Designation: D7768 – 12 (Reapproved 2018)

Standard Test Method for Speciated Organic Volatile Content of Waterborne Multi-Component Coatings by Gas Chromatography[1]

This standard is issued under the fixed designation D7768; 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 individual organic volatile compounds of waterborne multi-component coatings using gas chromatography (see Note 1).

1.2 The method has also been used successfully to determine the speciated volatile organic content of solvent-borne multi-component coatings. Work is continuing to develop this aspect of the method and will be added to the method at a later date.

NOTE 1—Currently there are no methods for the direct analysis of the VOC content of waterborne multi-component coatings. The VOC content of solvent-borne multi-component coatings is determined directly by a simple weight loss determination of the mixed components (Test Method D2369).

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

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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

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 Solvent-borne 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

3. Terminology

3.1 *Acronyms:*

3.1.1 *EB*—2-butoxyethanol; Butyl Cellosolve,[3] ethylene glycol monobutyl ether

3.1.2 *EGDE*—ethylene glycol diethyl ether

3.1.3 *FID*—flame ionization detector

3.1.4 *GC*—gas chromatogagphy

3.1.5 *MS*—mass spectrometry

3.1.6 *SPDE*—solid phase dynamic extraction

3.1.7 *SPME*—solid phase microextraction

4. Summary of Test Method

4.1 The components are mixed, a sample of the mixture is weighed into a 20 mL headspace vial, the vial is sealed with a crimp cap, and the mixture is allowed to cure for 24 h or longer at ambient temperature. After the initial cure, the sample is heated for 30 min at 110°C. After cooling, a known quantity of acetone containing an internal standard is added to the sealed

[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.

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

vial and the contents are mixed. The solution containing the organic volatile compounds is then analyzed by gas chromatograhpy (Note 2).

NOTE 2—If the cured coating contains free amines, acetone may be replaced with tetrahydrofuran (THF) as the extraction solvent. 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 method. 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 or GC/MS using solid phase microextraction (SPME) may be used to facilitate identification of the volatile compounds present in a coating (Note 3).

NOTE 3—The analyst should consult SDS and product data sheets for possible information regarding solvents which may be present in a particular coating.

5. Significance and Use

5.1 In using the methods of Practice D3960 to measure the VOC content of coatings, precision tends to be poor for waterborne coatings because the VOC weight fraction is determined indirectly. The present method first identifies and then quantifies the individual VOCs directly. The total VOC weight fraction is obtained by adding the individual weight fraction values.

6. Apparatus

6.1 *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.

6.2 *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 µm film thickness Confirmatory Column: 60 m by 0.25 mm Carbowax[4] (CW), 0.50 µm film thickness
Carrier Gas	Helium
Flow Rate	1.0 mL per min, constant flow
Split Ratio	50 to 1
Temperatures, °C	
Inlet	260°C
Detector	270°C
Initial	50°C for 4 min
Rate	20°C per min to 250°C, hold 6 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. The column designated as PDMS is available by the designations DB-1, SPB-1, HP-1, AT-1, BP-1, CP Sil 5 CB, Rtx-1. The column designated as Carbowax is available by the designations Suplecowax 10, DB-Wax, HP-Wax, AT-Wax, CP-Wax 52 CB. Rtx-Wax, BP-20.

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.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its used without lessening the accuracy of the determination.

7.2 *Carrier Gas,* helium of 99.995 % or higher purity.

7.3 *Acetone,* HPLC grade.

7.4 *Ethylene Glycol Diethyl Ether (EGDE),* 99 mole %.

7.5 *Fluorocarbon-faced Septum Vials,* 20 mL and 40 mL, *Headspace Vials* (20 mL), *Crimp Caps, and Cripmer,* Agilent Technologies part numbers: headspace vials, 5182–0837, crimp caps, 5183–4477, and crimper, 9301–0720, or equivalent.

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. Coating Analysis

9.1 Using a 100 mL volumetric flask, make up a concentrated internal standard solution containing ethylene glycol diethyl ether (EGDE) or other suitable internal standard in acetone at a concentration of approximately 1 g per 100 mL and known to the nearest 0.1 mg.

9.2 Using standard quantitative dilution techniques, dilute the concentrated internal standard solution to give a working internal standard solution such that the concentration is near 1 mg per mL. Calculate the actual concentration. Convert the concentration of the working internal standard solution from mg/mL to mg/g by dividing by the density of acetone (0.79 g/mL).

9.3 Determine the density of the individual components of the multi-component coating using Test Method D1475. Convert the manufacturer's recommended volume mix ratio to a weight mix ratio. Using a suitable container, prepare approximately 100 to 200 g of the mixture and mix using a spatula or paint shaker. Immediately after mixing, transfer approximately 100 mg of the mixture to a 20 mL headspace vial and weigh to

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

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States *Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.