INTERNATIONAL STANDARD ISO 2271

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Surface active agents – Detergents – Determination of anionic-active matter (direct two-phase titration procedure)

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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.

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

It was approved in August 1971 by the Member Bodies of the following countries :

Austria
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Surface active agents — Detergents — Determination of anionic-active matter (direct two-phase titration procedure)

1 SCOPE

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

2 FIELD OF APPLICATION

This method is applicable to the analysis of alkylbenzene sulphonates, alkyl sulphonates, sulphates and hydroxysulphates, alkylphenol and fatty alcohol ethoxysulphates and dialkylsulphosuccinates and to the determination of active materials containing one hydrophilic group per molecule.

NOTE — Low relative molar mass sulphonates present as hydrotropes (toluene, xylene) do not interfere when present in concentations up to 15 % (m/m) on active material. At higher levels, their influence must be evaluated in each particular case.

Soap, urea and ethylenediaminetetra-acetic acid salts do not interfere.

Typical inorganic components of detergent formulations such as sodium chloride, sulphate, borate, tripolyphosphate, perborate, silicate, etc., do not interfere but bleaching agents other than perborate should be destroyed before the analysis.

3 REFERENCES

ISO/R 385, *Burettes.*

ISO/R 648, *One-mark pipettes.*

ISO/R 1042, *One-mark volumetric flasks.*

4 PRINCIPLE

Determination of anionic-active matter in a medium consisting of an aqueous and a chloroform phase, by volumetric titration with a standard 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 red-pink colour.

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

5 REAGENTS

The water used shall be distilled water or water of at least equivalent purity.

The reagents used shall have the following properties :

5.1 Chloroform, $\rho_{20} = 1.48$ g/ml, distilling between 59.5 and 61.5 °C.

5.2 Sulphuric acid, 5 N solution.

Carefully add 134 ml of sulphuric acid, $\rho_{20} = 1.83$ g/ml, to 300 ml of water and dilute to 1 l.

5.3 Sulphuric acid, 1.0 N solution.

5.4 Sodium hydroxide, 1.0 N standard volumetric solution.

5.5 Sodium lauryl sulphate (sodium dodecyl sulphate) [$CH_3(CH_2)_{11}OSO_3Na$], 0.004 M standard volumetric solution.

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

5.5.1 *Determination of purity of sodium lauryl sulphate*

Weigh, to the nearest 1 mg, 5 ± 0.2 g of the product into a 250 ml round bottom flask with ground glass neck. Add exactly 25 ml of the sulphuric acid solution (5.3) and reflux under a water condenser. During the first 5 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 clarifies and foaming ceases. 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 (5.7), and titrate the solution with the sodium hydroxide solution (5.4).

Carry out a blank test by titrating 25 ml of the sulphuric acid solution (5.3) with the sodium hydroxide solution (5.4).

The purity of the sodium lauryl sulphate, expressed as a percentage, is equal to

$$\frac{28.84\,(V_1 - V_0)\,T_0}{m_1}$$

where

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

V_1 is the volume, in millilitres, of sodium hydroxide solution used for the sample;

m_1 is the mass, in grams, of the sodium lauryl sulphate to be checked.

T_0 is the exact normality of the sodium hydroxide solution.

5.5.2 *0.004 M sodium lauryl sulphate standard volumetric solution*

Weigh, to the nearest 1 mg, between 1.14 and 1.16 g of sodium lauryl sulphate and dissolve in 200 ml of water. Transfer to a ground glass stoppered 1 l one-mark volumetric flask and dilute to the mark with water.

Calculate the molarity, T_2, of the solution by means of the formula :

$$T_2 = \frac{m_2 \times \text{purity (\%)}}{288.4 \times 100}$$

where m_2 is the mass, in grams, of sodium lauryl sulphate.

5.6 Benzethonium chloride[1], 0.004 M standard volumetric solution.

Benzyl dimethyl -2- [2- *p* (1,1,3,3 -tetramethylbutyl) phenoxy-ethoxy]-ethyl ammonium chloride, monohydrate.

$[(CH_3)_3\text{-}C\text{-}CH_2\text{-}C\text{-}(CH_3)_2\text{-}C_6H_4OCH_2\text{-}CH_2\text{-}OCH_2\text{-}CH_2\text{-}N\text{-}(CH_3)_2\text{-}CH_2\text{-}C_6H_5]^+Cl^-, H_2O$

Weigh, to the nearest 1 mg, between 1.75 and 1.85 g of benzethonium chloride and dissolve in water.

Transfer to a ground glass stoppered 1 l one-mark volumetric flask and dilute to the mark with water.

NOTES

1 In order to prepare a 0.004 M solution, dry the benzethonium chloride at 105 °C, weigh 1.792 g, to the nearest 1 mg, dissolve in water and dilute to 1 l.

2 Tests which have been carried out 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 number 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 a dispute, only benzethonium chloride should be used.

5.7 Phenolphthalein, ethanolic solution containing 10 g/l.

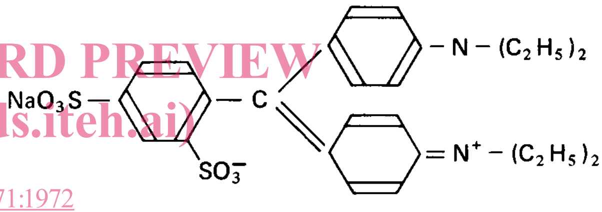
Dissolve 1 g of phenolphthalein in 100 ml of 95 % (V/V) ethanol.

5.8 Mixed indicator.[2]

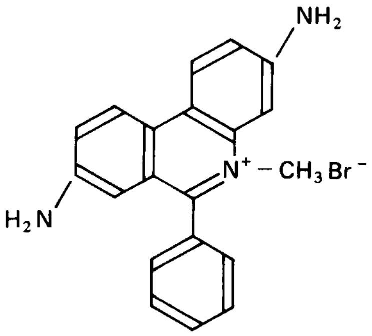
5.8.1 *Stock solution*

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

5.8.1.1 Acid blue 1[3] (C.I. 42045) (di-sodium-4′,4″-diaminodiethyltriphenylmethane-2,4-disulphonate)



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



5.8.1.3 Preparation of the stock solution

Weigh, to the nearest 1 mg, 0.5 ± 0.005 g of dimidium bromide (5.8.1.2) into a 50 ml beaker, and 0.25 ± 0.005 g of acid blue 1 (5.8.1.1) into a second 50 ml beaker.

Add between 20 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 10 % (V/V) ethanol.

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[1] The commercial product is also known under the name of "Hyamine 1622".

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

[3] This material is known commercially by, for example, the names Disulphine Blue VN 150 and Erioglaucine.

5.8.2 *Mixed acid indicator solution*

Add 200 ml of water to 20 ml of the stock solution (5.8.1) in a 500 ml one-mark volumetric flask. Add 20 ml of the 5 N sulphuric acid (5.2), mix and dilute to the mark with water. Store out of direct sunlight.

6 APPARATUS

Ordinary laboratory apparatus and

6.1 Bottles, 200 ml, glass stoppered, or **measuring cylinders,** 100 ml, glass stoppered.

6.2 Burettes, 25 ml and 50 ml, complying with class A of ISO/R 385.

6.3 One-mark volumetric flask, 1 l capacity, with ground glass stopper, complying with ISO/R 1042.

6.4 One-mark pipette, 25 ml, complying with Class A of ISO/R 648.

7 PROCEDURE

7.1 Standardization of benzethonium chloride solution

By means of the pipette (6.4), transfer 25 ml of the 0.004 M sodium lauryl sulphate solution (5.5) to a bottle or measuring cylinder (6.1); add 10 ml of water, 15 ml of the chloroform (5.1) and 10 ml of the mixed indicator solution (5.8).

Titrate with the 0.004 M benzethonium chloride solution (5.6); stopper the bottle or measuring cylinder after each addition and shake well. The lower layer will be coloured pink. Continue the titration, with repeated vigorous shaking. As the end point approaches, the emulsions formed during shaking tend 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.

The molarity, T_1, of the benzethonium chloride solution is given by the formula :

$$T_1 = \frac{T_2 \times 25}{V_2}$$

where

T_2 is the molarity of the sodium lauryl sulphate solution;

V_2 is the volume, in millilitres, of benzethonium chloride solution added.

7.2 Test portion

Weigh, to the nearest 1 mg, a sample which contains 3 to 5 milliequivalents of anionic-active matter.

NOTE – The table below, which has been calculated on the basis of a relative molar mass of 360, may be used as a rough guide.

TABLE – **Mass of test portion**

Amount of active matter in sample	Mass of test portion
% (m/m)	g
15	10.0
30	5.0
45	3.2
60	2.4
80	1.8
100	1.4

7.3 Determination

Dissolve the test portion in water. Add a few drops of the phenolphthalein solution (5.7) and neutralize to a faint pink colour with the sodium hydroxide solution (5.4) or sulphuric acid solution (5.3), as required.

Transfer to a 1 l one-mark volumetric flask (6.3) and dilute to the mark with water. Mix thoroughly and, by means of the pipette (6.4), transfer 25 ml of this solution to a bottle or measuring cylinder (6.1); add 10 ml of water, 15 ml of chloroform (5.1) and 10 ml of the mixed acid indicator solution (5.8). Titrate with the benzethonium chloride solution (5.6) as described in 7.1.

8 EXPRESSION OF RESULTS

8.1 Calculation

The content, as a percentage by mass, of anionic-active matter is equal to

$$\frac{V_3 \times T_1 \times 1\,000 \times M \times 100}{25 \times 1\,000 \times m_0} = \frac{4 \times V_3 \times T_1 \times M}{m_0}$$

The amount of active matter, expressed in milliequivalents per gram, is equal to

$$\frac{40 \times V_3 \times T_1}{m_0}$$

where

m_0 *is the mass, in grams, of the test portion;*

M is the relative molar mass of anionic-active matter;

T_1 is the molarity of the benzethonium chloride solution (5.6);

V_3 is the volume, in millilitres, of benzethonium chloride solution (5.6) used for the titration of a 25 ml aliquot of anionic-active matter solution.

8.2 Repeatability

The maximum difference found between the results of two determinations carried out on the same product simultaneously or rapidly one after the other by the same analyst using the same apparatus shall not exceed 1.5 % of the average value.

8.3 Reproducibility

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

9 TEST REPORT

The test report shall include the following information :

a) all information necessary for the complete identification of the sample;

b) the method used;

c) the results obtained;

d) the test conditions;

e) any operational details not specified in this International Standard, or optional, as well as all incidents likely to have influenced the results.