BRITISH STANDARD

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Surface active agents — Determination of the active matter content of alkylamidopropylbetaines

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ICS 71.100.40

National foreword

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A list of organizations represented on CII/34 can be obtained on request to its secretary.

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English Version

Surface active agents - Determination of the active matter content of alkylamidopropylbetaines

Agents de surface - Détermination de la teneur en matières actives des alkylamidopropylbétaïnes

Grenzflächenaktive Stoffe - Bestimmung des Aktivgehaltes von Alkylamidopropylbetainen

This European Standard was approved by CEN on 6 October 2006.

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EUROPÄISCHES KOMITEE FÜR NORMUNG

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Contents

Foreword

This document (EN 15109:2006) 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of an identical text or by endorsement, at the latest by May 2007, and conflicting national standards shall be withdrawn at the latest by May 2007.

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1 Scope

This European Standard specifies a method for the determination of the active matter content of alkylamidobetaines in commercial surface active agents.

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 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

The test sample to be analysed is alkalinized by addition of sodium hydroxide. In this way all substances present are converted into a defined form, namely:

— the betaine into its intermolecular salt form;

— the amidoamine into the free amidoamine;

— the acids (e.g. hydrochloric acid, fatty acids, chloroacetic acids and glycolic acid) into their sodium salt forms.

During the titration with perchloric acid in the non-aqueous medium:

— the betaine is changed into the protonated form;

— the amidoamine is changed into the amidoamine perchlorate;

— the excess sodium hydroxide and sodium salts of the different acids are transformed into weakly dissociated sodium perchlorate.

By using a solvent mixture which enables a good differentiation of varying pK(b) values, it is possible to differenciate the betaine from these accompanying substances.

Salts of chloroacetic acids, glycolic acid, fatty acid and amidoamine do not interfere. Short chain betaines are titrated together with long chain betaines.

4 Reagents

4.1 General

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 and have been checked in advance as to not interfere with the analytical results and water complying with grade 1 as defined in EN ISO 3696.

4.2 1,4-dioxane, minimum purity 99 % (CAS number: 123-91-1).

WARNING — This substance can cause irreversible effects and eye irritation.

4.3 Methoxyethanol, minimum purity 99 % (CAS number : 32718-54-0).

WARNING — This substance is considered as mutagenic.

4.4 Methanol, minimum purity 99,5 % (CAS number : 67-56-1).

WARNING — This substance is considered toxic by ingestion or inhalation.

4.5 Sodium hydroxide, *c*(NaOH) = 1,0 mol/l (CAS number : 1310-73-2).

4.6 Sodium acetate, minimum purity 99 % (CAS number : 127-09-3).

4.7 Sodium hydroxide/sodium acetate solution

Dissolve 80 g of sodium acetate in aqueous sodium hydroxide (*c*(NaOH) = 1,0 mol/l) into a 1 l volumetric flask. Make up to the volume with the same sodium hydroxide solution. Stopper and mix.

4.8 Potassium hydrogen phthalate, purity (100 ± 0,1) %, (CAS number : 877-24-7).

4.9 Acetic acid, minimum purity 99,8 % (CAS number : 64-19-7).

4.10 Perchloric acid standard volumetric solution, *c*($HClO_4$) = 0,1 mol/l (CAS number: 7601-90-3), in 1,4-dioxane.

Fill approximately 500 ml of dioxane in a 1 000 ml volumetric flask. Add the capacity of an ampoule for the preparation of 0,1 mol/l perchloric acid standard volumetric solution. Make up to the volume with 1,4-dioxane.

For the determination of the concentration of the perchloric acid standard volumetric solution, weigh about 0,18 g of dried potassium hydrogen phthalate to the nearest 0,1 mg into the titration beaker and dissolve in about 100 ml of acetic acid.

Switch the stirrer on, immerse the electrodes and titrate with the perchloric acid standard volumetric solution beyond the potential jump.

Calculate the concentration, f_c, of the perchloric acid standard volumetric solution, in moles per litre, using the Equation (1):

$$fc = \frac{m_0 \times 1000}{M \times V} \tag{1}$$

where

m_0 is the mass of potassium hydrogen phthalate, in grams;

M is the molar mass of potassium hydrogen phthalate (M = 204,23 g/mol);

V is the volume, in millilitres, of perchloric acid standard volumetric solution consumed to the inflection point.

5 Apparatus

Ordinary 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 pH glass electrode

5.3 Reference electrode Ag/AgCl

The instrument parameters shall be adjusted as to produce a curve similar to that shown in Figure 1.

6 Sampling and preparation of the test sample

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

7 Procedure

WARNING — Perform all titrations specified in a well ventilated hood.

Weigh 1,3 g of the test sample to the nearest 0,1 mg into the beaker. Add 20 ml of methanol and dissolve.

Add 0,5 ml of sodium hydroxide/sodium acetate solution measured with a graduated 1 ml pipette and allow to stand for 5 min at room temperature to react.

Add further 20 ml of methanol and 80 ml of methoxyethanol, both measured with a 100 ml graduated cylinder.

Switch the stirrer on, immerse the electrodes and titrate with the perchloric acid standard volumetric solution beyond the third potential jump. A typical titration curve is shown in Figure 1.

NOTE 1 Bad shaped curves can occasionally be obtained because of the following reasons:

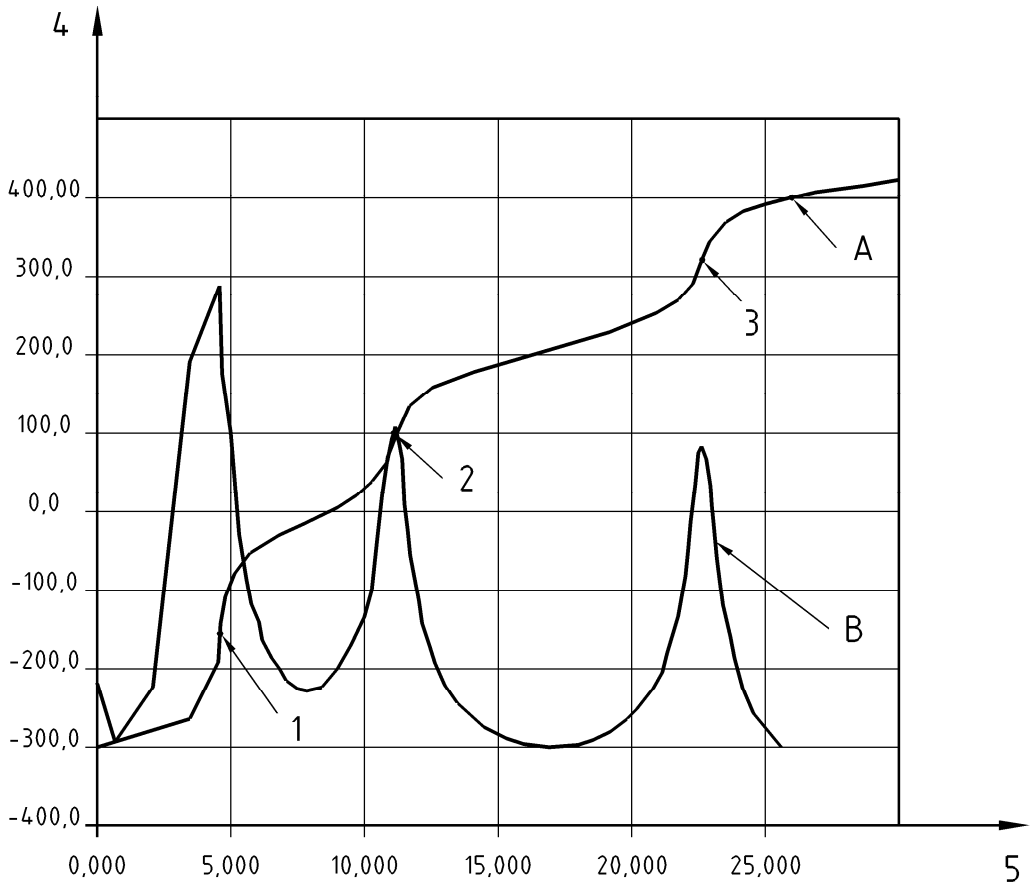
a) static electricity problems (to prevent these problems, special electronic arrangements (e.g. differential potentiometry) should be used);

b) clogging of the electrode diaphragm (remedy by scratching with a needle);

c) overaged perchloric acid standard volumetric solution (remedy by preparing a fresh solution).

NOTE 2 Typical curves start in the negative potential zone (between -100 mV and -400 mV) and show three distinct potential jumps (see Figure 1).

The first jump corresponds to the protonation of excess alkali. The second jump corresponds to the protonation of 1-hydroxy acetate, chloroacetates, fatty acid salts and free amine (i.e. amidoamine). It occurs at positive potential zone. The third jump corresponds to the protonation of betaines. Short chain betaines are also titrated at this point.



Key

1 first inflection point
2 second inflection point
3 third inflection point
4 voltage, in millivolts
5 volume consumed of perchloric acid standard volumetric solution, in millilitres

Figure 1 — Typical titration curve (A) and its first derivative (B)

8 Calculation and expression of results

The content of betaine, w_B, expressed as grams per 100 g, is calculated by the Equation (2):

$$w_B = \frac{(V_3 - V_2) \times M \times f_c}{m \times 10} \quad (2)$$

where

V_3 is the volume consumed of the perchloric acid standard volumetric solution until the third inflection point, in millilitres;

V_2 is the volume consumed of the perchloric acid standard volumetric solution until the second inflection point, in millilitres;

M is the molar mass of the betaine in grams per mole;

f_c is the exact concentration of the perchloric acid standard volumetric solution, in moles per litre;

m is the mass of the test sample, in grams.

The content of betaine, w_B shall be given to one decimal place.

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.

Typical precision data obtained in a ring test are given in Tables B.1 and B.2.

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.

Typical precision data obtained in a ring test are given in Tables B.1 and B.2.

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample tested;

b) a reference to this European Standard, i.e. EN 15109;

c) the test results;

d) details of any operation not specified in this European Standard or in the European Standards to which reference is made, and any operations regarded as optional, as well as any incidents like to have affected the results.

Annex A
(informative)

Titration parameters

The following parameters are settings for the Metrohm 716 DMS Titrino Titroprocessor [1)] and are intended to act as a guideline only (see Table A.1):

Table A.1 — Instrument settings

Parameter	Set point
Measuring point density	3
Minimum increment	10 µl
Titration rate	maximum
Signal, drift	10 mV/min
Equilibration time	52 s
Start volt	off
Pause	0 s
Measuring input	1

NOTE The designations of the parameters correspond to those given by the Metrohm 716 DMS Titrino Titroprocessor.

1) Metrohm 716 DMS Titrino Titroprocessor is an example of suitable apparatus commercially available. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the instruments named.

Annex B
(informative)

Statistical and other data derived from the results of inter-laboratory tests

The data for the repeatability and reproducibility limits of this method are the results of inter laboratory tests carried out by GAT (Common Committee for Analysis of Surfactants) in 1996 and CESIO (Comité Européen des agents de Surface et de leurs Intermédiaires Organiques)/AISE (International Association for Soaps, Detergents and Maintenance Products) in 1997. The evaluation of the laboratory test was performed in accordance with ISO 5725-2.

The alkylamidobetaine (Sample A) was analysed comparatively with samples B, C, and D that were obtained from sample A after addition of fatty acid amidoamine, glycolic acid and respectively fatty acid.

Table B.1 — GAT interlaboratory test of samples of commercial alkylamidopropylbetaines

Designation	Sample A	Sample B	Sample C	Sample D
Number of participating laboratories	8	8	8	8
Number of accepted test results	23	23	23	23
Mean value (w_B) (g/100 g)	27,65	27,54	27,42	27,43
Repeatability standard deviation (s_r)	0,11	0,16	0,14	0,13
Repeatability coefficient of variation	0,4%	0,6%	0,5%	0,5%
Repeatability limit, (r) ($2{,}8 \times s_r$)	0,32	0,45	0,39	0,36
Standard deviation of reproducibility (s_R)	0,17	0,25	0,28	0,31
Reproducibility coefficient of variation	0,6%	0,9%	1,0%	1,1%
Reproducibility limit, (R)($2{,}8 \times \cdot s_R$)	0,47	0,71	0,77	0,87
NOTE Sample B: Sample A spiked with added fatty acid amidoamine Sample C: Sample A spiked with added glycolic acid Sample D: Sample A spiked with added fatty acid				

Table B.2 — CESIO/AISE interlaboratory test of commercial alkylamidopropylbetaine

Designation	Sample E
Number of participating laboratories	8
Number of accepted test results	24
Mean value (w_B) (g/100 g)	32,76
Standard deviation of repeatability (s_r)	0,40
Repeatability coefficient of variation	1,2%
Repeatability limit, (r) ($2{,}8 \times s_r$)	1,14
Standard deviation of reproducibility (s_R)	0,69
Reproducibility coefficient of variation,	2,1%
Reproducibility limit, (R) ($2{,}8 \times s_R$)	1,94

Annex C
(informative)

EN 13270 and EN 15109 active matter comparative analysis

C.1 General

This annex aims to compare the analysis of active matter in an alkyldimethylbetaine and an alkylamidopropylbetaine with both methods EN 13270 and EN 15109.

C.2 Analysis of alkylamidopropylbetaines

C.2.1 General

An alkylamidopropylbetaine (Sample A) was comparatively analysed with EN 13270 and EN 15109.

The evaluation of the inter-laboratory test was performed in accordance with ISO 5725-2.

The results of the inter-laboratory test carried out by GAT (Common Committee for Analysis of Surfactants) in 1996 are listed in Table C.1.

Table C.1 — GAT inter-laboratory test of samples of commercial alkylamidopropylbetaines

Designation	**Sample A** (EN 15109)	**Sample A** (EN 13270)
Number of participating laboratories	8	10
Number of accepted test results	23	28
Mean value (w_B) (g/100 g)	27,65	27,7
Standard deviation of repeatability (s_r)	0,11	0,14
Repeatability coefficient of variation	0,4%	0,5%
Repeatability limit, (r) ($2{,}8 \times s_r$)	0,32	0,40
Standard deviation of reproducibility (s_R)	0,17	0,70
Reproducibility coefficient of variation	0,6%	2,5%
Reproducibility limit, (R) ($2{,}8 \times s_R$)	0,47	1,98

C.2.2 Student-t calculation:

The methods comparison has been done by means of the Student-t comparative test:

The calculated t(cal) resulted lower than the tabulated t(tab):

$$t(cal) = 0{,}17 < \quad t(tab) = 2{,}14 \text{ (95\% confidence)}$$

In this case the hypothesis that mean values are not equivalent is rejected.

Consequently both methods, EN 13270 and EN 15109, can be considered statistically equivalent for the analysis of active matter content in alkylamidopropylbetaines.

C.3 Analysis of alkyldimethylbetaines

C.3.1 General

An alkyldimethylbetaine (Sample F) was also comparatively analysed with the two methods.

The evaluation of the inter-laboratory test was performed in accordance with ISO 5725-2.

The results of the inter-laboratory test carried out by GAT (Common Committee for Analysis of Surfactants) in 1996 are listed in Tables C.2.

Table C. 2 — GAT inter-laboratory test of samples of commercial alkyldimethylbetaines

Designation	Sample F (EN 15109)	Sample F (EN 13270)
Number of participating laboratories	7	8
Number of accepted test results	19	18
Mean value (w_B) (g/100 g)	33,08	32,0
Standard deviation of repeatability (s_r)	0,08	0,13
Repeatability coefficient of variation	0,2%	0,4%
Repeatability limit, (r) ($2{,}8 \times s_r$)	0,21	0,37
Standard deviation of reproducibility (s_R)	0,18	0,27
Reproducibility coefficient of variation	0,5%	0,8%
Reproducibility limit, (R) ($2{,}8 \times s_R$)	0,49	0,75

C.3.2 Student-t calculation:

The methods comparison has been done by means of the Student-t comparative test:

The calculated t(cal) resulted higher than the tabulated t(tab):

t(cal) = 7,44 > t(tab)= 2,23 (95% confidence)

In this case the hypothesis that the mean values are not equivalent is accepted.

Consequently both methods, EN 13270 and EN 15109, can be considered statistically non-equivalent for the analysis of active matter content in alkyldimethylbetaines.

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*

[2] EN 13270, *Surface active agents — Determination of the active matter content in alkyldimethylbetaines*

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