



Designation: D6886 – 18

Standard Test Method for Determination of the Weight Percent Individual Volatile Organic Compounds in Waterborne Air-Dry Coatings by Gas Chromatography¹

This standard is issued under the fixed designation D6886; 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 is for the determination of the weight percent of individual volatile organic compounds in waterborne air-dry coatings (**Note 1**).

1.2 This method may be used for the analysis of coatings containing silanes, siloxanes, and silane-siloxane blends.

1.3 This method is not suitable for the analysis of coatings that cure by chemical reaction (this includes two-component coatings and coatings which cure when heated) because the dilution herein required will impede the chemical reaction required for these types of coatings.

1.4 Precision statistics for this method have been determined for waterborne coatings in which the volatile organic compound weight percent is below 5 percent. The method has been used successfully with higher organic content waterborne coatings and with solventborne coatings (**Note 2**).

1.5 This method may also be used to measure the exempt volatile organic compound content (for example, acetone, methyl acetate, *t*-butyl acetate and *p*-chlorobenzotrifluoride) of waterborne and solvent-borne coatings. Check local regulations for a list of exempt compounds. The methodology is virtually identical to that used in Test Method **D6133** which, as written, is specific for only exempt volatile compounds.

1.6 Volatile compounds that are present at the 0.005 weight percent level (50 ppm) or greater can be determined. A procedure for doing so is given in Section **9**.

1.7 Volatile organic compound content of a coating can be calculated using data from Test Method D6886 but requires other data (see **Appendix X2**.)

NOTE 1—Data from this method will not always provide the volatile organic compound content of a paint film equivalent to EPA Method 24. Some compounds and some semi-volatile compounds may be considered volatile using the GC conditions specified but will not fully volatilize

¹ This test method is under the jurisdiction of ASTM Committee **D01** on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee **D01.21** on Chemical Analysis of Paints and Paint Materials.

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during the one hour at 110°C conditions of EPA Method 24. Some or all of these materials remain in the paint film and therefore are not considered volatile organic compounds according to EPA Method 24. In addition, some compounds may decompose at the high inlet temperature of the GC. However, note the EPA Method 24 has poor precision and accuracy at low levels of volatile organic compounds.

NOTE 2—This method measures volatile organic compound weight of air-dry coatings directly as opposed to other methods in Practice **D3960** which measure the volatile organic compound weight percent indirectly. A direct measurement of the weight percent particularly in low volatile organic compound content waterborne coatings, generally gives better precision. California Polytechnic State University carried out an extensive study for the California Air Resources Board comparing the precision of the direct method with the indirect method (CARB Standard Agreement No. 04.329) Detailed results of this study may be found at http://www.arb.ca.gov/coatings/arch/Final_Report_6_11_09.pdf. This study may be used to decide if the present method or other methods in Practice **D3960** are preferred for a specific coating.

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

1.9 *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.*

1.10 *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:²

- D1475 Test Method for Density of Liquid Coatings, Inks, and Related Products
- D2369 Test Method for Volatile Content of Coatings

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.

- D3792 Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph
- D3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings
- D3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings
- D4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method
- D6133 Test Method for Acetone, *p*-Chlorobenzotrifluoride, Methyl Acetate or *t*-Butyl Acetate Content of Solventborne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Injection Into a Gas Chromatograph
- D7358 Test Method for Water Content of Paints by Quantitative Calcium Hydride Reaction Test Kit
- E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 Other Documents:

- EPA Method 24 —Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings
- 40 CFR 51.100 (s) List of components that EPA has classified as VOC-exempt
- SCAQMD M313 Determination of Volatile Organic Compounds (VOC) by Gas Chromatography/Mass Spectrometry/Flame Ionization Detection (GC/MS/FID)

3. Terminology

3.1 Acronyms:

- 3.1.1 *DB*—2-(2-butoxyethoxy)ethanol; Butyl Carbitol;³ diethylene glycol monobutyl ether
- 3.1.2 *DP*—diethylene glycol monopropyl ether
- 3.1.3 *DPM*—dipropylene glycol monomethyl ether
- 3.1.4 *DPnB*—dipropylene glycol monobutyl ether
- 3.1.5 *DPnP*—dipropylene glycol monopropyl ether
- 3.1.6 *EB*—2-butoxyethanol; Butyl Cellosolve;⁴ ethylene glycol monobutyl ether
- 3.1.7 *EG*—ethylene glycol
- 3.1.8 *EGDE*—ethylene glycol diethyl ether
- 3.1.9 *EP*—2-propoxyethanol
- 3.1.10 *FID*—flame ionization detector
- 3.1.11 *GC*—gas chromatograph
- 3.1.12 *MS*—mass spectrometer
- 3.1.13 *PG*—propylene glycol
- 3.1.14 *PnB*—propylene glycol monobutyl ether
- 3.1.15 *PnP*—propylene glycol monopropyl ether
- 3.1.16 *RRF*—relative response factor
- 3.1.17 *MRRF*—microreactor relative response factor
- 3.1.18 *SPME*—solid phase microextraction

- 3.1.19 *SPDE*—solid phase dynamic extraction
- 3.1.20 *THF*—tetrahydrofuran
- 3.1.21 *TMPD-IB*—2,2,4-trimethylpentane-1,3-diol, monoisobutyrate
- 3.1.22 *TMPD-DIB*—2,2,4-trimethylpentane-1,3-diol, diisobutyrate
- 3.1.23 *VOC*—volatile organic compound used in various air quality regulations

4. Summary of Test Method

4.1 A known weight of coating is dispersed in methanol or tetrahydrofuran (THF), internally standardized, and analyzed by capillary gas chromatography to give a speciated composition of the volatile organic compounds (Note 3). Summation of the individual volatile organic compound weight percents gives the total volatile organic content of the coating measured in weight percent.

NOTE 3—Methanol can be used as a first choice as a solvent for all waterborne coatings. THF can be used for solventborne coatings. Acetone may also be used for solventborne coatings but should not be used for waterborne coatings because it may react with ammonia and amines which are frequently found in waterborne coatings. Other solvents can be used if needed but the choice of solvent should be reported.

4.2 Direct GC/FID, GC/MS and solid phase microextraction (SPME) / gas chromatography of the coating may be used to facilitate identification of the volatile compounds present in a coating (Note 4). Table X1.1 lists the GC retention times for some of the volatile compounds which may be found in low volatile organic compound content air-dry coatings and for several possible internal standards, ordinarily not present in coatings, which may be used (Note 4).

NOTE 4—The analyst should consult SDS and product data sheets for information regarding solvents which are expected in a particular coating. Additional solvents, not shown on the SDS or PDS may also be present in the coating. Retention times given in Appendix X1 must be verified for each individual instrument.

NOTE 5—The accuracy of the volatile organic compound weight percent determined using Test Method D6886 is dependent on the proper identification of the compounds detected in the chromatogram. The response of the FID used in the GC is dependent on the compound detected. The accuracy of the determination requires proper identification (by GC/MS, by retention time, or by analyzing the sample on a GC column with a different stationary phase) and calibration of the GC for the compounds detected.

4.3 The methods for analysis are:

4.3.1 *Method A*—Analysis is performed using GC/FID by preparing and analyzing standards to determine response factors and using these response factors for determination of the weight concentrations of analytes.

4.3.2 *Method B*—Analysis is performed using GC/microreactor/FID (which converts all carbon-containing molecules into methane prior to detection in an FID) by first validating the system and subsequently quantifying using tabulated response factors.

4.3.3 *Method C*—Analysis is performed using GC/MS. This method is most often used in conjunction with either Method A or Method B, for identification of analytes. Precision statistics have not been determined for using GC/MS for quantification.

³ Butyl Carbitol is a registered trademark of The Dow Chemical Company.

⁴ Butyl Cellosolve is a registered trademark of The Dow Chemical Company.

5. Significance and Use

5.1 In using Practice D3960 to measure the volatile organic compound content of waterborne coatings, precision can be poor for low volatile organic compound content air-dry coatings if the volatile organic weight percent is determined indirectly. The present method directly identifies and then quantifies the weight percent of individual volatile organic compounds in air-dry coatings (Note 6). The total volatile organic weight percent can be obtained by adding the individual weight percent values (Note 7).

NOTE 6—The present method may be used to speciate solvent-borne air-dry coatings. However, since these normally contain high, and often complex, quantities of solvent, precision tends to be better using other methods contained in Practice D3960, where the volatile fraction is determined by a direct weight loss determination.

NOTE 7—Detectable compounds may result from thermal decomposition in a hot injection port or from reaction with the extraction solvent. If it can be shown that a material is a decomposition product, or is the result

of a reaction with the extraction solvent, then results for that compound should be discounted from the volatile measured by Test Method D6886.

6. Apparatus

6.1 *Gas Chromatograph, with Electronic Data Acquisition System FID Detection, FID/Microreactor Detection, or Mass Spectrometry Detection*—Any capillary gas chromatograph equipped with a flame ionization detector microreactor flame ionization detector, or mass spectrometer and temperature programming capability may be used. Electronic flow control, which gives a constant carrier gas flow, is highly recommended. Note that a full precision study has only been completed for GC with FID detection (Tables X1.2-X1.4). A preliminary precision study has been completed for GC/Microreactor/FID (Table X1.5).

6.2 *Standard GC/FID, GC/Microreactor/FID, and GC/MS Instrument Conditions:*

Instrument Conditions	GC/FID	GC/Microreactor ^A /FID	GC/MS
	Method A	Method B	Method C
Detector	Flame ionization	Microreactor/flame ionization	70 eV electron impact mass spectrometer ^B
Microreactor Air Supply Flow Rate		2.5 mL per min	
Microreactor Hydrogen Supply Flow Rate		35 mL per min	
Microreactor Temperature, °C,		450°	
Source Temperature, °C,			230°
Quadrupole Temperature °C,			150°
Transfer Line Temperature °C,			260°
Scanning Parameters			Mass 29 to 400 amu
FID Air Flow Rate	350 mL per min	350 per min	
FID H ₂ Air Rate	35 mL per min	1.5 per mL	
Columns		Primary column: 30 m by 0.25 mm 5 % phenyl/95 % methyl siloxane (PMPS) ^C , C 1.0 µm film thickness Confirmatory columns: 30 m by 0.25 mm polydimethylsiloxane (PDMS), 0.25 µm film thickness; 30 m by 0.25 mm Carbowax (CW), 0.25 µm film thickness	
Carrier Gas		Helium	
Flow Rate		1.0 mL per min, constant flow (24.9 cm/s at 40°)	
Split Ratio ^D		50 to 1	
Temperatures, °C,			
Primary Column			
Inlet			260°
Detector			270°
Initial			50° for 4 min
Rate			20° per min to 250°, hold 6 min (total run time = 20 min)
Temperatures, °C,			
Confirmatory Columns			
Inlet			260°
Detector			270°
Initial			40° for 4 min
Rate			10° per min to 250°, hold 25 min (total run time = 50 min)

^A The microreactor (for example, Polyarc, a registered trademark of Activated Research Company) is a two-step oxidation-reduction reactor that converts organic compounds to methane prior to detection in an FID.

^B Any mass spectrometer may be used. The conditions specified are for a quadrupole mass spectrometer and are listed as a reference only.

^C The column designated as PMPS is commercially available from several vendors by the following designations: DB-5, SPB-5, HP-5, AT-5, CP Sil 8 CB, RTx-5, BP-5. The column designated as PDMS is available by the designations DB-1, SPB-1, HP-1, AT-1, CP Sil 5 CB, Rtx-1. The column designated as Carbowax is available by the designations Supelcowax 10, DB-Wax, HP-Wax, AT-Wax, CP-Wax 52 CB, Rtx-Wax, BP-20. Inert versions (or other equivalent designations) of the columns listed above are recommended because they may provide better peak shapes.

^D Jennings Cup inlet liners with no glass wool are the recommended inlet liner type because they provide good reproducibility and complete volatilization of analytes across a large range in boiling points. An injection volume of 0.5 µL is recommended with the Jennings Cup liner. Any inlet liner that provides complete volatilization of analytes may be used.

NOTE 8—Some coatings may contain high-boiling components which elute from the GC capillary column after the specified run time of 20 min. It is advisable, therefore, to bake out the column between runs in these cases.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the available specifications of the Committee on

Analytical Reagents of the American Chemical Society. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Carrier Gas*, helium of 99.995 % or higher purity.

7.3 *THF*, HPLC grade.

7.4 *Methanol*, HPLC grade.

7.5 Possible internal standards: *1-Propanol*, *p*-fluorotoluene, *cyclohexanol*, *p*-chlorotoluene, *ethylene glycol diethylether* (EGDE).

7.6 *Fluorocarbon-faced Septum Vials*, 20 mL or 40 mL capacity.

7.7 *Ceramic Beads*, 0.5–1.0 mm diameter.

8. Column Conditioning

8.1 The capillary columns should be conditioned according to the manufacturer's recommendation. The columns may then be used indefinitely without further conditioning.

9. Preparation of Standards

9.1 Prepare a stock mixture of ethylene glycol (EG), propylene glycol (PG), triethylamine, *p*-xylene ethylene glycol monobutyl ether (EB), ethylene glycol diethyl ether (EGDE) [or other suitable internal standard], diethylene glycol monobutyl ether (DB), and 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (TMPD-IB) by weighing one or two grams of each into an appropriate 20 or 40 mL vial. The weight of each component should be approximately the same and determined to 0.1 mg. Mix the contents.

9.2 Transfer approximately 100 μL of the stock mixture to a septum-capped vial containing 10 mL of THF or methanol and mix the contents (Note 9). This solution will contain each of the known analytes at a concentration of approximately 2 mg/mL.

NOTE 9—The solvents EG, PG, EB, DB, and TMPD-IB are widely used in the manufacture of waterborne air-dry coatings and may be expected as probable components of these coatings.

9.3 Chromatograph the solution in 9.2 by injecting 0.5 to 1 μL into the PMPS column using the chromatographic conditions given in 6.2. Calculate the relative response factors for each of the analytes relative to the EGDE or other suitable internal standard using the relationship:

$$RF = \frac{AA \cdot MI}{AI \cdot MA} \quad (1)$$

where:

RRF = relative response factor,
AA = area of analyte,
MI = weight of internal standard (from 9.1),
AI = area of internal standard, and
MA = weight of analyte (from 9.1).

9.4 Method A:

9.4.1 The experimentally-determined RRFs will be used in Section 10 for calculation of weight fractions.

9.5 Method B:

9.5.1 Evaluate the performance of the GC/microreactor/FID system by determining the RRFs (in accordance with 9.3 and Eq 1) for ethylene glycol (EG), propylene glycol (PG), triethylamine, *p*-xylene, ethylene glycol monobutyl ether (EB), diethylene glycol monobutyl ether (DB), and 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (TMPD-IB) using ethylene glycol diethyl ether (EGDE) as the internal standard. Ensure that each of the individual RRFs are within 15 % of the

microreactor relative response factor (MRRF) values in Table X1.1 before proceeding.

9.5.2 Use the tabulated MRRF values in Table X1.1 for calculation of weight fractions in Section 10. Do not use experimentally-determined RRF values in Section 10. If a component is present in the sample, but not in Table X1.1, calculate the MRRF using the relationship:

$$MRRF = \frac{MWI \cdot CA}{MWA \cdot CI} \quad (2)$$

where:

MRRF = microreactor relative response factor,
MWI = molecular weight of internal standard,
CA = number of carbon atoms per analyte molecule,
MWA = molecular weight of analyte, and
CI = number of carbon atoms per internal standard molecule.

10. Paint Analysis

10.1 Analysis of Air-dry Solvent-borne and Waterborne Coatings by GC/FID:

10.1.1 Prepare duplicate samples by pipetting 10 mL of methanol (waterborne coatings) or THF (solventborne coatings) into each 20 or 40 mL vial containing 3 to 5 g of ceramic beads and close with a fluorocarbon-faced septum cap. Using a dedicated glass syringe (10 to 50 μL capacity), add 10 μL of EGDE or other internal standard and weigh to at least 0.1 mg. This solution must be analyzed by GC to determine if there are peaks that result from it rather than from the paint sample that is prepared in 10.1.2.

10.1.2 Pipette 10 mL of methanol or THF into a 20 or 40 mL vial containing 3 to 5 g ceramic beads and close with a fluorocarbon-faced septum cap. Using a disposable 1 mL syringe, add approximately 0.6 to 0.8 g of the well-mixed paint through the septum cap and weigh to 0.1 mg (Note 10). Using the dedicated syringe, add 10 μL of pure EGDE (or other internal standard) through the septum and weigh the amount added to at least 0.1 mg. Mix the contents vigorously by shaking for 1 min. Let the vial stand to permit pigments, if any, to settle.

NOTE 10—The paint should be drawn into the syringe without an attached syringe needle. Excess paint is wiped from the syringe and the needle is then attached for paint transfer. The mass of the paint may be determined by either the difference in the weight of the filled and empty syringe or by the difference in the weight of the vial before and after adding paint.

10.1.3 Chromatograph the solution in 10.1.2 by injecting 0.5 to 1 μL into the PMPS capillary column using the standard conditions described in 6.2. If necessary, adjust the split ratio to give well-defined chromatographic peaks. Integrate the volatile compounds which elute over a 20 min run time. Ensure all peaks present at a level of 0.005 weight percent or higher (when quantified in 10.1.4 or 10.1.5) are integrated. Methyl palmitate must elute at 18.4 ± 0.5 min. Any retention time marker eluting within the run time can be specified by a regulatory agency to define which peaks must be counted toward the total VOC emission (Note 11).

NOTE 11—When determining compliance with SCAQMD VOC rules, integration of peaks should end at the retention time of methyl palmitate

as per SCAQMD Test Method 313. Any compound that elutes prior to methyl palmitate should be counted as a VOC, unless otherwise excluded by SCAQMD.

10.1.4 Method A:

10.1.4.1 Calculate the weight percent of each peak using the relationship:

$$\%X = \frac{(AA)(MI)(100)}{(AI)(RRF)(MC)} \quad (3)$$

where:

- X = one of several possible volatile compounds in the coating,
- RRF = relative response factor of compound X,
- AA = peak area of compound X,
- MI = weight of internal standard,
- AI = peak area of internal standard, and
- MC = weight of coating.

10.1.4.2 For molecules that have not been identified, use the RRF for 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (TMPD-IB) for calculation of weight percent in 10.1.4.1.

10.1.5 Method B:

10.1.5.1 Calculate the weight percent of each peak using the relationship:

$$\%X = \frac{(AA)(MI)(100)}{(AI)(MRRF)(MC)} \quad (4)$$

where:

- X = one of several possible volatile compounds in the coating,
- MRRF = microreactor relative response factor of compound X (Table X1.1 or Eq 2),
- AA = peak area of compound X,
- MI = weight of internal standard,
- AI = peak area of internal standard, and
- MC = weight of coating.

10.1.5.2 For molecules that have not been identified, use the MRRF for 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (TMPD-IB) for calculation of weight percent in 10.1.5.1.

NOTE 12—If volatile compounds other than those in the standard (9.1) are present in the coating, the identity should be confirmed by FID retention time comparison with standard material or by GC/MS and the relative response factor should be determined as outlined in 9.1 – 9.3. Commercial 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (TMPD-IB) may contain small amounts of 2,2,4-trimethylpentane-1,3-diol which elutes approximately 0.5 min before butyl carbitol and 2,2,4-trimethylpentane-1,3-diol diisobutyrate (TMPD-IB) which elutes approximately 1.5 min after 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (TMPD-IB). Acetone and isopropyl alcohol have nearly the same retention time on a PMPS column and if either is found, their identities should be confirmed and quantitated on a Carbowax⁵ column or by using GC/MS. Isobutyl alcohol coelutes with the solvent (THF) and must be determined on a different column (Carbowax) or using a different solvent (methanol). SPME, SPDE and static headspace analysis are especially useful techniques for confirming that decomposition products are not being observed. Small quantities (up to 0.5 %) of acetic acid are sometimes found in coatings containing vinyl acetate resins. The acetic acid is formed as a decomposition product in the GC inlet and should not be counted as a volatile organic compound. Some coatings contain additives (for example, carbamate ester biocides) that may give decomposition products in the hot inlet of the gas chromatograph. If decomposition products are suspected,

a convenient procedure for determining this is to analyze the coating by static headspace gas chromatography. In using static headspace, a large sample of the coating (15 to 20 g) is internally standardized with 10 mg/g of EGDE, approximately 5 mL of ceramic beads are added, and manually mixed by shaking until the paint/internal standard mixture is homogeneous. The static headspace procedure is carried out on 40 to 60 mg of the internally standardized coating using a 20 mL crimp-cap headspace vial. Static headspace conditions are: Oven, 20 to 30 min at 130°C; Loop, 150°C; Transfer Line, 150°C. Chromatographic Conditions: as described in 6.2. Alternatively, if static headspace, SPME, or SPDE capability are not available, the analysis can be done using a lower inlet temperature as long as the selected temperature is high enough to fully volatilize the suspect compounds. Cool on-column injection can also be used to determine if a compound is being generated via thermal decomposition in the hot GC inlet.

10.2 Overlapping Chromatographic Peaks:

10.2.1 A number of organic compounds in solvent-borne paints containing commercial xylene can overlap. These include propylene glycol monomethyl ether acetate overlapping with ethylbenzene and butoxyethanol with o-xylene. Resolution can generally be obtained by simply changing the chromatographic heating rate.

10.3 Coatings Containing Silanes, Siloxanes and Silane-Siloxane Blends:

10.3.1 If the coating contains silanes, siloxanes, and silane-siloxane blends, approximately 50 mg of solid p-toluenesulfonic acid should be added to the solution in 10.1.2 thirty minutes prior to gas chromatography. The p-toluenesulfonic acid catalyzes the hydrolysis of alkoxy silanes to free alcohol (usually ethanol).

11. Reporting Results

11.1 Prepare a table (as indicated below) which contains information on each of the volatile organic compounds found. Only report volatile organic compounds present at a level of 0.005 weight percent or higher. Report the identity of the solvent used. Report the split ratio used if it deviates from 50:1. Report whether Method A or Method B was used for quantification. Report any deviations to the method.

Volatile Organic Compound	GC Retention Time	Weight % Found

Total weight percent of all speciated volatile organic compounds = .

11.2 List volatile organic compounds that are not identified as unknown (UK) and use the response factor for 2,2,4-trimethylpentane-1,3-diol monoisobutyrate to calculate the weight % for these unknowns. For compounds with concentrations greater than 0.1 weight percent (as determined using the response factor for 2,2,4-trimethylpentane-1,3-diol monoisobutyrate), the response factor for the actual molecule should be used.

12. Alternate Identification Methods

12.1 The use of GC/MS for volatile compound identification is highly desirable even when quantitation is carried out by GC/FID. A convenient procedure is to sample the headspace of the coating using an SPME or SPDE followed by thermal desorption onto any standard capillary column and subsequent

⁵ Carbowax is a registered trademark of The Dow Chemical Company.

mass spectral identification. This technique is especially valuable for identifying oxygenates, aromatics and other volatile organic compounds.

12.2 A split GC/MS system can be used with the GC/FID system or the GC/microreactor/FID system, and it allows for qualitative and quantitative information to be obtained with a single injection. A convenient setup for this includes the use of a post-column splitter controlled by an electronic pressure controller (EPC). Recommended conditions for this include a 0.6 m, 0.1 mm ID glass capillary restrictor connected to the MS, with a 0.8 m, 0.25 mm ID restrictor connected to the FID or a 0.5 m, 0.25 mm ID restrictor connected to the microreactor/FID. Using these conditions with a splitter pressure of 4 psig maintains a nearly-constant split ratio with changing oven temperature.

13. Precision and Bias⁶

13.1 *Interlaboratory Studies*—Three interlaboratory studies have been carried out (Note 13).

13.1.1 An interlaboratory study of the total weight percent volatile organic compounds was conducted in accordance with Practice E691 in seven laboratories with five materials, with each laboratory obtaining three test results for each material. Five commercial waterborne coatings, (a primer, a flat, a satin, a semi-gloss and a gloss), ranging in weight percent volatile content from 0.25 to 4.50, were analyzed. Each of the laboratories analyzed the coatings three times according to protocols specified in Practice E691.

13.1.2 In this study the participating laboratories knew the identities of the volatile organic compounds contained in each of the coatings and followed Test Method D6886-12.

13.1.3 Precision statistics were calculated for the total weight percent volatile organic compounds found in each of the five coatings and are presented in Table X1.2. The terms repeatability limit and reproducibility limit are used as specified in Practice E177.

13.1.4 *95 % Repeatability Limit (within laboratory)*—The within-laboratory coefficient of variation is 2.7 % relative. The 95 % confidence limit for the difference between two averages is 7.5 % of the test result.

13.1.5 *95 % Reproducibility Limit (between laboratories)*—The between-laboratory coefficient of variation is 5.8 % relative. The 95 % confidence limit for the difference between two averages is 16.2 % of the test result.

13.2 A second interlaboratory study of total weight percent volatile organic compounds was conducted in accordance with Practice E691. Eleven laboratories participated in the study, testing twelve coatings (five containing <2 wt% volatile and seven containing <0.21 wt% volatile). Each of the laboratories analyzed the coatings twice according to protocols specified in Practice E691.

13.2.1 In this study the samples were analyzed “blind,” that is, the participating laboratories had no knowledge of the

volatile organic compounds contained in each of the coatings and followed Test Method D6886-12.

13.2.2 The precision statement was determined through statistical examination of 264 results, from a total of eleven laboratories, on twelve coatings. The coatings were designated in the study as:

(1) Paints containing <0.21 wt% Volatile — cans 1-16, 17-32, 49-64, 97-112, 129-144, 145-160, 161-176.

(2) Paints containing <2 wt% Volatile — cans 33-48, 65-80, 81-96, 113-128, 177-192.

13.2.3 Precision statistics were calculated for the total weight percent volatile found in each of the five coatings and are presented in Table X1.3 and Table X1.4. The terms repeatability limit and reproducibility limit are used as specified in Practice E177.

13.2.4 *95 % Repeatability Limit (within laboratory)*—The 95 % confidence limit for the difference between two averages is 28.3 % for test results on paints containing <0.21 wt% volatile and 20.0 % for test results on paints containing <2 wt% volatile.

13.2.5 *95 % Reproducibility Limit (between laboratories)*—The 95 % confidence limit for the difference between two averages is 258 % for test results on paints containing <0.21 wt% volatile and 93.9 % for test results on paints containing <2 wt% volatile.

13.3 A third interlaboratory study of total weight percent volatile organic compounds was conducted using Method B in 2018. Two laboratories participated in this study. Each of the two laboratories reported ten replicate test results for five commercial waterborne coatings (a primer, a flat, a semi-gloss, a polyurethane, and a stain). Every “test result” reported represents an individual determination. Except for the use of only two laboratories, the design and analysis of the data in this study were based on Practice E691; the details are given in ASTM Research Report No. RR:D01-1184.⁷

13.3.1 This study is a preliminary study and did not include a comparison to Method A. A full round robin study will be performed to obtain comparative repeatability, reproducibility, and bias for Method A and Method B.

13.3.2 In this study the samples were analyzed “blind,” that is, the participating laboratories had no knowledge of the volatile organic compounds contained in each of the coatings and followed Test Method D6886-12.

13.3.3 The precision statement was determined through statistical examination of 100 results, from two laboratories, on five materials. These five coatings were described as Sample A, Sample B, Sample C, Sample D, and Sample E.

Sample Code	Sample Description
A	Zero VOC interior semi-gloss latex
B	Exterior latex primer
C	~50 g/L interior/exterior flat latex
D	Polyurethane waterborne wood coating
E	Waterborne exterior stain

13.3.4 Precision statistics were calculated for the total weight percent volatiles found in each of the five coatings and

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1178. Contact ASTM Customer Service at service@astm.org.

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1184. Contact ASTM Customer Service at service@astm.org.