



Standard Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent¹

This standard is issued under the fixed designation D1744; 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 covers the determination of water in the concentration from 50 to 1000 mg/kg in liquid petroleum products.

1.2 Values stated in SI units are to be regarded as the standard. Inch-pound units are provided for information only.

1.3 *This standard does not purport to address all of the safety problems, 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.* For specific precautionary statements see Section 7.

2. Referenced Documents

2.1 *ASTM Standards*:²

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

3. Summary of Test Method

3.1 The material to be analyzed is titrated with standard Karl Fischer reagent to an electrometric end point.

4. Significance and Use

4.1 Knowledge of the water content of petroleum products can be useful to predict quality and performance characteristics of the product.

5. Interferences

5.1 Free alkali, oxidizing and reducing agents, mercaptans, certain basic nitrogenous substances, or other materials that

react with iodine, interfere. One part per million of sulfur as mercaptan causes an error in the titration, equivalent to approximately 0.2 mg/kg of water.

6. Apparatus

6.1 Assemble the apparatus as described in the [Annex A1](#). (See [Note 1](#).)

NOTE 1—Any apparatus that will give equal or better precision is acceptable.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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 can 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 be understood to mean distilled water or water of equal purity. The solvents used must have low-water content, for example, less than 500 mg/kg mass.

7.3 *Karl Fischer Reagent, Solution* ([Note 2](#)), *Stock*—(**Warning**—Toxic.) For each litre of solution, dissolve 85 ± 1 g of iodine in 270 ± 2 mL of pyridine in a dry, glass-stoppered bottle. Add 670 ± 2 mL of methanol (99.9 %) ([Note 3](#)). Cool the mixture in an ice bath to below 3.9°C. Bubble gaseous sulfur dioxide (SO₂) ([Note 4](#)) through concentrated sulfuric acid (H₂SO₄, rel dens 1.84) (see warning information below) into the cooled mixture. Continue the addition of SO₂ until the volume is increased 50 ± 1 mL. Alternatively, add 50 ± 1 mL of freshly drawn liquid SO₂ in small increments to the precooled mixture in an ice bath. Mix well and set aside for at

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

least 12 h before using. (**Warning**—Poison. Corrosive. Strong oxidizer. Contact with organic material can cause fire. Can be fatal if swallowed. Liquid and vapor can cause severe burns. Harmful if inhaled. Contact with water liberates large amounts of heat. Spillage can cause fire.)

NOTE 2—Commercially prepared Karl Fischer Reagent may be used.

NOTE 3—If 99.9 % methanol is not commercially available, it can be prepared by dissolving 24 g of magnesium metal turnings in 200 mL of methanol. Caution, the reaction is vigorous. When the reaction is complete, add 3 L of methanol. Reflux for 5 h and distill directly into the container in which the 99.9 % methanol is to be kept. Vent the system through a drying tube during the distillation.

NOTE 4—Follow standard safety precautions for handling toxic gases.

7.4 *Karl Fischer Reagent, Dilute Solution*—Adjust the strength of the stock solution to a water equivalence of 2 to 3 mg of water per mL by dilution with pyridine.

7.5 *Sample Solvent*—Mix 1 volume of methanol (Note 4) with 3 volumes of chloroform. (**Warning**—Can be fatal if swallowed. Harmful if inhaled. Can produce toxic vapors if burned.)

8. Sampling

8.1 Take samples in accordance with the instructions in Practice D4057.

9. Standardization of Karl Fischer Reagent

9.1 The dilute Karl Fischer reagent should be standardized at least daily in accordance with either 9.1.1 to 9.1.3 or 9.1.4 to 9.1.8.

9.1.1 Add 50 mL of the sample solvent to a clean, dry titration flask. Insert the stopper and adjust the magnetic stirrer to give a smooth stirring action. Turn on the indicating circuit and adjust the potentiometer to give a reference point with approximately 1 μ A of current flowing. Add Karl Fischer reagent in suitable amounts to the solvent to cause the needle to deflect from the reference point. At first the needle will deflect due to local concentration of the unreacted reagent about the electrodes but will fall back to near the reference point. As the end point is approached, the needle will fall back more slowly after each addition of Karl Fischer reagent. The end point is reached when, after the addition of a single drop of reagent, the needle remains deflected at least 1 μ A from the reference point for at least 30 s.

9.1.2 To the solution in the titration flask add carefully, from a weighing pipet previously weighed to the nearest 0.1 mg, 1 drop of distilled water. Stopper the flask. Reweigh the weighing pipet. Titrate to the end point as described in 9.1.1.

9.1.3 Calculate the water equivalence of the Karl Fischer reagent as follows:

$$F = W/T \quad (1)$$

where:

F = water equivalence of Karl Fischer reagent, mg/mL,
 W = milligrams of water added, and
 T = millilitres of reagent required for titration of the added water.

9.1.4 Alternatively, add 50 mL of methanol as the titration solvent to the titration flask and titrate to the end point as described in 9.1.1.

9.1.5 From a tared weighing bottle, by means of a clean, dry spatula, transfer approximately 250 mg of sodium tartrate dihydrate to the pretitrated alcohol in the titration flask. Record the mass.

9.1.6 Dip the spatula into the solvent to ensure the removal of any adhering tartrate (Note 3). Stopper the flask and titrate to the end point as described in 9.1.1.

NOTE 5—To facilitate transfer 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.

9.1.7 Determine the total water content of the sodium tartrate dihydrate by drying a preweighed sample to a constant mass in an oven at $150 \pm 5^\circ\text{C}$.

9.1.8 Calculate the water equivalence of the Karl Fischer reagent as follows:

$$F = (A \times B)/100T \quad (2)$$

where:

F = the water equivalence of Karl Fischer reagent, mg/mL,
 A = milligrams of sodium tartrate dihydrate used,
 B = percentage of water in the sodium tartrate dihydrate, and
 T = millilitres of reagent required for titration of the water in the sodium tartrate dihydrate.

10. Procedure

10.1 Add 50 mL of solvent to the titration flask and titrate with standardized Karl Fischer reagent to the end point as described in 9.1.1. It is important to stopper the sample inlet tube as quickly as possible to prevent absorption of moisture from the atmosphere.

10.2 Obtain a hydrometer reading on the material to be tested and convert degrees API to relative density without correcting for temperature. Immediately pipet 50 mL of the sample into the titration flask. Alternatively, the sample can be weighed and added to the titration flask in any convenient manner.

10.3 Titrate the sample to the end point as described in 9.1.1. Record the millilitres of reagent used.

11. Calculation or Interpretation of Results

11.1 Calculate the water content of the sample as follows:

$$\text{Water, mg/kg} = (C F \times 1000) / [W \text{ or } A \times G] \quad (3)$$

where:

C = millilitres of reagent required for titration of the sample,
 F = water equivalence, milligrams mg water/mL,
 1000 = factor for converting to parts per million,
 W = grams of sample used = $A \times G$,
 A = millilitres of sample used, and
 G = relative density of the sample.

12. Precision and Bias

12.1 The precision of this test is not known to have been obtained in accordance with currently accepted guidelines (for example, in Committee D02 research report RR:D02-1007, Manual on Determining Precision Data for ASTM Methods on

Petroleum Products and Lubricants).² These results apply only to aviation turbine fuel. Difficulties encountered in distributing stable samples have prevented development of additional data.

12.2 The precision of the method as obtained by statistical examination of interlaboratory test results is as follows:

12.2.1 *Repeatability*—The difference between successive test 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 only one case in twenty:

Water Content, µg/g
50 to 1000

Repeatability, µg/g
11

12.2.2 *Reproducibility*—The reproducibility of the method has not been determined because of the difficulty encountered in maintaining sample integrity when distributing them to the cooperator's laboratories.

12.3 *Bias*—The bias of this test method has not been determined.

13. Keywords

13.1 Karl Fischer; petroleum products; water

ANNEX

(Mandatory Information)

A1. APPARATUS

A1.1 **Titration Assemblies**—The titration assembly (Fig. A1.1) shall include the following:

A1.1.1 *Buret*—A 10-mL buret graduated 0.05-mL subdivisions and fitted within a three-way stopcock. Some stopcock greases are affected by Karl Fischer reagent.

A1.1.2 *Reagent Reservoir*—Any convenient-size glass bottle.

A1.1.3 *Stirrer*—Magnetic stirrer.

A1.1.4 *Titration Flask*—A three-neck flask of approximately 500-mL capacity.

A1.1.5 Assemble the apparatus as shown in Fig. A1.1. All possible precautions must be taken to prevent absorption of moisture from the atmosphere. Cracks between glass and stoppers should be sealed with a suitable sealing material and necessary openings should be protected by the use of drying tubes containing anhydrous calcium sulfate.

A1.2 **Electrical Circuit**—The electrical circuit (Fig. A1.1) shall include the following:

A1.2.1 *Microammeter*—A d-c microammeter having a range from 0 to 50 µA and an internal resistance of approximately 1500 Ω.

A1.2.2 *Battery*—A 1.5-V dry cell.

A1.2.3 *Electrodes*—Suitable electrodes (Fig. A1.2) can be constructed as follows: Seal a piece of platinum wire approximately 25 mm (1 in.) in length (diameter of wire 0.3 to 0.8 mm (0.01 to 0.03 in.)) into a piece of small bore soft glass tubing approximately 160 mm long. Approximately 7.1 mm (0.28 in.) of the wire should extend above the seal on the inside of the tubing and approximately 15.2 mm (0.60 in.) extend outside the seal. Bend the glass tubing slightly about 20 to 30 mm above the seal as shown in Fig. A1.2. Make a small loop approximately 6.4 mm (0.25 in.) in diameter in the end of the platinum wire. Place sufficient mercury in the glass tube to provide contact for the leads to complete the circuit. Two electrodes are required. Care should be exercised that cracks do not develop around the seal, which will make the electrodes useless.

A1.2.4 *Potentiometer*—A potentiometer having a resistance of 2000 Ω.

A1.2.5 Assemble the circuit as shown in Fig. A1.1.

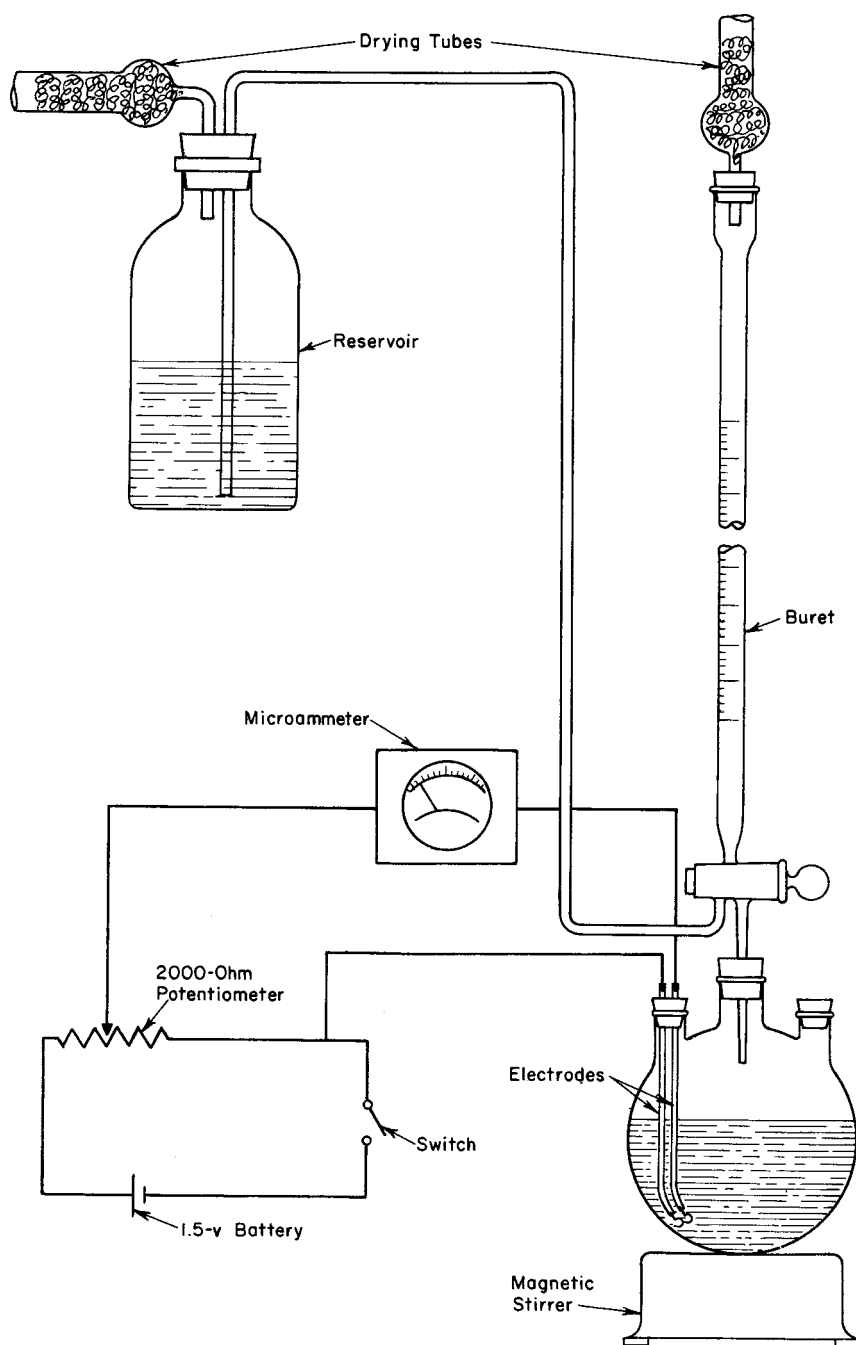


FIG. A1.1 Apparatus for Determination of Water by Karl Fischer Reagent

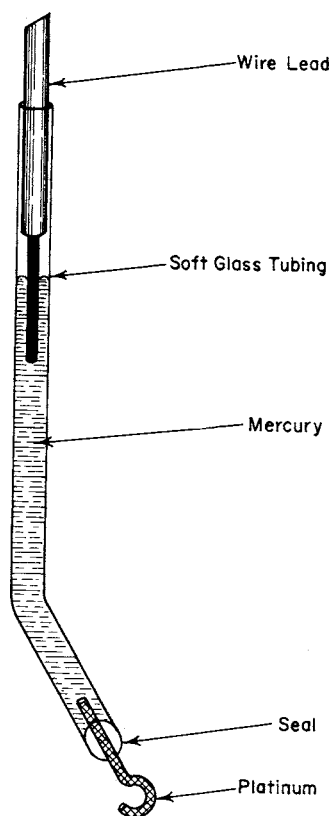


FIG. A1.2 Electrode

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