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.

Designation: D483 – 04 (Reapproved 2018)

Standard Test Method for Unsulfonated Residue of Petroleum Plant Spray Oils[1]

This standard is issued under the fixed designation D483; 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 standard. No other units of measurement are included in this 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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]

D1193 Specification for Reagent Water

D1250 Guide for Use of the Petroleum Measurement Tables

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

3. Terminology

3.1 *Definitions:*

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 °C ± 0.5 °C and 99.5 °C 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.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricantsand is the direct responsibility of Subcommittee D02.06 on Analysis of Liquid Fuels and 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.

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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 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 SO_3). (**Warning—**See 7.3 and7.4.)

7.3 *Sulfuric Acid (98.61 %)*—Prepare by blending reagent-grade fuming and concentrated sulfuric acids to a concentration of 98.61 % ± 0.1 % H_2SO_4 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 (H_2SO_4). (**Warning—**Corrosive. Health hazard. Oxidizer.).

8. Reference Spray Oil[4]

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 D4057 or D4177.

11. Procedure

11.1 Adjust the temperature of the boiling water bath to 99.5 °C 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 mm to 89 mm. Shake at the rate established by calibration within a tolerance of ±10 cycles/min.

11.2 Using Test Methods D1298 or D4052, 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 D1250.)

11.3 Weigh into a clean, dry sulfonation flask the equivalent of 4.9 mL 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 mL ± 0.5 mL of H_2SO_4 (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 min ± 1 min, remove the carrier and install it, with minimum delay, on the shaker. While wearing a face shield, shake for 10 s ± 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 min ± 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.

[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 *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.

[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 committee,[1] which you may attend.

11.6 After the final shaking, cool to approximately room temperature, and add sufficient H_2SO_4 (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 °C ± 0.5 °C for 10 min ± 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 bottom reading is generally sharp and straight across, and offers no problem. In reading the top, hold a black strip (about 10 mm 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.

12.2 Calculate the unsulfonated residue as follows:

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

TABLE 1 Rotation Speeds for Centrifuges of Various Diameters of Swing

Diameter of Swing, mm[A]	R/min at 80 rcf	R/min at 100 rcf
508	530	590
533	520	580
559	510	570
584	500	550
609	490	540

[A] Measured in millimetres between bottoms of opposite flasks when in rotating position.

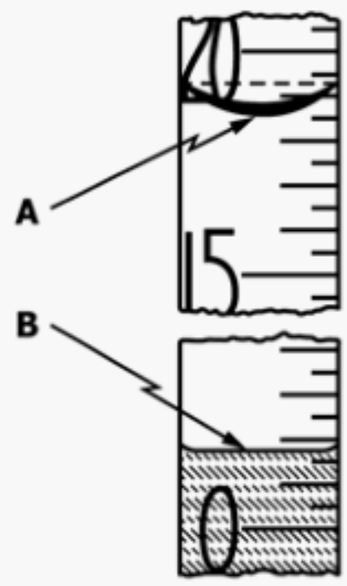

FIG. 1 Method for Reading Volume of Unreacted Oil

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, %	Repeatability (Machine Shaking)
79 to 97	0.5

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, %	Reproducibility (Machine Shaking)
79 to 97	2.0

13.2 The precision of this test method is not known to have been obtained in accordance with currently accepted guidelines.

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

ANNEX

(Mandatory Information)

A1. APPARATUS

A1.1 Apparatus

A1.1.1 *Sulfonation Flask,* as shown in Fig. A1.1. This is a standard Babcock test bottle known as "50 %, 9 g, 9 in., in 0.5 %, cream test bottle."

A1.1.2 To calibrate the graduated neck of the flask: first, fill exactly to the zero mark with water (see A1.1.2.2); then determine the true capacity to the 50 mark by adding water from a standardized 10 mL buret. Calculate a volume calibration factor.

A1.1.2.1 The buret shall be subdivided to 0.01 mL or 0.02 mL and be provided with a tip delivering drops of approximately 0.01 mL. Corrections to the nominal values of the buret should be obtained in the laboratory and used in the calculation.

A1.1.2.2 Water shall be reagent water conforming to Specification D1193, Type III.

A1.1.3 *Water Bath,* maintained at 25 °C ± 0.5 °C of sufficient depth to permit immersion of the sulfonation flask to the top graduation, and provided with a shelf at such a height that the flask, when placed on it, would be immersed to a point just below the bottom graduation.

A1.1.4 *Boiling-Water Bath,* maintained at 99.5 °C to 100 °C, and of sufficient depth to permit immersion of the sulfonation flask to a point between the 0 and 10 marks. The top of the bath shall be covered as completely as is consistent with the entry and withdrawal of the shaker bottle holder. This bath can be conveniently heated by an open steam coil.

A1.1.4.1 At altitudes above sea level, the required bath temperature must be attained by adding ethylene glycol to the water, and heating by means of a closed steam coil, gas, or electric immersion heater. The specified temperature shall be maintained by addition of make-up water. Use of an oil bath is not permissible.

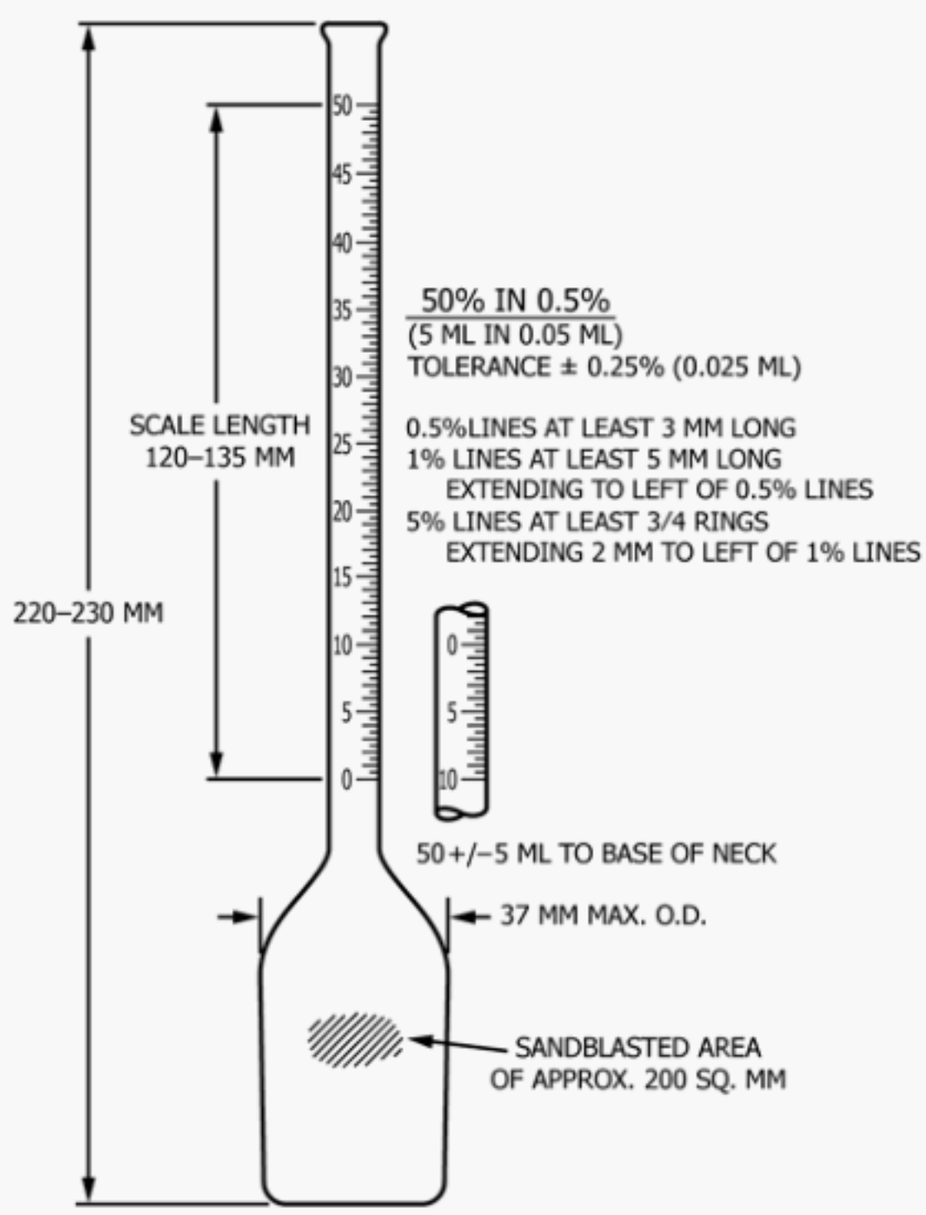

FIG. A1.1 Sulfonation Flask, Standard Babcock Bottle

A1.1.5 *Shaking Machine,* as shown in Fig. A1.2[5] comprising a carrier to which the sulfonation flask is attached in a nearly-vertical position, and a top-hinged frame for holding the carrier, attached to a motor-driven arm. The radius of arc, from the point of suspension of the frame to the bottom of the sulfonation flask shall be approximately 152 mm; travel of the bottom of the flask shall be approximately 28.6 mm. The machine shall be capable of quickly reaching, and maintaining for at least 10 s, any required rate of shaking in the range of 300 to 500 cycles/min, within a tolerance of ±10 cycles/min. Construct the flask carrier so that it can be detached quickly from the frame for transfer to the specified bath. The flask carrier may be constructed to hold from two to eight sulfonation flasks.

A1.1.6 *Centrifuge*— Capable of whirling two or more filled sulfonation flasks at a speed that can be controlled to give a relative centrifugal force (rcf) of between 80 and 100 at the bottom of the flasks. (See Note A1.1.) 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 breakage occurs. Calculate the speed of the rotating head as follows:

$$\text{Speed, rpm} = 265\sqrt{\text{rcf}/d} \qquad \text{(A1.1)}$$

where:

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

NOTE A1.1—The centrifuge usually specified for the rcf range of 500 to 700 is adaptable for this lower speed. Since separation is accomplished at the lower speed, it is considered inadvisable to increase speed and corresponding breakage hazard.

[5] A combination shaker and boiling-water bath is available from Koehler Instrument Co., Inc., 1595 Sycamore Ave., Bohemia, L.I., NY 11716. 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 committee,[1] which you may attend.

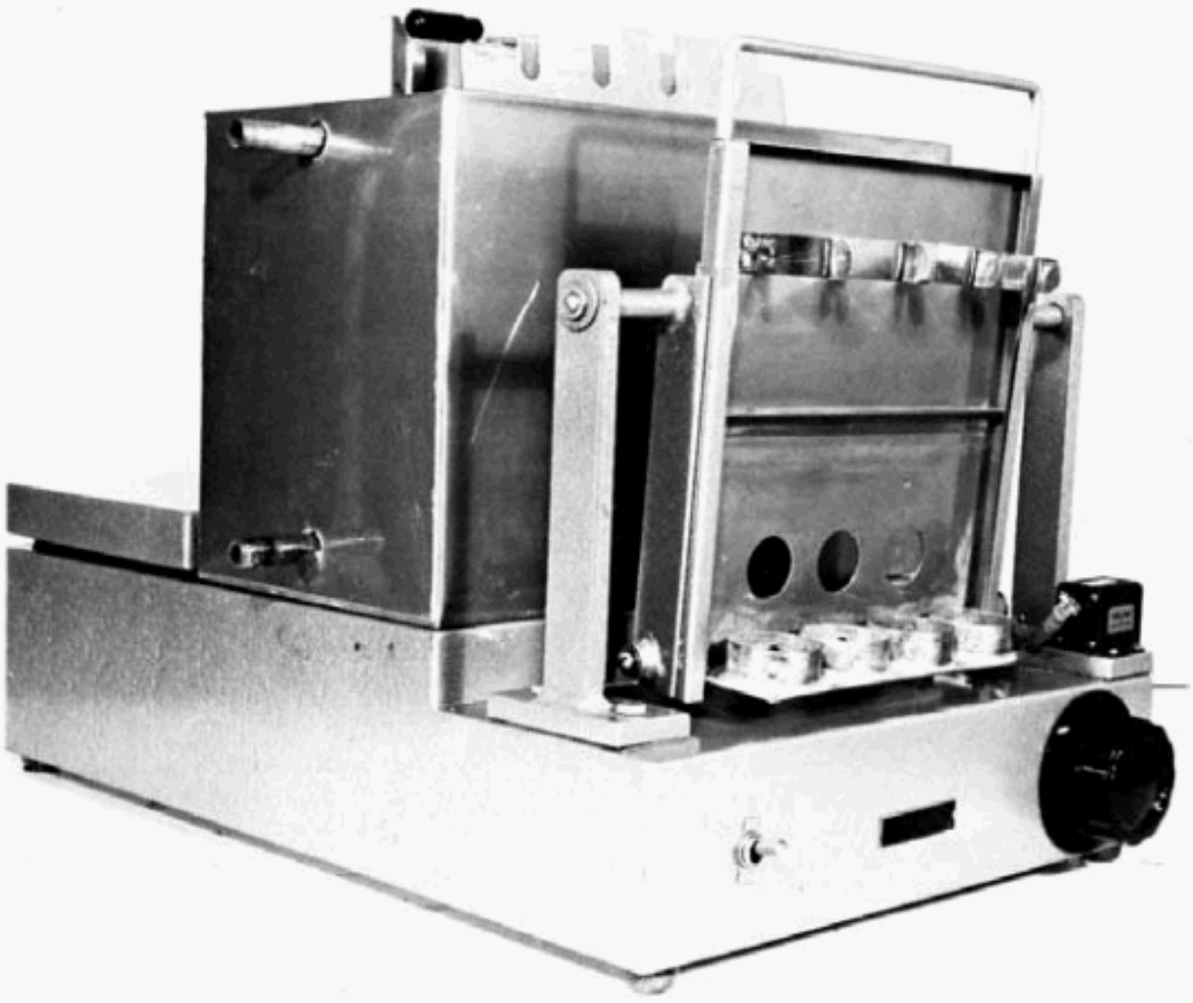

FIG. A1.2 Shaking Machine

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