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Standard Test Method for Water Using Volumetric Karl Fischer Titration¹

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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 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, health, and environmental 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 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

~~D789 Test Method for Determination of Relative Viscosity of Concentrated Polyamide (PA) Solutions~~

D803 Test Methods for Testing Tall Oil

D890 Test Method for Water in Liquid Pine Chemicals

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.

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

- D1123 Test Methods for Water in Engine Coolant Concentrate by the Karl Fischer Reagent Method
- ~~D1152 Specification for Methanol (Methyl Alcohol) (Withdrawn 2021)³~~
- 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
- ~~D4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration (Withdrawn 2020)³~~
- 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
- 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, 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.)

<https://standards.iteh.ai/catalog/standards/sist/beece7ab-7d81-42a8-b881-7c3a760cc554/astm-e203-23>

3.2 The general equation to this reaction is as follows:



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 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.

³ The last approved version of this historical standard is referenced on www.astm.org.

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

Acetals	Organic Compounds	Ethers
Acids (Note 1)		Halides
Acyl halides		Hydrocarbons (saturated and unsaturated)
Alcohols		Ketones, stable (Note 4)
Aldehydes, stable (Note 2)		Nitriles
Amides		Orthoesters
Amines, weak (Note 3)		Peroxides (hydro, dialkyl)
Anhydrides		Sulfides
Disulfides		Thiocyanates
Esters		Thioesters
	Inorganic Compounds	
Acids (Note 5)		Cupric oxide
Acid oxides (Note 6)		Desiccants
Aluminum oxides		Hydrazine sulfate
Anhydrides		Salts of organic and inorganic acids (Note 6)
Barium dioxide		
Calcium carbonate		

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 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 NaOCH₃ 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 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).

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

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—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,⁵ 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 Society⁶ 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 H and HHI or II of Specification D1193.

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 $\text{H}_2\text{O}/\text{mL}$ can be commercially obtained.

7.3.2 *Pyridine-Free Karl Fischer Solvent*—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

⁵ Automatic volumetric titrators specifically designed for KF determinations are manufactured by many different companies. Models are available from Metrohm, Mettler, Photovolt, Mitsubishi, and others.

⁶ *Reagent Chemicals, American Chemical Society Specifications, 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. (USP); (USPC), Rockville, MD.

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 H₂O) (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 g to 105 g of gaseous sulfur dioxide (SO₂) into the cooled mixture. Determine the amount of SO₂ added by the change in weight of the SO₂ cylinder or the increase in volume (about 70 mL) of the reagent mixture. Alternatively, add about 70 mL of freshly drawn liquid SO₂ 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 H₂O)—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 g to 105 g of gaseous sulfur dioxide (SO₂) into the cooled mixture. Determine the amount of SO₂ added by the change in weight of the SO₂ cylinder or the increase in volume (about 70 mL) of the reagent mixture. Alternatively, add about 70 mL of freshly drawn liquid SO₂ 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 H₂O).

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 ₂ O/mL	Litres of Diluent to Add/litre of 6 mg/mL KF reagent
3	0.85
2	1.6
1	3.2
0.5	5.7

These dilute solutions cannot be prepared by simple proportion, since water added with the diluent must be accounted for. The volumes to add, indicated above, are calculated assuming the diluent contains 0.05 % water.

7.4 Water Standard (1 mL = 1 mg H₂O)—This solution can be stored conveniently in a bottle with rubber cap and portions removed with a hypodermic syringe. Single use standards stored in ampoules are also acceptable for use.

7.5 Sodium Tartrate Dihydrate—Grind certified material (water content 15.61% to 15.71%) to a fine powder (preferably overnight in a sealed ball mill) and store the ground material in a stoppered bottle. If doubt exists as to its water content, dry a 2 to 3 -g sample in an oven at $155 \pm 5^\circ\text{C}$ to constant weight (min 4 h). (See **Note 16**.)

7.6 Solvents:

7.6.1 Acetic Acid, glacial.

7.6.2 Ethylene Glycol Monomethyl Ether, maximum 0.1 % water. (See **Note 1**.)

7.6.3 Methanol, max 0.15 % water, in accordance with Specification 0.15 mass % water. **D1152**. (See **Note 1**.)

7.6.4 Pyridine, maximum 0.1 % water. (See **Note 1**.)

7.7 Solvents, Mixed—In addition to the single solvents (7.6), (7.6), the following mixed solvents are useful for dissolving various samples:

7.7.1 Methanol—Chloroform (1 + 3)—Mix 1 volume of methanol with 3 volumes of chloroform. Use for liquid petroleum products.

7.7.2 Methanol—Salicylic Acid—Dissolve 150 g of salicylic acid in 1 L of methanol. Use for amines.

7.7.3 *Pyridine—Ethylene Glycol (1 + 4)*—Mix 1 volume of pyridine with 4 volumes of ethylene glycol. Use for compounds containing carbonyl groups.

7.7.4 *Pyridine—Methanol (1 + 4)*—Mix 1 volume of pyridine with 4 volumes of methanol. Use for organic acids.

7.8 *Sulfur Dioxide*, anhydrous grade. (See **Note 1** and **7.3.3**.)

8. Drying of Solvents

8.1 If it is necessary to prepare dry solvents in the laboratory, the following three methods can be used:

8.1.1 *Azeotropic Distillation Using Benzene*, to reduce the moisture to 0.05 %. Add 1 volume of benzene to 19 volumes of pyridine, ethylene glycol monomethyl ether, or mixtures thereof, and distill. Discard the first 5 % and use the dry residual 95 %.

8.1.2 *Molecular Sieves*—Solvents *other than methanol* may be dried to a moisture content of 0.05 % by passing upward through a molecular sieve column, using 1 part molecular sieve per 10 parts of solvent.

9. End Point Detection

9.1 There are many commercial titration assemblies on the market that are specifically designed for performing volumetric type KF titrations. All that is required of these units is pressing a “start titration” or “start” key on the instrument keyboard just prior to or after the sample has been added to the titration cell. End point detection is automatic and the amount of water in the sample is calculated once the operator enters the sample weight into the instrument’s memory. The method for color end point detection is given in **Appendix X1**.

10. Procedure for Soluble Materials, Either Liquid or Solid

10.1 Pipet 2525 mL to 50 mL of the selected solvent into the titration cell. Titrate the water in the solvent with KF reagent according to the instrument manufacturer’s instructions. The KF reagent that is used should be of appropriate titer as determined by the amount of water anticipated in the sample (see **10.2**).

10.2 Weigh or pipet a sample containing an anticipated water content that will give a fast and accurate titration. KF instrument operation manuals typically list suggested sample sizes, however, **Table 1** also can be used as a guideline for sample sizes of the three most common titrant titers. Keep in mind that very small sample amounts may be difficult to accurately weigh and transfer, whereas, very large sample amounts may result in incomplete miscibility with the chosen solvent.

NOTE 14—The KF technique described here is sometimes referred to as the “one component” method because all the reagents are in the titrant, and the solvent is used basically as a medium to dissolve the sample. There is also a “two component” KF volumetric titration in which the titrant contains the usual reagents, but the solvent also contains sulfur dioxide and a base. There are advantages to the two component system since strongly basic or acid samples can overcome the buffering capacity of the single component system and cause the pH of the reaction mixture to shift from the optimum range. The two component system provides initial sample buffering capacity in the solvent which may provide a faster reaction time. Rapid end point determination also can provide more accurate measurement of trace water concentrations. Two component reagents, however, are more susceptible to side reaction from noncomplexed sulfur dioxide than single component systems (**5**).

TABLE 1 Recommended Sample Amount

Water Content	1 mg H ₂ O/mL Titrant	2 mg H ₂ O/mL Titrant	5 mg H ₂ O/mL Titrant
100 %	25 to 50 mg
100 %	25 mg to 50 mg
10 %	25 to 50 mg	25 to 100 mg	50 to 250 mg
10 %	25 mg to 50 mg	25 mg to 100 mg	50 mg to 250 mg
1 %	0.1 to 0.5 g	0.2 to 1 g	0.5 to 2.5 g
1 %	0.1 g to 0.5 g	0.2 g to 1 g	0.5 g to 2.5 g
0.1 %	1 to 5 g	2 to 10 g	5 to 20 g
0.1 %	1 g to 5 g	2 g to 10 g	5 g to 20 g
100 ppm	5 to 10 g	10 to 20 g	...
100 ppm	5 g to 10 g	10 g to 20 g	...
25 ppm	>20 g

NOTE 15—The range of water indicated is for macro titrations. Considerably smaller amounts of water can be determined precisely on a micro scale. For example, less than 300 µg of water were titrated in ± 1 mL samples of benzene by a micro amperometric technique (6).

10.3 *Calculation*—Calculate the water content of the sample as follows:

$$\text{water, weight \%} = \frac{(A - B) \times F \times 0.001 \times 100}{W} \quad (2)$$

$$\text{water, \%mass} = \frac{(A - B) \times F \times 0.001 \times 100}{W} \quad (2)$$

where:

- A = millilitres of reagent required for titration of the sample,
- B = millilitres of reagent required to titrate solvent blank,
- F = water equivalent, in milligrams of water per millilitre of KF reagent, and
- W = grams of sample.

11. Standardization of Karl Fischer Reagent

11.1 Standardize the KF reagent daily or as necessary using the amounts of water, sodium tartrate dihydrate, or water-in-methanol shown below:

Water Equivalent F, mg/mL	Water, mg	Sodium Tartrate Dihydrate, g	Water-in-Methanol, Standard, mL
0.5	2.5–10	0.015–0.060	2.5–10
1	5–20	0.30–0.12	5–20
2	10–40	0.06–0.24	10–40
5	25–100	0.15–0.6	...

11.2 Pipet ± 0.01 mL to 50 mL of methanol or appropriate solvent to a clean, dry titration cell and pretitrate according to the instrument manufacturer's instructions.

11.3 Transfer the selected standard to the pretitrated solvent.

11.3.1 Weigh, to the nearest 0.0001 g, the indicated amount of water from a suitable weighing pipet, hypodermic syringe, or other device, or

11.3.2 Transfer the weighed sodium tartrate dihydrate by means of a dry spatula, dipping the spatula into the alcohol to ensure removal of any adhering tartrate (Note 16), or

11.3.3 Use a hypodermic syringe of suitable capacity to transfer the standard water-in-methanol solution to the titration flask.

NOTE 16—To facilitate transferral of the tartrate to vessels having constricted openings or narrow necks, a spatula with the tip bent at a right angle to the handle is satisfactory. If the tartrate is used for standardizing Karl Fischer reagent for use with samples containing more than 1 % water, a bias may exist which has been described in Ref (7).

11.4 Titrate with KF reagent to the instrument manufacturer's instructions.

11.5 *Calculation*—Calculate the water equivalent, *E*, of the KF reagent, in milligrams per millilitre, as follows: *Water as Standard*:

$$F = 1000 \times \frac{G}{A} \quad (3)$$

Water-in-Methanol as Standard:

$$F = D \times \frac{E}{A} \quad (4)$$

Sodium Tartrate Dihydrate as Standard: