



# 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

*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

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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).

\*A Summary of Changes section appears at the end of this standard.

**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°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<sup>®</sup> 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.