

INTERNATIONAL STANDARD

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6845**

Second edition
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Surface active agents — Technical alkane sulfonates — Determination of the mean relative molecular mass of the alkane monosulfonates and the alkane monosulfonate content

*Agents de surface — Alcane-sulfonates techniques — Détermination de la masse
moléculaire relative moyenne des alcanemonosulfonates et de leur teneur*



Reference number
ISO 6845 : 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 6845 was prepared by Technical Committee ISO/TC 91, *Surface active agents*.

This second edition cancels and replaces the first edition (ISO 6845 : 1982), of which it constitutes a minor revision.

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Surface active agents — Technical alkane sulfonates — Determination of the mean relative molecular mass of the alkane monosulfonates and the alkane monosulfonate content

1 Scope

This International Standard specifies a method for the determination of the mean relative molecular mass of the alkane monosulfonates present in technical alkane sulfonates which do not contain significant quantities of paraffins, as well as a method for the determination of the alkane monosulfonate content.

The method is applicable to all alkali metal salts of the products of sulfochlorination and sulfoxidation of paraffins.

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.*

3 Definition

For the purposes of this International Standard, the following definition applies.

alkane monosulfonate: Alkali metal salt of the monosulfonic acids present in the technical products of sulfochlorination and sulfoxidation of straight-chain paraffins, free from branched-chain compounds, with a chain length of between 12 and 20 carbon atoms.

4 Principle

Dissolution of a test portion in ethanol and acidification of the ethanolic solution with hydrochloric acid.

Extraction with light petroleum in a liquid-liquid extractor, giving quantitative separation of the alkane monosulfonic acids into the light petroleum phase and of the alkane disulfonates and sulfate ions into the aqueous/ethanolic phase.

Evaporation of the light petroleum phase and addition of ethanol.

Removal of traces of alkali by means of a cation-exchange column.

Neutralization of the eluate with carbonate-free sodium hydroxide solution. Drying and weighing of the sodium alkane monosulfonates so formed. Calculation of the mean relative molecular mass of the alkanemonosulfonates and the alkanemonosulfonate content.

5 Reagents

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

5.1 Acetone.

5.2 Ethanol, 95 % (V/V).

5.3 Ethanol, 50 % (V/V) aqueous solution.

5.4 Light petroleum, distilling between 40 °C and 60 °C.

5.5 Hydrochloric acid, ρ_{20} 1,18 g/ml.

5.6 Sodium hydroxide, aqueous/ethanolic standard volumetric solution, $c(\text{NaOH}) = 0,1 \text{ mol/l}$, free from carbonates.

5.6.1 Preparation of the solution

Weigh, to the nearest 1 mg, into a 250 ml conical flask fitted with a soda-lime tube, 8,1 g of sodium hydroxide pellets and dissolve them in 100 ml of the ethanol (5.2).

Allow to cool. The main part of the sodium carbonate present, which is insoluble, will settle. Then, using a pipette, transfer 10,0 ml of the clear solution to a 200 ml one-mark volumetric flask and dilute to the mark with carbon-dioxide-free water.

5.6.2 Standardization of the solution

Determine the exact concentration of the sodium hydroxide solution (5.6.1) using potassium hydrogen phthalate as the primary standard and phenolphthalein as the indicator.

5.6.3 Check for absence of carbonates

Check that the solution is free from carbonates by transferring a small amount of the solution to a test tube and adding the same volume of a 130 g/l barium nitrate solution. The solution shall remain clear for at least 5 min for the sodium hydroxide solution to be considered suitable.

5.7 Bromophenol blue, 1 g/l ethanolic solution.

5.8 Cation-exchange resin, strongly acidic (sulfonic group), with a degree of cross-linking corresponding to 2 % of divinylbenzene.

6 Apparatus

Usual laboratory equipment and

6.1 Liquid-liquid extractor, of capacity about 300 ml, with two ground glass joints (see figure 1).

6.2 Round-bottomed flask, of capacity 500 ml, with a ground glass neck to fit the lower glass joint of the extractor (6.1).

6.3 Flat-bottomed flask, of capacity 250 ml, with a ground glass neck and a ground glass stopper.

6.4 Reflux condenser, with a ground glass joint at its lower end to fit the upper ground glass joint of the extractor (6.1).

6.5 Beakers, of capacity 150 ml.

6.6 Burette, of capacity 50 ml, complying with the requirements of ISO 385-1, class A.

6.7 Column for ion-exchange resin, of internal diameter 12 mm and height 150 mm.

6.8 Boiling water bath.

6.9 Water baths, capable of being maintained at about 70 °C, and between 25 °C and 40 °C, respectively.

6.10 Vacuum oven, capable of being maintained at 120 °C ± 2 °C.

6.11 Magnetic stirrer.

6.12 Rotary evaporator, with flat-bottomed flasks of capacity 250 ml.

6.13 Desiccator, containing phosphorus(V) oxide (P₂O₅).

7 Sampling

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

8 Procedure

8.1 Test portion

From the laboratory sample, weigh, to the nearest 1 mg, into a 150 ml beaker (6.5), a test portion containing about 0,6 g to 0,8 g of alkane monosulfonate.

8.2 Preparation of the cation-exchange column

Into a 150 ml beaker (6.5), place 10 ml of the cation-exchange resin (5.8) and 30 ml of hydrochloric acid solution [prepared by mixing 10 ml of the hydrochloric acid (5.5) with 20 ml of water]. By means of the magnetic stirrer (6.11), stir slowly for 2 h.

Allow the resin to settle, replace the aqueous phase by 30 ml of the 95 % (V/V) ethanol (5.2) and stir slowly for 1 h.

Transfer the resin to the column (6.7). Stir the resin in the column to remove air bubbles and wash it with the ethanol (5.2) until chloride ions can no longer be detected in the eluate.

IMPORTANT — Do not allow the column to run dry. Ensure that the resin is always impregnated with liquid.

Adjust the rate of elution to about 6 ml/min for filling, washing or regeneration. If the resin has never been used before, wash it several times with hydrochloric acid and warm water before washing it with ethanol.

8.3 Regeneration of the column

After about 100 determinations, pass 30 ml of hydrochloric acid solution [prepared by mixing 10 ml of the hydrochloric acid (5.5) with 20 ml of water] through the column and wash with 50 ml of water followed by 50 ml of the ethanol (5.2). Continue washing with ethanol until chloride ions can no longer be detected in the eluate.

8.4 Determination

WARNING — Evaporate the petroleum and ethanolic solutions in a well-ventilated fume cupboard.

Dissolve the test portion (8.1) in 50 ml of the 50 % (V/V) ethanol (5.3) and 20 ml of the hydrochloric acid (5.5). Transfer the solution quantitatively from the beaker to the extractor (6.1), rinsing with 30 ml of ethanol (5.3).

Fit the extractor (6.1) to the flask (6.2) containing about 400 ml of the light petroleum (5.4) and fit the reflux condenser (6.4) to the extractor.

Heat the contents of the flask to boiling on the water bath (6.9), maintained at about 70 °C, and carry out the extraction for 5 h at a distillation rate of about 1,5 l/h.

NOTE — After extraction for about 4 h, the intermediate phase which often forms at the beginning of the extraction between the aqueous alcoholic and the light petroleum layers should disappear. If this is not the case, the proportions of water, ethanol and hydrochloric acid are unsatisfactory. It is then preferable to extract a new test portion.

Remove the flask (6.2) from the extractor (6.1) and evaporate to dryness on the water bath (6.9) maintained at about 70 °C, while passing a gentle current of nitrogen over the surface of the liquid in order to accelerate the evaporation, or evaporate using the rotary evaporator (6.12), on the water bath (6.9) maintained at between 25 °C and 40 °C, and under a vacuum produced by a water-jet suction pump, for instance.

Dissolve the residue in 50 ml of the 95 % (V/V) ethanol (5.2) and pass this solution through the previously prepared cation-exchange column (see 8.2).

Collect the eluate in the flat-bottomed flask (6.3) containing some antibumping granules and previously tared with its stopper. Wash the column with 100 ml of the ethanol (5.2), collecting the washings in the flask.

Add a few drops of the bromophenol blue solution (5.7) to the eluate. Stir this solution using the magnetic stirrer (6.11) and add the sodium hydroxide solution (5.6) by means of the burette (6.6) until a blue colour is obtained.

Evaporate the neutralized solution to dryness on the boiling water bath (6.8), while passing a gentle current of nitrogen over the surface of the solution, or evaporate using the rotary evaporator (6.12) on the water bath (6.9) maintained at between 25 °C and 40 °C, and under a vacuum produced by a water-jet suction pump, for instance.

To eliminate the last traces of water, carry out the following procedure three times: dissolve the residue in 10 ml of the acetone (5.1) and evaporate to dryness on the boiling water bath (6.8), while passing a gentle current of nitrogen over the surface of the solution, or by means of the rotary evaporator (6.12).

Dry the residue and the flask for 1 h in the vacuum oven (6.10), maintained at 120 °C ± 2 °C, allow to cool in the desiccator and weigh the stoppered flask (6.3) to the nearest 1 mg.

Repeat the operations of drying, cooling and weighing until the difference between two successive weighings does not exceed 1 mg.

9 Expression of results

9.1 Method of calculation

9.1.1 Mean relative molecular mass

The mean relative molecular mass, \bar{M}_r , of the sodium alkane monosulfonate present in the technical alkane sulfonate is given by the formula

$$\frac{m_1}{V \cdot c} \times 1\,000 = \frac{1\,000 m_1}{V \cdot c}$$

where

m_1 is the mass, in grams, of the sodium monosulfonate residue obtained in 8.4;

V is the volume, in millilitres, of the sodium hydroxide solution (5.6) used for neutralization of the extracted monosulfonic acid;

c is the exact concentration, in moles of NaOH per litre, of the sodium hydroxide solution (5.6).

9.1.2 Alkane monosulfonate content

The alkane monosulfonate content of the diluted sample, expressed as a percentage by mass, is given by the formula

$$\frac{m_1 \times 100}{m_0}$$

The alkane monosulfonate content of the raw material, expressed as a percentage by mass, is given by the formula

$$\frac{m_1 \times 100}{m_0} \times \frac{1}{f}$$

where

m_0 is the mass, in grams, of the test portion (8.1);

m_1 is as defined in 9.1.1;

f is the dilution factor of the laboratory sample.

9.2 Precision

9.2.1 Mean relative molecular mass

Comparative analyses on a sample in the form of a homogeneous aqueous solution containing about 25 % (m/m) of total soluble matter (comprising alkane mono-, di- and polysulfonates in the form of their sodium salts, sodium sulfate and small quantities of paraffins), carried out in 17 laboratories, have given the following statistical results:

- mean (mean relative molecular mass): 320
- standard deviation of repeatability, σ_r : 2,03
- standard deviation of reproducibility, σ_R : 6,49

9.2.2 Alkane monosulfonate content

Comparative analyses on a sample in the form of a homogeneous aqueous solution containing about 20 % (m/m) of total soluble matter (comprising alkane mono-, di- and polysulfonates in the form of their sodium salts, sodium sulfate and small quantities of paraffins), carried out in 24 laboratories, have given the following statistical results:

- mean [alkane monosulfonates, % (m/m)]: 16,92
- standard deviation of repeatability, σ_r : 0,15
- standard deviation of reproducibility, σ_R : 0,29

10 Test report

The test report shall include the following particulars:

- a) all the information necessary for the complete identification of the sample;
- b) the method used (a reference to this International Standard);
- c) the results and the way in which they have been expressed;
- d) 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, together with details of any incidents likely to have affected the results.

Dimensions in millimetres

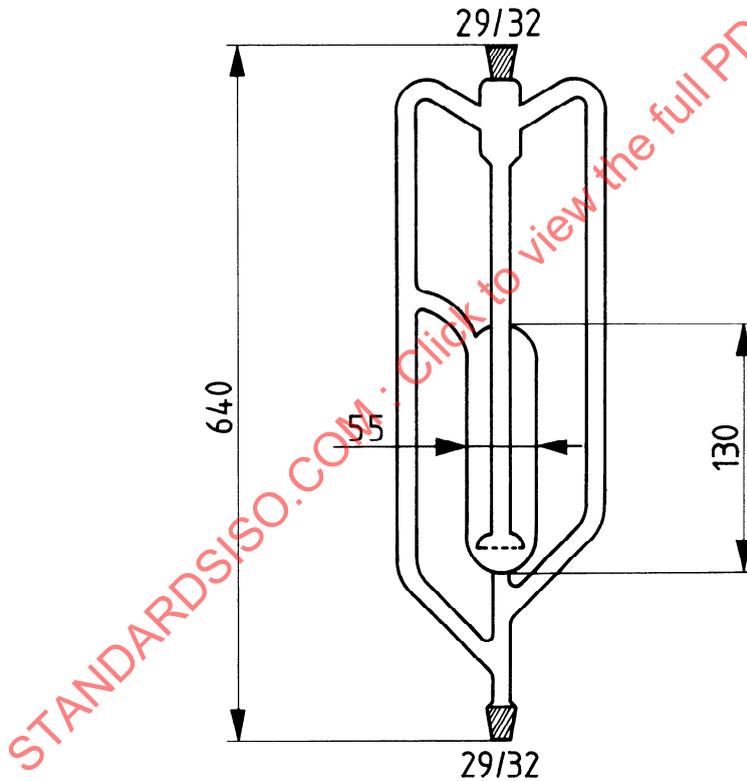


Figure 1 – 300 ml liquid-liquid extractor (6.1)