



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

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1. Scope

1.1 This test method covers the direct determination of water in the range of 10 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 Values stated in SI units are to be regarded as the 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:

- D 1193 Specification for Reagent Water²
- D 1298 Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method³
- D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter⁴
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products⁴
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products⁴

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D2.02 on Static Petroleum Measurement.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 5.01.

⁴ *Annual Book of ASTM Standards*, Vol 5.02.

D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products⁵

E 203 Test Method for Water Using Volumetric Karl Fischer Titration⁶

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 impedance in the effect of additives, and undesirable support of deleterious bacterial growth.

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 mass

⁵ *Annual Book of ASTM Standards*, Vol 5.03.

⁶ *Annual Book of ASTM Standards*, Vol 15.05.

%. For more information on substances that interfere in the determination of water by the Karl Fischer titration method, see Test Method E 203. 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 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 0.01 μL or better. This syringe is used in the standardization step (see Section 10).

6.2.2 Two hundred fifty microlitres, 500 μL , and 1 mL capacities and accurate to the nearest 1 μL , 1 μL , and 0.01 mL, respectively. 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 Society⁷, 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

⁷ *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.

defined by Type II of Specification D 1193.

7.3 *Xylene, Reagent Grade*, less than 100 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 and 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 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.

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 D 4057 and D 4177 and handled and mixed in accordance with Practice D 5854 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 in the expected water concentration.

9. Preparation of Apparatus

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