BRITISH STANDARD

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13926:2003

Surface active agents — Alkoxylated derivatives — Determination of hydroxyl value — N-methyl imidazole method

The European Standard EN 13926:2003 has the status of a
British Standard

ICS 71.100.40

British Standards

National foreword

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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:

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English version

Surface active agents - Alkoxylated derivatives - Determination of hydroxyl value - N-methyl imidazole method

Agents de surface - Dérivés alkyloxylés - Détermination de l'indice d'hydroxyle - Méthode à la N-méthylimidazole

Grenzflächenaktive Stoffe - Alkoxylierte Derivate - Bestimmung der Hydroxylzahl - N-Methylimidazol-Verfahren

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Contents

Foreword

This document (EN 13926:2003) 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of an identical text or by endorsement, at the latest by September 2003, and conflicting national standards shall be withdrawn at the latest by September 2003.

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, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a method for the determination of hydroxyl value of aliphatic and alicyclic hydroxyl compounds such as polyols, sorbitan esters, plasticisers and surface active agent alcohols and alkoxylates with hydroxyl values greater than 20 mg KOH/g.

2 Normative references

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.*

ISO 4314, *Surface active agents – Determination of free alkalinity or free acidity – Titrimetric method.*

3 Term and definition

For the purposes of this European Standard, the following term and definition apply.

3.1
hydroxyl value *I*(OH)
number of milligrams of potassium hydroxide needed to neutralize the acetic acid required to esterify the hydroxyl groups in 1 g of the material, or the number of milligrams of potassium hydroxide corresponding to the hydroxyl groups in 1 g of the material

4 Principle

A known mass of test sample is esterified with an excess of acetic anhydride/tetrahydrofuran solution using N-methyl imidazole as a catalyst. The excess of acetic anhydride is hydrolysed and then the formed acetic acid istitrated potentiometrically with ethanolic potassium hydroxide standard volumetric solution. The hydroxyl value is calculated from the difference in titration volumes of a blank test and the test sample.

5 Reagents

5.1 General

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.

WARNING — Tetrahydrofuran and N-methylimidazole being hazardous chemicals, all the operations shall be conducted under a well ventilated fume hood.

5.2 Tetrahydrofuran, C_4H_8O.

5.3 Acetic anhydride, $C_4H_6O_3$.

5.4 N-methyl imidazole, $C_4H_6N_2$.

5.5 Potassium hydrogen phthalate, $C_8H_5O_4K$, $w(C_8H_5O_4K) = 99$ % dried at (105 1) °C.

5.6 Ethanol, C_2H_5OH.

5.7 Potassium hydroxide standard volumetric solution in ethanol, $c(\text{KOH}) = 0{,}5$ mol/l.

Weigh 66,0 g of potassium hydroxide with a purity of 85 % (*m/m*) to the nearest 0,1 g and dissolve it in 250 ml freshly boiled water. Then transfer the solution into a 2 l volumetric flask and complete to the mark with ethanol (5.6). Allow the solution to stand for 24 h before standardization.

5.8 Acetylation reagent

Carefully mix 92 ml of tetrahydrofuran (5.2) and 8 ml of acetic anhydride (5.3). This solution is stable for up to one month.

6 Apparatus

6.1 General

Ordinary laboratory apparatus and the following.

6.2 Potentiometer, comprising a titrator with a combined glass/calomel electrode, automatic burette assembly and a magnetic stirrer.

6.3 Water bath, capable of maintaining a temperature of (45 ± 1) °C.

6.4 Air-cooler, with a length of 1 m.

6.5 Analytical balance, with an accurate to 0,000 1 g.

7 Sampling

Sample the material to be tested and store in accordance with ISO 607.

8 Procedure

8.1 Standardization of the ethanolic potassium hydroxide standard volumetric solution

Weigh approximately 1 g of dried potassium hydrogen phthalate (5.5) to the nearest 0,1 mg into a 150 ml beaker and dissolve it in 80 ml of freshly boiled water.

Immerse the electrode and a magnetic stir bar into the beaker, stir and titrate with the potentiometer (6.2) with the ethanolic potassium hydroxide standard volumetric solution (5.7).

Record the volume V_o of the ethanolic potassium hydroxide standard volumetric solution (5.7) at the first inflection point.

Carry out the standardization in triplicate.

8.2 Test portion

Calculate the quantity of the laboratory sample to be weighed, m, expressed in grams, by the equation (1):

$$m = \frac{168}{I(\text{OH})_\text{E}} \tag{1}$$

where

$I(\mathrm{OH})_E$ is the expected hydroxyl value, in milligrams KOH per gram of the material.

8.3 Determination

Fill the calculated mass of the test portion (8.2), m, weighed to the nearest 0,1 mg and not exceeding 10 g into a clean dry 150 ml stoppered conical flask.

Introduce with a pipette 10 ml of the acetylation reagent (5.8).

Add 2 ml of N-methyl imidazole (5.4) into the flask and dissolve the test portion.

Stop up the flask or connect the air cooler (6.4).

Place the flask in a water bath (6.3) at 45 °C for 15 min.

At the end of the reaction time, add 10 ml of water (taking care of washing the stopper or the air-cooler). Homogenise and allow to stand for 2 min.

Introduce the electrode and a magnetic stir bar into the flask, add enough ethanol to cover the tip of the electrode.

Titrate with the potentiometer (6.2) with the ethanolic potassium hydroxide standard volumetric solution (5.7) and note the volume (V_1) at the first inflection point.

Perform the laboratory sample analysis in duplicate.

8.4 Blank tests

Carry out two blank tests at the same time at the determination, using the same reagents, but without the test portion and note the volume at the first inflection as V_2.

9 Expression of results

9.1 Standardisation factor of the ethanolic potassium hydroxide standard volumetric solution

The standardisation factor, f, of the ethanolic potassium hydroxide standard volumetric solution (5.6) is calculated by the equation (2):

$$f = \frac{m_0 \quad w_0 \quad 10}{V_0 \quad M \quad c} \qquad (2)$$

where

m_o is the mass of potassium hydrogen phthalate (5.5), in grams;

w_o is the purity of potassium hydrogen phthalate (5.5), in percent (*m/m*);

V_o is the volume of the ethanolic potassium hydroxide standard volumetric solution (5.7) used for the standardisation (8.1), in millilitres;

M is the molar mass of potassium hydrogen phthalate (5.5), $M(C_8H_5O_4K)$ = 204,23 g/mol;

c is the concentration of the ethanolic potassium hydroxide standard volumetric solution (5.7), c(KOH) = 0,5 mol/l.

Take as the standardization factor the mean of three titrations performed according to 8.1.

9.2 Hydroxyl value

The experimental hydroxyl value, $I(\mathrm{OH})_o$, in milligrams of KOH per gram of the test portion, is calculated by the equation (3):

$$I(\mathrm{OH})_o = (V_2 \quad V_1) \quad c \quad f \quad \frac{56{,}11}{m} \tag{3}$$

where

V_2	is the mean volume of the ethanolic potassium hydroxide standard volumetric solution (5.7) used for the blank tests (see 8.4), in millilitres;
V_1	is the volume of the ethanolic potassium hydroxide standard volumetric solution (5.7) used for the determination (see 8.3), in millilitres;
c	is the concentration of the ethanolic potassium hydroxide standard volumetric solution (5.7), c(KOH) = 0,5 mol/l;
f	is the mean of standardisation factor of ethanolic potassium hydroxide the standard volumetric solution (5.7) from 9.1;
m	is the mass of the test portion (see 8.3), in grams.

For samples containing free acidity, the hydroxyl value, $I(\mathrm{OH})$, is calculated by the equation (4):

$$I(\mathrm{OH}) = I(\mathrm{OH})_o + AV \tag{4}$$

where

$I(\mathrm{OH})_o$	is the experimental hydroxyl value, in milligrams of KOH per gram of the test portion;
AV	is the acidity value of the sample in accordance with ISO 4314 or equivalent, in milligrams of KOH per gram of the test portion.

For samples containing free alkalinity, the hydroxyl value, $I(\mathrm{OH})$, is calculated by the equation (5):

$$I(\mathrm{OH}) = I(\mathrm{OH})_0 \quad BV \tag{5}$$

where

$I(\mathrm{OH})_o$	is the experimental hydroxyl value, in milligrams of KOH per gram of the test portion;
BV	is the alkalinity value of the sample in accordance with ISO 4314 or equivalent, in milligrams of KOH per gram of the test portion.

10 Precision

10.1 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 A.

10.2 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 annex A.

11 Test report

The test report shall include the following information:

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

b) a reference to this European Standard;

c) the test results;

d) details of any operations not specified in this European Standard, and any operations regarded as optional, as well as any incidents likely to have affected the results.

Annex A
(informative)

Results of interlaboratory test

The interlaboratory test was carried out by CESIO/AISE in 1998. The precision data were evaluated in accordance with ISO 5725-2. Four samples were analysed four times by 13 laboratories. These samples are shown in Table A.1.

Table A.1 – Test samples

Sample	Designation
A	Isotridecanole + 7EO
B	Sorbitan monolaurate
C	PO/EO-blockcopolymer
D	Lauryl alcohol

The ring test results are given in Tables A.2 and A.3.

Table A.2 – Results of interlaboratory test concerning the experimental hydroxyl values, $I(\mathrm{OH})_o$

Designation	Sample A	Sample B	Sample C	Sample D
Number of laboratories participating	12	13	13	13
Number of laboratories not eliminated	12	9	9	12
Total number of values (without outliers)	48	36	36	48
Mean value, in mg KOH/g	116,34	339,18	49,18	299,93
Repeatability standard deviation, s_r , in mg KOH/g	0,944	1,42	0,35	2,65
Repeatability limit, r : (r = 2,8 x s_r) in mg KOH/g	2,67	4,03	0,99	7,51
Repeatability coefficient of variation, in %	0,81	0,42	0,71	0,89
Reproducibility standard deviation, s_R in mg KOH/g	1,23	2,77	0,47	3,69
Reproducibility limit, R : (R =2,8 x s_R) in mg KOH/g	3,49	7,84	1,32	10,45
Reproducibility coefficient of variation, in %	1,06	0,82	0,95	1,24

Table A.3 – Results of interlaboratory test concerning the acidity respectively basicity values, I(OH)

Designation	Sample A	Sample B	Sample C	Sample D
Number of laboratories not eliminated	11	9	9	12
Total number of values (without outliers)	44	36	36	48
Mean value, in mg KOH/g	116,37	343,9	50,16	299,53
Repeatability coefficient of variation, in %	0,66	0,42	0,71	1,1
Reproducibility coefficient of variation, in %	1,04	0,99	1,47	1,45

Annex B
(informative)

Example for potentiometric operating parameters

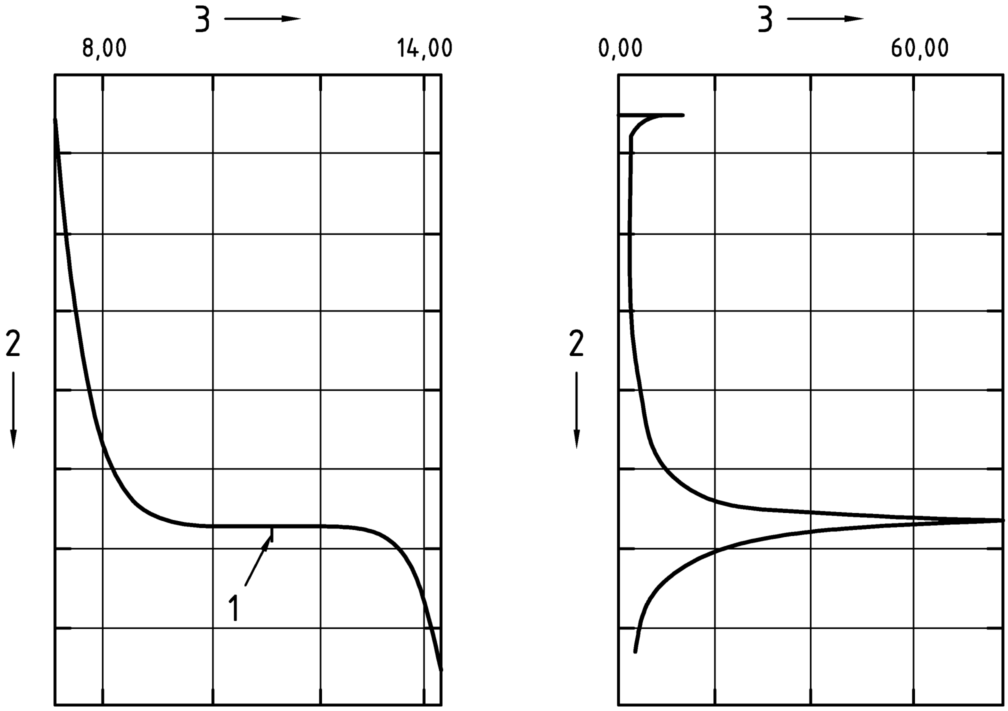
The following potentiometric operating parameters are given as a guideline (see Table B.1).

Table B.1 – Parameters for the dynamic equivalence point titration

Parameter	Measurable
Burette volume/Resolution	20 ml/2 l
Beginning volume addition	15 ml
Waiting time after beginning volume	20 s
Measuring point density	4
Minimum increment on titration	10,0 l
Drift	50 mV/min
Waiting time for measured value acquisition	26 s
End point criteria	30

Annex C
(informative)

Example for a typical titration curve and its derivative



a) Titration curve

b) Derivative of the titration curve

Key

1 Inflection point

2 Volume of the standard volumetric solution, in millilitres

3 Voltage, in millivolts

Figure C.1 – Example for a typical titration curve (a) and its derivative (b)

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.*

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