Designation: D4928 – 24

Manual of Petroleum Measurement Standards (MPMS), Chapter 10.9

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 U.S. Department of Defense.

1. Scope*

1.1 This test method covers the determination of water with true concentration range from 0.02 % to 5.00 % by mass or volume in crude oils using Procedures A and B and from 0.04 % to 3.75 % by mass or volume for Procedure C. 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(m)], the interference from these compounds is insignificant (see Section 6).

NOTE 1—To accommodate testing variations for Procedure C, refer to Section 16 for valid reporting range of test results.

1.2 This test method can be used to determine water in the 0.005 % to 0.02 % by 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 % by 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific warning statements, see Section 8.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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 Products by Hydrometer Method (API *MPMS* Chapter 9.1)

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 (API *MPMS* Chapter 8.1)

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

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

D5002 Test Method for Density, Relative Density, and API Gravity of Crude Oils by Digital Density Analyzer

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

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 1 Terms and Definitions Database

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

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, 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 Hydrocarbon Measurement for Custody Transfer (Joint ASTM-API). This test method has been approved by the sponsoring committees and accepted by the Cooperating Societies in accordance with established procedures.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. 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), 200 Massachusetts Ave., NW, Suite 1100, Washington, DC 20001, http://www.api.org.

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

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)

MPMS Chapter 9.1 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method (ASTM Test Method D1298)

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175 and the API *MPMS* Ch 1 Terms and Definitions Database.

3.1.2 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.

3.2.2 *coulometric titration, n—in reference to Karl Fischer titration methods*, a process of measuring the water content of a sample using an electrolytic process to generate iodine *in situ*.

3.2.3 *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.

3.2.4 *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 sample, a test specimen of that sample is injected into the titration 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 endpoint 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 can be determined.

4.2 The precision of this test method is critically dependent on the effectiveness of the homogenization step. The acceptability of the 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 Three procedures are provided for the determination of water in crude oils. In Procedure A, a weighed test specimen is injected into the titration cell and the mass % of water is determined. Procedure B 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 cell. Procedure C, in effect, uses a test specimen by weight of the sample placed into a glass vial and sealed. Toluene is added to be used as a co-solvent to enhance water extraction from the sample. The vial is heated in an oven to extract any water present into the headspace of the vial. The vaporized water in the headspace is carried into the Karl Fischer titration cell by a dried, nonreactive, carrier gas where it is titrated. The results may be presented on either a mass or volume basis. The contracting parties to any agreement should mutually agree on the method to be used.

5. Significance and Use

5.1 The accurate analysis of a crude oil sample to determine the water content 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(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(m)] as sulfur. For more information on substances that interfere in the determination of water by Karl Fischer titration 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 % by 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(m)] (as sulfur).

6.3 The indirect analysis method using an oven accessory (Procedure C) can reduce interferences, such as mercaptans.

6.3.1 A higher than appropriate extraction temperature can cause sample decomposition resulting in chemical interferences which can cause erroneously high results.

NOTE 2—For more information on chemical interferences, see X1.6.

7. Apparatus

7.1 *Karl Fischer Apparatus,* using electrometric endpoint detector. For Procedures A and B, the instrument may have anode and cathode reagents in separate compartments or diaphragm-less reagents in a single compartment. Instructions for operation of 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's specifications for the size of the mixer.

7.2.2 *Circulating Sample Mixer*—A device such as used with automatic crude oil sampling receivers, is acceptable providing it complies with the principles of Practice D5854 (API *MPMS* Chapter 8.3).

7.3 *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*—For gravimetric determination, any type of syringe that does not leak is appropriate. Syringe should have physical dimensions to fit on the balance appropriately.

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 *Oven Accessory (Procedure C)*—A standalone or automated device where the vial containing the test specimen with co-solvent is heated under controlled conditions, and the volatilized components are transferred using a dried carrier gas via a transfer line to a coulometric titration cell where they are titrated for water content.

7.5 *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.

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

NOTE 3—The use of balances on structures that are in motion may not be appropriate.

7.6 *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*—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*—Reagent grade. Less than 0.05 % water. (**Warning—**Flammable. Vapor harmful.)

8.4 *Toluene*—Reagent grade. Less than 0.02 % water. (**Warning—**Flammable. Vapor harmful.)

8.5 *Molecular Sieve,* or other suitable drying agent.

8.6 *Karl Fischer Reagent*—Commercial coulometric Karl Fischer (KF) reagents and reagent systems of various types are available for use with auto-titrators for water determination. Traditionally, pyridine was the organic base used in KF reagents. The pyridine-free reagents are less toxic, less odorous, and more stable than those containing pyridine. The use of pyridine-free reagents is recommended whenever possible. Coulometric titrations normally require two reagent solutions: an anolyte and a catholyte or generator solution. However, with the use of an integrated or diaphragm-less cell, a single solution that contains all of the reagents needed for a KF titration may be used.

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

8.6.2 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.

8.6.3 *Anode Reagent*—A mixture of commercial coulometric Karl Fischer anode 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.)

8.6.4 *Cathode Reagent*—Use standard commercially available coulometric Karl Fischer cathode reagent. (**Warning—**Flammable, can be fatal if inhaled, swallowed, or absorbed through skin. Possible cancer hazard.)

8.6.5 *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.

8.7 *Water Standards*—0.1 % and 1 % by mass or volume, commercially prepared in organic solvent are recommended. Other concentrations of prepared standards may be used. For Procedure C, oven accessory standards containing up to 5 % water are acceptable for use. Consult with the oven accessory manufacturer in the selection of standards.

8.8 *Nitrogen*—Used as a carrier for transferring moisture into the Karl Fischer titration vessel in Procedure C. Other dry gasses may be used.

8.9 Sample vials as described by the instrument manufacturer. The same vials will be used for check solutions, blanks and test specimens. It should comprise a sealing septum that will be used to allow the injection of co-solvent and the instrument to purge the sample into the test apparatus.

9. Sampling and Test Specimens

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

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[4] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.