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Standard Test Method for Water in Crude Oil by Distillation[1]

This standard is issued under the fixed designation D4006; 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 crude oil by distillation.

~~1.2~~

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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 6.1 and A1.1.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D95 Test Method for Water in Petroleum Products and Bituminous Materials by Distillation ~~D96Test Methods for Water and Sediment in Crude Oil by Centrifuge Method (Field Procedure) (API *MPMS* Chapter 10.4)~~

D473 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method

D665 Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water

D1796 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products ~~(API *MPMS* Chapter 8.2)~~

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4928 Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration

E123 Specification for Apparatus for Determination of Water by Distillation

2.2 *API Standards:*

MPMS Chapter 8.1 Manual Sampling of Petroleum and Petroleum Products (ASTM Practice D4057~~(API *MPMS* Chapter 8.1))~~)

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

MPMS Chapter 10.1 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method (ASTM Test Method D473)

MPMS Chapter 10.4 Determination of Water and/or Sediment in Crude Oil by the Centrifuge Method (Field Procedure) ~~(ASTM Test Method D96)~~

[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 D02.02.10 on Sediment and Water (API MPMS Chapter 10.0).

This test method was issued as a joint ASTM-API-IP standard in 1981.

Current edition approved ~~Aug.~~June 1, ~~2007.~~2011. Published ~~September 2007.~~August 2011. Originally approved in 1981. Last previous edition approved in ~~2005~~2007 as ~~D4006–81(2005).~~D4006–07. DOI: ~~10.1520/D4006-07.~~10.1520/D4006-11.

[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.

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

MPMS Chapter 10.5 Test Method for Water in Petroleum Products and Bituminous Materials by Distillation (ASTM Test Method D95)

MPMS Chapter 10.6 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure) (ASTM Test Method D1796)

MPMS Chapter 10.9 Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration (ASTM Test Method D4928)

3. Summary of Test Method

3.1 The sample is heated under reflux conditions with a water immiscible solvent which co-distills with the water in the sample. Condensed solvent and water are continuously separated in a trap—the water settles in the graduated section of the trap, and the solvent returns to the distillation flask.

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.

4.2 This test method may not be suitable for crude oils that contain alcohols that are soluble in water. In cases where the impact on the results may be significant, the user is advised to consider using another test method, such as Test Method D4928 (API *MPMS* Chapter 10.9).

5. Apparatus

5.1 The preferred apparatus, shown in Fig. 1, consists of a glass distillation flask, a condenser, a graduated glass trap,[3] and a heater. Other types of distillation apparatus are specified in Specification E123. Any of these apparatus will be acceptable for this test method provided it can be demonstrated that they operate within the precision established with the preferred apparatus.

5.1.1 *Distillation Flask*—A 1000-mL round-bottom, glass, distillation flask fitted with a 24/40 female taper joint shall be used. This flask receives a 5-mL calibrated, graduated water trap with 0.05-mL graduations. The trap will be fitted with a 400-mm Liebig condenser. A drying tube filled with desiccant (to prevent entrance of atmospheric moisture) is placed on top of the condenser.

5.1.2 *Heater*—Any suitable gas or electric heater that can uniformly distribute heat to the entire lower half of the flask may be used. An electric heating mantle is preferred for safety reasons.

[3] ~~ASTM standard withdrawn.~~

[3] Available on special order from Scientific Glass Apparatus Co., Bloomfield, NJ 07003.

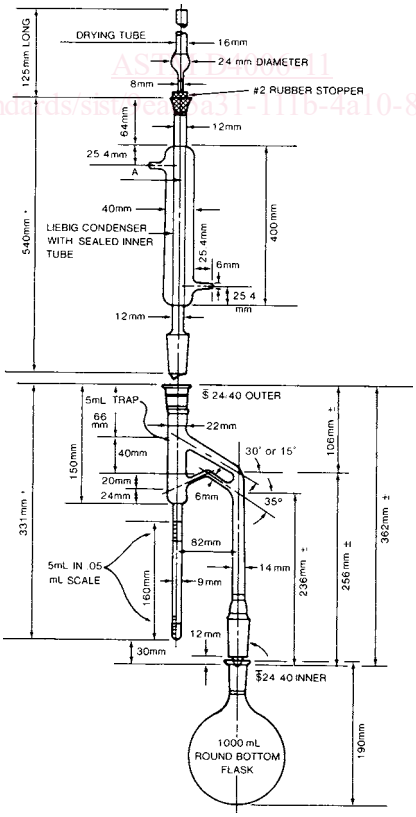

FIG. 1 Distillation Apparatus

5.1.3 The apparatus used in this test will be accepted when satisfactory results are obtained by the calibration technique described in Section 8.

6. Solvent

6.1 *Xylene*—reagent grade (**Warning**—Extremely flammable. Vapor harmful. See Annex A1.) A solvent blank will be established by placing 400 mL of solvent in the distillation apparatus and testing as outlined in Section 9. The blank will be determined to the nearest 0.025 mL and used to correct the volume of water in the trap as in Section 10.

6.2 The xylene used in this procedure is generally a mixture of ortho, meta, and para isomers and may contain some ethyl benzene. The typical characteristics for this reagent are:

Color (APHA)	not more than 10
Boiling range	137–144°C
Residue after evaporation	0.002 %
Sulfur compounds (as S)	0.003 %
Substances darkened by H_2SO_4	Color pass test
Water (H_2O)	0.02 %
Heavy metals (as Pb)	0.1 ppm
Copper (Cu)	0.1 ppm
Iron (Fe)	0.1 ppm
Nickel (Ni)	0.1 ppm
Silver (Ag)	0.1 ppm

7. Sampling, Test Samples, and Test Units

7.1 Sampling is defined as all steps required to obtain an aliquot of the contents of any pipe, tank, or other system and to place the sample into the laboratory test container.

7.1.1 *Laboratory Sample*—Only representative samples obtained as specified in Practice D4057 (API *MPMS* Chapter 8.1) and Practice <u>D4177</u> (API *MPMS* Chapter 8.2) shall be used for this test method.

7.1.2 *Preparation of Test Samples*—The following sample handling procedure shall apply in addition to those covered in 7.1.1.

7.1.2.1 The sample size shall be selected as indicated below based on the expected water content of the sample:

Expected Water Content, weight or volume %	Approximate Sample Size, g or mL
50.1–100.0	5
25.1– 50.0	10
10.1– 25.0	20
5.1– 10.0	50
1.1– 5.0	100
0.5– 1.0	200
less than 0.5	200

7.1.2.2 If there is any doubt about the uniformity of the mixed sample, determinations should be made on at least three test portions and the average result reported as the water content.

7.1.2.3 To determine water on a volume basis, measure mobile liquids in a 5, 10, 20, 50, 100, or 200-mL calibrated, graduated cylinder (NBS Class A) depending on the sample size indicated in 7.1.2.1. Take care to pour the sample slowly into the graduated cylinder to avoid entrapment of air and to adjust the level as closely as possible to the appropriate graduation. Carefully pour the contents of the cylinder into the distillation flask and rinse the cylinder five times with portions of xylene equivalent to one-fifth of the capacity of the graduated cylinder and add the rinsings to the flask. Drain the cylinder thoroughly to ensure complete sample transfer.

7.1.2.4 To determine water on a mass basis, weigh a test portion of sample in accordance with 7.1.2.1, pouring the sample directly into the distillation flask. If a transfer vessel (beaker or cylinder) must be used, rinse it with at least five portions of xylene and add the rinsings to the flask.

8. Calibration

~~8.1Calibrate~~<u>8.1 Calibrate</u> both the trap and the entire assembly prior to initial use and after any equipment changes as indicated in 8.1.1-8.1.3. Additionally, calibrate both the trap and the entire assembly periodically, at a frequency not to exceed yearly.

8.1.1 Verify the accuracy of the graduation marks on the trap by adding 0.05-mL increments of distilled water, at 20°C, from a 5-mL microburet or a precision micro-pipet readable to the nearest 0.01 mL. If there is a deviation of more than 0.050 mL between the water added and water observed, reject the trap or recalibrate.

8.1.2 Also calibrate the entire apparatus. Put 400 mL of dry (0.02 % water maximum) xylene in the apparatus and test in accordance with Section 9. When complete, discard the contents of the trap and add 1.00 ± 0.01 mL of distilled water from the buret or micro-pipet, at 20°C, directly to the distillation flask and test in accordance with Section 9. Repeat 8.1.2 and add 4.50 ± 0.01 mL directly to the flask. The assembly of the apparatus is satisfactory only if trap readings are within the tolerances specified here:

Limits Capacity of Trap at 20°C, mL	Volume of Water Added at 20°C, mL	Permissible for Recovered Water at 20°C, mL

5.00	1.00	1.00± 0.025
5.00	4.50	4.50 ± 0.025

8.1.3 A reading outside the limits suggests malfunctioning due to vapor leaks, too rapid boiling, inaccuracies in graduations of the trap, or ingress of extraneous moisture. These malfunctions must be eliminated before repeating 8.1.2.

9. Procedure

9.1 The precision of this test method can be affected by water droplets adhering to surfaces in the apparatus and therefore not settling into the water trap to be measured. To minimize the problem, all apparatus must be chemically cleaned at least daily to remove surface films and debris which hinder free drainage of water in the test apparatus. More frequent cleaning is recommended if the nature of the samples being run causes persistent contamination.

9.2 To determine water on a volume basis, proceed as indicated in 7.1.2.3. Add sufficient xylene to the flask to make the total xylene volume 400 mL.

9.2.1 To determine water on a mass basis, proceed as indicated in 7.1.2.4. Add sufficient xylene to the flask to make the total xylene volume 400 mL.

9.2.2 A magnetic stirrer is the most effective device to reduce bumping. Glass beads or other boiling aids, although less effective, have been found to be useful.

9.3 Assemble the apparatus as shown in Fig. 1, making sure all connections are vapor and liquid-tight. It is recommended that glass joints not be greased. Insert a drying tube containing an indicating desiccant into the end of the condenser to prevent condensation of atmospheric moisture inside the condenser. Circulate water, between 20 and 25°C, through the condenser jacket.

9.4 Apply heat to the flask. The type of crude oil being evaluated can significantly alter the boiling characteristics of the crude-solvent mixture. Heat should be applied slowly during the initial stages of the distillation (approximately ½ to 1 h) to prevent bumping and possible loss of water from the system. (Condensate shall not proceed higher than three quarters of the distance up the condenser inner tube (Point *A* in Fig. 1).) To facilitate condenser wash-down, the condensate should be held as close as possible to the condenser outlet. After the initial heating, adjust the rate of boiling so that the condensate proceeds no more than three quarters of the distance up the condenser inner tube. Distillate should discharge into the trap at the rate of approximately 2 to 5 drops per second. Continue distillation until no water is visible in any part of the apparatus, except in the trap, and the volume of water in the trap remains constant for at least 5 min. If there is a persistent accumulation of water droplets in the condenser inner tube, flush with xylene. (A jet spray washing tube, see Fig. 2, or equivalent device is recommended.) The addition of an oil-soluble emulsion breaker at a concentration of 1000 ppm to the xylene wash helps dislodge the clinging water drops. After flushing, redistill for at least 5 min (the heat must be shut off at least 15 min prior to wash-down to prevent bumping). After wash-down, apply heat slowly to prevent bumping. Repeat this procedure until no water is visible in the condenser and the volume of water in the trap remains constant for at least 5 min. If this procedure does not dislodge the water, use the TFE-fluorocarbon scraper, pick shown in Fig. 2, or equivalent device to cause the water to run into the trap.

9.5 When the carryover of water is complete, allow the trap and contents to cool to 20°C. Dislodge any drops of water adhering to the sides of the trap with the TFE-fluorocarbon scraper or pick and transfer them to the water layer. Read the volume of the water in the trap. The trap is graduated in 0.05-mL increments, but the volume is estimated to the nearest 0.025 mL.

10. Calculation

10.1 Calculate the water in the sample as follows:

$$\text{Volume \%} = \frac{(A - B)}{C} \times 100 \quad (1)$$

$$\text{Volume \%} = \frac{(A - B)}{C} \times 100 \quad (1)$$

$$\text{Volume \%} = \frac{(A - B)}{(M/D)} \times 100 \quad (2)$$

$$\text{Volume \%} = \frac{(A - B)}{(M/D)} \times 100 \quad (2)$$

~~(3) Mass % = (A – B)M×100~~

$$\text{Mass \%} = \frac{(A - B)}{M} \times 100 \quad (3)$$

where:

A = mL of water in trap,
B = mL of solvent blank,
C = mL of test sample,
M = g of test sample, and
D = density of sample, g/mL.

Volatile water-soluble material, if present, may be measured as water.

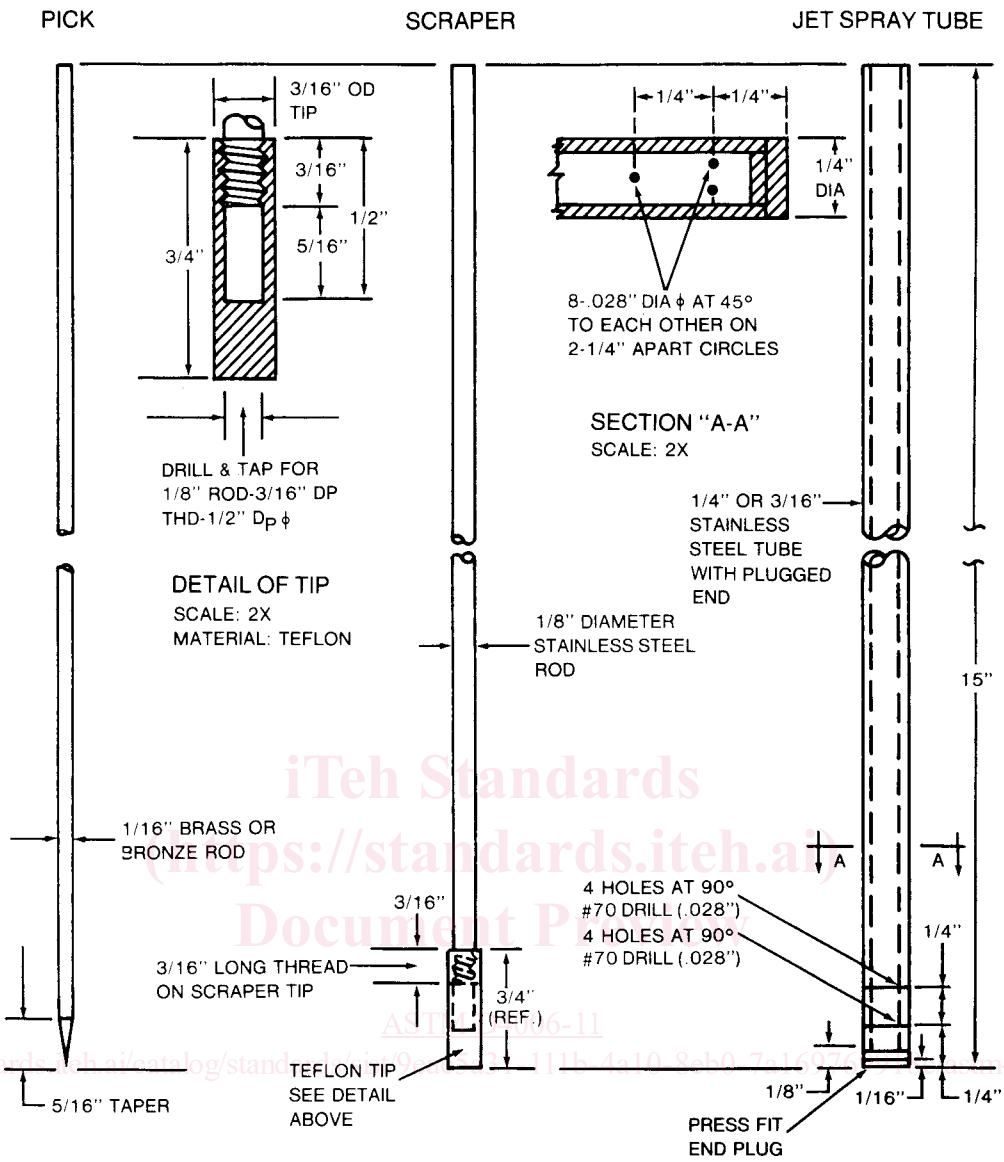

FIG. 2 Pick, Scraper, and Jet Spray Tube for Distillation Apparatus

11. Report

~~11.1Report~~11.1 Report the result as the water content to the nearest 0.025 %, reporting water content of less than 0.025 % as 0 %, and reference this Test Method D4006 (API *MPMS* Chapter 10.2) as the procedure used.

12. Precision and Bias

12.1 The precision of this test method, as obtained by statistical examination of interlaboratory test results in the range from 0.01 to 1.0 %, is described in 12.1.1 and 12.1.2.

12.1.1 *Repeatability*—The difference between successive test 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 value in only one case in twenty:

From 0.0 % to 0.1 % water, see Fig. 3.
Greater than 0.1 % water, repeatability is constant at 0.08.

12.1.2 *Reproducibility*—The difference between the two single and independent test results obtained by different operators working in different laboratories on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following value in only one case in twenty:

From 0.0 % to 0.1 % water, see Fig. 3
Greater than 0.1 % water, reproducibility is constant at 0.11.

13. Keywords

13.1 crude oil; distillation; water

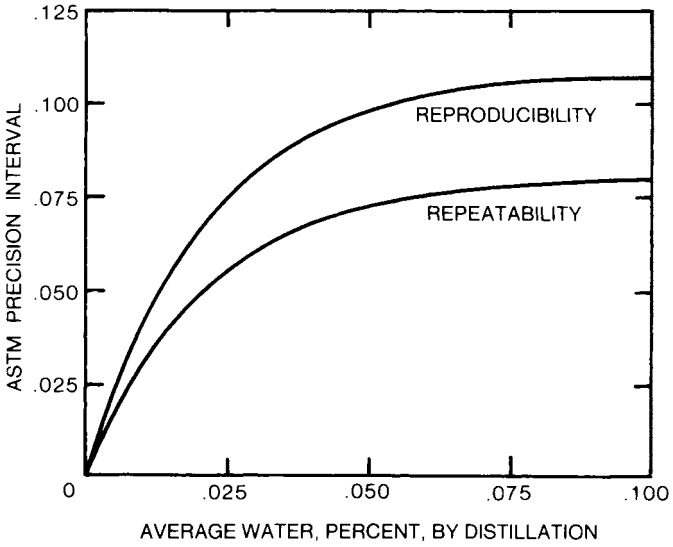

FIG. 3 Basic Sediment and Water Precision

ANNEX

(Mandatory Information)

A1. WARNING STATEMENT

A1.1 Xylene

A1.1.1 Keep away from heat, sparks, and open flame.
A1.1.2 Keep container closed.
A1.1.3 Use with adequate ventilation.
A1.1.4 Avoid breathing of vapor or spray mist.
A1.1.5 Avoid prolonged or repeated contact with skin.

APPENDIX

(Nonmandatory Information)

X1. PRECISION AND BIAS OF TEST METHODS FOR DETERMINING WATER IN CRUDE OILS

X1.1 Summary

X1.1.1 This round-robin testing program has shown that the distillation test method as practiced is somewhat more accurate than the centrifuge test method. The average correction for the distillation test method is about 0.06, whereas the centrifuge correction is about 0.10. However, this correction is not constant nor does it correlate well with the measured concentration.

X1.1.2 There is a slight improvement in the precision of the distillation test method over the present Test Method D95 (API *MPMS* Chapter 10.5): 0.08 versus 0.1 for repeatability and 0.11 versus 0.2 for reproducibility. These figures are applicable from 0.1 to 1 % water content; the maximum level studied in this program.

X1.1.3 The precision of the centrifuge test method is worse than the distillation: repeatability is about 0.12 and the reproducibility is 0.28.

X1.2 Introduction

X1.2.1 In view of the economic importance of measuring the water content of crude oils precisely and accurately, a working group of API/ASTM Joint Committee on Static Petroleum Measurement (COSM) undertook the evaluation of two test methods for determining water in crudes. A distillation test method (Test Method D95 (API *MPMS* Chapter 10.5)), and a centrifuge test method (Test Method D1796 (API *MPMS* Chapter 10.6)) were evaluated in this program. Both test methods were modified slightly in an attempt to improve the precision and accuracy.

X1.3 Experimental

X1.3.1 *Samples*—The following seven crude oils were obtained for this program: