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Standard Methods of Test for WATER AND SEDIMENT IN CRUDE OILS'

This Standard is issued under the fixed designation D 96; 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. This is also a standard of the American Petroleum Institute issued under the fixed designation API 2542.

These methods were adapted as a joint ASTM-API Standard in 1963.

1. Scope

1.1 These methods describe procedures for the determination of water and sediment in crude oils.

1.2 The methods appear in the following order:

1.3 The Gravity Settling Method for Crude Oils is in use in sbme areas of the United States for determining water and sediment in crude oil deliveries. Where used this method is well known. The most recent standard reference is Method D in ASTM Designation D 96 - 63; API Standard 2542, published-in the *1963 Book of ASTM Standards,* Part 18.

NOTE 1—The values stated in U.S. customary units are to be regarded as the standard.

2. Sample

2.1 The sample shall be thoroughly representative of the material in question and the portion used for the test shall be thoroughly representative of the' sample itself. This requires vigorous agitation of the sample immediately before transferring the sample to the tube. Cold samples should be warmed *to* facilitate mixing. The difficulties in obtaining representative samples for this determination are unusually great; hence, the importance of sampling cannot be too strongly emphasized.

METHOD A—LABORATORY CENTRIFUGE METHOD

3. Apparatus

3.1 *Centrifuge,* capable of whirling two or more filled centrifuge tubes at a speed which can be controlled to give a relative centrifugal force (rcf) of between *500* and 800 at the tip of the tubes. The revolving head, trunnion rings, and trunnion cups, including the cushion, 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. Calculate the speed of the rotating head as follows:

$$rpm = 265\sqrt{rcf/d}$$

where:

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

3.2 *Centrifuge Tubes,* cone-shaped, 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 constricted in shape for closure with a cork. Scale error tolerances and smallest graduations between

[1] These methods arc under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and the API Central Committee on Petroleum Measurement.

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various calibration marks are given in Table 2. and apply to calibrations made with air-free water at 20 C reading the bottom of a shaded meniscus.

3.3 *Bath for Centrifuge* Tubes—The bath shall be either a solid metal block or a liquid bath of sufficient depth for immersing the centrifuge tube in vertical position to the 100-ml mark. Means shall be provided for maintaining temperatures at 120 ± 2 F (49 ± 1 C) and 140 ± 2 F (60 ± 1 C).

4. Solvent

4.1 Toluene (Note 2) conforming to ASTM Specifications D 362, for Industrial Grade Toluene,[2] or benzene conforming to ASTM Specifications D 836, for Industrial Grade Benzene,[2] may be used as the solvent. A commercial demulsifier[3] may be added to the solvent but should not contribute to the water and sediment. The type and concentration is not limited, provided that the demulsifier itself does not contribute to the water and sediment. Commercial demulsifiers at a concentration of 7 ml per 1000 ml of solvent have been successfully used (Note 3).

NOTE 2—Toluene is the preferred solvent because of its lower toxicity.

NOTE 3—It is recognized that some crudes may require (1) other solvents or (2) solvent-demulsifier combinations. Such solvents and demulsifiers as agreed upon between the purchaser and the seller may be used after careful experimentation to determine suitability and desirability.

4.2 The solvent shall be saturated with water at ambient temperature but shall be free of suspended water. Saturation may be accomplished by the addition of 2 ml of water per 1000 ml of solvent. A mechanical stirring device is recommended, but if none is available, shaking will aid in saturation. Adequate settling time should be provided to ensure that the solvent is free of suspended water before use.

5. Procedure

5.1 Fill each of two centrifuge tubes (see 3.7) to the 50-ml mark with solvent; then pour immediately the well-shaken sample directly from the sample container into the centrifuge tubes until the total volume in each tube is 100 ml. Stopper the tubes tightly and shake vigorously until the contents are thoroughly mixed. Immerse the tubes to the 100-ml mark for 10 min in the bath (see 3.3) maintained at 120 ± 2 F (49 ± 1 C).

5.1.1 If wax contributes to the volume of water and sediment observed, preheat the oil-solvent mixture to 140 F (60 C) before each whirling; the final temperature of the mixture shall not drop below 115 F (46 C).

5.2 Invert the tubes to assure that the oil and the solvent are uniformly mixed. If necessary, shake cautiously. (Caution—The vapor pressure at 140 F is approximately double that at 100 F.) Place the tubes in trunnion cups on opposite sides of the centrifuge to establish a balanced condition, and whirl 10 min at a rate, calculated from the equation given in 3.1, sufficient to produce a relative centrifugal force (rcf) of between 500 and 800 at the tip of the whirling tuber. (For the relationship between diameter of swing, rcf, and rpm, see Table 1.) Read and record the conibined volume of water and sediment at the bottom of each tube to the nearest 0.05 ml from 0.1 to 1-ml graduation and to the nearest 0.1 above 1-ml graduation. Below 0.1 ml, estimate to the nearest 0.025 ml. Return the tubes without agitation to the centrifuge and whirl for 10 min at the same rate. Repeat this operation until the combined volume of water and sediment remains constant for two consecutive readings. In general, not more than two whirlings are required.

NOTE 4—With certain types of oil it is difficult to obtain a clean break between the oil layer and the separated water. In such cases one or more of the following remedies may be effective: (1) raise the temperature to 140 F and guard against allowing the temperature to drop below 115 F at the end of the run; (2) shake the mixture between whirlings in the centrifuge just sufficiently to disperse the emulsion; (3) use a different, or increased amount of demulsifier; however, it should not contribute to the water and sediment. After a satisfactory procedure for a particular type of oil has been worked out, it will ordinarily be found suitable for all samples of the same type.

5.3 Record the final volume of water and sediment in each tube and report the sum of these two readings as the percentage of water and sediment.

[2] *Annual Book of ASTM Standards*, Part 20.

[3] Tretolite F-46 and Tretolite C-10 have been successfully used.

6. Report

6.1 The report shall include the following:

6.1.1 The percentage of water and sediment. (Results lower than 0.05 percent reported either as zero or 0.05. whichever is closer.)

6.1.2 The name of and amount of demulsifier used.

6.1.3 The solvent used if different from those in Section 4.

6.1.4 The bath temperature.

7. Precision

7.1 The following criteria should be used for judging the acceptability of results (95 percent probability):

7.1.1 Repeatobiliry — Duplicate results by the same operator should be considered suspect if they differ by more than the values shown on the "repeatability" curve in Fig. 3.

7.1.2 Reproducibility — The results submitted by each of two laboratories should be considered suspect if they differ by more than the values shown on the "reproducibility" curve in Fig. 3.

METHOD B — FIELD CENTRIFUGE METHOD

a Apparatus

8.1 Centrifuge *for* Field *Use*, meeting the requirements prescribed in 3.1.

3.2 Centrifuge Tube, 8-in. (*203-mm*), cone-shaped as described in 3.2 and shown in Fig. I.

8.3 *Centrifuge* Tube, *6-in.* (*152-mm*), cone-shaped conforming to dimensions given in Fig. 4 and made of thoroughly annealed glass. The graduations, numbered as shown in Fig. 4, shall be clear and distinct, and the mouth constricted in shape for closure with a cork. Scale error tolerances and smallest graduations between various calibration marks are given in Table 3, and apply to calibrations made with air-free water at *20* C, reading the bottom of a shaded meniscus. While the use of the 8-in. tube is preferable. the 6-in. tube is included because of the extensive use of centrifuges of limited diameter.

8.4 Centrifuge Tube. *Pear-Sahped*, conforming to dimensions given in Fig. 5 and made of thoroughly annealed glass. The graduations, numbered as shown in Fig. *5* shall be clear and distinct. and the mouth constricted in shape for closure with a cork. Scale error and tolerances and smallest graduations between various calibration marks are given in Table 4 and apply to calibrations made with air-free water at 20 C reading the bottom of a shaded meniscus. (This tube has generally been superseded by tubes shown in Figs. I and 4, however, its use warrants inclusion in the method.)

8.5 Permissible Exception — When mutually agreeable, centrifuge tubes graduated in 200 parts; direct reading in percent water and sediment, may be used and may be 6-in. cone-shaped or pear-shaped. The use of these tubes is limited to testing with equal parts of solvent and oil.

9. Solvent

9.I The following solvents and demulsifiers have been reported as satisfactory for field testing.

Solvents	Demulsifiers
Stoddard Solvent	Commercial crude oil demulsifiers
Toluene	Phenol
Xylene	Nitrogen bans
Kerosine	Naphihenic acids
White gasoline	

9.1.1 Toluene and xylene shall be saturated with water at ambient or room temperature but shall be free of suspended water. Solvents are toxic and care should be exercised in their use. Gasoline containing tetraethyl lead or deicer should never be used. When Stoddard solvent, kerosine. and white gasoline are used they must have similar solvent characteristics with respect to the crude oil being tested.

9.1.2 The use of a demulsifier (resolving agent) with solvents shall be permitted subject to the mutual consent of all parties concerned when tests demonstrate that correct results cannot otherwise be determined. The type and concentration is not limited, provided that the demulsifier itself does not contribute to the water and sediment. Commercial demulsifiers,[3] at a concentration of 7 ml/1000 ml of solvent have been successfully used (Note 3).

10. Procedure

10.1 Fill the centrifuge tube to the 50-ml mark with solvent; then pour the well-shaken sample directly from the container into the tube until the total volume is 100 ml. Stopper

the tube and shake until the contents are thoroughly mixed. Immerse the tube in a bath or dry heating device and heat the contents of the tube to 120 F. Where field conditions do not permit the use of sensitive temperature control devices, pocket-type thermometers may be used. In such cases every effort should be made to ensure a reasonably consistent bath temperature for the same oil at each time of testing.

10.1.1 If wax contributes to the volume of water and sediment observed, preheat the oil-solvent mixture to 140 F before each whirling: the final temperature of the mixutre shall not drop below 115 F. A heated centrifuge may be required to maintain a final temperature of 115 F.

10.2 Invert the tube to assure that the oil and the solvent are uniformly mixed. If shaking is necessary, proceed cautiously because the vapor pressure at 140 F is approximately double that at 100 F. Place tubes in trunnion cups on opposite sides of the centrifuge to establish a balanced condition, and whirl for 3 to 10 min depending upon the character of the sample. at a rate calculated from the equation given in 3.1. sufficient to produce a relative centrifugal force (rcf) of between 500 and 800 at the tip of the whirling tubes. (For the relationship between diameter of swing. rcf, and rpm, see Table 2.)

10.3 Read and record the combined volume of water and sediment at the bottom of the tube to the nearest 0.05 ml from 0.1 to I-ml graduation and to the nearest 0.1 above I-ml graduation. Below 0.1 ml, estimate to the nearest 0.025 ml. If experience with the oil is limited, it is advisable to return the tube to the centrifuge without agitation and repeat the operation.

10.3.1 With certain types of oil it is difficult to obtain a clean break between the oil layer and the separated water. In such cases one or more of the following remedies may be effective: (I) raise the temperature to 140 F; *(2)* shake &he mixture between whirlings in the centrifuge just sufficiently to disperse the emulsion: (3) use a different. or increased amount of demulsifier: however. it should not contribute to the water and sediment: (*4*) use a different. or increased amount *of* solvent. After a satisfactory procedure for a particular type of oil has b a n worked out, it will ordinarily be found suitable for all samples of the same type.

11. Calculation

11.1 Multiply the reading obtained in accordance with the procedure described in 10.1, **10.2,** and **10.3** by two and record the results as the percentage of water and sediment. For example, if a reading is 0.025 ml. record the percentage of water and sediment as ***0.05.*** If a reading is 0.15 ml, record the percentage of water and sediment as 0.30. If the results are lower than **0.05** percent, record the percentage of water and sediment as described in Section **12.** When the ratio of solvent to oil is different than ***50*** percent, the reading obtained in 10.3 must be multiplied by the proper ratio factor in order to obtain the correct percentage of water and sediment.

12. Record

12.1 The record shall include the following:

12.1.1 The percentage of water and *sedi*ment. (Results lower than 0.05 percent reported either as zero or 0.05. whichever is closer.)

12.1.2 The solvent used.

12.1.3 The type of and amount of demulsifier if used.

12.1.4 The bath temperature.

13. Precision

13.1 For methods using the 8-in. conc shaped tube, as in Section 8, or the 6-in. conc shaped tube, the following criteria should t used for judging the acceptability of resul *(95* percent probability):

13.1.1 *Repeatability*—Duplicate results the same operator should be considered si pect if they differ by more than the valt shown on the "repeatability" curve (Fig. 6).

13.1.2 *Reproducibility*—The results st mitted by each of two separate parties sho be considered suspect if they differ by m than the values shown on the "reproduci ity" curve (Fig. 6).

13.2 For the method using pear-sha tube the following criteria should be used judging the acceptability of results *(95* per probability).

13.2.1 *Repeatability*—Duplicate results

the same operator should be considered suspect if they differ by more than the following:

Water and Sediment (Volume Percent)	Repeatability
0 to 0.5	0.1
0.5 to 1.5	0.2

13.2.2 Reproducibility figures are not available.

METHOD C—FIELD CENTRIFUGE METHOD—12.50-ML TUBE—CRUDE OILS

NOTE 5—This method is used for crude oil in some areas of the United States and is therefore included in the standard.

14. Apparatus

14.1 *Centrifuge for Field Use.* either hand- or electrically powered, meeting the requirements prescribed in 3.1 (see Table 2).

14.2 *Centrifuge Tube, API. 12.50-ml Capacity*—The capacity of this tube shall be 12.50 ml in the calibrated portion, with capacity, dimensions. graduations, tolerances. and markings as shown in Fig. 7 and Tables 5. 6. and 7.

14.2.1 *Limit of* Error (plus or minus tolerance) is based on the total calibrated volume of tube as shown in Table 7. Molded tubes are preferred. Blown tubes that comply with the stipulations on uniform wall thickness are satisfactory. All centrifuge tubes shall be retempered to remove manufacturing strains. The lower end of the centrifuge tube must be clear and perfectly rounded inside, with the same thickness of glass as in the main body of the tube.

15. Solvent

15.1 Solvents and demulsifiers to be used in this method are the same as given in Section 9 for Method B.

16. Procedure

16.1 Fill two tubes (Section 14) to the 50 percent mark, with tbe solvent, with or without demulsifier and then to the 100 percent mark with the sample of oil to be tested. Stopper the tubes and shake until the contents are thoroughly mixed, place them in the centrifuge and revolve at the rate of 1500 rpm for 3 to 10 min, depending upon the character of the sample. Remove the tubes and record the combined volume of water and sediment in each tube to the nearest 0.1 percent.

16.2 Replace the tubes in the centrifuge and revolve again for from 3 to 10 min. Again record the combined water and sediment. If there is a difference of more than 0.2 percent between the first and second readings, continue centrifuging until two consecutive readings check within 0.2 percent.

17. Calculation

17.1 The sum of the final readings on the two 12.50-ml centrifuge tubes represents the volume percentage of water and sediment in the crude oil tested.

18. Report

18.1 The report shall include:

18.1.1 The percentage of water and sediment.

18.1.2 The solvent used, and

18.1.3 The type and amount of demulsifier if used.

19. Precision

19.1 The precision of this method has not been established.

METHOD D—BASE METHOD

20. Procedure

20.1 The sum of the results obtained in accordance with ASTM Method D 95 - API 2560. Test for Water in Petroleum Products and Other Bituminous Materials.' and ASTM Method D 473 - API 2561, Test for Sediment in Crude and Fuel Oils by Extraction,' shall be assumed to be the correct value for water and sediment. These methods shall be considered as the "base method," and shall be used when agreement cannot be reached between the purchaser and the seller when using any of the other methods described. The base method shall be considered the standard method of test for crude oils and fuel oils having characteristics not suitable for test by the centrifuge method. The base method shall be used as a criterion to compare the effectiveness of solvents, with or without demulsifiers, used in Methods A. B. and C.

20.2 For crude oils containing sediment in accordance with Method D 473 - API 2561

[4] *Annual Book of ASTM Standards*, Part 18.

in excess of *0.02* weight percent, the results shall be converted to a volume basis because water and sediment values are commonly reported in volume percent. As the major portion of the sediment would probably be sand (silicon dioxide. which has a specific gravity of **2.32)** and **a** small amount of other natural-occurring materials (with a specific gravity lower than that of sand) an arbitrary specific gravity of **2.0** shall be used **for** the resulting sediment. Then, to obtain volume percent sediment. the weight percent sediment obtained in accordance with Method D **473** - **API 2561 shall** be divided by **two.**

21. Calculation

21.1 Calculate the percentage of water in accordance with Method D *95* - **API 2560.** Convert the weight percentage sediment **obtained** in accordance with Method D **473 API 2561** to volume percentage as described. Calculate the volume percentage of water and sediment **by** adding the two results.

22. Precision

22.1 *Water*—See Section **8** of Method D **95** - **API** 2560.

22.2 Sediment—See Section 7 of Method D **473** - **API 2561.**

TABLE I **Rotation Speeds** Applicable for **Centrifuges of Various Diameters of** swing

Diamctcr of Swing. in. (mm)[a]	Rpm at 500 rcf	Rpm at 800 rcf
12 (304)	1710	2160
13 (330)	I650	2080
14 (355)	1590	2000
I5 (381)	1530	1930
16 (406)	1480	1870
17 (431)	1440	1820
18 (457)	1400	1770
19 (482)	1360	1720
20 (508)	1330	1680
21 (533)	1300	1640
22 (558)	1270	1600
23 (584)	1240	1560
24 (609)	1210	1530

[a] Measured in inches (or millimeters) between tips of opposite tubes when in rotating position.

TABLE 2 **Centrifuge** Tube **Calibration Tolerances** for **8-** in. (203-mm) Tube

Range. ml	Subdivi-sion. ml	Volume Tolerance. ml
0 to 0.1	0.05	±0.02
Abovc 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
Abuvc 1.0 to 2.0	0.10	±0 10
Above 2.0 to 3.0	*0.20*	±0.10
Abovc 3.0to 5.0	*0.5*	±0.20
Abovc 5.0to 10	1.0	*t O* SO
Abovc 10 to 25	*5.0*	± 1 00
Above 25 to 100	*25*	± 1.00

TABLE 3 Centrifuge **Tube Calibration Tolerances for 6-** in. (152-mm) Tube

Range. ml	Subdivi-sion. ml	Volume Tolcrancc. ml
0 to 0.1	0.05	±0.02
Above 0.1 to 0.3	0.05	±0.03
Abovc 0.3 to 0.5	0.05	±0.05
Abovc 0.5 to 1.0	0.10	±0.075
Above 1.0 to 1.5	0.10	±0.10
Above 1.5 to 2	0.10	±0.20
Above 2 to 3	0.20	t0.30
Above 3 to 5	0.50	t0.50
Above 5 to 10	1	t0.75
Abovc 10 to 25	5	±1.0
at 50.75. and 100	...	±1.5

TABLE 4 Pear-Shaped **Centrifuge** Tube **Calibration Tolerances**

Range. ml	Smallest Scale Di-visiun. ml	Maximum Scale Error. ml
0 to 1.5	0.1	0.03
Over 1.5 to 3.0	0.5	0.20
Over 3.0 to 5.0	0.5	0.30
Over 5.0 to 10.0	1	0.50
Over 10 to 25	5	1.0
over 25 tu 100	25	2.0

TABLE 5 Capacity of 12.50-ml Centrifuge Tube

Indicated Percentage	Milliliters
1	0.125
2	0.250
3	0.375
5	0.625
10	1.250
15	1.875
20	2.500
25	3.125
30	3.750
35	4.375
40	5.000
45	5.625
50	6.250
100	12.500

TABLE 6 Specification. for 12.50-ml Ceatrifugc Tube

Graduations

Graduations shall be marked as follows:

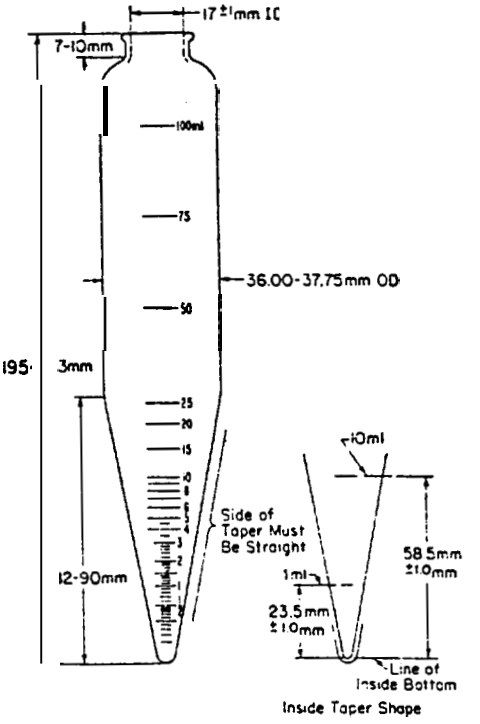
0 to 3 percent	0.2 of 1 percent
3 to 10 percent	0.5 of 1 percent
10 to 50 percent	1.0 percent
50 to 100 percent	blank

Specifications

Length. over-all: 118 ± 2 mm
Length, 0 to 50 percent: 66 ± 4 mm
Length, 50 to 100 percent: 35 ± 3 mm
Length, tapered pan: 56 to 62 mm
Length. untapered part: 58 to 60 mm
Rim thickness: 2 to 3 mm. included in over-all measurement
Diameter, untapered: 17 ± 0.25 mm
Diameter. bottom. at the 0.3 percent marking: 5 ± 1 mm
Normal thickness: perfect semicircle bottom.

TABLE 7 Tolerances for 12.50-ml Centrifuge Tube

Range percent	Tolerance. percent	Volumetric Capacity. ml
0 to 1	±0.1	±0.0125
1 to 2	±0.15	±0.0188
2 to 3	±0.2	±0.0250
3 to 5	±0.2	±0.0250
5 to 10	±0.4	±0.0500
10 to 25	±0.5	±0.0625
25 to 50	±1.0	±0.1250
50 to 100	±1.0	±0.1250



NOTE—For volumetric tolerances. see Table 2.

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

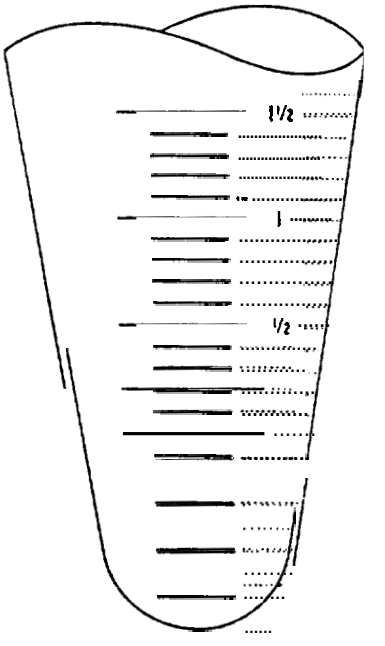


FIG. 2 Tip of 100-ml Cone-Shaped Tube.

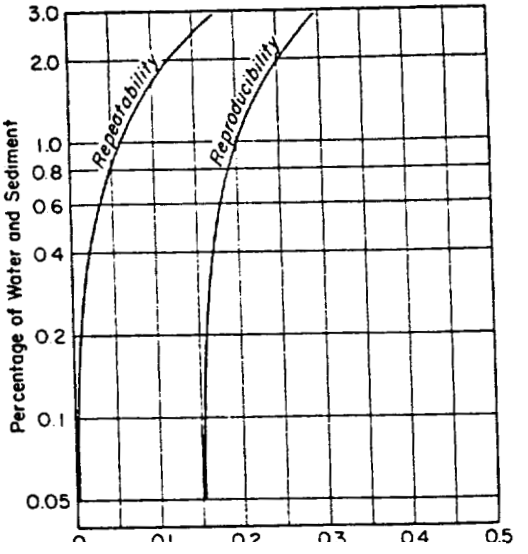


FIG. 3 Precision Curves for Centrifuge Tube Method.

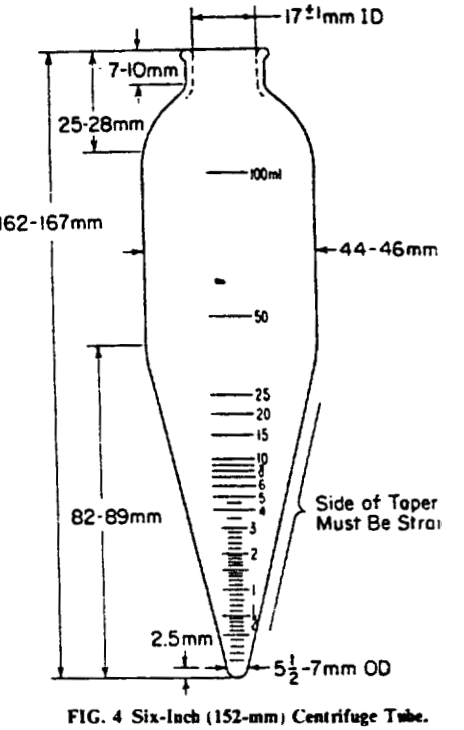
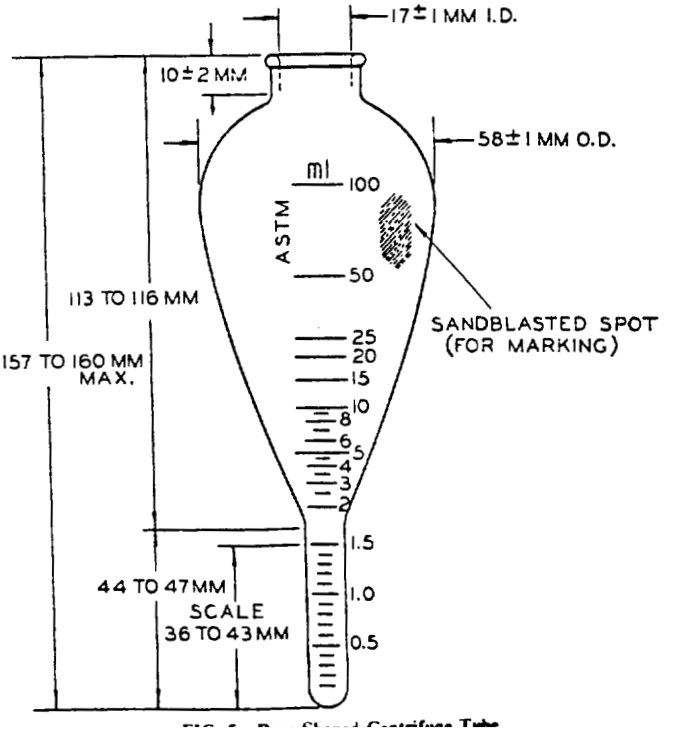


FIG. 4 Six-Inch (152-mm) Centrifuge Tube.



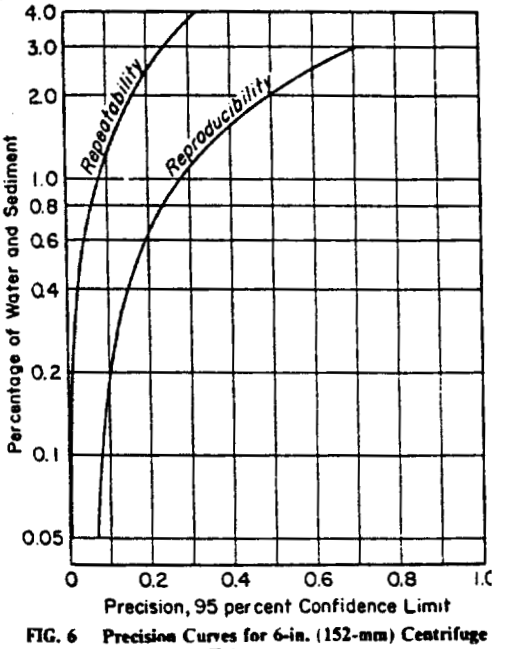


FIG. 6 Precision Curves for 6-in. (152-mm) Centrifuge Tube Method.

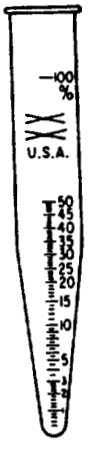


FIG. 7 Centrifuge Tube, 12.50-ml Capacity.