

Louise'e

**ISO**

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

**ISO RECOMMENDATION**  
**R 1104**

SURFACE ACTIVE AGENTS

**TECHNICAL SODIUM ALKYLARYLSULPHONATES**  
**METHODS OF ANALYSIS**

**1st EDITION**

September 1969

**COPYRIGHT RESERVED**

The copyright of ISO Recommendations and ISO Standards belongs to ISO Member Bodies. Reproduction of these documents, in any country, may be authorized therefore only by the national standards organization of that country, being a member of ISO.

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.

## CONTENTS

|                                                                                                                                                                                                                                    | Page |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Introduction . . . . .                                                                                                                                                                                                             | 5    |
| Part I — General . . . . .                                                                                                                                                                                                         | 5    |
| 1. Scope . . . . .                                                                                                                                                                                                                 | 5    |
| 2. Field of application . . . . .                                                                                                                                                                                                  | 6    |
| 3. Preparation of sample . . . . .                                                                                                                                                                                                 | 6    |
| 4. General principle . . . . .                                                                                                                                                                                                     | 7    |
| Part II — Determination of water content . . . . .                                                                                                                                                                                 | 8    |
| 1. Karl Fischer method . . . . .                                                                                                                                                                                                   | 8    |
| 2. Azeotropic method . . . . .                                                                                                                                                                                                     | 9    |
| Part III — Measurement of pH . . . . .                                                                                                                                                                                             | 10   |
| Part IV — Determination of free acidity or free alkalinity . . . . .                                                                                                                                                               | 11   |
| Part V — Determination of matter extractable by hexane . . . . .                                                                                                                                                                   | 12   |
| Part VI — Determination of sodium alkylarylsulphonates content . . . . .                                                                                                                                                           | 15   |
| Part VII — Determination of sodium sulphite content . . . . .                                                                                                                                                                      | 18   |
| Part VIII — Determination of organic sulphur content arising from the<br>sulphonate group (Wurzschnitt method) . . . . .                                                                                                           | 20   |
| Part IX — Determination of sodium sulphate content . . . . .                                                                                                                                                                       | 22   |
| Part X — Determination of sodium chloride content . . . . .                                                                                                                                                                        | 24   |
| Part XI — Report of the analysis . . . . .                                                                                                                                                                                         | 25   |
| Appendix W — General scheme of analysis . . . . .                                                                                                                                                                                  | 26   |
| Appendix X — Determination of water content (Karl Fischer method using two solutions) . . . . .                                                                                                                                    | 27   |
| Appendix Y — Determination of sodium alkylarylsulphonates content<br>(Rapid method) . . . . .                                                                                                                                      | 30   |
| Appendix Z — Determination of organic sulphur content arising from the<br>sulphonate group of sodium alkylarylsulphonates (isolated<br>in accordance with Part VI of this ISO Recommendation)<br>(Grote-Krekeler method) . . . . . | 33   |

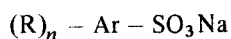
## SURFACE ACTIVE AGENTS

## TECHNICAL SODIUM ALKYLARYLSULPHONATES

## METHODS OF ANALYSIS

## INTRODUCTION

Sodium alkylarylsulphonates have the general formula



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 (Wurzschnitt 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

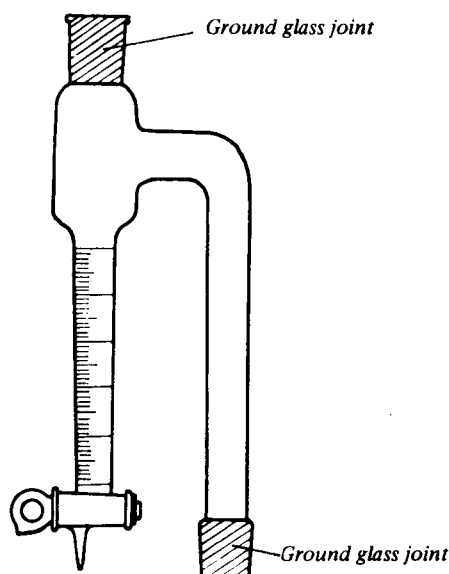
*Xylene, commercial quality* (any isomer or mixture of isomers in any proportion), saturated with water.

### 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 diagrammatically 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