



Designation: D6886 – 14^{ε1}

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.

^{ε1} NOTE—Research report was added editorially in August 2014.

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 This method can be used to determine the weight percent organic content of waterborne coatings in which the volatile organic compound weight percent is below 5 percent. The method has been used successfully with higher 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 of EPA Method 24.

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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Some compounds and some semi-volatile compounds may be considered volatile using the GC conditions specified but will not fully volatilize 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 and health practices and determine the applicability of regulatory limitations prior to use.*

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

D3792 Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph

D3925 Practice for Sampling Liquid Paints and Related

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.

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

3. Terminology

3.1 Acronyms:

3.1.1 *EGDE*—ethylene glycol diethyl ether

3.1.2 *DB*—2-(2-butoxyethoxy)ethanol; Butyl Carbitol;³ diethylene glycol monobutyl ether

3.1.3 *EB*—2-butoxyethanol; Butyl Cellosolve;⁴ ethylene glycol monobutyl ether

3.1.4 *EG*—ethylene glycol

3.1.5 *FID*—flame ionization detector

3.1.6 *GC*—gas chromatograph

3.1.7 *PG*—propylene glycol

3.1.8 *SPME*—solid phase microextraction

3.1.9 *SPDE*—solid phase dynamic extraction

3.1.10 *TMPD-IB*—2,2,4-trimethylpentane-1,3-diol, monoisobutyrate

3.1.11 *TMPD-DIB*—2,2,4-trimethylpentane-1,3-diol, diisobutyrate

3.1.12 *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.

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

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

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 / gas chromatography (SPME/GC) 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 MSDS and product data sheets for information regarding solvents which are expected in a particular coating. Additional solvents, not shown on the MSDS 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 flame ionization detector (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.

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, 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. Note that precision and accuracy have only been evaluated using GC with FID detection.

6.2 Standard GC/FID and GC/MS 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 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.

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 *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-trimethylpentane-1,3-diol monoisobutyrate (TMPD-IB) by weighing one or two grams of each into an appropriate 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, 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 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:

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

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:

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 fluorocarbon-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 10). Using the dedicated syringe, add 10 microliters 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 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. Identify the volatile compounds which elute over a 20 minute run time. An optional, late-eluting compound, such as methyl palmitate (retention time of 18.4 min) may be used to verify column performance and retention times. Note that methyl palmitate is not a marker to determine volatile organic compound/non-volatile organic compound status of eluted compounds. Calculate the weight fraction of each peak using the relationship:

$$\%X = \frac{(AA)(MI)(100)}{(AI)(RF)(MC)} \quad (2)$$

where:

X = one of several possible volatile compounds in the coating,
RF = 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.

NOTE 11—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 minutes before butyl carbitol and 2,2,4-trimethylpentane-1,3-diol diisobutyrate (TMPD-IB) which elutes approximately 1.5 minutes 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 minutes 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).

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