Designation: D7245 – 09 (Reapproved 2014)

Standard Test Method for Measuring Total Water and Volatiles in Liquid Coatings Which Produce Cure Water Upon Heating[1]

This standard is issued under the fixed designation D7245; 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 designed to measure total water which includes cure water resulting from the heat induced condensation reaction of coatings. Cure water cannot be measured directly by Test Method D4017. This task is accomplished by measuring water content in the vapors evolved during heating. This test method will yield total water content. This test method also permits for the simultaneous determination of total volatile content. The results of this test method may be used to calculate VOC content. Although this test method was designed for phenolic coatings, it can be used with other types of coatings.

1.2 Materials used for method development and evaluation had total water values from 20 to 37 %. Use of this test method on coatings outside these values will need to be validated by the user.

1.3 Sample heating is accomplished with a Brinkmann Instruments Model 832 drying oven,[2] or other mutually agreed upon alternative, passing all of the evolved vapors into a Karl Fischer titration vessel.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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 to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1193 Specification for Reagent Water

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

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 *Definitions:*

3.1.1 *cure water, n*—water produced as a product of condensation reaction during cure.

3.1.2 *total water, n*—water in the liquid coating plus cure water produced by the condensation reaction.

4. Summary of Test Method

4.1 A measured quantity of coating is added to a tared glass vial which is sealed and then placed into a preheated oven chamber for the required test duration. Sample is heated at 110°C for one hour. The volatiles are passed into a Karl Fischer titration vessel and total water determined. By subtracting the percent water found in regular Karl Fischer titration, Test Method D4017, from total water, the percent of cure water can be determined. With the weights being known and vial sealed, total volatile content is obtained with this method.

5. Significance and Use

5.1 In the determination of VOC, cure water is treated as a VOC in other test methods, as these methods are unable to

[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] Round-robin collaborators used the Model 832 drying oven which were loaned to them by Brinkmann Instruments Westbury, New York 11590. It is not known whether this method is applicable to other similar instruments.

[3] 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.

FIG. 1 Drying Oven

account for cure water. This test method allows taking credit for cure water as total water is measured, a value which includes cure water.

5.2 Total water content and volatile content results obtained with this method may be used in Practice D3960 to calculate VOC of the coating.

6. Apparatus

6.1 *Glass Vial*—A glass vial measuring 22 mm in diameter, 38 mm in height having a capacity of 6 ml capable of being sealed with a TFE-fluorocarbon septum.

6.2 *Analytical Balance*—Capable of weighing to ±0.0001 g.

6.3 *Drying Oven*—This instrument is essentially a closed system in which the sample is heated within the heating chamber and the vapors passed to the titration vessel through a connecting tube. See Fig. 1.

6.4 *Karl Fischer Apparatus*—See Test Method D4017.

6.5 *Syringe*—Minimum of 1 ml but no more than 5 ml capacity equipped without a needle, but with a cap, capable of properly dispensing the coating.

7. Reagents[4]

7.1 *Purity of Reagent*—Reagent grade chemicals shall be used in all tests unless otherwise indicated; it is intended that all reagents conform to the specifications of the committee on Analytical Reagents of the American Chemical Society where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit use.

7.2 *Purity of Water*—Unless otherwise indicated references to water shall be understood to mean reagent grade conforming to type II of Specification D1193.

7.3 *Karl Fischer Reagent*—For ketones.

7.4 *Methyl Propyl Ketone (MPK), or other appropriate solvent*—Technical Grade.

8. Preparation of Apparatus

8.1 Connect transfer line from the oven into the Karl Fischer unit so the end of the tubing is beneath the level of the liquid in the Karl Fischer titration vessel.

NOTE 1—Equipment tested came equipped with a tapered plug designed for the tubing to fit through and which was tapered to fit into the Karl Fischer unit.

NOTE 2—Transfer line should be insulated to avoid condensation of vapors in the line. The use of a heated transfer line is preferred.

8.2 The air-inlet port shall be attached to a source of desiccant-dried air or nitrogen.

NOTE 3—Testing found no appreciable difference between the two.

8.3 Check equipment for leaks.

8.4 Precondition the glass vials and septum by heating in an oven at 110ºC for 30 minutes and storing in a desiccator until needed.

9. Calibration and Standardization

9.1 Use the procedure specified in Test Method D4017 for calibration and standardization of the Karl Fischer apparatus.

9.2 Run a blank on the Methyl Propyl Ketone (MPK) to determine if it contains water. If there is water present in the solvent, proceed to 9.2.1.

9.2.1 Weigh a sample of MPK, record as $W_{solvent}$, to the nearest 0.1 mg.

9.2.2 Perform Test Method D4017, record the weight percent water results as W_{water}.

10. Procedure

10.1 Take a representative sample of the liquid coating in accordance with Practice D3925.

10.2 Thoroughly mix the sample to be analyzed.

NOTE 4—Mixing time of 5 minutes has proven adequate for most samples.

10.3 Should amount of cure water need to be known, determine percent water content on the coating in accordance with Test Method D4017 (W_{ws}).

10.4 Determine Total Water (W_{wt}) and Volatile content (W_v).

10.4.1 Preheat the Drying oven to 110 ± 2ºC.

10.4.2 Set the Airflow to 80 ml/min.

10.4.3 Purge transfer line for a period of 5 minutes at an airflow rate of 80 ml/min.

NOTE 5—Testing found use of empty sealed vial served this purpose.

10.4.4 Pretitrate contents of the Karl Fischer titration vessel to endpoint.

10.4.5 Weigh preconditioned empty vial and septum to the nearest 0.0001 g and record weight (W_t).

10.4.6 Using a syringe, draw a sample of coating and cap syringe.

10.4.7 Weigh to the nearest 0.0001 g and record (W_1).

[4] *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.

TABLE 1 Total Water (% by weight)

NOTE 1—This includes the water of polymerization and free water in the samples.

Material	Average[A] $\bar{X}$	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
A	15.97	0.45	0.52	1.27	1.45
B	8.35	0.13	0.69	0.35	1.93
C	8.95	0.16	0.46	0.45	1.29
D	10.64	0.34	0.77	0.95	2.14
E	3.53	0.15	0.78	0.42	2.19
F	12.46	0.48	1.35	1.33	3.78

[A] The average of the laboratories' calculated averages.

TABLE 2 Total Volatiles (% by weight)

Material	Average[A] $\bar{X}$	Repeatability Standard Deviation s_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
A	25.59	1.01	3.89	2.82	10.88
B	31.09	0.76	1.56	2.13	4.37
C	28.49	0.88	2.37	2.47	6.64
D	31.11	0.65	3.65	1.82	10.23
E	39.81	0.43	2.61	1.21	7.32
F	39.29	1.07	1.78	2.99	4.97

[A] The average of the laboratories' calculated averages.

10.4.8 Transfer approximately 0.2 ml (0.3 g) of the sample to the glass vial.

10.4.9 Cap syringe and re-weigh, record the weight (W_2).

10.4.10 Add approximately 0.8 ml of Methyl Propyl Ketone (MPK) or other mutually agreed upon acceptable solvent.

NOTE 6—If water was found in the MPK, the weight of the MPK is to be determined and recorded as $W_{solvent2}$.

10.4.11 Seal vial.

10.4.12 Shake the sealed vial well to mix.

10.4.13 Place vial in heating port and start the oven to run for a period of 1 hour with air flow at 80 ml/min.

10.4.14 Start the Karl Fischer Apparatus to determine total percent water (W_{wt}).

NOTE 7—If water was found in the MPK, then operator must include weight of MPK ($W_{solvent2}$) in the denominator of total water calculation.

10.4.15 Remove vial from the reaction port, place in a desiccant chamber to allow to cool to room temperature.

10.4.16 Weigh the vial with the residue in and record as (W_{nvc}).

10.4.17 Run a duplicate determination, steps 10.4.1 – 10.4.15, average the results.

11. Calculations

11.1 Percent Cure Water:

$$W_{wc} = W_{wt} - W_{ws} \quad (1)$$

11.2 Volatile content:

$$Volatile\ content = W_v = \left(1 - \left[\frac{(W_{nvc} - W_t)}{(W_1 - W_2)}\right]\right) \times 100 \quad (2)$$

11.3 Adjusted water percent if MPK contained water:

$$Adjusted\ water = \left[\frac{(((W_1 - W_2) + W_{solvent2}) \times W_{wt}) - (W_{solvent2} \times W_{water})}{(W_1 - W_2)}\right] \quad (3)$$

12. Report

12.1 Report the following information:

12.1.1 All data determined from the test and all calculated values.

13. Precision and Bias[5,6]

13.1 *Precision*—The precision of this test method is based on an interlaboratory study of Test Method D7245, conducted in 2008. Analytical results in this study were obtained from six laboratories, testing six different materials, for Total Water and Total Volatiles, run according to the standard in that the average of the duplicate was reported as a single individual determination. All participating laboratories were asked to report a duplicate test for each material. Practice E691 was followed for the design and analysis of the data.

13.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material. "*r*" is the interval representing the critical difference between two test

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1140. Contact ASTM Customer Service at service@astm.org.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1145. Contact ASTM Customer Service at service@astm.org.

results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

13.1.1.1 Repeatability limits are listed in Table 1 and Table 2.

13.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

13.1.2.1 Reproducibility limits are listed in Table 1 and Table 2.

13.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

13.1.4 The repeatability limit and the reproducibility limit should be considered as general guides, and the associated probability of 95 % as only a rough indicator of what can be expected.

13.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

13.3 The precision statement was determined through statistical examination of 144 data points, from six laboratories, on six materials. The six materials tested were identified as the following:

Material A:	Very low molecular weight phenolic resin, no solvent in the sample
Material B:	Solvent borne phenolic coating containing 55 % low-medium molecular weight phenolic resin
Material C:	Solvent borne phenolic coating containing 25 % low molecular weight phenolic resin and 25 % of very low molecular weight phenolic resin (material A)
Material D:	Solvent borne coating containing 60 % high molecular weight phenolic resin
Material E:	Solvent borne phenolic coating with 55 % very high molecular weight phenolic resin
Material F:	Solvent borne phenolic coating with 60 % very high molecular weight phenolic resin

NOTE 8—All the phenolic resin systems are of the phenol formaldehyde resol type.

13.4 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

14. Keywords

14.1 condensation reaction; cure water; drying oven; Karl Fischer; total water; VOC; volatile; volatile organic content