Designation: D4006 – 16$^{\varepsilon 1}$

Manual of Petroleum Measurement Standards (MPMS), Chapter 10.2

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 U.S. Department of Defense.

ε^1 NOTE—Subsections 5.1 and X1.3.3.2 were revised editorially in November 2016.

1. Scope*

1.1 This test method covers the determination of water in crude oil by distillation.

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 (API *MPMS* Chapter 10.5)

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

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) (API *MPMS* Chapter 10.6)

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)

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

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)

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)

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

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

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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 service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

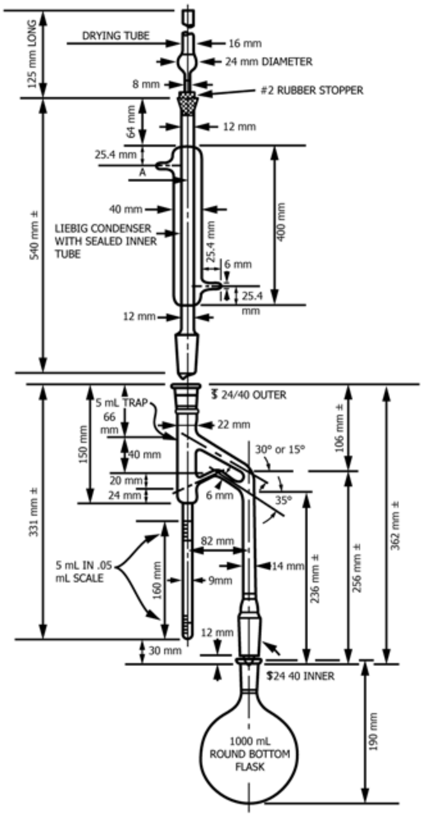

FIG. 1 Distillation Apparatus

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, 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.

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 °C to 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 D4177 (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 mL, 10 mL, 20 mL, 50 mL, 100 mL, 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

8.1 Calibrate 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 mL ± 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 mL ± 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.

9.1.1 To determine water on a volume basis, proceed as indicated in 7.1.2.3. In addition to the xylene added to rinse the oil sample transfer device, add sufficient xylene to the flask to make the total xylene volume 400 mL.

9.1.2 To determine water on a mass basis, proceed as indicated in 7.1.2.4. In addition to the xylene added to rinse the oil sample transfer device, add sufficient xylene to the flask to make the total xylene volume 400 mL.

9.2 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 °C 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 h 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 drops 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:

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

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

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

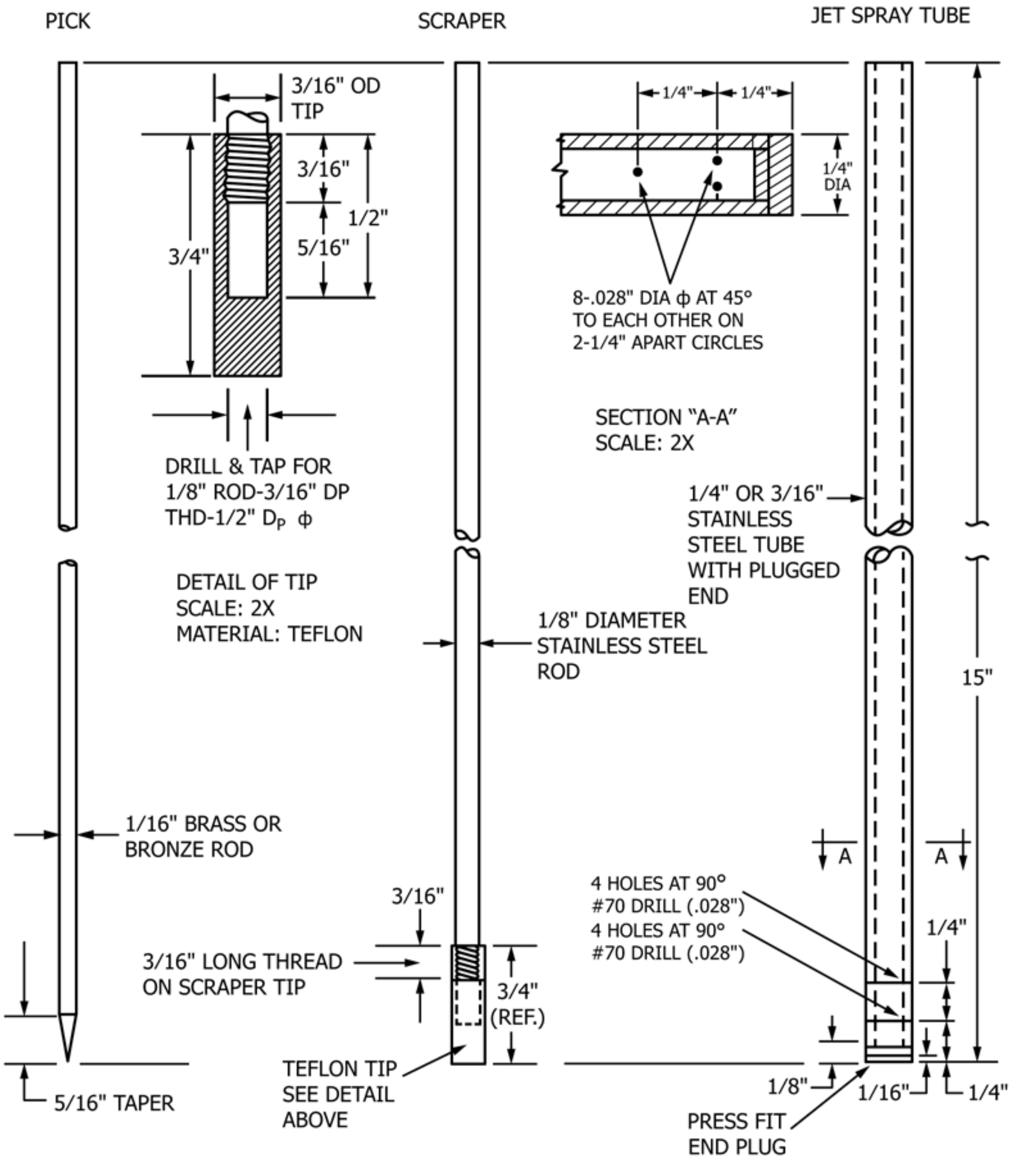

FIG. 2 Pick, Scraper, and Jet Spray Tube for Distillation Apparatus

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.

11. Report

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.

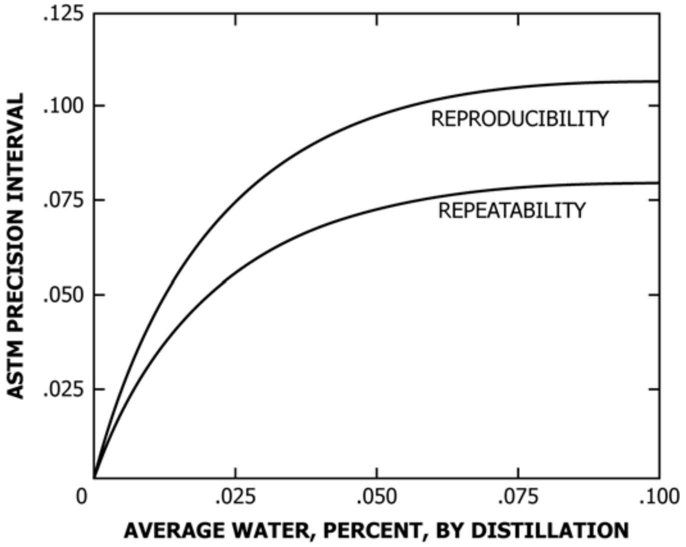

FIG. 3 Basic Sediment and Water Precision

13. Keywords

13.1 crude oil; distillation; water

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

TABLE X1.2 Base Case—Water Content of Crudes

Crude Oil	% H_2O
San Ardo	0.90
Arabian Light	0.15
Alaskan	0.25
Arabian Heavy	0.10
Minas	0.50
Fosterton	0.30
Nigerian	<0.05

TABLE X1.3 Water Content of Crude Oil Samples

Crude Source	%H_2O		
	Found	Added	Expect
San Ardo	0.90	0	0.90
		dried	0.0
		dried + 0.4	0.40
Arabian Light	0.15	0	0.15
		0.10	0.25
		0.90	1.05
Alaskan	0.25	0	0.25
		0.20	0.45
		0.80	1.05
Arabian Heavy	0.10	0	0.10
		dried	0.0
		dried + 0.1	0.10
Minas	0.50	0	0.50
		0.10	0.60
		0.50	1.00
Fosterton	0.30	0	0.30
		0.20	0.50
		0.80	1.10
Nigerian	0.05	0	<0.05
		0.40	0.45
		0.80	0.85

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:

Crude	Source
San Ardo	Texaco
Arabian Light	Mobil
Alaskan	Williams Pipe Line
Arabian Heavy	Exxon
Minas	Texaco
Fosterton	Koch Industries
Nigerian	Gulf

By removing all water or adding known amounts of water to the above crudes, 21 samples were prepared for testing. Each crude oil was represented at three levels of water concentration. The entire concentration range studied was from zero to 1.1 % water. These expected values were used to determine the accuracy of the test procedures.

X1.3.2 *Sample Preparation:*

X1.3.2.1 The crude oils were received from the suppliers in barrels. After mixing by rolling and turning, two 5 gal samples and one 250 mL sample were taken from each barrel. The Minas crude had to be heated to 66 °C (150 °F) with a barrel heater before samples could be drawn. The 250 mL samples of each crude, as received, were used to establish the base case in water content. Each sample was analyzed by Test Method D95 (API *MPMS* Chapter 10.5) to determine the water content. These starting points are shown in Table X1.1.

X1.3.2.2 To obtain "water-free" samples of crude oil, one 5 gal sample of each of two crudes was distilled over the temperature range of initial to 300 °F vapor temperature. This distillation was done using a 15 theoretical plate column at 1:1 reflux ratio.

X1.3.2.3 "Spiking" samples to a known water concentration was done using synthetic sea water (as described in Test Method D665. The mixing and homogenization was done with a static blender. The complete listing of samples with their expected water contents is shown in Table X1.2.

X1.3.2.4 The samples for each cooperator were bottled so that the entire sample had to be used for a given test. In this way, any effect due to settling or stratification of water was eliminated.

X1.3.2.5 Samples were coded to mask the presence of duplicates and a table of random numbers dictated the running order of tests.

X1.3.2.6 The participating laboratories were:

Chevron Research Co.
Exxon Research and Engineering Co.
Mobil Research and Development Corp.
Texaco, Inc.
Shell
Charles Martin, Inc.
Gulf Research and Development Co.

X1.3.3 *Test Modifications*—The base test methods studied were modified slightly in an effort to improve the performance. The modifications were as follows:

X1.3.3.1 *Test Method D95 (API MPMS Chapter 10.5)*—Sample size was standardized at 200 g and the solvent volume was increased to maintain the original solvent/sample ratio.

X1.3.3.2 *Test Method D1796 (API MPMS Chapter 10.6)*—A heated centrifuge (held near 60 °C (140 °F)) and use of a demulsifier were mandatory. Eight-inch centrifuge tubes were also specified. Toluene saturated with water at 140 °F was the only permissible solvent.

X1.4 Results and Discussion

X1.4.1 *Accuracy:*

X1.4.1.1 Accuracy or bias is defined as the closeness of the measured value to the "true value." Since there is no independent absolute test method available to determine this true value for these samples, some other means must be used. Two options were considered:

(1) Select one laboratory and one test method as the "reference system" and define these results as the true value, or

(2) Spike samples with known amounts of water. The measured difference between the original and unspiked samples can be compared to the known added water to determine the bias (accuracy). Both approaches were investigated in this study.

X1.4.1.2 Since Test Method API *MPMS* Chapter 10.4 defines the base test method as a combination of Test Methods D95 (API *MPMS* Chapter 10.5) and D473 (API *MPMS* Chapter 10.1), it was decided that data obtained by Test Method D95 (API *MPMS* Chapter 10.5) in one laboratory would be the "true value." Table X1.3 shows the expected

TABLE X1.5 Determination of Water in Crude Oils, % H_2O

Expected	Distillation	Centrifuge
0.90	0.90	0.79
0.0	0.04	0.05
0.40	0.42	0.021
0.15	0.10	0.12
0.25	0.21	0.13
1.05	0.86	0.78
0.25	0.21	0.14
0.45	0.39	0.32
1.05	0.92	0.98
0.10	0.11	0.04
0.0	0.06	0.02
0.10	0.18	0.10
0.50	0.45	0.34
0.60	0.53	0.47
1.00	0.96	0.97
0.30	0.18	0.07
0.50	0.33	0.20
1.10	0.86	0.77
0.05	0.02	0.01
0.45	0.35	0.32
0.85	0.65	0.65

value compared to each sample average using this criterion. It can be seen that both test methods are biased low. However, the distillation test method (Test Method D95 (API *MPMS* Chapter 10.5)) appears less biased than the centrifuge. Since the bias is not the same in every laboratory (Table X1.4), it is not possible to recommend inclusion of a correction factor in the test methods. This data treatment suggests that the centrifuge test method, on the average, yields results about 0.06 % lower than the distillation. The respective biases are −0.13 for the centrifuge and −0.07 for the distillation test method.

X1.4.1.3 A more reliable estimate of bias may be obtained if consideration is given only to those samples to which water was added. In this case, the measured differences between the unspiked sample and the spiked sample compared to the actual water added would be indicative of the bias. Table X1.5 shows these differences for each test method. On this basis the centrifuge bias has improved slightly, while the distillation is about the same. The difference between the two test methods is now 0.04 rather than 0.06. It should be noted that bias is greatest with both test methods at higher water contents.

X1.4.2 *Precision:*

X1.4.2.1 To estimate the precision of the tests, the data were analyzed following the ASTM guidelines published as Research Report RR:D02-1007, “Manual on Determining Precision Data for ASTM Methods on Petroleum Products” (1973).[3]

X1.4.2.2 Seven laboratories participated in the round robin. Basic sediment and water was measured on 21 crude oil samples in duplicate by the distillation test method (Test Method D95 (API *MPMS* Chapter 10.5)) and the centrifuge test method (Test Method D1796 (API *MPMS* Chapter 10.6)). The raw data are presented in Table X1.6.

X1.4.3 *Test for Outliers*—Procedures for rejecting outliers recommended in ASTM RR:D02-1007, “Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants” were followed.[3]

TABLE X1.6 Corrections to be Applied to Measured Values to Obtain “True” Water Content

Test Method	Laboratory	Correction
D1796 (API *MPMS* Chapter 10.6)		
Centrifuge	C	+ 0.152 ± 0.095
	E	+ 0.029 ± 0.125
	M	+ 0.196 ± 0.135
	T	+ 0.196 ± 0.100
	S	+ 0.160 ± 0.122
	I	+ 0.116 ± 0.126
	G	+ 0.121 ± 0.115
	Avg	+ 0.132
D95 (API *MPMS* Chapter 10.5)		
Distillation	C	+ 0.777± 0.082
	E	+ 0.048 ± 0.078
	M	+ 0.082 ± 0.077
	T	+ 0.064 ± 0.079
	S	+ 0.077 ± 0.107
	I	+ 0.061 ± 0.112
	G	+ 0.072 ± 0.096
	Average	+ 0.069

TABLE X1.7 Bias of Test Methods Estimated from Spiked Samples

Water Added,[A] %	D95 (API *MPMS* Chapter 10.5)		D1796 (API *MPMS* Chapter 10.6)	
	Found	Δ	Found	Δ
0.10	0.10	0	0.05	−0.05
0.10	0.08	−0.02	0.00	−0.10
0.10	0.10	0	0.10	0
0.20	0.16	−0.04	0.16	−0.04
0.20	0.15	−0.05	0.12	0.00
0.40	0.39	−0.01	0.16	−0.24
0.40	0.33	−0.07	0.30	−0.10
0.50	0.49	−0.01	0.52	+ 0.02
0.80	0.70	−0.10	0.73	−0.07
0.80	0.70	−0.10	0.70	−0.10
0.80	0.64	−0.16	0.63	−0.17
0.90	0.76	−0.14	0.69	−0.21
Average		−0.06		−0.10

[A] Equal water additions shown are to different crude oils.

X1.4.3.1 *Distillation Test Method*—The following table lists the outliers rejected and the substituted values:

Laboratory	Sample	Rejected Value	Substituted Value
1	14	0.75	0.53
3	3	0.35, 0.54	0.445
2	11	0.34	0.06
6	13	0.66	0.45
6	15	1.37	0.85

X1.4.3.2 *Centrifuge Test Method:*

(1) The data from Laboratory 5 were rejected outright because incorrect-size centrifuge tubes were used (letter, Shell Oil to E. N. Davis, cc: Tom Hewitt, February 9, 1979). Statistical tests showed that Laboratory 5’s data did not belong to the same population as the other data.

(2) Laboratory 2’s data were also suspect and did not appear to belong to the same population as the other data. However, it was learned that Laboratory 2’s results were closest to actual levels of water added to the samples. There is, therefore, a dilemma on whether or not to reject Laboratory 2’s data. As a compromise, precision was calculated with and without Laboratory 2’s results. The following table lists the

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1007.

TABLE X1.8 Round-Robin Results of Water in Crude Oils by ASTM D95 (API *MPMS* Chapter 10.5) and ASTM D1796 (API *MPMS* Chapter 10.6)

Distillation Test Method ASTM D95 (API *MPMS* Chapter 10.5)

Laboratories	Samples																				
	1	9	15	6	18	2	11	19	3	8	13	14	17	20	21	4	5	7	10	12	16
1	0.86	0.90	0.91	0.91	0.88	0.00	0.02	0.00	0.40	0.39	0.46	0.75	0.25	0.35	0.67	0.10	0.15	0.20	0.16	0.13	0.18
	0.86	0.92	0.92	0.86	0.85	0.01	0.02	0.02	0.39	0.40	0.46	0.53	0.38	0.33	0.66	0.09	0.21	0.21	0.20	0.13	0.15
2	0.90	0.94	0.99	0.90	0.90	0.05	0.34	0.04	0.43	0.40	0.48	0.53	0.39	0.35	0.70	0.09	0.25	0.25	0.18	0.11	0.20
	0.91	0.94	1.00	0.92	0.90	0.06	0.06	0.04	0.48	0.40	0.47	0.58	0.36	0.30	0.69	0.11	0.24	0.25	0.19	0.14	0.20
3	0.80	0.94	0.98	0.85	0.90	0.05	0.00	0.00	0.35	0.38	0.45	0.43	0.35	0.33	0.65	0.07	0.20	0.23	0.18	0.05	0.15
	0.85	0.94	0.98	0.83	0.90	0.02	0.03	0.00	0.54	0.40	0.43	0.55	0.33	0.33	0.65	0.10	0.15	0.23	0.15	0.07	0.16
4	0.93	0.92	0.89	0.90	0.88	0.07	0.02	0.00	0.42	0.40	0.42	0.52	0.35	0.35	0.66	0.10	0.19	0.23	0.18	0.10	0.20
	0.93	0.90	0.91	0.89	0.90	0.07	0.02	0.04	0.42	0.39	0.43	0.52	0.33	0.35	0.67	0.10	0.20	0.19	0.16	0.11	0.19
5	0.87	0.88	0.87	0.86	0.86	0.07	0.07	0.05	0.39	0.41	0.42	0.51	0.23	0.39	0.65	0.11	0.21	0.21	0.21	0.16	0.20
	0.86	0.92	0.83	0.80	0.80	0.07	0.09	0.04	0.39	0.40	0.37	0.47	0.35	0.35	0.60	0.12	0.20	0.24	0.24	0.18	0.16
6	0.98	0.94	0.85	0.79	0.74	0.04	0.02	0.00	0.58	0.39	0.45	0.44	0.36	0.38	0.61	0.11	0.24	0.23	0.20	0.07	0.24
	1.01	0.94	1.37	0.84	0.89	0.01	0.00	0.01	0.48	0.80	0.66	0.56	0.30	0.39	0.66	0.13	0.25	0.24	0.21	0.05	0.18
7	0.91	0.88	0.97	0.85	0.80	0.05	0.01	0.01	0.42	0.40	0.41	0.53	0.34	0.36	0.64	0.05	0.18	0.18	0.15	0.18	0.18
	0.97	0.92	1.03	0.84	0.80	0.02	0.13	0.01	0.39	0.35	0.45	0.47	0.35	0.38	0.65	0.15	0.20	0.23	0.15	0.11	0.15

Centrifuge Test Method D1796 (API *MPMS* Chapter 10.6)

Laboratories	Samples																				
	1	9	15	6	18	2	11	19	3	8	13	14	17	20	21	4	5	7	10	12	16
1	0.82	0.90	0.87	0.80	0.70	0.05	0.02	0.00	0.23	0.25	0.38	0.48	0.19	0.27	0.65	0.02	0.07	0.05	0.03	0.02	0.02
	0.79	0.89	0.88	0.81	0.74	0.05	0.02	0.02	0.23	0.31	0.35	0.41	0.17	0.29	0.61	0.02	0.06	0.06	0.03	0.02	0.04
2	1.03	1.09	1.06	0.74	0.95	0.19	0.07	0.00	0.19	0.40	0.50	0.58	0.38	0.45	0.61	0.15	0.20	0.20	0.20	0.06	0.20
	0.88	1.11	1.12	0.74	1.00	0.06	0.05	0.00	0.31	0.43	0.58	0.60	0.34	0.50	0.85	0.21	0.37	0.42	0.17	0.06	0.04
3	0.65	0.80	0.90	0.70	0.70	0.07	0.00	0.00	0.10	0.30	0.30	0.42	0.06	0.20	0.60	0.02	0.02	0.07	0.02	0.00	0.02
	0.60	0.85	0.90	0.60	0.70	0.07	0.00	0.02	0.10	0.34	0.40	0.50	0.10	0.20	0.45	0.02	0.02	0.12	0.02	0.00	0.02
4	0.73	0.95	0.88	0.85	0.80	0.00	0.00	0.00	0.18	0.27	0.33	0.46	0.15	0.30	0.63	0.00	0.10	0.10	0.05	0.00	0.05
	0.79	1.00	0.90	0.75	0.70	0.00	0.00	0.00	0.16	0.27	0.40	0.45	0.15	0.27	0.55	0.00	0.05	0.13	0.05	0.00	0.05
5	0.69	1.55	0.51	0.87	0.83	0.01	0.03	0.03	0.18	0.21	0.16	0.30	0.21	0.39	0.72	0.75	0.13	0.01	0.21	0.03	0.05
	0.76	1.10	0.87	0.93	0.41	0.01	0.05	0.02	0.30	0.54	0.20	0.07	0.19	0.01	0.69	0.06	0.11	0.02	0.09	0.03	0.12
6	0.72	0.75	1.59	0.85	0.65	0.07	0.05	0.05	0.35	0.33	0.25	0.52	0.20	0.45	0.75	0.05	0.15	0.05	0.05	0.05	0.05
	0.86	0.90	1.44	0.65	0.65	0.09	0.05	0.05	0.32	0.25	0.38	0.52	0.25	0.38	0.80	0.10	0.10	0.13	0.10	0.05	0.10
7	0.88	1.00	0.85	0.85	0.70	0.00	0.00	0.05	0.15	0.20	0.30	0.40	0.25	0.23	0.63	0.10	0.18	0.25	0.20	0.00	0.18
	0.90	0.85	0.80	0.80	0.80	0.00	0.00	0.05	0.10	0.35	0.30	0.35	0.13	0.25	0.60	0.18	0.20	0.30	0.15	0.00	0.10

outliers rejected and the substituted values when Laboratory 2's results are retained:

Laboratory	Sample	Rejected Value	Substituted Value
2	2	0.19	0.05
2	7	0.42	0.20
2	21	0.85	0.61
6	6	0.65	0.85
6	15	1.59, 1.44	0.922

With Laboratory 2's results omitted, only Laboratory 6's results listed above were rejected.

X1.4.4 *Calculation of Repeatability and Reproducibility*—Repeatability and reproducibility were obtained by fitting curves of the appropriate precision of the results on each sample versus the mean value of each sample. An equation of the form:

$$S = A\ \bar{x}\left(1 - \mathrm{e}^{-b\bar{x}}\right) \qquad (\text{X1.1})$$

where:

S = precision,

$\bar{x}$ = sample mean, and

A and b are constants.

was found to best fit the data. The values of the constants A and b were calculated by regression analysis of the linear logarithmic equation:

$$\log S = \log A/\log\left(1 - \mathrm{e}^{-b\bar{x}}\right) \qquad (\text{X1.2})$$

X1.4.4.1 The standard deviation for repeatability for each sample was calculated from pair-wise (repeat pairs) variances pooled across the laboratories. The standard deviation for reproducibility was calculated from the variance of the mean values of each pair. This variance is equal to the sum of two variances, the variance $\sigma_L{}^2$ due to differences between laboratories and the variance due to repeatability error $\sigma_L{}^2$ divided by the number of replicates:

$$\sigma_r{}^2 = \sigma_r{}^2/n + \sigma_L{}^2\ (n = 2) \qquad (\text{X1.3})$$

Using the data calculated above for each sample, the following values for the constants in Eq X1.1 were obtained:

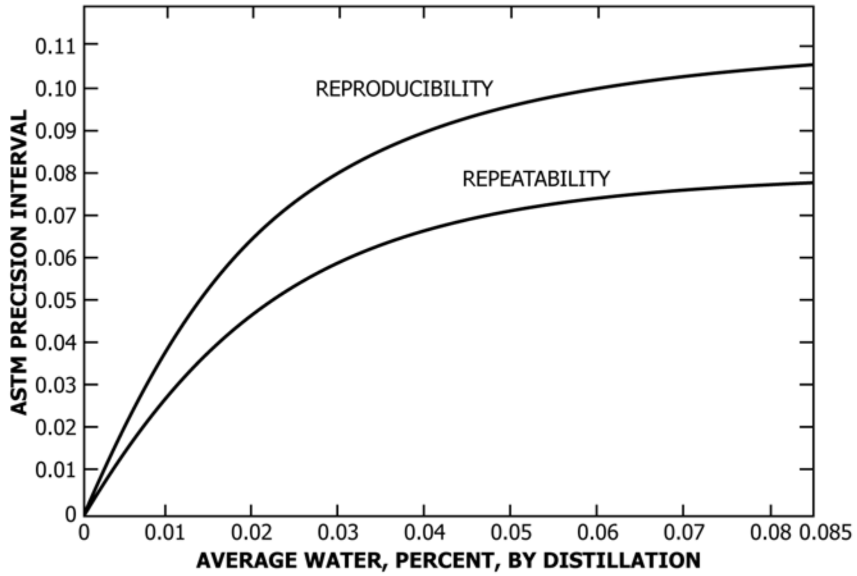

FIG. X1.1 Basic Sediment Water Precision for ASTM Test Method D95 (API *MPMS* Chapter 10.5) Distillation Method (Based on Seven Laboratories)

	Repeatability	Reproducibility
	Distillation Test Method 7 Laboratories	
Constant		
b	47.41	47.41
A	0.2883	0.0380
	Centrifuge Test Method 6 Laboratories	
Constant		
b	11.23	11.23
A	0.0441	0.1043
	5 Laboratories	
Constant		
b	17.87	17.87
A	0.0437	0.0658

The values of precision calculated by Eq X1.1 were multiplied by 2.828 $\left(2\times\sqrt{2}\right)$ to convert them to the ASTM-defined repeatability and reproducibility.

X1.4.4.2 The curves of repeatability and reproducibility for the distillation test method in the range 0 to 0.09 % water are shown in Fig. X1.1. These data are also tabulated in the Table X1.7. The curves for the centrifuge test method in the range 0 % to 0.2 % water are shown in Fig. X1.2 (five-laboratory case) and Fig. X1.3 (six-laboratory case).

X1.4.4.3 For higher levels of water the limiting repeatabilities and reproducibilities are:

Test Method	Repeatability Range of Concentration, %	Value, %
Distillation	≥0.085	0.08
Centrifuge (five-laboratory case)	≥0.155	0.12
Centrifuge (six-laboratory case)	≥0.235	0.12

Test Method	Reproducibility Range of Concentration, %	Value, %
Distillation	≥0.085	0.105
Centrifuge (five-laboratory case)	≥0.325	0.19
Centrifuge (six-laboratory case)	≥0.315	0.29

TABLE X1.12 ASTM Precision Intervals: ASTM D95 (API *MPMS* Chapter 10.5) (7 Laboratories)

% Water	Repeatability	Reproducibility	% Water
0.000	0.000	0.000	0.000
0.005	0.017	0.023	0.005
0.010	0.030	0.041	0.010
0.015	0.041	0.055	0.015
0.020	0.049	0.066	0.020
0.025	0.056	0.075	0.025
0.030	0.061	0.082	0.030
0.035	0.065	0.087	0.035
0.040	0.068	0.091	0.040
0.045	0.071	0.095	0.045
0.050	0.073	0.097	0.050
0.055	0.074	0.100	0.055
0.060	0.075	0.101	0.060
0.065	0.076	0.103	0.065
0.070	0.077	0.104	0.070
0.075	0.078	0.104	0.075
0.080	0.078	0.105	0.080
0.085	0.079	0.106	0.085
0.090	0.079	0.106	0.090
0.095	0.079	0.106	0.095
0.100	0.079	0.107	0.100
0.105	0.079	0.107	0.105
0.110	0.080	0.107	0.110
0.115	0.080	0.107	0.115
0.120	0.080	0.107	0.120
0.125	0.080	0.107	0.125
0.130	0.080	0.107	0.130

X1.4.4.4 It should be pointed out that at the lowest water levels, the precision "statements" for some of the analyses do not permit any pair of results to be considered suspect. This is because the precision interval exceeds twice the mean value. For example, in Fig. X1.1, the repeatability at 0.03 % water is 0.061 %. It is not possible to observe a difference of more than 0.06 and still average 0.03. Thus, a pair of observations of 0.00 and 0.06 are acceptable.

X1.4.4.5 Analyses of variance were performed on the data without regard to any functionality between water level and precision. The following repeatabilities and reproducibilities were found:

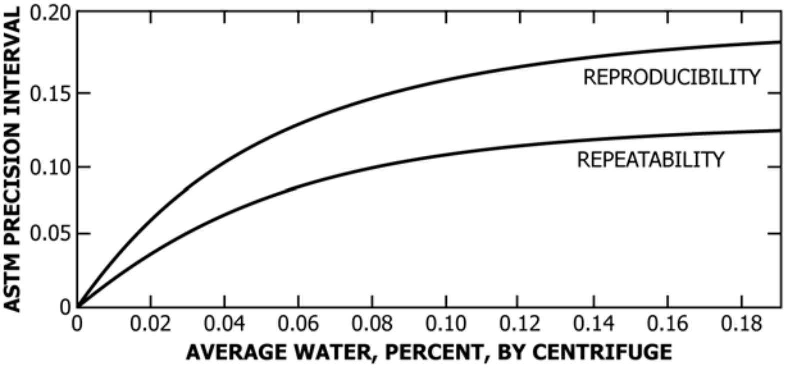

FIG. X1.2 Basic Sediment and Water Precision for ASTM Test Method D1796 (API *MPMS* Chapter 10.6) Centrifuge Method (Based on Five Laboratories)

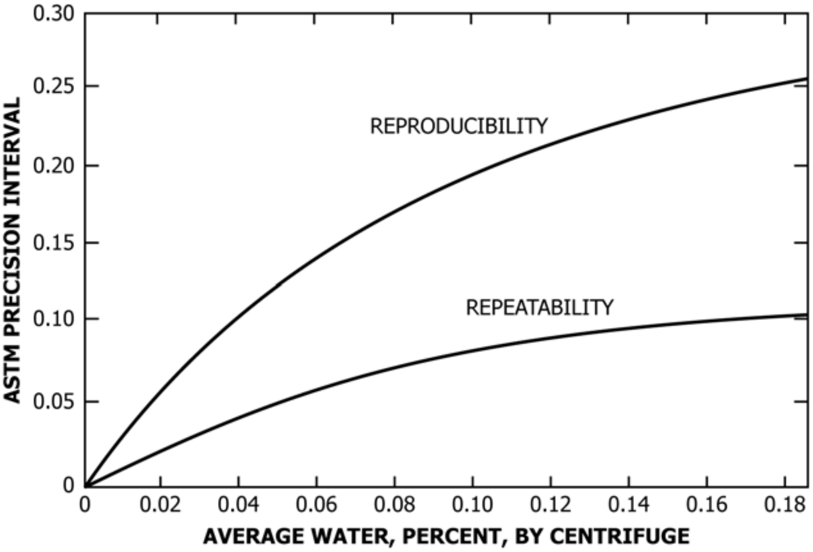

FIG. X1.3 Basic Sediment and Water Precision for ASTM Test Method D1796 (API *MPMS* Chapter 10.6) Centrifuge Method (Based on Six Laboratories)

Test Method	Repeatability	Reproducibility
Distillation (seven laboratories)	0.08	0.11
Centrifuge (six laboratories)	0.12	0.28

X1.4.4.6 These values are almost exactly the same as the limiting values obtained by curve fitting.

X1.5 Conclusions and Recommendations

X1.5.1 Data obtained in seven-laboratory round robin on measurement of basic sediment and water by the distillation test method (Test Method D95 (API *MPMS* Chapter 10.5)) and the centrifuge test method (Test Method D1796 (API *MPMS* Chapter 10.6)) in 21 crude oil samples were examined. The conclusions are:

X1.5.1.1 *Distillation Test Method:*

(1) Precision is related to water content up to about 0.08 % water.

(2) In the range from 0.01 to 0.08, repeatability varies from 0.020 to 0.078 and reproducibility from 0.041 to 0.105.

(3) Above 0.1 % water, the repeatability is 0.08 and the reproducibility is 0.11.

X1.5.1.2 *Centrifuge Test Method:*

(1) Repeatability is related to water content up to about 0.2 % water and reproducibility up to about 0.3 %.

(2) In the range 0.01 to 0.2, repeatability varies from 0.01 to 0.11 and reproducibility in the range 0.02 to 0.3 from 0.03 to 0.28.

X1.5.2 It is recommended that:

X1.5.2.1 Precision should be presented as a graph in the range where precision varies with water content.

X1.5.2.2 Precision should be presented as a statement where the precision is constant.

X1.5.3 In view of what appears to be lower bias and better precision, Test Method D95 (API *MPMS* Chapter 10.5) should be the specified test method for use in critical situations.

SUMMARY OF CHANGES

Subcommittee D02.02.08 has identified the location of selected changes to this standard since the last issue (D4006 – 11 (2012)$^{\varepsilon 1}$) that may impact the use of this standard. (June 1, 2016.)

(1) Revised subsection 9.1.

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