Designation: D7339 – 12

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

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 (ε) 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 standard 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 4×10^{-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 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. The method can be applied to analytes over a wide concentration range—typically 1 $\mu g/m^3$ to 1 mg/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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

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

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[1] 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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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Other Carbonyl Compounds in Air (Active Sampler Methodology)

D5337 Practice for Flow Rate Adjustment of Personal Sampling Pumps

D6196 Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds 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:*[3]

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:*[4]

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 (PPOR-B) 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 PPOR-B 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 PPOR-B sorbent or quartz/PPOR-B sorbent tube during vapor collection and which elute between n-C_6 and n-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 concentration and profile of vapors in the exhaust air of the emission chamber/cell are representative of the product under test. This standard 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.

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

[4] 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 Association (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

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—Note that inherent artifact levels will vary from sorbent to sorbent but are generally at sub-nanogram levels for quartz wool, PPOR-B and for 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 The method is suitable for sampling and analyzing vapor samples ranging up to 95 % relative humidity for all hydrophobic sorbents such as quartz wool, PPOR-B and graphitized carbon blacks. When less hydrophobic, strong sorbents such as carbonized molecular sieves are used in a secondary (back-up) tube, (see Note 3 and Note 8) care must 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 PPOR-B 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 PPOR-B 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—Note that use of a secondary back-up tube can serve as a useful check on the breakthrough volume of the primary PPOR-B or quartz/PPOR-B 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–µL liquid syringe readable to 0.1 µL.

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—Note that 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-µm 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, cyanopropylphenyl-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 ¼-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 PPOR-B 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 PPOR-B sorbent or quartz-PPOR-B 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—Note that much 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 PPOR-B sorbent. Practically, the analytical desorption temperature should not be greater that 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 other VOCs of interest (for example; styrene, caprolactam and 4-phenylcyclohexene) in methanol such that a 1 to 4 µL injection, via the calibration solution loading apparatus (see 7.7), introduces 20 to 2500 ng of each compound, or an

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

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

^{A}(1) and (2) refer to 75°C and 140°C preparation temperatures for the spiked tubes. The glass tubes were prepared at 75°C.

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 PPOR-B sorbent or quartz-PPOR-B 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 µL 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 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

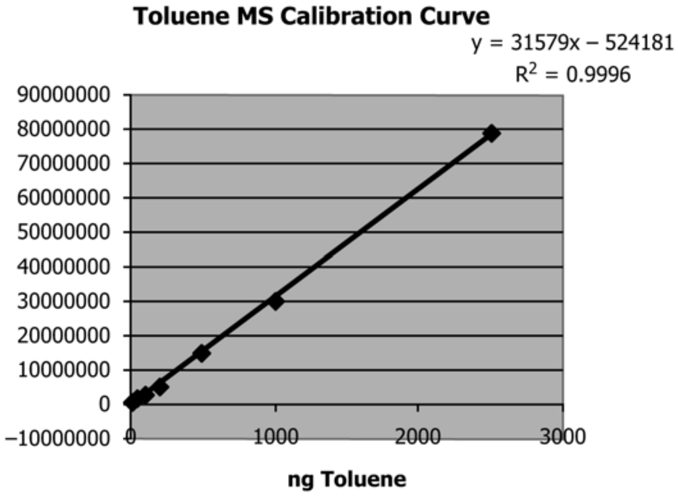

FIG. 1 Toluene MS Calibration Curve

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 (±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.

NOTE 7—Note that the sampling pump shall comply with 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 thorough 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 8—Note that 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 graphitized carbon blacks or carbon molecular sieves (see Practice D6196) may be attached to the primary PPOR-B sorbent or quartz-PPOR-B 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 9—Note that 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. PPOR-B sorbent or quartz-PPOR-B sorbent sample tubes do not require refrigerated storage. Controlled recovery studies have shown ~99 % recovery for VOCs from PPOR-B 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 connection between the thermal desorber and the GC/MS (FID) analytical system should ideally comprise uniformly heated capillary tubing, butt-connected to the analytical column to minimize risk of dead volumes, peak broadening, loss of sensitivity, or analyte losses.

11.3 Set up the gas chromatograph and mass spectrometer detector for the analysis of organic compounds from *n*-hexane to *n*-hexadecane or a wider volatility range as required by the relevant materials emissions test protocol. A typical GC temperature program using a PDMS capillary column (see 7.6.2) runs from 50 to 250 at 5°C/min, with an initial hold time of 5 min at 50°C and a final hold time of 5 min at 250°C.

11.4 *Checking Desorption Efficiency*—Desorption efficiency should be checked as described in Practice D6196, subsection 13.4, that is using either quantitative re-collection of split flow to repeat the analysis of one or more standards through the entire TD-GC/MS(FID) system (see Practice D6196, subsection 13.4.2); or by comparing calibration curves from the TD system with fresh calibration curves prepared on the same GC/MS (FID) system but using liquid injection (see Practice D6196, subsection 13.4.1). If the desorption efficiency is less than 95 % change the desorption parameters accordingly.

11.5 *Checking Blank Levels*—Analyze a laboratory blank tube under the normal analytical conditions to check system background. This is an identical tube to those used for emissions testing (that is, PPOR-B sorbent or quartz wool plus PPOR-B sorbent, packed at the same time and conditioned in the same way) but that is retained in the laboratory and kept sealed until the sampled tubes are ready for analysis. System blank levels, determined by analyzing the laboratory blank tube under routine analytical conditions, should be well below 2 ng for every individual VOC.

11.5.1 Most emissions testing practices/protocols also require field blanks to be collected by operating the entire emissions test apparatus as normal, but without the presence of a material/product sample. The sorbent tubes used for sampling the chamber/cell exhaust vapors during these blank tests, will also need to be analyzed under the normal operating conditions, and will be required to show individual VOC levels below prescribed levels, typically 2 ng per litre of exhaust air sampled as toluene, (2 µg/m^3) per individual VOC.

11.5.2 If the same profile/pattern of VOCs is observed in the field blanks as on the sample tubes, and if the levels of these components is 5 % or more of the sampled VOCs, careful attention must be paid to methods of sealing the tubes and other storage procedures in any future studies. If the profile of the VOCs on the field blanks matches that of the sampled tubes and if the area of the peaks in the field blanks are 10 % or more of the sampled tube levels, the sampled tube data are suspect and would imply that there is significant carryover in the sampling system.

11.6 *Qualitative Analysis—Confirmation of Component Identity:*

11.6.1 Samples and standards must be analyzed using the mass spectrometer in full scan mode to aid component identification. Compounds shall only be reported as positively identified if both the retention time and the mass spectrum match (>85 % match) that of a standard of the specific compound analyzed under identical conditions. If an IVOC of interest co-elutes chromatographically with another compound, spectral de-convolution should be used to separate the mass spectral data for that compound from interfering mass ions before a spectral comparison or standard library search is carried out.

11.6.2 If only a general mass spectral library search (NIST or Wiley libraries, for example) is used for component identification, the quality of the mass spectral match shall be reported and a comparison of the two mass spectra (unknown and library standard) shall be included in the report. “Probable” identification requires a mass spectral match of 85 % or better and reasonable retention times, unless a skilled analyst has a justifiable reason for a match less than 85 %. Any other compounds having mass spectral matches less than 85 %, without suitable justification for the lower quality match, shall be qualified with the word “tentative”.

11.7 *Quantitative Analysis of individual VOCs:*

11.7.1 Selective ion monitoring or ion extraction shall be used to quantify IVOCs. Examples of suitable mass ions include the 104, 78 and 91 for styrene and the 78, 104, and 158 ions for 4-phenylcyclohexene. Spectral de-convolution should be used to remove the contribution from interfering components with similar mass ions if necessary.

11.7.2 Individual VOCs (for example, styrene, 4-PCH, caprolactam, etc.) shall be quantified by comparing peak areas from the sample with those of authentic standards analyzed under the same conditions and quantified using the same mass ions (see 11.7.1). The specific IVOCs and the number of compounds to be quantified during analysis will be defined by the requirements of the specific testing protocol (Section 2.4), the particular product being tested, and the defined needs of the end user. Compounds detected in the *n*-C_6 to *n*-C_{16} retention time window (that is, minor components or non-target compounds) lacking suitable standard reference materials may be quantified using the MS average response factor for toluene. It should be made clear in the report which compounds were quantified using authentic standards, and which were quantified using the toluene response factor. Example calculations are shown below.

$$C_0(ng)_{IVOC} = \frac{(Peak\ Area - intercept)}{L.R.\ Slope} \tag{1}$$

where:

$C_0(ng)$ = concentration in nanograms of the compound of interest,

intercept = intercept from linear regression of standard calibration curve,

L.R. Slope = slope of linear regression of standard calibration curve, and

Peak Area = integrated peak area of the compound of interest after subtracting any blank contribution.

Alternatively, if using the average response factor,

$$C_0(ng)_{IVOC} = \frac{(Peak\ Area)}{RF} \tag{2}$$

where:

$C_0(ng)$ = concentration in nanograms of IVOC, *RF* = average response factor from standards (area/ng), and

Peak Area = integrated peak area of the compound of interest after subtracting any blank contribution.

$$C_0(\mu g/m^3)_{IVOC} = \frac{C_0(ng)}{Vol(m^3)*1000} \quad (3)$$

where:

$C_0(\mu g/m^3)$ = the concentration in micrograms per cubic metre of air pulled through the sorbent tube, and

$Vol\ (m^3)$ = the volume in cubic metres of air pulled through the sorbent tubes during the collection period.

11.7.3 Some commercial thermal desorption systems offer the facility to introduce a fixed volume, ppm-level gas phase internal standards onto the sampling end of sorbent tubes immediately after the leak test and before tube desorption. This should be used where available to check the analytical system stability, but not as a calibration scalar. Deuterated toluene is commonly used as a gas-phase internal standard because it is not present naturally. However, co-elution with toluene may cause a problem when used in conjunction with an FID.

11.7.4 Once the analytical system is calibrated, the mass of each IVOC on each unknown sample analyzed by that system can be calculated. If the field blanks contain measurable masses of one or more of the IVOCs of interest, this mass should be subtracted from those measured in the samples to give a corrected result (See restrictions given in 11.5). This data is then used to determine the emission levels of each compound from the sample of material/product under test. Example calculations to relate the mass of IVOC determined during TD-GC/MS(FID) analysis of the sorbent tubes, to area or mass specific emission rates for the carpet under test, are given in relevant practices/protocols for emissions testing.

12. System Performance

12.1 *Analytical Precision*—A detailed discussion of general sorbent tube sampling and thermal desorption analysis methods with respect to precision and bias is given in Section 15 of Practice D6196.

12.1.1 Analytical precision (MS and FID if required) should be checked (annually) by preparation and analysis of at least five replicates of the mid-level calibration standard. These standards should be prepared as described in 9.1 and contain toluene plus all IVOCs of interest. Mean, standard deviations, and relative standard deviations shall be calculated and recorded. The relative precision of these replicates shall be 10 % or better. Typical precision for eight measurements of six compounds by GC/MS from a single laboratory are shown in Table 2. Typical precision for eight measurements of six compounds by GC-FID from a single laboratory are shown in Table 3. Precision and recovery data from three different laboratories (MS data only) are shown in Table 4. The data from Tables 2-4 is from preloaded standard tubes, prepared by a third party and analyzed by multiple laboratories. The uncertainty associated with such standards includes variables relating to the standard preparation/introduction, storage, and transportation. Such data should not be confused with the desorption efficiency testing described in section 11.4.

12.2 *Recovery*—Typical recoveries for eleven selected carpet relevant IVOCs obtained by three laboratories are shown in Tables 2-4. Recoveries should be between 80 and 120 % of the known values of the measured compounds. Low recoveries listed in Table 2 and Table 3 for caprolactam and 2-EHA are attributed to incomplete desorption of the glass thermal desorption tubes. Table 1 shows the recovery results from both glass and stainless steel thermal desorption tubes, where care was taken to ensure that the glass wool, glass frit, or stainless steel screen holding the adsorbent in place in the tube was within the heated zone of the thermal desorber. In all four cases, the results are comparable and indicated that recoveries were not dependent upon standard preparation temperatures between 75°C and 140°C.

12.3 *Limits of Detection and Limits of Quantitation:*

12.3.1 If needed, a detection limit can be calculated each time a calibration curve is generated. The limit of detection is defined as:

$$DL = A + 3.3s \quad (4)$$

TABLE 2 Typical Single Laboratory Precision of Six Carpet Relevent IVOCs by GC/MS

Sample ID	Benzene, ng	Toluene, ng	Styrene, ng	4PCH[A], ng	Caprolactam, ng	2-EHA, ng
Tube 1	110	251	214.6	140.1	152.2	111.8
Tube 2	111	248	205.0	137.8	162.4	112.7
Tube 3	111	248	208.2	139.3	170.1	111.6
Tube 4	118	262	215.8	140.2	155.7	110.6
Tube 5	110	248	209.9	140.6	152.2	111.6
Tube 6	120	264	216.0	141.8	158.6	114.3
Tube 7	118	261	213.5	142.2	171.7	112.9
Tube 8	113	252	209.7	139.3	159.9	111.5
average (ng)	114	254	212	140	160	112
std dev	4	7	4	1	7	1
% RSD	3.7	2.7	1.9	1.0	4.6	1.0
Expected ng	125	275	275	125	275	275
Average % Recovery	91	92	85	112	58[B]	41[B]

[A] 4PCH = 4–phenylcyclohexene, 2–EHA = 2–ethylhexanoic acid

[B] See 12.2 for discussion of low recoveries for caprolactam and 2–EHA.

TABLE 3 Typical Single Laboratory Precision of Six Carpet Relevent IVOCs by GC-FID

Sample ID	Benzene, ng	Toluene, ng	Styrene, ng	4PCH, ng	Caprolactam, ng	2-EHA, ng
Tube 1	109.7	267.8	244.2	127.2	193.2	67.2
Tube 2	107.8	261.5	236.8	123.0	204.4	69.2
Tube 3	107.4	261.1	240.1	125.1	212.7	66.1
Tube 4	115.7	275.2	245.7	124.4	192.2	60.8
Tube 5	106.4	257.7	237.3	125.5	188.5	62.8
Tube 6	114.9	273.1	248.3	127.7	195.6	75.5
Tube 7	112.3	268.4	242.6	126.9	210.6	65.9
Tube 8	107.8	258.5	237.0	122.0	197.9	64.3
Average	110.3	265.4	241.5	125.2	199.4	66.5
Std Dev	3.6	6.7	4.4	2.0	8.9	4.5
% RSD	3.3	2.5	1.8	1.6	4.5	6.7
Expected ng	125	275	275	125	275	275
Average % Recovery	88	96	88	100	72[A]	24[A]

[A] See 12.2 for discussion of low recoveries for caprolactam and 2–EHA.

TABLE 4 Inter-Laboratory Recovery for Eleven Carpet Relevent Compounds by GC/MS

Compound	Expected Mass (ng)	Lab 1		Lab 2		Lab 3	
		Average % Recovery	% RSD	Average % Recovery	% RSD	Average % Recovery	% RSD
Benzene	125	105	4	114	5	111	13
Styrene	125	110	10	118	4	100	9
4-PCH	125	109	2	111	4	101	11
Toluene	125	101	4	126	4	114	10
Caprolactam	275	141[A]	35	103	3	80	16
2-EHA	275	115	2	106	6	97	13
Vinyl Acetate	275	55	1	104	3	79	21
Nonanal	275	112	2	141	5	133	8
Octanal	125	114	2	118	10	99	13
1-Methyl-2-pyrrolidinone	275	113	5	107	9	99	12
Naphthalene	125	107	3	119	5	110	11

[A] This value included a correction for a significant blank contribution.

where:

DL = the calculated detection limit in nanograms,
A = the intercept in ng from a least squares calibration curve fit,
s = the standard deviation of replicate determinations of the lowest level standard. (five replicates)

12.3.2 Specific analytical objectives or program requirements will determine minimal quantifiable limits that will depend on the volume sampled. For example, 3 ng of toluene retained on a Tenax tube equates to 0.75 $\mu g/m^3$ (0.75 ng/L) in a 4-L sample of exhaust air from the emission cell/chamber. Quantitation limit(s) of VOC(s) are typically the lowest calibration level(s). What this represents in terms of area specific emission rates will vary depending upon the type of chamber/cell, surface area of sample under test, air flow rate to the chamber, volume of exhaust air sampled, etc.

12.3.3 Speciated compound concentrations between the quantitation and detection limits shall be reported as present, but not quantifiable.

NOTE 10—See EPA Method TO-15 for additional discussion on limits of detection and limits of quantitation.

12.4 Mass Spectral Identification

12.4.1 Tuning of the mass spectrometer detector and associated performance criteria are described in 9.1.

13. Report Test Results

13.1 The analytical results, and a description of the method that was used to derive those results, shall be incorporated into an analytical study report. The report shall contain sufficient information that it is clear how the results were obtained. At a minimum, the analytical study report will contain the following sections:

13.1.1 Details of test facility

13.1.2 Test objectives

13.1.3 Citations of relevant standard methods and practices used in the testing

13.1.4 Description of the analytical equipment

13.1.5 Details of all analytical parameters

13.1.6 Calibration and relevant analytical quality assurance data including:

13.1.6.1 Calibration data (see requirements/details in 9.2, 9.4, and 9.5),

13.1.6.2 Laboratory blank levels (see requirements/details in 11.5),

13.1.6.3 Field blank levels (see requirements/details in 11.5),

13.1.6.4 Limits of detection (see requirements/details in 12.3),

13.1.6.5 Limits of quantification (see requirements/details in 12.3), and

13.1.6.6 An estimate of the Analytical Precision and Accuracy (see requirements/details in 12.1 and 12.2).

13.1.7 Analytical data—IVOC

13.1.8 Area (mass or volume) specific emission rates calculated from the analytical data

13.2 Additionally, if the analytical results are part of a complete emissions testing study, the report shall contain the following:

13.2.1 Detailed sample description including batch numbers, date of sample collection, source, transport and storage conditions, etc.,

13.2.2 Time, date and method of preparation of test specimen from the sample,

13.2.3 Details of all apparatus used for emissions testing, and

13.2.4 Details of all emissions testing parameters.

13.3 See Guide D5116 and Practice D6670 for additional reporting guidance.

NOTE 11—The level of detail required for the customer's report shall be determined by the customer requirements. Any data generated during the study is the property of the customer and shall be made available upon request.

14. Keywords

14.1 carpet; chamber; emission; gas chromatography; indoor air; mass spectrometry; thermal desorption; VOC; volatile organic compounds

APPENDIX

(Nonmandatory Information)

X1. APPENDIX

X1.1 See Table X1.1.

TABLE X1.1 Suggested Thermal Desorption Conditions

Desorption temperature	280°C (Suitable for tubes packed with PPOR-B sorbent or quartz plus PPOR-B sorbent. Note that other sorbents, which may be used in secondary (back-up) tubes for sampling very volatile organic compounds [VVOCs] may require different desorption conditions.)
Desorption time	5 to 10 minutes
Desorption flow rate	30 to 80 mL/min passing through the sample tube in the reverse direction to that used for sampling. The tube desorption flow rate is the sum of the flow through the cold focusing trap and the split flow (if any) during tube desorption
Cold trap low	Between -30°C and +30°C
Flow rate through trap for desorption	2 to 100 mL/min in the reverse direction to that used for focusing. The trap desorption flow rate is the sum of the flow through the analytical column and the split flow (if any) during trap desorption
Cold trap high	Heated as fast as possible (for example, 100°C/s) to 300°C for 3 minutes
Cold trap sorbent	Quartz wool and Tenax (backed up by a stronger carbon black or carbon molecular sieve adsorbent if VVOCs also of interest)
Carrier gas	Helium. Use back-pressure regulated electronic pneumatic control of the carrier gas head pressure through the entire TD-GC/MS(FID) analytical system, if available, such that stable retention times are maintained independent of split flow, trap temperature, etc.
Gas flows and split ratios	Split ratios between the sample tube and secondary trap, and between the secondary trap and analytical column should be selected dependent on expected vapor concentrations in the chamber/cell exhaust and the volume of gas sampled onto each sorbent tube. Typical desorption and split flows for vapor samples comprising 200-1000 ng per IVOC would be 50 mL/min tube desorption flow (comprising 30 mL/min flow through the cold focusing trap and 20 mL/min inlet split flow) and 22 mL/min trap desorption flow (comprising 2 mL/min column flow and 20 mL/min outlet split flow). This gives and inlet split ratio of 50:30, an outlet split ratio of 22:2 and an overall split ratio of 18:1.