Standard Test Methods for
Surface and Interfacial Tension of Solutions of Paints, Solvents, Solutions of Surface-Active Agents, and Related Materials[1]

This standard is issued under the fixed designation D1331; 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 These test methods cover the determination of surface tension and interfacial tension of a variety of liquid materials, including but not restricted to paints, solvents, and solutions of surface-active agents, as defined in Terminology D459. Four methods are covered as follows:

Method A—Surface Tension by du Noüy ring;

Method B—Interfacial Tension by du Noüy ring;

Method C—Surface Tension by Wilhelmy plate; and

Method D—Interfacial Tension by Wilhelmy plate.

1.2 Method A originally was written primarily to cover aqueous solutions of surface-active agents, but is also applicable to aqueous paints, nonaqueous solutions (including paints) and mixed solvent solutions.

1.3 Method B is applicable to two-phase solutions. More than one solute component may be present, including solute components that are not in themselves surface-active.

1.4 Method C is applicable to surface active liquids and, unlike du Noüy ring, no buoyancy corrections are needed and results are not affected by moderate viscosities (1-10 Pa-sec) of the liquid. It is the recommended method for use with paints and resin solutions.

1.5 Method D is applicable to two-phase solutions and mixtures.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *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.*

Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.

1.8 *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]

D459 Terminology Relating to Soaps and Other Detergents

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *du Noüy ring, n*—platinum wire ring.

3.1.2 *Wilhelmy plate, n*—flat, thin plate made of glass or platinum.

4. Summary of Test Methods

4.1 *du Noüy Ring Methods*—The ring is suspended from a tensiometer or balance. The test liquid is brought into contact with the ring until the latter is covered. For interfacial tension measurements, the ring must be at the interface between the two liquids. The ring is then slowly withdrawn until a maximum force is attained, from which the surface or interfacial tension may be calculated.

4.2 *Wilhelmy Plate Methods*—The plate is suspended from a tensiometer or balance. The test liquid or interface between two liquids is brought into contact with the bottom of the plate, causing the plate to be pulled down into the liquid by the surface tension force. The force applied to the plate from above

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[1] These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.24 on Physical Properties of Liquid Paints & Paint Materials.

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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.

is then increased to bring the bottom edge of the plate level with the flat surface of the liquid. The force acting on the plate is measured and used to calculate the surface tension of the liquid or the interfacial tension between two liquid phases.

5. Significance and Use

5.1 These methods provide data that are useful in evaluating the effectiveness of surface active agents in reducing surface tension. In addition, surface tension data can predict interactions between liquids and solid surfaces or other liquids and can be used to establish wetting properties of paints, solvents, and other liquids.

5.2 A number of laboratories have found the Wilhelmy plate to be easier to use, easier to clean and generally better for use with pigmented paints.

6. Interferences

6.1 The du Noüy ring is difficult to clean when used with pigmented paints. Paints high in titanium dioxide have a tendency to coat the ring with a layer that is almost impossible to remove. If left on the ring, this layer of material affects the surface tension values that are measured.

6.2 Paint measurements with the du Noüy ring are affected by viscosity above a level of 10 Poise (1 Pa-sec). Many coatings have a viscosity at rest greater than that level. Above 10 P, the resistance of the ring to being pulled is as much due to viscosity as to surface tension.

METHOD A—SURFACE TENSION BY DU NOÜY RING

7. Apparatus

7.1 *du Noüy Tensiometer*—Either the du Noüy precision tensiometer or the du Noüy interfacial tensiometer, equipped with either the 4 or the 6-cm circumference platinum ring, as furnished by the manufacturer, may be used. The tensiometer shall be placed on a sturdy support that is free from vibrations and other disturbances such as wind, sunlight, and heat. The wire of the ring shall be in one plane, free of bends or irregularities, and circular. When set in the instrument, the plane of the ring shall be horizontal, that is, parallel to the surface plane of the liquid being tested.

7.2 *Sample Container*—The vessel for holding the liquid shall be not less than 6 cm in diameter, and sufficiently large to ensure that the contact angle between the ring and the interface is zero.

8. Preparation of Apparatus

8.1 Clean all glassware thoroughly. The use of fresh chromic-sulfuric acid cleaning mixture, followed by a thorough rinsing in distilled water, is recommended.

8.2 Clean the platinum ring by rinsing thoroughly in a suitable solvent and in distilled water, before taking a set of measurements. Allow the ring to dry, and then heat to white heat in the oxidizing portion of a gas flame.

9. Calibration of Apparatus

9.1 Calibrate the tensiometer or balance according to the manufacturer's directions.

10. Procedure

10.1 After the tensiometer has been calibrated, check the level and insert the cleaned platinum ring (Note 1) that will be used in the measurement. Check the plane of the ring, and set the dial and vernier at zero. Adjust the rear adjusting screw so that the index level of the arm is opposite the reference mark on the mirror, that is, the ring system is at the zero position.

NOTE 1—Extreme care must be taken to have the sample vessel and platinum ring clean. Contamination of the liquid surface by dust or other atmospheric impurities during measurement should be avoided.

10.2 Place the solution to be tested (Note 2), contained in the thoroughly cleaned vessel (Note 1), on the sample platform. Raise the sample platform by means of its adjusting screw until the ring is just submerged.

NOTE 2—For surface active agents: since the surface tension of a solution is a function of the concentration, care must be taken that the concentration is adjusted and recorded within known limits. The presence of solutes other than the surface-active agent should be ascertained and reported qualitatively and quantitatively, insofar as possible. This includes hardness components in the water. Care should be taken that the solution is physically homogeneous. Measurements made near or above the cloud point or other critical solubility points can be in serious error. This is particularly true when the solute is a surface-active material.

10.3 Lower the platform slowly, at the same time applying torsion to the wire by means of the dial-adjusting screw. These simultaneous adjustments must be carefully proportioned so that the ring system remains constantly in its zero position. As the breaking point is approached, the adjustments must be made more carefully and more slowly. Record the force reading from the dial or the digital display when the ring detaches from the surface.

10.4 Make at least two measurements. Additional measurements shall be made if indicated by the over-all variation obtained, the total number of readings to be determined by the magnitude of that variation.

10.5 Record the temperature of the solution and the age of the surface at the time of testing. Since the submerging of the ring (10.2) may constitute a significant disturbance of the surface, take the age as the elapsed time between submersion and breakaway of the ring. The accuracy of this time observation may be indicated in the usual manner. In most cases an accuracy of ±5 s is reasonable, and sufficient for this test method.

11. Calculation and Report

11.1 The dial reading, obtained from a measurement carried out in the foregoing manner with a calibrated instrument, is actually the pull per linear centimetre on the ring (both inner and outer circumference being considered) at the break-point, expressed in dynes. This value, called the uncorrected surface tension, must be multiplied by a correcting factor, F, to give the corrected surface tension. F is a function of the contours of the liquid surface in the neighborhood of the ring at the instant of breakaway. It can be numerically specified in terms of R, the

mean radius, in centimetres, of the ring; r, the radius, in centimetres, of the wire from which the ring is made; and V, the maximum volume of liquid elevated above the free surface of the liquid. For liquids of low surface tension, such as surface-active agents, F is, in general, appreciably less than unity. It must, therefore, be ascertained and applied. Values of F in terms of two compounded parameters, R^3/V and R/r have been compiled and tabulated by Harkins and Jordan.[3] In order to look up F in the tables, the values of these two parameters must be calculated. Values for R and r are furnished by the manufacturer with each ring. The value of V is calculated from the following equation:

$$V = M/(D - d) \qquad (1)$$

where:

M = weight of liquid raised above the free surface of the liquid,
D = density of liquid, and
d = density of air saturated with vapor of the liquid.

To calculate M, multiply the tensiometer dial reading by the factor which converts this reading into grams pull on the ring. The factor D can be measured by the usual procedures, and the value d can be obtained from published data. The corrected surface tension in dynes per centimetre is obtained by multiplying the uncorrected surface tension value by F.

11.2 Unless specified, the surface tension values reported shall be corrected values. Report also the temperature at which the measurement was made. If it is desired to report the surface tension value of an aqueous solution at some standard temperature, for example, 25°C, and the measurement was actually made at a temperature within about 3°C of this value (that is, 22 to 28°C), a correction factor of 0.14 dynes/cm·°C may be used. Subtract this correction factor from the surface tension when the temperature of the test is lower than the reported temperature, and add it to the surface tension when the temperature of the test is higher than the reported temperature. This value for the correction factor is not valid for nonaqueous liquids, and should be used only where the solvent is preponderantly water.

METHOD B—INTERFACIAL TENSION BY DU NOÜY RING

12. Procedure

12.1 Determine interfacial tension as described in Section 10 for surface tension, with the following modifications:

12.1.1 Always move the ring from the aqueous side of the interface through to the nonaqueous side. With liquids lighter than water, it is accordingly possible to use the precision tensiometer as well as the interfacial tensiometer. With liquids heavier than water, where the ring must be pushed downward, the interfacial tensiometer should be used.

12.1.2 Use fresh solutions and a freshly cleaned ring for each determination.

12.1.3 When operating with a liquid heavier than the aqueous solution, place the two-layer system in the sample vessel and place the ring in the upper (aqueous) layer. Make the measurement by turning the torsion wire counter-clockwise and simultaneously keeping the ring system in the zero position, as in the measurement of surface tension, until the ring breaks through the interface.

12.1.4 When operating with a liquid (oil) lighter than the aqueous solution, first place the aqueous solution in the sample vessel and immerse the ring therein. Carefully pour the oil on top of the aqueous solution to form the two-layer system. Contact between the oil and the ring should be avoided during this operation. After allowing sufficient time for the interfacial tension to come to its equilibrium value (Note 3), make the measurement in the same manner as that used for measuring surface tension.

NOTE 3—Since the interfacial energy of a newly formed liquid-liquid interface generally requires some time to reach its equilibrium value, it is advisable to wait at least 5 min after the interface is formed before taking a measurement.

13. Calculation and Report

13.1 As in the case of surface tension, a correction factor, F, must be multiplied by the dial reading (pull on the ring in dynes) in order to obtain the corrected value for interfacial tension. Values for F have been published by Zuidema and Waters.[4] The factor F is, in this case, a function of the densities of the two liquids as well as of R and r, the radius of the ring and that of the wire, respectively.

13.2 Unless specified, interfacial tension values reported shall be corrected values. Report and adequately specify the nature of the nonaqueous liquid (oil) used in the determination. Also report the temperature at which the determination was made. In contrast to surface tension values, interfacial tension values cannot adequately be corrected for small temperature deviations by means of a simple formula.

METHOD C—SURFACE TENSION BY WILHELMY PLATE

14. Apparatus

14.1 *Balance or Tensiometer* with provision for attaching a Wilhelmy plate.

14.2 *Thin Platinum or Glass Plate* (microscope slides and cover slips have been used) with a means of connecting it to the balance or tensiometer.

15. Preparation of Apparatus

15.1 Clean all glassware thoroughly. The use of fresh chromic-sulfuric acid cleaning mixture, followed by a thorough rinsing in distilled water, is recommended.

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[3] Harkins, W. D., and Jordan, H. F., "A Method for Determination of Surface and Interfacial Tension from the Maximum Pull on a Ring," *Journal Am. Chemical Soc.*, Vol 52, 1930, p. 1751. These tables are also published in *Physical Methods of Organic Chemistry*, Interscience Publishers, Inc., New York, NY, Vol 1, 1945, pp. 182–184.

[4] Zuidema, H. H., and Waters, G. W., "A Ring Method for Determination of Interfacial Tension," *Industrial and Engineering Chemistry*, Analytical Edition, Vol 13, 1941, p. 312.

15.2 Clean platinum or glass plate by rinsing thoroughly in a suitable solvent and distilled water.

15.3 For a correct surface tension the surface of the plate must be roughened and with no bright spots on the plate.

16. Procedure

16.1 After the tensiometer or balance has been calibrated, check the level and insert the cleaned platinum or glass plate that will be used in the measurement. Extreme care must be taken to have the sample vessel and platinum or glass plate clean. Contamination of the liquid surface by dust or other atmospheric impurities during measurement should be avoided.

16.2 Check that the lower edge of the plate is exactly plane by ensuring the light gap between the edge of the plate and the surface is uniform.

16.3 Place the liquid to be tested, contained in the thoroughly cleaned vessel (16.1), on the sample platform. For surface active agents: since the surface tension of a solution is a function of the concentration, care must be taken that the concentration is adjusted and recorded within known limits. The presence of solutes other than the surface-active agent should be ascertained and reported qualitatively and quantitatively, insofar as possible. This includes hardness components in the water. Care should be taken that the solution is physically homogeneous. Measurements made near or above the cloud point or other critical solubility points can be in serious error. This is particularly true when the solute is a surface-active material.

16.4 Rinse the platform to just below the plate. Tare the force measuring system to zero.

16.5 Rinse the sample platform until the plate is just submerged and turn the mechanical drag pointer to set it at the reference mark.

16.6 Raise platform around another 5 mm to ensure the wetting of the plate and then lower platform until the drag pointer is pointing exactly to the reference mark again.

16.7 Record the force reading from the dial or the digital display.

16.8 Make at least two measurements. Additional measurements shall be made if indicated by the overall variation obtained, the total number of readings to be determined by the magnitude of that variation.

17. Calculation

17.1 The surface tension, γ, is computed from the force measurement, f, using:

$$\gamma = f/\{[2\ (1\ +\ t)]\}\cdot\ \cos\ \theta$$

where:
l = length of plate
t = thickness

The contact angle θ is often assumed to be zero for common liquids on clean glass or platinum plates, but one should be aware of the error caused by a non-zero contact angle. No other correction factors are necessary for this method and the fluid density does not need to be known.

METHOD D—INTERFACIAL TENSION BY WILHELMY PLATE

18. Procedure

18.1 Determine interfacial tension as described in the procedure for surface tension (Section 16), with the following modifications:

18.1.1 Always remove the plate from the aqueous side of the interface through to the nonaqueous side. With liquids lighter than water, it is accordingly possible to use the precision tensiometer as well as the interfacial tensiometer. With liquids heavier than water, where the plate must be pushed downward, the interfacial tensiometer should be used.

18.1.2 Use fresh solutions and a freshly cleaned plate for each determination.

18.1.3 When operating with a liquid heavier than the aqueous solution, place the two-layer system in the sample vessel and place the plate in the upper (aqueous) layer. Make the measurement by turning the torsion wire counter-clockwise and simultaneously keeping the plate system in the zero position, as in the measurement of the surface tension.

18.1.4 When operating with a liquid (oil) lighter than the aqueous solution, first place the aqueous solution in the sample vessel and immerse the plate therein. Carefully pour the oil on top of the aqueous solution to form the two-layer system. Contact between the oil and the plate should be avoided during this operation. After allowing the sufficient time for the interfacial tension to come to its equilibrium value (Note 4), make the measurement in the same manner as that used for measuring surface tension.

Note 4—Since the interfacial energy of a newly formed liquid-liquid interface generally requires some time to reach its equilibrium value, it is advisable to wait at least 5 min after the interface is formed before taking a measurement.

19. Calculations and Report

19.1 Calculate surface tension as in 17.1.

19.2 Report and adequately specify the nature of the nonaqueous liquid (oil) used in the determination. Also report the temperature at which the determination was made. In contrast to surface tension values, interfacial tension values cannot adequately be corrected for small temperature deviations by means of a simple formula.

20. Precision and Bias

20.1 The precision of these test methods is based on an interlaboratory study of ASTM D1331, Standard Test Methods for Surface and Interfacial Tension of Solutions of Paints, Solvents, Solutions of Surface-Active Agents, and Related Materials, conducted in 2018. A total of eight volunteer laboratories were asked to test four different materials. Every "test result" represents an individual determination, and all participants were instructed to report three replicate test results for each material. Practice E691 was followed for the design

and analysis of the data; the details are given in ASTM Research Report No. D01-2002.[5]

20.1.1 *Repeatability Limit (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

20.1.1.1 Repeatability can be interpreted as the maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

20.1.1.2 Repeatability limits are listed in Table 1 and Table 2.

20.1.2 *Reproducibility Limit (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus 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 20.

20.1.2.1 Reproducibility can be interpreted as the maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

20.1.2.2 Reproducibility limits are listed in Table 1 and Table 2.

20.1.3 Repeatability limit and reproducibility limit are used as specified in Practice E177.

20.1.4 Any judgment in accordance with statements 20.1.1 and 20.1.2 would have an approximate 95 % probability of being correct.

20.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

20.3 The precision statement was determined through statistical examination of 156 test results, from eight laboratories, on the four materials described as:

Material A: Waterborne Latex Paint;

Material B: Waterborne Latex Primer;

Material C: Solventborne Alkyd Paint; and

Material D: Surfactant Solution, 1 % by weight concentration.

20.4 To judge the equivalency of two test results, it is recommended to choose the material closest in characteristics to the test material.

21. Keywords

21.1 du Noüy ring; interfacial tension; surface tension; tensiometer; Wilhelmy plate

TABLE 1 Method A Surface Tension By du Noüy (dynes/cm)

Material	Number of Laboratories	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	n	$\bar{x}$	s_r	s_R	r	R
Material A	7	51.803	1.142	23.247	3.197	65.091
Material B	7	42.507	0.799	8.655	2.236	24.234
Material C	7	29.012	1.592	4.597	4.458	12.873
Material D	7	31.155	0.328	0.598	0.918	1.674

[A] The average of the laboratories' calculated averages.

TABLE 2 Method C Surface Tension By Wilhelmy Plate (dynes/cm)

Material	Number of Laboratories	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	n	$\bar{x}$	s_r	s_R	r	R
Material A	6	36.818	0.974	13.017	2.727	36.446
Material B	6	30.978	0.785	11.322	2.198	31.702
Material C	6	26.437	2.377	7.777	6.655	21.775
Material D	6	32.164	0.120	0.502	0.335	1.406

[A] The average of the laboratories' calculated averages.