Designation: D7923 – 17a

Standard Test Method for Water in Ethanol and Hydrocarbon Blends by Karl Fischer Titration[1]

This standard is issued under the fixed designation D7923; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the determination of water from 0.05 % to 5.0 % by mass in blends of ethanol, hydrocarbon, and corresponding blends. It is intended for measuring water content of gasoline or other hydrocarbon blendstock, denatured fuel ethanol as cited in Specification D4806, and ethanol fuel blends such as those cited in Specification D5798 and Practice D7794. This test method is not applicable to samples that are phase separated.

1.1.1 *Procedure A*—For measurement of water up to 2 % by mass in ethanol and hydrocarbon blends using coulometric Karl Fischer titration. This is the referee method for samples containing up to 2 % water.

1.1.2 *Procedure B*—For measurement of water up to 5.4 % by mass in ethanol and hydrocarbon blends using volumetric Karl Fischer titration.

1.2 This method measures mass percent water and allows for the alternative reporting of volume percent. This test method recommends the use of pyridine-free reagents.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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 precautionary statements are given in Section 8.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1152 Specification for Methanol (Methyl Alcohol)
D1193 Specification for Reagent Water
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D4806 Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
D5798 Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material
D7794 Practice for Blending Mid-Level Ethanol Fuel Blends for Flexible-Fuel Vehicles with Automotive Spark-Ignition Engines
E203 Test Method for Water Using Volumetric Karl Fischer Titration
E1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

3. Terminology

3.1 For general terminology, refer to Terminology D4175.

3.2 *Definitions:*

3.2.1 *denatured fuel ethanol, n*—fuel ethanol made unfit for beverage use by the addition of denaturants under formula(s) approved by the applicable regulatory agency to prevent the imposition of beverage alcohol tax. **D4806**

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Liquid Fuels and Lubricants.

Current edition approved July 1, 2017. Published July 2017. Originally approved in 2016. Last previous edition approved in 2017 as D7923 – 17. DOI: 10.1520/D7923-17A.

[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**

3.2.2 *hydrocarbon, n*—a compound composed solely of hydrogen and carbon. **D5798**

3.2.2.1 *Discussion*—The hydrocarbon mixtures used in ethanol fuel blends will be unleaded gasoline, gasoline blendstock for oxygenate blending (BOB), natural gasoline, or other hydrocarbons in the gasoline boiling range. The hydrocarbon blend components will also contain trace quantities of other elements.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *coulometric titration, n—in reference to Karl Fischer titration methods*, a process of measuring the water content of a sample using an electrolytic process to generate iodine in situ.

3.3.2 *pre-titration, n*—the process of adding titrant to react with any water in the Karl Fischer system so the system is totally dry prior to addition of a test sample.

3.3.3 *volumetric titration, n—in reference to Karl Fischer titration methods*, a process of measuring the water content of a sample by the physical delivery of a titration reagent containing iodine.

4. Summary of Test Method

4.1 This test method is based on the Karl Fischer (KF) reaction for determining water. Iodine is consumed by water in a one to one molar ratio in the presence of sulfur dioxide, organic base, and methanol or other alcohols. The coulometric method generates iodine from iodide by anodic oxidation while the iodine is already present in the volumetric KF reagents.

5. Significance and Use

5.1 Blends of fuel ethanol and hydrocarbon have a limited solvency for water that is dependent upon temperature and the ratio of ethanol to hydrocarbon. Good handling practices are important during the blending, storage, and transportation of fuel to avoid water contamination. High concentrations of water can cause haze or phase separation in ethanol and hydrocarbon blends and lead to freezing problems at low temperatures. Water has also been associated with corrosion and filter plugging.

6. Interferences

6.1 A number of functional groups are known to interfere with Karl Fischer titrations. In hydrocarbons, the most common interferences are mercaptans and sulfides. In ethanol, aldehydes and ketones are known to interfere with the Karl Fischer reagent. Some interferences can be mitigated with the use of applicable reagents. For fuel grade ethanol and gasoline in areas with stringent environmental regulations, the magnitude of the interference should be negligible under most circumstances. A list of several additional functional groups that can interfere with Karl Fischer titrations is included in the Appendix (X1.1.1).

7. Apparatus

7.1 *Automatic Titrator:*

7.1.1 *Coulometric Automatic Titrator,* consisting of a control unit, titration vessel, dual platinum sensing electrode, generator electrode assembly, and magnetic stirrer. The instrument is designed to coulometrically generate iodine that reacts stoichiometrically with the water present in the sample solution. The coulombs of electricity required to generate the reagent are converted to micrograms of water, which is obtained as a direct digital readout.

7.1.2 *Volumetric Automatic Titrator,* consisting of a control unit, titration vessel, dual platinum sensing electrode, dispensing buret, and magnetic stirrer. The instrument is designed to accurately dose an iodine containing titrant into the titration vessel that reacts stoichiometrically with the water present in the sample solution. The titrant solution is standardized to determine milligrams of water per milliliter of Karl Fischer reagent it will neutralize in the sample.

7.2 *Gas-tight Syringe,* fitted with a cannula needle of appropriate length and gauge for introducing sample into the titration chamber or removing excess solution from titration chamber (see Note 1). The syringe shall be made of glass or other suitably inert material. The volume of the syringe will depend on the sample size. When injecting by volume, the sample should occupy at least 25 % of the syringe volume.

7.2.1 Rinse all glass syringes and needles with dry methanol or ethanol after cleaning, then dry in an oven at 100 °C for at least 1 h and store in a desiccator.

7.3 *Sample Bottle,* suitable for collecting sample and maintaining an air-tight enclosure to prevent intrusion of atmospheric moisture.

7.4 *Oven,* temperature 100 °C ± 5 °C.

7.5 *Desiccator,* standard laboratory type with desiccant containing color change indicator.

7.6 *Analytical Balance,* capable of weighing to ±0.0001 g.

8. Safety Precautions

8.1 The reagents contain one or more of the following: iodine, organic base, sulfur dioxide, and methanol or other alcohol. Wear chemically resistant gloves when mixing the reagents and removing solution from the titration chamber. Exercise care to avoid inhalation of reagent vapors, or direct contact of the reagent with the skin.

9. Sampling

9.1 Sampling is defined as all of the steps required to obtain an aliquot representative of the contents of any pipe, tank or other system and to place the sample into a container for analysis by a laboratory or test facility. Sampling practices are covered in Practices D4057 and D4177.

9.2 Due to the low concentration of water to be measured, and the hygroscopic nature of ethanol, exercise care at all times to avoid contaminating the sample with moisture from the sample container, the atmosphere, or transfer equipment.

9.3 Samples shall be at room temperature at time of analysis.

9.4 Verify that samples are single phase before taking an aliquot to test. Water or water/ethanol blend will separate from hydrocarbon if the solubility limit is exceeded. The solubility limit depends on the gasoline makeup, concentration of ethanol or other emulsifiers, and sample temperature. Water is infinitely soluble in ethanol.

9.4.1 For a transparent container, this observation can be determined by visual inspection. If the material has two phases, shake the sample vigorously to combine. If the separate layer re-forms, the sample is not suitable for testing.

9.4.2 If the sample is contained in a non-transparent container, mix the sample and immediately pour a portion of the remaining sample into a clear glass container and observe for evidence of phase separation. If the separate layer forms, the sample is not suitable for testing.

9.4.3 Because of the volatile and hygroscopic nature of the samples, mixing with a mechanical or electronic mixer is not recommended.

9.5 Remove the test specimens for analysis from the sample bottle with a dry, inert gas-tight syringe.

PROCEDURE A (COULOMETRIC)

10. Reagents

10.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] 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.

10.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean Type II or Type III reagent water, conforming to Specification D1193, or better.

10.3 *Karl Fischer Reagents*—Commercial coulometric KF reagents and reagent systems of various types are available for use with autotitrators for water determination. Traditionally, pyridine was the organic base used in KF reagents. Pyridine-free formulations are available and are preferred by most KF instrument manufacturers for use with their equipment. The pyridine-free reagents are less toxic, less odorous, and more stable than those containing pyridine. The use of pyridine-free reagents is recommended whenever possible. Coulometric titrations normally require two reagent solutions: an anolyte and a catholyte or generator solution. However, with the use of an integrated or diaphragm-less cell, a single solution that contains all of the reagents needed for a KF titration may be used.

10.3.1 *Catholyte solution,* contains ammonium salts and methanol.

10.3.2 *Anolyte solution,* contains iodide, sulfur dioxide and imidazole buffer in a suitable solvent.

10.3.3 *One component solution,* iodide, sulfur dioxide, imidazole buffer, and bases in a suitable solvent. This solution may be used as the only solution in a coulometric system with a diaphragm-less generator cell or as the anolyte solution in a diaphragm cell if specified by the manufacturer.

10.3.4 *Water Standards,* 0.1 % by mass and 1 % by mass, commercially prepared in organic solvent recommended for this method.

11. Preparation of Apparatus

11.1 Clean, dry, and assemble the titration chamber as directed in the manufacturer's instructions. Care should be taken to ensure the vessel is sealed from atmospheric moisture. Replace the desiccant if saturated. Connect the leads from the sensing and generator electrodes to the titrator.

11.2 Add catholyte solution (10.3.1) to the generator electrode assembly and reseal the vessel according to manufacturer instructions.

11.3 Fill the anode reservoir with anolyte solution (10.3.2) as directed by the manufacturer. The level of the catholyte solution in the inner chamber shall be maintained slightly below the level of the anolyte solution to prevent backflow contamination of the titration (anolyte) solution. As samples are analyzed, the volume of the anolyte will increase. This may slow reactivity of the catholyte due to increased pressure across the membrane. A portion of the anolyte solution may have to be removed periodically to maintain the correct level. (Note 1)

NOTE 1—A coulometric system with a diaphragm-less generator electrode should be filled with the appropriate one component solution.

11.4 Agitate the titration solution by gently swirling the titration chamber to remove any residual moisture from the walls. Allow the solution to stir until inner atmosphere moisture is removed and the baseline has been established.

12. Verification of Calibration and Quality Control

12.1 Autotitrators vary in calibration procedures by manufacturer. Consult the operating manual for the autotitrator in use. Stable, prepackaged quality control (QC) water standards are commercially available with 0.1 % by mass and 1 % by mass water content for this purpose. It is desirable to verify calibration with a standard solution that approximates the same range of water expected to be in the samples.

12.2 It is recommended that a control chart measuring a QC standard sample be established and maintained according to generally accepted guidelines. Practice D6299 may be used for this purpose. Measure the control sample each day a sample(s) is tested. If the measured value exceeds ±5 % of the known amount, take appropriate action before proceeding with the sample test (see Note 2).

NOTE 2—This may require replacing the reagent solutions.

13. Procedure

13.1 Assemble a dry syringe and needle. Withdraw 1 mL to 2 mL of the sample into the syringe and discard the contents into a waste container. Repeat rinsing the syringe with sample two additional times to assure a representative sample and remove any residual moisture from the syringe. During sampling, minimize sample exposure to atmospheric moisture. Using the following table as a guide, withdraw the proper amount of test sample into the syringe. Invert the syringe and

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[3] *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.

eject to remove any air. Wipe any excess liquid from the needle. Obtain a mass to ±0.1 mg ($W1$). See Table 1.

13.1.1 A 1 mL gas tight syringe is suggested for single coulometric injections. If replicates of the same sample are required, a larger syringe with suitable volume may be used. The sample volume should occupy at least 25 % of the syringe volume. For increased precision, it is not recommended to inject less than 0.25 mL of sample into the coulometric cell.

13.2 With the analyzer stabilized, carefully insert the needle of the sample syringe through the septum and slightly below the level of solution in the titration chamber. Inject the sample carefully into the titration solution and begin titration per manufacturer directions. Withdraw the syringe needle and weigh to the nearest ±0.1 mg ($W2$) to determine the exact sample mass. Allow the titration to proceed until the end-point is indicated.

13.2.1 After numerous analyses, the level of solvent accumulated in the titration chamber may have to be reduced. This can be accomplished with a syringe of capacity of 20 mL or by partially draining the solution of the titration chamber. Discard the solution and replace with fresh anolyte solution if a stable reading cannot be obtained.

13.2.2 When a stable reading cannot be obtained, replace the reagents and follow the manufacturer procedure to condition the reagents.

13.3 *End Point Detection:*

13.3.1 During coulometric titrations, iodine is generated electrochemically by anodic oxidation of iodide to iodine. There is a quantitative relationship between the amount of electric current passed through the generator electrode and the amount of iodine generated. Iodine will be consumed as long as water is present.

13.3.2 End point is detected automatically and the water content is calculated based on the sample weight entered. During the titration a small constant polarization current is applied to the double platinum electrode and the voltage required to maintain this current is measured. When water is present in the titration vessel, the voltage required is high. Once there is a slight excess of iodine, the voltage required is reduced. This large change in voltage indicates the titration end point.

13.4 Record the micrograms of water determined for the sample titration.

14. Calculation

14.1 The water content is manually calculated in percent by mass using Eq 1 or percent by volume using Eq 2. Most instruments are equipped to provide a calculated result based upon the measured sample size.

TABLE 1 Recommended Sample Size (Coulometric)

Expected Water Content (mass percent)	Sample Size (g)
0 to 0.2	3 to 5
0.2 to 0.5	1 to 2
0.5 to 1.0	0.5 to1.0
1.0 to 2.0	0.5
>2.0	Please use Procedure B

$$(\text{water content, mass percent}) = \frac{\mu\text{g water}}{(W1 - W2) \times 10000} \tag{1}$$

$$\text{water content, volume percent} = (\text{water content, mass percent}) \times \frac{\text{density of sample at } t}{\text{density of water at } t} \tag{2}$$

where:

t = test temperature,
$W1$ = mass of sample and syringe before injection, g, and
$W2$ = mass of sample and syringe after injection, g.

15. Report

15.1 Report the percentage of water to the nearest 0.01 % by mass. Alternatively, report the percentage of water to the nearest 0.01 % by volume.

15.2 Report the water concentration in one of the defined units as obtained by Test Method D7923, Procedure A.

16. Precision and Bias

16.1 The statistical precision of this procedure, as determined by statistical examination of the 2015 interlaboratory test results, obtained from 12 laboratories on 12 samples, is as follows:

16.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values in one case in twenty.

$$\text{r} = 2.216\text{E-}02 \times X^{0.5746}\ \% \quad \text{by mass} \tag{3}$$

where:

X = the calculated result for percentage of water expressed as percent by mass.

16.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical material, would be in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

$$\text{R} = 3.356\text{E-}02 \times X^{0.5746}\ \% \quad \text{by mass} \tag{4}$$

where:

X = the calculated result for percentage of water expressed as percent by mass.

NOTE 3—The data in Table 2 shows repeatabilities and reproducibilities for water values obtained using the formulas given in 16.1.1 and 16.1.2.

TABLE 2 Calculated Precision Values for Water content by Procedure A

Water Content % by mass	Repeatability (*r*) % by mass	Reproducibility (*R*) % by mass	*r* as % of water	*R*as % of water
0.01	0.0016	0.0024	15.7	23.8
0.50	0.0149	0.0225	3.0	4.5
1.00	0.0222	0.0336	2.2	3.4
1.26	0.0253	0.0383	2.0	3.0
1.60	0.0290	0.0440	1.8	2.7

16.1.3 The precision statement was determined through statistical examination of 11 materials with blind duplicates from 12 laboratories. The materials included one sample of anhydrous ethanol, six ethanol blends ranging from a nominal 5 % to 85 % ethanol, three samples of denatured fuel ethanol, and one sample of gasoline. Water contents of the samples ranged from 0.002 % by mass to 1.63 % by mass by Procedure A.

16.2 *Bias*—This test method has no bias since the coulometric test method can be defined only in terms of this test method.

PROCEDURE B (VOLUMETRIC)

17. Reagents

17.1 *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 where such specifications are available.[3] 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.

17.2 *Purity of Water*—Unless otherwise indicated, references to water shall mean reagent water as defined by Type II and III of Specification D1193.

17.3 *Karl Fischer Reagents*—Pyridine-free formulations 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.

17.3.1 *One-component Karl Fischer Titrant*—Typically consists of a mixture of an organic base, sulfur dioxide and iodine dissolved in a solvent such as diethyleneglycol monoethyl ether. Reagents with titers of H_2O at 2.0 mg/mL are recommended for this method. Reagents with titers of H_2O at 5.0 mg/mL may also be used. See Note 4.

17.3.2 *Two-component Karl Fischer Titrant and Solvent*—Titrant typically consists of iodine and methanol or ethanol. Contains sulfur dioxide and organic base in anhydrous methanol or ethanol. See Note 4.

NOTE 4—The "one-component" KF volumetric titrant contains all the necessary reagents for titration of water and the solvent is used basically as a medium to dissolve the sample. The "two-component" KF volumetric titrant contains iodine and methanol or ethanol and the solvent contains sulfur dioxide and a base. The one component system is simple and allows for flexibility in solvent choice. However, because all of the necessary chemicals for titration are present, the titer decreases significantly over time. The two-component system will remain stable for longer periods of time and can provide more accurate measurement of trace water concentrations. Two-component reagents, however, are more susceptible to side reaction from non-complexed sulfur dioxide than single-component systems.

17.4 *Solvents:*

17.4.1 *Methanol,* max 0.15 % water, in accordance with Specification D1152. (See Note 5.)

17.4.2 *Denatured Ethanol,* max 0.15 % water.

NOTE 5—Solvents with low water content will consume less Karl Fischer reagents during the pre-titration process. Cosolvents are acceptable so long as solubility is not compromised.

17.5 *Water Standard*—Solvent mixture with precisely determined water content intended for calibrating volumetric KF reagents. Standards should come complete with a Certificate of Analysis. Standards containing 1.0 % water are recommended for this test method. High purity water may also be used for titrant standardization.

18. Preparation (Standardization of the Karl Fischer Titrant)

18.1 Standardize the KF reagent using high purity water or water standard daily. Standardization may be performed less frequently when using a daily check standard to verify KF reagent titer. Standard recovery should be within 97 % to 103 % of the certified value. Table 2 shows the suggested sample size that will require 2 mL to 10 mL of titrant for titration of the sample. Approximately 0.4 g to 1 g of 1.0 % water standard is recommended for standardization of a titrant with an expected titer of 2.0 mg/mL. Although pure water may be used to standardize KF titrants, weighing errors increase due to the small sample size required.

18.2 Prepare the dispensing buret and any tubing to ensure dispensed quantities are accurately measured. Care should be taken to ensure air bubbles are not dispensed during the titration.

18.3 Add approximately 25 mL to 50 mL or an appropriate amount of methanol or solvent if using two-component reagent to cover the electrode tip. See Note 6.

NOTE 6—The solvent volume should cover the double platinum electrode tip during stirring. Stir speed should be controlled to ensure proper mixing but should not create a vortex funnel.

18.4 Pre-titrate with KF reagent according to the instrument manufacturer's instructions.

18.5 Transfer standard to the pretitrated solvent.

18.5.1 Assemble a dry gas-tight 5 mL or 10 mL syringe and needle with suitable capacity to make three to five standardization titrations. See 7.2.

18.5.2 Rinse the syringe assembly by withdrawing approximately 0.25 mL of standard into the syringe. Eject to waste in an appropriate waste container. Repeat rinsing the syringe with standard two additional times to assure a representative sample and remove any residual moisture from the syringe.

18.5.3 Withdraw standard into the syringe according to the expected water content and titrant concentrations. Invert the syringe and eject to remove any air. Wipe any excess liquid from the needle. Obtain the mass of syringe and sample to ±0.1 mg ($W1$). See Table 2 and Note 4.

18.5.4 With the analyzer stabilized, carefully insert the needle of the sample syringe through the septum and below the level of solution in the titration chamber. Inject the sample slowly and carefully into the titration solution and begin titration. Withdraw the syringe needle and weigh to the nearest ±0.1 mg ($W2$) to determine the exact sample mass. Keep in mind that very small sample amounts can be difficult to accurately weigh and transfer.

18.6 Allow the titration to proceed until the end-point is indicated. After repeated injections, the level of solvent may need to be reduced or replaced. Follow the manufacturer's instructions. Discard solution and replace with fresh titration solution if a stable reading cannot be obtained.

18.7 *End Point Detection*—End point is detected automatically and the water content is calculated based on the sample mass entered. During the titration a small constant polarization current is applied to the double platinum electrode and the voltage required to maintain this current is measured. When water is present in the titration vessel, the voltage required is high. Once there is a slight excess of iodine, the voltage required is reduced. This large change indicates the titration end point.

18.8 Record the volume of titrant dispensed to reach the end point.

19. Calculation for Standardization of the KF Titrant

19.1 The water equivalent (titer) of the KF reagent, in milligrams per milliliter, can be manually calculated using Eq 5 if high purity water is used or Eq 6 if a certified water standard is used. Most instruments are equipped to provide a calculated result based upon the entered sample size.

High Purity Water:

$$\text{titer} = \frac{(W1 - W2) \times 0.001}{\text{titrant volume}} \quad (5)$$

Water Standard:

$$\text{titer} = \frac{(W1 - W2) \times \text{standard conc}}{\text{titrant volume}} \quad (6)$$

where:

titrant volume = milliliters of titrant required for titration of the sample,
standard conc = water content of standard, mg/g,
$W1$ = mass of sample and syringe before injection, g, and
$W2$ = mass of sample and syringe after injection, g.

20. Procedure

20.1 Prepare the dispensing buret and any tubing to ensure dispensed quantities are accurately measured. Ensure air bubbles are not dispensed during the titration.

20.2 Add 25 mL to 50 mL of the selected solvent into the titration cell. The volume of solvent should be added such that the metal portion of the electrode is completely submerged. See Note 7.

NOTE 7—If the titration vessel contains KF solvent that has been pre-titrated for standardization, there is no need to replace solvent. Proceed to 20.3.

20.3 Pre-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.

20.4 Transfer the sample to titration vessel.

20.4.1 Assemble a dry gas-tight syringe and needle with suitable capacity. See 7.2.

20.4.2 Rinse the syringe assembly by withdrawing approximately 0.5 mL of sample into the syringe. Eject to waste in an appropriate waste container. Repeat rinsing the syringe with sample two additional times to assure a representative sample.

20.4.3 Withdraw sample into the syringe according to the expected water content. Invert the syringe and eject to remove any air. Wipe any excess liquid from the needle. Obtain the weight of syringe and sample to ±0.1 mg ($W1$). KF instrument operation manuals typically list suggested sample sizes, however, Table 3 may be used as a guideline for sample sizes based on titrant concentrations. Keep in mind that very small sample amounts can be difficult to accurately weigh and transfer.

20.4.4 With the analyzer stabilized, carefully insert the needle of the sample syringe through the septum and below the level of solution in the titration chamber. Inject the sample slowly and carefully into the titration solution and begin titration. Withdraw the syringe needle and weigh to the nearest ±0.1 mg ($W2$) to determine the exact sample mass.

20.4.5 Allow the titration to proceed until the end-point is indicated. After repeated injections, the level of solvent may need to be reduced or replaced. Follow the manufacturer's instructions. Discard the solution and replace with fresh titration solution if a stable reading cannot be obtained.

20.5 *End Point Detection*—End point is detected automatically and the water content is calculated based on the sample weight entered. During the titration a small constant polarization current is applied to the double platinum electrode and the voltage required to maintain this current is measured. When water is present in the titration vessel the voltage required is high. Once there is a slight excess of iodine, the voltage required is reduced. This indicates the titration end point.

20.6 Record the volume of titrant dispensed to reach the end point.

21. Calculation of Sample Content

21.1 The water content may be manually calculated as percent by mass using Eq 7 or as percent by volume using Eq 8. Most instruments are equipped to provide a calculated result based upon the entered sample size.

$$\text{water content, percent by mass} = \frac{\text{titrant volume} \times \text{titer} \times 0.1}{(W1 - W2)} \quad (7)$$

TABLE 3 Recommended Sample Size (Coulometric)

Expected Water Content (mass percent)	Sample size at titrant strength, H_2O at 2 mg/mL, (g)
0.2	2 to 5
0.5	0.8 to 4
1.0	0.4 to 2
1.5	0.25 to 1.5
>3.0	0.2 to 0.4

$$\text{water content, percent by volume} = \frac{\text{titrant volume} \times \text{titer} \times 0.1}{\text{sample size } (W1 - W2)} \times \frac{\text{density of sample at } t}{\text{density of water at } t} \quad (8)$$

where:

titrant volume = amount required for titration of the sample, mL,

titer = equivalent amount of water in KF reagent, mg/mL,

t = test temperature, °C,

$W1$ = mass of sample and syringe before injection, g,

$W2$ = mass of sample and syringe after injection, g, and

0.1 factor = conversion factor, %.

22. Verification of Calibration and Quality Control

22.1 Autotitrators vary in calibration procedures by manufacturer. Consult the operating manual for the autotitrator in use. Stable, prepackaged quality control (QC) water standards are commercially available with 0.1 % by mass and 1 % by mass water content for this purpose. It is desirable to verify calibration with a standard solution that approximates the same range of water expected to be in the samples.

22.2 It is recommended that a control chart measuring a QC standard sample be established and maintained according to generally accepted guidelines. Practice D6299 can be used for this purpose. Measure the control sample each day a sample(s) is tested. If the measured value exceeds ±5 % of the known amount, take appropriate action before proceeding with the sample test.

23. Report

23.1 Report the percentage of water to the nearest 0.01 % by mass. Alternatively, report the percentage of water to the nearest 0.01 % by volume.

23.2 Report the water concentration in one of the defined units as obtained by Test Method D7923, Procedure B.

24. Precision and Bias

24.1 The statistical precision of this procedure, as determined by statistical examination of the 2015 interlaboratory test results, obtained from 8 laboratories on 14 samples, is as follows:

24.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values in one case in twenty.

$$r = 2.495\text{E-}02 \times (X + 0.0002)^{0.3144}\ \%\ \text{by mass} \quad (9)$$

where:

X = the calculated result for percentage of water expressed as percent by mass.

24.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical material, would be in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

$$R = 4.282\text{E-}02 \times (X + 0.0002)^{0.3144}\ \%\ \text{by mass} \quad (10)$$

where:

X = the calculated result for percentage of water expressed as percent by mass.

NOTE 8—The data in Table 4 shows repeatabilities and reproducibilities for water values obtained using the formulas given in 24.1.1 and 24.1.2.

24.1.3 The precision statement was determined through statistical examination of 14 materials with blind duplicates from eight laboratories. The materials included one sample of anhydrous ethanol, six ethanol blends ranging from a nominal 5 % to 85 % ethanol, three samples of denatured fuel ethanol, two samples of gasoline, and two samples of hydrous ethanol. Water contents of the samples ranged from 0.005 % by mass to 5.41 % by mass by Procedure B.

24.2 *Bias*—The bias of this test method has not been determined since no acceptable reference material has been identified.

24.3 *Relative Bias*—A relative bias assessment of Procedure B versus Procedure A of this test method for the determination of water by Karl Fischer titration was performed in accordance with the requirements of Practice D6708 with a successful outcome (type A4).

24.3.1 The degree of agreement between results from Procedure B (Volumetric Titration) and Procedure A (Coulometric Titration) can be further improved by applying the correction equation listed below (Research Report RR:D02-1839). Sample-specific bias, as defined in Practice D6708, was observed for some samples after applying the bias-correction. The bias was determined from eleven common samples of ethanol and hydrocarbon blends used in the precision study for the two procedures. The samples had water content ranging from 0.002 % by mass to 1.63 % by mass by Procedure A and 0.005 % by mass to 1.61 % by mass by Procedure B.

Correction Equation:

$$\text{bias-corrected } X = \text{predicted } Y = 1.01X - 2.55\text{e-}03 \quad (11)$$

where:

X = result by Procedure B (Volumetric Titration), % by mass,

bias-corrected X = predicted Y, % by mass, and

predicted Y = result that would have been obtained by Procedure A (Coulometric Titration) on the same sample.

TABLE 4 Calculated Precision Values for Water content by Procedure B

Water Content % by mass	Repeatability (*r*) % by mass	Reproducibility (*R*) % by mass	*r* as % of water	*R* as % of water
0.01	0.0059	0.0101	59.0	101.3
0.50	0.0201	0.0344	4.0	6.9
1.00	0.0250	0.0428	2.5	4.3
1.26	0.0268	0.0460	2.1	3.7
2.50	0.0333	0.0571	1.3	2.3
5.00	0.0414	0.0710	0.8	1.4

24.3.2 Differences between bias-corrected results from Procedure B and Procedure A from this method, for the sample types and property ranges studied, are expected to exceed the following between methods reproducibility (*RXY*), as defined in Practice D6708, about 5 % of the time. As a consequence of sample-specific biases, *RXY* may exceed the reproducibility for Procedure B, or the reproducibility for Procedure A, or both. Users intending to use Procedure B as a predictor of Procedure A, or vice versa, are advised to assess the required degree of prediction agreement relative to the estimated *RXY* to determine the fitness-for use of the prediction.

$$Rxy\ (\mathrm{D6708}) = SQRT\left(1.044\ \mathrm{E\text{-}03}\ (X + 2.000\ \mathrm{e\text{-}04})^{0.6288} + 6.237\ \mathrm{e\text{-}04} \times Y^{1.1492}\right) \quad (12)$$

25. Keywords

25.1 coulometric; ethanol; gasoline; hydrocarbon; Karl Fischer; pyridine-free; volumetric; water content

APPENDIX

(Nonmandatory Information)

X1. HELPFUL HINTS FOR KARL FISCHER WATER ANALYSIS

X1.1 The following precautions are suggested to obtain accurate and precise results by this test method. Some of these suggestions are also described in the text of the test method but are compiled here for easy reference.

X1.1.1 A number of chemicals interfere in this titration: mercaptans, sulfides, amines, ketones, aldehydes, oxidizing and reducing agents, and so forth. More information about interferences and how to prevent or circumvent them can be found in commercially available texts.

X1.1.2 At low water concentrations (<0.02 % by mass) the interference by mercaptan and sulfide (>500 mg/kg as sulfur) may be significant (see Test Method E203).

X1.1.3 All equipment should be scrupulously clean of moisture. Rinse all syringes, needles, and weighing bottles with dry ethanol or dry methanol after cleaning. Then dry in an oven at 100 °C for at least 1 h and store immediately in a desiccator.

X1.1.4 Fill the dry cooled sample bottle as rapidly as possible with the sample within 15 mm of the top and immediately seal.

X1.1.5 Although standardization is not necessary in coulometric titrations, reagent performance deteriorates with use and must be regularly monitored by accurately injecting a suitable water standard. Suggested intervals are initially with fresh reagent, and then after every ten determinations.

X1.1.6 Rinse the clean dry syringe at least three times with the sample and discard the aliquots before taking an aliquot for injecting into the titration vessel.

X1.1.7 During the blank measurement instrument preparation, high background current for a prolonged period may be due to moisture on the inside walls of the titration vessel. Wash the vessel walls by gently shaking or by more vigorously stirring.

X1.1.8 Follow the manufacturer's recommendation for cleaning and maintenance of the generator electrode.

X1.1.9 Any time one of the following situations occurs, replace the anode and the cathode solutions and then repeat the preparation of the apparatus (coulometric).

X1.1.9.1 Persistently high and unstable background current.

X1.1.9.2 Phase separation in the anode compartment or the sample coating the electrodes.

X1.1.9.3 The total amount of sample added to the titration vessel exceeds one fourth of the volume of solution in the anode compartment.

X1.1.9.4 The solutions in the titration vessel are over one week old.

X1.1.9.5 The results of a water standard is greater than ±5 % of the expected value.

X1.1.10 If the titration vessel gets contaminated with the sample, follow manufacturer's recommendation for cleaning. Never use acetone or similar ketones.

X1.1.11 Ensure that all titrant delivery lines are bubble-free and the delivery tip resting in the titration vessel is not blocked (volumetric).

X1.1.12 A rubber septum may be used to seal the tip of the gas-tight syringe needle when analyzing volatile and hygroscopic samples for more accurate and reproducible results.

SUMMARY OF CHANGES

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D7923 – 17) that may impact the use of this standard. (Approved July 1, 2017.)

(1) Revised subsection 1.1.1.

Subcommittee D02.06 has identified the location of selected changes to this standard since the last issue (D7923 – 16) that may impact the use of this standard. (Approved May 1, 2017.)

(1) Revised subsection 11.3.

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