# Manual of Petroleum Measurement Standards
# Chapter 10.9

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

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**Designation: D4928 – 12**

**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 Department of Defense.*

## 1. Scope*

1.1 This test method covers the determination of water in the range from 0.02 to 5.00 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 µg/g [ppm(m)], the interference from these compounds is insignificant (see Section 6).

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 warning statements, see Section 8.

## 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.

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 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

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[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**

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

## 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 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).

## 7. Apparatus

7.1 *Karl Fischer Apparatus,* using electrometric endpoint detector. The instrument must have anode and cathode reagents in separate compartments. 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 *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*—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.)

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[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.

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 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.)

8.4.4 *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.)

8.4.5 *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*—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.

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.

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.

**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 | 1250–12 500 |

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 *Sampling Method*—Representative samples obtained as specified in Practice D4057 (API MPMS Chapter 8.1) and Practice D4177 (API *MPMS* Chapter 8.2) should be used to obtain the sample.

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.

9.6 *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.

## 10. Preparation of Apparatus

10.1 Follow the manufacturer's directions for preparation and operation of the titration apparatus.

10.2 All joints and connections to the cell shall be sealed in order to prevent atmospheric moisture from entering the titration cell.

10.3 *Anode*—Add the appropriate mixture of xylene and Karl Fischer anode reagent to the level recommended by the manufacturer.

10.4 *Cathode*—Add the Karl Fischer cathode reagent. This reagent should be 2 to 3 mm below the level of the reagent in the anode compartment, or as recommended by the manufacturer.

10.5 Turn on the Karl Fischer titrator and start the stirrer. The stirrer should create a smooth, stirring action. Allow the residual moisture in the titration cell to be titrated until the endpoint is reached. If the time to reach an end point is excessive or there is high background current, this may be due to moisture on the inside walls of the titration cell. If this occurs, turn off the titration machine and gently swirl the liquid in the cell to wash the inside of the glassware. Repeat Karl Fischer titration until the end point is reached.

## 11. Verification of Equipment Calibration

11.1 Reagent performance deteriorates with use, so regular verification of reagent performance is required. This verification may be performed by injecting a known quantity of check solution (pure water) into the titration cell and confirming the result of the titration is consistent with the quantity injected. Suggested intervals are when the equipment is initially placed into use, when fresh reagent is introduced, and after every ten determinations (see 12.1.3). If the result is outside of tolerances, replace both the anode and cathode reagents.

11.1.1 *Mass Determination of Sample Size*—Fill a 10 µL syringe with water taking care to eliminate air bubbles, wipe the needle to remove any residual water from the needle and accurately determine the weight of the syringe plus water to 0.1 mg. Add the contents of the syringe to the titration cell ensuring that the tip of the needle is below the surface of the reagent. Reseal the titration cell immediately. Remove any reagent from the needle by wiping and reweigh the syringe to 0.1 mg. After the endpoint is reached, record the amount of titrated water. If the result is outside 10 000 ± 200 µg, replace both the anode and cathode reagents.

11.1.2 *Volume Determination of Sample Size*—Accurately fill a 10 µL syringe with water taking care to eliminate air bubbles, wipe the needle to remove any residual water. Add the contents of the syringe to the titration cell ensuring that the tip of the needle is below the surface of the reagent. Reseal the cell immediately. After the endpoint is reached, record the titrated water from the readout on the Karl Fischer apparatus. If the result is outside 10 000 ± 200 µg, or the equivalent as a percent water, replace both the anode and cathode reagents.

## 12. Procedure

12.1 *Mass Determination of Sample Size:*

12.1.1 Prepare the apparatus for use as described in Section 10.

12.1.2 Ensure the syringe is of suitable capacity (see 7.3 and Table 1). Immediately after the mixing step described in 9.6, withdraw at least three portions of the sample and discard to waste. Immediately withdraw a fourth portion, wipe the needle clean, weigh the syringe and contents to the nearest 0.1 mg, and inject the test specimen into the Karl Fischer reagent below the surface of the reagent in the titration cell. Withdraw the syringe and reweigh the syringe to the nearest 0.1 mg. After the endpoint is reached, record the result from the instrument.

NOTE 2—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.

12.1.3 Replace the reagents periodically as described in 8.4.

12.1.4 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 cell with the dropper. Reweigh the bottle. Titrate the sample as in 12.1.2

12.2 *Volume Determination of Sample Size:*

12.2.1 When measuring the test specimen by volume, the measurement of the volume is critical; special attention should be used in determining the test specimen volume.

12.2.2 Take care in filling the syringe to reduce the formation of gas bubbles. The presence of gas bubbles in the syringe can be a source of interference. The tendency of the crude to form gas bubbles may be a function of the crude type and corresponding vapor pressure.

12.2.3 Prepare the apparatus for use as described in Section 10. Ensure the syringe is of suitable capacity (see 7.3). Immediately after the mixing step described in 9.6, withdraw at least three portions of the sample and discard to waste. Immediately withdraw a fourth portion, wipe the needle clean, invert the syringe and allow any bubbles in the syringe to come to the outlet, expel the bubbles, wipe the needle, and record the volume in the syringe to the nearest 1 or 10 µL as appropriate. Inject the entire test specimen into the Karl Fischer reagent below the surface of the reagent in the titration cell. Inject the test specimen into the Karl Fischer reagent. After the endpoint is reached, record the results from the instrument

12.3 Prior to reporting the results, the results shall be checked against the repeatability requirement as discussed in 16.1.1.

## 13. Calculation

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

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

where:

$W_1$ = mass of water titrated, µg and
$W_2$ = mass of sample used, µg.

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

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

where:

$V_1$ = volume of water titrated, µL (same as the µg/1000 of water reported by the coulometric titrator), and

$V_2$ = volume of sample used, µL.

## 14. Report

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

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

## 15. Troubleshooting and Maintenance

15.1 *General Troubleshooting*—Consult the manufacturer's user manual for the proper operation and maintenance of the Karl Fischer instrument. While the Karl Fischer instrument is generally not serviceable by the user, the following can be checked in the field.

15.1.1 *Battery Power*—If the instrument is battery powered, follow the recommended guidelines for proper battery changing. Continued usage of the instrument once the battery charge has fallen below the level prescribed by the manufacturer may cause unpredictable results.

15.1.2 *Calibration Verifications*—Calibration verifications should be performed as described in Section 11. Observe the dates on the check solution and reagents to verify they are not beyond their expiration date. If the instrument results are outside of the prescribed tolerances, or if the instrument is abnormally slow to reach a result:

15.1.2.1 Change the electrode reagents and rerun the calibration verification.

15.1.2.2 Check that the electrode connections are secure.

15.1.2.3 Check that the cell is sealed. Endpoint creep is a sign of an incomplete cell seal.

15.1.2.4 Consult with the manufacturer.

15.1.3 *Results Out of the Expected Range*—There are multiple causes for results falling outside of the expected range:

15.1.3.1 Gas bubbles and entrained gasses. For determinations of water by volume, gas bubbles and gasses entrained in the test specimen can consume volume in the delivery syringe, and thus mask the true liquid volume of the specimen. To minimize this effect, care should be taken to use the correct syringe and test specimen for the water content of the crude. In addition, over-homogenizing the crude sample can lead to entrained air in the sample and should be avoided.

15.1.3.2 *Inadequate Stirring*—Follow the manufacturer's instructions to ensure the test sample, once injected, is mixed adequately in the sample chamber. Inadequate mixing may result in poor repeatability.

15.1.4 *Viscous Crudes*—Viscous crudes can cause difficulty with mixing and test specimen extraction.

15.1.4.1 *Dilution*—Kerosene, Stoddard Solvent, toluene, and xylene (**Warning—**Flammable, toxic by inhalation and if swallowed, avoid contact with skin.) are satisfactory diluents for crude oil. These diluents are mixed with the crude sample prior to withdrawing an aliquot for testing. The dilluent must be tested for water content and mixed in proportion to the crude with a precision of 0.5% of total volume or better,

**TABLE 2 Precision Intervals**

| % Water | Repeatability (*r*) | | Reproducibility (*R*) | |
|---|---|---|---|---|
| (Mass or Volume) | 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 |

15.1.4.2 *Larger Bore Syringe Needles*—Difficulties in drawing a test specimen of viscous crude into the syringe can sometimes be mitigated by using a larger bore (14 gauge) needle.

15.1.4.3 *Heating*—Heating the sample aliquot can reduce the viscosity of the sample. The temperature of the sample should be limited to 160°F.

15.2 *Maintenance*—Changing the electrode reagents and charging the battery of portable Karl Fischer instruments is part of routine maintenance. Frequency of use and the types of crudes analyzed will impact the required maintenance.

15.2.1 *Cell Cleaning*—Thoroughly clean the anode and cathode cell with xylene or other chemical if the cell becomes contaminated with crude.

NOTE 3—Never use acetone or similar ketones.

15.2.2 *Probe Maintenance*—In some cases the probes must be returned to the manufacturer for cleaning on a periodic basis.

NOTE 4—Clogging of the frit separating the cell compartments will cause instrument malfunction.

NOTE 5—Ensure the probes of the detector are not touching (follow manufacturer's guidelines for appropriate space. Ensure the screen on the bottom of the cathode cell has space between it and the generator glassware.

## 16. Precision and Bias

16.1 The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:[5]

16.1.1 *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. A minimum of 2 injections is required and, if the results are less than the stated *r* (see Table 2), the mean of the

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1246.

2 results are reported. If $r$ cannot be achieved within 5 consecutive injections, troubleshooting of the equipment should take place (see Section 15).

16.1.1.1 For determinations of water by mass,

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

where:

$X$ = sample mean from 0.02 to 5.00 mass %.

16.1.1.2 For determinations of water by volume,

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

where:

$X$ = sample mean from 0.02 to 5.00 volume %.

16.1.2 *Reproducibility (R)*—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).

16.1.2.1 For determinations of water by mass,

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

where:

$X$ = sample mean from 0.02 to 5.00 mass %.

16.1.2.2 For determinations of water by volume,

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

where:

$X$ = sample mean from 0.02 to 5.00 volume %.

16.2 *Bias:*

16.2.1 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.[5]

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

## 17. Keywords

17.1 coulometric; crude oils; homogenization; Karl Fischer; titration; water; water in crude oils

## SUMMARY OF CHANGES

Subcommittee D02.02 has identified the location of selected changes to this standard since the last issue (D4928–11) that may impact the use of this standard.

*(1)* Updated and modernized the existing standard to bring the content up to existing practices.

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