

English version

Surface active agents - Determination of quaternary ammonium
surface active agents in raw materials and formulated products -
Potentiometric two-phase titration method

Agents de surface - Détermination des agents de surface à
base d'ammonium quaternaire dans les matières premières
et les produits formulés - Méthode de titrage
potentiométrique dans deux phases

Grenzflächenaktive Stoffe - Bestimmung des Gehaltes an
quartären Ammoniumtensiden in Rohstoffen und
formulierten Produkten - Potentiometrische Zweiphasen-
Titration

This European Standard was approved by CEN on 19 May 2005.

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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 14668:2005) 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of an identical text or by endorsement, at the latest by December 2005, and conflicting national standards shall be withdrawn at the latest by December 2005.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 quaternary ammonium surface active agents in raw materials and formulated products, defined as being the amount of quaternary ammonium 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 2871-1 and ISO 2871-2) 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

Quaternary ammonium surface active agents are combined with anionic surface active agent 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 process 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 anionic surface active agent corresponds to that one of the test solution at the inflection point of the titration curve (Annex B).

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 recognized 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)($C_{12}H_{25}OSO_3Na$) ≥ 99 as determined following the method EN 14670.

4.3 Anionic surface active, agent standard volumetric solution, $c_a(\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}) = 0,005 \text{ mol/l}$:

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

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

4.6 Emulsifier, (TEGO Add¹⁾)

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.

4.7 Ethanol, denatured 96 % (V/V)

4.8 Methyl isobutyl ketone (MIBK), (CAS number: 108.10.1), 4-Methyl-2-pentanone

4.9 MIBK/ethanol-mixture

Measure 500 ml MIBK (4.8) and 500 ml ethanol (4.7) 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 been 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.

1) TEGO Add is the trade name of a 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 the product named. Equivalent products may be used if they can be shown to lead to the same results.

5.3 Combined glass pH-electrode.

5.4 Solvent-resistant surface-active agent sensitive electrode (Surfactrode Refill or Surfactrode Resistant)²⁾.

5.5 Ag/AgCl – double-junction ground joint diaphragm reference electrode, inner and outer chambers filled with potassium chloride solution (4.4).

6 Sampling and preparation of the test solution

6.1 Sampling

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

Solid samples shall be carefully melted in an oven at 60 °C taking care that they are firmly tight in order to avoid losing volatile matter.

6.2 Preparation of the test solution

6.2.1 Raw materials (organic solvent soluble)

The sample amount and the concentration of test solution shall be calculated in a way that the consumption of the titrant solution (4.3) used for the titration of 10 ml test solution is approximately 10 ml.

Weigh to the nearest 0,1 mg the homogenised sample in a 200 ml volumetric flask, make up to the mark with MIBK/ethanol-mixture (4.9) and mix well.

6.2.2 Formulated products (water soluble)

The sample amount and the concentration of the test solution shall be calculated in a way that the consumption of the titrant solution (4.3) used for the titration of 10 ml test solution is approximately 10 ml.

Weigh to the nearest 0,1 mg of the homogenised sample in a 200 ml volumetric flask, make up to the mark with water and mix well.

7 Procedure

7.1 Determination of quaternary ammonium surface active agents in organic solvent soluble products

Accurately transfer 10 ml of test solution (6.2.1) into the titration vessel and add about 70 ml water.

Adjust the pH to $3 \pm 0,2$ with the acid solution (4.5).

Add 20 ml of MIBK/ ethanol mixture (4.9) and 200 µl of emulsifier (4.6). Stir the mixture intensively for 60 s in order to form a stable emulsion.

Carry out the titration with the anionic surface-active agent standard volumetric solution (4.3) 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.

2) 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.

The quaternary ammonium surface active agent concentration is calculated according to Clause 8.

7.2 Determination of quaternary ammonium surface active agents in water soluble products

Accurately transfer 10 ml of test solution (6.2.2) into the titration vessel and add 60 ml water.

Adjust the pH to $3 \pm 0,2$ with the hydrochloric acid solution (4.5).

Add 30 ml of MIBK/ ethanol mixture (4.9) and 200 μ l of emulsifier (4.6). Stir the mixture intensively for 60 s in order to form a stable emulsion.

Carry out the titration with the anionic surface active agent standard volumetric solution (4.3) 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.

The quaternary ammonium surface active agent concentration is calculated according to Clause 8.

7.3 Cleaning, rinsing and conditioning of the measuring apparatus

Rinse the measuring apparatus with ethanol (4.7) after each titration. Condition it by stirring for 20 s in the titration beaker filled with ethanol (4.7).

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

8 Calculation and expression of results

The concentration of quaternary ammonium surface active agent (c_c), expressed in millimoles per 100 g is calculated according to the following equation (2):

$$c_c = \frac{c_a \times V}{m_1} \times \frac{V_1}{V_2} \times 100 \quad (2)$$

where

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

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

V is the volume consumption of anionic surface active agent standard volumetric solution, in millilitres;

V_1 is the total volume of the test solution, in millilitres (here 200 ml);

V_2 is the aliquot volume of the test solution used for the titration, in millilitres (here 10 ml).

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 and 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 information necessary for the complete identification of the sample;
- b) reference to this European Standard;
- c) test result;
- 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 settings for the Titroprocessor 726 and Titrinos 716/736/751³⁾ 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
Measuring point density :	0
Signal drift :	10 mV/min
Equilibration time :	120 s
Minimum increment :	150 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

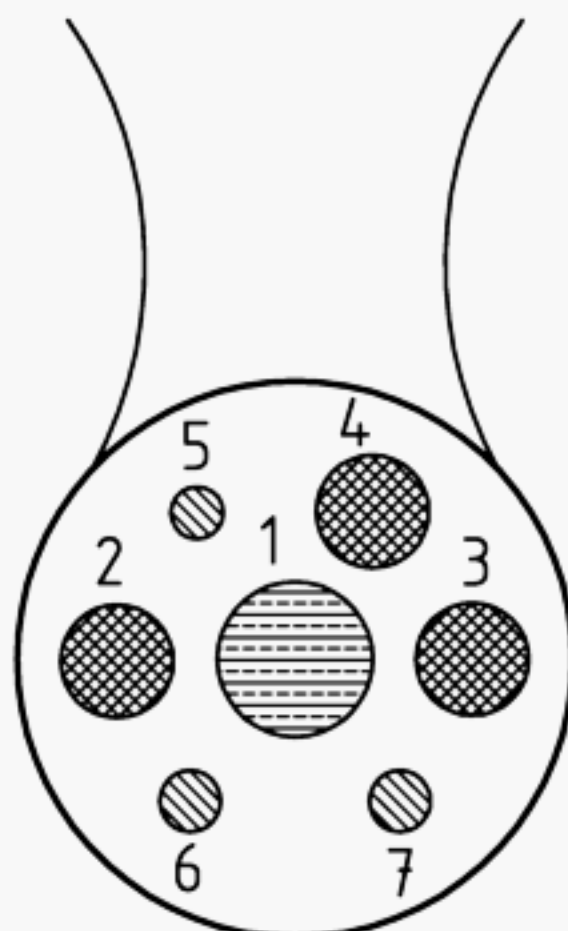
Special attention should be paid to the geometric arrangement of the immersing parts (electrodes, burette-tip, and stirrer). If arranged optimally, no foam will be produced, not even with heavy stirring.

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 6.2021.030⁴⁾. 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.

3) 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.

4) 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.



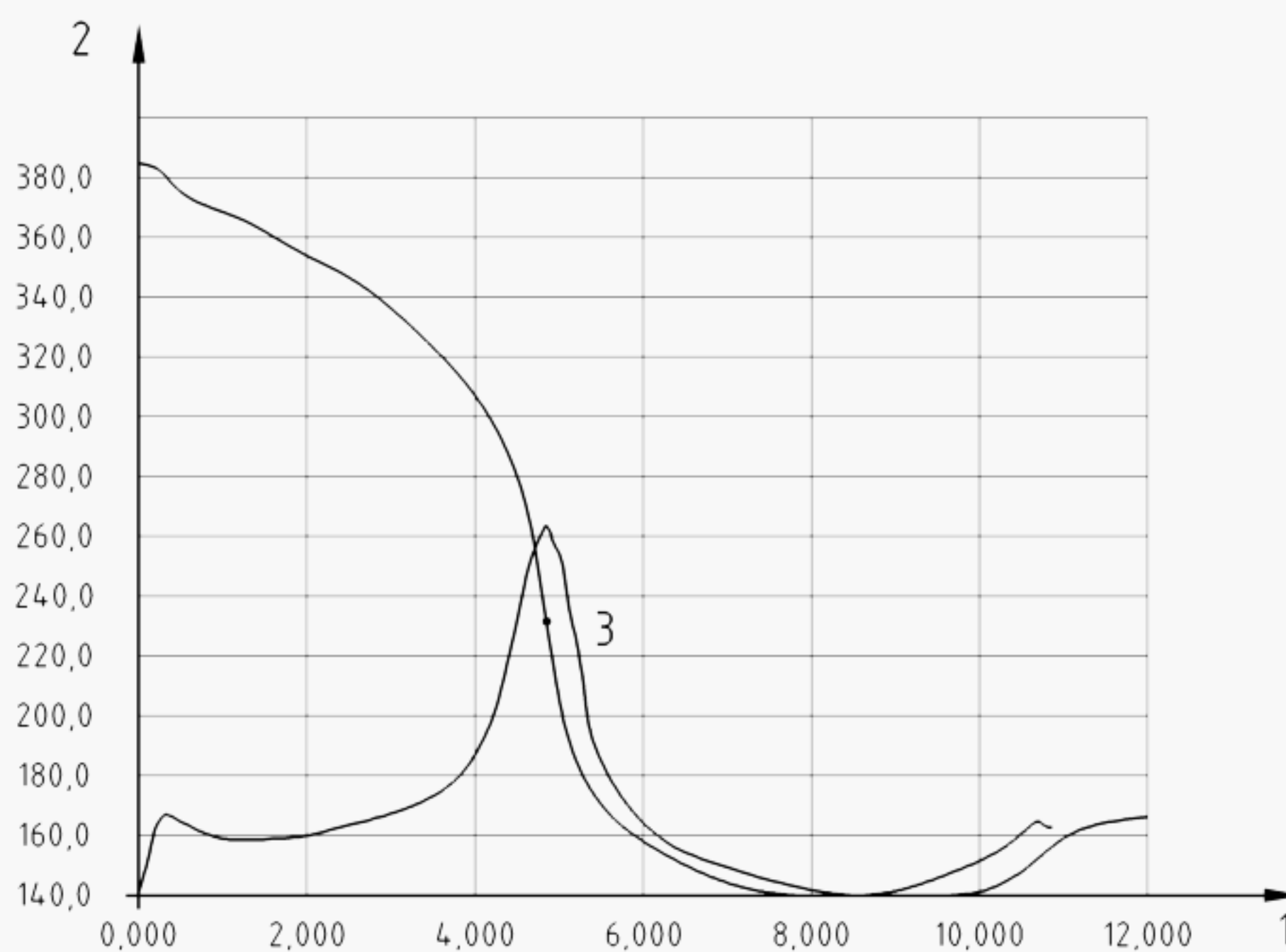
Key

- 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 an 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 2000 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 Table C.1).

Table C.1 — Results of inter-laboratory test

Designation	Benzylalkonium chloride	TEA Esterquat	Softener 1 ^a	Softener 2 ^a
Number of participating laboratories	8	8	15	15
Number of laboratories not eliminated	8	8	15	15
Number of individual measured values of all	72	81	126	132
Mean value in [mmol/100 g]	143,7	101,2	4,10	20,96
Repeatability standard deviation s_r , in mmol/100 g	0,73	1,06	0,069	0,24
Repeatability limit, $r = (2,8 \times s_r)$ in mmol/100 g	2,04	2,92	0,19	0,67
Variation coefficient of repeatability in %	0,51	1,04	1,68	1,15
Reproducibility standard deviation s_R in mmol/100 g	2,18	3,04	0,265	0,501
Reproducibility limit, $R = (2,8 \times s_R)$ in mmol/100 g	6,03	8,42	0,74	1,39
Variation coefficient of reproducibility in %	1,52	2,99	6,48	2,39
^a Formulated softener including TEA Esterquat.				

Table C.2 — Comparative results with ISO 2871-1 and ISO 2871-2^b

Designation	Methyltrioctylammonium Chloride		TEA-Esterquat	
	ISO 2871	Potentiometric	ISO 2871	Potentiometric
Number of participating laboratories	5	7	5	7
Number of laboratories not eliminated	5	7	5	7
Number of individual measured values of all	30	42	29	42
Mean value in [mmol/100 g]	201,6	201,2	109,4	108,4
Repeatability standard deviation s_r , in [mmol/100 g]	1,58	0,71	0,66	0,50
Repeatability limit, $r = (2,8 \times s_r)$ in mmol/100 g	4,42	1,98	1,85	1,40
Variation coefficient of repeatability in %	0,78	0,35	0,60	0,46
Reproducibility standard deviation s_R in mmol/100 g	4,39	1,65	1,35	1,11
Reproducibility limit, $R = (2,8 \times s_R)$ in mmol/100 g	12,3	4,62	3,78	3,11
Variation coefficient of reproducibility in %	2,17	0,82	1,23	1,03
^b Data obtained from a 2001 Goldschmidt internal ring test with four participating laboratories in repeatability and reproducibility conditions.				

Bibliography

- [1] EN ISO 2871-1, *Surface active agents — Detergents — Determination of cationic-active matter content — Part 1: High-molecular-mass cationic-active matter (ISO 2871-1:1988).*
- [2] EN ISO 2871-2, *Surface active agents — Detergents — Determination of cationic-active matter content — Part 2: Cationic-active matter of low molecular mass (between 200 and 500) (ISO 2871-2:1990).*
- [3] 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.*