UDC 661.185 : 543

Ref. No. : ISO/R 1104-1969 (E)

Louise

# ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

# ISO RECOMMENDATION

# R 1104

## SURFACE ACTIVE AGENTS

## TECHNICAL SODIUM ALKYLARYLSULPHONATES

## METHODS OF ANALYSIS

1st EDITION

September 1969





For each individual country the only valid standard is the national standard of that country.

Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

## BRIEF HISTORY

The ISO Recommendation R 1104, *Surface active agents – Technical sodium alkylarylsulphonates – Methods of analysis*, was drawn up by Technical Committee ISO/TC 91, *Surface active agents*, the Secretariat of which is held by the Association Française de Normalisation (AFNOR).

Work on this question led to the adoption of a Draft ISO Recommendation.

In December 1967, this Draft ISO Recommendation (No. 1037) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

| | | |
|---|---|---|
| Austria | Iran | Romania |
| Belgium | Ireland | South Africa, Rep. of |
| Canada | Israel | Spain |
| Chile | Italy | Sweden |
| Czechoslovakia | Japan | Switzerland |
| France | Korea, Rep. of | Turkey |
| Germany | Netherlands | U.A.R. |
| Greece | New Zealand | United Kingdom |
| Hungary | Poland | Yugoslavia |
| India | Portugal | |

No Member Body opposed the approval of the Draft.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in September 1969, to accept it as an ISO RECOMMENDATION.

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ISO Recommendation R 1104 September 1969

# SURFACE ACTIVE AGENTS

# TECHNICAL SODIUM ALKYLARYLSULPHONATES

# METHODS OF ANALYSIS



## INTRODUCTION

Sodium alkylarylsulphonates have the general formula

$$(R)_n - Ar - SO_3Na$$

and are used as surface active agents in a vast range of processes. They are sodium salts of alkylarylsulphonic acids in which the saturated aliphatic radical R may have a mean chain length of about 12 carbon atoms; $n$ may be equal to 1, 2 or 3 and Ar is an aromatic derivative of either benzene or naphthalene.

## PART I

## GENERAL

### 1. SCOPE

This ISO Recommendation describes methods of analysis of technical sodium alkylarylsulphonates. It covers the following :

(1) Determination of water content.

(2) Measurement of pH.

(3) Determination of free acidity or free alkalinity.

(4) Determination of matter extractable by hexane.

(5) Determination of sodium alkylarylsulphonate content.

(6) Determination of sodium sulphite content.

(7) Determination of organic sulphur derived from the sulphonate group (Wurzschmitt method).

(8) Determination of sodium sulphate content.

(9) Determination of sodium chloride content.

It also describes, in appendices,

(1) a general scheme of analysis;

(2) a method for the determination of water content, using the Karl Fischer technique with two solutions;

(3) a rapid method for the determination of sodium alkylarylsulphonates;

(4) a method for the determination of the content of organic sulphur arising from the sulphonate group of sodium alkylarylsulphonates, isolated in accordance with Part VI of this ISO Recommendation (Grote-Krekeler method).

## 2. FIELD OF APPLICATION

This ISO Recommendation applies to technical sodium alkylarylsulphonates, in paste or powder form, and free from any products extraneous to their manufacture.

It does not apply to liquid products since these often contain either solvents or additives, or both, which would interfere with the methods of analysis specified in this ISO Recommendation.

## 3. PREPARATION OF SAMPLE

### 3.1 Procedure

In all cases and as a first step, prepare a representative sample. The procedure depends on the physical nature of the product.

3.1.1 *Products in powder form.* If a suitable conical divider is available, proceed in accordance with ISO Recommendation R 607, *Surface active agents in powder form – Preparation of a reduced sample*, until a reduced sample of approximately 300 g is obtained.

If such a divider is not available, spread a representative mass of 1000 g of the product, in powder form, on a sheet of white filter paper. Crush any large grains by means of a spatula. Then, using the method of alternate quarters, form a representative sample of approximately 300 g.

3.1.2 *Products in paste form.* First of all determine the pH value of the paste by means of contact electrodes or a suitable indicator paper. If the pH is not below 7, the following procedure may be adopted : Stir the paste with a stout glass rod, at the same time exposing it to a moderate heat of 50 to 60 °C (water bath or hotplate) until a homogeneous mass is obtained. While still stirring it, let it cool to a temperature between 15 and 30 °C, in this way obtaining a very thick paste, which may be regarded as an average representative sample.

The mass (including the glass rod) should be determined both before and after the operation in order to determine any losses due to evaporation of water, which should be taken into consideration.

If, on the other hand, the pH value of the paste is below 7, for each 50 g of paste add five drops of 0.2 % alcoholic solution of phenolphthalein; stir with a strong nickel spatula, then, still stirring, add 0.5 N alcoholic potassium hydroxide, drop by drop, until a pink colour is obtained. Then proceed as specified above. (See Part III, section 2, and Part IV, section 3, of this ISO Recommendation.)

### 3.2 Storage

Pastes should not be stored in metal containers, but in wide-necked glass bottles with ground glass stoppers.

## 4. GENERAL PRINCIPLE*

Preparation of an aqueous alcoholic solution of a test portion of the raw material from which are isolated the products extractable by hexane.

Dilution of an aliquot portion of the remaining liquid with an appropriate quantity of propan-2-ol, saturation with anhydrous sodium carbonate, and separation of the sodium alkylarylsulphonates in solution in propan-2-ol by salting out. Determination of the organic sulphur content after evaporation of all the solvent.

On other aliquot portions of the same remaining liquid,

- determination of sodium sulphite content;
- determination of sodium chloride content.

On separate test portions of the representative sample of the raw material,

- determination of water content;
- measurement of pH;
- determination of free acidity or free alkalinity;
- determination of sodium sulphate content.



* See the general scheme of the method in Appendix W.

PART II

## DETERMINATION OF WATER CONTENT

Depending on the amount of water in the product, carry out the determination according to one of the two following methods :

(*a*) the Karl Fischer method, applicable to products having up to 10 % of water;

(*b*) the azeotropic method, which should be used only for products containing more than 5 % of water.

### 1. KARL FISCHER METHOD

#### 1.1 Introduction

The Karl Fischer reagent is a solution containing anhydrous pyridinium sulphite and iodine, which are transformed in the presence of the slightest trace of water into pyridinium sulphate and hydriodic acid respectively.

It is possible to proceed in one of two ways, as follows :

(*a*) by determining the water in the product directly with the Karl Fischer reagent as a single solution. As the liquid has reduced stability unless it has been specially stabilized, this technique is recommended only when the determination has to be carried out frequently enough for the single reagent to be used up each day, or when the stabilized reagent is available;

(*b*) by determining the water by means of the iodine solution after adding anhydrous pyridinium sulphite solution to the product. These two liquids can be kept much longer apart than when mixed and this technique, although also applicable in the other case, is particularly recommended when determinations have to be carried out at more or less regular intervals.

#### 1.2 Method using a single solution

In a solution or suspension, in methanol, of a test portion of the representative sample of the raw material, such that the water it contains requires a measurable quantity of Karl Fischer reagent, determine the water in accordance with ISO Recommendation R 760, *Determination of water by the Karl Fischer method.*

*Reproducibility*

The difference between the results obtained on the same sample, in two different laboratories, should not exceed 0.2 g of water for 100 g of sample.

#### 1.3 Method using two solutions

See Appendix X.

## 2. AZEOTROPIC METHOD

### 2.1 Principle

Entrainment of the water in the vapour state by boiling xylene.

### 2.2 Reagent

*Xylene, commercial quality* (any isomer or mixture of isomers in any proportion), saturated with water.

### 2.3 Apparatus

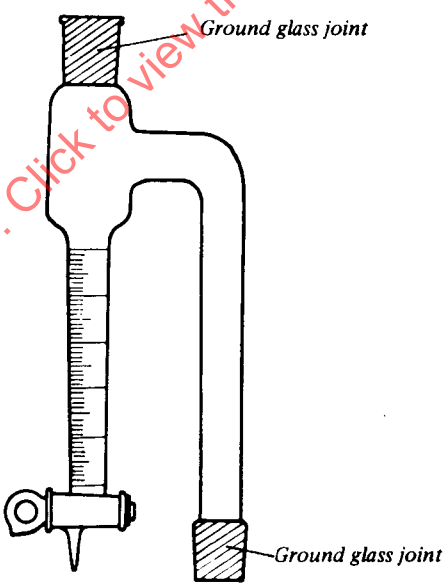
2.3.1 *Apparatus* comprising the following :

(*a*) *a short-neck round-bottomed flask*, of capacity not less than 500 ml, connected to the tube shown below by means of a ground glass joint;

(*b*) *a graduated cylindrical tube*, shown diagramatically below, with or without a discharge tap;

(*c*) *a straight reflux condenser*, connected to the tube by means of a ground glass joint.

2.3.2 *Analytical balance*




NOTE. – Before use, clean the graduated tube and the interior of the reflux condenser, so that they are free from all trace of fatty matter, for example, by washing them successively with chromic-sulphuric acid mixture, then with distilled water, and finally with acetone. Dry them. Perfect cleanliness of the apparatus is essential to the success of the test.

### 2.4 Procedure

**2.4.1** *Test portion.* Weigh, to the nearest 0.01 g, 10 to 50 g of the representative sample of the raw material into the flask according to whether it is a paste or a powder.

**2.4.2** *Determination.* Add to the test portion 100 to 300 ml of xylene (2.2) and a dry boiling aid, for example, a few fragments of pumice stone.

Connect the flask to the rest of the apparatus.

Heat gradually to boiling (2 to 3 drops per second) and maintain at this temperature until the distilled xylene becomes clear and water no longer separates from it.

If drops of water adhere to the sides of the tube, remove them, for example, by warming the tube carefully using a small flame.

If foaming is troublesome during the determination, it can be eliminated by adding dry paraffin wax or dry oleic acid to the flask.

Leave to settle until the water has completely separated without an emulsified layer.

Read the volume of the water in the graduated tube at the standard reference temperature of 20 °C.

### 2.5 Expression of results

**2.5.1** *Method of calculation and formula.* The percentage of water in the sample is equal to

$$V \times \frac{100}{M}$$

where

$M$ is the mass, in grammes, of the test portion;

$V$ is the volume, in millilitres, of the aqueous layer.

**2.5.2** *Reproducibility.* The difference between results obtained on the same sample, in two different laboratories, should not exceed 1 g of water per 100 g of sample

## PART III

## MEASUREMENT OF pH

### 1. PROCEDURE

Using distilled or deionized water with a pH between 6.5 and 7, prepare a 5 % (m/m) solution of the representative sample of the raw material (see section 2 below). Measure the pH to the nearest 0.1 pH unit by means of a pH meter suitable for this purpose.

Read the meter as rapidly as possible, i.e. between 30 seconds and 1 minute after immersion of the electrodes.

### 2. NOTE

In the case of products in paste form, a distinction has to be made between two cases, namely : during the preparation of the sample (see Part I, clause 3.1.2, of this ISO Recommendation) the raw material, in paste form, to be analysed has shown on preliminary examination either

(*a*) *a pH not below 7,* in which case it is possible to apply the procedure described in section 1 to a test portion of the representative sample of the raw material, prepared according to Part I, clause 3.1.2, of this ISO Recommendation; or

(*b*) *a pH below 7,* in which case it is necessary to apply the procedure described in section 1 to a test portion of the raw material as it is, whatever its state of homogeneity.

# PART IV

## DETERMINATION OF FREE ACIDITY OR FREE ALKALINITY

### 1. DEFINITION

By "free acidity" or "free alkalinity" is understood acidity or alkalinity determined, using phenolphthalein as indicator, under specified conditions. It is expressed as the acid value or the alkali value as the case may be.

### 2. PROCEDURE

Dissolve 10 g of the representative sample of the raw material (see section 3 below) in 100 ml of propan-2-ol, 50 % (V/V), previously neutralized, in the presence of phenolphthalein, and determine either the acidity or the alkalinity by titration with a suitable standard 0.1 N solution (0.1 N potassium hydroxide or 0.1 N hydrochloric or sulphuric acid).

### 3. NOTE

In the case of products in paste form, a distinction has to be made between two cases, namely : during the preparation of the sample (see Part I, clause 3.1.2, of this ISO Recommendation) the raw material, in paste form, to be analysed has shown on preliminary examination either

(*a*) *a pH not below 7,* in which case it is possible to apply the procedure described in section 2 to a test portion of the representative sample of the raw material, prepared according to Part I, clause 3.1.2; or

(*b*) *a pH below 7,* in which case it is necessary to apply the procedure described in section 2 to a test portion of the raw material as it is, whatever its state of homogeneity.

### 4. EXPRESSION OF RESULTS

Express the results as the acid value or alkali value, whichever is appropriate, that is in milligrammes of potassium hydroxide required to neutralize 1 g of the representative sample of the raw material.

The acid value (or alkali value) is equal to :

$$\frac{V \times 5.61}{M}$$

where

$M$ is the mass, in grammes, of the test portion;

$V$ is the volume, in millilitres, of the standard volumetric solution used.

NOTES

1. If the standard volumetric solution used is not exactly of strength 0.1 N, a suitable correction factor should be used in calculating the results.

2. When the value found is less than 0.3, express the result in the following form :

acid value, or alkali value (as appropriate) $< 0.3$

PART V

## DETERMINATION OF MATTER EXTRACTABLE BY HEXANE

### 1. INTRODUCTION

Matter extractable by hexane consists of sulphur-free products (non-sulphonated compounds and those which cannot be sulphonated) as well as, where applicable, products containing sulphur but not ionizable in an aqueous solution (sulphone, etc.).

### 2. PRINCIPLE

Extraction by means of hexane of the products specified in section 1, in the aqueous alcoholic solution of the test portion, taking into consideration the volatility of the products in question.

### 3. REAGENTS

3.1 *Propan-2-ol*, 15 % (V/V) solution in distilled water.

3.2 *Propan-2-ol*, 98 % (V/V) solution.

3.3 *Hexane*, not less than 95 % (V/V).*

3.4 *Sodium hydroxide*, approximately 0.1 N solution in distilled water.

3.5 *Sodium chloride*, 200 g/l solution in distilled water.

3.6 *Sodium sulphate*, neutral and anhydrous analytical reagent grade.

3.7 *Phenolphthalein*, 0.2 % solution in ethanol.

### 4. APPARATUS

*Ordinary laboratory apparatus* not otherwise specified, and the following items :

(*a*) *round-bottomed distillation flask*, 250 ml, with a standard socket;

(*b*) *fractionating column*, 20 cm long, with inside diameter approximately 10 mm, and a ground glass cone at its lower end to fit into the neck of the distillation flask;

(*c*) *three separating funnels*, 500 ml, with ground glass stopper;

(*d*) *straight condenser*, 80 cm long;

(*e*) *beaker*, 250 ml;

(*f*) *conical flask*, 250 ml;

(*g*) *volumetric flask*, 500 ml, with ground glass stopper.

(*h*) *glass beads;*

(*i*) *water bath;*

(*j*) *analytical balance.*

* If hexane is not available, freshly distilled light petroleum spirit, of boiling range 30 to 60 °C, may be used. In reporting the results, it should be stated which of the two solvents has been used.

## 5. PROCEDURE

### 5.1 Test portion

Weigh, to the nearest 0.01 g, a quantity of the representative sample of the raw material containing approximately 6 g of technical sodium alkylarylsulphonates, in the 250 ml beaker.

Let $M_0$ be the mass of the test portion.

### 5.2 Determination

Dissolve the test portion in 100 ml of distilled water. Heat if necessary, but not over 50 °C.

If necessary, render alkaline with sodium hydroxide (3.4), to the colour change shown by phenolphthalein (3.7). Transfer the solution quantitatively to a separating funnel and add 40 ml of propan-2-ol (3.2).

Carry out five extractions, using two separating funnels alternately, using 30 ml of hexane (3.3) each time.

During each extraction shake vigorously and allow the layers to settle well after each separation.

Combine the hydrocarbon extracts in a third separating funnel and wash four times with 40 ml portions of propan-2-ol solution (3.1). Run off the hexane layer. If an emulsion forms add sodium chloride solution (3.5) 5 ml at a time, shaking the flask and allowing the contents to settle after each addition until the emulsion is destroyed and complete separation occurs. One 5 ml portion will usually be sufficient. The quantity of sodium chloride (3.5) used to destroy the emulsion should be correct to ± 0.03 ml, in order to allow account to be taken of it in the sodium chloride determination (see Part X of this ISO Recommendation).

Return the propan-2-ol solution used for washing to the stock solution.

Transfer the hexane layer quantitatively from the third separating funnel to the 250 ml conical flask containing approximately 10 g of sodium sulphate (3.6). Shake for at least 3 minutes and then allow to stand for about 5 minutes.

Transfer the combined aqueous alcoholic layers that remain, quantitatively, into the 500 ml volumetric flask. Rinse each of the three separating funnels with 20 ml of propan-2-ol (3.1) three times. Add the rinsing solution to the volumetric flask, and make up to the mark with propan-2-ol solution (3.1). This solution, $L_1$, will be used for other determinations.

Filter the hexane layer through fast-running filter paper into the 250 ml distillation flask, containing a few glass beads, and previously tared. Wash the sodium sulphate, the conical flask and the filter with hexane (3.3) until no grease marks remain on the filter paper.

Attach the fractionating column to the distillation flask and distil, using a water bath. If water is present in material extracted with hexane, redissolve the material in hexane (3.3), filter and repeat the distillation. After distillation allow the flask to cool and remove the last traces of the solvent under a reduced pressure of 20 mbars (about 15 mmHg) at 30 °C so that the difference between subsequent weighings made at 20 minute intervals is only apparent in the third significant figure.

NOTE. – If only very little water is found in the extract (and in droplet form) an attempt can be made to remove it by adding about 3 ml of acetone and repeating the process of evaporation as indicated above.

## 6. EXPRESSION OF RESULTS

### 6.1 Method of calculation and formula

The percentage of matter extractable by hexane in the representative sample of the raw material is equal to

$$M_1 \times \frac{100}{M_0}$$

where

$M_0$ is the mass, in grammes, of the test portion (representative sample);

$M_1$ is the mass, in grammes, of the residue obtained.

### 6.2 Reproducibility

The difference between the results obtained, on the same sample, in two different laboratories, should not exceed 1 g of products extractable by hexane per 100 g of sample.

# PART VI

## DETERMINATION OF SODIUM ALKYLARYLSULPHONATES CONTENT

### 1. PRINCIPLE

Addition to 98 % propan-2-ol of an aliquot portion of the aqueous alcoholic liquor $L_1$, resulting from the previous determination (see Part V, clause 5.2 of this ISO Recommendation), then saturation with sodium carbonate at 45 to 50 °C.

The sodium alkylarylsulphonates are salted out and passed into solution in the propan-2-ol which separates.

Isolation of the sodium alkylarylsulphonates by evaporation of the solvent.

### 2. REAGENTS

2.1 *Propan-2-ol,* 98 % (V/V) solution,

2.2 *Sodium carbonate,* neutral, anhydrous, analytical reagent grade,

2.3 *Sulphuric acid,* 0.1 N standard volumetric solution in distilled water.

2.4 *Phenolphthalein,* 0.2 % solution in ethanol.

2.5 *1,4-Dioxan.*

### 3. APPARATUS

*Ordinary laboratory apparatus* not otherwise specified, and the following items :

(*a*) *two crystallizing dishes,* 80 mm in diameter and 200 ml capacity;

(*b*) *volumetric flask,* 250 ml;

(*c*) *conical flask,* 300 ml, with ground glass stopper;

(*d*) *separating funnel,* 250 ml;

(*e*) *water bath;*

(*f*) *sintered glass filter funnel,* 15 to 40 µm porosity;

(*g*) *oven,* regulated at 100 to 105 °C;

(*h*) *pipettes,* 50 and 100 ml;

(*i*) *analytical balance.*

## 4. PROCEDURE

### 4.1 Test portion

Using a pipette take 100 ml of the aqueous alcoholic solution $L_1$ produced during the previous analysis (see Part V, section 5, of this ISO Recommendation), and place it in the 300 ml conical flask.

### 4.2 Determination

Add 70 ml of propan-2-ol (2.1) to the test portion. Warm the water bath to 45 to 50 °C. Stirring all the time, add sodium carbonate (2.2) 4 to 5 g at a time until it fails to dissolve (30 g is generally sufficient).

Close the conical flask and shake vigorously, using a suitable method, for 5 minutes, keeping the temperature at 45 to 50 °C. Leave the liquid to settle at this temperature (if settling is unsatisfactory add 2 ml of 1,4-dioxan (2.5)).

Allow to cool without stirring *for 2 hours* at 30 °C. It is advisable not to allow the temperature to fall below this value, to avoid the sodium carbonate crystallizing out when the solution is transferred to the separating funnel as this would make separation very difficult. For the same reason it is advisable to warm the separating funnel to 40 to 50 °C before transferring the contents of the conical flask.

Transfer the liquid in the conical flask to the separating funnel. Run off the lower aqueous layer. Wash the sediment in the conical flask twice with 20 ml of propan-2-ol (2.1) and add the washings to the separating funnel.

Where applicable remove carefully all the aqueous phase. Transfer the propan-2-ol layer to the 250 ml volumetric flask, filtering on the sintered glass filter if necessary. Wash the filter and the separating funnel with propan-2-ol (2.1), add the washings to the volumetric flask and dilute to the mark.

Add to each crystallizing dish, previously weighed, exactly 50 ml of the solution in propan-2-ol using a 50 ml pipette. Evaporate nearly to dryness over the water bath in a fume cupboard and add with the pipette a further 50 ml of the solution in propan-2-ol to each of the dishes. Evaporate to dryness over the water bath in a fume cupboard and dry in the oven at 100 to 105 °C until constant mass is attained. The difference between two successive weighings made at an interval of 30 minutes should be apparent only in the third significant figure.

One of the two residues so obtained, $R_1$, is used in the determination of the organic sulphur derived from the sulphonate group (see Part VIII of this ISO Recommendation). The other residue, $R_2$, is dissolved in distilled water, heated if necessary to achieve complete solution. Check that this solution is alkaline to phenolphthalein, and determine the content of sodium carbonate which may have been carried over, with sulphuric acid (2.3) using phenolphthalein (2.4) as indicator. On the remaining aqueous liquor, determine the content of $Cl^-$ ions from any sodium chloride which may have been carried over, using the argentimetric method given in Part X of this ISO Recommendation.

## 5. EXPRESSION OF RESULTS

### 5.1 Method of calculation and formula

The percentage of sodium alkylarylsulphonates in the raw material is equal to

$$\frac{M_1 + M_2}{2} \times \left(1 - \frac{0.0106\,V_0 + 0.00585\,V_1}{M_2}\right) \times \frac{250}{100} \times \frac{500}{100} \times \frac{100}{M_0}$$

$$= \frac{M_1 + M_2}{2} \times \left(1 - \frac{0.0106\,V_0 + 0.00585\,V_1}{M_2}\right) \times \frac{1250}{M_0}$$

where

$M_0$ is the mass, in grammes, of the test portion specified in Part V, clause 5.1, of this ISO Recommendation (representative sample);

$M_1$ is the mass, in grammes, of the residue used for the determination of organic sulphur content;

$M_2$ is the mass, in grammes, of the residue used for the determination of sodium carbonate and of $Cl^-$ ions;

$V_0$ is the volume, in millilitres, of sulphuric acid (2.3) used in the determination of sodium carbonate content;

$V_1$ is the volume, in millilitres, of 0.1 N silver nitrate used in the determination of $Cl^-$ ion content (see Part X of this ISO Recommendation).

NOTE. – If the standard volumetric solution used is not exactly of strength 0.1 N, a suitable correction factor should be used in calculating the results.

### 5.2 Reproducibility

The difference between results obtained, on the same sample, in two laboratories, should not exceed 1 g of sodium alkylarylsulphonates per 100 g of sample.

NOTE. – For a check on the values by the method described above (content in raw material of technical sodium alkylarylsulphonates), see Appendix Y.

PART VII

## DETERMINATION OF SODIUM SULPHITE CONTENT

### 1. PRINCIPLE

Iodometric determination on a 100 ml aliquot portion of solution $L_1$. (See Part V, clause 5.2 of this ISO Recommendation.)

### 2. REAGENTS

2.1. *Iodine*, 0.1 N standard volumetric solution in distilled water,

2.2 *Hydrochloric acid*, 0.1 N volumetric solution in distilled water,

2.3 *Sodium thiosulphate*, 0.1 N standard volumetric solution in distilled water,

2.4 *Starch solution.*

### 3. APPARATUS

*Ordinary laboratory apparatus* not otherwise specified, and the following items :

(*a*) *pipettes*, 25 ml and 100 ml;

(*b*) *conical flask*, 500 ml.

### 4. PROCEDURE

#### 4.1 Test portion

Take 100 ml of solution $L_1$ remaining after the determination described in Part VI, clause 4.2, of this ISO Recommendation.

#### 4.2 Determination

Using a 25 ml pipette transfer 25 ml of iodine solution (2.1) into the conical flask and acidify with 100 ml of hydrochloric acid (2.2). Stir, and add the test portion, using the 100 ml pipette. Stir again and then back-titrate with sodium thiosulphate solution (2.3) using starch (2.4) as indicator.

#### 4.3 Blank test

Carry out a blank test under the same conditions.

## 5. EXPRESSION OF RESULTS

### 5.1 Method of calculation and formula

The percentage of sodium sulphite in the raw material is equal to

$$(V_0 - V_1) \times 0.003\,152 \times \frac{500}{100} \times \frac{100}{M_0} = \frac{1.576\,(V_0 - V_1)}{M_0}$$

where

$M_0$ is the mass, in grammes, of the test portion (see Part V, clause 5.1 of this ISO Recommendation);

$V_0$ is the volume, in millilitres, of sodium thiosulphate solution (2.3) used in the blank test;

$V_1$ is the volume, in millilitres, of sodium thiosulphate solution (2.3) used in the determination.

NOTE. – If the standard volumetric solution of sodium thiosulphate used is not exactly of strength 0.1 N, a suitable correction factor should be used in calculating the results.

### 5.2 Reproducibility

The difference between the results obtained, on the same sample, in two different laboratories, should not exceed 0.2 g of sodium sulphite per 100 g of sample.

NOTE. – A sodium sulphite content of less than 0.1 % should be described as "traces".

PART VIII

## DETERMINATION OF ORGANIC SULPHUR CONTENT ARISING FROM THE SULPHONATE GROUP (Wurzschmitt method)

### 1. PRINCIPLE

Conversion of the organic sulphur (from the sulphonate group of the sodium alkylarylsulphonates isolated as described in Part VI of this ISO Recommendation) by oxidative ashing to sulphate ion which is estimated gravimetrically as barium sulphate.

The oxidative ashing is carried out in a nickel bomb (the Wurzschmitt method).

NOTE. – See Appendix Z in which is described a method for the determination of organic sulphur (sulphur from the sulphonate group) by combustion in a current of air (the Grote-Krekeler method). This method may give additional analytical information.

### 2. REAGENTS

2.1 *Sodium peroxide.*

2.2 *Ethanediol.*

2.3 *Bromine.*

2.4 *Hydrochloric acid,* ($\rho_{20}$ = 1.19 g/ml), analytical reagent grade.

2.5 *Ammonia solution* ($\rho_{20}$ = 0.925 g/ml), analytical reagent grade.

2.6 *Methyl orange,* 0.2 % solution in distilled water.

2.7 *Barium chloride dihydrate,* ($BaCl_2.2H_2O$), 100 g/l solution in distilled water.

### 3. APPARATUS

*Usual laboratory apparatus* not otherwise specified, and the following items :

(*a*) *squat-form beakers,* 600 ml;

(*b*) *bomb,* pure nickel, 22 ml capacity, for sodium peroxide combustion*;

(*c*) *protective shield* and micro-burner;

(*d*) *analytical balance.*

* For example, the Parr bomb.

## 4. PROCEDURE

### 4.1 Test portion

Weigh, to the nearest 0.1 mg, about 0.3 g of the sodium alkylarylsulphonates, isolated as described in Part VI of this ISO Recommendation (residue $R_1$), into the nickel crucible of the bomb.

Let $M_0'$ be the mass of the material weighed.

### 4.2 Determination

Add several drops (about 0.15 to 0.20 g) of ethanediol (2.2) to the test portion from a pipette, then cover it with 6 to 8 g of sodium peroxide (2.1). Assemble the bomb and place it in the protective shield. Regulate the micro-burner so that the flame just plays on the bottom of the bomb. Combustion starts in 10 to 20 seconds. Leave the micro-burner under the bomb for a further 50 seconds.

Allow the bomb to cool, then open it and wash the bomb and lid quantitatively with hot distilled water in a 600 ml beaker. Place the nickel crucible in the 600 ml beaker and cover with 200 ml of hot distilled water.

Withdraw the crucible when the contents have dissolved, rinsing it quantitatively with hot distilled water.

Add 5 to 6 drops of bromine (2.3) to the solution. Boil it for 10 minutes. Cool, acidify it with hydrochloric acid (2.4) and boil it until bromine vapour is no longer evolved.

Filter it through paper into a second 600 ml beaker. Wash the filter paper quantitatively with distilled water.

Render the filtrate slightly alkaline with ammonia solution (2.5) then acidify it to methyl orange (2.6) with hydrochloric acid (2.4) adding an excess of 1 ml.

Bring it to the boil, then precipitate the $SO_4^{--}$ ion with barium chloride (2.7), determining it gravimetrically as barium sulphate.

## 5. EXPRESSION OF RESULTS

### 5.1 Method of calculation and formula

The percentage of sulphur (derived from the sulphonate group) in the sodium alkylarylsulphonates isolated in accordance with Part VI of this ISO Recommendation is equal to

$$M_3 \times 0.1374 \times \frac{100}{M_0' \left(1 - \frac{0.0106\, V_0 + 0.00585\, V_1}{M_2}\right)} = \frac{13.74\, M_3}{M_0' \left(1 - \frac{0.0106\, V_0 + 0.00585\, V_1}{M_2}\right)}$$

where

$M_0'$ is the mass, in grammes, of the test portion (sodium alkylarylsulphonates, residue $R_1$; see Part VI of this ISO Recommendation);

$M_2$ is the mass, in grammes, of residue $R_2$, obtained as in Part VI of this ISO Recommendation;

$M_3$ is the mass, in grammes, of barium sulphate;

$V_0$ is the volume, in millilitres, of 0.1 N sulphuric acid used in the determination of sodium carbonate content of residue $R_2$ (see Part VI, section 5, of this ISO Recommendation);

$V_1$ is the volume, in millilitres, of 0.1 N silver nitrate solution used in the determination of $Cl^-$ ions (see Part X of this ISO Recommendation).

NOTE. – If the standard volumetric solution used is not exactly of strength 0.1 N, a suitable correction factor should be used in calculating the results.

### 5.2 Reproducibility

The difference between results obtained, on the same sample, in two different laboratories, should not exceed 0.4 g of organic sulphur per 100 g of sample.

# PART IX

# DETERMINATION OF SODIUM SULPHATE CONTENT

## 1. PRINCIPLE

Complete separation, from a test portion of the representative sample of the raw material dissolved in distilled water, after treatment with hot hydrochloric acid, of alkylarylsulphonic acids as well as other organic compounds (see Part V of this ISO Recommendation) with pentan-l-ol. Determination of the content of $SO_4^{--}$ ions in the remaining acid solution by precipitation as barium sulphate.

## 2. REAGENTS

2.1 *Pentan-1-ol* (*n*-amyl alcohol)

2.2 *Hydrochloric acid* ($\rho_{20}$ = 1.19 g/ml), analytical reagent grade.

2.3 *Hydrochloric acid*, dilute solution ($\rho_{20}$ = 1.06 g/ml), prepared by the addition of 1 volume of hydrochloric acid (2.2) to 2 volumes of distilled water.

2.4 *Ammonia solution*, ($\rho_{20}$ = 0.925 g/ml), analytical reagent grade.

2.5 *Methyl orange*, 0.2 % solution in distilled water.

2.6 *Barium chloride dihydrate* ($BaCl_2.2H_2O$), 100 g/l solution in distilled water.

## 3. APPARATUS

*Ordinary laboratory apparatus*, not otherwise specified, and the following items :

(*a*) *volumetric flask*, 500 ml, with ground glass stopper;

(*b*) *three separating funnels*, 250 ml, with ground glass stopper;

(*c*) *beaker*, 100 ml;

(*d*) *analytical balance*.

## 4. PROCEDURE

### 4.1 Test portion

Weigh, to the nearest 0.01 g, about 3 g of the representative sample of the raw material in powder form or 10 g in paste form, as appropriate, into the 100 ml beaker.
Let the mass be $M_0$.

### 4.2 Determination

Add 50 ml of distilled water to the test portion and stir with a glass rod, heating if necessary until the material has dissolved completely. Add 24 ml of hydrochloric acid (2.2). Boil for 1 minute to drive off any sulphur dioxide which may have been formed and allow to cool. Transfer the solution quantitatively to a separating funnel. Shake three times with 30 ml portions of pentan-1-ol (2.1). Combine the extracts and wash them three times with 20 ml portions of hydrochloric acid (2.3).

Combine quantitatively the remaining acid solutions and the acid used for washing in the 500 ml volumetric flask. Dilute to the mark with distilled water.

Determine the sulphate ion content using the method described below, either on the whole sample or on an aliquot portion to obtain between 0.02 and 0.2 g of barium sulphate.

Neutralize with ammonia solution (2.4) using methyl orange indicator (2.5), then acidify with hydrochloric acid (2.2) adding an excess of 1 ml. Bring to the boil, then add barium chloride solution (2.6) and determine the $SO_4^{--}$ ion content gravimetrically, as barium sulphate precipitated.

## 5. EXPRESSION OF RESULTS

### 5.1 Method of calculation and formula

The percentage of sodium sulphate in the raw material is equal to

$$0.6086 \times M_1 \times \frac{500}{V} \times \frac{100}{M_0} = \frac{60.86\, M_1 \times 500}{M_0 \times V}$$

where

$M_0$ is the mass, in grammes, of the test portion;

$M_1$ is the mass, in grammes, of the precipitate;

$V$ is the volume, in millilitres, of the aliquot portion.

### 5.2 Reproducibility

The difference between results obtained, on the same sample, in two different laboratories, should not exceed 0.2 g of sodium sulphate per 100 g of sample.

NOTE. – A sodium sulphate content of less than 0.1 % should be described as "traces".

# PART X

## DETERMINATION OF SODIUM CHLORIDE CONTENT

### 1. PRINCIPLE

Argentimetric determination of the content of $Cl^-$ ions, in a 100 ml aliquot portion of solution $L_1$ (see Part V, clause 5.2, of this ISO Recommendation), by potentiometry.

### 2. REAGENTS

2.1 *Nitric acid* ($\rho_{20}$ = 1.33 g/ml), analytical reagent grade.

2.2 *Silver nitrate*, 0.1 N standard volumetric solution in distilled water.

### 3. APPARATUS

*Ordinary laboratory apparatus* not otherwise specified, and the following items :

(*a*) *beaker*, 300 ml;

(*b*) *graduated measuring cylinder*, 10 ml;

(*c*) *potentiometric titration apparatus*, of good construction, with a silver working electrode and a mercury/mercurous sulphate reference electrode (with potassium sulphate solution as bridge):

NOTE. – If a reference electrode of this type is not available, a calomel electrode may be used instead but it should be connected by a potassium nitrate/agar bridge to the beaker in which the titration is carried out and into which the silver working electrode is immersed.

A bridge of this kind can easily be made as follows: saturate 100 ml of distilled water with approximately 32 g of potassium nitrate of analytical reagent quality and then add 4 g of agar. Heat at 70 °C until solution is complete. Fill a U-shaped capillary tube (internal diameter 2 to 3 mm, length of legs 8 to 10 cm, distance between legs about 6 cm), keeping it at about 70 °C, with the above solution and then let it cool. During cooling keep the open ends of the legs in the solution.

(*d*) *magnetic stirrer;*

(*e*) *pipette*, 100 ml;

(*f*) *analytical balance.*

### 4. PROCEDURE

#### 4.1 Test portion

Using the pipette take 100 ml of solution $L_1$, remaining after the determination described in Part VI of this ISO Recommendation, and place it in the 300 ml beaker.

#### 4.2 Determination

Drive off the alcohol by heating on a water bath. Then add 100 ml of distilled water and 10 ml of nitric acid (2.1), measured with the graduated measuring cylinder, and place the magnetic stirrer in position. Stir for a few moments, then titrate with the silver nitrate solution (2.2).

The volume, in millilitres, of silver nitrate (2.2) used is obtained from the curve, mV/ml, or from the differential curve.

## 5. EXPRESSION OF RESULTS

### 5.1 Method of calculation and formula

The percentage of sodium chloride in the raw product is equal to

$$V_1 \times 0.005\ 85 \times \frac{500}{100} \times \frac{100}{M_0} = \frac{2.925\ V_1}{M_0}$$

where

$M_0$ is the mass, in grammes, of the test portion (see Part V of this ISO Recommendation);

$V_1$ is the volume, in millilitres, of silver nitrate (2.2) used.

NOTES

1. A sodium chloride content of less than 0.1 % should be described as "traces".
2. Take into account the quantity of sodium chloride added in the determination of matter extractable in hexane (see Part V of this ISO Recommendation).

### 5.2 Reproducibility

The difference between the results obtained, on the same sample, in two different laboratories, should not exceed 0.2 g of sodium chloride per 100 g of sample.



## PART XI

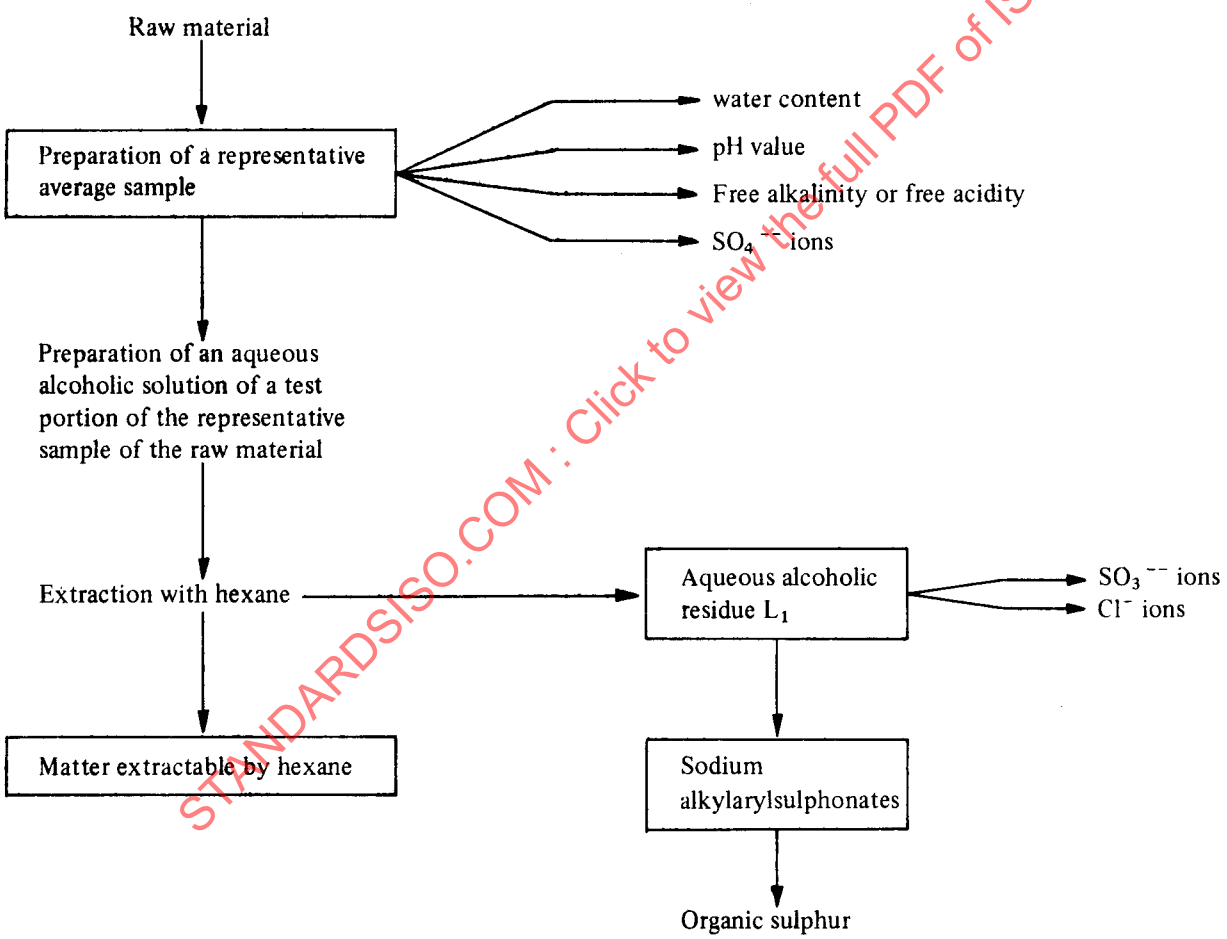
## REPORT OF THE ANALYSIS

The report of the analysis should indicate the methods used and the results obtained. It should also mention any details of procedure not specified in this ISO Recommendation, or any optional details, together with any circumstances which may have affected the results.

The report should include all details required for the complete identification of the sample.

APPENDIX W

## GENERAL SCHEME OF ANALYSIS



# APPENDIX X

## DETERMINATION OF WATER CONTENT

## (Karl Fischer method using two solutions)

### X.1 PRINCIPLE

Reaction of any water present on iodine and sulphur dioxide in a solution of methanol and pyridine (Karl Fischer reagent).

### X.2 REAGENTS

**X.2.1** *Karl Fischer reagent A*

Solution containing 100 g of anhydrous sulphur dioxide in 1000 ml of a solution (1/1 by volume) of absolute methanol and pyridine.

**X.2.2** *Karl Fischer reagent B*

Solution containing 80 g of resublimed iodine in 1000 ml of absolute methanol.

**X.2.3** *Standard reference solution,* as follows :

- *distilled water,*
- or *oxalic acid,* with 2 molecules of water of crystallization, analytical reagent grade,
- or *citric acid,* with 1 molecule of water of crystallization, analytical reagent grade,
- or *sodium tartrate,* with 2 molecules of water of crystallization, analytical reagent grade.

NOTE. – The two Karl Fischer reagents, A (X.2.1) and B (X.2.2), should be kept in flasks with ground glass stoppers and away from light and atmospheric humidity.

### X.3 APPARATUS

**X.3.1** *Karl Fischer apparatus,* which enables the titration to be carried out under protection from moisture in the air. It consists of two 25 ml volumetric burettes (A) and (B) graduated in 0.05 ml and provided with bulbs, with an electrometric titration device which indicates the end of titration.

**X.3.2** *Ordinary laboratory apparatus,* not otherwise specified, and the following items :

(*a*) *suitable titration vessels,* completely dry and clean, kept in a desiccator;

(*b*) *desiccator;*

(*c*) *precision pipettes,* 1 ml, which can be read to 0.05 ml;

(*d*) *magnetic stirrer;*

(*e*) *analytical balance.*

## X.4 PROCEDURE

### X.4.1 Test portion

Into a titration vessel, weigh to the nearest 0.001 g a quantity of the representative sample of the raw material such that the water which it contains requires a measurable quantity of Karl Fischer reagent (solution B).

### X.4.2 Blank test and determination of the water equivalent of solution B (X.2.2)

With the titration apparatus assembled and ready for titration, introduce exactly 25 ml of solution A (X.2.1) into the titration vessel, fitted with its magnetic stirrer, by means of burette (A).

Operate the magnetic stirrer, then using burette (B), introduce solution B (X.2.2) drop by drop until the end point is reached.

It is advisable to repeat the operation in order to verify the constancy of the volume of solution B (X.2.2) used.

Let $V_0$ be the volume, in millilitres, of solution B (X.2.2) used.

In another titration vessel, place by means of a precision pipette approximately 50 to 100 mg of distilled water*. Weigh to the nearest 0.1 mg. Fit the titration vessel in place and carry out the titration as above.

Let $V_1$ be the volume in millilitres of solution B (X.2.2) used.

The water equivalent, $EQ$, in milligrammes of water per millilitre of solution B (X.2.2), is given by the equation

$$EQ = \frac{M_1}{V_1 - V_0}$$

where

$M_1$ is the mass, in milligrammes, of water weighed;

$V_1$ is the volume, in millilitres, of solution B (X.2.2) used for the titration of the water weighed;

$V_0$ is the volume, in millilitres, of solution B (X.2.2) used for the titration of solution A (X.2.1).

### X.4.3 Determination proper

Place the magnetic stirrer in the titration vessel containing the test portion (X.4.1) and then fit the vessel to the titration apparatus. Using burette (A) introduce exactly 25 ml of solution A (X.2.1) into the titration vessel. Operate the stirrer for 5 minutes.

Then titrate with solution B (X.2.2), drop by drop, rapidly to begin with, and then more slowly, until the end point is reached.

Let $V_2$ be the volume, in millilitres, of solution B (X.2.2) used.



* or the equivalent mass of one of the other standard substances (X.2.3).