



Designation: D 483 – 04

Standard Test Method for Un sulfonated Residue of Petroleum Plant Spray Oils¹

This standard is issued under the fixed designation D 483; 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 covers the determination of unsulfonated residue in plant spray oils of petroleum origin and applies only to the petroleum oil content. It provides a measure of the degree of refinement of plant spray oils by determining the extent to which the oil is attacked by 98.61 % sulfuric acid under closely standardized conditions. Since the relationship between unsulfonated residue and the actual composition of the oil is not known, this test method should be applied only for measuring the degree of refinement and not for the determination of aromatics or olefins, or both.

1.2 The values stated in SI units are to be regarded as the standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D 1193 Specification for Reagent Water

D 1250 Guide for Petroleum Measurement Tables

D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

3. Terminology

3.1 *Definition:*

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.06 on Analysis of Lubricants.

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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.

3.1.1 *unsulfonated residue, n—in oils*, that portion of an oil remaining unsulfonated after treatment with concentrated sulfuric acid.

4. Summary of Test Method

4.1 A measured volume of sample is shaken with 98.61 % sulfuric acid at 100°C in a Babcock bottle, shaking mechanically for 10 s at 10-min intervals. The volume not absorbed by the acid is a measure of the unsulfonated residue in the sample.

5. Significance and Use

5.1 This test method is useful for distinguishing between oils that are adaptable to various types of spraying application, with a higher unsulfonated oil being required for leaf spraying as compared to dormant vegetation application.

6. Apparatus

6.1 *Sulfonation Flask*—The flask is shown in Fig. A1.1 and described in Annex A1.

6.2 *Meniscus Viewing Lens*, focusing type, consisting of eyepiece and objective to facilitate reading the meniscus with a minimum of parallax, is recommended.

6.3 *Water Baths*—Two water baths maintained at $25 \pm 0.5^\circ\text{C}$ and 99.5 to 100°C, and conforming to the requirements prescribed in Annex A1.

6.4 *Shaking Machine*—The exact design described in the appendix is required for uniform control of shaking and precision results. Hand shaking is permissible if technique is developed to correlate results by machine shaking.

6.5 *Centrifuge*—A centrifuge as described in Annex A1 is recommended.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be

³ "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 *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.

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

used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1.1 Commercially prepared solutions may be used when they meet or exceed the specifications set in 7.1.

7.2 *Fuming Sulfuric Acid* (approximately 15 % free SO₃). (**Warning**—See 7.3 and 7.4.)

7.3 *Sulfuric Acid (98.61 %)*—Prepare by blending reagent-grade fuming and concentrated sulfuric acids to a concentration of 98.61 ± 0.1 % H₂SO₄ as determined by titration. (**Warning**—Corrosive. Health hazard. Oxidizer.) (**Warning**—While preparing the reagent, protect the face with a safety mask and place the flask in a tray.)

7.4 *Sulfuric Acid (sp gr 1.84, approximately 95 %)*—Concentrated sulfuric acid (H₂SO₄). (**Warning**—Corrosive. Health hazard. Oxidizer.)

8. Reference Spray Oil⁴

8.1 Test results for unsulfonated residue are highly dependent upon rate of shaking. A reference spray oil has been calibrated for unsulfonated residue by a group of cooperating laboratories using both machine and hand shaking. Instructions are given in Section 8 for using this reference oil as a guide to ensure that the rate of shaking is correct.

9. Calibration

9.1 *Machine Shaking Rate*—A rate of 425 cycles/min was used in the cooperative work to establish the unsulfonated residue of the reference spray oil. There are small variations in severity of shaking between individual machines, even when they are newly built and of the same make; and these differences can increase with use. Consequently, each laboratory shall run occasional tests on the reference spray oil. If an unsulfonated residue is found which differs by more than ±0.4 % from the established value, the rate of shaking shall be adjusted accordingly. A faster rate tends to give a lower unsulfonated residue, and vice versa.

9.2 *Hand Shaking Rate*—Each operator shall standardize his technique of shaking so as to obtain the established value (within ± 0.4 %) on the reference spray oil. A rate of 300 cycles/min was used in the manual shaking tests in the cooperative program on the reference oil; however, an individual operator's calibrated rate can differ appreciably from 300 cycles/min.

10. Sampling

10.1 Obtain a sample for this test method using Practices D 4057 or D 4177.

11. Procedure

11.1 Adjust the temperature of the boiling water bath to 99.5 to 100°C and keep it in this temperature range throughout the test. Adjust the shaker rate and check it before and after each

test to make sure that the rate does not deviate more than ±10 cycles/min from the rate established by calibration. (**Warning**—When hand shaking, protect the face with a safety mask and point the Babcock bottle away from other personnel. Protect hands by wearing suitable safety gloves.)

NOTE 1—If hand shaking is used, shake the sulfonation flask by grasping the neck between the thumb and index finger and swinging the flask through an arc of approximately 20° so that the bottom of the flask passes through a distance of 64 to 89 mm (2.5 to 3.5 in.). Shake at the rate established by calibration within a tolerance of ±10 cycles/min.

11.2 Using Test Methods D 1298 or D 4052, determine the density at 25°C in grams per millilitre by means of data obtained from Vol VIII and Vol XI/XII of the Petroleum Measurement Tables. (See Guide D 1250.)

11.3 Weigh into a clean, dry sulfonation flask the equivalent of 4.9 to 5.1 mL of the sample at 25°C, weighed to the nearest 0.005 g, adding the oil to the flask by pipet, and taking care to deposit as little oil as possible on the neck of the flask. From the weight of the sample, calculate its volume at 25°C.

11.4 Slowly introduce 20 ± 0.5 mL of H₂SO₄ (98.61 %) into the flask in such a way that oil adhering to the neck of the flask will be washed down. Transfer the flask to the carrier, and suspend the carrier in the boiling water bath, with the flask immersed to a point between the 0 and 10 marks, noting the time when this is done. Close the cover of the bath, and direct a gentle stream of air across the top of the flask to blow away any steam arising from the opening.

11.5 After the flask has been in the bath for 10 ± 1 min, remove the carrier and install it, with minimum delay, on the shaker. While wearing a face shield, shake for 10 ± 1 s at the rate established in the calibration with the reference spray oil. (**Warning**—Certain samples of low unsulfonated residue can foam excessively when shaken. Stop the shaker when the foam rises in the neck of the flask, and shake intermittently but at the specified rate. Substitute the counter for the timer and shake a total number of cycles equal to one-sixth of the number representing the established rate in cycles per minute, even though it requires more than 10 s for example, if the rate is 425 cycles/min, shake 71 cycles.) After shaking, return the carrier to the bath as quickly as possible. Repeat the shaking at 10 ± 1 min intervals for a total of six shaking periods, so that an hour has elapsed between the time of placing the flask in the bath, and the removal for the final shaking.

11.6 After the final shaking, cool to approximately room temperature, and add sufficient H₂SO₄ (95 %) to raise the oil into the neck of the flask nearly to the top graduation. Place the flask in the centrifuge, balancing as necessary, and centrifuge for 10 min at a speed calculated by the equation given in A1.1.6, or taken from Table 1 to give a relative centrifugal force between 80 and 100 at the bottom of the flask. Transfer the flask to a water bath maintained at 25 ± 0.5°C for 10 ± 1 min, with the graduated neck immersed to the upper oil level.

NOTE 2—The use of rubber cushions in the centrifuge carrier tubes to avoid breakage is recommended.

11.7 Transfer the flask to the shelf in the 25°C bath. Using a suitable light source, and the aid of a viewing lens, record the reading on the graduated neck at the top and bottom of the oil column, estimating to one fifth of the smallest division. The

⁴ The reference spray oil may be obtained from R. E. Carroll, Inc., P.O. Box 5806, 1570 North Olden Ave., Trenton, NJ 08638. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee¹, which you may attend.

TABLE 1 Rotation Speeds for Centrifuges of Various Diameters of Swing

Diameter of Swing, mm (in.) ^A	Rpm at 80 rcf	Rpm at 100 rcf
508 (20)	530	590
533 (21)	520	580
559 (22)	510	570
584 (23)	500	550
609 (24)	490	540

^A Measured in millimetres (inches) between bottoms of opposite flasks when in rotating position.

bottom reading is generally sharp and straight across, and offers no problem. In reading the top, hold a black strip (about 10 by 50 mm) at the back of the neck, and about 5 mm below the top of the oil column, which makes the lowest meniscus appear as a black curve. Install the viewing lens at a right angle to the neck of the flask at the proper height, focus it, and read the lowest black meniscus. The upper and lower levels on the oil layer are represented by points *A* and *B* in Fig. 1. Point *A* denotes the lowest portion of the boundary between the clear oil and the darkest part of the air-liquid interface, and point *B* refers to the lowest portion of the interface between the clear oil and sulfonation acid.

11.8 Repeat the centrifuging and temperature equilibration (11.6 and 11.7), until constant readings have been obtained.

12. Calculation and Report

12.1 Correct the readings at the upper and lower oil surfaces in accordance with the calibration error.

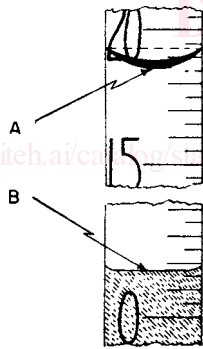


FIG. 1 Method for Reading Volume of Unreacted Oil

12.2 Calculate the unsulfonated residue as follows:

$$\text{Unsulfonated residue, volume \%} = [(A - B)/V] \times 100 \quad (1)$$

where:

A = corrected scale reading, at upper oil level, mL,
B = corrected scale reading at lower oil level, mL, and
V = volume of sample used, mL.

12.3 Report all results to the nearest 0.2 %.

13. Precision and Bias

13.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

13.1.1 *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 values only in one case in twenty:

Range of Unsulfonated Residue, % 79 to 97	Repeatability (Machine Shaking) 0.5
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13.1.2 *Reproducibility*—The difference between two single and independent 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 values only in one case in twenty:

Range of Unsulfonated Residue, % 79 to 97	Reproducibility (Machine Shaking) 2.0
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13.2 The precision of this test method is not known to have been obtained in accordance with currently accepted guidelines.⁵

13.3 *Bias*—There being no criteria for measuring bias in these test product combinations, no statement of bias can be made.

14. Keywords

14.1 petroleum plant spray oils; unsulfonated residue

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1007.