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## Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation<sup>1</sup>

This standard is issued under the fixed designation D 95; 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 ( $\epsilon$ ) 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 organizations in accordance with established procedures.*

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope

1.1 This test method covers the determination of water in the range from 0 to 25 % volume in petroleum products, tars, and other bituminous materials by the distillation method.

NOTE 1—Volatile water-soluble material, if present, may be measured as water.

1.2 The specific products considered during the development of this test method are listed in Table 1. For bituminous emulsions refer to Test Method D 244. For crude oils, refer to Test Method D 4006.

NOTE 2—With some types of oil, satisfactory results may be obtained from Test Method D 1796.

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

1.4 *This standard may involve hazardous materials, operations, and equipment. 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 hazard statements, see Section 5 .

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 244 Test Methods for Emulsified Asphalts<sup>2</sup>

D 1796 Test Method for Water and Sediment in Fuel Oils by

**TABLE 1 Type of Solvent-Carrier Liquid Versus Material to Be Tested**

Type of Solvent-Carrier Liquid	Material to be Tested
Aromatic	asphalt, tar, coal tar, water gas tar, road tar, cut-back bitumin, liquid asphalt, tar acid
Petroleum distillate	road oil, fuel oil, lubricating oil, petroleum sulfonates
Volatile spirits	lubricating grease

the Centrifuge Method (Laboratory Procedure)<sup>3</sup>  
D 4006 Test Method for Water in Crude Oil by Distillation<sup>4</sup>  
D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>4</sup>  
D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products<sup>4</sup>  
D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products<sup>5</sup>  
E 123 Specification for Apparatus for Determination of Water by Distillation<sup>6</sup>  
2.2 *API Manual of Petroleum Measurements Standards:*<sup>7</sup>  
Chapter 8.1 Manual Sampling of Petroleum and Petroleum Products (ASTM Practice D 4057)  
Chapter 8.2 Automatic Sampling of Petroleum and Petroleum Products (ASTM Practice D 4177)  
Chapter 8.3 Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products  
Chapter 10.2 Determination of Water in Crude Oil by the Distillation Method (ASTM Test Method D 4006)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and API Committee on Petroleum Measurement and is the direct responsibility of Subcommittee D02.02, the Joint ASTM-API Committee on Static Petroleum Measurement.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 04.03.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 05.03.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>7</sup> Available from American Petroleum Institute, 1220 L St., N.W., Washington, DC 20005.

Chapter 10.6 Determination of Water and Sediment in Fuel Oil by the Centrifuge Method (ASTM Test Method D 1796)

### 3. Summary of Test Method

3.1 The material to be tested is heated under reflux with a water-immiscible solvent, which co-distills with the water in the sample. Condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and the solvent returning to the still.

### 4. Significance and Use

4.1 A knowledge of the water content of petroleum products is important in the refining, purchase, sale, and transfer of products.

4.2 The amount of water as determined by this test method (to the nearest 0.05 volume %) may be used to correct the volume involved in the custody transfer of petroleum products and bituminous materials.

4.3 The allowable amount of water may be specified in contracts.

### 5. Solvent-Carrier Liquid

5.1 A solvent-carrier liquid appropriate to the material being tested (see Table 1) shall be used.

5.1.1 *Aromatic Solvent*—The following aromatic solvents are acceptable:

5.1.1.1 *Industrial Grade Xylene.*

NOTE 3—**Warning:** Flammable. Vapor harmful.

5.1.1.2 A blend of 20 volume % industrial grade toluene and 80 volume % industrial grade xylene.

NOTE 4—**Warning:** Flammable. Vapor harmful.

5.1.1.3 *Petroleum or Coal Tar Naphtha*, free of water, yielding not more than 5% distillates at 125°C (257°F) and not less than 20% at 160°C (320°F) and with a relative density (specific gravity) not lower than 0.8545 at 15.56/15.56°C (60/60°F).

NOTE 5—**Warning:** Extremely flammable. Harmful if inhaled. Vapors may cause fire.

5.1.2 *Petroleum Distillate Solvent*—A petroleum distillate solvent, 5% boiling between 90 and 100°C (194 and 212°F) and 90% distilling below 210°C (410°F), shall be used. Percent may be determined by mass or by volume. These solvents are available from most chemical companies under the name of stoddard solvent or ligroine.

NOTE 6—**Warning:** Flammable. Vapor harmful.

5.1.3 *Volatile Spirits Solvent*—The following volatile spirits solvents are acceptable:

5.1.3.1 *Petroleum Spirit*, with a boiling range from 100 to 120°C (212 to 248°F).

NOTE 7—**Warning:** Flammable. Vapor harmful.

5.1.3.2 *Isooctane*, of 95% purity or better.

NOTE 8—**Warning:** Extremely flammable. Harmful if inhaled. Vapors may cause fire.

5.2 *Solvent Blank*—The water content of the solvent shall

be determined by distilling an equivalent amount of the same solvent used for the test sample in the distillation apparatus and testing as outlined in Section 9. The blank shall be determined to the nearest scale division and used to correct the volume of water in the trap in Section 10.

### 6. Apparatus

6.1 *General*—The apparatus comprises a glass or metal still, a heater, a reflux condenser, and a graduated glass trap. The still, trap, and condenser may be connected by any suitable method that produces a leakproof joint. Preferred connections are ground joints for glass and O-rings for metal to glass. Typical assemblies are illustrated in Fig. 1, Fig. 2, and Fig. 3. The stills and traps should be chosen to cover the range of materials and water contents expected. On assembly, care should be taken to prevent the joints from freezing or sticking. This may be prevented by the application of a very thin film of stopcock grease.

6.2 *Still*—A glass or metal vessel with a short neck and suitable joint for accommodating the reflux tube of the trap shall be used. Vessels of 500, 1000, and 2000-mL nominal capacity have proved satisfactory.

6.3 *Heater*—A suitable gas burner or electric heater may be used with the glass still. A gas ring burner with ports on the inside circumference shall be used with the metal still. The gas ring burner shall be of such dimensions that it may be moved up and down the vessel when testing materials that are likely to foam or solidify in the still.

6.4 *Glassware*—Dimensions and descriptions of typical glassware for use in this test method are provided in Specification E 123.

NOTE 9—Instead of standardizing on a particular apparatus specification with respect to dimensions and style, a given apparatus will be deemed satisfactory when accurate results are obtained by the standard addition technique described in Section 8.

### 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

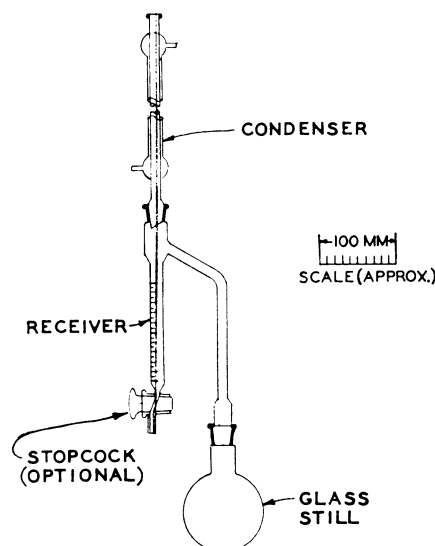
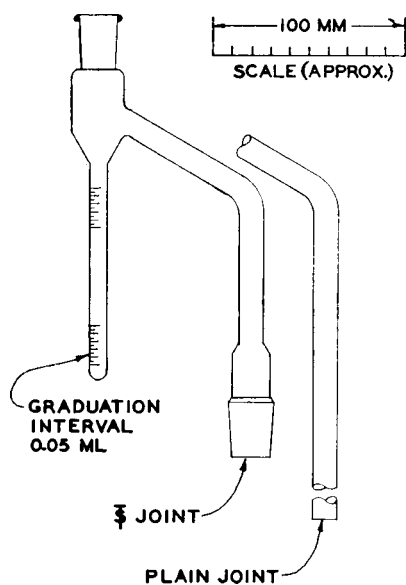


FIG. 1 Typical Assembly with Glass Still



**FIG. 2 Two-millilitre Receiver Showing Alternative Connections to Glass Still**

place the sample into the laboratory test container. Only representative samples obtained as specified in Practices D 4057 (API Chapter 8.1) and D 4177 (API Chapter 8.2) shall be used for this test method.

7.2 The size of the test portion should be based on the expected water content of the sample, such that the water yield does not exceed the capacity of the trap (unless a trap with a stopcock is used permitting excess water to be withdrawn into a graduated cylinder).

7.3 Practice D 5854 (API Chapter 8.3) contains information on sampling and homogenization efficiency of unknown mixers. This test method should not be followed without strict adherence to Practice D 5854.

## 8. Standardization

8.1 The accuracy of the graduation marks on the trap shall be certified or verified, using only national or international standards, such as National Institute of Standards and Technology (NIST)<sup>8</sup> traceable equipment. Verification shall be with a traceable 5 mL Micro Burette or Micro Pipette, readable to the nearest 0.01 mL.

8.1.1 In styles A, B, C, and D, as specified in Table 2 (Table 1 in Specification E 123), each subdivision (that is, 0.1 mL through 1.0 mL) in the conical portion of the tube shall be verified. Thereafter, each major subdivision (that is, 2.0 mL, 3.0 mL, 4.0 mL, and up to the total volume of the trap) shall be verified.

8.1.2 In styles E and F, as specified in Table 2, each major subdivision (0.1 mL, 1.0 mL, 2.0 mL, 4.0 mL, and 5.0 mL in the case of Style E; 0.05 mL, 0.5 mL, 1.0 mL, 1.5 mL, and 2.0 mL in the case of Style F) shall be verified.

8.2 The entire glassware assembly shall be calibrated prior to use as follows.

8.2.1 Put 400 mL of dry (0.02 % water maximum) xylene or the solvent to be utilized in the analysis of unknown samples into the apparatus and test in accordance with Section 9. When complete, discard the contents of the trap and add the volume of water as specified as first test in Table 3 directly to the distillation flask and test in accordance with Section 9.

8.2.2 Repeat the test in 8.2.1, and add the volume specified as second test in Table 3 directly to the flask. The assembly of the apparatus is satisfactory only if the trap readings are within the tolerances specified in Table 3.

8.3 A reading outside the permissible limits suggests a malfunction resulting from vapor leaks, too rapid boiling, inaccuracies in calibration of the trap, or ingress of extraneous moisture. Eliminate these factors before repeating the standardization.

## 9. Procedure

NOTE 10—**Caution:** The precision of this test method will be affected by water droplets adhering to surfaces in the apparatus and therefore not settling into the water trap to be measured. To minimize the problem, all apparatus must be cleaned chemically at least daily to remove surface films and debris, which hinder free drainage of water in the test apparatus. More frequent cleaning is recommended if the nature of samples being run causes persistent contamination.

9.1 Measure a suitable amount of sample to an accuracy of  $\pm 1\%$  and transfer it to the still.

9.2 Measure ordinary liquid samples in a graduated cylinder of an appropriate size. Rinse the material adhering to the cylinder with one 50-mL and two 25-mL portions of the solvent-carrier liquid (see Section 5 and Table 1). Drain the cylinder thoroughly after the sample transfer and each rinsing.

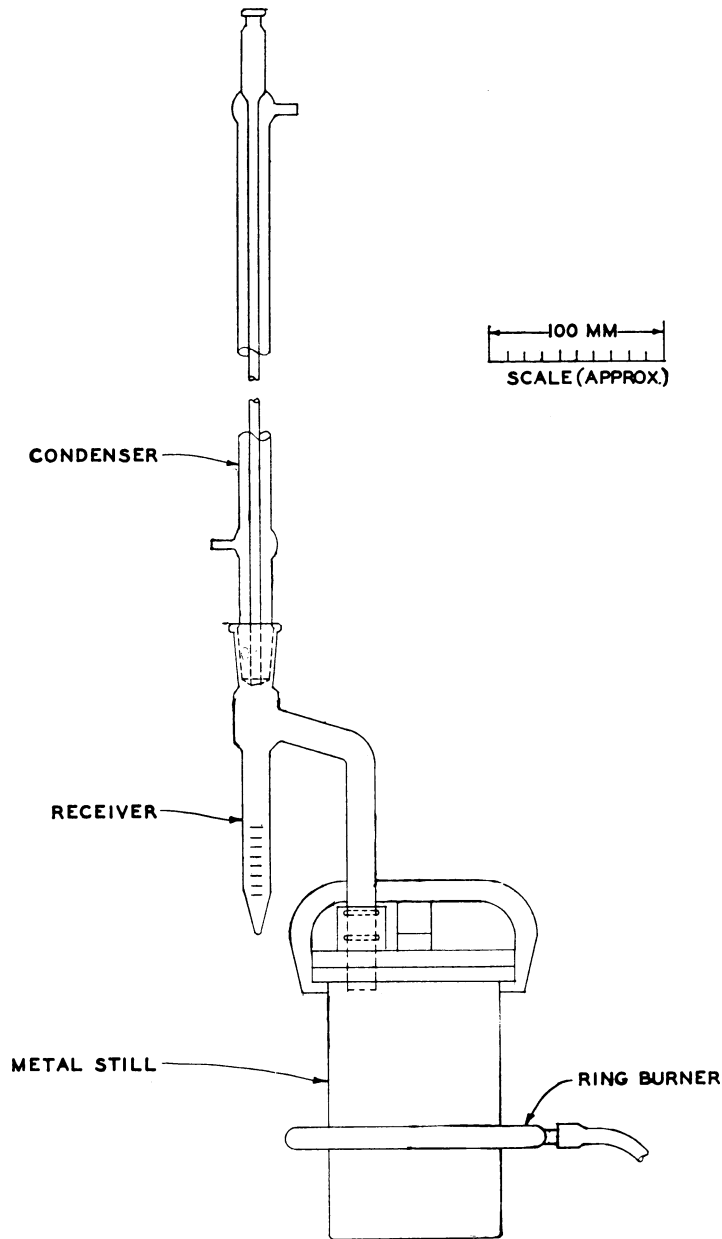
9.3 Weigh solid or viscous materials directly into the still and add 100 mL of the selected solvent-carrier liquid. In cases of material with a low-water content when large samples must be used, a solvent-carrier liquid volume in excess of 100 mL may be necessary.

9.4 Glass beads or other boiling aids may be added, if necessary, to reduce bumping.

9.5 Assemble the components of the apparatus, as illustrated in Fig. 1, Fig. 2, and Fig. 3, choosing the trap in accordance with the expected water content of the sample and making all connections vapor and liquid tight. If a metal still with a removable cover is used, insert a gasket of heavy paper, moistened with solvent, between the still body and the cover. The condenser tube and trap must be chemically clean to ensure free drainage of water into the bottom of the trap. Insert a loose cotton plug in the top of the condenser to prevent condensation of atmospheric moisture inside it. Circulate cold water through the jacket of the condenser.

9.6 Apply heat to the still, adjusting the rate of boiling so that condensed distillate discharges from the condenser at the rate of two to five drops per second. If the metal still is used, start heating with the ring burner about 76 mm (3 in.) above the bottom of the still and gradually lower the burner as the distillation proceeds. Continue distillation until no water is visible in any part of the apparatus except in the trap and the volume of water in the trap remains constant for 5 min. If there is a persistent ring of water in the condenser tube, carefully

<sup>8</sup> National Institute of Standards and Technology, U.S. Department of Commerce, Gaithersburg, MD 20899.



NOTE 1—Trap shall be 15 to 16 mm in inside diameter

**FIG. 3 Typical Assemblies with Metal Still**

**TABLE 2 Specifications and Sizes of Traps**

Description							
Style	Top of Graduated Tube	Bottom of Graduated Tube	Bottom of Vapor Tube	Size of Trap mL	Range mL	Smallest Scale Division, mL	Scale Error Maximum, mL
A	ST Joint	Conical	ST Joint	10	0 to 1.0 >1.0 to 10.0	0.1 0.2	0.05 0.1
B	ST Joint	Conical	ST Joint	25	0 to 1.0	0.1	0.05
C	ST Joint	Conical	Plain	25	>1.0 to 25	0.2	0.1
D	ST Joint	Conical	Plain	25	1.0 to 25	0.2	0.1
E	ST Joint	Round	ST Joint	5	0 to 5.0	0.1	0.05
				10	0 to 10.0	0.1	0.1
F	ST Joint	Round	ST Joint	2	0 to 2.0	0.05	0.025

**TABLE 3 Permissible Limits in Milliliters**

Capacity of Receiver at 20°C		Volume of Water Added to Flask at 20°C	Permissible Limits for Recovered Water at 20°C
Round trap			
2	1 <sup>st</sup> Test	1	1 ± 0.05
2	2 <sup>nd</sup> Test	1.9	1.9 ± 0.05
5	1 <sup>st</sup> Test	1	1 ± 0.05
5	2 <sup>nd</sup> Test	4.5	4.5 ± 0.05
10	1 <sup>st</sup> Test	5	5 ± 0.1
10	2 <sup>nd</sup> Test	9	9 ± 0.1
Conical trap			
10	1 <sup>st</sup> Test	1	1 ± 0.1
10	2 <sup>nd</sup> Test	9	9 ± 0.2
25	1 <sup>st</sup> Test	12	12 ± 0.2
25	2 <sup>nd</sup> Test	24	24 ± 0.2

increase the rate of distillation or cut off the condenser water for a few minutes.

9.7 When the evolution of water is complete, allow the trap and contents to cool to room temperature. Dislodge any drops of water adhering to the sides of the trap with a glass or polytetrafluoroethylene (PTFE) rod or other suitable means and transfer them to the water layer. Read the volume of the water in the trap to the nearest scale division.

9.8 A solvent blank shall be established, as outlined in 5.2.

## 10. Calculation

10.1 Calculate the water in the sample, as weight or volume percent, in accordance with the basis on which the sample was taken, as follows:

10.1.1 Water, % (V/V) =

$$\frac{(\text{Volume in water trap, mL}) - (\text{Water in solvent blank, mL})}{\text{Volume in test sample, mL}} \times 100 \quad (1)$$

10.1.2 Water, % (V/m) =

$$\frac{(\text{Volume of water in trap, mL}) - (\text{Water in solvent blank, mL})}{\text{Mass of test sample, g}} \times 100 \quad (2)$$

## 11. Report

11.1 Report the results as the water content to the nearest 0.05% if the 2-mL receiver has been used and to the nearest

0.1% if the 10-mL or 25-mL receiver has been used with a 100-mL or 100-g sample.

## 12. Precision and Bias

12.1 *Precision*—The criteria described in 12.1.1 and 12.1.2 should be used to judge the acceptability of results (95% probability) when using the 10 or 25-mL traps. The precision when using the 2-mL trap has not been established.

NOTE 11—Practice D 6300 was not used in obtaining precision data.

12.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 4 in only one case in twenty.

12.1.2 *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 values in Table 4 in only one case in twenty.

12.2 *Bias*—As there is no accepted reference material suitable for determining bias for the procedure described in this test method for measuring water in petroleum products and bituminous materials by distillation, no statement about bias is made.

## 13. Keywords

13.1 bituminous materials; distillation; petroleum products; solvent carrier liquid; water by distillation; water content

**TABLE 4 Precision**

Type	Water Collected, mL	Difference, mL
Repeatability	0.0–1.0	0.1
	1.1–25	0.1 or 2 % of the mean, whichever is greater
Reproducibility	0.0–1.0	0.2
	1.1–25	0.2 or 10 % of the mean, whichever is greater

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