ENTERED

Colon, Vanessa, NMENV

From: Jeffrey Smith <jsmith@ACTEnviro.com>
Sent: Wednesday, February 20, 2019 4:20 PM
To: Colon, Vanessa, NMENV
Subject: [EXT] RE: ACT Treatment - ASTM Method manual
Attachments: ASTM E203.udda0545.pdf

Subject: ASTM Method doc.

Hi Vanessa,

Attached is the correct ASTM method document. Please let me know if you have any questions.

Thank you,

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From: Jeffrey Smith
Sent: Tuesday, February 19, 2019 8:17 PM
To: 'Colon, Vanessa, NMENV' <Vanessa.Colon@state.nm.us>
Subject: RE: ACT Treatment - ASTM Method manual

Hi Vanessa,

I will follow up tomorrow on this topic. A copy of the ASTM method did not come with our equipment so I purchased a copy. Unfortunately I purchased the wrong ASTM method and need to get it corrected tomorrow. I will forward it over as soon as I have it.

Thank you,

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Please print this email only if necessary.

From: Jeffrey Smith
Sent: Friday, February 15, 2019 1:58 PM
To: 'Colon, Vanessa, NMENV' <Vanessa.Colon@state.nm.us>
Subject: ACT Treatment - ASTM Method manual

Hi Vanessa,

We are still trying to track down a copy of the ASTM manual for our Karl Fischer machine. I have my documents lady looking and will have a copy to you one way or another on Tuesday 19th. My apologies for the delay.

Thank you,

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Designation: E203 – 16

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 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 Methods for Determination of Solution Viscosities of Polyamide (PA)

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

D1152 Specification for Methanol (Methyl Alcohol)

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

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

[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.

Current edition approved April 1, 2016. Published May 2016. Originally approved in 1962 as E203 – 62 T. Last previous edition approved in 2008 as E203 – 08. DOI: 10.1520/E0203-16.

[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**

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
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.)

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 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	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 $NaOCH_3$ 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 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 Society[6] 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 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 H_2O/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 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).

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
1	3.2
0.5	5.7

[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*, 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), Rockville, MD.

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 H_2O)—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 ± 5°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 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), 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—Salicyclic Acid*—Dissolve 150 g of salicyclic 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 25 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)**.

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:

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

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.

TABLE 1 Recommended Sample Amount

Water Content	1 mg H_2O/mL Titrant	2 mg H_2O/mL Titrant	5 mg H_2O/mL Titrant
100 %	...	...	25 to 50 mg
10 %	25 to 50 mg	25 to 100 mg	50 to 250 mg
1 %	0.1 to 0.5 g	0.2 to 11 g	0.5 to 2.5 g
0.1 %	1 to 5 g	2 to 10 g	5 to 20 g
100 ppm	5 to 10 g	10 to 20 g	...
25 ppm	>20 g	...	...

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 25 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:*

$$F = 1000 \times \frac{G}{A} \tag{3}$$

Water-in-Methanol as Standard:

$$F = D \times \frac{E}{A} \tag{4}$$

Sodium Tartrate Dihydrate as Standard:

$$F = 156.6 \times \frac{C}{A} \tag{5}$$

where:

G = grams of water used,
C = grams of sodium tartrate dihydrate used,
A = millilitres of reagent required for titration of the standard,
D = millilitres of water-in-methanol standard required, and
E = milligrams of water per millilitre in the water-in-methanol standard.

12. Procedure for Insoluble Solids

12.1 In case the sample is insoluble in the solvent or solvent mixture used, one of two modifications may be applied. The entire sample-solvent slurry may be titrated, or after stirring and standing, an aliquot of the clear supernatant liquid may be withdrawn and titrated. The latter modification is particularly useful for alkaline samples which are relatively insoluble in the solvent used (**8**).

12.2 Weigh the sample into a clean and dry titration cell, add 25 to 50 mL of the selected solvent (Section 7) and stopper the cell. Extract the water by stirring with a magnetic stirrer for 15 min or longer, or warming if indicated. Titrate the mixture at room temperature with KF reagent as described in 11.2 (Note 17). Also titrate the same volume of solvent as a blank.

NOTE 17—If desired, a known excess of KF reagent may be added to the cell, allowed to stand, and then back-titrated with standard water-in-methanol reagent, as described in Test Methods D1348.

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

$$\text{water, weight \%} = \frac{(A - B) \times F \times 0.001 \times 100}{W} \tag{6}$$

where:

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

12.4 Alternatively, add 50 to 100 mL of the solvent to the sample in a volumetric flask, stopper, and extract as before. Make up to the mark with solvent, mix, and allow to stand until clear. Transfer a suitable aliquot of the supernatant liquid to a titration cell, and titrate with KF reagent as described in 11.2. Also titrate the same volume of the solvent, as a blank.

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

$$\text{water, weight \%} = \frac{(A - B) \times F \times 0.001 \times 100 \times R}{W} \tag{7}$$

where:

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

13. Report

13.1 Report the percentage of water to the nearest 0.001 %.

14. Precision and Bias

14.1 Sensitivity, precision, and bias depend on several factors, for example, concentration of the KF reagent, titration technique, apparatus, quantity of water titrated, and nature of material being analyzed.

14.2 When using pyridine-based reagents, sensitivity is less than 0.02 mg of water when measurements are made using the amperometric endpoint.

14.3 The following (see Note 18) is an example of the precision attained at an interlaboratory study for determining water with pyridine-based reagents on two samples of acetone containing 0.1 % and 0.4 % water and two samples of methyl ethyl ketone containing 0.05 % and 0.17 % water.

14.3.1 *Repeatability (Single Analyst)*—The 95 % for the difference between two runs is 0.008 %.

14.3.2 *Laboratory Precision (Within-Laboratory, Between-Days, Variability)*—The 95 % limit for the difference between two averages of duplicates by the same analyst obtained on different days is 0.015 %.

14.3.3 *Reproducibility (Multiple Laboratory)*—The 95 % limit for the difference between two results (each the average of duplicates) obtained by analysts in different laboratories is 0.027 % absolute.

NOTE 18—The interlaboratory study was carried out by ASTM Committee D01 on Paint, Varnish, Lacquer, and Related Products, Subcommittee D01.35 on Solvents, Plasticizers, and Chemical Intermediates. Seven laboratories participated, with a single analyst performing duplicate determinations on each of two days, using two methods on the four samples described above. Test Method D1364 was the subject of the test program being compared with each laboratory's own version of a KF method. As neither the means nor the variances of the two sets of data proved significantly different, all of the results were pooled to give estimates of the repeatability based on 55 df and reproducibility based on 47 df. Practice E180 was used to develop the precision estimates.

14.4 The following is an example of the precision attained in an interlaboratory study for determining water with *pyridine-free reagents* on one sample each of *n*-butyl acetate and methyl amyl ketone (see Note 19).

14.4.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0034 % absolute at 40 df. The 95 % limit for the difference between two such runs is 0.010 % absolute.

14.4.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0050 % absolute at 20 df. The 95 % limit for the difference between two such averages is 0.014 % absolute.

14.4.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories has been estimated to be 0.0277 % absolute at 8 df. The 95 % limit for the difference between two such averages 0.078 % absolute.

NOTE 19—The above precision estimates are based on an interlaboratory study of analyses performed in 1994 on a sample of *n*-butyl acetate containing approximately 0.096 % water and a sample of methyl amyl ketone containing approximately 0.066 % water. One analyst in each of 12 laboratories performed duplicate determinations on the *n*-butyl acetate sample and repeated one day later, for a total of 48 determinations. The methyl amyl ketone sample was analyzed in a similar manner except 11 laboratories participated for a total of 44 determinations.[7] The analysts were not restricted to any particular instrumentation, titrant, or solvent system. Practice E180 was used in developing these precision estimates.

14.5 *Bias*—Because of the wide scope of this test method and varying degrees of interferences, it is impractical to estimate the bias of this test method.

15. Keywords

15.1 free water; Karl Fischer reagent; pyridine-free; volumetric; water; water of hydration

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1043. Contact ASTM Customer Service at service@astm.org.

APPENDIXES

(Nonmandatory Information)

X1. SUGGESTED APPARATUS FOR KARL FISCHER METHOD

X1.1 *Scope*—Described in this Appendix is a manual procedure for the KF method using a visual means of detecting the titration end point.

X1.2 *Titration Assembly:*

X1.2.1 The storage and dispensing assembly shall consist of the following parts (see Fig. X1.1):

X1.2.1.1 *Buret,* automatic, with TFE-fluorocarbon resin plug and automatic zero, reservoir bottle, and connecting tube. Select the size buret and bottle needed. An overhead reservoir with micro buret may also be used.

X1.2.1.2 *Tube, Drying,* calcium chloride, one bulb, 200 mm long.

X1.2.1.3 *Bottle, Aspirator,* with outlet for tubing connections, 500-mL capacity.

X1.2.1.4 *Stirrer, Magnetic,* with stirring bar coated with TFE-fluorocarbon resin.

X1.2.1.5 *Flask, Titration,* 250-mL capacity.

X1.2.1.6 *Rubber Cap,* 38 mm in outside diameter. Punch two holes, 3 to 4 mm in diameter, through the cap.

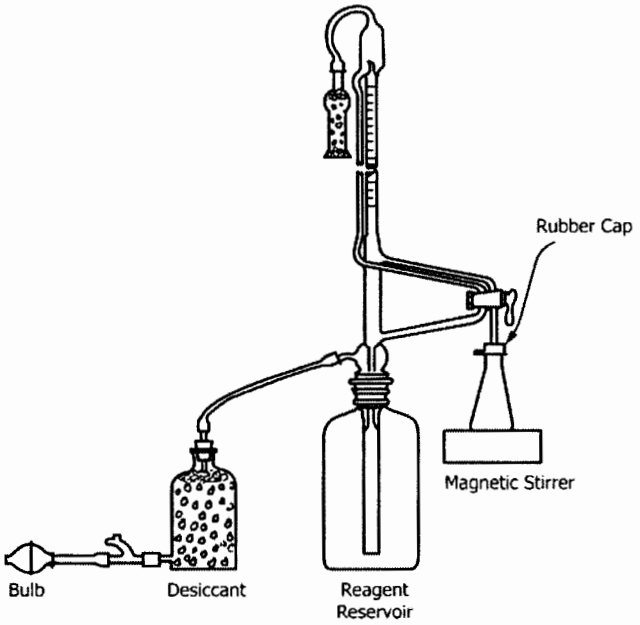
X1.3 *Assembly of Apparatus:*

X1.3.1 Assemble the apparatus as shown in Fig. X1.1. Fill the drying tube and aspirator bottle with desiccant. Insert the buret tip through one hole in the rubber cap. Use the other hole for inserting a pipet or hypodermic syringe containing liquid samples. Under humid conditions, keep the second hole plugged except when introducing a sample, or pass a slow stream of dry nitrogen into the flask.

X1.4 *Reagents*—Refer to Section 7.

X1.5 *Drying of Solvents* —Refer to Section 8.

X1.6 *End Point Detection:*



NOTE 1—Not to scale.

FIG. X1.1 Karl Fischer Titration Apparatus Assembly

X1.6.1 *Color End Point*—The titration to a visual end point is not as accurate or precise as the electrometric end point, and cannot be used for highly colored samples. It may be adequate, however, for routine determinations of water above 0.1 to 0.2 %, in a relatively colorless system. The end point is taken during titration when the color changes from yellow to orange-red and persists for at least 30 s. The sensitivity of this titration is about 0.1 mg of water.

X1.7 *Standardization of Karl Fischer Reagent:*

X1.7.1 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, g	Sodium Tartrate Dihydrase, g	Water-in-Methanol Standard, mL
0.5	0.01 to 0.02	0.1 to 0.15	10 to 20
1	0.03 to 0.05	0.2 to 0.3	30 to 50
3	0.09 to 0.15	0.6 to 0.9	...
6	0.18 to 0.30	1.1 to 1.9	...

X1.7.2 Pipet 25 to 50 mL of solvent to a clean, dry titration flask containing a stirring bar. Close the neck of the flask with a two-hole-rubber cap. Adjust the magnetic stirrer to give a smooth stirring action. Titrate with KF reagent to the color end point.

X1.7.3 Continue as described in 11.3 – 11.3.3.

X1.7.4 Titrate with KF reagent to the color end point.

X1.7.5 *Calculations*—Calculate the water equivalent, *F*, of the KF reagent as in 11.5.

X1.8 *Procedure for Soluble Materials, Either Liquid or Solid:*

X1.8.1 Pipet 25 to 50 mL of the selected solvent and proceed as in X1.7.2.

X1.8.2 Continue as described in 10.2, except use color end point.

X1.8.3 *Calculations*—Calculate water content of sample as in 10.3.

X1.9 *Report*—Report the percentage of water to nearest 0.01 %.

X1.10 *Procedure for Insoluble Solids*—Follow 12.1, 12.2, 12.3, 12.4, and 12.5, using color end point procedure.

X1.11 *Report*—Report the percentage of water to nearest 0.01 %.

X2. INTERFERING COMPOUNDS THAT REACT STOICHIOMETRICALLY WITH KF REAGENT, THEREBY ENABLING FREE WATER TO BE CALCULATED AFTER APPLYING CORRECTION

X2.1 Many interfering substances react stoichiometrically with constituents of the KF reagent. Consequently, when independent analyses can be made for these compounds, suitable corrections can be applied to the apparent water results. Also in many cases moisture can be separated from the interfering substance by extraction with a water-miscible liquid in which the sample is insoluble or by distillation, preferably using a carrier that forms a homogeneous azeotrope, for example, dioxane, ethanol-benzene. Materials in this class are given in Table X2.1.

X2.2 Some compounds react only partially with KF reagent when titrated under normal conditions. These include the following:[8,9]

Methylolurea[8]
Peroxides, diacyl[9]
Peracids[9]
Quinone
Arsenious oxide
Chromates
Dichromates
Iron oxide
Nickel oxide
Sodium peroxide
Sodium sulfide

[8] Interference of methylolurea can be eliminated by titration at – 40°C (2).

[9] Diacyl peroxides and peracids fairly rapidly oxidize the HL of spent KF reagent. After a short time interval following addition of KF reagent, this reaction may be quantitative (2).

TABLE X2.1 Materials Reacting Stoichiometrically With KF Reagent

Class or Compound	Moles of Apparent H_2O per Mole Compound	Do Not React
Ascorbic acid	1	
Hydrazine derivatives	1	hydrazine sulfate
Mercaptans	0.5	
Silanols, R_3SiOH	1	
$R_2Si(OH)_2$	2	
Arsenate, $RAsO_4$	3	
Arsenite, $RAsO_2$	2	
Boric acid, H_3BO_3	3	
HBO_2	2	
Boric oxide, B_2O_3	3	
Bicarbonates	1	
Carbonates	1	calcium carbonate
Cupric salts	0.5	
Ferric salts	0.5	ferric fluoride
Metal hydroxides, MOH	1	
$M(OH)_2$	2	
Metal oxides, CaO, MgO, ZnO, Ag_2O, HgO, Cu_2O, MnO_2, PbO^A, $PbO_2{}^A$	1	aluminum, cupric, barium oxides
Pb_3O_4	3	
Pyrosulfites	1	pyrosulfate
Sodium nitrite[B]	0.5	
Sulfites	1	hyposulfite
Stannous salts	1	
Tetraborate	7	
Thiosulfate	0.5	

[A] The lead oxides react only partially when dispersed in methanol, probably because of insolubility. In acetic acid solution, however, these oxides react quantitatively.

[B] Reaction is fairly slow. Apparently free water can be determined in presence of $NaNO_2$ by rapid titration with KF reagent.

X3. OTHER ASTM KARL FISCHER REAGENT WATER METHODS

Designation	Sponsoring Committee	Title of Method
D789	D20	Test Methods for Determination of Solution Viscosities of Polyamide (PA)
D803	D01	Test Methods for Testing Tall Oil
D890	D01	Test Method for Water in Liquid Naval Stores
D1123	D15	Test Method for Water in Engine Coolant Concentrate by the Karl Fischer Reagent Method
D1348	D01	Test Methods for Moisture in Cellulose
D1364	D01	Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)
D1533	D27	Test Method for Water in Insulating Liquids (Karl Fischer)
D1568	D12	Methods for Sampling and Chemical Analysis of Alkylbenzene Sulfonates
D1631	D16	Test Method for Water in Phenol and Related Materials by the Iodine Reagent Method
D2072	D01	Test Method for Water in Fatty Nitrogen Compounds
D2575	D01	Methods of Testing Polymerized Fatty Acids
D3277	D27	Test Methods for Moisture Content of Oil-Impregnated Cellulosic Insulation
D3401	D26	Test Method for Water in Halogenated Organic Solvents and Their Admixtures
D4017	D01	Test Method for Water and Paint Materials by Karl Fischer Method
D4377	D02	Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration
D4672	D20	Test Methods for Polyurethane Raw Materials: Determination of Water Content of Polyols
D4928	D02	Test Methods for Water in Crude Oils by Coulometric Karl Fischer Titration
D5460	D11	Test Method for Rubber Compounding Materials Water in Rubber Additives
D5530	D34	Test Method for Total Moisture of Hazardous Waste Fuel by Karl Fischer Titrimetry
D6304	D02	Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration
E1064	E15	Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

X4. DETERMINATION OF WATER IN GASES

X4.1 Procedures for determining moisture in gases are described in the literature **(2, 9, 10, 11, 12)**.

X4.2 As mentioned in Section 1, this test method does not include procedures for samples that are gaseous at room temperature. The safe handling and analysis of gases require a thorough knowledge of their properties and also the use or special apparatus and techniques. The moisture content may range from 1000 down to 2 to 3 mg/kg.

X4.3 The manufacturers of gases have developed very precise KF procedures for measuring moisture down to a few milligrams per kilograms **(11, 12)**. They should be consulted when need arises. Also, there are available commercial instruments that operate on the dew point, infrared, conductance, electrolysis principle, etc., which are rapid and accurate for determining moisture in gas samples **(2, 10)**.

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SUMMARY OF CHANGES

Subcommittee E15.01 has identified the location of selected changes to this standard since the last issue (E203-08) that may impact the use of this standard.

(1) Revised 7.4.
(2) Deleted vendor specific Footnotes 4, 8, 9, 10, 11, 12, 13, 15, 16, 17, 18, and 19.