



# Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration<sup>1</sup>

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*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope

1.1 This test method covers the determination of water from 0 to 2.0 % in liquid organic chemicals, with Karl Fischer reagent, using an automated coulometric titration procedure.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 Review the current material safety data sheets (MSDS) for detailed information concerning toxicity, first-aid procedures, handling, and safety precautions.

1.4 *This standard does not purport to address all of the safety problems, 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 precautionary statements are given in Section 8.

## 2. Referenced Documents

### 2.1 ASTM Standards:

E 1193 Specifications for Reagent Water<sup>2</sup>

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals<sup>3</sup>

E 203 Test Method for Water Using Karl Fischer Reagent<sup>3</sup>

## 3. Summary of Test Method

3.1 This test method is based on the Karl Fischer reaction for determining water—the reduction of iodine by sulfur dioxide in the presence of water to form sulfur trioxide and hydriodic acid. The reaction becomes quantitative only when pyridine and methyl alcohol are present. Unlike the volumetric Karl Fischer reagents that include iodine, the coulometric technique electrolytically generates iodine, with 10.71 C of generating current corresponding to 1 mg of water in accordance with Faraday's law.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 15.05.

## 4. Significance and Use

4.1 The coulometric technique is especially suited for determining low concentrations of water in organic liquids which would yield small titers by the Karl Fischer volumetric procedure. The precision and accuracy of the coulometric technique decreases for concentrations of water much greater than 2.0 % because of the difficulty in measuring the small size of sample required. The test method assumes 100 % efficiency of coulombs in iodine production. Provision is made for verifying this efficiency.

## 5. Interferences

5.1 Interfering substances are the same as are encountered in the volumetric Karl Fischer titration and include free halogens, ketones, aldehydes, most acids, and oxidizing or reducing agents. A detailed discussion of interfering substances can be found in the treatise on "Aquametry."<sup>4</sup>

5.2 Test Method E 203 discusses organic compounds in which water may be determined directly and compounds in which water cannot be determined directly, but in which interferences may be eliminated by suitable chemical reactions.

## 6. Apparatus

6.1 *Automatic Titrator*,<sup>5,6,7</sup> consisting of a control unit, titration vessel, dual platinum sensing electrode, generator assembly, and magnetic stirrer. The instrument is designed to coulometrically generate iodine that reacts stoichiometrically with the water present in the sample solution. The coulombs of electricity required to generate the reagent are converted to

<sup>4</sup> J. Mitchell, Jr. and D. M. Smith, "Aquametry"—*A Treatise on Methods for the Determination of Water, Part III—The Karl Fischer Reagent*, 2nd Ed., J. Wiley and Sons, Inc., New York, NY 1990.

<sup>5</sup> An apparatus of this type is patented by the Photovolt Corporation under U.S. Patent 3,726,778. A detailed drawing is available from ASTM Headquarters. Request Adjunct No. 12-415330-00.

<sup>6</sup> The Mitsubishi automatic moisture titrator distributed by Cosa Corporation is patented under U.S. Patent 3,950,237.

<sup>7</sup> Basic references to the automatic coulometric titrator: M. T. Kelley, R. W. Stelzner, W. R. Laing, and D. J. Fisher, *Analytical Chemistry* 31, No. 2, 220 (1959) and A. W. Meyer, Jr. and C. M. Boyd, *Analytical Chemistry* 31, No. 2, 215 (1959).

micrograms of water, which is obtained as a direct digital readout.

6.2 *Glass Syringe*, 50-mL, fitted with an 11.5-cm hypodermic needle for removing excess solution from the titration chamber.

NOTE 1—All syringes and needles should be rinsed with anhydrous acetone after cleaning, then dried in an oven at 100°C for at least 1 h and stored in a desiccator.

6.3 *Glass Syringe*, 20-mL, fitted with an 11.5-cm hypodermic needle for introduction of neutralizing solution into the titration chamber (see Note 1).

6.4 *Glass Syringes*, 1- and 5-mL, fitted with 11.5-cm hypodermic needles for introduction of samples into titration chamber (see Note 1).

6.5 *Glass Syringe*, 5  $\mu$ L, fitted with 11.5-cm hypodermic needle for standardization of instrument (see Note 1).

6.6 *Fluorocarbon Sealing Grease*,<sup>8</sup> to seal the titration chamber against atmospheric moisture.

6.7 *Septa*, to seal sample port but allow introduction of samples by a needle with a minimum of moisture contamination. Serum caps and septa should be replaced as required to prevent air leakage as indicated by instrument drift.

## 7. Reagents

7.1 *Purity of Reagents*—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.<sup>9</sup> 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 Type II or Type III reagent water, conforming to Specification D 1193.

7.3 *Generator Solution*, containing iodine, pyridine, sulfur dioxide, methanol, and 2-methoxyethanol to provide iodine in the reaction mixture.<sup>10</sup>

7.4 *Titration Solution*, prepared as per instrument specifications.

7.5 *Neutralizing Solution*, methanol containing approximately 20 mg H<sub>2</sub>O/mL.

## 8. Safety Precautions

8.1 The reagents contain one or more of the following: iodine, pyridine, sulfur dioxide, and methanol. Chemical resistant gloves should be worn when mixing the reagents and removing solution from the titration chamber. Care must be exercised to avoid inhalation of reagent vapors, or direct contact of the reagent with the skin.

<sup>8</sup> A suitable sealing grease can be obtained from Halocarbon Products, 8 Burlews Ct., Hackensack, NJ 07601.

<sup>9</sup> *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.

<sup>10</sup> Reagents are available from the instrument manufacturer.

## 9. Sampling

9.1 Because of the low concentration of water to be measured, maximum care must be exercised at all times to avoid contaminating the sample with moisture from the sample container, the atmosphere, or transfer equipment.

9.1.1 Dry the sample bottles and caps overnight in an oven at 100°C before using. Seal the bottles immediately after removing from the oven.

9.1.2 Fill the sample bottle as rapidly as possible to within 1 in. of the top and immediately seal.

9.2 The test specimens for analysis are removed from the sample bottle with a dry hypodermic syringe. Dry nitrogen is injected into the sample bottle with the syringe to displace the sample that is removed.

## 10. Preparation of Apparatus

10.1 Clean, dry, and assemble the titration chamber as directed in the manufacturer's instructions. Use fluorocarbon grease to seal the upper and lower sections of the chamber from atmospheric moisture. Connect the leads from the sensing and generator electrodes to the titrator.

10.2 Prepare the titration solution (7.4) as directed by the instrument manufacturer and fill the instrument reservoir as directed by the manufacturer.

10.3 Add the generator solution (7.3) to the generator assembly and replace the cover cap. The surface of the generator solution must be below the level of the titration solution to prevent backflow contamination of the titration solution. The generator solution may have to be removed periodically to maintain the lower level.

10.4 Agitate the titration solution by gently swirling the titration chamber to remove any residual moisture from the walls. Allow the solution to stir for at least 20 min to dry and stabilize the inner atmosphere.

NOTE 2—The Mitsubishi automatic moisture analyzer does not require the steps in 10.4.

10.5 Attach an 11.5-cm hypodermic needle to a 20-mL syringe and withdraw about 15 mL of neutralizing solution (7.5). Insert the needle through the sample port septum and lower it until the tip is just below the surface of the titration solution.

10.6 Slowly inject the neutralizing solution into the titration solution until the color changes from brown to light red. This indicates that the end point is near. Continue the addition very slowly until the ON light comes on, indicating an excess of water is present, then carefully withdraw the syringe and needle. The total volume of neutralizing solution required will range from 5 to 15 mL. Allow the system to stabilize for 1 h.

## 11. Verification of Calibration

11.1 To determine if the instrument is functioning properly, the calibration can be checked by determining the recovery value for a known amount of water as follows: carefully inject 5  $\mu$ L of water below the surface of the titration solution using a 5- $\mu$ L syringe. Titrate the water added. The instrument should indicate  $5000 \pm 250 \mu\text{g}$ .

## 12. Procedure

12.1 Assemble a dry syringe and needle and attach a small

piece of rubber septum to the needle tip. Obtain a tare weight to  $\pm 0.1$  mg. Withdraw 1 to 2 mL of the sample into the syringe and discard the contents into a waste container. Using the following table as a guide, withdraw the proper amount of sample into the syringe and seal with the rubber septum. Again weigh to  $\pm 0.1$  mg to determine the exact sample weight. See Note 3 and Note 4.

Expected Water Content	Sample Size, mL
0 to 500 ppm	5
500 to 1000 ppm	2
1000 to 2000 ppm	1
0.2 to 0.5 %	0.5
0.5 to 2.0 %	0.1

NOTE 3—If multiple analyses are performed on the same sample or if an appreciable volume of sample is withdrawn, a slight pressure should be maintained on the sample bottle by means of a hypodermic needle attached to a dry nitrogen source.

NOTE 4—Alternatively, if syringes of suitable accuracy are available, a measured volume of sample can be injected and the weight calculated from the volume and density.

12.2 With the analyzer stabilized carefully insert the needle of the sample syringe through the septum and below the level of solution in the titration chamber. Inject the sample slowly into the titration solution and begin titration. Rinse the syringe several times by backfilling with and discharging the titration solution to assure quantitative transfer of the sample. Withdraw the syringe needle. Allow the titration to proceed until the endpoint is indicated. Record the micrograms of water determined.

NOTE 5—After numerous analyses, the level of solvent accumulated in the titration chamber may have to be reduced. This can be accomplished with a 50-mL syringe or by partially draining the solution if the titration chamber is provided with a stopcock. Discard the solution and replace with fresh titration solution if a stable reading cannot be obtained.

NOTE 6—Replace the generator solution when it becomes yellow and a stable reading cannot be obtained.

### 13. Calculation

13.1 Calculate the water content of the sample to the nearest 0.001 % as follows:

$$\text{water content, \%} = \frac{\mu\text{g water found}}{\text{g sample} \times 10\,000} \quad (1)$$

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### 14. Report

14.1 Report the percentage of water to the nearest 0.001 %.

14.2 The coefficient of variation has been estimated at 1.39 % relative with 61 degrees of freedom (see Note 7). Duplicate determinations (same day) that agree within 3.9 % relative are acceptable for averaging (95 % probability).

### 15. Precision and Bias

15.1 *Precision*—The following criteria should be used to judge the acceptability of results (see Note 7):

15.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 1.39 % relative at 61 DF. The 95 % limit for the difference between two such runs is 3.9 % relative.

15.1.2 *Laboratory Precision (Within-Laboratory, Between Days Variability, formerly called repeatability)*—The coefficient of variation of results (each the average of duplicate determinations), obtained by the same analyst on different days, was estimated to be 2.00 % relative at 31 DF. The 95 % limit for the difference between two such averages is 5.6 % relative.

15.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicate determinations), obtained by analysts in different laboratories, has been estimated to be 6.12 % relative at 7 DF. The 95 % limit for the difference between two such averages is 17.1 % relative.

15.2 *Bias*—The bias of this test method has not been determined since no acceptable reference material has been identified.

NOTE 7—The above precision estimates are based on an inter-laboratory study on samples of toluene, ethyl acetate, ethanol, and acetonitrile, containing approximately 0.02, 0.16, 0.52, and 2.04 % water, respectively. One analyst in each of 8 laboratories performed duplicate determinations on two different days, for a total of 128 determinations. Five values for toluene were judged to be outliers. Practice E 180 and a special computer program for the analysis of variance of unbalanced nested experiment designs were used to develop these precision estimates.

### 16. Keywords

16.1 coulometric; Karl Fischer; organic liquids; water