



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

This standard is issued under the fixed designation D 4017; 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 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 *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.* Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paint and Related Coatings³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals⁴

E 203 Test Method for Water Using Volumetric Karl Fischer Titration⁴

2.2 Other Standard:

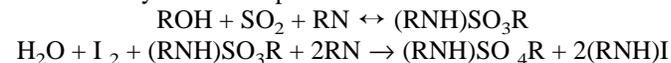
EPA Federal Reference Method 24—Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁵

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).⁶

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.

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 E 203. Apparatus should be equipped with a 25-mL buret, Class A, or equivalent.

5.2 *Syringe*, 100- μL capacity, with needle.

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

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. Current edition approved Jan. 10, 2002. Published March 2002. Originally published as D 4017 – 81. Last previous edition D 4017 – 96a.

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.01.

⁴ *Annual Book of ASTM Standards*, Vol 15.05.

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

⁶ Available from Hoechst Celanese Corporation, Hydranal Technical Center, U.S. Highway 43, Bucks, AL 36512.

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.⁷ 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 D 1193.

6.3 *Classical Karl Fischer Reagent*.⁸

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

6.4 *Pyridine*.

6.5 *1-Ethylpiperidine*.⁹

6.6 *Hydrochloric Acid (HCl)*, concentrated.

NOTE 1—All reagents must be fresh. Do not use reagents that are more than 9 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

8.1 *Standardization of Karl Fischer Reagent:*

⁷ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁸ So-K-3 available from Fischer Scientific Co., or equivalent has been found suitable for this purpose.

⁹ Use 1-ethylpiperidine, manufactured by the Aldrich Chemical Co., Milwaukee, WI 53233, for the best results.

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 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 2—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 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 3—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 dessicant.

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 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.⁶ 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 dessicant 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 Bias¹⁰

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 E 180. 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

¹⁰ Supporting data are available from ASTM International Headquarters. Request RR:D01-1096.

(Nonmandatory Information)
X1. TEST METHOD FOR KARL FISCHER WATER DETERMINATION FOR LATEX PAINTS USING EXTRACTION WITH METHANOL¹¹
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:

D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals⁴

X1.2.2 Other Standard:

EPA Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁵

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 D 4017.

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 Section X1.12, Recommendations for Good Results.

X1.4.5 For further information see Practice D 3960, EPA

Reference Method 24, and Manual 4.¹²

X1.5 Apparatus

X1.5.1 *Karl Fischer Titration Apparatus.*¹³

X1.5.2 *Disposable Syringe*, 1-cc tuberculin with cap and needle.¹⁴

X1.5.3 *Disposable Syringe*, 1-cc tuberculin with cap and *no* needle.¹⁵

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

X1.5.5 *Sonic Bath.*¹⁶

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)¹⁷ 5 mg/mL titre.

X1.6.2 *Reagent Grade Methanol* or commercial anhydrous methanol.¹⁸

X1.6.3 *4A Molecular Sieve*, 8–12 mesh beads (required only if drying your own material).¹⁹

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.

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.

¹² MNL, 4, *Manual on Determination of Volatile Organic Compound (VOC) Content in Paints, Inks, and Related Coating Products*, ASTM, 1993.

¹³ 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.

¹⁴ Disposable syringe, BD 9625, available from many scientific supply companies, has been found suitable for this purpose.

¹⁵ Disposable syringe, BD 9602, available from many scientific supply companies, has been found suitable for this purpose.

¹⁶ Sonic bath, VWR Catalogue No. 21812-119 or equivalent has been found suitable for this purpose. VWR Scientific, Box 232, Boston, MA 02101.

¹⁷ Hydranal® 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).

¹⁸ Reagent grade methanol, VWR Catalogue No. 34801 or equivalent has been found suitable for this purpose.

¹⁹ Sieve, VWR Catalogue No. EM-MX 1583L-1 or equivalent has been found suitable for this purpose.

¹¹ Isopropanol has also been found suitable in some cases.

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 Appendix X1.13).

X1.9 Blank Determination

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

X1.9.2 Place the instrument in “Standby”.

X1.9.3 Pipete 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 Section 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.

X1.11 Calculation and Report

X1.11.1 Most instruments calculate automatically. To calculate manually, use the equation as follows:

$$\% \text{ water}^{20} = \frac{(\text{mL KFR used} - \text{mL for blank}) \times F \times 100}{\text{grams sample}} \quad (\text{X1.3})$$

Record to the second decimal, for example 70.35 %.

X1.11.2 Report the average of two results.

X1.11.3 If the results differ from each other by more than 2.3 % relative, run another set of duplicates. For example, results of 50.05 % and 51.25 % would be considered suspect.

X1.12 Precision¹⁰

X1.12.1 *Precision* —The precision estimates are based on an interlaboratory study in which one operator in each of five different laboratories analyzed in quadruplicate six samples of water-based paints of various types containing from 35 to 70 % water.¹⁰ The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 0.81 % relative for duplicates, at 58 df,

²⁰ Units arrived as follows:

$$\% \text{ water} = \frac{\text{mL} \times F \times 10 \times 100}{\text{g} \times 1000} \quad (3)$$

where:

10 = dilution factor,

100 = converts into percentage, and

1000 = converts grams into milligrams.

and the between-laboratory coefficient of variation was found to be 2.55 % at 23 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

X1.12.1.1 *Repeatability*—Two results obtained by the same operator should be considered suspect if they differ by more than 2.28 % relative.

X1.12.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained in different laboratories, should be considered suspect if they differ by more than 7.46 % relative.

X1.12.2 *Bias*—Bias cannot be determined because there are no accepted standards for water content of paints.

X1.13 Recommendations for Good Results

X1.13.1 Clean the titration vessel by rinsing with fresh methanol. Pyridine or *n*-methyl pyrrolidone may also be used for difficult residues.

X1.13.2 Check frequently to be sure that all drying tubes are in good condition and tightly connected. Replace the desiccant when any color change is observed.

X1.13.3 To ensure against an unrepresentative sample due to settling, draw sample into the syringe right after mixing, and

carry out the entire operation immediately. Always use a new syringe for the second sample.

X1.13.4 Check titre and blank values at least daily.

X1.13.5 Stir rapidly and titrate slowly (~3 mL/min)

X1.13.6 The methanol solutions in the 100-mL flasks should not be allowed to stand around for a long time, as methanol will absorb water from the atmosphere, even when the flasks are stoppered, especially on humid days. All flasks and apparatus must be kept closed except when adding or withdrawing material.

X1.13.7 Problems with end points are often traceable to the electrode. If experiencing problems with repeatability or poor end points, try the following, in order. Try a titration after each step, to see if the next one is needed:

X1.13.7.1 Wipe the electrode with a clean paper towel,

X1.13.7.2 Dip the electrode in concentrated nitric acid for 1 min. Then rinse with deionized water, followed by methanol. If any residue remains, remove with a fine abrasive such as a crocus cloth,

X1.13.7.3 Replace the electrode, and

X1.13.7.4 Check the instrument operability in accordance with the manufacturer's supplied manual.

X2. TEST METHOD FOR KARL FISCHER DETERMINATION OF WATER CONTENT IN PAINT USING A HOMOGENIZER ACCESSORY

X2.1 Scope

X2.1.1 If variable results are obtained with the pyridine method, the use of the homogenizer method is recommended.

X2.1.2 This test method is applicable to water-based paints, which may not be sufficiently soluble in the solvents specified in the pyridine titration method. Some solvent-based paints will "ball up" in contact with methanol and not disperse.

X2.1.3 *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.*

X2.2 Referenced Documents

X2.2.1 *ASTM Standards:*

D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

X2.2.2 *Other Standard:*

EPA Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁵

X2.3 Summary of Test Method

X2.3.1 Samples are titrated in methanol after being homogenized with a specialized accessory that quickly disperses insoluble material by reducing it to very low particle size.

X2.4 Significance and Use

X2.4.1 The latex polymers in some modern coatings are not

soluble, and do not readily give up their water in pyridine or other solvents specified in Test Method D 4017. This procedure is designed to disperse insoluble specimens so to quantitatively extract the water in a reasonable time into methanol, so the water can be easily titrated. The principle is the same as in the "Methanol Extraction" procedure (Appendix X1), but with the advantage of eliminating some steps, thus saving time and eliminating sources of error. This test method may not be applicable to all coating types. It is offered only as an alternative to the Test Method D 4017 direct titration method, and the methanol extraction method in Appendix X1.

X2.4.2 This test method has been found to give precise and consistent results for water content.

X2.4.3 The specimen size assumes a paint which has 50 to 90 % water content. If the product being tested has a lower expected water content, larger specimens should be taken.

X2.4.4 Good results are dependent on close attention to detail. See Section X2.11, "Recommendations for Good Results".

X2.5 Apparatus

X2.5.1 *Karl Fischer Titration Apparatus.*²¹

X2.5.2 *Homogenizer.*²²

²¹ The Metrohm Model E-701 was used in the development of this test method. (Brinkman 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. Several companies market equivalent instruments.

²² Model No. 2000, available from Brinkmann Instruments. The homogenizer may be used with other company's titrators; however no accessory comparable to the Brinkmann Homogenizer is known to be available from other vendors.

X2.5.3 *Disposable Syringe*,¹⁴ 1 cc tuberculin with cap and needle.

X2.5.4 *Disposable Syringe*,¹⁵ 1 cc tuberculin with cap and no needle.

X2.5.5 *Analytical Balance*, with tare bar, readable to 0.0001 g.

X2.6 Reagents

X2.6.1 *Non-Pyridine Composite Karl Fischer Reagent*,¹⁷ 5 mg/mL titre.

X2.6.2 *Reagent Grade Methanol*.¹⁸

X2.7 Titre Determination

X2.7.1 If possible, use the following instrument settings for all titrations in this test method:

Homogenizer settings: 30 s, lowest speed

Extraction Time: – 60 s, (prevents titration from starting until 30 s after homogenizer stops),

End point delay time: 20 s,

Report mode: mass fraction, mean value (to read out as percent water and average the results).

X2.7.2 Fill the titration vessel with enough methanol to cover the homogenizer blades and the electrodes with stirrer on.

X2.7.3 Titrate out the water using the non-pyridine composite KF titrant. On most instruments, this is done automatically in the “condition” mode.

X2.7.4 RUN A “DUMMY” TITRATION. That is, run the homogenizer for 30 s, wait 30 s, and start the titration, with NO SPECIMEN ADDED. Throw out the result.

X2.7.5 Fill a 1-cc syringe with needle with deionized water. Draw back the plunger ¼ in. (5 mm), wipe off any excess water, and cap the syringe.

X2.7.6 Place the capped syringe on a 4-place analytical balance. Tare out the weight to zero.

X2.7.7 With the needle tip at the solvent surface, add 2 to 3 drops (0.0250 to 0.0500 g) into the titration solvent. After removing the syringe, withdraw the plunger ¼ in. (5 mm) and cap the titration vessel.

X2.7.8 Weigh the syringe on the tared balance and record the weight to the fourth decimal. Ignore the minus sign.

X2.7.9 Run the homogenizer for 30 s, then wait for 30 s. (Will be done automatically on instruments that accept the above settings.) Titrate the water to the end point that holds for 20 s. Stir rapidly. Titration rate should be about 3 mL/min.

X2.7.10 *Calculation*: Most instruments will calculate the titre automatically, after entering the weight. To calculate manually, use the following equation as follows:

$$\text{Titre (F)} = \frac{\text{grams of water added} \times 1000}{\text{mL KFR used}} \quad (\text{X2.1})$$

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

X2.7.11 REPEAT X2.7.6 TO X2.7.9 AT LEAST TWO MORE TIMES. The Karl Fischer titre should be the average of at least three determinations. (Many instruments will average automatically). If the range of values exceeds 0.1, check the instrument (see Section X1.3).

X2.8 Sample Determination

X2.8.1 If possible, set the following parameters on your

instrument:

Homogenizer settings: 30 s, lowest speed

Extraction Time: – 60 s, (prevents titration from starting until homogenizer stops),

End point delay time: 20 s,

Report mode: mass fraction, mean value (to read out as percent water and average the results).

X2.8.2 Add fresh methanol to cover the homogenizer blades and the electrodes when the stirrer is on.

X2.8.3 RUN A “DUMMY” TITRATION. That is, run the homogenizer for 30 s, wait 30 s, and start the titration, with NO SPECIMEN ADDED. Throw out the result.

X2.8.4 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 ¼ in. (5 mm), wipe off the excess paint, and cap the syringe.

X2.8.5 Place the capped syringe on the balance pan and tare to zero.

X2.8.6 Remove the syringe cap, and add 2 to 3 drops (equivalent to 0.0300 to 0.0500 g of water for a sample which has about 50 % water) into the titration vessel.²³ Draw back the plunger ¼ in. (5 mm), and immediately cap the syringe and close the titration vessel.

X2.8.7 Weigh the syringe on the tared balance and record to the fourth place after the decimal. Ignore the minus sign. Transfer the weight to the titrator, if required for your instrument.

X2.8.8 Run the homogenizer for 30 s, then wait for 30 s. (Will be done automatically on instruments that accept the above settings.) Titrate the water to the end point that holds for 20 s. Stir rapidly. Initial titration rate should be about 3 mL/min.

X2.8.9 Repeat X2.8.4 to X2.8.8 for a duplicate specimen.

X2.9 Calculation and Report

X2.9.1 Calculate percent water as follows:

$$\% \text{ water} = \frac{\text{mL KFR} \times F \times 100}{\text{mg of specimen}} \quad (\text{X2.2})$$

X2.9.2 Report the average of results on two specimens.

X2.9.3 A set of duplicates with a range of more than 2.2 % relative should be considered suspect and be rerun. For example, duplicate results of 50.05 and 51.20 % would be suspect.

X2.10 Precision

X2.10.1 *Precision* —The precision estimates are based on an interlaboratory study in which one operator in each of nine different laboratories analyzed in quadruplicate six samples of water-based paints of various types containing from 35 to 70 % water.¹⁰ The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 0.79 % relative for duplicates, at 98 df, and the between-laboratory coefficient of variation was found to be 1.47 % at 43 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

²³ Other specimen sizes may be used.

X2.10.1.1 *Repeatability*—Two results obtained by the same operator should be considered suspect if they differ by more than 2.20 % relative.

X2.10.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained in different laboratories should be considered suspect if they differ by more than 4.20 % relative.

X2.10.2 *Bias*—Bias cannot be determined because there are no accepted standards for water content of paints.

X2.11 Recommendations for Good Results

X2.11.1 Clean the titration vessel by rinsing with fresh methanol. Pyridine or *n*-methyl pyrrolidone are suggested for difficult residues.

X2.11.2 Check frequently to be sure that all drying tubes are in good condition and tightly connected. Replace the desiccant when any color change is observed.

X2.11.3 To ensure against an unrepresentative sample due to settling, draw sample into the syringe right after mixing, and

carry out the entire operation immediately. Always use a new syringe for the second sample.

X2.11.4 Check titre values daily.

X2.11.5 Stir rapidly and titrate slowly (~3 mL/min).

X2.11.6 Problems with end points are often traceable to the electrode. If experiencing problems with repeatability or drifting end points, try the following steps, in order. Try a titration after each step, to see if the next one is needed:

X2.11.6.1 Wipe the electrode with a clean paper towel.

X2.11.6.2 Dip the electrode in concentrated nitric acid for 1 min. Then rinse with deionized water, followed by methanol. If any residue remains, remove with a fine abrasive such as a crocus cloth.

X2.11.6.3 Replace the electrode.

X2.11.6.4 Check the instrument operability in accordance with the manufacturer's supplied manual

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