



Designation: D4017 – 22

Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method¹

This standard is issued under the fixed designation D4017; 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 applicable to all paints and paint materials, including resins, monomers, and solvents, with the exception of aldehydes and certain active metals, metal oxides, and metal hydroxides. While the evaluation was limited to pigmented products containing amounts of water in the 30 % to 70 % range, there is reason to believe that higher and lower concentrations can be determined by this test method.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Specific hazard statements are given in Section 7.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

D3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Spe-

cialty Chemicals (Withdrawn 2009)³

E203 Test Method for Water Using Volumetric Karl Fischer Titration

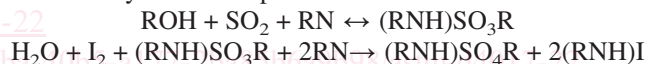
2.2 *Other Standard:*

EPA Federal Reference Method 24 Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁴

3. Summary of Test Method

3.1 The material is dissolved in a suitable solvent, and titrated directly with standardized Karl Fischer reagent, to an electrometric end point. The sluggish reaction with water in pyridine is accelerated with a chemical catalyst, 1-ethylpiperidine.

3.1.1 Karl Fischer reagent is a mixture of iodine, amine, sulfur dioxide, and an alcohol. In the reaction with water, iodine is reduced to hydrogen iodide. Once all the water is consumed, the appearance of free iodine is detected electrochemically and the titration is stopped. The following depicts the chemistry that takes place:



3.2 In classical Karl Fischer titrations the base used is pyridine, and the solvent either methanol or methoxy ethanol. In order to accelerate the reaction when pyridine is used, 1-ethylpiperidine is used as a catalyst/buffer. The additional buffer capacity is usually already built in to most nonpyridine based reagents such as hydranal (see Hydranal Manual).⁵

4. Significance and Use

4.1 Control of water content is often important in controlling the performance of paint and paint ingredients, and it is critical in controlling volatile organic compound (VOC) content.

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 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.

⁵ Available from Hoechst Celanese Corporation, Hydranal Technical Center, U.S. Highway 43, Bucks, AL 36512.

4.2 Paint materials are often insoluble in common Karl Fischer solvents such as methanol. Pyridine has been found to be a nearly universal solvent for these materials; however, the Karl Fischer reaction is too slow in that solvent at room temperature. To speed it up, 1-ethylpiperidine is added at 5 % as a buffer, or “catalyst.”

4.3 For nonpyridine-based reagents, a number of different solvent systems are available to increase solubility and to minimize interferences from ketones and aldehydes.

5. Apparatus

5.1 *Karl Fischer Apparatus*, manual or automatic, encompassed by the description in Test Method E203. Apparatus should be equipped with a 25-mL buret, Class A, or equivalent.

5.2 *Syringe*, 100- μ L capacity, with needle.

5.3 *Syringes*, 1-mL and 10-mL capacity, without needle, but equipped with caps.

6. Reagents

6.1 *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.⁶ Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

TABLE 1 Specimen Guidelines

Expected water, %	Approximate Specimen Weight, g	Approximate Titrant Volume at 5 mg/mL titre, mL
0.5–1.0	5	5–10
1–3	2–5	10–20
3–10	1–2	10–20
10–30	0.4–1.0	20–25
30–70	0.1–0.4	15–25
>70	0.1	20

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

6.3 *Classical Karl Fischer Reagent*.⁷

6.3.1 *Nonpyridine Based Karl Fischer Reagent (KFR)*.

6.4 *Pyridine*.

6.5 *1-Ethylpiperidine*.⁸

⁶ *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.

⁷ So-K-3 available from Fischer Scientific Co., or equivalent has been found suitable for this purpose.

⁸ Use 1-ethylpiperidine, manufactured by the Aldrich Chemical Co., Milwaukee, WI 53233, for the best results.

6.6 *Hydrochloric Acid (HCl)*, concentrated.

NOTE 1—All reagents must be fresh. Do not use reagents that are more than nine months old. Karl Fischer reagent deteriorates with age. Check expiration dates on the reagent bottle.

7. Hazards

7.1 Karl Fischer reagent contains four toxic compounds, namely iodine, sulfur dioxide, pyridine, and methanol or glycol ether. Prepare and dispense the reagent in a hood. Care must be exercised to avoid inhalation or skin contact. Following accidental contact or spillage, wash with large quantities of water.

7.2 Treat pyridine and methanol solvents with the same care as Karl Fischer reagent.

7.3 1-ethylpiperidine is of unknown toxicity and, therefore, handle with the same care as the materials listed in 7.1 and 7.2.

7.4 Handle also nonpyridine based reagents with the same care as the chemicals listed in 7.1 and 7.2.

8. Procedure

NOTE 2—Some instruments perform many of the following procedures and calculations automatically; consult instrument manual for details.

8.1 *Standardization of Karl Fischer Reagent*:

8.1.1 Add enough fresh solvent to cover the electrode tip. If using pyridine, also add 1 mL of 1-ethylpiperidine catalyst per 20 mL of pyridine. Catalyst performs best at a concentration of about 5 % of the volume present.

8.1.2 Fill the 100- μ L syringe to about half full with distilled water and weigh to the nearest 0.1 mg.

8.1.3 Pretitrate the solvent to the end point indicated by the equipment manufacturer, by adding just enough Karl Fischer Reagent I (KFR) to cause the end point to hold for at least 30 s.

8.1.3.1 The use of the catalyst greatly increases the reaction rate between water and Karl Fischer reagent. To obtain reliable results, increase the electrode sensitivity and reduce titration rate to a minimum. Most instruments have controls for these functions. Consult the instructional manual for information on these controls.

8.1.4 Empty the contents of the syringe into the titrator vessel. Immediately replace the stopper of the sample port and titrate with KFR to the end point as described in 8.1.3.

8.1.5 Repeat standardization until replicate values of F agree within 1 %. Determine the mean of at least two such determinations. Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

8.1.6 *Calculation*:

8.1.6.1 Calculate the KFR titre F as follows:

$$F = J/P \quad (1)$$

where:

J = water added, g, and

P = KFR used, mL.

The value for F should be recorded to the four significant digits and should be the mean of at least two determinations. Typical values are in the range of 0.004000 g/mL to 0.006000 g/mL.

8.2 Analysis of Samples With More Than 0.5 % Water:

8.2.1 The titration vessel should already contain pretitrated solvent and catalyst, as described in 8.1.1 and 8.1.3 in the standardization procedure. Best results are obtained with fresh solvent, that is, containing no previously titrated specimen in the vessel.

8.2.2 With a 1-mL or 10-mL syringe, draw the amount of material indicated in Table 1.

NOTE 3—Paint samples tend to settle in the syringe and give high percent water content. Obtain a freshly stirred or mixed specimen for each test run.

8.2.2.1 Remove the syringe from the specimen, pull the plunger out a little further, wipe the excess material off the syringe, and place a cap on the syringe tip. Weigh the filled syringe to the nearest 0.1 mg.

8.2.3 Remove the cap, and empty the syringe contents into the pretitrated solvent vessel. Pull the plunger out and replace the cap.

8.2.4 Stir rapidly for 1 min to 2 min before starting titration. Some instruments can be set to do this automatically. If the specimen is still not dissolved or dispersed, continue stirring until it is dissolved, or use a different solvent in place of solvent in 8.2.1.

8.2.5 Titrate the specimen *slowly* with KFR to the end point described in 8.1.3.

8.2.6 Reweigh the emptied syringe, and calculate the specimen weight by difference.

8.2.7 Calculation:

8.2.7.1 Calculate the percent water L as follows:

$$L = (P \times F \times 100) / S \quad (2)$$

8.3 Analysis of Materials With Less Than 0.5 % Water:

8.3.1 For 0.1 % to 0.5 %, follow procedure in 8.2 (1-g specimen), except substitute a 1-mL microburet for the 25-mL buret in the Karl Fischer apparatus.

8.3.2 For less than 0.1 %, use a 1-mL microburet and increase specimen size as much as needed, up to 10 g. It should be possible to measure moisture levels down to 1 ppm (0.0001 %) by this approach.

NOTE 4—Specimens with less than 0.1 % water may require special handling techniques to prevent pickup of atmospheric moisture. The precision of this test method was determined with specimens containing higher water levels.

9. Recommendations for Good Results

9.1 Make sure electrodes are clean.

9.2 Follow manufacturer's instructions to ensure that venting into the titration vessel is only through a desiccant.

9.3 Samples should be thoroughly mixed before taking a specimen.

9.4 Use an appropriate solvent/reagent for the paint/coating being analyzed. Paints and paint materials are often slow to dissolve or disperse. To ensure that all of the water is extracted into the pyridine or solvent, stir rapidly for 1 min or 2 min before starting the titration.

9.5 Run the titration slowly with rapid stirring.

9.6 Throw out the first result in fresh pyridine.

9.7 Use only Aldrich's 1-ethylpiperidine.⁵ It has been found that other brands produce variable results.

9.8 For difficult-to-dissolve samples, extract the water with a suitable solvent, such as dry methanol. An example of this procedure is outlined in Appendix X1.

10. Maintenance

10.1 *Cleanup*—Clean the titration vessel by rinsing with fresh pyridine. Do not use methanol or other solvents.

10.2 *Dryness*—Check frequently to be sure that all drying tubes are in good condition and tightly connected. Replace desiccant when indicator color changes through *half of the tube*.

10.3 *Electrode Performance*—If electrode response is sluggish or otherwise off standard, take the following steps, in turn, to correct the problem. Test the electrode with a titration after each step, to determine if the next step is required.

10.3.1 Wipe the electrode tip with a clean paper towel.

10.3.2 Wash the electrode by dipping in concentrated hydrochloric acid for at least 1 min. Rinse first with distilled water, then with methanol.

10.3.3 Follow manufacturer's instructions on resetting end point meter.

10.3.4 Replace power source. See manual for replacement procedure.

10.3.5 Replace the electrode.

11. Precision and Bias⁹

11.1 The precision estimates are based on an interlaboratory study in which one operator in each of seven different laboratories analyzed in duplicate on two different days seven samples of water-based paints of various types containing between 25 % to 75 % water. The results were analyzed statistically in accordance with Practice E180. The within-laboratory coefficient of variation was found to be 0.9 % relative at 23 df, and the between-laboratory coefficient of variation was 1.9 % relative, at 18 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

11.1.1 *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 3.5 % relative.

11.1.2 *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 5.5 % relative.

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

12. Keywords

12.1 Karl Fischer reagent method; moisture content; water content

⁹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1096. Contact ASTM Customer Service at service@astm.org.

APPENDIXES

(Nonmandatory Information)

X1. TEST METHOD FOR KARL FISCHER WATER DETERMINATION FOR LATEX PAINTS USING EXTRACTION WITH METHANOL¹⁰

X1.1 Scope

X1.1.1 If variable results are obtained with the pyridine method, the methanol extraction method is recommended.

X1.1.2 This test method is applicable to paints based on latex technology, which may not be sufficiently soluble in the solvents specified in the direct titration method. Some solvent-based paints will “ball up” in contact with methanol.

X1.1.3 *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.*

X1.2 Referenced Documents

X1.2.1 *ASTM Standards:* **D3960** Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

X1.2.2 *Other Standard:* EPA Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁴

X1.3 Summary of Test Method

X1.3.1 Water is quantitatively extracted from a sample with anhydrous methanol, and an aliquot is titrated for water content using commercial non-pyridine based reagents.

X1.4 Significance and Use

X1.4.1 The latex polymers in some modern coatings are not soluble, and do not readily give up their water, in pyridine or other solvents used in this test method. This procedure is designed to quantitatively extract the water, in a reasonable time, into anhydrous methanol, so it can be easily titrated. This test method may not be applicable to all coating types, and is offered as an alternative to the direct titration method in Test Method D4017.

X1.4.2 This test method is specifically designed to obtain VOC content of waterborne coatings with minimum error.

X1.4.3 The specimen size assumes a paint that has 50 to 90 % water content. If the product being tested has a lower expected water content, larger specimens should be taken.

X1.4.4 Good results are dependent on close attention to detail. See **X1.12**, Recommendations for Good Results.

X1.4.5 For further information see Practice **D3960**, EPA Reference Method 24, and Manual 4.¹¹

X1.5 Apparatus

X1.5.1 *Karl Fischer Titration Apparatus.*¹²

X1.5.2 *Disposable Syringe*, 1-cc tuberculin with cap and needle.¹³

X1.5.3 *Disposable Syringe*, 1-cc tuberculin with cap and *no* needle.¹⁴

X1.5.4 *Analytical Balance*, with tare bar, readable to 0.0001 g.

X1.5.5 *Sonic Bath.*¹⁵

X1.5.6 *Flasks*, 100-mL, Class A volumetric.

X1.5.7 *Pipetes*, 10 mL, Class A volumetric.

X1.6 Reagents

X1.6.1 *Non-Pyridine Composite Karl Fischer Reagent*, (KFR)¹⁶ 5 mg/mL titre.

X1.6.2 *Reagent Grade Methanol* or commercial anhydrous methanol.

X1.6.3 *4A Molecular Sieve*, 8–12 mesh beads (required only if drying your own material).¹⁷

X1.7 Sample Preparation

X1.7.1 *Dry Methanol:* Put about 200 g of 4A molecular sieve beads into a fresh 4-L bottle of reagent grade methanol and allow to stand overnight.

¹¹ *MNL, 4, Manual on Determination of Volatile Organic Compound (VOC) Content in Paints, Inks, and Related Coating Products*, ASTM, 1993.

¹² The Metrohm Model E-358 was used in the development of this test method. (Brinkmann Instruments, Cantiague Rd., Westbury, NY 11590). A few references to its features are mentioned in the Procedure. Most modern Karl Fischer titrators have comparable features. This model is no longer available, but several companies, including Brinkmann, market equivalent instruments.

¹³ Disposable syringe, BD 9625, available from many scientific supply companies, has been found suitable for this purpose.

¹⁴ Disposable syringe, BD 9602, available from many scientific supply companies, has been found suitable for this purpose.

¹⁵ Sonic bath, VWR Catalogue No. 21812-119 or equivalent has been found suitable for this purpose. VWR Scientific, Box 232, Boston, MA 02101.

¹⁶ Hydranal, a registered trademark of Sigma-Aldrich Biotechnology LP and Sigma-Aldrich Co., Composit 5, Catalogue No. 34801, (Crescent Chemical Co., 1324 Motor Parkway, Hauppauge, NY 11788), was used in the development of this test method. Several companies market equivalent reagents, however care should be exercised to ensure that they are equivalent. Samples containing ketones, Hydranal Composite 5K, combined with Hydranal Working Medium K, or equivalent reagents from other suppliers, have been found to give excellent results (see Catalogue Nos. 34816 and 34817, respectively).

¹⁷ Sieve, VWR Catalogue No. EM-MX 1583L-1 or equivalent has been found suitable for this purpose.

¹⁰ Isopropanol has also been found suitable in some cases.

X1.7.2 Into two 100-mL volumetric flasks, add about 80 mL of dry methanol and stopper.

X1.7.3 Fill a 1-mL disposable syringe (the type with no needle) with freshly mixed sample of the paint to be tested. Draw back the plunger a little, wipe off the excess paint, and cap the syringe.

X1.7.4 Place the capped syringe on the balance pan and tare to zero.

X1.7.5 Remove the cap and empty the syringe into one of the flasks, being careful not to get any sample on the neck or top of the flask. Pull the plunger back a little and cap the syringe and re-stopper the flask.

X1.7.6 Place the empty, capped syringe on the balance and record the weight to the nearest 0.0001 g.

X1.7.7 Repeat X1.7.3 to X1.7.6 with a duplicate sample. Be sure to number the flasks.

X1.7.8 Add dry methanol to the mark in each flask.

X1.7.9 Place the two flasks in a sonic bath and run for 15 min. Make sure that the flasks are tightly stoppered by taping them shut with masking tape.

X1.7.10 If the flask contents are warm, cool to room temperature, or until the meniscus returns to the mark. Ensure that the flask contents are uniform by turning them upside down three or four times.

X1.8 Titre Determination Procedure

X1.8.1 Use the following instrument settings for all titrations in this test method:

END POINT DELAY: 20 s

EXTRACTION TIME: 0 min

REPORT MODE: Mass fraction, mean value

X1.8.2 Fill the titration vessel with enough dry methanol to cover the electrode.

X1.8.3 Titrate out the water using the non-pyridine KF reagent. On some instruments, this is done automatically in the “condition” mode.

X1.8.4 Fill a 1-cc syringe with needle with deionized water. Draw back the plunger a little, wipe off any excess water, and cap the syringe.

X1.8.5 Place the capped syringe on a 4-place analytical balance. Tare out the weight to zero.

X1.8.6 With the needle tip at the solvent surface, add 2 to 3 drops into the titration solvent. After removing the syringe, withdraw the plunger a little and cap the titration vessel.

X1.8.7 Weigh the syringe on the tared balance and record the weight to the fourth decimal. Ignore the minus sign.

X1.8.8 Titrate the water to the endpoint that holds for 20 s. Stir rapidly. Titration rate should be about 3 mL/min.

X1.8.9 *Calculation:* Most instruments will calculate the titre automatically, after entering the weight. To calculate manually, use the equation as follows:

$$\text{Titre (F)} = \frac{\text{grams of water added} \times 1000}{\text{mL KFR used}} \quad (\text{X1.1})$$

Record to the third decimal, for example 5.238 mg/mL.

X1.8.10 Repeat X1.8.3 to X1.8.8 at least two more times. Make sure that the Karl Fischer titre is the average of at least three determinations. (Many instruments will average automatically). If all values do not agree within 0.05, check the instrument. (see X1.13).

X1.9 Blank Determination

X1.9.1 The titration vessel should contain pretitrated methanol as previously described (see X1.8.2 and X1.8.3).

X1.9.2 Place the instrument in “Standby.”

X1.9.3 Pipette 10.00 mL of dry methanol into the titration vessel.

X1.9.4 Titrate at the slowest rate. On some instruments, this is best done by pressing the “Condition” button. Record the volume at the end point. It will typically be in the range of 0.3 to 0.5 mL.

X1.9.5 Repeat X1.9.3 and X1.9.4 two more times. Average the three volumes.

X1.9.6 Calculate the average milligrams of water in 10.00 mL of dry methanol as follows:

$$\text{milligrams water in blank} = \text{average titration} \times F \quad (\text{X1.2})$$

For instruments with automatic blank correction in milligrams of water, enter this value in memory.

X1.9.6.1 If the instrument does not have this feature, use the average volume and calculate manually as shown under Section X1.11, Calculation

X1.9.7 The blank value will change fairly quickly, so determine this whenever a sample is run, or run it once a day if there are several samples to be done.

X1.10 Analysis of Samples

X1.10.1 The titration vessel should already contain pretitrated methanol as described under X1.8.

X1.10.2 Mix the volumetric flask by turning upside down once or twice.

X1.10.3 Pipete 10.00 mL into the titration vessel and titrate at about 3 mL/min.

X1.10.4 Repeat the above for the second volumetric flask.