



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

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

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 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 , 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