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Standard Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure)[1]

This standard is issued under the fixed designation D 4007; 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. This method was issued as a joint ASTM-API-IP standard in 1981.~~

~~ε[1] NOTE—Editorial changes were made throughout in September 1995.~~

[1] This test method is under the jurisdiction of ASTM Committee ~~D-2~~ D02 on Petroleum Products and Lubricants and the API Committee on Petroleum Measurement, and is the direct responsibility of Subcommittee D-02.02/COMQ, the joint ASTM-API Committee on Static Petroleum Measurement.

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This test method has been approved by the sponsoring committees and accepted by the Cooperating Societies in accordance with established procedures. This method was issued as a joint ASTM-API-IP standard in 1981.

1. Scope

1.1 This test method describes the laboratory determination of water and sediment in crude oils by means of the centrifuge procedure. This centrifuge method for determining water and sediment in crude oils is not entirely satisfactory. The amount of water detected is almost always lower than the actual water content. When a highly accurate value is required, the revised procedures for water by distillation ~~(~~, Test Method D 4006 (API *MPMS* Chapter 10.2) (Note ~~1))~~ 1), and sediment by extraction ~~(~~, Test Method ~~D 473) must~~ D 473 (API *MPMS* Chapter 10.1), shall be used.

NOTE 1—Test Method D 4006 (API *MPMS* Chapter 10.2) has been determined to be the preferred and most accurate method for the determination of water.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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 precautionary statements, see ~~6.1 and 7.~~ 6.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 95 Test Method for Water in Petroleum Products and Bituminous Materials by Distillation (API *MPMS* Chapter 10.5)[2]

D ~~96~~473 Test Method~~s~~ for ~~Water and~~ Sediment in Crude Oil~~s~~ and Fuel Oils by ~~Centrifuge~~ the Extraction Method ~~(Field Procedure)~~ (API *MPMS* Chapter 10.1)[2]

~~D 362 Specification for Industrial Grade Toluene[3]~~

~~D 473 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method[2]~~

~~D 665 Test~~ 665 Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water[2]

D 1796 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure) (API *MPMS* Chapter 10.6)[2]

D 4006 Test Method for Water in Crude Oil by Distillation (API *MPMS* Chapter 10.2)[3]

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol ~~06.03.~~ 05.02.

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products (API *MPMS* Chapter 8.1)[3]
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products (API *MPMS* Chapter 8.2)[3]
D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products (API *MPMS* Chapter 8.3)[4]
E 969 Specification for Glass Volumetric (Transfer) Pipets[5]

2.2 *API Standards:*[6]
MPMS Chapter 8.1 "Manual Sampling of Petroleum and Petroleum Products"[5] (ASTM Practice D 4057)

[4] *Annual Book of ASTM Standards*, Vol 05.023.
[5] ~~Available from the American Petroleum Institute, 1220 L St., N.W., Washington, DC 20005.~~
[5] *Annual Book of ASTM Standards*, Vol 14.02.
[6] Available from the ~~Institute of Petroleum, 61 New Cavendish~~ American Petroleum Institute, 1220 L St., ~~London, W.I., England.~~ NW, Washington, DC 20005.

MPMS Chapter 8.2 Automatic Sampling of Petroleum and Petroleum Products (ASTM Practice D 4177)
MPMS Chapter 8.3 Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products (ASTM Practice D 5854)
MPMS Chapter 10.1 Determination of Sediment in Crude Oils and Fuel Oils by the Extraction Method (ASTM Test Method D 473)
MPMS Chapter 10.2 Determination of Water in Crude Oil by Distillation (ASTM Test Method D 4006)
MPMS Chapter 10.4 Determination of Sediment and Water in Crude Oil by the Centrifuge Method (Field Procedure)
MPMS Chapter 10.5 Determination of Water in Petroleum Products and Bituminous Materials by Distillation (ASTM Test Method D 95)
MPMS Chapter 10.6 Determination of Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedures) (ASTM Test Method D 1796)

2.3 *IP Standard:*[7]
Methods Book, Appendix B Specification for Methylbenzenes (Toluenes)

2.4 *ISO Standard:*[8]
ISO 5272:1979 Tolue−ne for Industrial Use—Specifications

3. Summary of Test Method

3.1 Equal volumes of crude oil and water-saturated toluene are placed into a cone-shaped centrifuge tube. After centrifugation, the volume of the higher ~~gravity~~ density water and sediment layer at the bottom of the tube is read.

4. Significance and Use

4.1 The water and sediment content of crude oil is significant because it can cause corrosion of equipment and problems in processing. A determination of water and sediment content is required to measure accurately net volumes of actual oil in sales, taxation, exchanges, and custody transfers.

5. Apparatus

5.1 *Centrifuge*:

5.1.1 A centrifuge capable of spinning two or more filled cone-shaped, 203-mm (8-in.) centrifuge tubes at a speed that can be controlled to give a relative centrifugal force (rcf) of a minimum of 600 at the tip of the tubes shall be used (see 5.1.6).

5.1.2 The revolving head, trunnion rings, and trunnion cups, including the cushions, shall be soundly constructed to withstand the maximum centrifugal force capable of being delivered by the power source. The trunnion cups and cushions shall firmly support the tubes when the centrifuge is in motion. The centrifuge shall be enclosed by a metal shield or case strong enough to eliminate danger if any breakage occurs.

5.1.3 The centrifuge shall be heated and ~~should be~~ controlled thermostatically to avoid unsafe conditions. It ~~should~~ shall be capable of maintaining the sample temperature during the entire run at 60 ± 3°C (140 ± 5°F). The thermostatic control shall be capable of maintaining the temperature within these limits and operate safely if there is a flammable atmosphere.

5.1.4 Electric powered and heated centrifuges must meet all safety requirements for use in hazardous areas.

5.1.5 Calculate the necessary minimum speed of the rotating head in revolutions per minute (r/min) as follows:

$$\text{r/min} = 1335\sqrt{\text{rcf}/d} \tag{1}$$

where:
rcf = relative centrifugal force and
d = diameter of swing measured between tips of opposite tubes when in rotating position, mm, or

~~$$\text{rpm} = 265\sqrt{\text{rcf}/d}$$~~ (2)

$$\text{r/min} = 265\sqrt{\text{rcf}/d} \tag{2}$$

where:
rcf = relative centrifugal force and
d = diameter of swing measured between tips of opposite tubes when in rotating position, in.

5.1.6 Calculate the relative centrifugal force from a measured speed (r/min) as follows:

$$\text{rcf} = d\left(\frac{\text{r/min}}{1335}\right)^2 \tag{3}$$

where:

[7] ~~Tret-O-Lite is a registered trademark of Tretolite Div., Petrolite Corp., 369 Marshall Ave., St. Louis, MO. Even though Tret-O-Lite F65 was used during~~
[7] Available from the ~~round-robin, there are many demulsifiers on the market that may be useful.~~ Institute of Petroleum, 61 New Cavendish Street, London, W1G 7AR, U.K.
[8] Available from the American National Standards Institute, 1819 L Street, NW, Suite 600, Washington, DC 20036.

d = diameter of swing measured between tips of opposite tubes when in rotating position, mm, or

$$\text{rcf} = d\left(\frac{\text{r/min}}{265}\right)^2 \quad (4)$$

where:

d = diameter of swing measured between tips of opposite tubes when in rotating position, in.

5.2 *Centrifuge Tubes*—Each centrifuge tube shall be a 203-mm (8-in.) cone-shaped tube, conforming to dimensions given in Fig. 1 and made of thoroughly annealed glass. The graduations, numbered as shown in Fig. 1, shall be clear and distinct, and the mouth shall be constricted in shape for closure with a cork. Scale error tolerances and the smallest graduations between various calibration marks are given in Table 1 and apply to calibrations made with air-free water at 20°C (68°F), when reading the bottom of the shaded meniscus. The accuracy of the graduations on the centrifuge tube shall be volumetrically verified, before use of the tube. The verification shall include calibration at each mark up to the 0.25 mL mark (as shown in Fig. 2), and at the 0.5, 1.0, 1.5, 2.0, 50.0, and 100 mL marks. The tube shall not be used if the scale error at any mark exceeds the applicable tolerance from Table 1.

5.3 *Bath*—The bath shall be either a solid metal block bath or a liquid bath of sufficient depth for immersing the centrifuge tube in the vertical position to the 100-mL mark. Means shall be provided for maintaining the temperature at 60 ± 3°C (140 ± 5°F).

NOTE 2—By contractual agreement 49 5°F). For some crude oils, temperatures of 71 ± 3°C (1260 ± 5°F) may be required to melt wax crystals in crude oils. For these crude oils, the test temperature shall be maintained high enough to ensure the absence of wax crystals.

5.4 *50 mL Pipet*, Class A, or equivalent volume dispensing device, capable of delivering a volume of 50 ± 0.05 mL (see Specification E 969) for use in the test.

6. Solvent

6.1 *Toluene* (—conforming to the IP Specification for Methylbenzenes (Toluenes) or to ISO 5272. (**Warning**—See Note 3.) conforming —Flammable. Keep away from heat, sparks, and open flame. Vapor harmful. Toluene is toxic. Particular care must be taken to Specification D 362 or avoid breathing the vapor and to protect the IP Specification for Toluole.

NOTE 3—**Warning:** Flammable. eyes. Keep container closed. Use with adequate ventilation. Avoid prolonged or repeated contact with the skin.)

6.1.1 Typical characteristics for this material are reagent are:

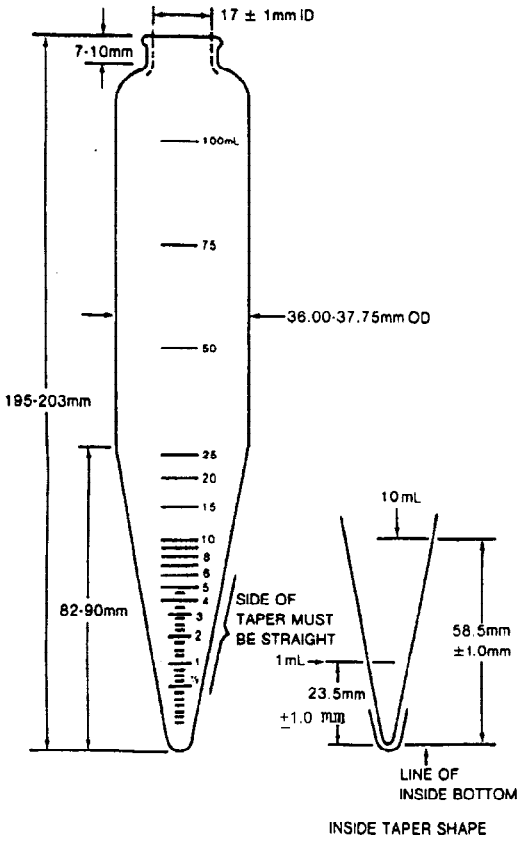

FIG. 1 Eight-Inch (203-mm) Centrifuge Tube

TABLE 1 Centrifuge Tube Calibration Tolerances for ~~8-in. (~~ 203-mm (8-in.) Tube

~~Range, mm~~	~~Subdivision, mm~~	~~Volume Tolerance, mm~~
Range, mm	Subdivision, mL	Volume Tolerance, mL
0 to 0.1	0.05	±0.02
Above 0.1 to 0.3	0.05	±0.03
Above 0.3 to 0.5	0.05	±0.05
Above 0.5 to 1.0	0.10	±0.05
Above 1.0 to 2.0	0.10	±0.10
Above 2.0 to 3.0	0.20	±0.10
Above 3.0 to 5.0	0.5	±0.20
Above 5.0 to 10	1.0	±0.50
Above 10 to 25	5.0	±1.00
Above 25 to 100	25.0	±1.00

~~Molecular weight~~	~~92.14~~
Molecular weight $C_6H_5CH_3$	92.14
Color (APHA)	10
~~Boiling range (initial to dry point)[A]~~	~~2.0°C (36°F)~~
Boiling range (initial to dry point)[A]	2.0°C (3.6°F)
Residue after evaporation	0.001 %
Substances darkened by H_2SO_4	passes ACS test
Sulfur compounds (as S)	0.003 %

[A] Recorded boiling point 110.6°C

~~[A]Recorded boiling point 110.6°C~~

6.1.2 The solvent shall be water-saturated at 60 ± 3°C (140 ± 5°F) (see ~~Note 2)~~ 5.3) but shall be free of suspended water. See Annex A1 for the solvent-water saturation procedure.

6.2 *Demulsifier*—A demulsifier should be used to promote the separation of water from the sample and to prevent its clinging to the walls of the centrifuge tube. The recommended stock solution is 25 % demulsifier to 75 % toluene. For some crude oils a different ratio of demulsifier to toluene may be required. Demulsifiers used in the concentration and quantity recommended will not add to the water and sediment volume determined. The solution must be stored in a dark bottle that is tightly closed.

7. Sampling

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.

7.2 Only representative samples obtained as specified in ~~the API MPMS, Chapter 8 (or Practice~~ Practices D 4057 (API *MPMS* Chapter 8.1) and Practice D 4177 (API *MPMS* Chapter 8.2)~~,~~ shall be used for this test method.

7.3 *Sample Mixing*— is typically required to obtain a test portion representative of the bulk sample to be tested, but precautions shall be taken to maintain the integrity of the sample during this operation. Mixing of volatile crude petroleum containing water or sediments, or both, may result in the loss of light components. Additional information on the mixing and handling of liquid samples can be found in Practice D 5854 (API *MPMS* Chapter 8.3).

8. Procedure

8.1 Fill each of two centrifuge tubes (5.2) to the 50-mL mark with sample directly from the sample container. ~~Then, with~~ Using a pipet or other suitable volume transfer device (see 5.4), add 50 ± 0.05 mL of toluene, which has been water saturated at 60°C (140°F) or ~~49°C (120°F)~~ 71°C (160°F) (see ~~Note 2).~~ 5.3). Read the top of the meniscus at both the 50 and 100-mL marks. Add 0.2 mL of demulsifier solution (6.2) to each tube, using a 0.2-mL pipet. ~~A~~ or other suitable volume transfer device, such as an automatic ~~pipettor may be used.~~ pipettor. Stopper the tube tightly and invert the tubes ten times to ensure that the oil and solvent are uniformly mixed.

8.2 In the case where the crude oil is very viscous and mixing of the solvent with the oil would be difficult, the solvent may be added to the centrifuge tube first to facilitate mixing. ~~Care must be taken in order not~~ Take care to not fill the centrifuge tube past the 100-mL mark with the sample.

8.3 Loosen the stoppers slightly and immerse the tubes to the 100-mL mark for at least 15 min in the bath maintained at 60 ± 3°C (140 ± 5°F) (see ~~Note 2).~~ 5.3). Secure the stoppers and again invert the tubes ten times to ensure uniform mixing of oil and solvent. (**Warning**—The vapor pressure at 60°C (140°F) is approximately double that at 40°C (104°F).)

8.4 Place the tubes in the trunnion cups on opposite sides of the centrifuge to establish a balanced condition. (If the tubes cannot be counter-balanced by eye, place them, in their trunnion cups, on either side of a balance and equalize their masses by the addition of water to the trunnion cups.) Retighten the corks and spin for 10 min at a minimum relative centrifugal force of 600 calculated from the equation given in 5.1.5~~5~~6.

8.5 Immediately after the centrifuge comes to rest following the spin, read and record the combined volume of water and sediment at the bottom of each tube, to the nearest 0.05 mL from 0.1 to 1-mL graduations, and to the nearest 0.1-mL above 1-mL

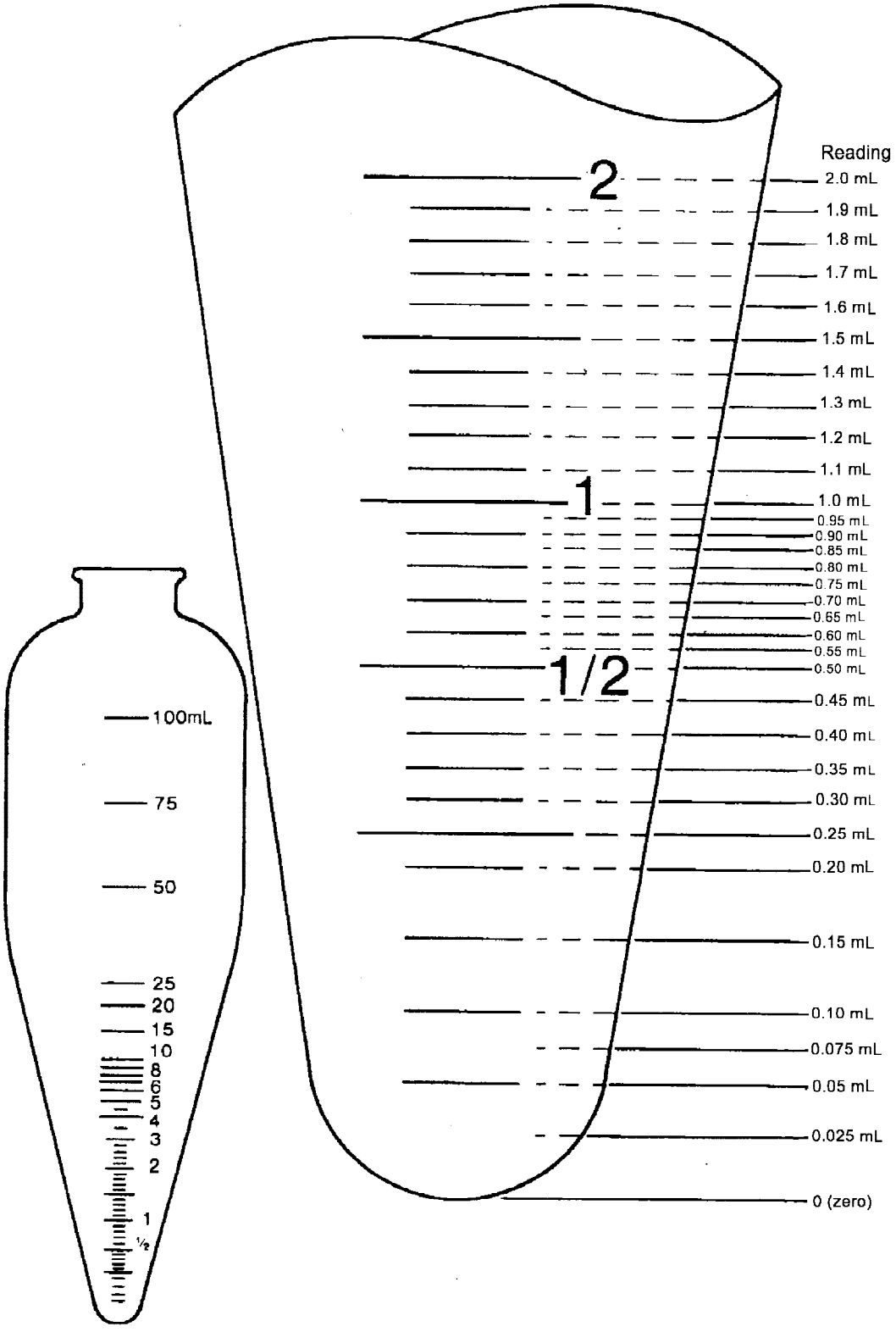

FIG. 2 Procedure for Reading Water and Sediment When Using an ASTM 100-mm Cone-Shaped Centrifuge Tube

graduations. Below 0.1 mL, estimate to the nearest 0.025 mL (refer to Fig. 2). Return the tubes without agitation to the centrifuge and spin for another 10 min at the same rate.

8.6 Repeat this operation until the combined volume of water and sediment remains constant for two consecutive readings. In

general, not more than two spinnings are required.

8.7 The temperature of the sample during the entire centrifuging procedure ~~should~~ shall be maintained at 60 ± 3°C (140 ± 5°F) (see ~~Note 2).~~ 5.3).

8.8 To avoid the danger of tubes breaking in the cups, care must be taken that the tubes are bedded onto the bottom cushion so that no part of the tube is in contact with the rim of the cup.

9. Calculation

9.1 Record the final volume of water and sediment in each tube. If the difference between the two readings is greater than one subdivision on the centrifuge tube (see Table 1) or 0.025 mL for readings of 0.10 mL and below, the readings are inadmissible and the determination shall be repeated.

9.2 Express the sum of the two admissible readings as the percentage by volume of water and sediment; report the results as shown in Table 2.

TABLE 2 Expression of Results, ~~mm~~[A] L

Tube 1	Tube 2	Total Percent Water and Sediment, % (*V/V*)
~~No visible water and sediment~~	~~No visible water and sediment~~	—
No visible water and sediment	No visible water and sediment	0.00
No visible water and sediment	0.025	0.025
0.025	0.025	0.05
0.025	0.05	0.075
0.05	0.05	0.10
0.05	0.075	0.125
0.075	0.075	0.15
0.075	0.10	0.175
0.10	0.10	0.20
0.10	0.15	0.25

[A] ~~For volumetric tolerances, see Table 1.~~

10. Precision and Bias

10.1 *Precision*—The precision of this test method, as ~~obtained~~ determined by statistical examination of interlaboratory test results in the range from 0.01 to 1.0 %, is described in 10.1.1 and 10.1.2.

10.1.1 *Repeatability*—The difference between ~~successive~~ two 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 0.3 % water, see Fig. ~~3.~~

~~From~~ 3.

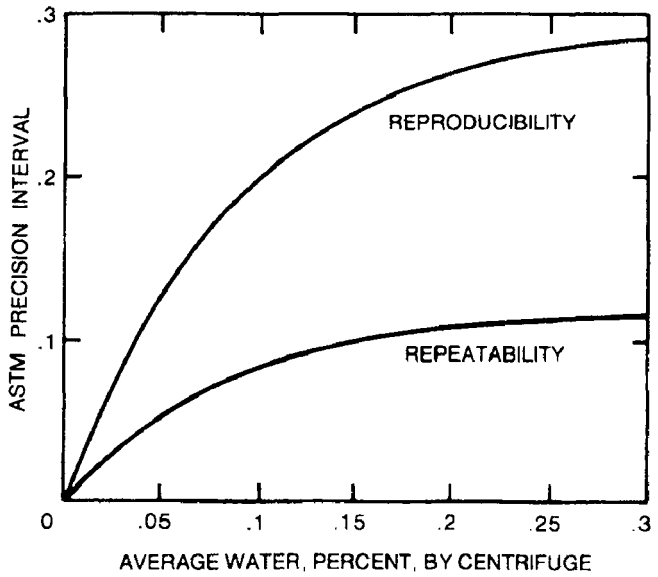

FIG. 3 Basic Sediment and Water Precision

From 0.3 % to 1.0 % water, repeatability is constant at 0.12.

10.1.2 *Reproducibility*—The difference between 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 0.3 % water, see Fig. 3.

From 0.3 % to 1.0 % water, reproducibility is constant at 0.28.

10.2 *Bias*—The procedure in this test method has no bias because the value of water and sediment can be defined only in terms of a test method.

11. Keywords

11.1 centrifuge; centrifuge tube; crude oil; laboratory procedure; sampling; sediment and water; solvent

ANNEXES

(Mandatory Information)

A1. PROCEDURE TO WATER-SATURATE TOLUENE

A1.1 Scope

A1.1.1 This method is satisfactory for the water saturation of toluene to be used for determination of water and sediment in crude oils by the centrifuge method.

A1.2 Significance

A1.2.1 Fig. A1.1 shows that water is soluble in toluene to a significant extent. The percentage of water that will dissolve increases as the temperature is increased from about 0.03 % at 21°C (70°F) to about 0.17 % at 70°C (158°F). Toluene, as normally supplied, is relatively dry and if used in an as-received condition, will dissolve a portion of or even all of any water present in a crude oil sample. This would reduce the apparent sediment and water level in the crude sample. To determine water and sediment accurately by centrifuge on a crude oil sample, the toluene must first be saturated at the centrifuge test temperature.

A1.3 Reagents

A1.3.1 *Toluene* conforming to ~~Specification D 362 or to~~ the IP Specification for Methylbenzenes (Toluolenes) or ISO 5272.

A1.3.2 *Water*, either distilled or tap water.

A1.4 Apparatus

A1.4.1 *Liquid-Heating Bath* of sufficient depth for immersing a 1-qt or 1-L bottle to its shoulder. Means shall be provided for maintaining the temperature at 60 ± 3°C (140 ± 5°F) (see 5.3).

A1.4.2 *Glass Bottle*, 1-qt or 1-L, with screw top.

A1.5 Procedure

A1.5.1 Adjust the heating bath to the temperature at which the centrifuge test is to be run. Maintain the bath temperature to ±3°C (±5~~0~~°F).

A1.5.2 Fill the glass bottle with 700 to 800 mL of toluene. Add ~~25~~ sufficient water (at least 2 mL but not more than 25 mL) to maintain a visual indication of excess water. Screw the cap on the bottle and shake vigorously for 30 s.

A1.5.3 Loosen the cap and place the bottle in the bath for 30 min. Remove the bottle, tighten the cap, and shake cautiously for 30 s.

A1.5.4 Repeat the above procedure (A1.5.3) ~~three~~ 3 times. (**Warning**—The vapor pressure of toluene at 60°C (140°F) is approximately twice that at 38°C (100°F).)

A1.5.~~4.1~~5 Allow the bottle with the water-toluene mixture to sit in the bath 48 h before using. This will ensure complete equilibrium between the toluene and the free water as well as complete saturation at the desired temperature. If it is necessary to use the water-saturated toluene before the 48-h equilibration time has been completed, the solvent must be poured into centrifuge tubes and centrifuged in the same equipment at the same relative centrifuge force and temperature that is used for the centrifuge test. The toluene must be carefully pipetted from the centrifuge tube so that any free water that may be in the bottom of the tube is not disturbed.

A1.5.~~4.2~~6 Saturation is time- and temperature-dependent. It is recommended that bottles of the toluene-water mixture be kept at test temperature in the bath at all times so that saturated solvent will be available whenever tests are to be run.~~.~~

~~A2. Precautionary Statement~~

~~A2.1 Toluene—Precaution Keep away from heat, sparks, and open flame.~~

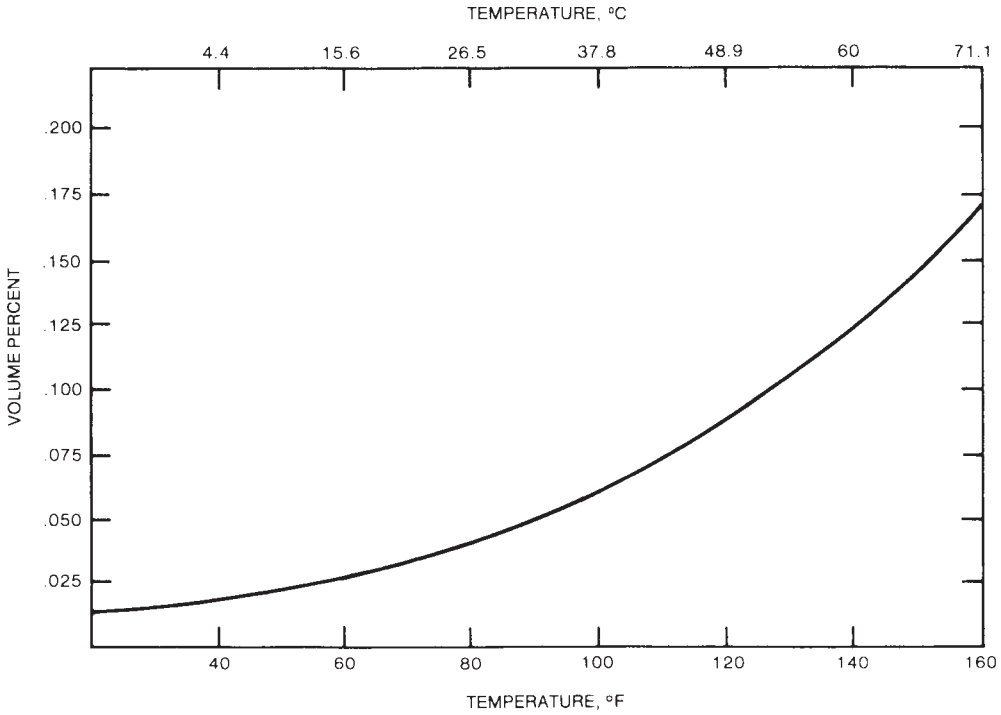

FIG. A1.1 Solubility of Water in Toluene

~~Vapor harmful.~~
~~Toluene is toxic.~~
~~Particular care must be taken to avoid breathing the vapor and to protect the eyes.~~
~~Keep container closed.~~
~~Use with adequate ventilation.~~
~~Avoid prolonged or repeated contact with the skin.~~

APPENDIX

(Nonmandatory Information)

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

X1.1 Summary

X1.1.1 This round-robin testing program has shown that the distillation method as practiced is somewhat more accurate than the centrifuge method. The average correction for the distillation 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 method over the present Test Method D 95 (API *MPMS* Chapter 10.5): 0.08 repeatability versus 0.1, 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 method is worse than the distillation method: 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 ~~C~~ Subcommittee on Static Petroleum Measurement ~~(COSM)~~ undertook the evaluation of two methods

for determining water in crudes. A distillation method (, Test Method D 95 (API *MPMS* Chapter 10.5), and a centrifuge method (, Test Method D 1796 (API *MPMS* Chapter 10.6), were evaluated in this program. Both methods were modified slightly in an attempt to improve the precision and accuracy.

X1.3 Experimental Procedure

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~~
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 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 D 95 (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 D 665). 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 methods studied were modified slightly in an effort to improve the performance. The modifications were as follows:

X1.3.3.1 *Test Method D 95 (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 D 1796*

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

TABLE X1.1 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 X1.2 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~~
		~~0.30~~	~~1.10~~
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

demulsifier used was a Tret-O-Lite material, F65.[9]

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 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 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 D 96 defines the base method as a combination of Test Methods D 95 and D 473, it was decided that data obtained by Test Method D 95 in one laboratory would be the" true value." Table X1.3 shows the expected value~~

[9] Tret-O-Lite is a registered trademark of Tretolite Div., Petrolite Corp., 369 Marshall Ave., St. Louis, MO. Even though Tret-O-Lite F65 was used during the round robin, there are many demulsifiers on the market that may be useful.

TABLE X1.3 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

compared to each sample average using this criterion. It can be seen that both methods are biased low. However, the distillation test method (Test Method D 95) appears less biased than the centrifuge. Since the bias is not the same in every laboratory (Table X1.4 study.), it is not possible to recommend inclusion of

X1.4.1.2 Since API *MPMS* Chapter 10.4 defines the base method as a correcombination of Test Method D 95 (API *MPMS* Chapter 10.5) and Test Method D 473 (API *MPMS* Chapter 10.1), it was decided that data obtained by Test Method D 95 (API *MPMS* Chapter 10.5) in one laboratory would be the methods. This data treatment suggests that "true value." Table X1.3 shows the expectend value compared to each sample averifage using this criterion. Both method,s are biased on the average, yields results about 0.06 % lower low side. However, the distillation test method, Test Method D 95 (API *MPMS* Chapter 10.5) appears less biased than the distillation. The respective biases are − 0.13 for the centrifuge and − 0.07 for the distillation method.

X1.4.1.3 A more reliable estimate of method. Since the bias may be obtained if consideration is given only to those samples to which water was added. In this case, not 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 same in every laboratory (Table X1.4), it is not possible to recommend inclusion of a correction factor in the methods. This data treatment suggests that the centrifuge method, on the average, yields results about 0.06 % lower than the distillation method. The respective biases are −0.13 for the centrifuge method and −0.07 for the distillation 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 method. On this basis the centrifuge bias has improved slightly, while the distillation method bias is about the same. The difference between the two methods is now 0.04 rather than 0.06. It should be noted that bias is greatest with both methods at higher water content.

TABLE X1.4 Corrections to be Applied to Measured Values to Obtain "True'' Water Content

Method	Laboratory	Correction
D 1796 Centrifuge	C	+ 0.152±0.095
D 1796 (API *MPMS* Chapter 10.6)	C	+ 0.152±0.095
	E	+ 0.029±0.125
Centrifuge	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
	Average	+ 0.132
D 95 Distillation	C	+ 0.777±0.082
D 95 (API *MPMS* Chapter 10.5)	C	+ 0.777±0.082
	E	+ 0.048±0.078
Distillation	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 X1.5 Bias of Methods Estimated from Spiked Samples

Water Added,[A] %	D 95 (API *MPMS* Chapter 10.5)		D 1796 (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.

X1.4.2 *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-D-2-1007, "Manual on Determining Precision Data for ASTM methods on Petroleum Products"[4] (1973).~~ a research report.[10]

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 D 95 (API *MPMS* Chapter 10.5) and the centrifuge test method ~~(~~, Test Method D 1796 (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:D-02–1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants," were followed.

X1.4.3.1 *Distillation 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 Method:*—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 ~~l~~ Laboratory 5's data did not belong to the same population as the other data.

~~(a)~~*(1)* 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 outliers rejected and the substituted values when Laboratory 2's results are retained:

Laboratory	Sample	Rejected Value	Substituted Value
2	2	0.19	0.06
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

(~~b~~2) With Laboratory 2's results omitted, only Laboratory 6's results listed above were rejected.

X1.4.4 *Calculation of Repeatability and Reproducibility*:

X1.4.4.1 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:

~~$$S = Ax\,(1 - e^{-b\bar{x}})$$~~ (X1.1)

$$S = A\,\bar{x}(1 - e^{-b\bar{x}})$$ (X1.1)

where:

S = precision,
$\bar{x}$ = sample mean, and
A and b = are constants.

[10] This research report was filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1007.

TABLE X1.6 Round-Robin Results of Water in Crude Oils by ASTM D 95 (API *MPMS* Chapter 10.5) and ASTM D 1796 (API *MPMS* Chapter 10.6)

~~Distillation Test Method ASTM D 95~~

Distillation Test Method ASTM D 95 (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~~
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	0.88	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 D 1796~~

Centrifuge Test Method D 1796 (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

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:

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

X1.4.4.2 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:

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

Using the data calculated above for each sample, the ~~following~~ values listed in Table X1.7 for the constants in Eq X1.1 were ~~obtained:~~

TABLE X1.7 ASTM PrecisiCon Instervalnts: ASTM D 95 (7 Laboratoriesee Eq X1.1)

	Distillation Method 7 Laboratories		Centrifuge Method 6 Laboratories	5 Laboratories
% WConstanter	Repeatability	Reproducibility	% WRepeater	
0.000	0.000	0.000	0.000	
0.000ability	Reproducibility	Repeatability	Reproducibility	
0.005	0.017	0.023	0.005	
b	47.41	47.41	0.005	
0.010	0.030	0.041	0.010	
0.011.23	11.23	17.87	17.87	
0.015	0.041	0.055	0.015	
A	0.2883	0.0380	0.04415	
0.020	0.049	0.066	0.020	
0.020	0.1043	0.0437	0.020	
0.025	0.0560.0750.025			
0.025	0.05650.025			
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	

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

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

X1.4.4.3 The curves of repeatability and reproducibility for the distillation method in the range 0 to 0.09 % water are shown in Fig. X1.1. These data are also tabulated in Table X1.7 X1.8. The curves for the centrifuge 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).

X1.4.4.4 For higher levels of water the limiting repeatabilities and reproducibilities are:

Method	Repeatability Range of Concentration, %	- Value, %
Distillation	≥.085	0.08
Centrifuge (five-laboratory case)	≥.155	0.12
Centrifuge (six-laboratory case)	≥.235	0.12

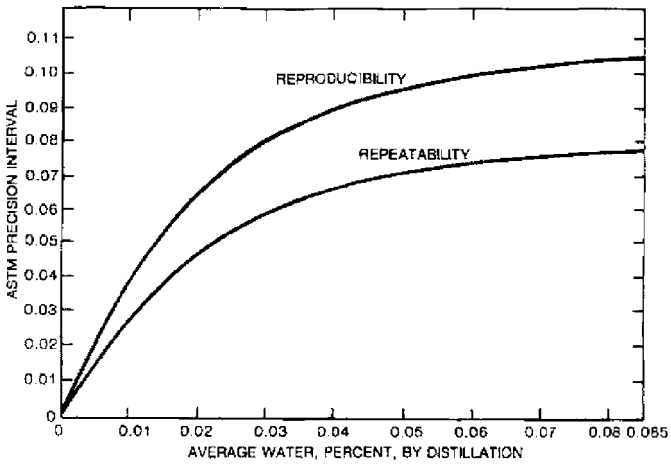

FIG. X1.1 Basic Sediment and Water Precision for ASTM Test Method D 95 (API *MPMS* Chapter 10.5) Distillation (Based on Seven Laboratories)

TABLE X1.8 ASTM Precision Intervals: ASTM D 95 (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

~~Method~~ ~~Range of Concentration, %~~ ~~Reproducibility Value, %~~

~~Distillation ≥0.085 0.105~~
~~Centrifuge (five-laboratory case) ≥0.325 0.19~~
~~Centrifuge (six-laboratory case) ≥0.315 0.29~~

are listed in Table X1.9.

X1.4.4.5 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.

X1.4.4.6 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:

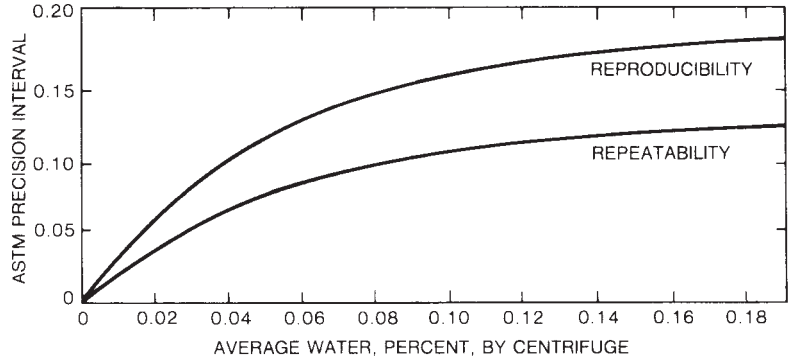

FIG. X1.2 Basic Sediment and Water Precision for ASTM Test Method D 1796 (API *MPMS* Chapter 10.6) Centrifuge (Based on Five Laboratories)

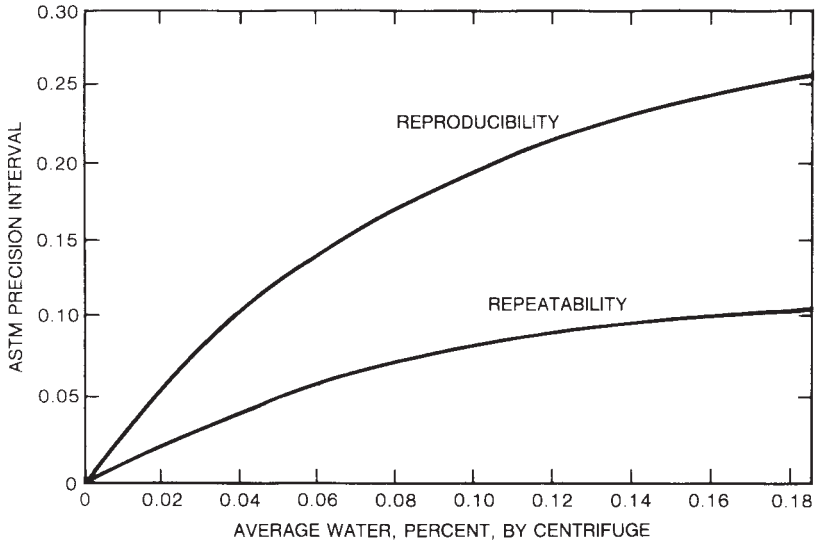

FIG. X1.3 Basic Sediment and Water Precision for ASTM Test Method D 1796 (API *MPMS* Chapter 10.6) Centrifuge (Based on Six Laboratories)

TABLE X1.9 Limiting Repeatabilities and Reproducibilities

Method	Repeatability		Reproducibility	
	Range of Concentration, %	Value, %	Range of Concentration, %	Value, %
Distillation	≥0.085	0.08	≥0.085	0.105
Centrifuge (five-laboratory case)	≥0.155	0.12	≥0.325	0.19
Centrifuge (six-laboratory case)	≥0.235	0.12	≥0.315	0.29

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

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 D 95 (API *MPMS* Chapter 10.5) and the centrifuge test method (, Test Method D 1796 (API *MPMS* Chapter 10.6) in 21 crude oil samples were examined. The conclusions are:

X1.5.1.1 *Distillation Method*:

(a)(1) Precision is related to water content up to about 0.108 % water.

(b)(2) In the range from 0.01 to 0.108, repeatability varies from 0.020 to 0.078 and reproducibility from 0.041 to 0.105.

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

X1.5.1.2 *Centrifuge Method*:

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

(b)(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 D 95 (API *MPMS* Chapter 10.5) should be the specified method for use in critical situations.

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