



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
 - EPA 450/3-83-013R, U.S. Environmental Protection

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.

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:

(weight percent of total volatiles less water less (1)

$$VOC = \frac{(\text{exempt volatile compounds})(\text{density of coating})}{100\% - (\text{volume percent of water}) - (\text{volume percent of exempt volatile compounds})}$$

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 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:

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

10.2.2.2 For solventborne coatings that contain an exempt volatile compound but do not contain water (see section 3.1.3 and Note 3):

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

10.2.2.3 For solventborne coatings that contain water but do not contain exempt volatile compounds (see 3.1.3 and Note 3):

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

10.2.2.4 For solventborne coatings that contain both an exempt volatile compound and water, use Eq 1 in 10.2.1 (see 3.1.3 and Note 3).

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 4 in 10.2.2.3 (see 3.1.3 and Note 3).

10.2.3.2 For waterborne coatings that contain exempt volatile compounds, use Eq 1 in 10.2.1 (see 3.1.3 and Note 3).

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 D 6093 and D 2697, 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 Weight of VOC per Weight of Solids*:

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

$$W_o = (W_v - W_w - W_{ex}) \quad (7)$$

$$VOC_b = \frac{W_o}{W_s}$$

where:

VOC_b = VOC content in weight VOC per unit weight of solids, 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 VOC; VOC calculations; VOC content; VOC content of paint; VOC content; test precision

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 D 3960. 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 E 180. As was suspected from previous round robins conducted to evaluate Practice D 3960 (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 or volume percent of exempt solvent in the VOC expression (Eq 1, Eq 3, and Eq 5) can be obtained using Test Methods D 4457 and D 1475 if the solvent is methylene chloride or 1,1,1-trichloroethane.

X2.2 Two or More Exempt Solvents—For solvent or waterborne coatings containing more than one exempt solvent, the values for W_{ex} and $(W_{ex})(D_c/D_{ex})$ to be used in Eq 1 or Eq 3 (10.2.1, 10.2.2.2, 10.2.2.4 or 10.2.3.2) are the summations of the values of W_{ex} and $(W_{ex})(D_c/D_{ex})$ for each individual solvent. Also, the value for W_{ex} to be used in 10.3.1 (to determine W_o in Eq 5) is the summation of the individual W_{ex} values.

X2.3 Volume Nonvolatile Content—The volume percent nonvolatile content, V_n , in Eq 5 (10.3.1) 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):

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

where:

- $(V_n)_j$ = volume of nonvolatile 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 D 5201.

NOTE X2.2—Eq X2.1 is meant to clarify the equation (II-4) currently in

the EPA certification manual 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 (X2.3):

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

where:

VOA = Amount of volatile organic compounds in g/L of coating including water and exempt volatile compounds.

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 Applicable to EPA regulations governing the preparation of state implementation plans (SIP’s) which are required under Title I of the Clean Air Act [Act].^{6,7}

X3.1.1 Section 51.100 Definitions:

X3.1.1.1 Volatile Organic Compounds (VOC), means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

(1) This includes any such organic compound other than

the following, which have been determined to have negligible photochemical reactivity: Methane; methyl acetate; ethane; methylene chloride (dichloromethane); 1,1,1-trichloroethane (methyl chloroform); 1,1,1-trichloro-2,2,2-trifluoroethane (CFC-113); trichlorofluoromethane (CFC-111); dichlorodifluoromethane (CFC-12); chlorodifluoromethane (CFC-22); trifluoromethane (FC-23); 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114); chloropentafluoroethane (CFC-115); 1,1,1-trifluoro 2,2-dichloroethane (HCFC-123); 1,1,1,2-tetrafluoroethane (HF-134a); 1,1-dichloro 1-fluoroethane (HCFC-141b); 1-chloro 1,1-difluoroethane (HCFC-142b); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentafluoroethane (HFC-125); 1,1,2,2-tetrafluoroethane (HFC-134); 1,1,1-trifluoroethane (HFC-143a); 1,1-difluoroethane (HFC-152a); parachlorobenzotrifluoride (PCBTF); cyclic, branched or linear completely methylated siloxanes; acetone; and perfluorocarbon compounds that fall into these classes:

⁶ U.S. Environmental Protection Agency, “Glossary for Air Pollution Control of Industrial Coating Operations,” EPA-450/3-83-013R, Environmental Protection Agency, Washington, DC, December 1983.

⁷ 40 CFR Part 51, “Requirements for Preparation, Adoption and Submittal of Implementation Plans: Approval and Promulgation of Implementation Plans,” Federal Register, Vol 57, No. 22, February 22, 1992, pp. 3941-46.

(a) (a) Cyclic, branched, or linear, completely fluorinated alkanes;

(b) (b) Cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;

(c) (c) Cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and

(d) (d) Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.

(1) For purposes of determining compliance with emissions limits. VOC will be measured by the test methods in the approved state implementation plan (SIP) or 40 CFR part 60,⁵ appendix A, as applicable. Where such a method also measures compounds with negligible photochemical reactivity, these negligibility-reactive compounds may be excluded as VOC if the amount of such compounds is accurately quantified and such exclusion is approved by the enforcement authority.

(2) As a precondition to excluding these compounds as VOC or at any time thereafter, the enforcement authority may require an owner or operator to provide monitoring or testing methods and results demonstrating, to the satisfaction of the enforcement authority, the amount of negligible-reactive compounds in the source's emissions.

(3) For purposes of Federal enforcement for a specific source, the EPA will use the test methods specified in the applicable EPA-approved SIP in a permit issue pursuant to a program approved or promulgated under Title V of the Act, or under 40 CFR part 51,⁵ subpart I or appendix S, or under 40 CFR parts 52⁵ or 60.⁵ The EPA will not be bound by any state determination as to appropriate methods for testing or monitoring negligibly-reactive compounds if such determination is not reflected in any of the above provisions.

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