Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration

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 (ε) 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.

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 H₂S) 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 problems, 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 Notes 1, 2, 3, 4, and 5.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water
D 1744 Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent
D 4006 Test Method for Water in Crude Oil by Distillation
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D 4177 Test Method for Automatic Sampling of Petroleum and Petroleum Products
E 203 Test Method for Water Using Karl Fischer Reagent

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 μg/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. A suggested assembly of the apparatus is described in Appendix X1 of Test Method D 1744.

6.1.2 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, 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:

---

1 This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.


3 Annual Book of ASTM Standards, Vol 05.01.

4 Annual Book of ASTM Standards, Vol 05.02.

5 Annual Book of ASTM Standards, Vol 15.05.

---

Some of the referenced documents are from the following volumes:

- Annual Book of ASTM Standards, Vol 11.01
- Annual Book of ASTM Standards, Vol 05.01
- Annual Book of ASTM Standards, Vol 05.02
- Annual Book of ASTM Standards, Vol 15.05

Copyright © 1998 by ASTM International

www.astm.org
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 Needle 10 μL, 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 Crude Oil Samples, 2.5 mL, 5 mL, and 10 mL (see Section 10).
6.3.1.3 Sample Solvent, 20 mL or larger.

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. 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).

NOTE 1: 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.

NOTE 2: Warning—Combustible. Harmful if swallowed, inhaled, or absorbed through the skin.

7.4.2 Pyridine-Free Karl Fischer (one-component) reagent diluted with xylene—Dilute three parts pyridine-free Karl Fischer (one-component) reagent (1 mL = 5 mg water) to 1 part xylene. Fresh Karl Fischer reagent must be used. (Warning—See Note 2) Must be used with solvent in 7.6.2.
7.5 Methanol (anhydrous), Maximum 0.1% water but preferably less than 0.05% water.

NOTE 3: 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 Note 1.)
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 (contains SO₂ 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—See Notes 2 and 4.)
7.7 Xylene, reagent grade. Less than 0.05 % water.

7.8 Chloroform, reagent grade.

NOTE 5: 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 and D 4177 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 6—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 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.

<table>
<thead>
<tr>
<th>TABLE 1 Test Sample—% Water Content Based on Sample Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expected Water Content, %</td>
</tr>
<tr>
<td>---------------------------</td>
</tr>
<tr>
<td>0.3-1</td>
</tr>
<tr>
<td>1-2</td>
</tr>
</tbody>
</table>


8 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 Dehnen—Composite 5 and Hydranal—solvent.
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 as prescribed in Test Method D 1744. Add Karl Fischer reagent from the buret until the end point is reached. 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 7—After adding water do not shake the cell.

NOTE 8—When wiping the needle exercise care, so not to siphon liquid through the tip of the needle.

9.3.2 Fill a 10-µL syringe with water taking care to eliminate air bubbles, wipe the needle with a paper towel 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 towel 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:

\[ F = \frac{W}{T} \]

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 towel, 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 Notes 7 and 9).

NOTE 9—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 10—After adding the sample do not shake the cell.

11. Calculations

11.1 Calculate the water content of the sample as follows:

\[ \text{water, mass} \% = \frac{CF}{W}(10) \]

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.

12. Precision and Bias

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

12.1.1 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.

\[
\begin{align*}
12.1.1.1 & \text{Standard Karl Fischer Reagents:} \\
& \quad r = 0.034 (X^{1/3}) \\
12.1.1.2 & \text{Pyridine-Free Karl Fischer Reagents:} \\
& \quad r = 0.032 (X^{1/3})
\end{align*}
\]

Supporting data are available from ASTM Headquarters. Request RR:D02-1173.
where: $X = \text{sample mean from 0.0 to 2 \%}$. 

12.1.2 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.

12.1.2.1 Standard Karl Fischer Reagents:

$$R = 0.111 (X^{1/3})$$

12.1.2.2 Pyridine-Free Karl Fischer Reagents:

$$R = 0.095 (X^{1/3})$$

where:

$X = \text{sample mean from 0.00 to 2 \%}$. 

12.2 Bias:

12.2.1 Compared to the results of Test Method D 4006, no significant bias was found.

12.2.2 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 \(\mu\text{g/g (ppm)}\) (0.03 mass \%) water by this test method. The validity of correcting measured water contents for known mercaptan/sulfide sulfur levels has not been evaluated.

ANNEX

(Mandatory Information)

A1. HOMOGENIZATION EFFICIENCY OF UNKNOWN MIXERS

A1.1 The homogenization efficiency of each unknown mixer must be evaluated before use. The grade of crude oil, the sample size, and the sample container expected to be used with the mixer should be used in this test. The specifications of this test should be met before running this method and any changes in the mixing procedure should be re-evaluated by this test. The crude oil used in this test should be dry (less than 0.1 \% water).

A1.2 Weigh the sample container to the nearest 0.01 g. Fill the container between (or the level normally used) with the dry crude. Immerse the mixer into the crude with the bottom of the mixer 5 mm above the bottom of the container and mix the crude at the speed and for the amount of time you expect to use. Suggested mixing time is between 1 and 5 min at 5 to 7 thousand rpm/s. Immediately determine the water content in duplicate (10.1) of the dry crude. Obtain the average of the duplicate results.

A1.3 Weigh the crude and container to the nearest 0.01 g. Immerse the mixer into the crude at 5 mm above the bottom of the container and mix the crude at the speed and for the amount of time you expect to use. Suggested mixing time is between 1 and 5 min at 5 to 7 thousand rpm/s. Immediately determine the water content in duplicate (10.1) of the dry crude. Obtain the average of the duplicate results.

A1.4 Without additionally mixing the crude, determine the water content of the crude 15 and 30 min after the initial mixing in A1.3.

A1.5 Remix the sample in the same manner as A1.2. Immediately after mixing, determine the water content in duplicate.

A1.6 The water contents of the crude determined in A1.3, A1.4, and A1.5 minus the base determined in Section A1.2 should agree within 0.05 \% absolute of the added water and to each other. If they do not agree, this test should be repeated while changing the mixing time, the mixing speed, or the height of the mixer, in the crude or a combination thereof, until these conditions are met.