



Designation: D 6886 – 03

# Standard Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 6886; 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 ( $\epsilon$ ) 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 low VOC content waterborne latex air-dry coatings. The method is intended primarily for analysis 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.

1.2 This method may also be used to measure the exempt volatile organic compound content (acetone, methyl acetate, and *p*-chlorobenzotrifluoride) of waterborne coatings. The methodology is virtually identical to that used in Test Method D 6133 and similar to that used in Test Method D 6438.

1.3 Volatile compounds that are present at the 0.05 weight percent level or greater can be determined. Solid phase microextraction will detect volatile compounds at lower levels.

1.4 *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:

- D 1475 Test Method for Density of Liquid Coatings, Inks, and Related Products<sup>2</sup>
- D 2369 Test Method for Volatile Content of Coatings<sup>2</sup>
- D 3792 Test Method for Water Content of Coatings by Direct Injection Into a Gas Chromatograph<sup>2</sup>
- D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings<sup>2</sup>
- D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings<sup>2</sup>
- D 4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method<sup>2</sup>
- D 6133 Test Method for Acetone *p*-Chlorobenzotrifluoride

<sup>1</sup> 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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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 06.01.

Methyl Acetate or *t*-Butyl Acetate Content of Solventborne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Injection into a Gas Chromatograph<sup>2</sup>

D 6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography<sup>2</sup>

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods<sup>3</sup>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>3</sup>

## 3. Terminology

### 3.1 Abbreviations:

- 3.1.1 *CW/DVB*—Carbowax<sup>™</sup>/divinylbenzene
- 3.1.2 *DB*—2-(2-butoxyethoxy)ethanol; Butyl Carbitol<sup>™</sup>; diethylene glycol monobutyl ether
- 3.1.3 *EB*—2-butoxyethanol; Butyl Cellosolve<sup>™</sup>; 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)
- 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 *Std Dev*—standard deviation
- 3.1.12 *TX*—2,2,4-trimethylpentane-1,3-diol, monoisobutyrate; Texanol<sup>™</sup>
- 3.1.13 *VOC*—volatile organic compound
- 3.1.14 *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 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

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

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 1).

NOTE 1—Using the provisions of Practice D 3960, 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 D 3792 or Test Method D 4017) or the nonvolatile fraction (Test Method D 2369) may be determined indirectly in the application of Practice D 3960. The equations for calculating regulatory 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 waterborne air-dry coatings. Table X1.1 also lists possible internal standards for use in the analysis and minor volatile components which are sometimes found in waterborne coatings (Note 2).

NOTE 2—The analyst should consult MSDS and product data sheets for possible information regarding solvents which may be present in a particular coating. SPME/GC may be used to ascertain that decomposition volatiles are not measured.

## 5. Significance and Use

5.1 In using Practice D 3960 to measure the regulatory VOC content of coatings, precision tends to be poor for low VOC content waterborne coatings because the VOC weight fraction is determined indirectly. The present method first identifies and then quantifies the weight fraction of individual VOCs directly in low VOC content waterborne air-dry coatings. The total VOC weight fraction can be obtained by adding the individual weight fraction values (Note 3).

NOTE 3—An effort is currently underway in California to consider changing mass-based VOC regulations for architectural coatings to reactivity-based VOC regulations. In California, reactivity based regulations have already been implemented for aerosol coatings, that is, MIR-indexed regulations (California Air Resources Board). Reactivity based regulations would require knowing the weight fractions of each individual volatile compound present in a coating.

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 *SPME Sampling Apparatus and Fibers*,<sup>4</sup> manual SPME holders fitted with a 70  $\mu\text{m}$  Carbowax<sup>™</sup>/Divinylbenzene (CW/DVB) StableFlex fiber assembly.

6.2 *Gas Chromatograph, FID Detection with Electronic Data Acquisition System*—Any capillary gas chromatograph equipped with a flame ionization detector and temperature programming capability may be used. Electronic flow control, which gives a constant carrier gas flow, is highly recommended.

### 6.3 Standard FID Instrument Conditions:

Detector	Flame ionization
Columns	Primary column: 30 m by 0.25 mm 5 % phenyl/95 % methyl siloxane (PMPS) (Note 4) , 1.0 $\mu\text{m}$ film thickness. Confirmatory Columns: 30 m by 0.25 mm polydimethylsiloxane (PDMS), 0.25 $\mu\text{m}$ film thickness; 30 m by 0.25 mm Carbowax <sup>™</sup> (CW), 0.25 $\mu\text{m}$ film thickness.
Carrier Gas	Helium
Flow Rate	1.0 mL per min, constant flow (24.9 cm/s at 40°)
Split Ratio	Variable
Temperatures, °C	
Inlet	260°
Detector	270°
Initial	40° for 4 min
Rate	10° per min to 250°, hold 5 min

NOTE 4—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.

## 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 *1-Propanol, p-fluorotoluene, cyclohexanol, p-chlorotoluene and p-cymene*, 99 + mole %.

7.5 The volatile organic compounds listed in Table X1.1.

7.6 *Fluorocarbon-faced septum vials*, 20 mL and 40 mL capacity.

## 8. Column and Fiber 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.

8.2 The SPME fiber should be conditioned and used according to the manufacturer's recommendation.

8.3 The SPME fiber should be inserted into a 260°C injection port for 30 s prior to each sampling event.

## 9. Preparation of Standards

9.1 Prepare a stock mixture of ethylene glycol (EG), propylene glycol (PG), ethylene glycol monobutyl ether (EB), p-cymene (CY) [or other suitable internal standard], diethylene

<sup>4</sup> Available from the Supelco Company, Supelco Park, Bellefonte, PA 16823-0048.

glycol monobutyl ether (DB), and Texanol (TX) 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  $\mu\text{L}$  of the stock mixture to a septum-capped vial containing 10 mL of THF 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 and Texanol are widely used in the manufacture of low VOC content waterborne air-dry coatings and may be expected as highly probable components of these coatings. The tetrahydrofuran solvent must be analyzed by GC to determine if possible impurities interfere/coelute with the analytes being tested.

9.3 Chromatograph the solution in 9.2 by injecting 1  $\mu\text{L}$  into the PMPS column using the chromatographic conditions given in 6.3. Calculate the relative response factors for each of the analytes relative to the p-cymene internal standard using the relationship:

$$RF = \frac{AA * MI}{AI * MA} \quad (3)$$

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 Using a 100 mL volumetric flask, make up a concentrated standard solution containing p-cymene (or other suitable internal standard) in THF at a concentration of approximately 1 g per 100 mL and known to the nearest 0.1 mg.

10.2 Using standard quantitative dilution techniques, dilute the concentrated standard solution to give a working standard solution such that the internal standard concentration is near 1 mg per mL. Calculate the actual concentration.

10.3 Pipette 10 mL of working standard solution into a 20 or 40 mL vial 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). Mix the contents vigorously by shaking for 1 min followed by sonication for 5 min. Let the vial stand to permit pigments, if any, to settle.

NOTE 6—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. When adding the paint to the THF in the vial, care should be taken that the paint falls directly into the THF solution containing the internal standard.

10.4 Chromatograph the solution in 10.3 by injecting 1  $\mu\text{L}$  into the PMPS capillary column using the standard conditions described in 6.3. Adjust the split ratio to give well-defined chromatographic peaks. Identify the volatile compounds present (Note 7) and calculate the weight fraction of each in the coating using the relationship:

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

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 in 10 mL THF,

*AI* = peak area of internal standard, and

*MC* = weight of coating.

NOTE 7—If volatile compounds other than those in the standard (9.1) are present in the coating, the identity should be confirmed by retention time comparison with authentic material and the relative response factor should be determined as outlined in 9.1-9.3. Commercial Texanol may contain small amounts of 2,2,4-trimethylpentane-1,3-diol which elutes approximately 0.5 min before butyl carbitol. Acetone and isopropyl alcohol have nearly the same retention time on a 5 % phenyl/95 % PDMS column and if either is found, their identities should be confirmed on a different column. Isobutyl alcohol coelutes with the solvent (THF) and must be determined on a different column. SPME (11.2) is especially useful for confirming the presence of isobutyl alcohol since no THF is used in this procedure.

## 11. Solid Phase Microextraction Procedure

11.1 Since a dispersion of coating in THF is injected into a relatively hot GC injection port, peaks representing decomposition products may be observed and should not be considered as VOCs. Solid phase microextraction allows sampling of most VOCs at low temperature and may be used to determine if GC peaks observed in the direct GC analysis (Section 10) are actual VOCs or decomposition products. If desired, the SPME procedure may be used prior to direct analysis to determine which VOCs are present in the coating. If GC/MS is available, the SPME procedure is especially useful for identification of VOCs and exempt compounds present in a coating sample.

11.2 Place approximately 5 to 10 g of liquid waterborne coating into a 40 mL fluorocarbon-faced septum vial. If using a smaller vial, reduce the coating amount. Close the vial with a fluorocarbon-faced septum cap and heat to 55 to 60°C in an oven or other suitable heat source (oil bath, water bath, heated metal block). Do not let the contents contact the inside face of the septum cap. Insert the SPME fiber through the septum cap and sample the headspace for 3 to 4 min using a conditioned CW/DVB SPME fiber. Desorb the fiber for 10 s onto the capillary column and obtain the gas chromatogram using the standard chromatographic conditions described in 6.3. Identify the volatile components present in the liquid paint using retention time values given in Table X1.1. The peaks found by this SPME procedure should correspond to the peaks found by the direct procedure. If peaks found in the direct procedure are not found by the SPME procedure, decomposition may be taking place in the direct method (Note 8).

NOTE 8—Ethylene glycol and propylene glycol, which are often present in waterborne air-dry coatings, are not sufficiently volatile to give a strong SPME response. If propylene glycol or ethylene glycol are present in the coating being analyzed, peaks for these analytes will be substantially larger when carrying out the direct analysis and should be reported as VOCs. In carrying out the SPME procedure, a number of small peaks are usually observed which may not appear in the direct analysis. These peaks normally correspond to low levels of monomers, or monomer impurities