A.5. SURFACE TENSION

1. **METHOD**

The methods described are based on the OECD Test Guideline (1). The fundamental principles are given in reference (2).

1.1 INTRODUCTION

The described methods are to be applied to the measurement of the surface tension of aqueous solutions.

It is useful to have preliminary information on the water solubility, the structure, the hydrolysis properties and the critical concentration for micelles formation of the substance before performing these tests.

The following methods are applicable to most chemical substances, without any restriction in respect to their degree of purity.

The measurement of the surface tension by the ring tensiometer method is restricted to aqueous solutions with a dynamic viscosity of less than approximately 200 mPa s.

1.2. DEFINITIONS AND UNITS

The free surface enthalpy per unit of surface area is referred to as surface tension.

The surface tension is given as:

N/m (SI unit) or

mN/m (SI sub-unit)

1 N/m = 103 dynes/cm

1 mN/m = 1 dyne/cm in the obsolete cgs system

1.3. REFERENCE SUBSTANCES

Reference substances do not need to be employed in all cases when investigating a new substance. They should primarily serve to check the performance of the method from time to time and to allow comparison with results from other methods.

Reference substances which cover a wide range of surface tensions are given in references 1 and 3.

1.4. PRINCIPLE OF THE METHODS

The methods are based on the measurement of the maximum force which it is necessary to exert vertically, on a stirrup or a ring in contact with the surface of the liquid being examined placed in a measuring cup, in order to separate it from this surface, or on a plate, with an edge in contact with the surface, in order to draw up the film that has formed.

Substances which are soluble in water at least at a concentration of 1 mg/l are tested in aqueous solution at a single concentration.

1.5. QUALITY CRITERIA

These methods are capable of greater precision than is likely to be required for environmental assessment.

1.6. DESCR1PTION OF THE METHODS

A solution of the substance is prepared in distilled water. The concentration of this solution should be 90% of the saturation solubility of the substance in water; when this concentration exceeds 1 g/l, a concentration of 1 g/l is used for testing. Substances with a water solubility lower than 1 mg/l need not be tested.

1.6.1. Plate method

See ISO 304 and NF T 73-060 (Surface active agents -determination of surface tension by drawing up liquid films).

1.6.2. Stirrup method

See lSO 304 and NF T 73-060 (Surface active agents -determination of surface tension by drawing up liquid films).

1.6.3. Ring method

See ISO 304 and NF T 73-060 (Surface active agents - determination of surface tension by drawing up liquid films).

1.6.4. OECD harmonized ring method

1.6.4.1. Apparatus

Commercially available tensiometers are adequate for this measurement. They consist of the following elements:

-mobile sample table,

-force measuring system,

The force measuring system (see figure) is located above the sample table. The error of the force measurement shall not exceed $\pm 10^{-6}$ N, corresponding to an error limit of $\pm 0,1$ mg in a mass measurement. In most cases, the measuring scale of commercially available tensiometers is calibrated in mN/m so that the surface tension can be read directly in mN /m with an accuracy of 0,1 mN/m.
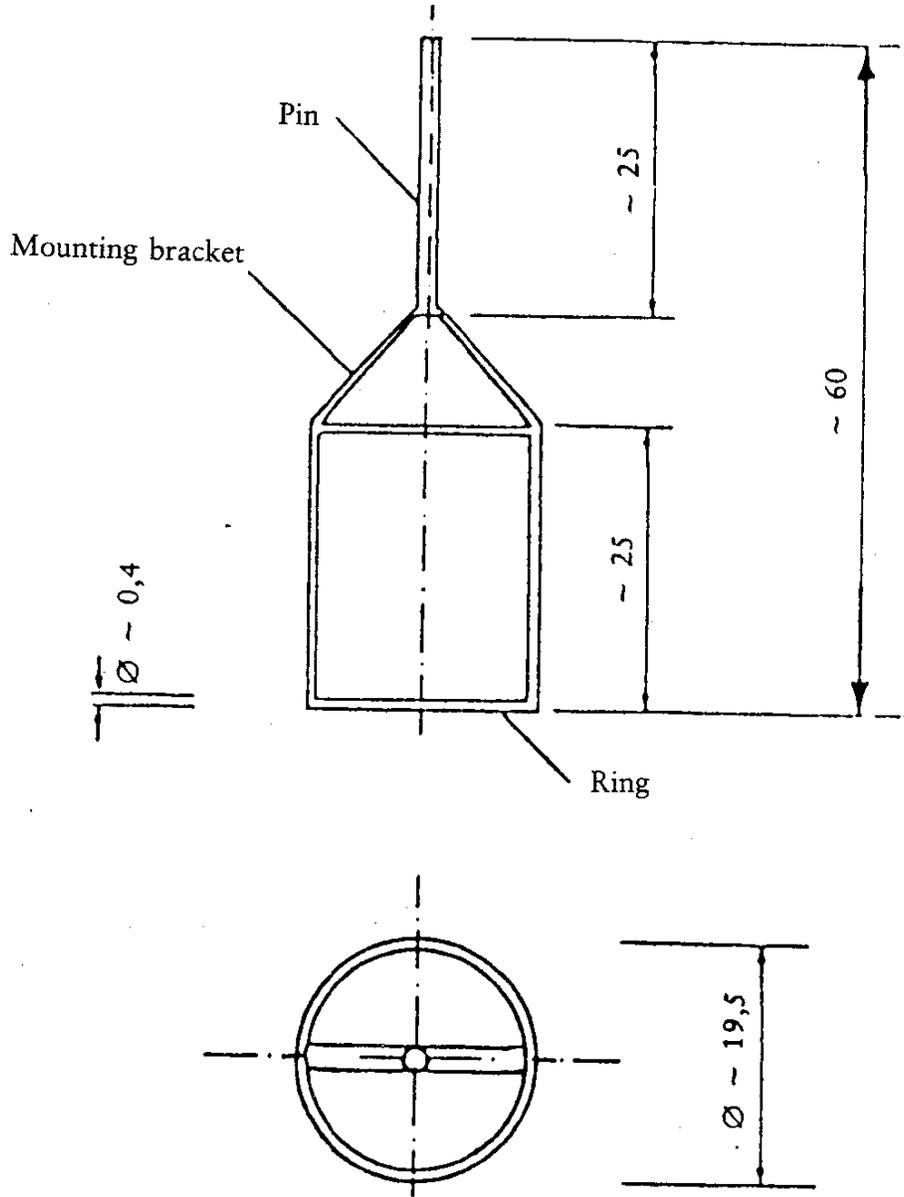
1.6.4.1.3. Measuring body (ring)

The ring is usually made of a platinum-iridium wire of about 0,4 mm thickness and a mean circumference of 60 mm. The wire ring is suspended horizontally from a metal pin and a wire mounting bracket to establish the connection to the force measuring system (see figure).

Figure

Measuring body
(All dimensions expressed in millimetres)

Pin

Mounting bracket

Ring

$\emptyset \sim 0,4$

~ 25

~ 25

~ 60

$\emptyset \sim 19,5$

1.6.4.1.4. Measurement vessel

The measurement vessel holding the test solution to be measured shall be a temperature-controlled glass vessel. It shall be designed so that during the measurement the temperature of the test solution liquid and the gas phase above its surface remains constant and that the sample cannot evaporate. Cylindrical glass vessels having an inside diameter of not less than 45 mm are acceptable.

1.6.4.2. Preparation of the apparatus

1.6.4.2.1. Cleaning

Glass vessels shall be cleaned carefully. If necessary they shall be washed with hot chromo-sulphuric acid and subsequently with syrupy phosphoric acid (83 to 98% by weight of H_3PO_4), thoroughly rinsed in tap water and finally washed with double-distilled water until a neutral reaction is obtained and subsequently dried or rinsed with part of the sample liquid to be measured.

The ring shall first be rinsed thoroughly in water to remove any substances which are soluble in water, briefly immersed in chromo-sulphuric acid, washed in double-distilled water until a neutral reaction is obtained and finally heated briefly above a methanol flame.

Note:

Contamination by substances which are not dissolved or destroyed by chromo-sulphuric acid or phosphoric acid, such as silicones, shall be removed by means of a suitable organic solvent.

1.6.4.2.2. Calibration of the apparatus

The validation of the apparatus consists of verifying the zero point and adjusting it so that the indication of the instrument allows reliable determination in mN/m.

Mounting:

The apparatus shall be levelled, for instance by means of a spirit level on the tensiometer base, by adjusting the levelling screws in the base.

Zero point adjustment:

After mounting the ring on the apparatus and prior to immersion in the liquid, the tensiometer indication shall be adjusted to zero and the ring checked for parallelism to the liquid surface. For this purpose, the liquid surface can be used as a mirror.

Calibrations:

The actual test calibration can be accomplished by means of either of two procedures:

(a) Using a mass: procedure using riders of known mass between 0,1 and 1,0 g placed on the ring. The calibration factor, Φ_a by which all the instrument readings must be multiplied, shall be determined according to equation (1).

$$\Phi_a = \frac{\sigma_r}{\sigma_a}$$

where

$$\sigma_r = \frac{mg}{2b}(mN/m)$$

m = mass of the rider (g)

g = gravity acceleration (981 cm s^{-2} at sea level)

b = mean circumference of the ring (cm)

σ_a = reading of the tensiometer after placing the rider on the ring (mN/m).

(b) Using water: procednre using pure water whose surface tension at, for instance, 23 °C is equal to 72,3 mN/m. This procedure is accomplished faster than the weight calibration but there is always the danger that the surface tension of the water is falsified by traces of contamination by surfactants.

The calibration factor, Φ_b by which all the instrument readings shall be multiplied, shall be determined in accordance with the equation (2):

$$\Phi_b = \frac{\sigma_o}{\sigma_g}$$

where:

σ_o = value cited in the literature for the surface tension of water (mN/m)

σ_g = measured value of the surface tension of the water (mN/m)

both at the same temperature.

1.6.4.3. Preparation of samples

Aqueous solutions shall be prepared of the substances to be tested, using the required concentrations in water, and shall not contain any non-dissolved substances.

The solution must be maintained at a constant temperature ($\pm 0,5$ °C). Since the surface tension of a solution in the measurement vessel alters over a period of time, several measurements sh all be made at various times and a curve plotted showing surface tension as a function of time. When no further change occurs, a state of equilibrium has been reached.

Dust and gaseous contamination by other substances interfere with the measurement. The work shall therefore be carried out under a protective cover.

1.6.5. Test conditions

The measurement shall be made at approximately 20 °C and shall be controlled to within $\pm 0,5$ °C.

1.6.6. Performance of test

The solutions to be measured shall be transferred to the carefully cleaned measurement vessel, taking care to avoid foaming, and subsequently the measurement vessel shall be placed onto the table of the test apparatus. The table-top with measurement vessel shall be raised until the ring is immersed below the surface of the solution to be measured. Subsequently, the table-top shall be lowered gradually and evenly (at a rate of approximately 0,5 cm/min) to detach the ring from the surface until the maximum force has been reached. The liquid layer attached to the ring must not separate from the ring. After completing the measurements, the ring shall be immersed below the surface again and the measurements repeated until a constant surface tension value is reached. The time from transferring the solution to the measurement vessel shall be recorded for each determination. Readings shall be taken at the maximum force required to detach the ring from the liquid surface.

2. **DATA**

In order to calculate the surface tension, the value read in mN/m on the apparatus shall be first multiplied by the calibration factor Φ_a or Φ_b (depending on the calibration procedure used). This will yield a value which applies only approximately and therefore requires correction.

Harkins and Jordan (4) have empirically determined correction factors for surface-tension values measured by the ring method which are dependent on ring dimensions, the density of the liquid and its surface tension.

Since it is laborious to determine the correction factor for each individual measurement from the Harkins and Jordan tables, in order to calculate the surface tension for aqueous solutions the simplified procedure of reading the corrected surface-tension values directly from the table may be used. (Interpolation shall be used for readings ranging between the tabular values.)

TABLE: CORRECTION OF THE MEASURED SURFACE TENSION
Only for aqueous solutions, $\rho \cong 1$ g/cm3

R = 9,55 mm (average ring radius)

r = 0,185 mm (ring wire radius)

Experimental Value (mN/m)	Corrected Value (mN/m)	
	Weight calibration (see 1.6.4.2.2(a))	Water calibration (see 1.6.4.2.2(b))
20	16,9	18,1
22	18,7	20,1
24	20,6	22,1
26	22,4	24,1
28	24,3	26,1
30	26,2	28,1
32	28,1	30,1
34	29,9	32,1
36	31,8	34,1
38	33,7	36,1
40	35,6	38,2
42	37,6	40,3
44	39,5	42,3
46	41,4	44,4
48	43,4	46,5
50	45,3	48,6
52	47,3	50,7
54	49,3	52,8
56	51,2	54,9
58	53,2	57,0
60	55,2	59,1
62	57,2	61,3
64	59,2	63,4
66	61,2	65,5
68	63,2	67,7
70	65,2	69,9
72	67,2	72,0
74	69,2	—
76	71,2	—
78	73,2	—

This table has been compiled on the basis of the Harkins-Jordan correction. It is similar to that in the DIN Standard (DIN 53914) for water and aqueous solutions (density $\rho = 1$ g/cm^3) and is for a commercially available ring having the dimensions R = 9,55 mm (mean ring radius) and r = 0,185 mm (ring wire radius). The table provides corrected values for surface-tension measurements taken after calibration with weights or calibration with water.

Alternatively, without the preceding calibration, the surface tension call be calculated according to the following formula:

$$\sigma = \frac{f \times F}{4\pi R}$$

where:

F = the force measured on the dynamometer at the breakpoint of the film

R = the radius of the ring

f = the correction factor (1)

3. **REPORTING**

3.1. TEST REPORT

The test report shall, if possible, include the following information:

-method used,

-type of water or solution used,

-precise specification of the substance (identity and impurities),

-measurement results: surface tension (reading) stating both the individual readings and their arithmetic mean as well as the corrected mean (taking into consideration the equipment factor and the correction table),

-concentration of the solution,

-test temperature,

-age of solution used; in particular the time between preparation and measurement of the solution,

-description of time dependence of surface tension after transferring the solution to the measurement vessel,

-all information and remarks relevant for the interpretation of results have to be reported, especially with regard to impurities and physical state of the substance.

3.2. INTERPRETATION OF RESULTS

Considering that distilled water has a surface tension of 72,75 mN/m at 20 °C, substances showing a surface tension lower than 60 mN/m under the conditions of this method should be regarded as being surface-active materials.

4. **REFERENCES**

(1) OECD, Paris, 1981, Test Guideline 115, Decision of the Council C(81) 30 final.

(2) R. Weissberger ed.: Technique of Organic Chemistry, Physical Methods of Organic Chemistry, 3rd ed., Interscience Publ., New York, 1959, Vol. I, Part I, Chapter XIV

(3) Pure Appl. Chem., 1976, vol. 48,511.

(4) Harkins, W.D., Jordan, H.F., J. Amer. Chem. Soc., 1930, vol. 52, 1751.