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## Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration<sup>1</sup>

This standard is issued under the fixed designation D 4377; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This test method has been approved by the sponsoring committees and accepted by the cooperating societies in accordance with established procedures.*

*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 2 % in crude oils. Mercaptan and sulfide ( $S^-$  or  $H_2S$ ) sulfur are known to interfere with this test method (see Section 5).

1.2 This test method is intended for use with standard Karl Fischer reagent or pyridine-free Karl Fischer reagents.

1.3 The 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.* Specific precautionary statements are given in Section 7.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

D 4006 Test Method for Water in Crude Oil by Distillation<sup>3</sup>

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>3</sup>

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>3</sup>

E 203 Test Method for Water Using Volumetric Karl Fischer Reagent<sup>4</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and API Committee on Petroleum Measurement and is the direct responsibility of Subcommittee D02.02, the joint ASTM-API Committee on Static Petroleum Measurement.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 15.05.

#### 2.2 API Standards:<sup>5</sup>

Manual of Petroleum Measurement Standards (MPMS):  
Chapter 8.1 Manual Sampling of Petroleum and Petroleum Products

Chapter 8.2 Automatic Sampling of Petroleum and Petroleum Products

Chapter 10.2 Determination of Water in Crude Oil by Distillation

### 3. Summary of Test Method

3.1 After homogenizing the crude oil with a mixer, an aliquot of the crude, in a mixed solvent, is titrated to an electrometric end-point using Karl Fischer reagent.

### 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 class 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. At levels of less than 500  $\mu\text{g/g}$  (ppm) (as sulfur) the interference from these compounds is insignificant. For more information on substances that interfere in the determination of water using the (Karl Fischer reagent) titration method see Test Method E 203.

### 6. Apparatus

6.1 *Karl Fischer Apparatus*, using electrometric end-point.

<sup>5</sup> Available from American Petroleum Institute, 1220 L St., NW, Washington, DC 20005-4070.

A suggested assembly of the apparatus is described in Annex A2.

6.1.1 Presently there is available on the market commercial Karl Fischer titration assemblies, some of which automatically stop the titration at the end-point. Instructions for operation of these devices are provided by the manufacturer and not described herein. This test method is not intended for use with coulometric Karl Fischer titrators.

6.2 *Mixer*, to homogenize the crude sample.

6.2.1 *Non-Aerating, High-Speed, Shear Mixer*,<sup>6</sup> capable of meeting the homogenization efficiency test described in Annex A1. The sample size is limited to that suggested by the manufacturer for the size of the probe.

6.3 *Syringes*:

6.3.1 Samples and base liquid 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/blocking whilst sampling. Suggested syringe sizes are as follows:

6.3.1.1 *Syringe*, 10  $\mu\text{L}$ , with a needle long enough to dip below the surface of the base solution in the cell during the standardization procedure (see Section 9).

6.3.1.2 *Syringes*, 2.5 mL, 5 mL, and 10 mL for crude oil samples (see Section 10).

6.3.1.3 *Syringe*, 20 mL or larger for sample solvent.

## 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.<sup>7</sup> 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 *1-Ethylpiperidine* (99 + percent). (**Warning**—Irritant. Flammable.)

7.4 *Karl Fischer Reagents*, Standard reagent containing pyridine (7.4.1) or pyridine-free reagent (7.4.2).

7.4.1 *Karl Fischer Reagent Ethylene Glycol Monomethyl Ether Solution*, stabilized, containing pyridine, (1 mL = 5 mg of water)—Fresh Karl Fischer reagent must be used. Must be used with solvent in 7.6.1. (**Warning**—Combustible. Harmful if swallowed, inhaled, or absorbed through the skin.)

<sup>6</sup> The following mixers were used in a cooperative program and have been found satisfactory for samples under 300 mL; Ultra Turrax Model TP 18/10, available from Tekmar Co., P. O. Box 37202, Cincinnati, OH 45222; Brinkman Polytron Model PT 35, Available from Brinkman Instruments Inc., Cantiagu Road, Westbury, NY 11590; and Kraft Apparatus Model S-25, SGA, Bloomfield, NJ.

<sup>7</sup> *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.

7.4.2 *Pyridine-Free Karl Fischer* (one-component) reagent diluted with xylene—Dilute three parts pyridine-free Karl Fischer (one-component) reagent<sup>8</sup> (1 mL = 5 mg water) to 1 part xylene. Fresh Karl Fischer reagent must be used. (**Warning**—See 7.4.1) Must be used with solvent in 7.6.2.

7.5 *Methanol (anhydrous)*, Maximum 0.1 % water but preferably less than 0.05 % water. (**Warning**—Flammable. Vapor harmful. May be fatal or cause blindness if swallowed or inhaled. Cannot be made nonpoisonous.)

7.6 *Sample Solvent*—Use 7.6.1 for standard Karl Fischer reagent containing pyridine and 7.6.2 for pyridine-free Karl Fischer reagent.

7.6.1 *Sample Solvent*—Mix 40 mL of 1-ethylpiperidine, 20 mL of methanol, and 40 mL of Karl Fischer reagent in a sealable glass bottle. Allow this mixture to sit overnight before adding 200 mL of xylene. Additional methanol may be required in some cases for the proper function of the electrodes. (**Warning**—see 7.3.)

7.6.2 *Sample Solvent for Pyridine-Free Reagents*—Mix 3 parts chloroform to 1 part pyridine-free solvent using solvent part of two-component reagent<sup>8</sup> (contains  $\text{SO}_2$  and odorless amine dissolved in methanol) and store in a sealable glass bottle. An evaluation of a number of crude oils has demonstrated that xylene can be substituted for chloroform with no apparent change in accuracy of this test method. (**Warning**—Flammable. Vapor harmful.) (Also, see 7.4.1.)

7.7 *Xylene*, reagent grade. Less than 0.05 % water.

7.8 *Chloroform*, reagent grade. (**Warning**—Harmful if inhaled or swallowed. Carcinogen (animal positive). Skin and eye irritant. May produce toxic vapors if burned.)

## 8. Sampling and Test Samples

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 the laboratory test container. The laboratory test container and sample volume shall be of sufficient dimensions and volume to allow mixing as described in 8.1.2.1.

8.1.1 *Laboratory Sample*—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 for this test method.

8.1.2 *Test Samples*—The following sample handling procedure shall apply in addition to those covered in 8.1.1.

8.1.2.1 Mix the test sample of crude oil immediately (within 15 min) before analysis to insure complete homogeneity. Mix the test sample at room temperature (25°C) in the original container.

NOTE 1—The sample should be mixed at room temperature (25°C) or less. Mixing of the sample should not increase the temperature of the sample more than 10°C, or a loss of water may occur. The type of mixer depends on the quantity of crude. Before any unknown mixer is used, the specifications for the homogenization test, Annex A1, must be met. The

<sup>8</sup> Pyridine-free Karl Fischer reagent and two-component solvent used in the cooperative program and found to be satisfactory are available from Crescent Chemical Co., Inc., 1324 Motor Parkway, Hauppauge, NY 11788 under the name of Hydranal a registered trademark of Riedel Dehaen—Composite 5 and Hydranal—solvent.

mixer must be re-evaluated for any changes in the type of crude, quantity of crude, or shape of the sample container.

8.1.2.1.1 For small sample volumes, 50 to 500 mL, a non-aerating, high speed, shear mixer is required. Use the mixing time, mixing speed, and height above the bottom of the container found to be satisfactory to Annex A1. Clean and dry the mixer between samples.

8.1.2.2 The test sample size is selected as indicated in Table 1 based on the expected water content.

## 9. Calibration and Standardization

9.1 Standardize the Karl Fischer reagent at least once daily.

9.2 Add enough solvent to the clean, dry titration vessel to cover the electrodes. The volume of solvent depends on the size of the titration vessel. Seal all openings to the vessel and start the magnetic stirrer for a smooth stirring action. Turn on the indicating circuit and adjust the potentiometer to give a reference point with approximately 1  $\mu$ A of current flowing. Add Karl Fischer reagent in suitable amounts to the solvent to cause the needle to deflect from the reference point. At first the needle will deflect due to local concentration of the unreacted reagent about the electrodes but will fall back to near the reference point. As the end-point is approached, the needle will fall back more slowly after each addition of Karl Fischer reagent. The end-point is reached when, after the addition of a single drop of reagent, the needle remains deflected at least 1  $\mu$ A from the reference point for at least 30 s. Swirl the titration vessel to dry the inside walls of the vessel. Add more Karl Fischer reagent, if needed, until a steady end-point is reached for at least 30 s.

9.3 Standardize the Karl Fischer reagent with distilled water by one of the following methods:

9.3.1 From a water filled weighing pipet or syringe previously weighed to the nearest 0.1 mg, add 1 drop of distilled water (about 20 mg) to the sample solvent at end-point conditions and reweigh the syringe. Record the weight of the water added. Titrate the water with Karl Fischer reagent added from the buret until a steady end point is reached for at least 30 s. Record to the nearest 0.01 mL the volume of the Karl Fischer reagent needed to reach the end-point.

NOTE 2—After adding water do not shake the cell.

NOTE 3—When wiping the needle exercise care, so not to siphon liquid through the tip of the needle.

9.3.2 Fill a 10- $\mu$ L syringe with water taking care to eliminate air bubbles, wipe the needle with a paper tissue to remove any residual water from the needle and accurately determine the weight of syringe plus water to 0.1 mg. Add the contents of the syringe to the sample solvent in the cell which has been adjusted to the end point ensuring that the tip of the needle is below the surface of the sample solvent. Reseal the vessel immediately. Remove any solvent from the needle by wiping

with a paper tissue and reweigh the syringe to 0.1 mg. Titrate the water with Karl Fischer reagent as in 9.3.1.

9.4 Calculate the water equivalence of the Karl Fischer reagent as follows:

$$F = W/T \quad (1)$$

where:

$F$  = water equivalence of the Karl Fischer reagent, mg/mL,

$W$  = water added, mg, and

$T$  = reagent required for titration of the added water, mL.

9.5 Duplicate values of water equivalence should agree within 2 % relative. If the variation between the two titrations is greater than 2 % relative, discard the contents of the titration vessel. Introduce a further portion of sample solvent into the vessel and repeat the standardization procedure. If the titrations for two further portions of distilled water still vary by more than 2 %, it is likely that either the Karl Fischer reagent or the sample solvent, or both, have aged. Replace these with fresh reagents and repeat the procedure for calibration and standardization.

9.6 Determine and record the mean water equivalence value.

## 10. Procedure

10.1 Add the fresh sample solvent to the titration vessel and bring the solvent to end-point conditions as described in 9.2.

10.2 Add the crude to the titration vessel immediately after the mixing step described in 8.1.2.1 using one of the following methods:

10.2.1 Starting with a clean, dry syringe (10 or 5 mL), rinse the syringe two times with the sample and discharge to waste. Withdraw the required amount of sample and discharge any air bubbles. Weigh the syringe to the nearest 0.1 mg. Inject the sample into the titration vessel, clean the needle with a paper tissue, and reweigh the syringe. Titrate the sample until a steady end-point for at least 30 s is reached and record the volume of Karl Fischer reagent to the nearest 0.01 mL (see Note 2 and Note 4).

NOTE 4—The solvent should be changed when the sample content exceeds 2 g of crude per 15 mL of solvent or when 4 mL of titrant per 15 mL of solvent has been added to the titration vessel.

10.2.2 For viscous crudes, 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 10.2.1.

NOTE 5—After adding the sample do not shake the cell.

## 11. Calculations

11.1 Calculate the water content of the sample as follows:

$$\text{water, mass \%} = CF/W(10) \quad (2)$$

where:

$C$  = Karl Fischer reagent required to titrate the sample, mL,

$F$  = water equivalence of Karl Fischer reagent, mg/mL,

$W$  = sample used, g, and

10 = factor for converting to percent.

**TABLE 1 Test Sample—% Water Content Based on Sample Size**

Expected Water Content, %	Sample Size, g
0–0.3	5
0.3–1	2
1–2	1