

English version

Surface active agents - Determination of anionic surface active agents and soaps in detergents and cleansers - Potentiometric two-phase titration method

Agents de surface - Détermination des agents de surface anioniques et des savons dans les détergents et produits de nettoyage - Méthode de titrage potentiométrique dans deux phases

Grenzflächenaktive Stoffe - Bestimmung des Gehaltes an anionischen grenzflächenaktiven Stoffen und Seifen in Detergenzien und Reinigern - Potentiometrische Zweiphasen-Titration

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

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Foreword

This European Standard (EN 14669:2005) 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of an identical text or by endorsement, at the latest by December 2005, and conflicting national standards shall be withdrawn at the latest by December 2005.

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 anionic surface active agents and soaps in detergents and cleansers, defined as being the amount of anionic surface active agents expressed in millimoles per 100 g of product.

NOTE 1 The applicability in products different than those tested should be checked in each particular case.

NOTE 2 In comparison to usual laboratory two-phase titration with visual endpoint determination (see ISO 2271), potentiometric titration offers the advantage of automation; operator-dependent differences in recognising the equivalence point can be neglected, and a non-critical solvent replaces the toxicologically critical chloroform.

2 Normative references

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

EN 14670, *Surface active agents – Sodium dodecyl sulfate – Analytical method*.

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

Anionic surface active agents and soaps are combined with cationic surface active agents to form water-insoluble ion pairs which are immediately extracted into a water immiscible organic solvent. This fundamental reaction is the basis for the titration of equivalents of ionic surface active agents with an oppositely charged surface active agent standard volumetric solution in the two-phase titration.

This procedure is supported by intensively stirring the two-phase mixture of aqueous solution and organic phase. The potential, which is formed in the emulsion during the titration, is recorded with the help of a special solvent-resistant surface active agent-sensitive electrode in combination with a silver/silver chloride reference electrode against the amount of titrant added. The equivalence point of the added cationic surface active agent corresponds to that one of the test solution at the inflection point of the titration curve (Annex B).

The titration is carried out twice, once under acidic conditions for the determination of the anionic surface active agents and then under alkaline conditions in order to determine the sum of soaps and anionic surface active agents. The soap concentration is calculated from the difference of the titrant consumptions.

4 Reagents

WARNING — Your attention is drawn to the regulations covering the handling of hazardous substances. Technical, organisational and personal protection measures should be observed.

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 Sodium dodecyl sulfate, $C_{12}H_{25}OSO_3Na$, % (m/m)($C_{12}H_{25}SO_4Na$) ≥ 99 as determined following the method EN 14670.

4.3 Anionic surface active agent standard volumetric solution, $c(C_{12}H_{25}OSO_3Na) = 0,005 \text{ mol/l}$.

Weigh 1,455 g of sodium dodecyl sulfate (4.2) with a known active content to the nearest 1 mg, in a conical flask, and dissolve in about 500 ml water. Transfer quantitatively the solution into a 1000 ml volumetric flask and make up to the mark with water and mix well.

The concentration of the anionic surface active agent standard volumetric solution, c_a , expressed in millimoles per millilitre is calculated in accordance with the following equation (1):

$$c_a = \frac{m \times w}{M \times 100} \quad (1)$$

where

m is the mass of sodium dodecyl sulfate (4.2) in grams;

w is the active matter content of sodium dodecyl sulfate (4.2) in grams per 100 g;

M is the molar mass of sodium dodecyl sulfate, in grams per mole (288,4 g/mol).

4.4 1,3-didecyl-2-methyl-imidazolium chloride (e.g. TEGO Trant A100¹⁾).

4.5 Cationic surface active agent, standard volumetric solution, $c = 0,005 \text{ mol/l}$:

Weigh 2,00 g of 1,3-didecyl-2-methyl-imidazolium chloride (4.4), to the nearest 1 mg, in a conical flask and dissolve it in about 500 ml water. Transfer quantitatively the solution into a 1000 ml volumetric flask, make up to the mark with water and mix well. Standardize the solution as specified in 7.1.

Standardize the cationic surface active agent solution only when the solution has reached its equilibrium, i.e. after standing for at least one day.

NOTE Cationic surface active agents adsorb on glass surfaces like such of the burette and reagent bottle of the titration unit.

4.6 Potassium chloride solution, $c(KCl) = 3 \text{ mol/l}$.

4.7 Hydrochloric acid, $c(HCl) = 0,5 \text{ mol/l}$.

4.8 Sodium hydroxide solution, $c(NaOH) = 0,5 \text{ mol/l}$.

1) TEGO Trant A100 is the trade name of product supplied by Metrohm Ltd. (CH-9101 Herisau, Switzerland). This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product. Equivalent product may be used if it can be shown to lead to the same results.

4.9 Emulsifier (TEGO Add²⁾).

NOTE The emulsifier has the task of supporting the formation of a stable emulsion and at the same time of preventing the deposition of the ion associate formed during the titration on the electrode surface.

4.10 Propan-2-ol (Isopropanol) (C_3H_8O) $\geq 99\%$.

4.11 Ethanol denatured 96% (V/V).

4.12 Methyl isobutyl ketone (MIBK) (CAS number: 108.10.1), 4-methyl-2-pentanone, % (m/m) ($C_6H_{12}O$) ≥ 99 .

4.13 MIBK / propan-2-ol - mixture

Measure 600 ml MIBK (4.12) and 400 ml propan-2-ol (4.10) using a measuring cylinder, transfer into a 1000 ml flask and mix well.

5 Apparatus

Normal 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 Propeller stirring system.

In a potentiometric two-phase titration a thorough blending is required. Hence, a stirring propeller is compulsory. The stirrer should be constructed so that an optimal emulsification of the vessel contents is achieved with a simultaneous low degree of air entrapment. Propeller stirrers shaped like ship screws have proven effective, while magnetic stirrers are not suitable. It is advisable to pay special attention to the geometric arrangement of the immersing parts (electrodes, burette tip, and stirrer). If arranged optimally, no foam is produced, not even with heavy stirring.

5.3 Combined glass pH-electrode.

5.4 Solvent-resistant- surface active agent -sensitive electrode (Surfactrode Refill or Surfactrode Resistant³⁾).

5.5 Ag/AgCl- double-junction ground joint diaphragm reference electrode, inner and outer chambers filled with potassium chloride solution (4.6).

2) TEGO Add is the trade name of product supplied by Metrohm Ltd. (CH-9101 Herisau, Switzerland). This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product. Equivalent product may be used if it can be shown to lead to the same results.

3) Surfactrode Refill and Surfactrode Resistant are trade names of products supplied by Metrohm Ltd. (CH-9101 Herisau, Switzerland). This information is given for the convenience of users of this document and does not constitute an endorsement by CEN. Equivalent products may be used if they can be shown to lead to the same results.

6 Sampling and preparation of the test solution

6.1 Sampling

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

6.2 Preparation of the test solution

Powder detergents and powdery cleansers shall be homogenised by additional milling if amounts lower than 10 g are used.

The sample amount and the concentration of test solution shall be calculated in a way that the consumption of the titrant solution (4.5) used for the titration of 10 ml test solution is approximately 10 ml.

Weigh, to the nearest 0,1 mg, the homogenised sample (m_1) in a glass beaker and add approximately 100 ml water. Stir the mixture using a magnetic stirrer until the substance is dissolved and possibly insoluble product ingredients are suspended homogeneously in the solution. For soap raw material heating is necessary to achieve complete dissolution. For fatty acids instead of water, ethanol is used as solvent.

Transfer quantitatively the sample solution into a 200 ml volumetric flask, to minimise foaming add a small quantity of ethanol (4.11). Make up to the mark with water and mix well.

7 Procedure

7.1 Standardisation of the cationic surface active agent standard volumetric solution

Accurately transfer 10 ml of the sodium dodecyl sulfate standard volumetric solution (4.3) into the titration vessel and add about 70 ml of water.

Adjust the pH to $3 \pm 0,2$ with the hydrochloric acid solution (4.7).

Add 10 ml of methyl isobutyl ketone (MIBK) (4.12), 10 ml of ethanol (4.11) and 200 μ l of emulsifier (4.9). Stir the mixture intensively for 60 s in order to form a stable emulsion.

Carry out the titration with the cationic surface active agent standard volumetric solution (4.5) under intensive stirring (5.2).

Record the reagent consumption, V , at the inflection point of the titration curve (see Figure B.1).

NOTE Examples for instrument settings are given in Annex A.

Calculate the factor, f_i , of the cationic surface active agent standard volumetric solution (4.5) by the equation (2):

$$f_i = \frac{c_a \times V_1}{V \times c_b} \quad (2)$$

where

c_a is the concentration of the anionic surface active agent standard volumetric solution expressed in millimoles per millilitre (4.3);

c_b is the concentration of the cationic surface active agent standard volumetric solution expressed in millimoles per millilitre (here 0,005 mmol/ml);

V_1 is the volume of anionic surface active agent standard volumetric solution used, in millilitres (here: 10 ml);

V is the consumption of cationic surface active agent standard volumetric solution (4.5), in millilitres.

Repeat the determination at least three times and calculate from the factors f_i the average factor f .

7.2 Determination of anionic surface active agents

Accurately transfer 10 ml of test solution (6.2) into the titration vessel and add 70 ml water.

Carry out the determination as specified in 7.1.

The anionic surface active agent concentration is calculated according to 8.1.

7.3 Determination of soaps and anionic surface active agents

Accurately transfer 10 ml of test solution (6.2) into the titration vessel and add 70 ml water.

Adjust the pH to 11,5 with the sodium hydroxide solution (4.8).

NOTE 1 It is not advisable to use Surfactrode Resistant at this pH value of 11,5.

Add 25 ml of MIBK/ propan-2-ol mixture (4.13), 10 ml ethanol (4.11) and 200 µl of emulsifier (4.9). Stir the mixture intensively for 60 s in order to form a stable emulsion.

NOTE 2 If ethanol is used for the preparation of the test solution this amount should be taken into account when the ethanol is added.

Carry out the titration with the cationic surface-active agent standard volumetric solution (4.5) under intensive stirring (5.2).

Record the reagent consumption at the inflection point of the titration curve (see Figure B.1).

The content of anionic surface active agent is calculated according to 8.1.

The soap content is calculated according to 8.2.

7.4 Cleaning, rinsing and conditioning of the measuring apparatus

Rinse the measuring apparatus with ethanol (4.11) after each titration. Condition it by stirring for 20 s in the titration beaker filled with ethanol (4.11).

For the surfactrode resistant, it is recommended to carry out three or four titrations before taking into account the results.

8 Calculation and expression of results

8.1 Anionic surface active agent content

The content of anionic surface active agent, c_a , expressed in millimoles per 100 g is calculated according to the following equation (3):

$$c_a = \frac{c_b \times f \times V_2}{m_1} \times \frac{V_3}{V_4} \times 100 \quad (3)$$

where

m_1 is the mass of the test sample, in grams (6.2);

c_b is the concentration of the cationic surface active agent standard volumetric solution (4.5), in millimoles per millilitre (here 0,005 mmol/ml);

f is the factor of the cationic surface active agent standard volumetric solution (4.5) calculated in 7.1;

V_2 is the volume consumption of cationic surface active agent standard volumetric solution (4.5), in millilitres;

V_3 is the total volume of the test solution, in millilitres (here 200 ml);

V_4 is the aliquot volumes of the test solution used for the titration, in millilitres (here 10 ml).

8.2 Soap content

The soap content, C_s , expressed in millimoles per 100 g of mixtures of soaps and anionic surface active agents is calculated by subtracting the result of the acidic titration (7.2) from the result of the alkaline titration (7.3) according to the following equation (4) :

$$C_s = C_2 - C_1 \quad (4)$$

where

C_1 is the content of anionic surface active agent determined following (7.2), in millimoles per 100 g;

C_2 is the content of anionic surface active agent and soap determined following (7.3), in millimoles per 100 g.

For samples containing soap as the only anionic surface active agent the content is calculated directly from the result of the alkaline titration (7.3)

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 C.

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 C.

10 Test report

The test report shall include the following information:

- a) all necessary information for the complete identification of the sample;
- b) reference to this European Standard;
- c) test results;
- d) details of any operations not specified in this document or in the European 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 Titroprocessor 726 and Titrinos 716/736/751⁴⁾ 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 | Anionic surface active agent | Anionic surface active agent plus soap |
|-----------------------------|------------------------------|--|
| pH | 2,0 | 11,5 |
| Measuring point density : | 2 | 0 |
| Signal drift | off | 5 mV / min |
| Equilibration time | 15 s | 15 s |
| Minimum increment | 50 µl | 150 µl |
| Burette volume/Resolution : | 20 ml / 2 µl | 20 ml / 2 µl |

NOTE The designations of the parameters correspond to those given by the Titroprocessor 726 and Titrinos 716/736/751

A.2 Propeller stirring equipment

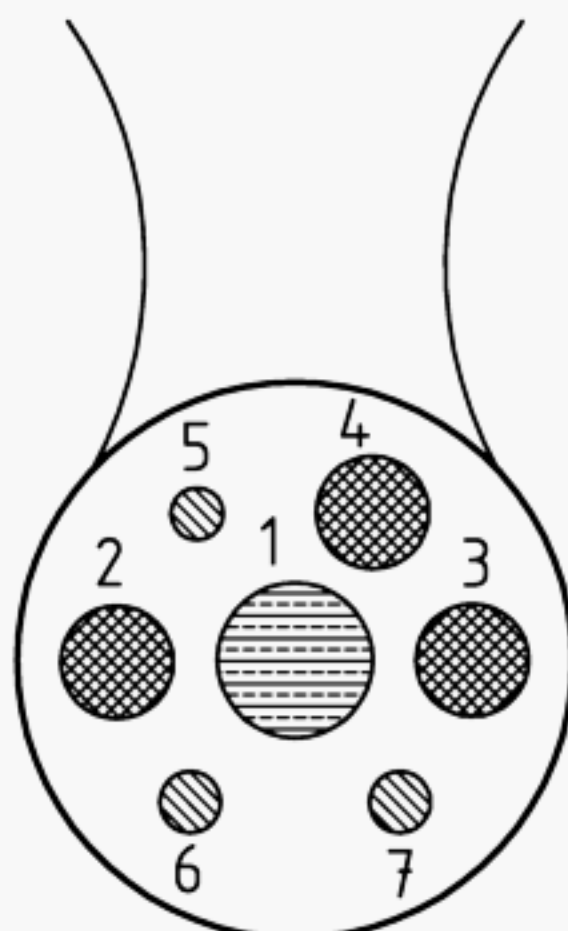
Special attention should be paid to the geometric arrangement of the immersing parts (electrodes, burette-tip, and stirrer). If arranged optimally, no foam will be produced, not even with heavy stirring.

Suitable apparatus available commercially are e.g. Metrohm Titroprocessor 726 or Titrinos 716/736/751, with titration stand 722, ship screw shape stirring propeller 6.1909.010 and electrode holder with rinsing device 6.2021.030⁵⁾. Using a Metrohm Titroprocessor 726, the stirring rate of 9 is set maximum.

A top view of a suitable arrangement of electrodes, burette tip and stirrer is shown in Figure A.1.

4) Metrohm Titroprocessor 726 and Titrinos 716/36/751 are examples of suitable apparatus commercially available. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of the instruments named.

5) Metrohm Titroprocessor 726, Titrinos 716/736/751, titration stand 722, stirring propeller 6.1909.010 and electrode holder with rinsing device 6.2021.036 are examples of suitable apparatus available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of these apparatus.



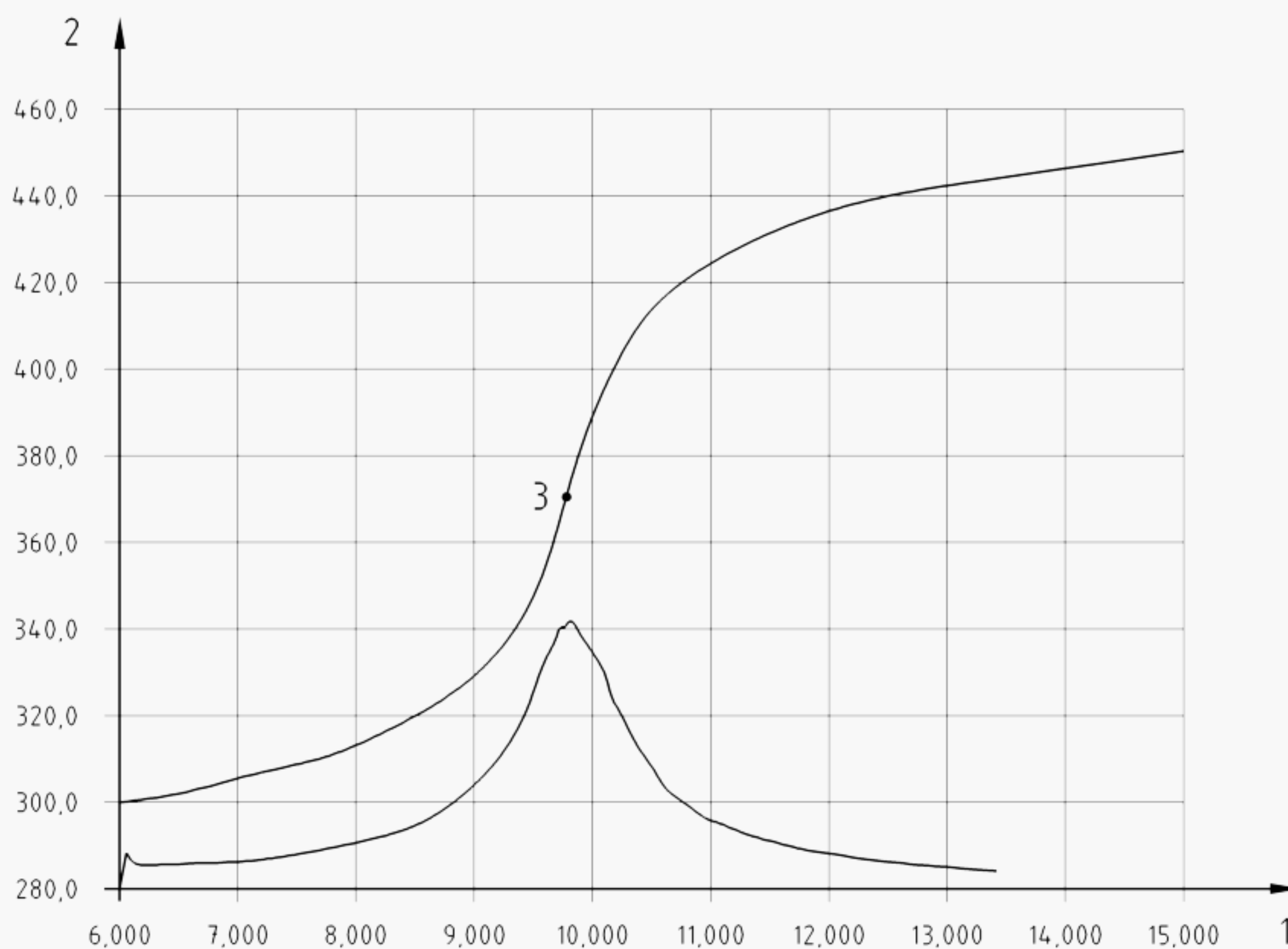
Key

- 1 Propeller stirrer (5.2)
- 2 Solvent resistant -surface active agent -sensitive electrode (5.4)
- 3 Reference-electrode Ag/AgCl (5.5)
- 4 Combined glass pH-electrode (5.3)
- 5 Olive connector for rinsing equipment
- 6 Burette tip of cationic surface active agent standard volumetric solution
- 7 Not occupied

Figure A.1 — Top view of arrangement of electrodes, burette tip and stirrer

Annex B (informative)

Potentiometric two-phase titration- typical titration curve



Key

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

Figure B.1 — Typical titration curve of potentiometric two-phase titration

Annex C (informative)

Results of inter-laboratory test

The inter-laboratory test was carried out in 1999 by AISE/CESIO 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 Tables C.1 to C.3).

Table C.1 — Results of inter-laboratory test on detergent 1

| Designation | Anionic surface active agent content | Anionic surface active agent plus soap content | Soap content |
|---|--------------------------------------|--|--------------|
| Number of laboratories participating | 12 | 11 | |
| Number of laboratories not eliminated | 11 | 10 | |
| Number of individual measured values of all laboratories | | | |
| Mean value, in mmol/100 g | 49,85 | 53,00 | 3,31 |
| Repeatability standard deviation s_r , in mmol/100 g | 0,571 | 0,345 | 0,611 |
| Repeatability limit $r = (2,8 \times s_r)$, in mmol/100 g | 1,58 | 0,96 | 1,69 |
| Variation coefficient of repeatability, in % | 1,15 | 0,65 | 18,47 |
| Reproducibility standard deviation s_R , in mmol/100 g | 1,013 | 1,060 | 1,057 |
| Reproducibility limit, $R = (2,8 \times s_R)$, in mmol/100 g | 2,81 | 2,94 | 2,93 |
| Variation coefficient of reproducibility, in % | 2,03 | 2,00 | 31,94 |

Table C.2 — Results of inter-laboratory test on detergent 2:

| Designation | Anionic surface active agent content | Anionic surface active agent plus soap content | Soap content |
|---|--------------------------------------|--|--------------|
| Number of laboratories participating | 12 | 11 | |
| Number of laboratories not eliminated | 12 | 10 | |
| Number of individual measured values of all laboratories | | | |
| Mean value, in mmol/100 g | 32,62 | 49,88 | 17,40 |
| Repeatability standard deviation s_r , in mmol/100 g | 0,981 | 0,426 | 0,857 |
| Repeatability limit, $r = (2,8 \times s_r)$, in mmol/100 g | 2,72 | 1,18 | 2,38 |
| Variation coefficient of repeatability, in % | 3,01 | 0,85 | 4,93 |
| Reproducibility standard deviation s_R , in mmol/100 g | 1,478 | 1,469 | 1,875 |
| Reproducibility limit, $R = (2,8 \times s_R)$, in mmol/100 g | 4,10 | 4,07 | 5,20 |
| Variation coefficient of reproducibility, in % | 4,53 | 2,94 | 10,78 |

Table C.3 — Results of inter-laboratory test on raw materials

| Designation | Fatty Acids mixture | Soap (raw material) |
|--|---------------------|---------------------|
| Number of laboratories participating | 9 | 9 |
| Number of laboratories not eliminated | 8 | 6 |
| Number of individual measured values of all laboratories | | |
| Mean value, in mmol/100 g | 353,6 | 302,9 |
| Repeatability standard deviation s_r , in mmol/100 g | 1,72 | 3,90 |
| Repeatability limit $r = (2,8 \times s_r)$ in mmol/100 g | 4,77 | 10,81 |
| Variation coefficient of repeatability, in % | 0,49 | 1,29 |
| Reproducibility standard deviation s_R , in mmol/100 g | 6,93 | 4,78 |
| Reproducibility limit $R = (2,8 \times s_R)$, in mmol/100 g | 19,22 | 13,26 |
| Variation coefficient of reproducibility, in % | 1,96 | 1,58 |

Bibliography

- [1] ISO 2271, *Surface active agents – Detergents – Determination of anionic-active matter by manual or mechanical direct two-phase titration procedure.*
- [2] 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.*