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Standard Test Methods for Water in Crude Oils by Coulometric Karl Fischer Titration¹

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This standard has been approved for use by agencies of the Department of Defense.

^{ε1} NOTE—Footnote 1 and the Referenced Documents were corrected editorially to comply with the ASTM-API joint standard contract in October 2002.

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 $\mu\text{g/g}$ (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 *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:

D 1193 Specification for Reagent Water²

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products (API MPMS Chapter 8.1)³

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products (API MPMS Chapter 8.2)³

D 5854 Practice for Mixing and Handling Liquid Samples

of Petroleum and Petroleum Products (API MPMS Chapter 8.3)⁴

E 203 Test Method for Water Using Karl Fischer Titration⁵

2.2 API Standards:⁶

MPMS Chapter 8.1 Manual Sampling of Petroleum and Petroleum Products (ASTM Practice D 4057)

MPMS Chapter 8.2 Automatic Sampling of Petroleum and Petroleum Products (ASTM Practice D 4177)

MPMS Chapter 8.3 Mixing and Handling Liquid Samples of Petroleum and Petroleum Products (ASTM Practice D 5854)

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.

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 D 5854 (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

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/COMQ, the joint ASTM-API Committee on Static Petroleum Measurement.

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² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 05.02.

⁴ Annual Book of ASTM Standards, Vol 05.03.

⁵ Annual Book of ASTM Standards, Vol 15.05.

⁶ Published as Manual of Petroleum Standards. Available from the American Petroleum Institute (API), 1220 L St., NW, Washington, DC 20005.

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 E 203).

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 D 5854 (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 D 5854 (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.⁷ 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 D 1193.

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.

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 D 4057 (API *MPMS* Chapter 8.1) and Practice D 4177 (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

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.

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 D 5854 (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 D 5854 (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 D 5854 (API *MPMS* Chapter 8.3) and Practice D 4177 (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 $10\,000 \pm 200$ µg, replace both the anode and cathode solutions.

11. Procedure

11.1 Mass Determination of Sample Size:

11.1.1 Add fresh solvents to the anode and cathode compartments of the titration vessel and bring the solvent to end-point conditions as described in Section 9.

11.1.2 Add an aliquot of the crude oil test specimen to the titration vessel immediately after the mixing step described in 8.4 using the following method.

11.1.2.1 Starting with a clean, dry syringe of suitable capacity (see Table 1 and Note 4), withdraw at least three portions of the sample and discard to waste. 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 sample. Withdraw the syringe and reweigh the syringe to the nearest 0.1 mg. After the end-point is reached, record the titrated water from the digital readout on the instrument.

NOTE 4—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 can then be made as necessary.

11.1.2.2 When the background current or titration rate returns to a stable reading at the end of the titration as discussed in 9.5, additional samples can be added in accordance with 11.1.2.1.

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

11.1.3.1 Persistently high and unstable background current.

11.1.3.2 Phase separation in the anode compartment or crude oil coating the electrodes.

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

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

11.1.3.5 The instrument displays error messages that directly or indirectly suggest replacement of the electrodes—see

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

the instrument operating manual.

11.1.3.6 The result from a 10- μL injection of water is outside $10\,000 \pm 200\ \mu\text{g}$.

11.1.4 Thoroughly clean the anode and cathode compartments with xylene if the vessel becomes contaminated with crude. Never use acetone or similar ketones.

NOTE 5—Clogging of the frit separating the vessel compartments will also cause instrument malfunction.

11.1.5 For crudes too viscous to draw into a syringe, add the sample to a clean, dry dropper bottle and weigh the bottle and crude. Quickly transfer the required amount of sample to the titration vessel with the dropper. Reweigh the bottle. Titrate the sample as in 11.2.

11.2 Volume Determination of Sample Size:

11.2.1 This procedure is applicable only when conditions warrant, that is, when the vapor pressure and viscosity of the crude permit an accurate determination of the volume of the crude oil. Viscous crudes are difficult to measure accurately with a syringe.

11.2.2 Take care in filling the syringe to reduce the formation of gas bubbles.

NOTE 6—The presence of gas bubbles in the syringe can be a source of interference. The tendency of the crude to form gas bubbles is a function of the crude type and corresponding vapor pressure.

11.2.3 The referee procedure for determination of water in crude oil by coulometric Karl Fischer titration is the mass measurement of the crude oil in 11.1.

11.2.4 The basic steps are the same as those for mass determination (see 11.1) with the following exception. With a clean, dry syringe of suitable capacity (see Table 1), withdraw at least three portions of sample and discard to waste. Immediately withdraw a further portion of sample, expel any gas in the syringe, clean the needle with a paper tissue, and record the volume in the syringe to the nearest 1 or 10 μL as appropriate (see 6.3.1.2). Insert the needle through the port inlet septum, start the titration, and with the tip of the needle just below the liquid surface, inject the entire contents of the syringe. After the end-point is reached, record from the digital readout on the instrument the micrograms titrated.

12. Calculation

12.1 Calculate the mass % water in a crude oil sample as follows:

$$\text{Water, mass \%} = \frac{W_1}{W_2} \times 100 \quad (1)$$

where:

W_1 = mass of water titrated, μg and

W_2 = mass of sample used, μg .

12.2 Calculate the volume % water in a crude oil sample as follows:

$$\text{Water content, volume \%} = \frac{V_1}{V_2} \times 100 \quad (2)$$

where:

V_1 = volume of water titrated, μL (same as the μg of water reported by the coulometric titrator) and

V_2 = volume sample used, μL .

13. Report

13.1 When determining % water by mass, report the water content to the nearest 0.01 mass %.

13.2 When determining % water by volume, report the water content to the nearest 0.01 volume %.

14. Precision and Bias

14.1 The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:⁸

14.1.1 *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 only in one case in twenty (see Table 2).

14.1.1.1 For determinations of water by mass,

$$r = 0.040 (X^{2/3}) \quad (3)$$

where:

X = sample mean from 0.02 to 5 mass %.

14.1.1.2 For determinations of water by volume,

$$r = 0.056 (X^{2/3}) \quad (4)$$

where:

X = sample mean from 0.02 to 5 volume %.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty (see Table 2).

14.1.2.1 For determinations of water by mass,

$$R = 0.105 (X^{2/3}) \quad (5)$$

⁸ Supporting data are available from ASTM Headquarters, Request RR: D02-1246.

TABLE 2 Precision Intervals

% Water (Mass or Volume)	Repeatability (r)		Reproducibility (R)	
	Mass	Volume	Mass	Volume
0.01	0.002	0.003	0.005	0.005
0.02	0.003	0.004	0.008	0.008
0.05	0.005	0.008	0.014	0.015
0.1	0.01	0.01	0.02	0.02
0.3	0.02	0.03	0.05	0.05
0.5	0.03	0.04	0.07	0.07
0.7	0.03	0.04	0.08	0.09
1.0	0.04	0.06	0.11	0.11
1.5	0.05	0.07	0.14	0.15
2.0	0.06	0.09	0.17	0.18
2.5	0.07	0.10	0.19	0.21
3.0	0.08	0.12	0.22	0.23
3.5	0.09	0.13	0.24	0.26
4.0	0.10	0.14	0.26	0.28
4.5	0.11	0.15	0.29	0.31
5.0	0.12	0.16	0.31	0.33

where:

X = sample mean from 0.02 to 5 mass %.

14.1.2.2 For determinations of water by volume,

$$R = 0.112 (X^{2/3}) \quad (6)$$

where:

X = sample mean from 0.02 to 5 volume %.

14.2 *Bias*:

14.2.1 No significant difference was found between the average water content obtained by this test method and the expected water content (based on the amount of added water) for the crude oil samples analyzed in the round robin used to evaluate the precision of this test method.⁸

14.2.2 The interference from mercaptan sulfur follows the theoretical stoichiometry of 1 to 0.28, that is 1000 $\mu\text{g/g}$ (ppm) of mercaptan sulfur can generate a response equivalent to 280 $\mu\text{g/g}$ (ppm) water by this test method. The interference from H_2S sulfur follows the stoichiometry of 1 to 0.56, that is 1000 $\mu\text{g/g}$ (ppm) of hydrogen sulfide sulfur can generate a response equivalent to 560 $\mu\text{g/g}$ (ppm) water by this test method. The validity of correcting measured water contents for known mercaptan/sulfide levels has not yet been determined.

15. Keywords

15.1 coulometric; crude oils; homogenization; Karl Fischer; shear mixer; titration; water; water in crude oils

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