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Standard Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration[1]

This standard is issued under the fixed designation D4928; 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 Department of Defense.

1. Scope*

1.1 This test method covers the determination of water in the range from 0.02 to 5 mass or volume % in crude oils. Mercaptan (RSH) and sulfide (S^- or H_2S) as sulfur are known to interfere with this test method, but at levels of less than 500 µg/g (ppm), the interference from these compounds is insignificant (see Section 5).

1.2 This test method can be used to determine water in the 0.005 to 0.02 mass % range, but the effects of the mercaptan and sulfide interference at these levels has not been determined.

1.3 This test method is intended for use with standard commercially available coulometric Karl Fischer reagent.

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

1.5 *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.* For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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

2.2 *API Standards:*[3]

MPMS Chapter 8.1 Practice for Manual Sampling of Petroleum and Petroleum Products (ASTM Practice D4057)

MPMS Chapter 8.2 Practice for Automatic Sampling of Petroleum and Petroleum Products (ASTM Practice D4177)

MPMS Chapter 8.3 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products (ASTM Practice D5854)

3. Summary of Test Method

3.1 After homogenizing the crude oil with a mixer, an aliquot is injected into the titration vessel of a Karl Fischer apparatus in which iodine for the Karl Fischer reaction is generated coulometrically at the anode. When all 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, one mole of iodine reacts with one mole of water, thus the quantity of water is proportional to the total integrated current according to Faraday's Law.

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and the API Committee on Petroleum Measurement~~,~~ and is the direct responsibility of Subcommittee D02.02.10 on Sediment and Water (API MPMS Chapter 10.0).

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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] Published as Manual of Petroleum Standards. Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, http://www.api.org.

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

3.2 The precision of this test method is critically dependent on the effectiveness of the homogenization step. The efficiency of the mixer used to achieve a homogeneous sample is determined by the procedure given in Practice D5854 (API *MPMS* Chapter 8.3).

3.3 Two procedures are provided for the determination of water in crude oils. In one procedure, a weighed aliquot of sample is injected into the titration vessel and the mass % of water is determined. The other procedure provides for the direct determination of the volume % of water in the crude oil by measuring the volume of crude oil injected into the titration vessel.

4. Significance and Use

4.1 A knowledge of the water content of crude oil is important in the refining, purchase, sale, or transfer of crude oils.

5. Interferences

5.1 A number of substances and classes of compounds associated with condensation or oxidation-reduction reactions interfere in the determination of water by Karl Fischer. In crude oils, the most common interferences are mercaptans and sulfides (not total sulfur). At levels of less than 500 µg/g (ppm) (as sulfur), the interference from these compounds is insignificant. Most crude oils, including crude oils classified as "sour crude," have mercaptan and sulfide levels of less than 500 µg/g (ppm) as sulfur. For more information on substances that interfere in the determination of water by Karl Fischer titration method (see Test Method E203).

5.2 The significance of the mercaptan and sulfide interference on the Karl Fischer titration for water levels in the 0.005 to 0.02 mass % range has not been determined experimentally. At these low water levels, however, the interference may be significant for mercaptan and sulfide levels of less than 500 µg/g (ppm) (as sulfur).

6. Apparatus

6.1 *Karl Fischer Apparatus*, using electrometric end-point. Presently there are available on the market a number of commercial coulometric Karl Fischer titration assemblies. Instructions for operation of these devices are provided by the manufacturer and not described herein.

6.2 *Mixer*, to homogenize the crude sample.

6.2.1 *Non-Aerating, High-Speed, Shear Mixer*—The mixer shall be capable of meeting the homogenization efficiency test described in Practice D5854 (API *MPMS* Chapter 8.3). The sample size is limited to that suggested by the manufacturer for the size of the mixing probe.

6.2.2 Circulating sample mixers, such as those used with automatic crude oil sampling receivers, are acceptable providing they comply with the principles of Practice D5854 (API *MPMS* Chapter 8.3).

6.3 *Syringes*:

6.3.1 Samples are most easily added to the titration vessel by means of accurate glass syringes with LUER fittings and hypodermic needles of suitable length. The bores of the needles used should be kept as small as possible but large enough to avoid problems arising from back pressure and blocking while sampling. Suggested syringe sizes are as follows:

6.3.1.1 *Syringe*, 10 µL with a needle long enough to dip below the surface of the anode solution in the cell when inserted through the inlet port septum. This syringe is used in the calibration step (Section 10). It should be of suitable graduations for readings to the nearest 0.1 µL or better.

6.3.1.2 *Syringes*, 250 µL, 500 µL, and 1000 µL (1 mL), for crude oil samples. For the volumetric determination procedure, the syringes should be accurate to 5 µL, 10 µL, and 20 µL (0.02 mL), respectively.

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.[4] 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type IV of Specification D1193.

7.3 *Xylene*, reagent grade. Less than 0.05 % water. (**Warning**—Flammable. Vapor harmful.)

7.4 *Karl Fischer Reagent*—Standard commercially available reagents for coulometric Karl Fischer titrations.

7.4.1 *Anode Solution*, shall be 6 parts of commercial Karl Fischer anode solution with 4 parts of reagent grade xylene. Fresh Karl Fischer anode solution shall be used. Anode solution shall not be used past its expiration date. Anode solution should be replaced after 7 days in the titration vessel. (**Warning**—Flammable, toxic by inhalation and if swallowed, avoid contact with skin.)

NOTE 1—Other proportions of anode solution and xylene can be used and should be determined for a particular reagent and apparatus. The precision and bias were established using the designated anode solution and xylene.

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[4] *Reagent Chemicals, American Chemical Society Specifications*~~,~~, American Chemical Society, Washington, DC. For ~~s~~Suggestions on the testing of reagents not listed by the American Chemical Society, see ~~*Analar*~~*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.

7.4.2 *Cathode Solution*, use standard commercially available Karl Fischer cathode solution. Cathode solution shall not be used after the expiration date and should be replaced after 7 days in the titration vessel. (**Warning** —Flammable, can be fatal if inhaled, swallowed, or absorbed through skin. Possible cancer hazard.)

8. Sampling and Test Specimens

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. The laboratory sample container and sample volume shall be of sufficient dimensions and volume to allow mixing as described in 8.4.

8.2 *Laboratory Sample*—The sample of crude oil presented to the laboratory or test facility for analysis by this test method. Only representative samples obtained as specified in Practice D4057 (API *MPMS* Chapter 8.1) and Practice D4177 (API *MPMS* Chapter 8.2) shall be used to obtain the laboratory sample.

NOTE 2—Examples of laboratory samples include sample bottles from manual sampling, receptacles from automatic crude oil samplers, and storage containers holding a crude oil from a previous analysis.

8.3 *Test Specimen*—The sample aliquot obtained from the laboratory sample for analysis by this test method. Once drawn, the entire portion of the test specimen will be used in the analysis. Mix the laboratory sample properly as described in 8.4 before drawing the test specimen.

8.4 Mix the laboratory sample of crude oil immediately (within 15 min) before drawing the test specimen to ensure complete homogeneity. Mix the sample at room temperature (15 to 25°C) or less in the laboratory sample container and record the temperature of the sample in degrees Celsius immediately before mixing. The type of mixer depends on the quantity of crude oil in the laboratory sample container. Before any unknown mixer is used, the specifications for the homogenization test, Practice D5854 (API *MPMS* Chapter 8.3), shall be met. Reevaluate the mixer for any changes in the type of crude, volume of crude in the container, the shape of the container, or the mixing conditions (such as mixing speed and time of mixing).

8.5 For small laboratory sample containers and volumes, 50 to 500 mL, a non-aerating, high-speed, shear mixer is required. Use the mixing time, mixing speed, and height of the mixer probe above the bottom of the container found to be satisfactory in Practice D5854 (API *MPMS* Chapter 8.3). For larger containers and volumes, appropriate mixing conditions shall be defined by following a set of procedures similar to those outlined in Practice D5854 (API *MPMS* Chapter 8.3) and Practice D4177 (API *MPMS* Chapter 8.2) but modified for application to the larger containers and volumes. Clean and dry the mixer between samples.

8.6 Record the temperature of the sample in degrees Celsius immediately after homogenization. The rise in temperature between this reading and the initial reading before mixing (8.4) is not to exceed 10°C, otherwise loss of water can occur or the emulsion can become unstable.

8.7 Select the test specimen size as indicated in Table 1 based on the expected water content.

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 to the anode (outer) compartment the mixture of xylene and Karl Fischer anode solutions which has been found suitable for the particular reagent and apparatus being used. Add the solutions to the level recommended by the manufacturer.

9.4 Add to the cathode (inner) compartment the Karl Fischer cathode solution to a level 2 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.

NOTE 3—High background current for a prolonged period can be due to moisture on the inside walls of the titration vessel. Gentle shaking of the vessel (or more vigorous stirring action) will wash the inside with electrolyte. Keep the titrator on to allow stabilization to a low background current.

10. 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 10 µL of pure water. Suggested intervals are initially with fresh reagent and then after every ten determinations (see Section 11.1.3). If the result is outside 10 000 ± 200 µg, replace both the anode and cathode solutions.

TABLE 1 Approximate Test Specimen Size Based on Expected Water Content

Expected Water Content, %	Sample Size, g or mL	Water Titrated, µg
0.02–0.1	1.0	200–1000
0.1–0.5	0.5	500–2500
0.5–5.0	0.25	1250–12500