Designation: D3960 – 05 (Reapproved 2013)

Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings[1]

This standard is issued under the fixed designation D3960; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This practice measures the volatile organic compound (VOC) content of solventborne and waterborne paints and related coatings as determined from the quantity of material released from a sample under specified bake conditions and subtracting exempt volatile compounds and water if present.

NOTE 1—The regulatory definition, under the control of the U.S. EPA, can change. To ensure currency, contact the local air pollution control agency.

1.2 This practice provides a guide to the selection of appropriate ASTM test methods for the determination of VOC content.

1.3 Certain organic compounds that may be released under the specified bake conditions are not counted toward coating VOC content because they do not participate appreciably in atmospheric photochemical reactions. Such negligibly photochemically reactive compounds are referred to, as exempt volatile compounds in this practice.

NOTE 2—Information on the US EPA definition of VOC and a list of the current US EPA approved exempt volatile compounds which have been used in coatings, are provided in Appendix X3.

1.4 VOC content is calculated as a function of (*1*) the volume of coating less water and exempt volatile compounds, and (*2*) the volume of coating solids, and (*3*) the weight of coating solids.

1.5 The values stated in SI units are to be regarded as 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:*[2]

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

D2369 Test Method for Volatile Content of Coatings

D2697 Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings

D2832 Guide for Determining Volatile and Nonvolatile Content of Paint and Related 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

D4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method

D4457 Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph

D5095 Test Method for Determination of the Nonvolatile Content in Silanes, Siloxanes and Silane-Siloxane Blends Used in Masonry Water Repellent Treatments

D5201 Practice for Calculating Formulation Physical Constants of Paints and Coatings

D5403 Test Methods for Volatile Content of Radiation Curable Materials

D6093 Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer

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

D6419 Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks

[1] This practice 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.

Current edition approved Nov. 1, 2013. Published November 2013. Originally approved in 1981. Last previous edition approved in 2005 as D3960 – 05. DOI: 10.1520/D3960-05R13.

[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.

D6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction-Gas Chromatography

D6886 Test Method for Determination of the Weight Percent Individual Volatile Organic Compounds in Waterborne Air-Dry Coatings by Gas Chromatography

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

2.2 *Other Documents:*

EPA Federal Reference Method 24 Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings[4]

EPA 450/3-84-019 U.S. Environmental Protection Agency Procedures for Certifying Quantity of Organic Compound Emitted by Paint, Ink, and Other Coatings[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *exempt volatile compound, n*—organic compounds that do not participate significantly in atmospheric photochemical reactions.

3.1.2 *nonvolatile material, n*—the solid material remaining after volatiles have been removed from a coating under specified test conditions.

3.1.3 *volatile organic compound (VOC), n*—any organic compound that participates in atmospheric photochemical reactions.

3.1.3.1 *Discussion*—Information on the US EPA definition of VOC and a list of the current US EPA and approved exempt volatile compounds which have been used in coatings, are provided in Appendix X3.

3.1.4 *volatile organic compound content (VOC content), n*—the mass of VOC released from a coating under specified test conditions.

3.1.4.1 *Discussion*—VOC content is expressed in this practice as a function of: (*1*) the coating volume less water and exempt volatile compounds, and (*2*) the volume of coating solids and (*3*) the weight of coating solids.

4. Summary of Practice

4.1 Take a representative sample of the liquid coating in accordance with Practice D3925. Mix thoroughly before taking specimens for individual tests. If air bubbles become entrapped, stir by hand until the air has been removed.

4.2 The volatile content, density, water content, volume solids and exempt solvent content of the coating are determined in accordance with designated methods and instructions. For multicomponent coatings, the components are first mixed in the appropriate ratios and the applicable values determined on the mixture. These values are combined using specified equations to calculate the VOC content of the coating.

NOTE 3—In Reference Method 24 the U.S. EPA defines a waterborne coating as any coating with more than 5 % water by weight in its volatile fraction, and requires/allows water determination for waterborne coatings only.

5. Significance and Use

5.1 This practice discusses applicable ASTM test methods used in the determination of the VOC content of paints and related coatings and provides equations for calculating the VOC content expressed as the mass of VOC: (*1*) per unit volume of coating less water and exempt volatile compounds, and (*2*) per unit volume of coating solids and (*3*) per unit mass of coating solids.

5.2 Volatile organic compound content is used to compare the amount of VOC released from different coatings used for the same application, that is, to coat the same area to the same dry film thickness (assuming the same application efficiency).

5.3 VOC content data are required by various regulatory agencies.

5.4 Only the expression of VOC content as a function of the volume of coating solids gives a linear measure of the difference in VOC released from different coatings used for the same application.

NOTE 4—Thus assuming the same transfer efficiency, a coating with VOC content of 3 lb of VOC/gal of solids would release ½ the VOC that would a coating with 6 lb of VOC/gal of solids.

5.5 When VOC content is expressed as a function of the volume of coating less water and exempt solvents, the values obtained do not account for differences in the volume solids content of the coatings being compared: this expression, therefore, does not provide a linear measure of the difference in VOC emitted from different coatings used for the same application.

NOTE 5—Thus, a coating with VOC content of 3 lb of VOC/gal less water and exempt volatile compounds would release about 85 % less VOC than a coating with 6 lb of VOC/gal less water and exempt volatile compounds.

6. Nonvolatile and Volatile Content

6.1 Guide D2832 includes suggested time/temperature drying schedules for the determination of the nonvolatile and volatile content of various types of coatings.

NOTE 6—For regulatory compliance testing, follow the method and conditions specified in the applicable regulation. Federal Reference Method 24 specifies the use of Test Method D2369.

6.2 Test Method D2369 includes a specific drying schedule and sample weight, and heating 1 h at 110 ± 5°C for the determination of the weight percent volatile content of solvent-borne and waterborne coatings.

6.2.1 For multicomponent coatings, Test Method D2369 specifies the components should be mixed first, then the volatile content should be determined on the mixture. Test specimens are held in the aluminum dish for at least 1 h before baking.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

NOTE 7—Other induction periods are used. See U.S. EPA Reference Method 24.

6.2.2 The nonvolatile content of silanes, siloxanes, and silane/siloxane blends used in masonry water repellent treatments is defined using Test Method D5095. In this standard, applicable to both solvent and water reducible materials, the test specimen, containing an added catalyst, is allowed to stand at room temperature for 1 h prior to heating in an oven at 110° ± 5°C for 60 min.

NOTE 8—In VOC determinations, for 6.2.2 only, the density and water content (if applicable) are measured on the test material without the added catalyst.

6.2.3 The nonvolatile content of radiation curable coatings, inks, and adhesives is defined using Test Methods D5403. These materials contain volatile reactive components that become nonvolatile after radiation curing. Test Method A is applicable to radiation curable materials that are essentially 100 % reactive but may contain traces (no more than 3 %) of volatile materials as impurities or introduced by the inclusion of various additives. Test Method B is applicable to all radiation curable materials but must be used for materials that contain volatile solvents intentionally introduced to control application viscosity and that are intended to be removed from the material to cure.

6.2.4 The volatile content of sheet-fed and coldset web offset printing inks is defined using Test Method D6419. This standard is based on Test Method D2369, but has tighter controls for specimen weight and oven temperature. Interlaboratory studies have shown this necessary to improve the precision of test results for these inks. It also allows the use of ink knives or taper knives for transferring the specimen to the aluminum dish from the sample container.

6.2.5 Test Method D6886 is a direct gas chromatographic method for the determination of individual and total volatile organic compounds in low VOC content waterborne latex air-dry coatings. This method is intended primarily for analysis of waterborne coatings in which the material VOC content is below 5 weight percent. It is the only method for the speciation of VOCs in low VOC content waterborne latex air-dry coatings. This method provides a direct determination of weight percent VOC content, in contrast to the indirect determination (total volatiles minus water) of weight percent VOC of waterborne coatings presented in Practice D3960.

7. Water Content

7.1 To determine the water content of coatings two test methods are available:

7.1.1 In Test Method D3792, a paint specimen is diluted with dimethyl formamide, an internal standard (2-propanol) is added, and an aliquot of the mixture is injected directly into a gas chromatograph.

7.1.2 Test Method D4017 offers three options for determining water content by Karl Fischer titration.

7.1.2.1 A specimen is dissolved in pyridine or another suitable solvent and titrated in the presence of a buffer, 1-ethyl piperidine. The use of newer non-pyridine titration reagents is also allowed.

7.1.2.2 The water in a latex paint is first extracted into anhydrous methanol, then an aliquot of the methanol extract is titrated with non-pyridine reagent in methanol solvent (see Appendix X1 of Test Method D4017).

7.1.2.3 The specimen is dispersed in methanol solvent using a homogenizer accessory, then directly titrated with non-pyridine reagent (see Appendix X2 of Test Method D4017).

7.1.3 With multicomponent coatings, the components are first mixed in the appropriate ratios, then water content is determined using Test Methods D3792 or D4017.

8. Density

8.1 The density of the paint or coating at 25°C is determined in accordance with Test Method D1475. Although both the pycnometer and weight-per-gallon cup are covered by the test method, and the former is more accurate and precise, the weight-per-gallon cup is recommended because of its speed and ease of use.

8.2 With multicomponent coatings, first mix the components in appropriate ratios in sufficient quantity to determine the weight-per-gallon using Test Method D1475.

9. Exempt Volatile Compounds

9.1 In Test Method D4457 an internal standard (1-propanol) is added to the test specimen, and then the specimen is injected directly into a gas chromatograph.

9.2 In Test Method D6133 an internal standard is added to the whole paint, and the mixture injected directly into the gas chromatograph.

9.3 In Test Method D6438 an internal standard is added to whole paint, followed by solid phase microextraction (SPME) headspace sampling and subsequent injection into a gas chromatograph.

9.4 With multicomponent coatings, the exempt volatile compound content is determined on the mixture of the components.

10. Calculation of VOC Content

10.1 In this practice VOC content is expressed in three ways: (*1*) as the mass of VOC per unit volume of the coating less water and exempt volatile compounds, (*2*) as the mass of VOC per unit volume of coating solids, and (*3*) the mass of VOC per unit mass of coatings solids. The following equations should be used to calculate VOC content and may be used for coatings both “as supplied” and “as applied” (see Note 8).

NOTE 9—For compliance with VOC regulations, the VOC content should be calculated after any thinning or dilution (“as applied”). Instructions for VOC calculations of such diluted coatings are available in EPA 450/3-84-019.

10.2 *VOC Content Expressed as the Mass of VOC per Unit Volume of Coating Less Water and Exempt Volatile Compounds:*

10.2.1 *General Expression:*

$$VOC = \frac{[(\text{weight percent of total volatiles less water less exempt volatile compounds})(\text{density of coating})]}{[100\ \% - (\text{volume percent of water}) - (\text{volume percent of exempt volatile compounds})]} \quad (1)$$

or

$$VOC = \frac{(W_o)(D_c)}{100\,\% - V_w - V_{ex}} \quad (2)$$

$$= \frac{(W_v - W_w - W_{ex})(D_c)}{100\,\% - (W_w)(D_c/D_w) - (W_{ex})(D_c/D_{ex})}$$

where:

VOC = VOC content in g/L of coating less water and exempt volatile compound (see Note 9),
W_o = weight of organic volatiles, % ($W_v - W_w - W_{ex}$),
W_v = weight of total volatiles, % (100 % – weight % nonvolatiles, see Test Method D2369),
W_w = weight of water, % (see Test Methods D3792 or D4017),
W_{ex} = weight of exempt volatile compound, % (see 3.1.3.1, Note 11, and Test Methods D4457, D6133, and D6438),
V_w = volume of water, % (W_w)(D_c/D_w),
V_{ex} = volume of exempt volatile compound, % (see 3.1.3.1, Note 11), = (W_{ex})(D_c/D_{ex}),
D_c = density of coating, g/L, at 25°C, (see Test Method D1475),
D_w = density of water, g/L, at 25°C, (0.997×10^3), and
D_{ex} = density of exempt volatile compound g/L, at 25°C, (see Test Method D1475).

NOTE 10—To convert from g/L to lb/gal, multiply the result (VOC content) by 8.345×10^{-3} (lb/gal/g/L). To convert g/L to kg/L, divide the result by 10^3.

NOTE 11—See X2.1 and X2.2 for comments on coatings containing one or more exempt volatile compounds.

10.2.2 *Solventborne Coatings*—Calculate the VOC content in grams of VOC per litre of coating less water and exempt volatile compounds using the appropriate equation:

10.2.2.1 For solventborne coatings that do not contain water or exempt volatile compounds:

$$VOC = \frac{(W_v)(D_c)}{100\,\%} \quad (3)$$

10.2.2.2 For solventborne coatings that contain an exempt volatile compound but do not contain water (see section 3.1.3.1 and Note 2):

$$VOC = \frac{(W_v - W_{ex})(D_c)}{100\,\% - (W_{ex})(D_c/D_{ex})} \quad (4)$$

10.2.2.3 For solventborne coatings that contain water but do not contain exempt volatile compounds (see 3.1.3.1 and Note 2):

$$VOC = \frac{(W_v - W_w)(D_c)}{100\,\% - (W_w)(D_c/D_w)} \quad (5)$$

10.2.2.4 For solventborne coatings that contain both an exempt volatile compound and water, use Eq 1 and Eq 2 in 10.2.1 (see 3.1.3.1 and Note 2).

10.2.3 *Waterborne Coatings*—Calculate the VOC content in grams of VOC per litre of coating less water and exempt volatile compound using the appropriate equation.

10.2.3.1 For waterborne coatings that contain no exempt volatile compounds, use Eq 5 in 10.2.2.3 (see 3.1.3.1 and Note 2).

10.2.3.2 For waterborne coatings that contain exempt volatile compounds, use Eq 1 and Eq 2 in 10.2.1 (see 3.1.3.1 and Note 2).

10.3 *VOC Content Expressed in Terms of the Mass of VOC per Unit Volume of Coating Solids (Nonvolatiles):*

10.3.1 Calculate the VOC content in grams of VOC per litre of coating solids according to the following equation:

$$VOC_m = \frac{(W_o)(D_c)}{V_n} \quad (6)$$

where:

VOC_m = VOC content in g/L of coating solids,
W_o = $W_v - W_w - W_{ex}$ (terms defined as in 10.2.1), and
V_n = volume of nonvolatile content of the liquid coating, % (see Test Methods D6093 and D2697, and Note 12 and Note 13).

NOTE 12—The EPA Reference Method 24 does not include an analytical method for determining V_n, but states that the value be calculated from the coating manufacturer's formulation.

NOTE 13—An expression for calculating formula V_n from the coating formulation is included in X2.3, Eq X2.1.

10.4 *VOC Content Expressed in Terms of the Mass of VOC per Unit Mass of Coating Solids (Nonvolatiles):*

10.4.1 Calculate the VOC content in grams of VOC per gram of coating solids according to the following equations:

$$VOC_b = \frac{W_o}{W_S} \quad (7)$$

where:

VOC_b = VOC content in g/g of coating solids,
W_o = $W_v - W_w - W_{ex}$ (terms defined as in 10.2.1, and
W_S = weight of solids, %.

NOTE 14—The calculated VOC is expressed as weight of VOC/weight of solids. This may be "lb VOC per lb solids" or "Kg of VOC per Kg of solids."

11. Keywords

11.1 test precision; VOC; VOC calculations; VOC content; VOC content of paint

APPENDIXES

(Nonmandatory Information)

X1. AUTOMOTIVE COATINGS SUPPLIERS ROUND ROBIN

X1.1 A round robin was conducted at the laboratories of automotive coatings suppliers for determination of VOC using Practice D3960. The analysts involved were persons experienced in running all the test methods involved in VOC determination. The data was analyzed statistically in accordance with Practice E180. As was suspected from previous round robins conducted to evaluate Practice D3960 (which involved some laboratories not familiar with these test methods), when well experienced analysts conduct the tests, the precision data is much improved.

X1.2 The interlaboratory study involved four laboratories and six samples; four solventborne automotive topcoats and two waterborne automotive topcoats. One operator in each of the four laboratories analyzed the sample in duplicate on 2 different days. The following duplicates, repeatability, and reproducibility coefficients of variation were obtained.

Automotive Topcoats	Duplicates, %	Repeatability, % (Within Laboratory)	Reproducibility, % (Between Laboratory)
Solventborne	0.86	1.62	2.86
Waterborne	3.94	5.29	9.75

X2. CALCULATION OF VOC CONTENT (SECTION 10)

X2.1 *Measurement of Exempt Volatile Compound Content*—The value of the weight percent of exempt volatile compound, W_{ex}, used in the VOC expression in Eq 2 and Eq 4 and to determine W_o for Eq 6, Eq 7, and Eq X2.2 can be obtained using Test Method D4457 for methylene chloride and 1, 1, 1 trichloroethane, and either Test Methods D6133 or D6438 for acetone, p-chlorobenzotrifluoride and methyl acetate.

X2.2 *Two or More Exempt Volatile Compounds*—For solvent or waterborne coatings containing more than one exempt volatile compound, the values for W_{ex} and (W_{ex}) (D_c/D_{ex}) to be used in Eq 2 and Eq 4, and to determine W_o for Eq 6, Eq 7, and Eq X2.2 (10.2.1, 10.2.2.2, 10.3.1, 10.4.1, X2.4) are the summations of the values of W_{ex} and $(W_{ex})(D_c/D_{ex})$ for each individual exempt volatile compound. For example, for a coating with three exempt volatile compounds use $(W_{ex1} + W_{ex2} + W_{ex3})$ for W_{ex} and use $((W_{ex1})(D_c/D_{ex1} + (W_{ex2})D_c/D_{ex2}) + (W_{ex3})(D_c/D_{ex3}))$ for $(W_{ex})(D_c/D_{ex})$.

X2.3 *Volume Nonvolatile Content*—The volume percent nonvolatile content, V_n, in Eq 6 (10.4.1) can be calculated from the summation of the individual contributions of each component in the coating formulation ("p" components) using the following equation (Eq X2.1 and Eq X2.2):

$$V_n = \sum_{j=1}^{p} [([V_n]_j)(V_j/100\,\%)] \qquad (X2.1)$$

where:

$(V_n)_j$ = volume of nonvolatile content of component "j," % [(100 %) × (volume of nonvolatiles of "j" per unit volume of "j")], and

V_j = volume of component "j" in the coating % [(100 %) × (volume of "j" used)/(total volume of coating)].

NOTE X2.1—Instructions for calculating the value for the formula percent volume solids (or formula volume percent nonvolatile) content of the coating are provided in Practice D5201.

NOTE X2.2—Eq X2.1 is meant to clarify the equation (II-4) currently in the EPA document EPA-450/3-84-019 for the expression of calculated volume percent nonvolatile content, V_n.

X2.4 *Amount of VOC in a Coating Expressed in Terms of Mass of VOC per Unit Volume of Coating Including Water and Exempt Volatile Compounds*—The amount of volatile organic compounds in both solvent- and waterborne coatings can be expressed in terms of the mass of volatile organic compounds per unit volume of coating including water and exempt volatile compounds according to the following equation (Eq X2.2):

$$VOA = \frac{(W_o)(D_c)}{100\,\%} \qquad (X2.2)$$

where:

VOA = amount of volatile organic compounds in g/L of coating including water and exempt volatile compounds, and

W_o = $W_v - W_w - W_{ex}$ (terms defined as in 10.2.1.

NOTE X2.3—Calculation of the amount of volatile organic compound based on the total volume of coating (including water and exempt volatile compounds), as illustrated in Eq X2.2, does not provide a measure of the amount of VOC that would be released from two coatings used for the same application (that is, to coat the same area to the same dry film thickness assuming the same application efficiency for each coating) *when one or both of the coatings contain water or exempt solvents*. These units do not identify which of the coatings will release the greater amount of VOC as they treat water and exempt volatile compounds as coating solids. These units, therefore, have not been used, recommended or accepted by U.S. EPA for demonstration of compliance with VOC content regulations as such calculations yield misleading results for coatings that contain water or exempt volatile compounds.

NOTE X2.4—The expression in X2.2 is useful for the calculation of the mass of VOC released per unit of time (for example, the mass of VOC per unit of volume including water and exempt volatile compounds times the volume of total coating used per unit of time). This expression may also be useful for certain labeling purposes where the amount of VOC per unit container is desired.

X3. DEFINITION OF VOLATILE ORGANIC COMPOUNDS (VOC)

X3.1 The US EPA definition of VOC is published in the Code of the Federal Register Regulations at 40 CFR 51.100(s). The US EPA definition uses the term "negligibly photochemical reactivity" rather than exempt volatiles compound as used in this practice.

X3.2 The US EPA definition was last amended on November 29, 2004.[5]

X3.3 The exempt volatile compounds are listed in paragraphs (1) and (5) of the US EPA definition.

X3.4 The following exempt volatile compounds have been used in coatings:

(a) methylene chloride (dichloromethane)

(b) 1,1,1–trichloroethane (methy chloroform)

(c) parachlorobenzotrifluoride (PCBTF)

(d) cyclic, branched, or linear completely methylated siloxanes

(e) acetone

(f) perchloroethylene (tetrachloroethylene)

(g) methyl acetate

(h) *t*-butyl acetate

X3.5 Certain VOC record keeping, emissions reporting, photochemical dispersion modeling and inventory requirements apply to *t*-butyl acetate as described in paragraph (5) of the US EPA definition.

[5] *Federal Register*, Vol. 69, No. 228, pp. 69290–69298 and 69298–69304.