



Designation: D 3960 – 02

Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings¹

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This standard has been approved for use by agencies of the 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 classified as VOC as they do not participate in atmospheric photochemical reactions. Such nonphotochemically reactive compounds are referred to as exempt volatile compounds in this practice.

NOTE 2—A list of the current US EPA approved exempt volatile compounds is found in Appendix Appendix X3, paragraph X3.1.1.1.

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.

2. Referenced Documents

2.1 ASTM Standards:

- D 1475 Test Method for Density of Liquid Coatings, Inks, and Related Products²
- D 2369 Test Method for Volatile Content of Coatings²
- D 2697 Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings²
- D 2832 Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings²
- D 3792 Test Method for Water Content of Coatings by

- Direct Injection into a Gas Chromatograph²
- D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings²
- D 4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method²
- D 4457 Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph²
- D 5095 Test Method for Determination of the Nonvolatile Content in Silanes, Siloxanes and Silane-Siloxane Blends Used in Masonry Water Repellent Treatments³
- D 5201 Practice for Calculating Formulation Physical Constants of Liquid Paints and Coatings²
- D 5403 Test Methods for Volatile Content of Radiation Curable Materials³
- D 6093 Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer²
- D 6133 Test Method for Acetone *p*-Chlorobenzotrifluoride, Methyl Acetate or *t*-Butyl Acetate Content of Solvent-Reducible and Water-Reducible Paints, Coatings, Resins, and Raw Materials by Direct Injection into a Gas Chromatograph²
- D 6419 Test Method for Volatile Content of Sheet-Fed and Coldset Web Offset Printing Inks³
- D 6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints and Coatings by Solid Phase Microextraction-Gas Chromatography²
- E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴
- 2.2 Other Documents:
- EPA Federal Reference Method 24—Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁵
- EPA 450/3-84-019, U.S. Environmental Protection Agency Procedures for Certifying Quantity of Organic Compound Emitted by Paint, Ink, and Other Coatings⁵

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.

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² Annual Book of ASTM Standards, Vol 06.01.

³ Annual Book of ASTM Standards, Vol 06.02.

⁴ Annual Book of ASTM Standards, Vol 15.05.

⁵ Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

EPA 450/3-83-013R, U.S. Environmental Protection Agency Glossary for Air Pollution Control of Industrial Coatings Operations⁵

3. Terminology

3.1 Definitions:

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

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

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

3.1.3.1 *Discussion*—The definition of VOC adopted by the U.S. EPA and a list of exempt volatile compounds are included in Appendix X3.

3.1.4 *volatile organic compound content (VOC content)*—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 solids.

4. Summary of Practice

4.1 Take a representative sample of the liquid coating in accordance with Practice D 3925. 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 D 2832 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 D 2369.

6.2 Test Method D 2369 includes a specific drying schedule and sample weight, and heating 1 h at $110 \pm 5^\circ\text{C}$ for the determination of the weight percent volatile content of solvent-borne and waterborne coatings.

6.2.1 For multicomponent coatings, Test Method D 2369 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.

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 D 5095. 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 $110^\circ \pm 5^\circ\text{C}$ 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 D 5403. 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 D 6419. This standard is based on Test Method D 2369, 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.

7. Water Content

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

7.1.1 In Test Method D 3792, 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 D 4017 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).

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).

7.1.3 With waterborne multicomponent coatings, the components are first mixed in the appropriate ratios, then water content is determined using Test Methods D 3792 or D 4017.

8. Density

8.1 The density of the paint or coating at 25°C is determined in accordance with Test Method D 1475. 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 D 1475.

9. Exempt Solvents

9.1 In Test Method D 4457 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 D 6133 an internal standard is added to the whole paint and injected directly into the gas chromatograph.

9.3 In Test Method D 6438 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 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, and (2) as the mass of VOC per unit volume of coating solids and (3) the weight of VOC per unit weight of 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:*

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

or

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

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

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 D 2369),

W_w = weight of water, % (see Test Methods D 3792 or D 4017),

W_{ex} = weight of exempt volatile compound, % (see 3.1.3.1, Note 10, and Test Method D 4457),

V_w = volume of water, % ($W_w)(D_c/D_w)$,

V_{ex} = volume of exempt volatile compound, % (see 3.1.3.1, Note 10), = ($W_{ex})(D_c/D_{ex})$,

D_c = density of coating, g/L, at 25°C, (see Test Method D 1475),

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 D 1475).

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 solvents: