures specified by the tube supplier or manufacturer should always be followed.

NOTE 6—Less stringent conditions are required for cleaning used tubes (for example 10 minutes at a temperature ~20°C higher than that to be used for analysis), provided this doesn't exceed the maximum safe temperature for W-PP sorbent. Practically, the analytical desorption temperature should not be greater than 300°C because higher temperatures may lead to the production of trace amounts of benzene. Tubes used for trace level monitoring (individual VOC levels below 20 ng/L) can often be re-used immediately after analysis (that is, without further cleaning).

8.4 *Calibration Solutions*—Following guidance given in Practice D6196, prepare standard solutions of toluene and

**TABLE 1 Average Recoveries for GC/MS Analysis of Six IVOCs spiked into Glass and Stainless Steel Thermal Desorption Tubes**

	Average % Recovery	Average % Recovery	Average % Recovery	Average % Recovery	Average % Recovery	Average % Recovery
	Toluene	Benzene	4-PCH	Styrene	2-EHA	Caprolactam
Glass Tube (Glass Wool)	102	97	98	99	120	70
Glass Tube (Glass Frit)	101	94	99	97	119	72
Stainless Steel (1) <sup>A</sup>	94	92	89	86	109	66
Stainless Steel (2) <sup>A</sup>	98	98	97	93	127	73

<sup>A</sup> (1) and (2) refer to 75°C and 140°C preparation temperatures for the spiked tubes. The glass tubes were prepared at 75°C.

other VOCs of interest (for example; styrene, caprolactam and 4-phenylcyclohexene) in methanol such that a 1 to 4  $\mu\text{L}$  injection, via the calibration solution loading apparatus (see 7.7), introduces 20 to 2500 ng of each compound, or an alternative mass range if more appropriate to the samples being tested. In any event, the lowest and highest concentration standards must be prepared such that the mass of the analyte introduced in the highest level standard is at least a factor of 20 higher than that introduced in the lowest standard.

**9. Tuning and Calibration of the TD-GC/MS(FID) Analytical System**

9.1 Tuning and mass standardization is performed in accordance with the manufacturer’s instructions, generally using perfluorotributylamine (FC-43) commonly known as PFTBA. This process may vary among instruments. Consult the tuning instructions for the specific instrument being used for the appropriate tune conditions. The FC-43 is introduced directly into the ion source through a molecular leak. Instrument parameters are adjusted to give acceptable relative ion abundances. An example of the ranges for the relative ion abundances based on the NIST02 mass spectral database are given below.

Mass	% Relative Abundance
69	100
131	25–55
219	45–75
502	3–7

The mass range scanned is 35 amu to 450 amu with an allowable scan rate  $>0.5$  Hz. The mass spectrometer should be tuned prior to an initial calibration, after vacuum is broken (column change, new source installed, etc.), and if the calibration check has failed.

9.2 Standard calibration curves will be required for MS (and on FID, if required by the relevant materials emissions testing protocol) for each compound of interest comprising at least five points within the range of 20 to 2500 ng of each compound. The standard concentrations distribution should not be greater than five times the concentration of the next lower standard (for example 20, 100, 500, 1750, 2500 ng). See Fig. 1 for a typical

example of an MS calibration curve (area response versus ng toluene loaded on a thermal desorption tube). Prepare loaded tubes by injecting aliquots of standard solutions onto clean W-PP sorbent or quartz-W-PP sorbent tubes as follows: Fit the sampling end of the clean sorbent tube into the injection unit (see 7.7) through which inert purge gas is typically passing at 50-100 mL/min and introduce a 1 to 4  $\mu\text{L}$  aliquot of an appropriate standard solution injected through the septum. After 1 to 5 minutes, disconnect the tube and seal it using long term storage caps (see 7.3). This multi-level calibration shall be carried out when the calibration check (see 9.4 and 9.5) falls outside the specified range. The MS response factors shall agree within 20 % across all calibration levels or demonstrate an  $R^2$  value of  $>0.995$ .

9.3 The use of a linear regression of the standards for quantification is recommended. Use of a linear regression of the standard responses does not eliminate the possibility of large systematic errors if the intercept value is large relative to the quantity being measured. The analyst needs to be aware of unusually large intercepts which may bias the results. Typically observed intercept values for toluene, benzene, styrene, 4PCH, caprolactam, and 4-ethylhexanoic acid have ranged from 5 to 50 nanograms.

9.4 Split or splitless injections can be used for these analyses. In either case, care must be taken to ensure that the calibration standards do not exceed the capacity of the sorbent material, column, or the detector. Appendix X1 gives suggested split conditions, however the analyst may need to adjust the split flow (or lack thereof) to accommodate the sensitivity needed, the breakthrough volume of the compounds of interest, or the capacity of the column and/or detector.

9.5 If an FID is used, a single, mid-point calibration check of detector response will be carried out before and after the analysis of a series of sorbent tubes collected during emissions testing of a single sample of carpet. The FID response factor shall agree within 10 % to the average of that obtained from all five standards during the most recent multi-level calibration. If

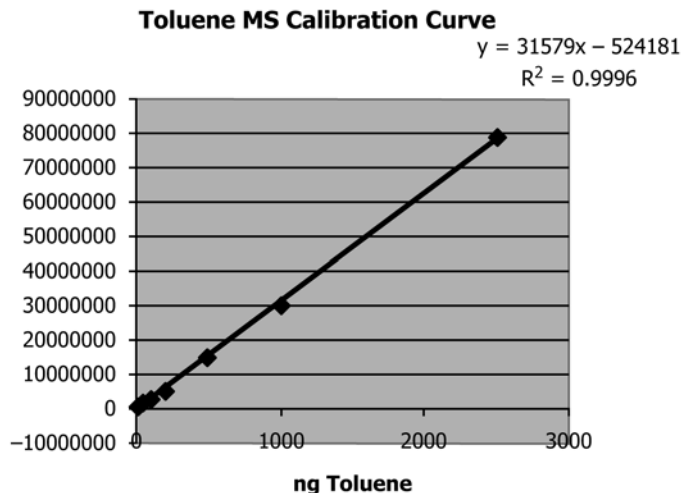


FIG. 1 Toluene MS Calibration Curve

this is not the case, the five-level calibration curves must be repeated before proceeding with the analysis.

9.6 A check on MS response for each target VOC will be carried out at the midpoint level of the calibration curve before the analysis of a series of sorbent tubes collected during emissions testing, after every ten samples or every twelve hours thereafter during continuous analyses. The average MS response factors obtained for each compound shall agree within 20 % to the average of that obtained from all five standards during the most recent multi-level calibration. If this is not the case, the five-level calibration curves must be repeated before proceeding with the analysis.

9.7 Certified reference standard tubes pre-loaded with toluene and other VOCs are available commercially and should be used as an independent check on analytical quality assurance on a quarterly basis. Experimental data for each compound should agree ( $\pm 15\%$ ) to the actual mass of each analyte on the certified reference standard tubes.

## 10. Collecting VOCs from the Exhaust Gas of Emission Chambers/Cells

10.1 Clean, conditioned sorbent tubes (see 8.3), with blank levels below 2 ng for toluene and each individual VOC of interest, should be used for this test method. Each tube used should be indelibly etched with a unique identification number and the numbers of the tubes selected should be recorded and batched according to date of packing and number of thermal cycles. Analyze a representative, randomly-selected proportion (at least 10 %) of the batch of sorbent tubes using routine analytical parameters, to ensure that the thermal desorption blank is sufficiently small (see 11.5). If the blank is unacceptable, the tubes should be reconditioned by repeating the procedure outlined in 8.3. Sorbent tubes should be sealed with long term storage caps (see 7.3) until the start of sample collection and should be resealed with the same caps immediately after sample collection unless they are to be analyzed immediately. Tubes will be required for recovery measurements (testing for sink effects), for sample collection and for use as field blanks during emissions testing. Consult the emissions testing practice and protocols used for details of how many sample and blank tubes will be required.

10.2 Calibrate the pump with a representative sorbent tube assembly in line, using an appropriate external calibrated meter (refer to Practices D3686 and D5337). The pump should be attached to the non-sampling end of the sorbent tube using appropriate connecting tubing. The chosen air sampling pump shall meet any certifications required by local safety regulations.

10.3 The sampling end of the sorbent tube should be connected to the exhaust of the materials emissions chamber/cell using inert fittings. Follow chamber/cell manufacturer's instructions and relevant materials emissions testing standards/protocols. The pump flow rate and time used to sample vapors from the exhaust stream of the emission chamber or cell should be set in accordance with the requirements of the emissions testing protocol selected, but should not, in any event exceed 500 mL/min even for short term (<15 minute) sampling. If the

velocity is greater than 500 mL/min, through standard, 5 mm I.D. stainless steel or silica-coated stainless steel tubes, the analytes of interest will pass through the adsorbent resin too quickly to permit efficient trapping of the volatiles on the adsorbent resin. The maximum short term sample gas flow rate through the adsorbent resin bed should not exceed 250 mL/min for the 4.0-mm I.D. Desorption tubes and 150 mL/min for the 3.0 mm diameter desorption tubes. Higher flow rates will not permit the efficient trapping of volatiles on the adsorbent resin.

NOTE 7—Collecting sample volumes above 5.0 L can be used but this may exceed retention volumes for the more volatile VOCs such as *n*-hexane (see Practice D6196). Tests for breakthrough, using two tubes in series, are described in Practice D6196, subsection 11.1.6. If larger sample volumes are required, a secondary (back-up) tube containing a stronger sorbent, such as one of the MS-GCB or CMS (see Practice D6196) may be attached to the primary W-PP sorbent or quartz-W-PP sorbent tube using the coupling described in 7.2. The secondary (back-up) tube will need to be analyzed separately from the primary tube.

NOTE 8—Flow rates above 200 mL/min should only be used for short sampling periods up to 15 minutes for tubes with 4 or 5 mm I.D.

10.4 Batches of sealed sampled tubes should be stored and transported in clean, airtight, non-outgassing containers such as uncoated paint cans or air tight, non-emitting plastic containers. W-PP sorbent or quartz-W-PP sorbent sample tubes do not require refrigerated storage. Controlled recovery studies have shown ~99 % recovery for VOCs from W-PP sorbent after eleven months storage at ambient temperature (see Practice D6196, subsection 16.2 and Table 11). If refrigerated storage conditions are used, tube seals must be retightened once the tubes have reached minimum storage temperatures and tubes must be allowed to re-equilibrate with room temperature before seals are removed immediately prior to analysis (see Practice D6196, subsection 16.3). This prevents humidity from the laboratory air condensing inside the cold tube and interfering in the subsequent analysis. Samples comprising chemically stable compounds of interest should ideally be analyzed within 30 days. If target compounds include more reactive species, samples should be analyzed as soon as possible.

## 11. Desorption and Analysis

11.1 When ready for analysis, remove the long-term storage seals from blank and sampled tubes and fit analytical end caps if required by the TD apparatus in use. Place the sorbent tube(s) into suitable thermal desorption apparatus (see 7.5) and begin the automatic process of leak testing, purging, primary (tube) desorption and secondary trap desorption. Analytical parameters will vary to some extent depending on the make of the TD equipment used, but desorption conditions should be chosen such that desorption efficiency exceeds 95 % for all analytes (see 11.4). Typical analytical thermal desorption parameters are tabulated in Appendix X1.

11.2 Set the sample flow path temperature (transfer line temperature and main valve) high enough to prevent analyte condensation but not so high as to cause degradation. *n*-Hexadecane and more volatile analytes do not require flow path temperatures above 150°C. Higher flow path temperatures (for example, 200°C or higher) will be required for the simultaneous analysis of VOC and semi-VOC (that is, compounds with a higher vapor pressure than *n*-hexadecane.). The