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Standard Test Method for ~~Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography~~ Determination of the Individual Volatile Organic Compounds (VOCs) in 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 ~~low VOC content waterborne latex air-dry coatings. The method is intended primarily for analysis~~ 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~~ 1.3 The method may also be used to measure the exempt volatile organic compound content (acetone, methyl acetate, t-butyl acetate and p-chlorobenzotrifluoride) of waterborne and solvent-borne coatings. The methodology is virtually identical to that used in Test Method D6133 ~~and similar to that used in Test Method D6438.~~

~~1.3~~ 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~~ 1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

~~1.5~~ 1.5 *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:*

D1475 Test Method For Density of Liquid Coatings, Inks, and Related Products³

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.

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

³ Available from the Supelco Company, Supelco Park, Bellefonte, PA 16823-0048.

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.

- 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
- ~~D6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography~~
- 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 ~~*CW/DVB*—Carbowax[®]/divinylbenzene~~ *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)
- 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-trimethylpentane-1,3-diol, monoisobutyrate; Texanol[®]~~
- 3.1.13 *TX*—2,2,4-trimethylpentane-1,3-diol, monoisobutyrate
- 3.1.14 *VOC*—volatile organic compound
- ~~3.1.14~~
- 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); (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 1—Using the provisions of Practice D3960 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. The equations for calculating regulatory VOC content when no exempt volatile compounds are present are:—) 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:

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

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

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

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or

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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 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 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. 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 regulatory VOC content of waterborne coatings, precision tends to be poor for low VOC content waterborne air-dry coatings because when 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 34).

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. 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 *SPME Sampling Apparatus and Fibers*, manual SPME holders fitted with a 70 μ m Carbowax[™]/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* 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:

Detector

Flame ionization

Columns

Primary column: 30 m by 0.25 mm 5% phenyl/95% methyl siloxane (PMPS) (Note 4) , 1.0 μ m film thickness.

Confirmatory Columns: 30 m by 0.25 mm polydimethylsiloxane (PDMS), 0.25 μ m film thickness; 30 m by 0.25 mm Carbowax[™] (CW), 0.25 μ 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.

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

7.5 The volatile organic compounds listed in Table X1.1: *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* Fluorocarbon-faced Septum Vials, 20 mL and 40 mL capacity.

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

8. Column and Fiber Conditioning—Column Conditioning

8.1 The capillary columns should be conditioned according to the manufacturer's recommendation. The columns may then be

TABLE 1 Standard FID Instrument Conditions

Instrument Conditions	FID	GC/MS
<u>Detector</u>	Flame ionization	70 eV electron impact mass spectrometer
<u>Columns</u>	Primary column: 30 by 0.25 mm 5 % phenyl/95 % methyl siloxane (PMPS), ⁴ 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), ⁴ 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.
<u>Carrier Gas</u>	Helium	Helium
<u>Flow Rate</u>	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°)
<u>Split Ratio</u>	50 to 1	50 to 1
<u>Temperatures, °C, Primary Column</u>		
<u>Inlet</u>	260°	260°
<u>Detector</u>	270°	270°
<u>Initial</u>	50° for 4 min	50° for 4 min
<u>Rate</u>	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)
<u>Temperatures, °C, Confirmatory Columns</u>		
<u>Inlet</u>	260°	260°
<u>Detector</u>	270°	270°
<u>Initial</u>	40° for 4 min	40° for 4 min
<u>Rate</u>	10° per min to 250°, hold 25min	10° per min to 250°, hold 25min
<u>Source</u>		230°
<u>Quadrupole</u>		230°
<u>Transfer Line</u>		260°
<u>Scanning Parameters</u>		Mass 29–400 amu

⁴ 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 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.

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)~~ ethylene glycol diethyl ether (EGDE) [or other suitable internal standard], diethylene glycol monobutyl ether (DB), and ~~Texanol~~ 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (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 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 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.~~ 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 ~~6.36.2~~. Calculate the relative response factors for each of the analytes relative to the ~~p-cymene~~ EGDE or other suitable internal standard using the relationship:

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iteh Standards (<https://standards.iteh.ai>) Document Preview

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<https://standards.iteh.ai/catalog/standards/sist/bbb3fd5-7c00-4381-ae27-d743304ed038/astm-d6886-12>

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 (

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 fluorocarbon-faced septum cap. Using a dedicated glass syringe (25 or 50 microliter capacity), add 10 μ L 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). 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. 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 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.

10.4.1.3 Chromatograph the solution in 10.3.10.1.2 by injecting 1 μ 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: 6.2. Adjust the split ratio to give well-defined chromatographic peaks. Identify the volatile compounds which elute over a 20 minute run time. An internal marker, methyl palmitate (BP = 338°C) should elute at approximately 18.4 minutes. Calculate the weight fraction of each peak using the relationship:

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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, weight of internal standard,
 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 FID retention time comparison with authentic material or by GC/MS 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. Commercial 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (TX) 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 (TXIB) which elutes approximately 1.5 minutes after 2,2,4-trimethylpentane-1,3-diol monoisobutyrate (TX). 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 Carbowax⁶ 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

⁶ Carbowax is a registered trademark of The Dow Chemical Company.