Designation: ~~D4007 – 11ε1~~ D4007 – 11 (Reapproved 2016)

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.

~~ε[1] NOTE—Referenced Documents and API information was editorially corrected in July 2013.~~

1. ~~Scope*~~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. ~~The values given in parentheses are for information only.~~

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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements appear in 6.1, 8.3, and A1.5.4.

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)

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 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 of Petroleum and Petroleum Products (ASTM Practice D5854)

[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.

[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**

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. 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 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. 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.

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 *Centrifuge:*

5.1.1 A centrifuge capable of spinning two or more filled cone-shaped, ~~203-mm (8-in.)~~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 controlled thermostatically to avoid unsafe conditions. It shall be capable of maintaining the sample temperature during the entire run at ~~60~~60 °C ± ~~3°C (140~~3 °C (140 °F ± ~~5°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.

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

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

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:

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

[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.

where:

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.)~~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),~~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~~ 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~~ 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.

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~~100 mL mark. Means shall be provided for maintaining the temperature at ~~60~~60 °C ± ~~3°C (140~~3 °C (140 °F ± ~~5°F).~~5 °F). For some crude oils, temperatures of ~~71~~71 °C ± ~~3°C (160~~3 °C (160 °F ± ~~5°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.

5.4 ~~*50 mL*~~ *50 mL Pipet,* Class A, or equivalent volume dispensing device, capable of delivering a volume of ~~50~~50 mL ± ~~0.05 mL~~ 0.05 mL (see Specification E969) for use in the test.

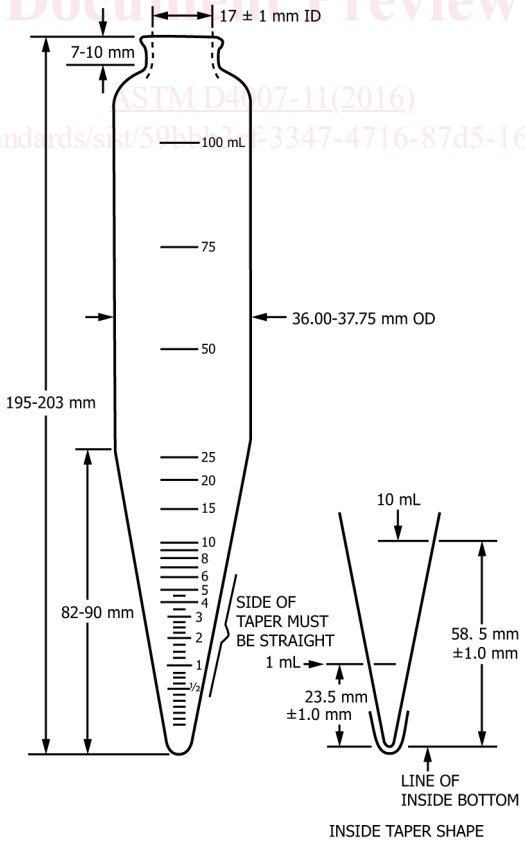

FIG. 1 Eight-Inch ~~(203-mm)~~(203 mm) Centrifuge Tube

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

6. Solvent

6.1 *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.)

6.1.1 Typical characteristics for this reagent are:

Assay	99.5+ %
Color (APHA)	10
~~Boiling range (initial to dry point) (Recorded boiling point 110.6°C)~~	~~2.0°C~~
Boiling range (initial to dry point) (Recorded boiling point 110.6°C)	2.0 °C
Residue after evaporation	0.001 % max – wt/wt
Substances darkened by H_2SO_4	passes test
Sulfur compounds (as S)	0.003 % max – wt/wt
Water (H_2O) (by Karl Fischer titration)	0.03 % max – wt/wt

6.1.2 The solvent shall be water-saturated at ~~60~~60 °C ± ~~3°C (140~~3 °C (140 °F ± ~~5°F)~~5 °F) (see 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 Practices D4057 (API *MPMS* Chapter 8.1) and Practice D4177 (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 D5854 (API *MPMS* Chapter 8.3).

8. Procedure

8.1 Fill each of two centrifuge tubes ~~(5.2)~~(5.2) to the ~~50-mL~~50 mL mark with sample directly from the sample container. Using a pipet or other suitable volume transfer device (see 5.4), add ~~50~~50 mL ± ~~0.05 mL~~ 0.05 mL of toluene, which has been water saturated at ~~60°C (140°F) or 71°C (160°F)~~60 °C (140 °F) or 71 °C (160 °F) (see 5.3). Read the top of the meniscus at both the ~~50~~50 mL and ~~100-mL~~100 mL marks. Add ~~0.2 mL~~ 0.2 mL of demulsifier solution (6.2) to each tube, using a ~~0.2-mL~~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.

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

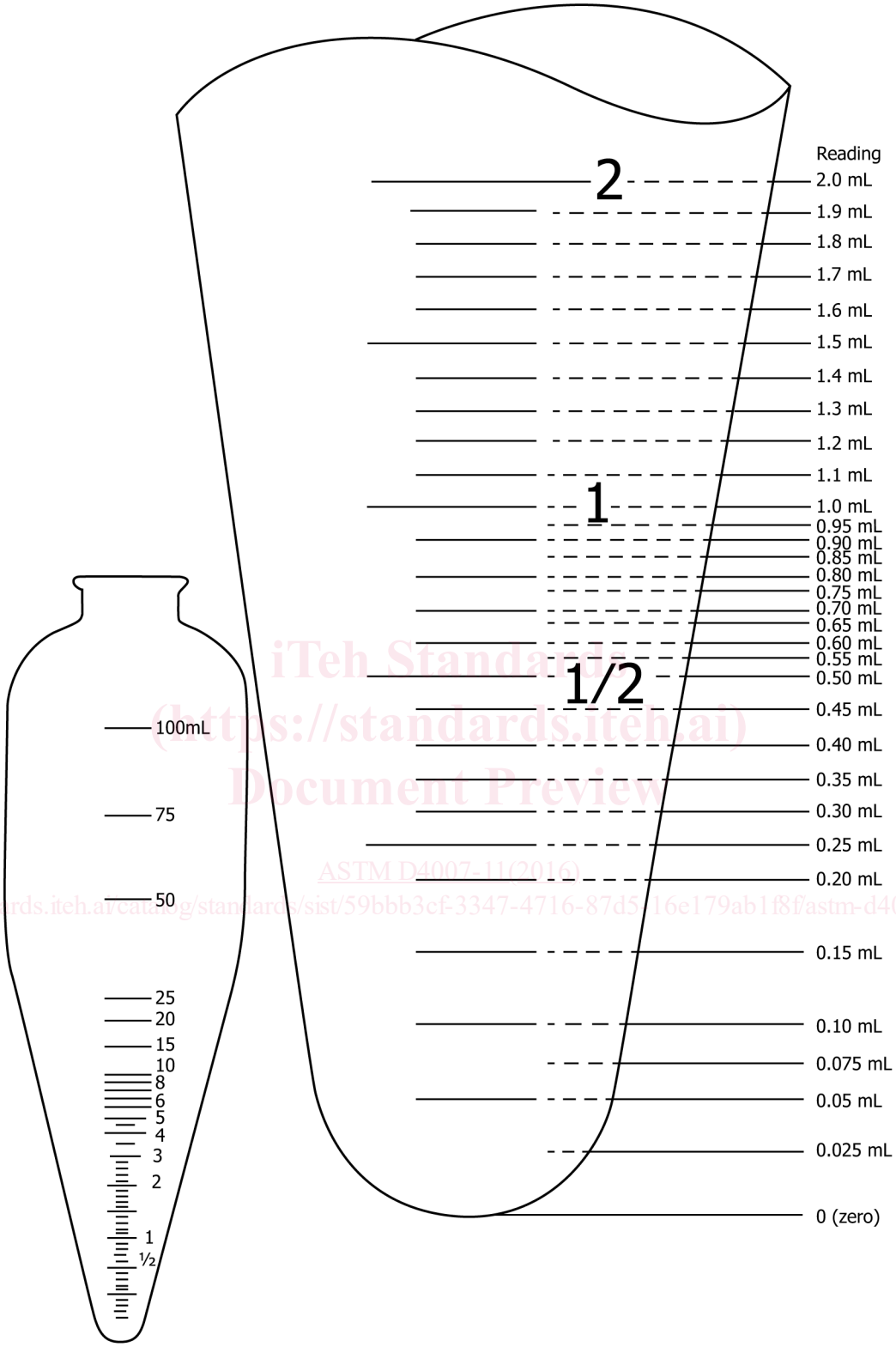

FIG. 2 Procedure for Reading Water and Sediment When Using an ASTM 100-mm Cone-Shaped Centrifuge Tube

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

8.3 Loosen the stoppers slightly and immerse the tubes to the ~~100-mL~~100 mL mark for at least ~~15 min~~ 15 min in the bath maintained at ~~60~~60 °C ± ~~3°C (140~~3 °C (140 °F ± ~~5°F)~~5 °F) (see 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)~~60 °C (140 °F) is approximately double that at ~~40°C (104°F).)~~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 5.1.6.

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~~ 0.05 mL from ~~0.1~~0.1 mL to ~~1-mL~~1 mL graduations, and to the nearest ~~0.1-mL~~0.1 mL above ~~1-mL~~1 mL graduations. Below ~~0.1 mL,~~ 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~~ 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 shall be maintained at ~~60~~60 °C ± ~~3°C (140~~3 °C (140 °F ± ~~5°F)~~5 °F) (see 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~~ 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.

10. Precision and Bias

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

10.1.1 *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.

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:

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