Designation: E 203 – 08

Standard Test Method for Water Using Volumetric Karl Fischer Titration[1]

This standard is issued under the fixed designation E 203; 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 intended as a general guide for the application of the volumetric Karl Fischer (KF) titration for determining free water and water of hydration in most solid or liquid organic and inorganic compounds. This test method is designed for use with automatic titration systems capable of determining the KF titration end point potentiometrically; however, a manual titration method for determining the end point visually is included as Appendix X1. Samples that are gaseous at room temperature are not covered (see Appendix X4). This test method covers the use of both pyridine and pyridine-free KF reagents for determining water by the volumetric titration. Determination of water using KF coulometric titration is not discussed. By proper choice of the sample size, KF reagent concentration and apparatus, this test method is suitable for measurement of water over a wide concentration range, that is, parts per million to pure water.

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

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.* Specific warnings are given in 3.1 and 7.3.3.

1.4 Review the current Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions for chemicals used in this test procedure.

2. Referenced Documents

2.1 A list of existing ASTM Karl Fischer methods, their applications to various products, and the sponsoring committees is given in Appendix X3.

2.2 *ASTM Standards:*[2]

D 789 Test Methods for Determination of Solution Viscosities of Polyamide (PA)
D 803 Test Methods for Testing Tall Oil
D 890 Test Method for Water in Liquid Naval Stores
D 1123 Test Methods for Water in Engine Coolant Concentrate by the Karl Fischer Reagent Method
D 1152 Specification for Methanol (Methyl Alcohol)
D 1193 Specification for Reagent Water
D 1348 Test Methods for Moisture in Cellulose
D 1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)
D 1533 Test Method for Water in Insulating Liquids by Coulometric Karl Fischer Titration
D 1568 Test Methods for Sampling and Chemical Analysis of Alkylbenzene Sulfonates
D 1631 Test Method for Water in Phenol and Related Materials by the Iodine Reagent Method
D 2072 Test Method for Water in Fatty Nitrogen Compounds[3]
D 2575 Methods of Testing Polymerized Fatty Acids[3]
D 3277 Test Methods for Moisture Content of Oil-Impregnated Cellulosic Insulation
D 3401 Test Methods for Water in Halogenated Organic Solvents and Their Admixtures
D 4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method
D 4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration
D 4672 Test Methods for Polyurethane Raw Materials: Determination of Water Content of Polyols
D 4928 Test Methods for Water in Crude Oils by Coulometric Karl Fischer Titration
D 5460 Test Method for Rubber Compounding Materials—

[1] 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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[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] Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

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

Water in Rubber Additives
D 5530 Test Method for Total Moisture of Hazardous Waste Fuel by Karl Fischer Titrimetry
D 6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration
E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals
E 1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

3. Summary of Test Method

3.1 The sample, containing a maximum of 100 mg of water, is dissolved or dispersed in a suitable liquid and titrated with KF reagent, which consists of iodine, sulfur dioxide, organic base, and a solvent (typically an alcohol, such as methanol, ethylene glycol, or 2-methoxyethanol). The titration end point is determined potentiometrically with a platinum electrode which senses a sharp change in cell resistance when the iodine is reduced by sulfur dioxide in the presence of water. (**Warning—**KF reagent contains four toxic compounds, namely, iodine, sulfur dioxide, pyridine or other organic bases, and methanol or glycol ether. The reagent should be dispensed in a well-ventilated area. Care must be exercised to avoid inhalation of the reagent or direct contact of the reagent with the skin.)

3.2 The general equation to this reaction is as follows:

$$H_2O + I_2 + SO_2 + R'OH + 3\,RN > (RNH)SO_4R' + 2(RNH)I \quad (1)$$

where:
RN = an organic base such as pyridine, and
R′OH = alcohol.

4. Significance and Use

4.1 Titration techniques using KF reagent are one of the most widely used for the determination of water.

4.2 Although the volumetric KF titration can determine low levels of water, it is generally accepted that coulometric KF titrations (see Test Method E 1064) are more accurate for routine determination of very low levels of water. As a general rule, if samples routinely contain water concentrations of 500 mg/kg or less, the coulometric technique should be considered.

4.3 Applications can be subdivided into two sections: (*1*) organic and inorganic compounds, in which water may be determined directly, and (*2*) compounds, in which water cannot be determined directly, but in which interferences may be eliminated by suitable chemical reactions or modifications of the procedure. Further discussion of interferences is included in Section 5 and Appendix X2.

4.4 Water can be determined directly in the presence of the following types of compounds:

Organic Compounds
Acetals
Acids (Note 1)
Acyl halides
Alcohols
Aldehydes, stable (Note 2)
Amides
Amines, weak (Note 3)
Anhydrides
Disulfides
Esters
Ethers
Halides
Hydrocarbons (saturated and unsaturated)
Ketones, stable (Note 4)
Nitriles
Orthoesters
Peroxides (hydro, dialkyl)
Sulfides
Thiocyanates
Thioesters

Inorganic Compounds
Acids (Note 5)
Acid oxides (Note 6)
Aluminum oxides
Anhydrides
Barium dioxide
Calcium carbonate
Cupric oxide
Desiccants
Hydrazine sulfate
Salts of organic and inorganic acids (Note 6)

NOTE 1—Some acids, such as formic, acetic, and adipic acid, are slowly esterified. For high accuracy with pyridine-based reagents, use 30 to 50 % pyridine in methanol as the solvent. When using pyridine-free reagents, commercially available buffer solutions[4] can be added to the sample prior to titration. With formic acid, it may be necessary to use methanol-free solvents and titrants (**1**).[5]

NOTE 2—Examples of stable aldehydes are formaldehyde, sugars, chloral, etc. Formaldehyde polymers contain water as methylol groups. This combined water is not titrated. Addition of an excess of $NaOCH_3$ in methanol permits release and titration of this combined water, after approximate neutralization of excess base with acetic acid (see Note 9).

NOTE 3—Weak amines are considered to be those with K_b value $<2.4 \times 10^{-5}$.

NOTE 4—Examples of stable ketones are diisopropyl ketone, camphor, benzophenone, benzil, dibenzolacetone, etc.

NOTE 5—Sulfuric acid up to a concentration of 92 % may be titrated directly; for higher concentrations see Note 13.

NOTE 6—Compounds subject to oxidation-reduction reactions in an iodine-iodide system interfere.

5. Interferences

5.1 Condensation and oxidation-reduction reactions cause interference in this titrimetric method. Also, a number of substances and classes of compounds interfere in the determination of water by this method. Complete descriptions may be found in the literature (**2**).

5.2 Interferences of many classes of compounds can be eliminated by chemical reactions to form inert compounds prior to titration. The following are in this category:

Aldehydes and ketones, active (Note 7)
Amines, strong (Note 8)
Ammonia (Note 9)
Ferric salts (Note 10)
Hydrazine derivatives (Note 9)
Hydroxylamine salts (Note 11)
Mercaptans (Note 12)
Sodium methylate (Note 9)
Sulfuric acid (Note 13)
Thioacids (Note 12)
Thiourea (Note 12)

NOTE 7—This interference may be reduced by use of pyridine rather than methanol as solvent for the same or by the use of KF reagent and solvent prepared with ethylene glycol monomethyl ether in place of methanol. For pyridine-free reagents, use ethylene glycol monomethyl-ether, ethylene glycol, benzyl alcohol or dimethylformamide in place of the methanol solvent and use a methanol-free titrant (**1**). The cyanhydrin reaction may be used to eliminate the interference (**2**).

NOTE 8—Strong amines are considered to be those with $K_b$value $>2.4 \times 10^{-5}$. Use salicylic acid-methanol solution (Section 7). Glacial acetic acid is applicable in certain cases.

NOTE 9—Addition of acetic acid eliminates the interference.

[4] Cresent Chemicals, 1324 Motor Parkway, Hauppauge, NY, 11788, Hydranal® buffer has been found satisfactory.

[5] The boldface numbers in parentheses refer to the list of references at the end of this test method.

NOTE 10—Ferric fluoride does not interfere. Reaction with 8-hydroxyquinoline is reported to eliminate this interference (**3**).

NOTE 11—With pyridine-based reagent, add 1 mol/L SO_2 in 1 + 1 pyridine-methanol or spent KF reagent. With pyridine-free reagents, the two component reagent methods should be used and 1 mL of sulfuric acid is added to the solvent prior to titration (Note 15).

NOTE 12—Olefin addition reaction eliminates interferences (**2**). Oxidation with neutral iodine solution eliminates the interference of mercaptans (**4**).

NOTE 13—Sulfuric acid, above 92 %. Add the sample (10 g) to a large excess of pyridine (35 mL), swirl to dissolve precipitate, and titrate. Addition of 8 mL of 1 + 1 pyridine-dioxane/1 g of sample also is satisfactory, maintaining a homogeneous solution throughout the titration.

5.3 If there is a question of compounds listed in 5.2 causing an interference, the recovery of spiked additions of water to the sample matrix should be checked.

5.4 Many materials react stoichiometrically with KF reagent. When their concentration is known, suitable corrections can be applied. A list of such materials is given in Appendix X2.

6. Apparatus

6.1 Karl Fischer Volumetric Titrator,[6] consisting of a titration cell, dual platinum electrode, magnetic stirrer, dispensing buret and control unit. Many manufacturers of general purpose laboratory titrators offer optional accessories that allow their instrument to perform KF titrations.

7. Reagents

7.1 *Purity of Reagents*—Use reagent grade chemicals in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society[7] where such specifications are available. 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, references to water shall mean reagent water as defined by Type II and III of Specification D 1193.

7.3 *Karl Fischer Reagents*—Traditionally, pyridine was the organic base used in KF reagents. Pyridine-free formulations, however, are available now and are preferred by most KF instrument manufacturers for use with their equipment. These reagents are less toxic, less odorous, and more stable than those containing pyridine. The use of pyridine-free reagents is recommended whenever possible.

7.3.1 *Pyridine-Free Karl Fischer Titrant*—Typically consists of a mixture of an organic base, sulfur dioxide and iodine dissolved in a solvent such as methanol or 2-methoxyethanol. Reagents with titers of 1.00, 2.00, and 5.00 mg H_2O/mL can be commercially obtained.

7.3.2 *Pyridine-Free Karl Fischer Solvent*[8]—Anhydrous methanol is the most frequently used solvent, however, other alcohols including glycols and glycol ethers are used. Some commercially available solvents also contain an organic base and sulfur dioxide.

7.3.3 *Karl Fischer Reagent Containing Pyridine*—The KF reagent may be either prepared in the laboratory or purchased. Two types of reagent are commonly used. Directions for preparing these and diluting if necessary, along with commercial sources of supply, are as follows: (**Warning—**Follow standard precautions for handling toxic gases in preparing the reagents (*1*) or (*2*) as described in 7.3.3.1 and 7.3.3.2. Carry out all operations in a hood. Wear rubber gloves and a face shield when handling pyridine and sulfur dioxide and when mixing chemicals. Special precautions must be observed when dispensing sulfur dioxide to prevent drawback of the solution into the gas cylinder, which might cause an explosion. This is best accomplished by placing a trap in the line between the gas cylinder and absorption vessel.)

7.3.3.1 *Karl Fischer Reagent (Ethylene Glycol Monomethyl Ether Solution, 1 mL = 6 mg H_2O) (2)*—For each litre of solution, dissolve 133 ± 1 g iodine in 425 ± 5 mL of pyridine in a dry glass-stoppered bottle. Add 425 ± 5 mL of ethylene glycol monomethyl ether. Cool to below 4°C in an ice bath. Bubble 102 to 105 g of gaseous sulfur dioxide (SO_2) into the cooled mixture. Determine the amount of SO_2 added by the change in weight of the SO_2 cylinder or the increase in volume (about 70 mL) of the reagent mixture. Alternatively, add about 70 mL of freshly drawn liquid SO_2 in small increments. Mix well and set aside for at least 12 h before using. (**Warning—**see 7.3.3.)

7.3.3.2 *Karl Fischer Reagent (Methanol Solution, 1 mL = 6 mg H_2O)*—For each litre of solution, dissolve 133 ± 1 g of iodine in 425± 5 mL of pyridine in a dry, glass-stoppered bottle. Add 425 ± 5 mL of methanol. Cool the mixture in an ice bath to below 4°C. Bubble 102 to 105 g of gaseous sulfur dioxide (SO_2) into the cooled mixture. Determine the amount of SO_2 added by the change in weight of the SO_2 cylinder or the increase in volume (about 70 mL) of the reagent mixture. Alternatively, add about 70 mL of freshly drawn liquid SO_2 in small increments. Mix well and set aside for at least 12 h before using. (**Warning—**see 7.3.3.)

7.3.3.3 *Karl Fischer Reagent (Ethylene Glycol Monomethyl Solution, Stabilized*, 1 mL = 6 mg H_2O).[9,10]

7.3.3.4 *Karl Fischer Reagent, Dilute*—Prepare more dilute solutions of the KF reagent by diluting with the proper solvent as follows:

Desired Strength, mg H_2O/mL	Litres of Diluent to Add/litre of 6 mg/mL KF reagent
3	0.85
2	1.6

[6] Automatic volumetric titrators specifically designed for KF determinations are manufactured by many different companies. Models are available from EM Science, Metrohm, Mettler, Photovolt, Mitsubishi, and others.

[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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[8] Pyridine-free KF reagents can be purchased from Cresent Chemical, JT Baker, EM Science, GFS Chemicals, and others.

[9] Fisher Scientific Co., Catalog No. SK 3-500 has been found satisfactory for this purpose.

[10] Mallinckrodt Catalog No. 5651 has been found satisfactory for this purpose.