



Designation: D6304 – 16

Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration¹

This standard is issued under the fixed designation D6304; 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 direct determination of water in the range of 10 mg/kg to 25 000 mg/kg entrained water in petroleum products and hydrocarbons using automated instrumentation. This test method also covers the indirect analysis of water thermally removed from samples and swept with dry inert gas into the Karl Fischer titration cell. Mercaptan, sulfide (S^- or H_2S), sulfur, and other compounds are known to interfere with this test method (see Section 5).

1.2 This test method is intended for use with commercially available coulometric Karl Fischer reagents and for the determination of water in additives, lube oils, base oils, automatic transmission fluids, hydrocarbon solvents, and other petroleum products. By proper choice of the sample size, this test method may be used for the determination of water from mg/kg to percent level concentrations.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Prod-

ucts by Hydrometer Method

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products

E203 Test Method for Water Using Volumetric Karl Fischer Titration

3. Summary of Test Method

3.1 An aliquot is injected into the titration vessel of a coulometric Karl Fischer apparatus in which iodine for the Karl Fischer reaction is generated coulometrically at the anode. When all of the water has been titrated, excess iodine is detected by an electrometric end point detector and the titration is terminated. Based on the stoichiometry of the reaction, 1 mol of iodine reacts with 1 mol of water; thus, the quantity of water is proportional to the total integrated current according to Faraday's Law.

3.2 The sample injection can be done either by mass or volume.

3.3 The viscous samples can be analyzed by using a water vaporizer accessory that heats the sample in the evaporation chamber, and the vaporized water is carried into the Karl Fischer titration cell by a dry inert carrier gas.

4. Significance and Use

4.1 A knowledge of the water content of lubricating oils, additives, and similar products is important in the manufacturing, purchase, sale, or transfer of such petroleum products to help in predicting their quality and performance characteristics.

4.2 For lubricating oils, the presence of moisture could lead to premature corrosion and wear, an increase in the debris load resulting in diminished lubrication and premature plugging of filters, an impedence in the effect of additives, and undesirable support of deleterious bacterial growth.

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.

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

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

TABLE 1 Test Sample Size Based on Expected Water Content

Expected Water Concentration	Sample Size g or mL	µg Water Titrated
10 mg/kg to 100 mg/kg or µg/mL	3.0	30 to 300
10 mg/kg to 500 mg/kg or µg/mL	2.0	200 to 1000
0.02 % to 0.1 %	1.0	200 to 1000
0.1 % to 0.5 %	0.5	500 to 2500
0.5 % to 2.5 %	0.25	1250 to 6250

5. Interferences

5.1 A number of substances and classes of compounds associated with condensation or oxidation-reduction reactions interferes in the determination of water by Karl Fischer titration. In petroleum products, the most common interferences are mercaptans and sulfides. At levels of less than 500 mg/kg as sulfur, the interference from these compounds is insignificant for water concentrations greater than 0.02 % by mass. For more information on substances that interfere in the determination of water by the Karl Fischer titration method, see Test Method E203. Some interferences, such as ketones, may be overcome if the appropriate reagents are used.

5.2 The significance of the mercaptan and sulfide interference on the Karl Fischer titration for water in the 10 mg/kg to 200 mg/kg range has not been determined experimentally. At these low water concentrations, however, the interference may be expected to be significant for mercaptan and sulfide concentrations of greater than 500 mg/kg as sulfur.

5.3 Helpful hints in obtaining reliable results are given in Appendix X1.

6. Apparatus

6.1 *Coulometric Karl Fischer Apparatus (using electrometric end point)*—A number of automatic coulometric Karl Fischer titration assemblies consisting of titration cell, platinum electrodes, magnetic stirrer, and a control unit are available on the market. Instructions for operation of these devices are provided by the manufacturers and are not described herein.

6.1.1 *Water Vaporizer Accessory*—A number of automatic water vaporizer accessories are available on the market. Instructions for the operation of these devices are provided by the manufacturers and are not described herein.

6.2 *Syringes*—Samples are most easily added to the titration vessel by means of accurate glass or disposable plastic syringes with luer fittings and hypodermic needles of suitable length to dip below the surface of the anode solution in the cell when inserted through the inlet port septum. The bores of the needles used shall be kept as small as possible, but large enough to avoid problems arising from back pressure or blocking while sampling. Suggested syringe sizes are as follows:

6.2.1 Ten microlitres, with a needle long enough to dip below the surface of the anode solution in the cell when inserted through the inlet port septum and graduated for readings to the nearest 0.1 µL or better. This syringe can be used to accurately inject a small quantity of water to check reagent performance as described in Section 10.

6.2.2 As identified in Table 1, syringes of the following

capacities: 250 µL accurate to the nearest 10 µL; 500 µL accurate to the nearest 10 µL; 1 mL accurate to the nearest 0.01 mL; 2 mL accurate to the nearest 0.01 mL; and 3 mL accurate to the nearest 0.01 mL. A quality gas-tight glass syringe with a TFE-fluorocarbon plunger and luer fitting is recommended.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society³, where such specifications are available. Use other grades, provided 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 reagent water as defined by Type II of Specification D1193.

7.3 *Xylene, Reagent Grade*, less than 100 mg/kg to 200 mg/kg water, dried over a molecular sieve (**Warning**—Flammable. Vapor harmful).

7.4 *Karl Fischer Reagent*, standard commercially available reagents for coulometric Karl Fischer titrations.

7.4.1 *Anode Solution*—Mix six parts of commercial Karl Fischer anode solution with four parts of reagent grade xylene on a volume basis. Newly made Karl Fischer anode solution shall be used. Other proportions of anode solution and xylene may be used and determined for a particular reagent, apparatus, and sample tested. Some samples may not require any xylene, whereas others will require the solvent effect of the xylene (**Warning**—Flammable, toxic if inhaled, swallowed, or absorbed through skin).

NOTE 1—Toluene may be used in place of xylene. However, the precision data in Section 17 were obtained using xylene.

7.4.2 *Cathode Solution*—Use standard commercially available cathode Karl Fischer solution. Newly made solution shall be used (**Warning**—Flammable, may be fatal if inhaled, swallowed, or absorbed through skin. Possible cancer hazard.).

7.4.3 If the sample to be analyzed contains ketone, use commercially available reagents that have been specially modified for use with ketones.

NOTE 2—Some laboratories add the ketone suppressing reagent as part of their standard analytical procedure since often the laboratory does not know whether the sample contains ketone.

7.5 *Hexane, Reagent Grade*, less than 100 mg/kg to 200 mg/kg water (**Warning**—Flammable. Vapor harmful). Dried over molecular sieve.

7.6 *White Mineral Oil*—Also called paraffin oil or mineral oil. Reagent grade.

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 *Annual 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.

7.7 *Molecular Sieve* 5Å—8 to 12 mesh.

8. Sampling

8.1 Sampling is defined as all 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.

8.2 *Laboratory Sample*—The sample of petroleum product presented to the laboratory or test facility for analysis by this test method. Only representative samples obtained as specified in Practices **D4057** and **D4177** and handled and mixed in accordance with Practice **D5854** shall be used to obtain the laboratory sample.

NOTE 3—Examples of laboratory samples include bottles from a manual sampling, receptacles from automatic samplers, and storage containers holding a product from a previous analysis.

8.3 *Test Specimen*—The aliquot obtained from the laboratory sample for analysis by this test method. Once drawn, use the entire portion of the test specimen in the analysis.

8.4 Select the test specimen size as indicated in **Table 1** based on the expected water concentration.

9. Preparation of Apparatus

9.1 Follow the manufacturer's directions for preparation and operation of the titration apparatus.

9.2 Seal all joints and connections to the vessel to prevent atmospheric moisture from entering the apparatus.

9.3 Add the Karl Fischer anode solution to the anode (outer) compartment. Add the solution to the level recommended by the manufacturer.

9.4 Add the Karl Fischer cathode solution to the cathode (inner) compartment. Add the solution to a level 2 mm to 3 mm below the level of the solution in the anode compartment.

9.5 Turn on the apparatus and start the magnetic stirrer for a smooth stirring action. Allow the residual moisture in the titration vessel to be titrated until the end point is reached. Do not proceed beyond this stage until the background current (or background titration rate) is constant and less than the maximum recommended by the manufacturer of the instrument.

NOTE 4—High background current for a prolonged period may be due to moisture on the inside walls of the titration vessel. Gentle shaking of the vessel (or more rigorous stirring action) will wash the inside with electrolyte. Keep the titrator on to allow stabilization to a low background current.

10. Calibration and Standardization

10.1 In principle, standardization is not necessary since the water titrated is a direct function of the coulombs of electricity consumed. However, reagent performance deteriorates with use and shall be regularly monitored by accurately injecting a known quantity of water (see **7.2**) that is representative of the typical range of water concentrations being determined in samples. As an example, one may accurately inject 10 000 µg or 10 µL of water to check reagent performance. Suggested intervals are initially with fresh reagent and then after every ten determinations (see **11.3**).

11. Procedure A (by Mass)

11.1 Add newly made solvents to the anode and cathode compartments of the titration vessel and bring the solvent to end-point conditions as described in Section **9**.

11.2 Add the petroleum product test specimen to the titration vessel using the following method:

11.2.1 Starting with a clean, dry syringe of suitable capacity (see **Table 1** and **Note 5**), withdraw and discard to waste at least three portions of the sample. Immediately withdraw a further portion of sample, clean the needle with a paper tissue, and weigh the syringe and contents to the nearest 0.1 mg. Insert the needle through the inlet port septum, start the titration, and with the tip of the needle just below the liquid surface, inject the test specimen. Withdraw the syringe, wipe clean with a paper tissue, and reweigh the syringe to the nearest 0.1 mg. After the end point is reached, record the micrograms of water titrated.

NOTE 5—If the concentration of water in the sample is completely unknown, it is advisable to start with a small trial portion of sample to avoid excessive titration time and depletion of the reagents. Further adjustment of the aliquot size may then be made as necessary.

11.2.2 When the background current or titration rate returns to a stable reading at the end of the titration as discussed in **9.5**, additional specimens may be added as per **11.2.1**.

11.3 Replace the solutions when one of the following occurs and then repeat the preparation of the apparatus as in Section **9**.

11.3.1 Persistently high and unstable background current.

11.3.2 Phase separation in the anode compartment or oil coating the electrodes.

11.3.3 The total oil content added to the titration vessel exceeds one quarter of the volume of solution in the anode compartment.

11.3.4 The solutions in the titration vessel are greater than one week old.

11.3.5 The instrument displays error messages that directly or indirectly suggest replacement of the electrolytes—see instrument operating manual.

11.3.6 The result of a 10 µL injection of water is outside 10 000 µg ± 200 µg.

11.4 Thoroughly clean the anode and cathode compartment with xylene if the vessel becomes contaminated with product. Never use acetone or similar ketones. Clogging of the frit separating the vessel compartments will cause instrument malfunction.

11.5 For products too viscous to draw into a syringe, add the sample to a clean, dry bottle and weigh the bottle and product. Quickly transfer the required amount of sample to the titration vessel by suitable means, such as with a dropper. Reweigh the bottle. Titrate the sample as in **11.2**.

12. Procedure B (by Volume)

12.1 Follow steps **11.2.1** through **11.5** from Procedure A, taking sample by volume instead of mass.

NOTE 6—A volume aliquot of the product is titrated to an electrometric end point using a coulometric Karl Fischer apparatus. The steps described