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Manual of Petroleum Measurement Standards (MPMS), Chapter 10.3

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 D4007; 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.

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 D4006 (API MPMS Chapter 10.2) (Note 1), and sediment by extraction, Test Method D473 (API MPMS Chapter 10.1), shall be used.

NOTE 1—Test Method D4006 (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 standard.

1.2.1 *Exception*—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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements appear in 7.1, 9.3, and A1.5.4.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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. 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)

D4006 Test Method for Water in Crude Oil by Distillation (API MPMS Chapter 10.2)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products (API MPMS Chapter 8.1)

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

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)

D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products (API MPMS Chapter 8.3)

E969 Specification for Glass Volumetric (Transfer) Pipets

2.2 API Standards:³

MPMS Chapter 1 Terms and Definitions Database

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 8.3 Mixing and Handling of Liquid Samples

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, www.api.org.

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

of Petroleum and Petroleum Products (ASTM Practice D5854)

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

MPMS Chapter 10.2 Determination of Water in Crude Oil by Distillation (ASTM Test Method D4006)

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 D95)

MPMS Chapter 10.6 Determination of Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedures) (ASTM Test Method D1796)

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

2.3 IP Standard:⁴

Methods Book, Appendix B Specification for Methylbenzenes (Toluenes)

2.4 ISO Standard:⁵

ISO 5272:1979 Toluene for Industrial Use—Specifications

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175 and the API MPMS Chapter 1 Terms and Definitions Database.

4. Summary of Test Method

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

5. Significance and Use

5.1 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. It is not anticipated that this test method, which is written with a dedicated laboratory facility in mind, is likely to be used in field test rooms or sample rooms due to safety concerns for proper ventilation and handling.

5.2 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).

6. Apparatus

6.1 Centrifuge:

6.1.1 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 6.1.6).

6.1.2 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.

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

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

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

$$r/\text{min} = 1335 \sqrt{\text{rcf}/d} \quad (1)$$

where:

rcf = relative centrifugal force and

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

$$r/\text{min} = 265 \sqrt{\text{rcf}/d} \quad (2)$$

where:

rcf = relative centrifugal force and

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

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

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

where:

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

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

where:

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

6.2 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),

⁴ Available from Energy Institute, 61 New Cavendish St., London, WIG 7AR, U.K., <http://www.energyinst.org.uk>.

⁵ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

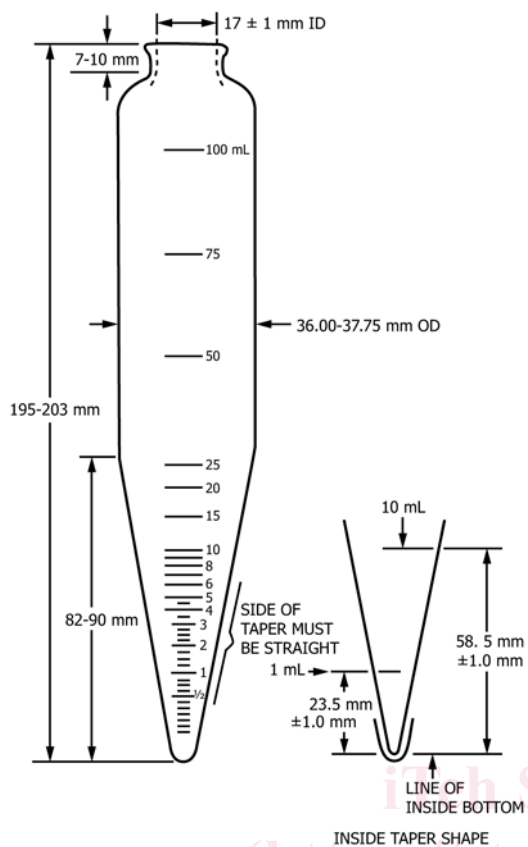


FIG. 1 Eight-Inch (203 mm) Centrifuge Tube

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

Range, mL	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

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 mL, 1.0 mL, 1.5 mL, 2.0 mL, 50.0 mL, and 100 mL marks. The tube shall not be used if the scale error at any mark exceeds the applicable tolerance from Table 1.

6.3 *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 °C ± 3 °C (140 °F ± 5 °F). For some crude oils, temperatures of 71 °C ± 3 °C (160 °F ± 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.

6.4 *50 mL Pipet, Class A*, or equivalent volume dispensing device, capable of delivering a volume of 50 mL ± 0.05 mL (see Specification E969) for use in the test.

7. Solvent

7.1 *Toluene*—Reagent grade conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS)⁶ or to Grade 2 of ISO 5272 or conforming to the EI Specification for Methylbenzenes (Toluenes). (**Warning**—Flammable. Keep away from heat, sparks, and open flame. 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.)

7.1.1 Typical characteristics for this reagent are:

Assay	99.5+ %
Color (APHA)	10
Boiling range (initial to dry point)	2.0 °C
(Recorded boiling point 110.6°C)	
Residue after evaporation	0.001 % max – wt/wt
Substances darkened by H ₂ SO ₄	passes test
Sulfur compounds (as S)	0.003 % max – wt/wt
Water (H ₂ O) (by Karl Fischer titration)	0.03 % max – wt/wt

7.1.2 The solvent shall be water-saturated at 60 °C ± 3 °C (140 °F ± 5 °F) (see 6.3) but shall be free of suspended water. See Annex A1 for the solvent-water saturation procedure.

7.2 *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.

8. Sampling

8.1 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.

8.2 Only representative samples obtained as specified in Practices D4057 (API MPMS Chapter 8.1) and Practice D4177 (API MPMS Chapter 8.2) shall be used for this test method.

8.3 *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 D5854 (API MPMS Chapter 8.3).

⁶ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

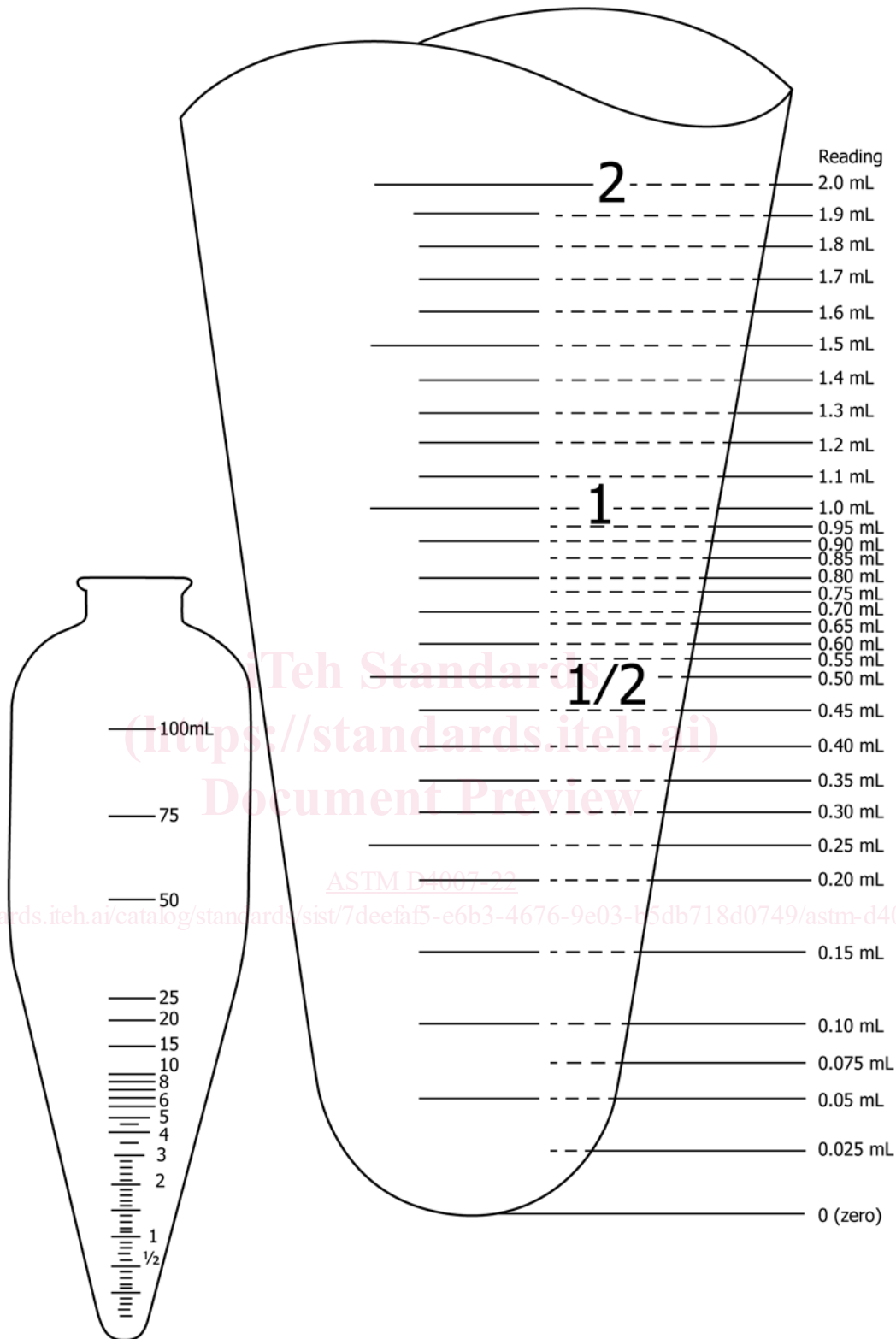


FIG. 2 Procedure for Reading Water and Sediment When Using an ASTM 100-mm Cone-Shaped Centrifuge Tube

9. Procedure

9.1 Fill each of two centrifuge tubes (6.2) to the 50 mL mark with sample directly from the sample container. Using a pipet or other suitable volume transfer device (see 6.4), add 50 mL ± 0.05 mL of toluene, which has been water saturated at 60 °C (140 °F) or 71 °C (160 °F) (see 6.3). Read the top of the meniscus at both the 50 mL and 100 mL marks. Add 0.2 mL of demulsifier solution (7.2) to each tube, using a 0.2 mL pipet or other suitable volume transfer device, such as an automatic pipettor. Stopper the tube tightly and invert the tubes ten times to ensure that the oil and solvent are uniformly mixed.

9.2 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. Take care to not fill the centrifuge tube past the 100 mL mark with the sample.

9.3 Loosen the stoppers slightly and immerse the tubes to the 100 mL mark for at least 15 min in the bath maintained at 60 °C ± 3 °C (140 °F ± 5 °F) (see 6.3). 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).)

9.4 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 6.1.6.

9.5 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 mL to 1 mL graduations, and to the nearest 0.1 mL above 1 mL 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.

9.6 Repeat this operation until the combined volume of water and sediment remains constant for two consecutive readings. In general, not more than two spinings are required.

9.7 The temperature of the sample during the entire centrifuging procedure shall be maintained at 60 °C ± 3 °C (140 °F ± 5 °F) (see 6.3).

9.8 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.

10. Calculation

10.1 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.

10.2 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.

11. Precision and Bias

11.1 *Precision*—The precision of this test method, as determined by statistical examination of interlaboratory test results in the range from 0.01 % to 1.0 %, is described in 11.1.1 and 11.1.2.

11.1.1 *Repeatability*—The difference between 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 0.3 % to 1.0 % water, repeatability is constant at 0.12.

11.1.2 *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.

11.2 *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.

12. Keywords

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

TABLE 2 Expression of Results, mL

Tube 1	Tube 2	Total Percent Water and Sediment, % (V/V)
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

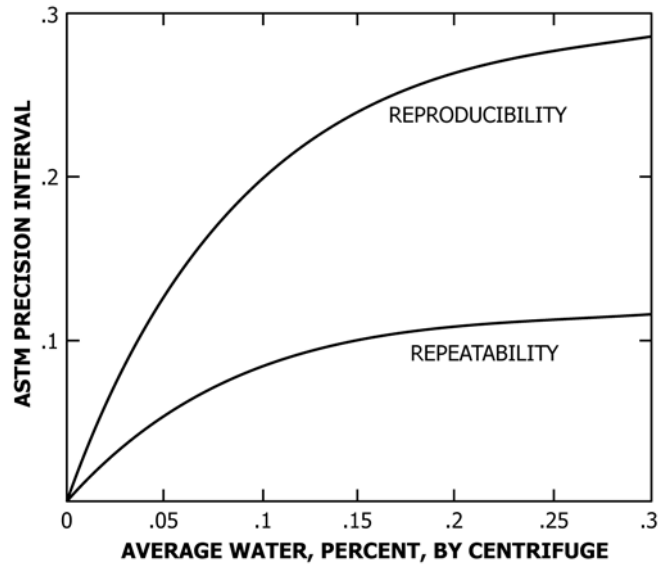


FIG. 3 Basic Sediment and Water Precision

ANNEX

(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

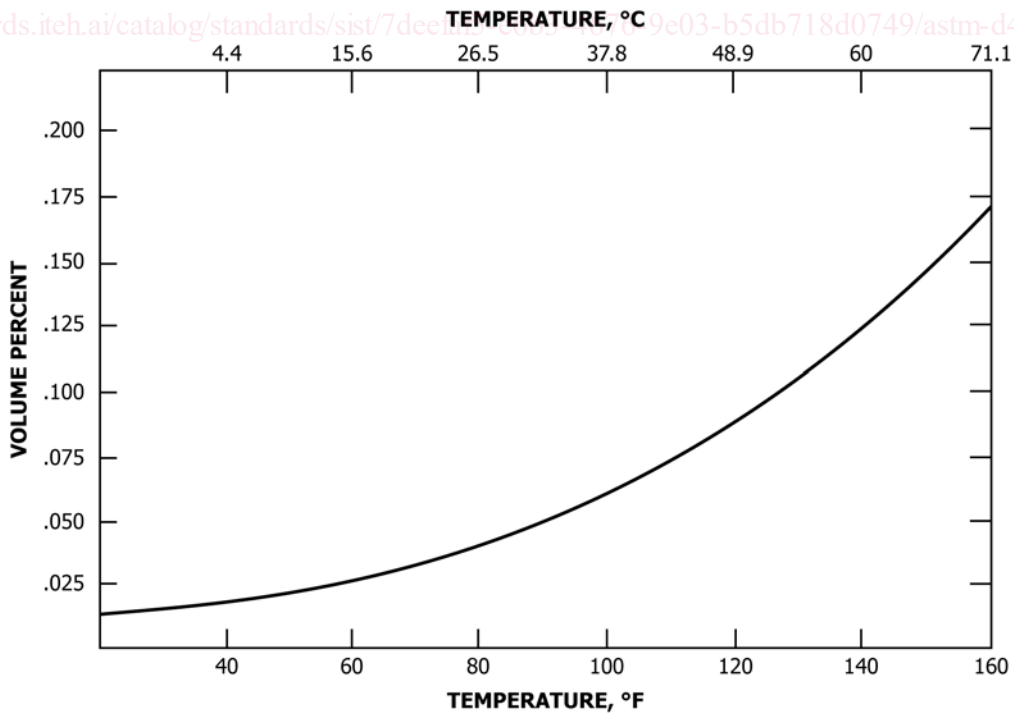


FIG. A1.1 Solubility of Water in Toluene

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*—Reagent grade conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS)⁶ or to Grade 2 of ISO 5272, or conforming to the EI Specification for Methylbenzenes (Toluenes).

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 °C ± 3 °C (140 °F ± 5 °F) (see 6.3).

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 °F).

A1.5.2 Fill the glass bottle with 700 mL to 800 mL of toluene. Add 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) 3 times. (**Warning**—The vapor pressure of toluene at 60 °C (140 °F) is approximately twice that at 38 °C (100 °F).)

A1.5.5 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.

A1.5.6 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.

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 D95 (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 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 Subcommittee on Static Petroleum Measurement undertook the evaluation of two methods for determining water in crudes. A distillation method, Test Method D95 (API MPMS Chapter 10.5), and a centrifuge method, Test Method D1796 (API MPMS Chapter 10.6), were evaluated in this program. Both methods were modified slightly in an attempt to improve the precision and accuracy.