Designation: E1064 – 24

Standard Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration[1]

This standard is issued under the fixed designation E1064; 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.

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 Safety Data Sheets (SDS) 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 8.

1.5 *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

D4672 Test Method for Polyurethane Raw Materials: Determination of Water Content of Polyols

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E203 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 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 5.)

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."[4]

[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.04 on Instrumental Analysis.

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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] 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.

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

TABLE 1 Sample Size Estimation

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

5.2 Test Method E203 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,*[5] 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 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 mL and 5 mL, fitted with 115 mm hypodermic needles for introduction of samples into titration chamber (see Note 1).

6.5 *Syringe,* 5 µL, 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 °C ± 5 °C.

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

6.11 *Analytical Balance,* capable of weighing to ±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.[6] 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 I or Type II reagent water, conforming to Specification D1193.

7.3 *Karl Fischer Reagents*—Commercial pyridine-free coulometric KF reagents and reagent systems of various types are available for use with autotitrators for water determination. 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®[7] Manual-Eugen Schotz Reagents for Karl Fischer Titration, from Riedel-deHaen (www.rdhlab.de) or Sigma Aldrich (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, 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_2O/mL.

8. Safety Precautions

8.1 The reagents contain one or more of the following: iodine, 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.

[5] 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).

[6] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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] Hydranal® is a registered trademark of Sigma-Aldrich, Inc, St. Louis, MO.