

English Version

Surface active agents - Determination of inorganic sulphate  
content in anionic surface active agents - Potentiometric lead  
selective electrode titration method

Agents de surface - Détermination de la teneur en sulfate  
inorganique dans les agents de surface anioniques -  
Méthode potentiométrique de titrage avec électrode à  
membrane sélective au plomb

Grenzflächenaktive Stoffe - Bestimmung des Gehaltes an  
anorganischen Sulfaten in anionischen grenzflächenaktiven  
Stoffen - Potentiometrische Titration mit einer bleiselektiven  
Elektrode

This European Standard was approved by CEN on 8 July 2005.

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## Foreword

This European Standard (EN 14880:2005) has been prepared by Technical Committee CEN/TC 276 "Surface active agents", the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2006, and conflicting national standards shall be withdrawn at the latest by February 2006.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

## 1 Scope

This European Standard specifies a method for the determination of the content of inorganic sulphate in anionic surface active agents. It can be applied to  $\alpha$ -olefin sulphonates and n-olefin sulphonates, alcohol sulphates, alcohol ether sulphates, alkyl benzene sulphonates and other alkyl sulphonates. This method is used also for the determination of inorganic sulphate in alkyl benzene sulphonates or other alkyl sulphonates in their acid form. This method also applies to deep-coloured samples.

NOTE Sulphate can be present as sulphuric acid, ionic salts of this acid or mixture of these.

## 2 Normative references

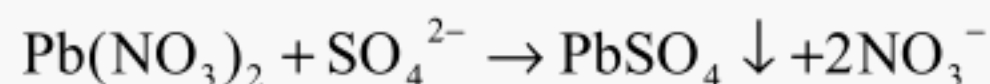
The following referenced documents are indispensable for the application of this European Standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 3696, *Water for analytical laboratory use – Specification and test methods (ISO 3696:1987)*

ISO 607, *Surface active agents and detergents – Methods of sample division*

## 3 Principle

Potentiometric titration of the test sample containing inorganic sulphate is performed in non-aqueous medium with a lead nitrate standard volumetric solution. The reaction is the following:



Lead sulphate precipitate is formed during the titration and the non-aqueous medium decreases its solubility. Nitric acid is added to remove possible interference from carbonates. The endpoint is related to an increase in lead ion activity, as measured by a lead-selective electrode.

## 4 Reagents

During the analysis, unless otherwise specified, use only reagents of recognised analytical grade that have been checked in advance as to not interfere with the analytical results.

**4.1 Water**, complying with grade 3 as defined in EN ISO 3696.

NOTE If the water is purified via ion-exchange resins, ensure that no cationic or anionic species from the resins cause interference.

**4.2 Nitric acid**, solution  $c(\text{HNO}_3) = 1 \text{ mol/l}$ .

**4.3 Lead nitrate standard volumetric solution**,  $c(\text{Pb}(\text{NO}_3)_2) = 0,01 \text{ mol/l}$ .

Weigh 3,312 g of lead nitrate, previously dried at 150 °C in a vacuum oven, dissolve in water, by using a small beaker. Quantitatively transfer the solution into a 1 000 ml volumetric flask and add water up to the mark.

**4.4 Lead nitrate standard volumetric solution**,  $c(\text{Pb}(\text{NO}_3)_2) = 0,005 \text{ mol/l}$ .

Weigh 1,656 g of lead nitrate, previously dried at 150 °C in a vacuum oven, dissolve in water, by using a small beaker. Quantitatively transfer the solution into a 1 000 ml volumetric flask and add water up to the mark.

#### 4.5 Potassium sulphate solution, $c(\text{K}_2\text{SO}_4) = 0,01 \text{ mol/l}$ .

Weigh approximately 1,74 g ( $m$ ) of  $\text{K}_2\text{SO}_4$ , previously dried in an oven at 180 °C, dissolve with water in a 1 000 ml volumetric flask, make up to the mark and homogenize.

Calculate the factor,  $f$ , of the solution, according to the Equation (1):

$$f = \frac{m}{1,7425} \quad (1)$$

where

$m$  is the mass of potassium sulphate weighted, in grams;

1,742 5 is the mass, in grams, of 0,01 mole of potassium sulphate  $\text{K}_2\text{SO}_4$ .

#### 4.6 Propan-2-ol ( $\text{C}_3\text{H}_8\text{O}$ )

### 5 Apparatus

Ordinary laboratory apparatus and the following:

**5.1 Automatic potentiometric titration apparatus**, with drift-controlled data acquisition and dynamic titrimetric dosing equipped with a piston burette delivery system of 20 ml capacity.

**5.2 Lead-selective electrode** (Metrohm 6.0502.170<sup>1</sup>), or similar).

**5.3 Reference electrode Ag/AgCl** filled with a saturated sodium nitrate ethanolic solution.

### 6 Sampling and preparation of the test solution

#### 6.1 Sampling

The laboratory sample shall be taken and stored in accordance with ISO 607.

#### 6.2 Preparation of the test solution

For non-homogeneous products, it will be better to dissolve a large sample (for example 5 g) in a suitable solvent (for example propan-2-ol/water) and take an aliquot for the titration.

Exactly weigh, in a 150 ml beaker, a quantity of the sample ( $m_0$ ) so as to consume a maximum of 10 ml of  $\text{Pb}(\text{NO}_3)_2$  solution (4.3 or 4.4) during the titration (typically, the mass is in the range 0,3 g to 1 g).

### 7 Procedure

#### 7.1 Standardisation of the lead nitrate standard volumetric solution

Pipette 5,00 ml of the potassium sulphate solution (4.5) into a 150 ml beaker. Add approximately 1 ml of nitric acid solution (4.2) and 100 ml of propan-2-ol (4.6).

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1) Metrohm 6.0502.170 is the trade name of instruments supplied by Metrohm Ltd. (CH-9101 Herisau, Switzerland). This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of these instruments named.

Prepare the potentiometer (5.1) for operation, immerse the electrodes in the solution and stir by using the electromagnetic stirrer.

Titrate with the lead nitrate volumetric solution (4.3 or 4.4). Record the reagent consumption,  $V_2$ , at the inflection point of the titration curve.

NOTE An example for instrument settings and a titration curve are given in Annex A.

Run the standardization in triplicates. The concentration of the lead nitrate standard volumetric solution,  $c_a$ , expressed in moles per litre is calculated in accordance with the following Equation (2):

$$c_a = \frac{V_1 \times c \times f}{V_2} \quad (2)$$

where

$V_1$  is the volume of potassium sulphate solution (4.5), in millilitres;

$c$  is the concentration of the lead nitrate solution, in moles per litre;

$f$  is the factor of the potassium sulphate solution determined according to 4.5;

$V_2$  is the average volume of lead nitrate standard volumetric solution used in the titration, in millilitres.

NOTE In alternative, a solution of sulphuric acid,  $c(\text{H}_2\text{SO}_4) = 0,01 \text{ mol/l}$ , can be used to standardize the lead nitrate solution. In this case the sulphuric acid solution can be prepared diluting in the suitable ratio a standard reagent.

## 7.2 Determination

If the expected sulphate content is lower than 1% m/m, use the  $\text{Pb}(\text{NO}_3)_2$ ,  $c(\text{Pb}(\text{NO}_3)_2) = 0,005 \text{ mol/l}$  for the titration, otherwise use the  $\text{Pb}(\text{NO}_3)_2$ ,  $c(\text{Pb}(\text{NO}_3)_2) = 0,01 \text{ mol/l}$ .

Exactly weigh, in a 150 ml beaker, a quantity of the sample ( $m_0$ ) so as to consume a maximum of 10 ml of  $\text{Pb}(\text{NO}_3)_2$  standard volumetric solution during the titration.

NOTE Weighing more than 1g of surfactant should be avoided because the electrical behaviour of the ion-selective electrode is strongly dependent on the surfactant concentration and could give bad potentiometric curves. Approximately 1 ml of nitric acid solution (4.2) and 100 ml of propan-2-ol (4.6) should be added.

The solution should be acidic (lower than pH 3) before titration. If 1 ml of nitric acid solution (4.2) is not sufficient to achieve this, more acid should be added.

Prepare the potentiometer (5.1) for operation, immerse the electrodes in the solution and stir by using the electromagnetic stirrer.

Titrate with the lead nitrate volumetric solution (4.3 or 4.4). Record the reagent consumption,  $V$ , at the inflection point of the titration curve

Clean the ion-selective electrode tip before each titration by using a soft cloth or paper together with propan-2-ol.



## 8 Calculation and expression of results

The content of inorganic sulphate in the sample,  $c_b$ , expressed in percent by mass of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) is calculated according to the Equation (3):

$$c_b = \frac{c_a \times 142,04 \times V}{m_0 \times 10} \quad (3)$$

where

$m_0$  is the mass of the test sample, in grams;

$c_a$  is the concentration of the lead nitrate standard volumetric solution, in moles per litre;

$V$  is the average volume consumption of lead nitrate standard volumetric solution.

NOTE The value 142,04 is the molecular mass of  $\text{Na}_2\text{SO}_4$  in grams.

## 9 Precision

### 9.1 Repeatability limit

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will not exceed the repeatability limit,  $r$ , in more than 5 % of cases.

Precision data are given in Annex B.

### 9.2 Reproducibility limit

The absolute difference between two independent single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, will not exceed the reproducibility limit,  $R$ , in more than 5 % of cases.

Precision data are given in Annex B.

## 10 Test report

The test report shall include the following information:

- all necessary information for the complete identification of the sample;
- method used (a reference to this European Standard, i.e. EN 14880);
- test results;
- details of any operations not specified in this European Standard or in the standards to which reference is made, and any operations regarded as optional, as well as any incidents likely to have affected the results.

## Annex A (informative)

### Titration apparatus settings

#### A.1 Automatic potentiometric titration apparatus

The following parameters are the settings for the automatic potentiometric titration apparatus and are intended to act as a guideline, only (see Table A.1). The titration is carried out with dynamic dosing.

For samples of known concentration providing a suitable starting volume can shorten the titration time.

**Table A.1 — Instrument settings**

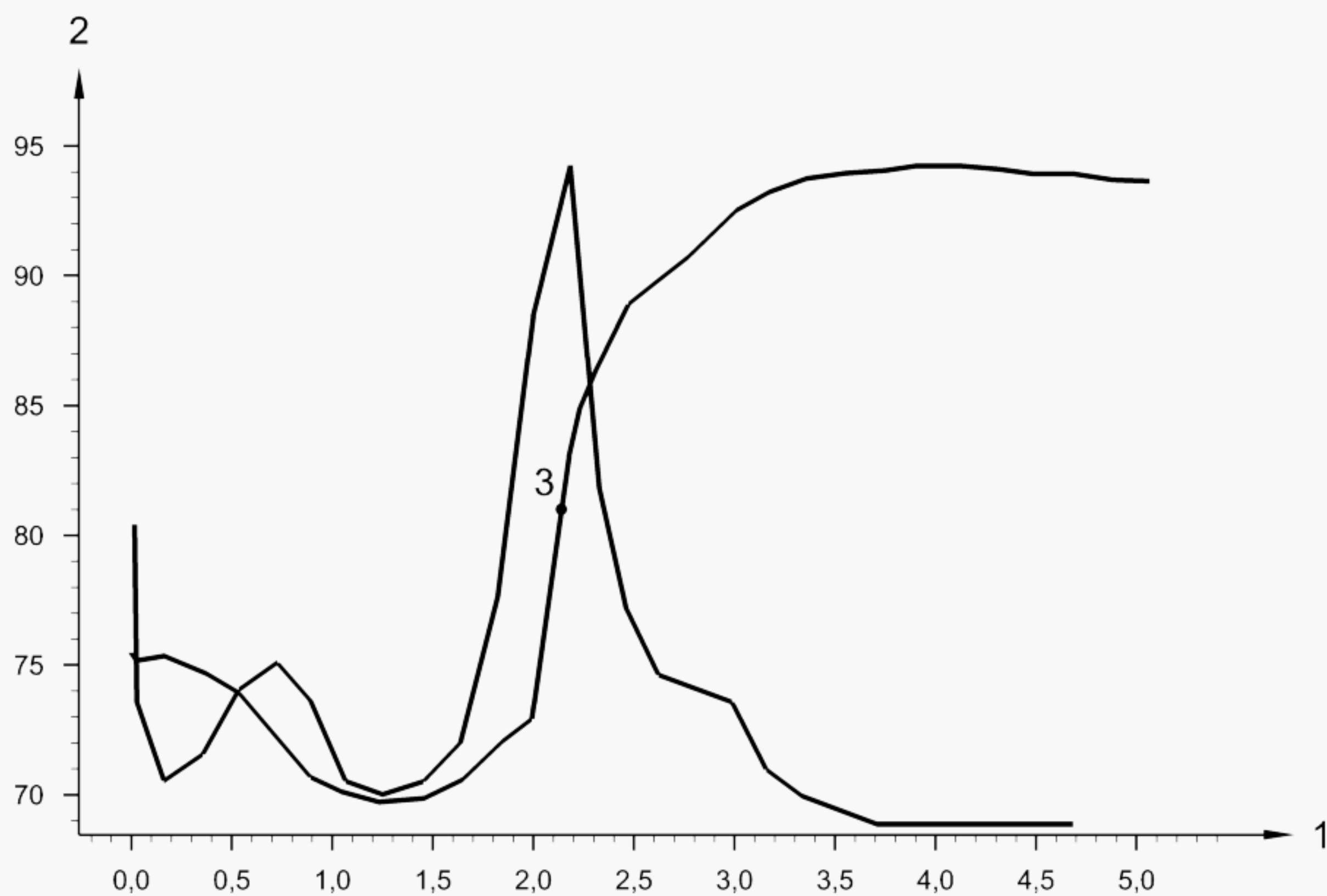
Parameter	Set point
Start volume	0 ml
Measuring point density	2
Signal drift	20 mV/min
Equilibration time	38 s
Minimum increment	10 µl
Burette volume/resolution	20 ml/2 µl
Dose rate, max.	2 ml/min
Pause	300 s
Evaluation end point criteria	5

NOTE 1 The parameter "Start volume" can be changed depending on the final titration volume of the lead nitrate solution. For instance, if the final titration volume is higher than 4 ml or 5 ml, "Start volume" can be set to 2 ml (that is just to save time).

NOTE 2 The parameter "Pause" is the waiting time before the start of the titration. The value of 300 s is just a conservative time for products difficult to solubilize. In the case of soluble products this time can be decreased to 60 s or 120 s.



## A.2 Example of titration curve



### Key

- 1 Volume, ml
- 2 Voltage, mV
- 3 Inflection point

Figure A.1 — Typical titration curve

## Annex B (informative)

### Results of inter-laboratory test

The inter-laboratory test was carried out in 2002 by CESIO/AISE WG "Surfactant Analysis". The test samples were commercial products (raw materials and formulated products). The results of inter-laboratory test were evaluated in accordance with ISO 5725-2 (see Table B.1).

**Table B.1 — Results of inter-laboratory test**

Designation	A	B	C	D	E
Number of participating laboratories	6	6	6	6	6
Number of not eliminated laboratories	5	6	5	5	5
Number of individual measured values	27	33	29	30	30
Mean value, in % m/m	1,16	2,27	0,094	0,106	0,128
Repeatability standard deviation $s_r$ , in % m/m	0,012	0,038	0,006 8	0,006 5	0,005 5
Repeatability limit $r = (2,8 \times s_r)$ , in % m/m	0,03	0,11	0,019	0,018	0,015
Variation coefficient of repeatability, in %	1,0	1,7	7,2	6,1	4,3
Reproducibility standard deviation $s_R$ , in % m/m	0,023	0,14	0,012 2	0,010 4	0,009 9
Reproducibility limit, $R = (2,8 \times s_R)$ , in % m/m	0,064	0,38	0,034	0,029	0,028
Variation coefficient of reproducibility, in %	1,95	6,1	12,9	9,8	7,8

Sample	Definition	CAS name	CAS number
A	Linear Alkyl Benzene Sulphonic Acid	Benzenesulphonicacid, 4-C10-13-sec-alkyl derivs.	85536-14-7
B	Heavy Alkylate Sulphonate	Benzene, mono-C10-14 alkyl. Derivs., fractionation bottoms	85117-41-5
C	Alcohol Ether Sulphate (Linear)	Poly(oxy-1,2-ethanediyl), alpha-sulpho, omega-hydroxy-, C12-14-alkyl ethers, sodium salt	68891-38-3
D	Alcohol Ether Sulphate (Branched)	Poly(oxy-1,2-ethanediyl), alpha-sulpho, omega-hydroxy-, C10-16-alkyl ethers, sodium salt	68585-34-2
E	Alcohol Sulphate	Sulphuric acid, mono-C12-13-alkyl ester, sodium salt	91783-23-2

## Bibliography

- [1] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*