Designation: D7768 – 12

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 and health practices and determine the applicability of regulatory limitations prior to use. Some specific hazards statements are given in Section 7 on Hazards.*

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 chromatogaphy

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 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

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[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.

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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:

$$VOC = \frac{f_{VOC}\,(D_P)}{1 - [(1 - f_{NV} - f_{VOC})\,(D_P / D_W)]} \tag{1}$$

or

$$VOC = \frac{f_{VOC}\,(D_P)}{1 - [f_W\,(D_P / D_W)]} \tag{2}$$

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 MSDS 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 0.1 mg. Add a paper clip to the vial and then seal the vial with a crimp cap immediately after adding the coating mixture and paper clip. Using an external magnet, spread the coating mixture evenly over the bottom surface of the vial. Prepare two more samples in the same way.

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[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.

9.4 Determine the volatile content of the multi-component mixture prepared in 9.3 using Test Method D2369 immediately after preparing the mixture. Allow the coating in the capped vials from 9.3 to cure for a minimum of 24 h at ambient temperature and then heat the vials for 30 min at 110°C for 30 min. Using a dedicated glass syringe, add 3 to 4 mL of the working internal standard solution from 9.2 to each of the cooled headspace vials by injecting the solution into the capped vial. Determine the weight of solution added to 0.1 mg. Mix the contents by briefly shaking the contents followed by sonication for 15 to 30 min.

9.5 Chromatograph the solution in 9.4 by injecting 1 µL into the PMPS capillary column using the standard conditions described in 6.2. Adjust the split ratio to give well-defined chromatographic peaks. Identify the volatile compounds present (Note 5) and calculate the weight percent of each in the coating using the relationship:

$$\%X = \frac{(A\ A)\ (M\ I)\ (100)}{(A\ I)(R\ F)(M\ C)} \qquad (3)$$

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 5—Analytes may be identified using information available from product data sheets, MSDS, GC/MS, or FID retention time comparison with known compounds (see Table 1).

10. Preparation of Standards

10.1 After identification of the VOCs present in the coating (from 9.5), prepare a mixture of the identified pure components and the internal standard (EGDE) by weighing approximately 1 g (to 0.1 mg) of each into an appropriate vial and mix the contents.

10.2 Dilute a portion of the mixture from 10.1 with acetone to give a solution with a concentration of each analyte of approximately 1 to 2 mg/mL.

10.3 Chromatograph the solution in 10.2 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 internal standard using the relationship:

$$RF = \frac{AA^*\ MI}{AI^*\ MA} \qquad (4)$$

where:

RF = relative response factor,

AA = area of analyte,

MI = weight of internal standard,

AI = area of internal standard, and

MA = weight of analyte.

11. Chromatographic Resolution

11.1 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 using a Carbowax capillary column.

11.2 Using a PMPS column and the chromatographic conditions of 6.2, certain compounds co-elute. These include, and are not limited to: PM acetate/ethylbenzene and 2-butoxyethanol(EB)/o-xylene. Separation may be obtained by changing the chromatographic heating rate.

12. Reporting Results

12.1 Prepare a table (as indicated below) that contains information on each of the VOC species found.

VOC Found	GC Retention Time	Weight % Found

Total weight percent of all speciated VOCs =

12.2 List VOCs that are not identified as unknown (UK) and use the relative response factor of EGDE to calculate the weight % for unknown VOCs.

13. Alternate Identification Methods

13.1 The use of GC/MS for volatile compound identification is highly desirable. A convenient procedure is to sample the headspace of the cured coating in one of the headspace vials using an SPME fiber. Solid phase dynamic extraction (SPDE) and dynamic headspace analysis have also been used successfully to identify volatile components. Table 1 lists the relative retention times of a wide variety of compounds which have been found in various coatings. The retention times must be reconfirmed whenever a new or different capillary column is placed into service.

14. Precision and Bias

14.1 A within laboratory study of total weight percent VOC was conducted in accordance with Practice E691 with three waterborne multi-component materials. Three test results were obtained for each material. The three coatings analyzed had a range in weight percent VOC content of 4.16 to 9.40.

14.2 Precision statistics were calculated for the total weight percent VOC found in each of the three coatings and are presented in Table 2. The term repeatability limit is used as specified in Practice E177.

14.3 *95 % Repeatability Limit (within laboratory)*—The within-laboratory coefficient of variation is 4.3 % relative. The 95 % confidence limit for the difference between two such averages is 12.0 % of the test result.

14.4 *Bias*—Bias has not been determined.

15. Keywords

15.1 gas chromatography; multicomponent VOC analysis; waterborne multicomponent coating analysis

TABLE 1 Retention Times (in Minutes) and FID Relative Response Factors (RRF) of Possible Volaile Organic Compounds and Exempt Compounds in Waterborne Multi-Component Coatings Using the Chromatographic FID Conditions Described in 6.2

		Retention Time, min		
Compound	RRF	PMPS	Carbowax	PDMS
methanol	0.66	2.35	5.16	1.97
ethanol	1.00	2.75	5.85	2.08
acetone	1.02	3.12	3.93	2.21
2-propanol	1.02	3.13	5.71	2.19
t-butyl alcohol		3.42		
methyl acetate	0.60	3.59	4.1	2.31
1-propanol		3.82	7.91	2.44
vinyl acetate		4.40		
methyl ethyl ketone	1.25	4.74	5.24	2.7
2-butanol	1.18	4.78	7.63	2.72
ethyl acetate	0.83	5.05		
tetrahydrofuran (THF)		5.31	4.65	3.05
isobutyl alcohol	1.62	5.31	8.94	2.97
1-butanol	1.59	5.97	9.92	3.39
propylene glycol monomethyl ether	0.79	6.18	9.66	3.62
ethylene glycol	0.55	6.42	16.94	3.91
ethyl acrylate		6.48		
t-butyl acetate	1.22	6.65	5.31	4.18
methyl methacrylate		6.74		
2-ethoxyethanol	0.70	6.83		
methyl pivalate		7.00		
propylene glycol	0.73	7.18	16.48	4.8
AMP-95	0.84	7.46		
toluene	2.07	7.82	8.02	5.44
p-fluorotoluene		8.03		
ethylene glycol diethyl ether (EGDE)	1.00	8.12		
2-propoxyethanol (EP)	1.00	8.27	12.58	6.41
butyl acetate	1.16	8.33		
propylene glycol monopropyl ether (PnP)	1.01	8.72	11.65	7.32
diacetone alcohol		8.73		
furfuryl alcohol	0.93	8.88		
ethylbenzene	2.04	8.92	10.87	7.75
parachlorobenzotrifluoride	1.02	8.93		
propylene glycol mono t-butyl ether	1.16	8.96	12.58	7.67
propylene glycol, methyl ether acetate	0.86	8.99		
p-xylene	2.17	9.19	9.72	7.6
m-xylene	2.17	9.19	9.87	7.81
butyl ether		9.20	9.99	7.81
2-heptanone	1.46	9.32		
cyclohexanol		9.32		
butyl acrylate		9.32		
butyl propionate		9.45		
o-Xylene	2.17	9.47		
2-butoxyethanol (EB)	1.11	9.51	10.78	8.28
hexylene glycol		9.62	14.05	8.6
diethylene glycol monomethyl ether	0.70	9.81	16.89	
propylene glycol monobutyl ether (PnB)	1.09	9.87	16.52	
diethylene glycol diethyl ether	0.68	9.88		
PnB (minor component)		10.05	13.15	9.41
glycerin	0.65	10.12		
diethylene glycol	0.57	10.14		
p-chlorotoluene		10.17	13.97	9.66
butyl methacrylate				
dipropylene glycol monomethyl ether (DPM)	0.80	10.46, 10.51, 10.71		
diethylene glycol monoethyl ether	0.69	10.49		
p-cymene	2.13	10.84	15.62	10.67
benzyl alcohol	1.65	10.89		
N-methylpyrrolidinone	0.72	10.96	12.18	10.94
ethylene glycol butyl ether acetate		11.25	17.73	
diethylene glycol monopropyl ether (DP)		11.34	14.8	11.85

TABLE 1 *Continued*

Compound	RRF		Retention Time, min	
		PMPS	Carbowax	PDMS
dipropylene glycol monopropyl ether (DPnP)	0.76	11.79, 11.82		
2,2,4-trimethylepentane-1,3-diol		11.85	16.68	
diethylene glycol monobutyl ether (DB)	0.93	12.12		
napthalene	2.03	12.43		
2-(2-ethylhexyl)ethanol		12.51		
triethylene glycol	0.58	12.53		
dipropylene glycol monobutyl ether (DPnB)	1.04	12.53, 12.58	18.86	13.41
propylene glycol monophenyl ether	1.14	12.67		
2,2,4-trimethylpentane-1,3-diol monoisobutyrate (TX)	1.27	13.62, 13.74		
tetraethylene glycol	0.59	14.54		
2,2,4-trimethylpentane-1,3-diol, diisobutyrate (TXIB)	1.17	15.15		
2-ethylhexyl benzoate	1.39	16.05		
methyl palmitate		18.40		
dibutyl phthalate	1.16	18.50		
Mineral Spirits	2.23	9 to 11		
Aromatic100	2.10	9.2 to 10.6		

TABLE 2 Within Precision Statistics Waterborne Multi-Component Coatings

Material	VOC, wt %, avg	Std Dev	Std Dev, %	Repeatability Limit, r	VOC % Reported by Supplier
1	9.40	0.19	2.07	5.81	10.03
2	7.91	0.37	4.74	13.28	7.85
3	4.16	0.25	6.04	16.92	4.54

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