BRITISH STANDARD

BS EN
13717:2002

Surface active agents — Determination of primary, secondary and tertiary amino nitrogen — Potentiometric titration

The European Standard EN 13717:2002 has the status of a British Standard

ICS 71.100.40

National foreword

This British Standard is the official English language version of EN 13717:2002.

The UK participation in its preparation was entrusted to Technical Committee CII/34, Methods of test for surface active agents, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

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This British Standard, having been prepared under the direction of the Materials and Chemicals Sector Policy and Strategy Committee, was published under the authority of the Standards Policy and Strategy Committee on 20 December 2002

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English version

Surface active agents - Determination of primary, secondary and tertiary amino nitrogen - Potentiometric titration

Agents de surface - Détermination de la teneur en azote sous forme amine primaire, secondaire et tertiaire - Titrage potentiométrique

Grenzflächenaktive Stoffe - Bestimmung des Gehalts an Primär-, Sekundär- und Tertiär-Aminstickstoff - Potentiometrische Titration

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Contents

Foreword

This document (EN 13717:2002) 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of an identical text or by endorsement, at the latest by June 2003, and conflicting national standards shall be withdrawn at the latest by June 2003.

The annexes A, B and C are informative.

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

1 Scope

This European Standard specifies the methods for the determination of primary, secondary and tertiary amino nitrogen content in surface active agents by potentiometric titration.

2 Normative reference

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

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

3 Principle

3.1 The sum of primary and secondary amino nitrogen

After reaction of the primary and secondary amino nitrogen with carbon disulfide, the resulting dithiocarbamic acids are titrated with sodium hydroxide standard volumetric solution (see also NOTE in 7.1).

3.2 The sum of secondary and tertiary amino nitrogen

After reaction of the primary amino nitrogen with salicylaldehyde to give a Schiff's base, the sum of secondary and tertiary amino nitrogen is determined by potentiometric titration with hydrochloric acid standard volumetric solution.

3.3 Tertiary amino nitrogen

After reaction of the primary and secondary amino nitrogen with acetic acid anhydride, the tertiary amino nitrogen is determined by titration with standard trifluoromethane sulfonic acid solution.

NOTE Alternatively, a reaction with phenylisothiocyanate and a subsequent titration with hydrochloric acid standard volumetric solution can be carried out.

4 Reagents

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.

4.1 Sodium hydroxide standard volumetric solution, c (NaOH) = 0,1 mol/l.

4.2 Carbon disulfide, purity 99,7 % (minimum).

WARNING This substance is highly flammable and toxic. It causes serious damage to health by prolongated exposure through inhalation and is a possible risk of impaired fertility as well as harm to the unborn child. This substance irritates to eyes and skin.

4.3 2-Propanol, purity 99,5 % (minimum).

4.4 Hydrochloric acid standard volumetric solution, c (HCl) = 0,1 mol/l, in 2-propanol.

4.5 Salicylaldehyde, purity 99 % (minimum).

4.6 Acetic acid anhydride, purity 98,5 % (minimum).

4.7 Trifluoromethane sulfonic acid standard volumetric solution, c (HSO_3CF_3) = 0,1 mol/l, in glacial acetic acid.

NOTE Perchloric acid, c ($HClO_4$) = 0,1 mol/l, in glacial acetic acid can also be used.

4.8 Glacial acetic acid, purity 100 %.

4.9 Phenolphthalein solution, = 1 g/100 ml, in ethanol, as indicator.

4.10 Phenylisothiocyanate, purity 98 % (minimum).

5 Apparatus

Ordinary laboratory apparatus and the following.

5.1 Potentiometric titrating apparatus, comprising a titrator with a combined pH glass electrode, a 20 ml plunger burette and a stirrer.

NOTE An example of instrument settings is given in Annex A.

5.2 Beaker, capacity 150 ml.

5.3 Analytical balance, reading to the nearest 0,1 mg.

5.4 Magnetic stirrer, with hot plate.

5.5 Oven.

5.6 Pressure bottles, encased in plastics, capacity 250 ml, with plastics screw caps and polytetrafluoroethylene (PTFE) seal.

5.7 Fume cupboard.

6 Sampling and preparation of the sample

The laboratory sample of surface active agent shall be prepared and stored in accordance with ISO 607.

7 Procedure

7.1 Titration of the primary and secondary amino nitrogen

Weigh into the beaker (5.2) a quantity of the sample (m_1) to be tested which contains about 0,5 mmol to 1 mmol of total base nitrogen to the nearest 0,1 mg. Dissolve the sample in 50 ml of 2-propanol (4.3). Add a few drops of phenolphthalein solution (4.9). Then add sodium hydroxide standard volumetric solution (4.1) until the colour changes to faint pink.

Add 5 ml of carbon disulfide (4.2) and stir for 1 min at room temperature (work in a fume cupboard).

Immerse the electrode, stir and titrate with sodium hydroxide standard volumetric solution (4.1).

Record the amount consumed at the equivalent (inflexion) point (volume V_1) ; (see Annex B).

NOTE To avoid the use of carbon disulfide, the test method in accordance with EN 13716 can be alternatively applied to determine the content of total base nitrogen, w_t, the primary amino nitrogen content is calculated by the equation $w_1 = w_t - w_2$ when w_2 is determined in 7.2.

7.2 Titration of the secondary and tertiary amino nitrogen

Weigh into the beaker (5.2) an amount of the sample (m_2) to be tested which contains about 0,5 mmol to 1 mmol of total base nitrogen to the nearest 0,1 mg. Dissolve the sample in 50 ml of 2-propanol (4.3).

Add 5 ml of salicylaldehyde (4.5) and heat at 80 °C for 15 min (work in a fume cupboard). Allow the solution to cool to room temperature.

Immerse the electrode, stir and titrate with hydrochloric acid standard volumetric solution (4.4).

Record the consumption at the equivalent (inflexion) point (volume V_2) ; (see Annex B).

7.3 Titration of the tertiary amino nitrogen (acetic acid anhydride method)

Weigh into a pressure bottle (5.6) a quantity of the sample (m_3) to be tested which contains about 0,5 mmol to 1 mmol of total base nitrogen to the nearest 0,1 mg. Dissolve the sample in 20 ml of glacial acetic acid (4.8). Then add 30 ml of acetic acid anhydride (4.6).

Seal the pressure bottle (5.6) securely and heat at 60 °C in the oven (5.5) for 30 min.

Allow to cool to room temperature; open the pressure bottle and rinse down the cap and the sides of the bottle with glacial acetic acid (4.8).

Immerse the electrode, stir and titrate with trifluoromethane sulfonic acid standard volumetric solution (4.7).

Record the consumption at the equivalent (inflexion) point (volume V_3) ; (see annex B).

7.4 Titration of the tertiary amino nitrogen (phenylisothiocyanate method)

Weigh into the beaker (5.2) an amount of the sample (m_4) to be tested which contains about 0,5 mmol to 1 mmol of total base nitrogen to the nearest 0,1 mg. Dissolve the sample in 50 ml of 2-propanol (4.3). Then add 5 ml of phenylisothiocyanate (4.10) and heat the solution at 60 °C for 30 min (work in a fume cupboard). Allow the solution to cool to room temperature.

Immerse the electrode, stir and titrate with hydrochloric acid standard volumetric solution (4.4).

Record the consumption at the equivalent (inflexion) point (volume V_4) ; (see Annex B).

8 Expression of results

8.1 Calculation of the sum of primary and secondary amino nitrogen

Calculate the sum of primary and secondary amino nitrogen, w_1, expressed as grams per 100 g, by the equation (1) :

$$w_1 = \frac{V_1 \times c_1 \times f_1 \times M \times 100}{m_1 \times 1\,000} \qquad (1)$$

where

V_1 is the volume of sodium hydroxide standard volumetric solution (4.1) according to 7.1, in millilitres ;

c_1 is the concentration of the sodium hydroxide standard volumetric solution (4.1), in moles per litre ;

f_1 is the factor of the sodium hydroxide standard volumetric solution (4.1) ;

M is the molar mass of nitrogen, M = 14 g/mol ;

m_1 is the mass of sample according to 7.1, in grams.

8.2 Calculation of the sum of secondary and tertiary amino nitrogen

Calculate the sum of secondary and tertiary amino nitrogen, w_2, expressed as grams per 100 g, by the equation (2) :

$$w_2 = \frac{V_2 \times c_2 \times f_2 \times M \times 100}{m_2 \times 1\,000} \qquad (2)$$

where

V_2 is the volume of hydrochloric acid standard volumetric solution (4.4) according to 7.2, in millilitres ;

c_2 is the concentration of hydrochloric acid standard volumetric solution (4.4), in moles per litre ;

f_2 is the factor of the hydrochloric acid standard volumetric solution (4.4) ;

M is the molar mass of nitrogen, M = 14 g/mol ;

m_2 is the mass of sample according to 7.2, in grams.

8.3 Calculation of the tertiary amino nitrogen

a) Calculate the tertiary amino-nitrogen content, w_3, expressed as grams per 100 g, by the equation (3) :

$$w_3 = \frac{V_3 \times c_3 \times f_3 \times M \times 100}{m_3 \times 1\,000} \qquad (3)$$

where

V_3 is the volume of trifluoromethane sulfonic acid standard volumetric solution (4.7) according to 7.3, in millilitres ;

c_3 is the solution concentration of the trifluoromethane sulfonic acid standard volumetric solution (4.7), in moles per litre ;

f_3 is the factor of the trifluoromethane sulfonic acid standard volumetric solution (4.7) ;

M is the molar mass of nitrogen, M = 14 g/mol ;

m_3 is the mass of the sample according to 7.3, in grams.

b) Calculate the tertiary amino nitrogen content, w_4, expressed as grams per 100 g, by the equation (4) :

$$w_4 = \frac{V_4 \times c_4 \times f_4 \times M \times 100}{m_4 \times 1\,000} \quad (4)$$

where

V_4 is the volume of hydrochloric acid standard volumetric solution (4.4) according to 7.4, in millilitres ;

c_4 is the concentration of the hydrochloric acid standard volumetric solution (4.4) in moles per litre ;

f_4 is the factor of the hydrochloric acid standard volumetric solution (4.4) ;

M is the molar mass of nitrogen, M = 14 g/mol ;

m_4 is the mass of sample according to 7.4, in grams.

The results shall be given to two decimal places.

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 Annex C.

9.2 Reproducibility limit

The absolute difference between two 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 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) the method used (a reference to this European Standard);

c) the results obtained and the way which they have been expressed;

d) details of any operations 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 likely to have affected the results.

Annex A
(informative)

Instrument settings

Data given are settings for the Metrohm Titroprocessor 682 [1)] and are intended to act as a guideline, only.

Pause 1:	20 s
Electrical input:	1
Titration rate:	1,50 ml/min
Anticipation:	40
Stop volume:	15,00 ml
Temperature:	25 °C
Equivalent point (EP) criterion:	1

1) Metrohm Titroprocessor 682 is the trade name of an instrument 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 the instrument named.

Annex B
(informative)

Typical titration curves

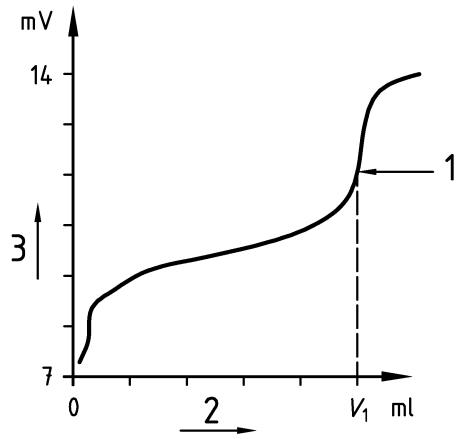

Figure B.1 — Titration of the primary and amino nitrogen

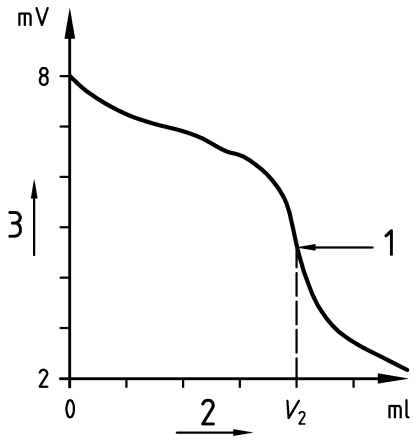

Figure B.2 — Titration of the secondary and tertiary amino nitrogen

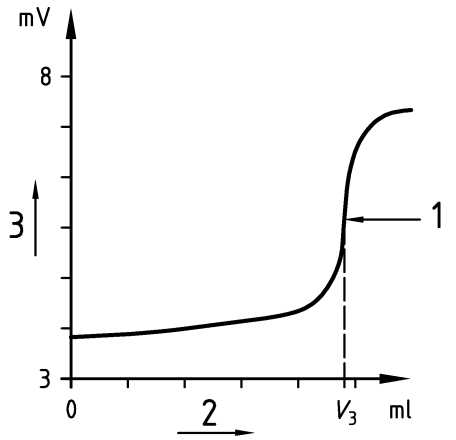

Figure B.3 — Titration of the tertiary amino nitrogen (acetic acid anhydride method)

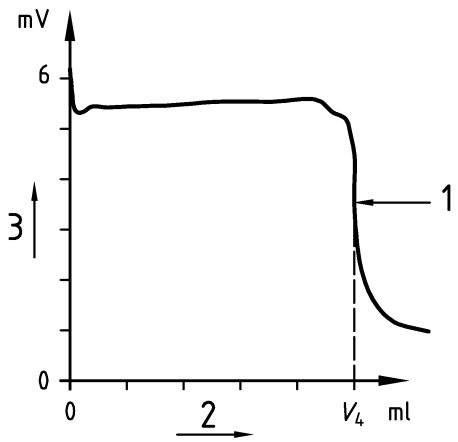

Figure B.4 — Titration of the tertiary amino nitrogen (phenylisothiocyanate method)

Key for Figures B.1 to B.4

1 Equivalent point
2 Consumption of the standard volumetric solution, in millilitres
3 Voltage, in millivolts

Annex C
(informative)

Results of interlaboratory test

The interlaboratory test was carried out in 1997 by the AISE/CESIO WG "Surfactant Analysis". The test samples were commercial products (laurylpropylene diamine and cocofattyamine 2 C_2H_4O).

Table C.1 — Results of laurylpropylene diamine (primary and secondary amino nitrogen)

Denomination	Laurylpropylene diamine (primary and secondary amino nitrogen)
Number of laboratories participating	10
Number of laboratories not eliminated	10
Number of individual test results of all laboratories on each sample	30
Mean value, w, in g/100 g	10,85
Repeatability standard deviation, s_r, in g/100 g	0,142
Repeatability limit r, ($r = s_r$ 2,8), in g/100 g	0,40
Reproducibility standard deviation, s_R, in g/100 g	0,282
Reproducibility limit R, ($R = s_R$ 2,8), in g/100 g	0,79
Repeatability coefficient of variation, in %	1,3
Reproducibility coefficient of variation, in %	2,6

Table C.2 — Results of laurylpropylene diamine (secondary and tertiary amino nitrogen)

Denimonation	Laurylpropylene diamine (secondary and tertiary amino nitrogen)
Number of laboratories participating	13
Number of laboratories not eliminated	13
Number of individual test results of all laboratories on each sample	37
Mean value, w, in g/100 g	5,51
Repeatability standard deviation, s_r, in g/100 g	0,029
Repeatability limit r, ($r = s_r$ 2,8), in g/100 g	0,08
Reproducibility standard deviation, s_R, in g/100 g	0,080
Reproducibility limit R, ($R = s_R$ 2,8), in g/100 g	0,22
Repeatability coefficient of variation, in %	0,5
Reproducibility coefficient of variation, in %	1,5

Table C.3 — Results of cocofatty amine 2 C_2H_4O (tertiary amino nitrogen)

Denomination	Cocofatty amine 2 C_2H_4O (tertiary amino nitrogen)	
	Acetic acid anhydride method	Phenylisothiocyanate method
Number of laboratories participating	13	14
Number of laboratories not eliminated	13	14
Number of individual test results of all laboratories on each sample	39	42
Mean value, w, in g/100 g	4,83	4,90
Repeatability standard deviation, s_r, in g/100 g	0,029	0,028
Repeatability limit r, ($r = s_r$ 2,8), in g/100 g	0,08	0,08
Reproducibility standard deviation, s_R, in g/100 g	0,044	0,067
Reproducibility limit R, (R = 2,8 s_R), in g/100 g	0,12	0,19
Repeatability coefficient of variation, in %	0,6	0,6
Reproducibility coefficient of variation, in %	0,9	1,4

Bibliography

EN 13716, *Surface active agents – Determination of total base nitrogen – Potentiometric titration.*

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