Designation: D95 – 13 (Reapproved 2018)

Manual of Petroleum Measurement Standards (MPMS), Chapter 10.5

Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation[1]

This standard is issued under the fixed designation D95; 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 standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 This test method covers the determination of water in the range from 0 % to 25 % by 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 D244. For crude oils, refer to Test Method D4006 (API *MPMS* Chapter 10.2).

NOTE 2—With some types of oil, satisfactory results may be obtained from Test Method D1796 (API *MPMS* Chapter 10.6).

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.4 *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.* For specific hazard statements, see Section 6.

1.5 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D235 Specification for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Dry Cleaning Solvent)

D244 Test Methods and Practices for Emulsified Asphalts

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)

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

E123 Specification for Apparatus for Determination of Water by Distillation

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)

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

MPMS Chapter 10.6 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure) (ASTM Test Method D1796)

[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 practice has been approved by the sponsoring committees and accepted by the Cooperating Societies in accordance with established procedures.

Current edition approved Oct. 1, 2018. Published November 2018. Originally approved in 1921. Last previous edition approved in 2013 as D95 – 13$^{\varepsilon 1}$. DOI: 10.1520/D0095-13R18.

[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] Published as Manual of Petroleum Measurement Standards. Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, http://www.api.org..

3. Terminology

3.1 *Definitions:*

3.1.1 *bituminous material, n—in petroleum technology*, a black or dark-colored very viscous liquid or semi-solid composed principally of high molecular weight condensed aromatic, or naphthenic compounds, or both.

4. Summary of Test Method

4.1 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.

5. Significance and Use

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

5.2 The amount of water as determined by this test method (to the nearest 0.05 % or 0.1 % by volume, depending on the trap size used) may be used to correct the volume involved in the custody transfer of petroleum products and bituminous materials.

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

6. Solvent-Carrier Liquid

6.1 A water-immiscible solvent-carrier liquid that is miscible in the material being tested (see Table 1) shall be used.

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

6.1.1.1 *Industrial Grade Xylene*—(**Warning—**Flammable. Vapor harmful.)

6.1.1.2 A blend of 20 % by volume industrial grade toluene and 80 % by volume industrial grade xylene. (**Warning—** Flammable. Vapor harmful.)

6.1.1.3 *Petroleum Naphtha 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 °C/15.56 °C (60 °F/60 °F). (**Warning—**Extremely flammable. Harmful if inhaled. Vapors may cause fire.)

6.1.2 *Petroleum Distillate Solvent*—A petroleum distillate solvent containing at least 2 % (V/V) aromatics and with an initial boiling point (IBP) greater than 80 °C (176 °F); and a final boiling point (FBP) below 250 °C (482 °F) shall be used.

NOTE 3—Examples of suitable solvents include Types I and IV and Classes A and B of Specification D235.

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

Type of Solvent-Carrier Liquid	Material to be Tested
Aromatic	asphalt, bitumen, tar, and related products
Petroleum distillate	fuel oil, lubricating oil, lubricating oil additives
Volatile spirits	greases

NOTE 4—It is recommended to use a wide boiling range solvent with 10 % boiling below 100 °C to help to ensure an even distillation rate.

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

6.1.3.1 *Petroleum Spirit,* with a boiling range from 100 °C to 120 °C (212 °F to 248 °F). (**Warning—**Flammable. Vapor harmful.)

6.1.3.2 *Iso-octane,* of 95 % purity or better. (**Warning—** Extremely flammable. Harmful if inhaled. Vapors may cause fire.)

6.2 *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 10. The blank shall be determined to the nearest scale division and used to correct the volume of water in the trap in Section 11.

7. Apparatus

7.1 *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 shall be taken to prevent the joints from freezing or sticking. Always apply a very thin film of stopcock grease to prevent the glassware joints from seizing.

7.2 *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 mL, 1000 mL, and 2000 mL nominal capacity have proved satisfactory.

7.3 *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

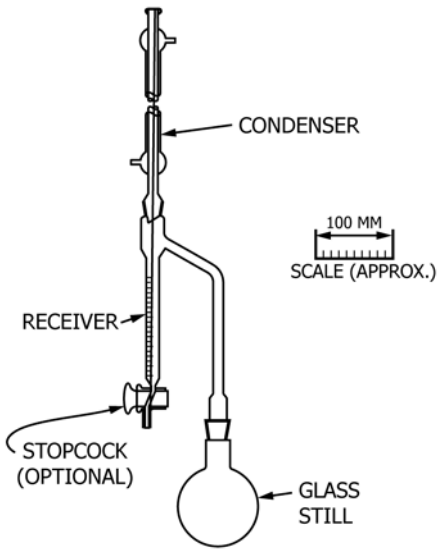


FIG. 1 Typical Assembly with Glass Still

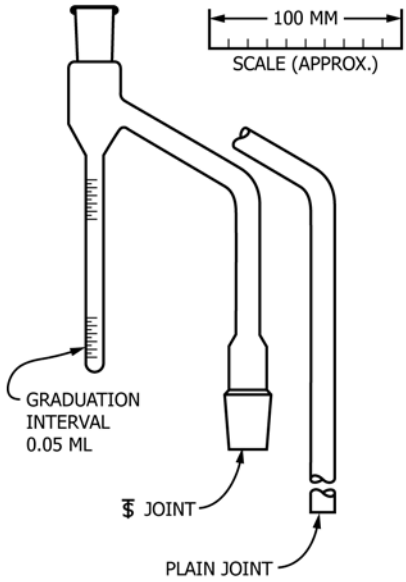


FIG. 2 Two-millilitre Receiver Showing Alternative Connections to Glass Still

up and down the vessel when testing materials that are likely to foam or solidify in the still.

7.4 *Glassware*—Dimensions and descriptions of typical glassware for use in this test method are provided in Specification E123.

NOTE 5—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 9.

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

8.2 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).

8.3 Practice D5854 (API *MPMS* 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 D5854 (API *MPMS* Chapter 8.3).

9. Verification

9.1 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)[4] traceable equipment. Verification shall be with a traceable 5 mL Micro Burette or Micro Pipette, readable to the nearest 0.01 mL.

9.1.1 In styles A, B, C, and D, as specified in Table 2 (Table 1 in Specification E123), 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.

9.1.2 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.

9.2 The entire glassware assembly shall be verified prior to first use and at a regular frequency thereafter as follows.

9.2.1 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 10. 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 10.

9.2.2 Repeat the test in 9.2.1, 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.

9.3 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 verification.

10. Procedure

NOTE 6—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.

10.1 Measure a suitable amount of sample to an accuracy of ±1 % and transfer it to the still.

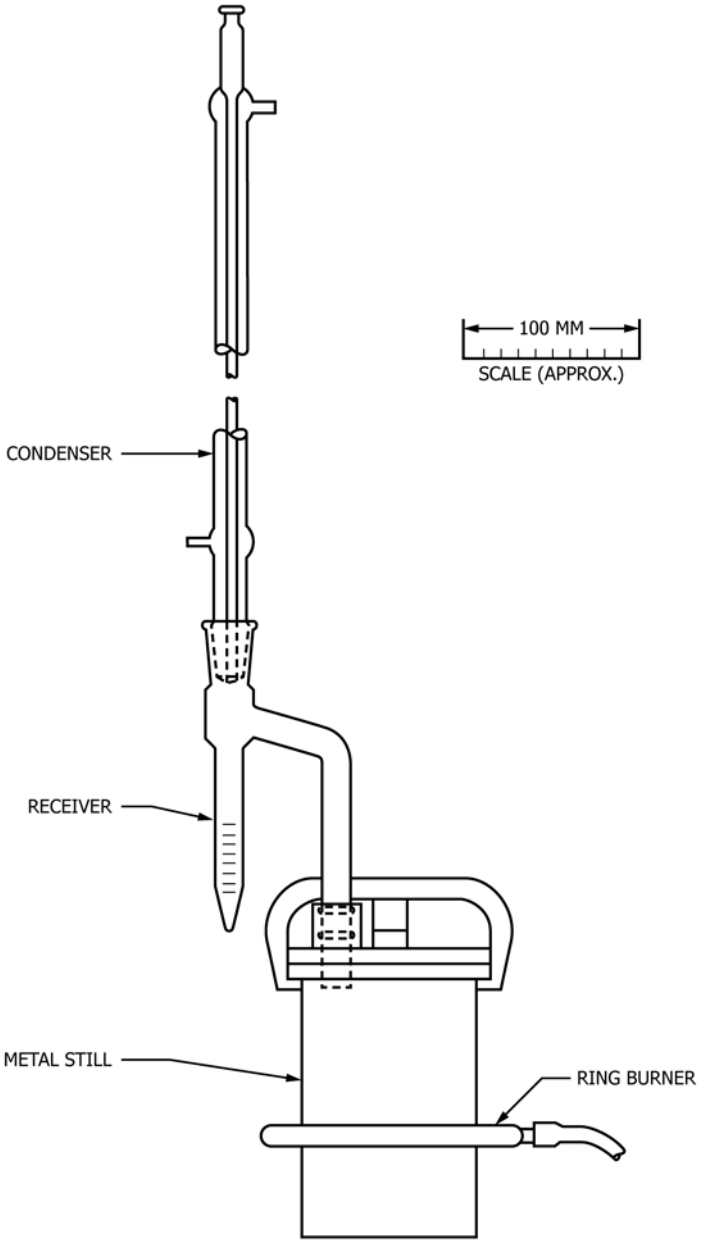
10.2 Measure ordinary liquid samples in a graduated cylinder of an appropriate size. Rinse the material adhering to the cylinder with one 50 mL and two 25 mL portions of the solvent-carrier liquid (see Section 6 and Table 1). Drain the cylinder thoroughly after the sample transfer and each rinsing.

10.3 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.

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

10.5 Assemble the components of the apparatus, as illustrated in Fig. 1, Fig. 2, and Fig. 3, choosing the trap in

[4] National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, http://www.nist.gov.



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	0.1	0.05
					>1.0 to 10.0	0.2	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
				5	0 to 5.0	0.05	0.025
				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 Millilitres

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	1st Test	1	1 ± 0.05
2	2nd Test	1.9	1.9 ± 0.05
5 (0.05 mL subdivisions)	1st Test	1	1 ± 0.05
5 (0.05 mL subdivisions)	2nd Test	4.5	4.5 ± 0.05
5 (0.1 mL subdivisions)	1st Test	1	1 ± 0.1
5 (0.1 mL subdivisions)	2nd Test	4.5	4.5 ± 0.1
10	1st Test	5	5 ± 0.1
10	2nd Test	9	9 ± 0.1
Conical trap			
10	1st Test	1	1 ± 0.1
10	2nd Test	9	9 ± 0.2
25	1st Test	12	12 ± 0.2
25	2nd Test	24	24 ± 0.2

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.

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

10.7 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.

10.8 A solvent blank shall be established, as outlined in 6.2.

11. Calculation

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

11.1.1 Water, % (V/V) =

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

11.1.2 Water, % (V/m) =

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

12. Report

12.1 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 and to the nearest subdivision if a 5 mL receiver has been used with a 100 mL or 100 g sample.

13. Precision and Bias

13.1 *Precision*—The criteria described in 13.1.1 and 13.1.2 should be used to judge the acceptability of results when using the 10 mL or 25 mL traps. The precision when using the 2 mL trap or a 5 mL trap has not been established.

NOTE 7—Practice D6300 was not used in obtaining precision data.

13.1.1 *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.

TABLE 4 Precision

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

13.1.2 *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.

13.2 *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.

14. Keywords

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