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English Version

Surface active agents - Determination of N-(3-dimethylaminopropyl)-alkylamide content in alkylamidopropylbetaines - Gas chromatographic method

Agents de surface - Détermination de la teneur en N-(3-diméthylaminopropyl)-alkylamide dans les alkylamidopropylbétaïnes - Méthode par chromatographie en phase gazeuse

Grenzflächenaktive Stoffe - Bestimmung des Gehaltes an N-(3-dimethyl-aminopropyl)-alkylamid in Alkylamidopropylbetainen - Gaschromatographisches Verfahren

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

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COMITÉ EUROPÉEN DE NORMALISATION
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Foreword

This European Standard (EN 14881:2005) 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of an identical text or by endorsement, at the latest by February 2006, and conflicting national standards shall be withdrawn at the latest by February 2006.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 free N-(3-dimethylaminopropyl)-alkylamides (amidoamine) in alkylamidopropylbetaines, expressed in grams per 100 g of product.

This method is applicable in the range between 0,02 g and 1,0 g of amidoamine per 100 g of product.

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

The method is based on the amidoamine extraction with diethyl ether at alkaline pH and subsequent analysis of the organic extract by GLC-FID. The chromatogram resolves the different amidoamines according to their alkyl chain length. The result is calculated from the sum of all the chain homologues.

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 not interfering 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 Ethanol

4.3 Diethyl ether

4.4 N-(3-dimethylaminopropyl)-undecylamide (amidoamine-C11), purity ≥ 98 % m/m.

NOTE The N-(3-dimethylaminopropyl) alkylamide standard preparation and purity determination are given in Annex A.

4.5 Potassium hydroxide, ethanolic solution *c* (KOH)= 1 mol/l.

4.6 Internal standard solution

Weigh in a 50 ml volumetric flask, to the nearest 0,1 mg, approximately 0,2 g of the amidoamine-C11 (4.4). Dissolve and make up to the mark with ethanol (4.2). Keep tightly closed.

4.7 Sodium chloride, aqueous solution, 30 % m/m.

4.8 Phenolphthalein, solution of 1 % m/*V* in ethanol.

5 Apparatus

Ordinary laboratory apparatus and the following.

5.1 Gas chromatograph, with capillary split injector, flame ionisation detector and integrator or computer.

5.2 Fused silica capillary column, coating with bonded deactivated poly (5 % diphenyl/95 % dimethyl) siloxane, length 30 m, internal diameter 0,25 mm, film thickness 0,50 µm (PTA-5[1)]).

5.3 Syringe, capacity 1 µl.

6 Sampling and preparation of the sample

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

7 Procedure

7.1 Calibration

Since it is assumed that the response factor of the different homologues is the same no extra calibration is needed (see Annex C).

7.2 Determination

Weigh to the nearest 0,1 mg, approximately 3,0 g of sample in a 15 ml vial with snap cap.

Add 2 ml of NaCl solution (4.7), and homogenise.

Add 1 ml of internal standard solution (4.6), measured with a one-mark pipette.

Add two drops of the phenolphthalein solution (4.8) and enough potassium hydroxide solution (4.5) to red change and add few extra drops of potassium hydroxide solution.

Add 4 ml of diethyl ether (4.3) measured with a measuring cylinder.

Stopper and shake the tube vigorously for about 1 min.

Let stand until the phases separate (usually 2 min will be enough).

Analyse the organic phase by injecting 1 µl of the organic layer directly into the gas chromatograph (5.1).

Set up the gas chromatograph to give results similar to the reference chromatogram in Figure B.1.

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1) PTA-5 is the trade name of product supplied by Supelco (U.S.A). This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the product named.

8 Calculation and expression of results

The content of total free amidoamine, *c*, in the sample, expressed in grams per 100 g of the product, is calculated by the equation:

$$c=\frac{m_{\mathrm{is}}\times A\times w}{m\times A_{\mathrm{is}}} \qquad (1)$$

where

m_{IS} is the mass of the internal standard, in grams, present in 1 millilitre;

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

A_{IS} is the peak area of the internal standard in the chromatogram of the sample solution;

A is the sum of the areas of all the peaks corresponding to alkylamidoamine homologues (except that of the internal standard) in the chromatogram of the sample solution;

w is the purity of internal standard in grams per 100 g (see Annex A).

The relative response factor of all the N-(3-dimethylaminopropyl)- alkylamide homologues with respect to the internal standard N-(3-dimethylaminopropyl)- undecylamide is assumed to be 1 (see Annex C).

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 the cases.

Precision data are given in Annex D.

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 the cases.

Precision data are given in Annex D.

10 Test report

The test report shall include the following information:

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

b) method used (a reference to this European Standard, i.e. EN 14881);

c) test results;

d) details of any operation 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 like to have affected the results.

Annex A
(informative)

N-(3-dimethylaminopropyl)-undecylamide

A.1 Preparation of N-(3-dimethylaminopropyl)-undecylamide

250 g (1,34 mol) undecanoic acid of about 98 % purity is weighed together with 1,5 g of 50 % hypophosphorous acid into a 500 ml four-neck round-bottom flask equipped with an immersion thermometer, an addition funnel, a mechanical stirrer, condenser and nitrogen purge systems.

206 g (2,01 mole) dimethylaminopropylamine (DMAPA) is added drop wise during 30 min at 140 ºC under N_2 atmosphere. Temperature is then raised up to 200 ºC within 3 h while the water is removed. The reaction is completed at 200 ºC for an additional 2 h, when the acid value becomes lower than 1 mg KOH/g.

The reactor content is cooled down to 180 ºC and the condenser system removed.

Keeping the system at 180 ºC under a reduced pressure of 2 mm/Hg for an additional 2 h distils off the residual DMAPA.

A.2 Determination of purity of N-(3-dimethylaminopropyl)-undecylamide standard

The N-(3-(dimethylaminopropyl)-undecylamide standard purity is determined as follows:

$$w=\left(100-\left(\frac{186\times AV}{56,1\times 10}\right)\right)\times\frac{r}{100} \qquad \text{(A.1)}$$

where

w is the concentration of the N-(3-dimethylaminopropyl)-undecylamide (internal standard) in grams per 100 grams;

AV is the acid value of the N-(3-dimethylaminopropyl)-undecylamide, in milligrams KOH per gram;

r is the relative percentage of alkyl chain C 11 obtained by gas chromatograph.

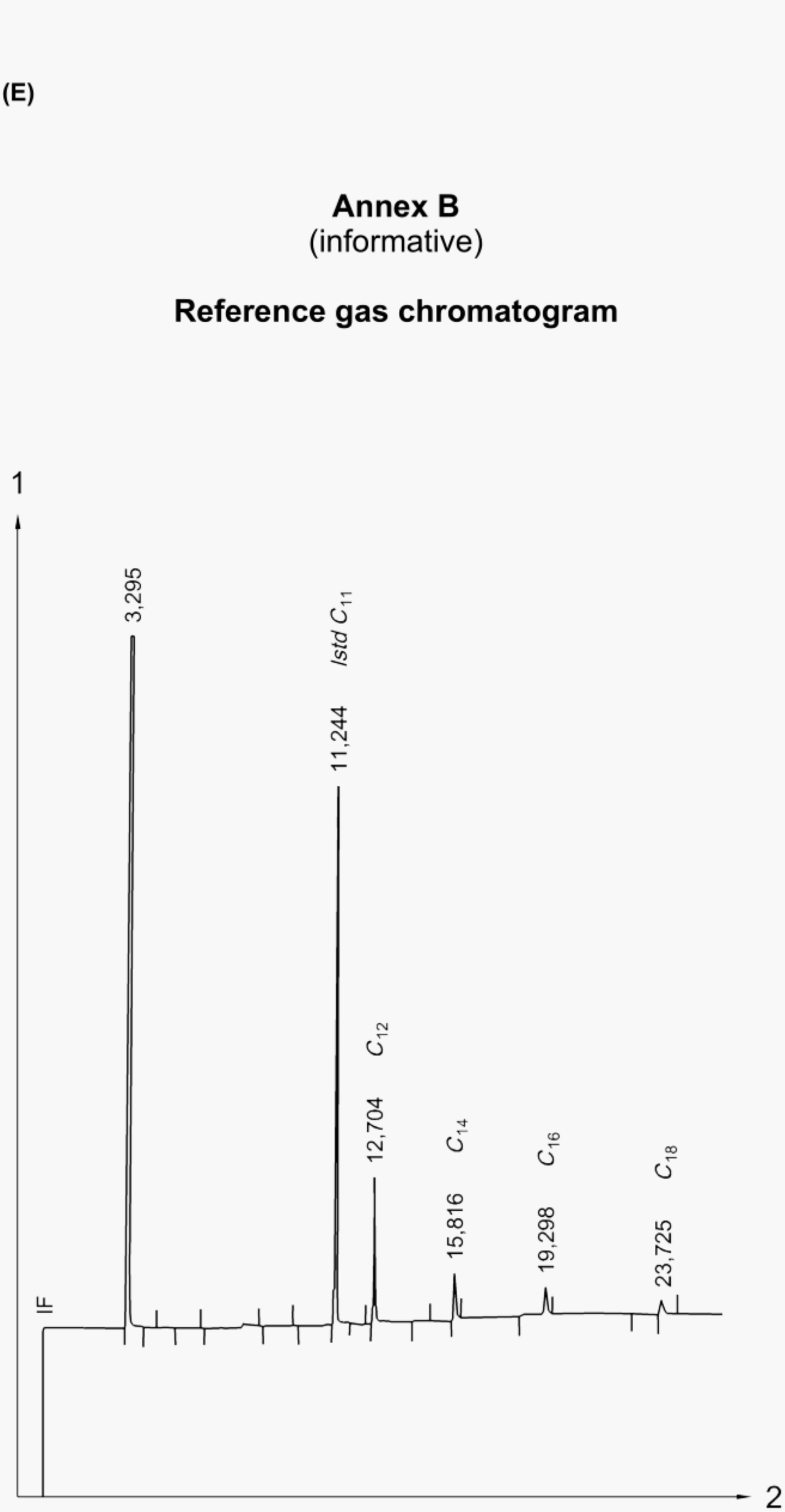
186 is the molecular weight of the undecanoic acid.

NOTE 1 The acid value (AV) corresponds to the determination of free undecanoic acid by potentiometric titration with a potassium hydroxide standard volumetric solution c (KOH) = 0,1 mol/l in ethanol (see EN ISO 660).

NOTE 2 The alkyl chain purity (r) is determined by analysing an ethanolic solution of 5 % (m/V) by gas chromatography following the same conditions specified in 7.2 and calculated by areas normalisation in percentage.

Annex B
(informative)

Reference gas chromatogram



Key
1 response
2 time

Figure B.1 – Reference gas chromatogram

The following GC conditions have be found to be suitable:

Column	PTA-5[2)] (30 m, 0,25 mm, film thickness 0,50 µm)
Carrier gas	Helium
Column head pressure	48 kPa
Split	50 ml/min
Injection volume	1µl
Injector temperature	230 °C
Detector temperature: FID	330 °C
Temperature programme	220 °C (0 min) to 300 °C with 5 °C/min; 300°C (10 min)

[2]) PTA-5 is the trade name of product supplied by Supelco (U.S.A). This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the product named.

Annex C
(informative)

Validation method

C.1 Selectivity

All the signals corresponding to alkylamidoamine and the internal standard are perfectly separated. The relative retention factor between the signals of C 11 and C 12 is α = 1,2.

C.2 Linearity

Range studied: 0,02 % to 1,0 % of coconut alkylamidopropylamine.

The adjusted regression line of A_{IS}/A_{C12} versus c_{IS}/c_{C12} (within the studied range) fits the linearity requirements specified:

	Experimental	**Tolerance**
Correlation coefficient (*r*)	0,999 6	> 0,98 %
S_b relative (%)	1,134	< 2,0 %
Proportionality test	0,019 ± 0,517 9	includes 0

$$A_{IS}/A_i = 1{,}0150 \times c_{IS}/c_i \qquad \text{(C.1)}$$

Since the slope is quite close to 1, it can be assumed that the relative response factor between all the alkylamidopropylamines is 1.

C.3 Precision

Fits the established criteria CV ≤ CV (Horwitz) where:

CV = 5,82 % ≤ CV (Horwitz) = 6,28 %

Resulting of n = 6 analysis under repeatability conditions.

C.4 Recovery

The recovery is 100,35 % with a CV (Recovery) of 4,5 % in an alkylamidopropylbetaine with 0,1 % of alkylamidopropylamine, and fits the criteria: $t_{exp} \leq t_{tab}$ where $t_{exp} = 0{,}133 < t_{tab} = 3{,}18$.

Annex D
(informative)

Inter-laboratory test results

The inter-laboratory test was carried out in 2002.

Table D.1 — Results of inter-laboratory test

Designation	Precision data
Numbers of laboratories participating	7
Numbers of laboratories not eliminated	7
Number of individual test results of all laboratories	20
Mean value, m, in % m/m	0,087
Repeatability standard deviation s_r, % m/m	0,003 2
Repeatability limit r (s_r x 2,8), in % m/m	0,008 9
Repeatability coefficient of variation, in %	3,6
Reproducibility standard deviation s_R, in % m/m	0,003 9
Reproducibility limit R (s_R x 2,8), in % m/m	0,011
Reproducibility coefficient of variation, in %	4,4

Bibliography

[1] EN ISO 660, *Animal and vegetable fats and oils – Determination of acid value and acidity (ISO 660:1996)*