

INTERNATIONAL STANDARD

**ISO
2271**

Second edition
1989-10-15

Surface active agents — Detergents — Determination of anionic-active matter by manual or mechanical direct two-phase titration procedure

*Agents de surface — Détergents — Détermination de la teneur en matière active
anionique selon une méthode manuelle ou mécanique par titrage direct
dans deux phases*



Reference number
ISO 2271 : 1989 (E)

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 2271 was prepared by Technical Committee ISO/TC 91, *Surface active agents*.

This second edition cancels and replaces the first edition (ISO 2271 : 1972), of which it constitutes a minor revision.

Annex A of this International Standard is for information only.

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International Organization for Standardization

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Surface active agents — Detergents — Determination of anionic-active matter by manual or mechanical direct two-phase titration procedure

1 Scope

This International Standard specifies a manual or mechanical method for the determination of anionic-active matter present in detergents.

The method is applicable to solids or to aqueous solutions of the active material. The relative molecular mass of the anionic active matter has to be known.

The method is not applicable if cationic surface active agents are present.

The manual method is thus applicable to the determination of alkylbenzene sulfonates; alkane sulfonates, sulfates and hydroxysulfates; alkylphenol sulfates; fatty alcohol methoxy- and ethoxysulfates; dialkylsulfosuccinates and other active materials containing one hydrophilic group per molecule.

The mechanical method is applicable to all the above-mentioned products provided it gives results comparable with those obtained using the manual method.

NOTE — Low relative molecular mass sulfonates present as hydrotropes (toluene, xylene) do not interfere when present in concentrations of up to 15 % (*m/m*) relative to the active matter. At higher levels, their influence should be evaluated in each particular case.

Soap, urea and salts of (ethylenedinitrilo)tetraacetic acid do not interfere.

In the presence of non-ionic surface agents, their influence should be evaluated in each particular case.

Typical inorganic components of detergent formulations, such as sodium chloride, sulfates, borates, tripolyphosphates, perborates, silicates, etc., do not interfere, but bleaching agents other than perborate should be destroyed before the analysis, and the sample should be completely soluble in water.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1 : 1984, *Laboratory glassware — Burettes — Part 1: General requirements*.

ISO 607 : 1980, *Surface active agents and detergents — Methods of sample division*.

ISO 648 : 1977, *Laboratory glassware — One-mark pipettes*.

ISO 1042 : 1983, *Laboratory glassware — One-mark volumetric flasks*.

3 Principle

Determination of the anionic-active matter in a medium consisting of an aqueous and a chloroform phase by titration with a standard volumetric cationic-active solution (benzethonium chloride) in the presence of an indicator which consists of a mixture of a cationic dye (dimidium bromide) and an anionic dye (acid blue 1).

NOTE — The chemical process is as follows: the anionic-active matter forms a salt with the cationic dye which dissolves in the chloroform to give this layer a reddish pink colour.

In the course of the titration, the benzethonium chloride displaces the dimidium bromide from this salt and the pink colour disappears from the chloroform layer as the dye passes into the aqueous phase. Excess benzethonium chloride forms a salt with the anionic dye, which dissolves in the chloroform layer and colours it blue.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Chloroform, ρ_{20} 1,48 g/ml, distilling between 59,5 °C and 61,5 °C.

4.2 Sulfuric acid, approximately 245 g/l solution.

Carefully add 134 ml of sulfuric acid, ρ_{20} 1,83 g/ml, to 300 ml of water and dilute to 1 litre.

4.3 Sulfuric acid, standard volumetric solution, $c(1/2 \text{ H}_2\text{SO}_4) = 1,0 \text{ mol/l}$.

4.4 Sodium hydroxide, standard volumetric solution, $c(\text{NaOH}) = 1,0 \text{ mol/l}$.

4.5 Sodium lauryl sulfate (Sodium dodecyl sulfate)
 $[\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}]$, standard volumetric solution,
 $c(\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}) = 0,004 \text{ mol/l}$.

Check the purity of the sodium lauryl sulfate and simultaneously prepare the standard volumetric solution.

4.5.1 Determination of purity of sodium lauryl sulfate

Weigh, to the nearest 1 mg, $5 \text{ g} \pm 0,2 \text{ g}$ of the product into a 250 ml round bottom flask with ground glass neck. Add exactly 25 ml of the standard volumetric sulfuric acid solution (4.3) and reflux using a water condenser. During the first 5 min to 10 min, the solution will thicken and tend to foam strongly; control this by removing the source of heat and swirling the contents of the flask.

In order to avoid excessive foaming, instead of refluxing, the solution may be left on a boiling water bath for 60 min.

After a further 10 min, the solution will become clear and foaming will cease. Reflux for a further 90 min.

Remove the source of heat, cool the flask and carefully rinse the condenser with 30 ml of ethanol followed by water.

Add a few drops of the phenolphthalein solution (4.7), and titrate the solution with the sodium hydroxide solution (4.4).

Carry out a blank test by titrating 25 ml of the sulfuric acid solution (4.3) with the sodium hydroxide solution (4.4).

Calculate the purity τ , expressed as a percentage by mass, of the sodium lauryl sulfate using the formula

$$\frac{28,84(V_1 - V_0)c_0}{m_1}$$

where

V_0 is the volume, in millilitres, of sodium hydroxide solution (4.4) used for the blank test;

V_1 is the volume, in millilitres, of sodium hydroxide solution used for the test portion of sodium lauryl sulfate taken;

c_0 is the exact concentration, expressed in moles of NaOH per litre, of the sodium hydroxide solution (4.4);

m_1 is the mass, in grams, of the test portion of sodium lauryl sulfate taken.

4.5.2 Preparation of standard volumetric sodium lauryl sulfate solution

Weigh, to the nearest 1 mg, between 1,14 g and 1,16 g of sodium lauryl sulfate and dissolve in 200 ml of water. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask (5.3) fitted with a ground glass stopper, and dilute to the mark with water.

Calculate the exact concentration c_2 , expressed in moles of $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$ per litre, of the solution thus obtained, using the formula

$$\frac{m_2\tau}{288,4 \times 100}$$

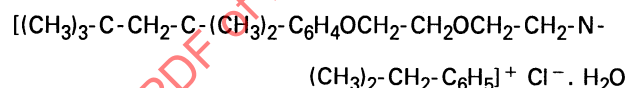
where

m_2 is the mass, in grams, of sodium lauryl sulfate used to prepare the solution;

τ has the same meaning as in 4.5.1.

4.6 Benzethonium chloride¹⁾, standard volumetric solution, $c(\text{C}_{27}\text{H}_{42}\text{ClNO}_2) = 0,004 \text{ mol/l}$.

Benzyl dimethyl-2-[2-4(1,1,3,3-tetramethylbutyl)phenoxy-ethoxy]ethyl ammonium chloride, monohydrate:



4.6.1 Preparation of the solution

Weigh, to the nearest 1 mg, between 1,75 g and 1,85 g of benzethonium chloride and dissolve in water.

Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask (5.3) fitted with a ground glass stopper, and make up to the mark with water.

NOTE — In order to prepare a 0,004 mol/l solution, dry the benzethonium chloride at 105 °C, allow to cool in a desiccator, weigh 1,792 g to the nearest 1 mg, dissolve in water and dilute to 1 000 ml.

Tests indicate that other cationic reagents, such as cetyl trimethyl ammonium bromide and benzalkonium chloride, give results identical to those obtained using benzethonium chloride. However, these tests have not been carried out in sufficient numbers to make it possible to state that the results will be identical no matter what the product analysed; for this reason, if benzethonium chloride is not available it is permitted to use another reagent provided that this is stated in the test report. However, in case of doubt, and always in case of dispute, only benzethonium chloride shall be used.

4.6.2 Standardization of the solution

By means of a pipette (5.4), transfer 25 ml of the standard volumetric sodium lauryl sulfate solution (4.5) to a bottle or measuring cylinder (5.1) or the titration vessel (5.5), and add 10 ml of water, 15 ml of chloroform (4.1) and 10 ml of the mixed indicator solution (4.8).

Titrate against the benzethonium chloride solution (4.6.1). If a bottle or measuring cylinder (5.1) is used, stopper the bottle or

1) Hyamine 1622 is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

measuring cylinder after each addition and shake well; if the titration vessel (5.5) with stirrer is used, run the stirrer for at least 4 s and then switch it off. The lower layer will be coloured pink. Continue the titration, with repeated vigorous shaking (if using 5.1) or stirring (if using 5.5). As the end point approaches, the emulsion formed during shaking tends to break easily. Continue the titration drop by drop, shaking after each addition of titrant, until the end point is reached. This is at the moment when the pink colour is completely discharged from the chloroform layer, which becomes a faint greyish blue.

4.6.3 Calculation of the concentration

Calculate the exact concentration c_1 of the benzethonium chloride solution, expressed in moles of $C_{27}H_{42}ClNO_2$ per litre, using the formula

$$\frac{c_2 \times 25}{V_2}$$

where

V_2 is the volume, in millilitres, of the benzethonium chloride solution used for the titration in 4.6.2;

c_2 has the same meaning as in 4.5.2.

4.7 Phenolphthalein, ethanolic solution containing 10 g/l

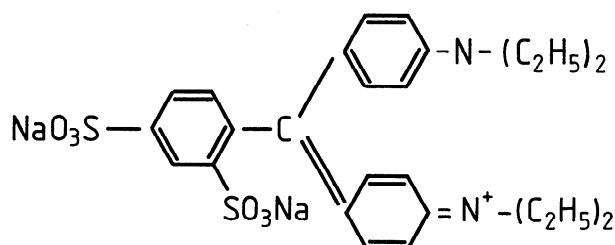
Dissolve 1 g of phenolphthalein in 100 ml of 95 % (V/V) ethanol.

4.8 Mixed indicator solution.¹⁾

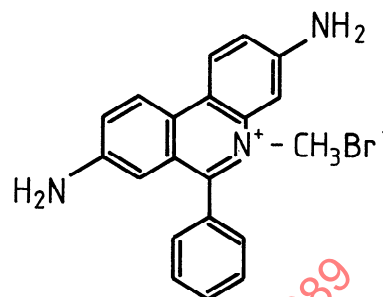
4.8.1 Stock solution

This solution shall be prepared from acid blue 1 and dimidium bromide.

4.8.1.1 Acid blue 1²⁾ (Colour Index 42045) (disodium-4',4''-dinitrilotriphenylmethane-2,4-disulfonate):



4.8.1.2 Dimidium bromide (3,8-diamino-5-methyl-6-phenyl-phenanthridinium bromide):



4.8.1.3 Preparation of the stock solution

Weigh, to the nearest 1 mg, 0,5 g $\pm$ 0,005 g of dimidium bromide (4.8.1.2) into a 50 ml beaker, and 0,25 g $\pm$ 0,005 g of acid blue 1 (4.8.1.1) into a second 50 ml beaker.

Add between 20 ml and 30 ml of hot 10 % (V/V) ethanol to each beaker.

Stir until dissolved and transfer the solutions to a 250 ml one-mark volumetric flask. Rinse the beakers into the volumetric flask with the ethanol and dilute to the mark with the ethanol.

4.8.2 Acid solution

Add 200 ml of water to 20 ml of the stock solution (4.8.1) in a 500 ml one-mark volumetric flask. Add 20 ml of the approximately 245 g/l sulfuric acid solution (4.2), mix and dilute to the mark with water. Store in the dark.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Bottles or measuring cylinders, 100 ml capacity, with ground glass stoppers.

5.2 Burettes, 25 ml and 50 ml capacity, complying with the requirements of class A of ISO 385-1.

5.3 One-mark volumetric flask, 1 000 ml capacity, with ground glass stopper, complying with the requirements of ISO 1042.

5.4 One-mark pipettes, 25 ml capacity, complying with the requirements of Class A of ISO 648.

5.5 Titration vessel, with suitable stirrer (see figure 1) driven by a motor.

5.6 Automatic burette, motorized piston type, 20 ml capacity, of accuracy similar to those specified in 5.2.

1) This mixed indicator is available commercially in the form of a basic solution, which should be acidified and diluted before use.

2) Acid blue 1, VS blue and disulfine blue VN 150 are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

6 Sampling

The laboratory sample shall be prepared and stored in accordance with the instructions given in ISO 607.

7 Procedure

WARNING — Comply with safety regulations relating to the handling of toxic solvents.

7.1 Test portion

Weigh, to the nearest 1 mg, into a 150 ml beaker, an amount of the laboratory sample (see clause 6) which contains about 0,003 mol to 0,005 mol of anionic-active matter.

NOTE — Table 1 below, which has been calculated on the basis of a relative molecular mass of 360, may be used as a rough guide.

Table 1 — Mass of test portion

Amount of active matter in sample % (m/m)	Mass of test portion g
15	10,0
30	5,0
45	3,2
60	2,4
80	1,8
100	1,4

7.2 Determination

Dissolve the test portion in water. Add a few drops of the phenolphthalein solution (4.7) and neutralize to a faint pink colour with the sodium hydroxide solution (4.4) or sulfuric acid solution (4.3), as required.

Transfer quantitatively to a 1 000 ml one-mark volumetric flask (5.3) with ground glass stopper, and dilute to the mark with water. Mix thoroughly and, by means of a pipette (5.4), transfer 25 ml of this solution to a bottle or measuring cylinder (5.1) or the titration vessel (5.5), and add 10 ml of water, 15 ml of chloroform (4.1) and 10 ml of the mixed acid indicator solution (4.8).

Titrate against the benzethonium chloride solution (4.6) as described in 4.6.2, beginning at the second paragraph.

8 Expression of results

8.1 Calculation

The anionic-active matter content, expressed as a percentage by mass, is given by the formula

$$\frac{V_3 c_1 M_r \times 1\,000 \times 100}{m_0 \times 25 \times 1\,000}$$

$$= \frac{4 V_3 c_1 M_r}{m_0}$$

where

V_3 is the volume, in millilitres, of benzethonium chloride solution (4.6) used for the titration of a 25 ml aliquot of anionic-active matter solution;

M_r is the relative molecular mass of the anionic-active matter;

m_0 is the mass, in grams, of the test portion (see 7.1);

c_1 is as defined in 4.6.3.

8.2 Precision

8.2.1 Repeatability

The difference between the results of two determinations carried out on the same sample simultaneously or in rapid succession by the same analyst using the same apparatus should not exceed 1,5 % of the mean value.

8.2.2 Reproducibility

The difference between the results obtained on the same sample in two different laboratories should not exceed 3 % of the mean value.

9 Test report

The test report shall include the following particulars:

- all information necessary for the complete identification of the sample;
- the method used (a reference to this International Standard and whether the manual or automatic method was used);
- the results obtained and the way in which they have been expressed;
- details of any operations not specified in this International Standard or in the International Standards to which reference is made, and any operations regarded as optional, as well as any incidents likely to have affected the results.