Designation: E203 – 24

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

This standard is issued under the fixed designation E203; 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 U.S. 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 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific warnings are given in 3.1.

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

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 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]

D803 Test Methods for Testing Tall Oil

D890 Test Method for Water in Liquid Pine Chemicals

D1123 Test Methods for Water in Engine Coolant Concentrate by the Karl Fischer Reagent Method

D1193 Specification for Reagent Water

D1348 Test Methods for Moisture in Cellulose (Withdrawn 2017)[3]

D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)

D1533 Test Method for Water in Insulating Liquids by Coulometric Karl Fischer Titration

D1568 Test Methods for Sampling and Chemical Analysis of Alkylbenzene Sulfonates (Withdrawn 2023)[3]

D1631 Test Method for Water in Phenol and Related Materials by the Iodine Reagent Method

D2072 Test Method for Water in Fatty Nitrogen Compounds (Withdrawn 2007)[3]

D2575 Methods of Testing Polymerized Fatty Acids (Withdrawn 2007)[3]

D3277 Test Methods for Moisture Content of Oil-Impregnated Cellulosic Insulation (Withdrawn 2010)[3]

D3401 Test Methods for Water in Halogenated Organic Solvents and Their Admixtures

D4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method

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

D4928 Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration

D5460 Test Method for Rubber Compounding Materials—Water in Rubber Additives

[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.

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

D5530 Test Method for Total Moisture of Hazardous Waste Fuel by Karl Fischer Titrimetry
D6304 Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration
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]
E1064 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, 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, 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 E1064) 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. When using pyridine-free reagents, commercially available buffer solutions can be added to the sample prior to titration. With formic acid, it may be necessary to use methanol-free solvents and titrants (**1**).[4]

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—Use ethylene glycol monomethylether, 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.

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

NOTE 11—The two component reagent methods should be used and 1 mL of sulfuric acid is added to the solvent prior to titration (Note 15).

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