Designation: D6886 − 12

Standard Test Method for
Determination of the Individual Volatile Organic Compounds (VOCs) in Air-Dry Coatings by Gas Chromatography[1]

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 air-dry coatings.

1.2 The method can be used to determine the weight fraction VOC content of waterborne coatings in which the material VOC content is below 5 weight percent. The method has been used successfully with higher VOC content waterborne coatings and with solvent-borne coatings (Note 1).

1.3 The method may also be used to measure the exempt volatile organic compound content (acetone, methyl acetate, t-butyl acetate and p-chlorobezotrifluoride) of waterborne and solvent-borne coatings. The methodology is virtually identical to that used in Test Method D6133 which, as written, is specific for only exempt volatile compounds.

1.4 Volatile compounds that are present at the 0.005 weight percent level or greater can be determined.

NOTE 1—This test method may be used for the VOC analysis of coatings containing silanes, siloxanes, and silane-siloxane blends. The test 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 dilution with a solvent would impede the chemical reaction required for these types of coatings. This test method measures the VOC weight fraction of air-dry coatings directly as opposed to the methods of Practice D3960 which measure the VOC weight fraction of air-dry waterborne coatings indirectly. A direct measurement of VOC weight fraction, particularly in low VOC 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).[2] This study may be used to decide if the present method or the methods of Practice D3960 are preferred as an analysis method for obtaining the best possible precision for measuring the mass-based VOC content of a specific coating.

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

1.6 *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:*[3]

D2369 Test Method for Volatile Content of Coatings
D3792 Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph
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 Solvent-borne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Injection Into a Gas Chromatograph
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

3. Terminology

3.1 *Abbreviations:*

3.1.1 *EGDE*—ethylene glycol diethyl ether

3.1.2 *DB*—2-(2-butoxyethoxy)ethanol; Butyl Carbitol;[4] diethylene glycol monobutyl ether

3.1.3 *EB*—2-butoxyethanol; Butyl Cellosolve;[5] ethylene glycol monobutyl ether

3.1.4 *EG*—ethylene glycol

3.1.5 *FID*—flame ionization detector

3.1.6 *F-VOC*—formulation data calculated volatile organic compound in g/(L-water)

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[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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[2] Detailed results of this study may be found at http://www.arb.ca.gov/coatings/arch/Final_Report_6_11_09.pdf.

[3] 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.

[4] Butyl Carbitol is a registered trademark of The Dow Chemical Company.

[5] Butyl Cellosolve is a registered trademark of The Dow Chemical Company.

3.1.7 *GC*—gas chromatograph

3.1.8 *PG*—propylene glycol

3.1.9 *% RSD*—percent relative standard deviation

3.1.10 *SPME*—solid phase microextraction

3.1.11 *SPDE*—solid phase dynamic extraction

3.1.12 *Std Dev*—standard deviation

3.1.13 *TX*—2,2,4-trimethypentane-1,3-diol, monoisobutyrate

3.1.14 *VOC*—volatile organic compound

3.1.15 *X-VOC*—experimental volatile organic compound in g/(L-water)

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 and exempt organic compounds, if any, present in the coating. Summation of the individual volatile organic compound weight fractions gives the total VOC content of the coating measured in weight percent (Note 2).

NOTE 2—Methanol should be used as a solvent for all waterborne coatings. THF should 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. Using the provisions of Practice D3960, the VOC content of coatings measured in g/L minus water, or other units, may be determined. Since the determination of weight percent VOC in the present method is by direct measurement, either the water fraction (Test Method D3792 or Test Method D4017) or the nonvolatile fraction (Test Method D2369) may be determined indirectly in the application of Practice D3960. Since precision is better for the determination of the nonvolatile content, this is the preferred method for the indirect calculation of water content in this test method. The equations for calculating coating VOC content when no exempt volatile compounds are present are:

$$VOC = \frac{f_{VOC}(D_P)}{1 - [(1 - f_{NV} - f_{VOC})(D_P/D_W)]} \quad (1)$$

or

$$VOC = \frac{f_{VOC}(D_P)}{1 - [f_W(D_P/D_W)]} \quad (2)$$

where:

D_P, f_{NV}, f_{VOC}, and f_W = coating density, nonvolatile fraction, VOC fraction, and water fraction, respectively.

4.2 Direct GC/FID, GC/MS and solid phase microextraction / gas chromatography (SPME/GC) of the coating may be used to facilitate identification of the volatile compounds present in a coating. Table X1.1 lists the GC retention times for the volatile compounds which may be found in low VOC content air-dry coatings and several possible internal standards, ordinarily not present in coatings, which may be used (Note 3).

NOTE 3—The analyst should consult MSDS and product data sheets for possible information regarding solvents which may be present in a particular coating. Retention times given in X1.1 must be verified for each individual instrument.

5. Significance and Use

5.1 In using Practice D3960 to measure the VOC content of waterborne coatings, precision tends to be poor for low VOC content air-dry coatings when the VOC weight fraction is determined indirectly. The present method first identifies and then quantifies the weight fraction of individual VOCs directly in air-dry coatings. The total VOC weight fraction can be obtained by adding the individual weight fraction values (Note 4).

NOTE 4—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 the methods contained in Practice D3960, where the VOC fraction is determined by a direct weight loss determination.

5.2 SPME/GC makes it possible to identify very low levels of volatile compounds in a coating and could serve to make it possible to identify the presence of hazardous air pollutants (HAPs).

6. Apparatus

6.1 *Gas Chromatograph, FID Detection or Mass Spectrometry Detection with Electronic Data Acquisition System*—Any capillary gas chromatograph equipped with a 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.

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

6.2.1 See Table 1.

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 *Tetrahydrofuran (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 and 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), ethylene glycol monobutyl ether (EB), ethylene glycol diethyl ether (EGDE) [or other suitable internal standard], diethylene glycol monobutyl ether (DB), and 2,2,4-trimethylepntane-1,3-diol monoisobutyrate (TX) by weighing one or two grams of each into an appropriate vial. The weight

TABLE 1 Standard FID Instrument Conditions

Instrument Conditions	FID	GC/MS
Detector	Flame ionization	70 eV electron impact mass spectrometer
Columns	Primary column: 30 by 0.25 mm 5 % phenyl/95 % methyl siloxane (PMPS),[A] 1.0 µm film thickness Confirmatory Columns: 30 by 0.25 mm polydimethylsiloxane (PDMS), 0.25 µm film thickness; 30 by 0.25 mm Carbowax (CW), 0.25 µm film thickness.	Primary column: 30 by 0.25 mm % phenyl/95 % methyl siloxane (PMPS),[A] 1.0 µm film thickness Confirmatory Columns: 30 by 0.25 mm polydimethylsiloxane (PDMS), 0.25 µm film thickness; 30 by 0.25 mm Carbowax (CW), 0.25 µm film thickness.
Carrier Gas	Helium	Helium
Flow Rate	1.0 mL per min, constant flow (24.9 cm/s at 40°)	1.0 mL per min, constant flow (24.9 cm/s at 40°)
Split Ratio	50 to 1	50 to 1
Temperatures, °C, Primary Column		
Inlet	260°	260°
Detector	270°	270°
Initial	50° for 4 min	50° for 4 min
Rate	20° per min to 250°, hold 6 min (total run time = 20 min)	20° per min to 250°, hold 6 min (total run time = 20 min)
Temperatures, °C, Confirmatory Columns		
Inlet	260°	260°
Detector	270°	270°
Initial	40° for 4 min	40° for 4 min
Rate	10° per min to 250°, hold 25min	10° per min to 250°, hold 25min
Source		230°
Quadrupole		230°
Transfer Line		260°
Scanning Parameters		Mass 29–400 amu

[A] Some coatings may contain high-boiling components which elute from the GC capillary column after the specified run time of 20 minutes. It is advisable, therefore, to bake out the column in these cases. 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 8CB, RTx-5, BP-5. The column designated as PDMS is available by th 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.

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 5). This solution will contain each of the known analytes at a concentration of approximately 2 mg/mL.

NOTE 5—The solvents EG, PG, EB, DB TX are widely used in the manufacture of waterborne air-dry coatings and may be expected as highly probable components of these coatings.

9.3 Chromatograph the solution in 9.2 by injecting 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:

$$RF = \frac{AA^{*}MI}{AI^{*}MA} \tag{3}$$

where:

RF = 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).

10. Paint Analysis

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

10.1.1 Prepare duplicate samples by pipetting 10 mL of methanol (waterborne coatings) or THF (solventborne coatings) into a vial containing 3 to 5 g of ceramic beads and close with a fluorcarbon-faced septum cap. Using a dedicated glass syringe (25 or 50 microliter 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 6). Using the dedicated syringe, add 10 microliters of pure EGDE (or other internal standard) through the septum and weigh the