Standard Test Method for
Water Content of Coatings by Direct Injection Into a Gas Chromatograph[1]

This standard is issued under the fixed designation D3792; 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 test method is for the determination of the total water content of waterborne paints. It has been evaluated for latex systems (styrene-butadiene, poly(vinylacetate)-acrylic, acrylic), epoxy acrylic resin systems and acrylic systems. The established working range of this test method is from 15 to 90 %. There is no reason to believe that it will not work outside of this range.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *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]

D1193 Specification for Reagent Water

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

3. Summary of Test Method

3.1 A suitable aliquot of whole paint is internally standardized, diluted with dimethylformamide, and then injected into a gas chromatographic column containing a porous polymer packing that separates water from other volatile components.

4. Significance and Use

4.1 In order to calculate volatile organic content (VOC) in waterborne paints, it is necessary to know the water content. This gas chromatographic test method provides a relatively simple and direct way to determine water content.

5. Apparatus

5.1 *Gas Chromatography*—Any gas-liquid chromatographic instrument equipped with a thermoconductivity detector may be used. Temperature programming capability is preferable, but isothermal operations may be adequate. See Table 1.

5.2 *Column*—The column should be at least 1.22 m (4 ft) of 3.2-mm (⅛-in.) outside diameter tubing of stainless steel, or other suitable material, lined with a TFE-fluorocarbon coating packed with 60/80 mesh (180 to 250 µm) porous polymer packing material.[4] A longer 1.83 m (6-ft) column can be used to improve resolution.

5.3 *Integrator*—Any electronic integrator that can accurately quantify a gas chromatographic peak is acceptable. Alternatively, a recording potentiometer with a full-scale deflection of 1-10mV, full scale response time of 2 s or less and sufficient sensitivity and stability to meet the requirements of 5.1.

5.4 *Liquid Charging Devices*—Micro syringes of 5–10-µL capacity with a precision of ±0.01 µL. Automatic injection of samples improves the precision of this test method.

6. Column Conditioning

6.1 *Procedure*—Install the packed column in the gas chromatographic unit leaving the exit end disconnected from the detector. This will prevent any contamination of the detector with the column bleed.

6.1.1 Set the carrier gas flow rate at 20 to 30 mL/min if a 3.2-mm (⅛-in.) outside diameter column is used. Purge the column 5 or 10 min before heating.

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

[4] HayeSep R (silanized), was used in the round robin. Any other porous polymer packing or other column giving equivalent or superior performance may be used. These products are available from most gas chromatography suppliers and distributors.

TABLE 1 Suggested Instrument Conditions

Detector	thermal conductivity
Column	1.22 m × 3.2 mm TFE-fluorocarbon coating coated stainless steel
Packing	60/80 mesh porous polymer
Temperatures, °C	
Sample inlet	240
Detector	250
Column	
Initial	140
Final	240
Program rate	40/min
Carrier gas	helium
Flow rate, ml/min	22.0-22.5
Detector current	150 mA
Specimen size	1-2 µl

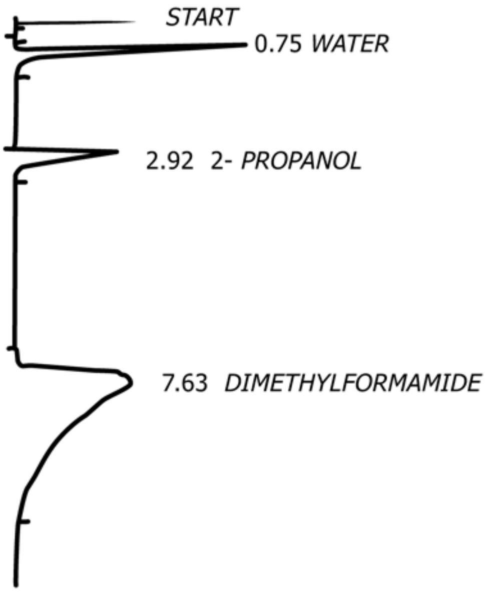

FIG. 1 Typical Chromatogram

6.1.2 Heat the column from room temperature to 200°C at 5°C/min and hold this temperature for at least 12 h (overnight). At the end of this time, heat the column at 5°C/min to 250°C (the maximum temperature for this packing) and hold for several hours. Cool the column to room temperature and connect to the detector.

6.1.3 Reheat the column to 250°C at 5°C/min to observe if there is column bleed. Optimum conditioning of this column may take several cycles of the heating program before a flat recorder baseline is achieved.

6.2 Before each calibration and series of determinations (or daily) condition the column at 200°C for 1 h with carrier gas flow and to eliminate any residual volatile compounds retained on the column.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D1193.

7.3 *Carrier Gas*—Helium of 99.995 % or higher purity. High-purity nitrogen may also be used.

NOTE 1—Care should be taken that any moisture that may be present in the carrier gas is eliminated through the use of a suitable carrier gas purifier. Trace levels of water will accumulate on the column at low oven temperatures and may affect the reproducibility as well as the accuracy of the determination.

7.4 *Dimethylformamide (DMF) (Anhydrous)* gas chromatography, spectrophotometric quality (See Note 2).

7.5 *2-Propanol (Anhydrous) (Isopropanol)*—See Note 2.

7.6 *Methanol (Anhydrous)*—See Note 2.

7.7 *Septum Sample Vials,* 10-mL capacity with fluorocarbon-faced septa are preferred.

7.8 *Molecular Sieve,* 2A-3A, 8-12, mesh.

NOTE 2—Dry the DMF, 2-propanol and methanol with the molecular sieve. Verify the absence of water by analysis of the solvents by this GC method.

8. Hazards

8.1 *Dimethylformamide* is hazardous. Check the supplier's Safety Data Sheet (SDS) before use.

9. Preparation of Apparatus

9.1 Install the column in the chromatograph and establish the operating conditions required to give the desired separation (see Table 1).

9.2 Allow sufficient time for the instrument to reach equilibrium as indicated by a stable baseline.

9.3 Control the detector temperature so that it is constant to within 1°C without thermostat cycling, which causes an uneven baseline.

9.4 Adjust the carrier-gas flow to a constant value.

10. Calibration

10.1 Using the information in Table 1 (as a guide), select the conditions of temperature and carrier gas flow that give baseline resolution of the water and internal standard.

10.2 *Determination of Relative Response Factors:*

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[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.

10.2.1 Anhydrous 2-propanol or methanol is used as an internal standard.[6]

10.2.2 The response factor to water relative to the internal standard is determined by means of the following procedure. See Fig. 1 for a typical chromatogram. It is good practice to determine the relative retention time daily or with each series of determinations. Failure of this value to remain relatively constant may indicate a chromatographic problem.

10.2.3 Weigh about 0.9 g of water and 0.9 g of 2-propanol or appropriate amount of an alternate internal standard to 0.1 mg into a septum sample vial. Weigh 9.0 g of dimethylformamide (DMF) into the vial. If the DMF is anhydrous, simply add 9 mL of it as weighing is not necessary.

10.2.4 Inject a 1- or 2-µl aliquot of the above solution into the column and record the chromatogram. The retention order and approximate retention times after the air peak are (*1*) water; (*2*) internal standard, (see Note 3), and (*3*) DMF (see Fig. 1).

10.2.5 Calculate the response factor for water by means of the following equation:

$$R = \frac{(W_i)\,(A_{H_2O})}{(W_{H_2O})\,(A_i)} \qquad (1)$$

where:

W_i = weight of internal standard,
W_{H_2O} = weight of water added,
A_{H_2O} = area of water peak, and
A_i = area of internal standard peak.

NOTE 3—Initially, each paint specimen should be analyzed to check for the presence of methanol or isopropanol so that the proper internal standard can be used. Check each paint system to be analyzed for interfering peaks. Coalescing agents do not interfere with this determination.

11. Procedure

11.1 Weigh to 0.1 mg, 0.6 g of waterborne paint and 0.6 g of internal standard into a septum vial. Add 7.0 g of DMF into the vial. Seal the vial.

11.2 Shake the vials on a wrist action shaker or other suitable device for 15 min, (dry mixing beads added to the vials have proved beneficial with viscous samples). To facilitate settling of solids allow the vials to stand for 5 min just prior to injection into the chromatograph. Low-speed centrifugation may also be used.

11.3 Inject a 1- or 2-µL sample of the supernatant from the prepared solutions into the gas chromatograph. Record the chromatograms using the conditions described in Table 1. Make duplicate determinations.

12. Calculations

12.1 With the integrator set up to measure the area of the water and the internal standard peaks, multiply each area by the appropriate attenuation factor to express the peak areas on a common basis. Use of an electronic integrator is recommended to obtain the best accuracy and precision.

12.2 Calculate the water concentration in the paint by means of the following equation:

$$H_2O,\ \% = \frac{A_{H_2O} \times W_i \times 100}{A_i \times W_p \times R} \qquad (2)$$

where:

A_{H_2O} = area of water peak,
A_i = area of internal standard,
W_i = weight of internal standard,
W_p = weight of paint, and
R = response factor determined in 10.2.

12.3 Report H_2O, %, the mean of duplicate determinations if the relative percent difference is 1.6 % or less. If the relative percent difference between the two values is greater than 1.6 %, repeat the determinations in duplicate.

12.4 *Correction for Water Content of Solvent:*

12.4.1 If the blank indicates the presence of a detectable peak for water in the dimethylformamide used as solvent, make a correction in the calculation.

12.4.2 The water content of the dimethylformamide determined by either chromatography or preferably, Karl Fischer titration is used to make the correction. Calculate the water content due to the solvent by using the following equation:

$$H_2O(S),\ \% \ \frac{(W_s)(P)100}{W_p} \qquad (3)$$

where:

W_s = weight of dimethylformamide,
W_p = weight of paint, and
P = weight % of water in DMF/100.

12.4.3 The water content of the paint in this case is the difference between the total percent determined in 12.2 and the correction for the solvent water content as determined in 12.4.2.

13. Precision and Bias[7]

13.1 The precision estimates are based on an interlaboratory study in which five different laboratories analyzed in duplicate on two days six samples of waterborne paints containing from 34 to 76 % H_2O. The results obtained were analyzed statistically in accordance with Practice E180. The within-laboratory coefficient of variation was found to be 0.77 % relative at 27 df and the between-laboratories coefficient of variation 1.72 % relative at 21 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

13.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 1.6 % relative.

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[6] Select an internal standard compound that is not part of the paint or coating formulation, or is not formed during the cure. Any compound that elutes free of interferences relatively close to water and gives approximately the same peak height and peak width could be used. Both 2-propanol and methanol have been found to be good internal standard compounds. An alternative internal standard may be considered.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1022 and RR:D01-1027. Contact ASTM Customer Service at service@astm.org.

13.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 5.0 % relative.

13.2 *Bias*—Bias cannot be determined because there are no accepted standards for water content of coatings.

14. Keywords

14.1 gas chromatograph; water content of paints by gas chromatography

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