



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

This standard is issued under the fixed designation E 1064; 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 covers the determination of water from 0 to 2.0 % mass in most liquid organic chemicals, with Karl Fischer reagent, using an automated coulometric titration procedure. Use of this test method is not applicable for liquefied gas products such as Liquid Petroleum Gas (LPG), Butane, Propane, Liquid Natural Gas (LNG), etc.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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:*<sup>2</sup>

**D 1193** Specification for Reagent Water

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

**E 203** Test Method for Water Using Volumetric Karl Fischer Titration

## 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 or other organic base and methanol or other 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.

## 4. Significance and Use

4.1 The coulometric technique is especially suited for determining low concentrations of water in organic liquids that 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. (See **Table 1** and Note 6.)

## 5. Interferences

5.1 Interfering substances are the same as are encountered in the volumetric Karl Fischer titration. A detailed discussion of interfering substances can be found in the treatise on "Aquametry."<sup>3</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>4</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

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.01 on General Standards.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</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>4</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).

**TABLE 1 Sample Size Estimation**

| Expected Water Content | Sample Size, mL |
|------------------------|-----------------|
| 0 to 500 mg/kg         | 5               |
| 500 to 1000 mg/kg      | 2               |
| 1000 to 2000 mg/kg     | 1               |
| 0.2 to 0.5 % mass      | 0.5             |
| 0.5 to 2.0 % mass      | 0.1             |

water present in the sample solution. The coulombs of electricity required to generate the reagent are converted to micrograms of water, which is obtained as a direct digital readout.

6.2 *Syringe*, 50-mL, fitted with an 115-mm hypodermic needle for removing excess solution from the titration chamber.

NOTE 1—Rinse all glass syringes and needles with anhydrous acetone after cleaning, then dry in an oven at 100°C for at least 1 h and store in a desiccator. Plastic syringes shall be disposed of following use.

6.3 *Syringe*, 20-mL, fitted with an 115-mm hypodermic needle for introduction of neutralizing solution into the titration chamber (see **Note 1**).

6.4 *Syringes*, 1- and 5-mL, fitted with 115-mm hypodermic needles for introduction of samples into titration chamber (see **Note 1**).

6.5 *Syringe*, 5  $\mu$ L, fitted with 115-mm hypodermic needle for standardization of instrument (see **Note 1**).

6.6 *Fluorocarbon Sealing Grease or TFE-Fluorocarbon*, 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. Replace serum caps and septa as required to prevent air leakage as indicated by instrument drift.

6.8 *Serum Bottles*.

6.9 *Oven*, temperature  $100 \pm 5^\circ\text{C}$ .

6.10 *Dessicator*, standard laboratory type with color change indicator.

6.11 *Analytical Balance*, capable of weighing to  $\pm 0.0001$  g.

## 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>5</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 *Karl Fischer Reagents*—Commercial coulometric KF reagents and reagent systems of various types are available for use with autotitrators for water determination. Traditionally,

pyridine was the organic base used in KF reagents. Pyridine-free formulations are available and are preferred by most KF instrument manufacturers for use with their equipment. The pyridine-free reagents are less toxic, less odorous, and more stable than those containing pyridine. The use of pyridine-free reagents is recommended whenever possible. Coulometric titrations normally require two reagent solutions. An anolyte or solvent titration solution and a catholyte or generator titrant solution. However, now reagents can be purchased in one or two component reagent systems. A one component reagent system contains all the components required for a Karl Fischer titration in a single solution. A two component system incorporates separate solutions for the solvent and titrant.

NOTE 2—Two good references on pyridine-free reagents are the Hydranal® Manual-Eugen Schotz Reagents for Karl Fischer Titration, from Riedel-deHaen ([www.rdhlab.de](http://www.rdhlab.de)) or Sigma Aldrich ([www.sigma-aldrich.com](http://www.sigma-aldrich.com)) and Moisture Measurement by Karl Fischer Titrimetry, 2nd ed., by GFS Chemicals, Inc., January 2004.

7.3.1 *Generator Titrant Solution (catholyte)*, containing iodine, sulfur dioxide, pyridine or other organic base and methanol or other alcohol to provide iodine in the reaction mixture.

7.3.2 *Solvent Titration Solution (anolyte)*, prepared as per instrument specifications.

7.3.3 *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 or other organic base, sulfur dioxide, and methanol or other alcohol. Wear chemical resistant gloves 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.

## 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. Allow to cool in a desiccator before filling and sealing.

9.1.2 Fill the sample bottle as rapidly as possible to within 25 mm of the top and immediately seal.

9.2 Remove the test specimens for analysis from the sample bottle with a dry hypodermic syringe. Inject dry nitrogen 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 or TFE-fluorocarbon 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.

<sup>5</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.

10.2 Prepare the titration solution (7.3.2) as directed by the instrument manufacturer and fill the instrument reservoir as directed by the manufacturer.

10.3 Add the generator solution (7.3.1) 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 3—Mitsubishi automatic moisture analyzers do 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 (7.3.3). 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 Different autotitrators may vary in calibration procedures. Consult the operating manual for the autotitrator in use. Stable, prepackaged Quality Control (QC) water standards are commercially available with 10 mg/kg, 100 mg/kg and 1 % (m/m) water content for this purpose. It is desirable to verify calibration with a standard solution that approximates the same range of water expected to be in the samples.

11.2 It is recommended that a control chart measuring a QC standard sample be established and maintained according to generally accepted guidelines.<sup>6</sup> Measure the control sample each time a test sample(s) is tested. If the measured value exceeds  $\pm 5$  % of the known amount, take appropriate action before proceeding with the sample test.

NOTE 4—This may require replacing or regenerating the reagent solutions.

<sup>6</sup> ASTM Manual on Presentation of Data and Control Chart Analysis, 7th Edition, ASTM Manual Series MNL 7A, (revision of Special Technical Publication (STP) 15D).

## 12. Procedure

12.1 Assemble a dry syringe and needle and attach a small piece of rubber septum to the needle tip. 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 test sample into the syringe and seal with the rubber septum. Obtain a tare weight to  $\pm 0.1$  mg. See Table 1, Note 5 and Note 6.

NOTE 5—If multiple analyses are performed on the same test sample or if an appreciable volume of test 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 6—Alternatively, if syringes of suitable accuracy are available, a measured volume of sample can be injected and the mass 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. Withdraw the syringe needle, seal and again weigh to the nearest  $\pm 0.1$  mg to determine the exact sample mass. Allow the titration to proceed until the end-point is indicated. Record the micrograms of water determined.

NOTE 7—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 8—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 % mass as follows:

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

## 14. Report

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

## 15. Precision and Bias

15.1 In 2007, ASTM International Committee E15 on Industrial and Specialty Chemicals conducted and completed Interlaboratory Study No. 52 to determine Precision data for six test methods used in the analysis of glycols. The precision of this test method is based on the interlaboratory study of E 1064, Standard Test Method for the Determination of Water in Organic Liquids by Coulometric Karl Fischer Titration, conducted in 2007. Each of seventeen laboratories were asked

TABLE 2 E 1064 Water in Organic Liquids by Coulometric Karl Fischer Titration

| Test Result % mass | Sample | Average over all Laboratories | Repeatability Standard Deviation | Intermediate Standard Deviation | Reproducibility Standard Deviation | Repeatability Limit | Intermediate Unit | Reproducibility Limit |
|--------------------|--------|-------------------------------|----------------------------------|---------------------------------|------------------------------------|---------------------|-------------------|-----------------------|
| Water              | MEG    | 0.0086                        | 0.0009                           | 0.0014                          | 0.0025                             | 0.0026              | 0.0038            | 0.0071                |
| Water              | DEG    | 0.0649                        | 0.0012                           | 0.0014                          | 0.0049                             | 0.0032              | 0.0039            | 0.0137                |
| Water              | TEG    | 0.0498                        | 0.0019                           | 0.0129                          | 0.0157                             | 0.0054              | 0.0361            | 0.0439                |

to test three different materials. Fourteen laboratories tested MEG, 13 laboratories tested DEG and 13 laboratories tested TEG. Every “test result” represents an individual determination. Two test results were conducted on each of two days for a total of four test results per assay. Note that in the combined study, 8 laboratories used a single analyst, 7 laboratories used two analysts (on different days) and 2 laboratories did not record this information. In the event that there were missing values for one or more laboratories, this information was noted in the results.<sup>7</sup>

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

**15.1.2 Reproducibility**—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 difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

**15.1.3 Intermediate Precision**—The day-to-day standard deviation within a laboratory for results produced by the same operator, determined through statistical analysis following ASTM E 180, Standard Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals. E 180 was used to conform to this particular study design which required an estimate of intermediate precision.

The statistical analysis was conducted using the SAS statistical analysis software, Version 8.0.

**15.1.3.1** The E 180 analysis considers the two test results from each day as being run under repeatability, intermediate, and reproducibility precision for each assay. The repeatability precision would be estimated from the two sets of duplicate test results within each day, and the intermediate precision would be estimated from the agreement between the two days, all pooled over laboratories. Caveat: Since two days is a short time period, the intermediate precision would probably be underestimated by the E 180 analysis.

**15.1.4** Any judgment in accordance with these two statements would have an approximate 95 % probability of being correct.

**15.2 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.

**15.3** The precision statement was determined through statistical examination of qualified results, from seventeen laboratories, on three materials. These three materials were described as the following:

Fluid 1: Monoethylene Glycol

Fluid 2: Diethylene Glycol

Fluid 3: Triethylene Glycol

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

## 16. Keywords

16.1 coulometric; Karl Fischer; organic liquids; pyridine; pyridine-free; water

<sup>7</sup> The details of this study are given in ASTM Research Report No. E15-1062.

## SUMMARY OF CHANGES

Committee E15 has identified the location of selected changes to this standard since the last issue (E 1064-05) that may impact the use of this standard.

(1) A new Precision and Bias section was added.

(2) Table 2 was added.

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