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Manual of Petroleum Measurement Standards (MPMS), Chapter 10.9



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

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 55.00 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~~), [ppm(m)], the interference from these compounds is insignificant (see Section 56).

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. For the range 0.005 to 0.02 mass %, there is no precision or bias statement.

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~~warning statements, see Section 78.

2. Referenced Documents

2.1 ASTM Standards:²

D1193 Specification for Reagent Water

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

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

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

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. Terminology

3.1 The following terms are used with respect to sampling (see Section 9).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *aliquot, n*—a small portion of a larger sample which is analyzed and assumed to represent the whole sample.

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 on Hydrocarbon Measurement for Custody Transfer (Joint ASTM-API).

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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

3.2.2 sample, n—portion extracted from the contents of any pipe, tank, or other system, and intended to be representative of that system, placed in a primary sample container for analysis.

3.2.3 test specimen, n—the representative sample taken from the primary or intermediate sample (aliquot) container for analysis. The entire test specimen is used in the analysis.

4. Summary of Test Method

4.1 After homogenizing the crude oil with a mixer, an aliquot sample, a test specimen of that sample is injected into the titration vessel cell 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 endpoint detector and the titration is terminated. Based on the stoichiometry of the reaction, one mole of iodine reacts with one mole of water, water thus the quantity of water is proportional to the total integrated current according to Faraday's Law can be determined.

4.2 The precision of this test method is critically dependent on the effectiveness of the homogenization step. The efficiency acceptability of the mixer mixing used to achieve a homogeneous sample is determined by the procedure given in Practice D5854 (API MPMS Chapter 8.3). In addition, if the test method is performed on a volume basis, the precision of the test method is critically dependent on the accuracy and repeatability of the volume injected.

4.3 Two procedures are provided for the determination of water in crude oils. In one procedure, a weighed aliquot of sample test specimen is injected into the titration vessel cell 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 cell.

5. Significance and Use

5.1 A knowledge of The accurate analysis of a crude oil sample to determine the water content of crude oil is important in the refining, purchase, sale, or transfer of crude oils.

6. Interferences

6.1 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)[ppm(m)] (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)[ppm(m)] as sulfur. For more information on substances that interfere in the determination of water by Karl Fischer titration method (see method, see Test Method E203).

6.2 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)[ppm(m)] (as sulfur).

7. Apparatus

7.1 Karl Fischer Apparatus, using electrometric end-point. Presently there are available on the market a number of commercial coulometric Karl Fischer titration assemblies, endpoint detector. The instrument must have anode and cathode reagents in separate compartments. Instructions for operation of these Karl Fischer titration devices are provided by the manufacturer and not described herein.

7.2 Mixer, to homogenize the crude sample.

7.2.1 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 manufacturer's specifications for the size of the mixing probe mixer.

7.2.2 Circulating Sample Mixer—Circulating sample mixers, A device 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).

7.3 Syringes—Syringes—Test specimens are most easily added to the titration cell by means of accurate glass syringes with Luer Lok 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 injecting a test specimen. The syringe size should be selected such that the test specimen is not less than half the total volume contained by the syringe, the needle should be long enough to permit the injection of the test specimen into the fluid, below the surface of the fluid in the titration cell.

7.3.1 Syringes for Gravimetric Determination—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: For gravimetric determination, any type of syringe that does not leak is appropriate. Syringe should have physical dimensions to fit on the balance appropriately.

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.

7.3.2 *Syringe for Volumetric Determination*—For volumetric determination a certified syringe capable of delivering the volumetric quantity with an accuracy 0.5% of the contained volume is required.

7.4 *Balance for Mass Determination*—Any analytical balance with an accuracy and resolution of 0.1 mg, and capable of weighing up to 100 g can be used.

7.4.1 The balance for determining the weight of the test specimen injected into the titration cell shall be calibrated.

NOTE 1—The use of balances on structures that are in motion may not be appropriate.

7.5 *Titration Cell*—Sunlight can cause disassociation of the iodine in the Karl Fischer reagent, resulting in false results. A titration cell made of opaque material may reduce this effect.

8. Reagents and Materials

8.1 *Purity of Reagents*—~~Reagent grade chemicals~~ Chemicals of reagent grade or higher purity 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.

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

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

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

8.4.1 Anode and cathode reagents shall not be used past the manufacturer's expiration date.

8.4.2 The need to replace the anode and cathode reagent is a function of number of tests run and the amount of water previously titrated. An abnormally slow titration is an indication that the reagents should be replaced.

8.4.3 *Anode Solution, Reagent*—~~shall be 6 parts~~ A mixture of commercial coulometric 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.~~ reagent and reagent grade xylene, typically in a 6:4 mixture. Other proportions of anode reagent and xylene can be used and should be determined for a particular reagent and apparatus. The precision and bias were established using a 6 parts Karl Fischer reagent and 4 parts xylene. (**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.

8.4.4 *Cathode Solution, Reagent*—~~use~~ Use standard commercially available coulometric 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. reagent. (**Warning**—Flammable, can be fatal if inhaled, swallowed, or absorbed through skin. Possible cancer hazard.)

8.4.5 *Check Solution*—NIST Traceable check solution used for verifying the calibration of the Karl Fischer instrument. In the absence of an available check solution, pure water may be used.

9. Sampling and Test Specimens

9.1 *Sample Container*—~~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~~ It shall be constructed of a material to which water does not adhere 8.4. with a sealable lid or other mechanism to prevent rain or humidity from contaminating the sample.

9.1.1 If a non-aerating high-speed shear mixer is to be used, the sample container shall be of sufficient dimensions to allow mixing as described in 9.6 and consistent with the sample container used in any mixer efficiency testing.

9.1.2 If a circulating sample mixer is to be used, the primary sample container shall be designed for direct connection to the mixing system without transfer to an intermediate sample container. Internals should be constructed to ensure fluid circulation results in efficient homogenization of the sample. This can be accomplished with spray nozzles, dispersion tubes or other proprietary designs.

⁴ *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.

9.1.3 Sample Container Preparation—The sample container shall be clean and dry prior to use. Inspect the integrity of sample container lid seals.

9.2 Sample Volume—The volume required for a test specimen to be analyzed is very small (typically 1 mL or less) so the primary constraint for sample volume is that it be sufficient to allow mixing as described in 9.6, and withdrawal of multiple test specimens for repeat testing.

9.3 Sampling Apparatus—Sample lines and other sampling apparatus that comes into contact with the fluid being sampled shall be constructed of a material to which water does not adhere. The apparatus shall be constructed so that water does not collect in deadlegs and low spots. There may be unique requirements specified in the sampling method listed in 9.5. Prior to extracting a sample, sample apparatus should be appropriately purged or cleaned to prevent contamination.

9.4 Sample Storage and Handling—Samples should be properly labeled and secured as appropriate to prevent tampering. Samples can be stored indefinitely as long as the container is constructed to prevent ingress or egress of vapors, and the fluid being tested can be rehomogenized. No additional environmental constraints apply to properly sealed containers.

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

9.5.1 Sampling Viscous Crude Oil—Application of this method of viscous crude oils may present challenges in two different areas; sample mixing and test specimen extraction. Mixing apparatus may operate less efficiently. It may be difficult or impossible to extract and deliver an exact quantity of test specimen (see Section 15). Equipment or procedure modifications if required may invalidate the precision statement in this method. Validation of any modifications are required.

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).

9.6 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. Sample Mixing:

9.6.1 In order for the test specimen to be representative of the sample, the sample must first be homogenized. This is accomplished by mixing the sample using an appropriate mixer for a specified period of time.

9.6.2 The mixer shall meet the specifications for the homogenization test, Practice D5854 (API MPMS Chapter 8.3). 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).

9.6.2.1 For small sample containers and volumes in the 50 to 500 mL range, a non-aerating, highspeed, shear mixer may be used. Use the parameters found to be satisfactory in the Practice D5854 (API MPMS Chapter 8.3) homogenization test.

9.6.2.2 For larger containers and volumes larger than 500 mL, appropriate mixing conditions shall be defined by following a set of procedures similar to those outlined in Practice D5854 (API MPMS Chapter 8.3) but modified for application to the larger containers and volumes.

9.6.2.3 Ensure the mixer is clean and dry before use.

9.6.3 An excessive rise in temperature during mixing (exceeding 10°C) may result in the loss of water or destabilization of the emulsion. Record the temperature of the sample immediately before and after mixing.

9.6.4 Mix the sample of crude oil immediately before drawing the test specimen to ensure the sample remains homogeneous.

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

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.