



Designation: D7923 – 16

# Standard Test Method for Water in Ethanol and Hydrocarbon Blends by Karl Fischer Titration<sup>1</sup>

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 ( $\epsilon$ ) 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 % ethanol.

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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

D1152 Specification for Methanol (Methyl Alcohol)

<sup>1</sup> 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.

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<sup>2</sup> 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.

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**

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.<sup>3</sup> 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

<sup>3</sup> *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.

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 below the level of the anolyte solution to prevent backflow contamination of the titration (anolyte) solution. The anolyte solution may have to be removed periodically to maintain the lower 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  $\pm 5$  % 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 eject to remove any air. Wipe any excess liquid from the needle. Obtain a mass to  $\pm 0.1$  mg (W1). See **Table 1**.

**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 to 1.0
1.0 to 2.0	0.5
>2.0	Please use Procedure B

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 analyte 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.

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

water content, volume percent =

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

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.

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

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.

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

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.

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.

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