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15168:2006

Surface active agents — Determination of hydroxyl value — p-Toluensulfonyl isocyanate (TSI) method and potentiometric titration with tetrabutylammonium hydroxide

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ICS 71.100.40

British Standards

National foreword

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Surface active agents - Determination of hydroxyl value - p-Toluensulfonyl isocyanate (TSI) method and potentiometric titration with tetrabutylammonium hydroxide

Agents de surface - Détermination de l'indice d'hydroxyle - Méthode à la p-toluènesulfonylisocyanate (TSI) et titrage potentiomètrique avec l'hydroxyde de tétrabutylammonium

Grenzflächenaktive Stoffe - Bestimmung der Hydroxylzahl - p-Toluolsulfonylisocyanat-(TSI-) Verfahren und potentiometrische Titration mit Tetrabutylammoniumhydroxid

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

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Contents

Foreword

This document (EN 15168:2006) 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of an identical text or by endorsement, at the latest by May 2007, and conflicting national standards shall be withdrawn at the latest by May 2007.

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, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

1 Scope

This European Standard specifies a method for the determination of hydroxyl value of aliphatic and cyclic hydroxyl compounds with hydroxyl groups attached to primary and secondary carbon atoms.

This European Standard is applicable to polyacetals, temperature sensitive materials, high solids polymer polyols and rigid polyols and phenols.

This European Standard is not suitable for determination of hydroxyl groups attached to tertiary carbon atoms.

NOTE This method is currently recommended for neutral refined products. However for products that contain an excess of acidic species a validation should be carried out to show that the acidic species either does not interfere or that the acidic species interference has been obviated.

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 Terms and definitions

For the purposes of this document, the following term and definition applies.

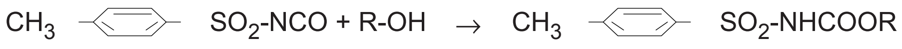
3.1
hydroxyl value, ***OHV***
number of milligrams of potassium hydroxide corresponding to the hydroxyl groups in 1 g of material

4 Principle

A known mass of test sample is reacted with an excess of p-toluenesulfonyl isocyanate to form an acidic carbamate. Water is added to convert un-reacted isocyanate to sulfonamide followed by direct potentiometric titration of the acidic carbamate with tetra-n-butyl ammonium hydroxide in non-aqueous medium.

The reactions occurring are as follows:

a) formation of acidic carbamate;



b) hydrolysis of the excess of isocyanate;

c) titration of the acidic carbamate formed.

5 Reagents

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.

WARNING — Acetonitrile, p-toluenesulfonyl isocyanate and tetrabutylammonium hydroxide being hazardous chemicals: conduct all the operations under a well-ventilated fume hood.

5.1 Water complying with grade 3 as defined in EN ISO 3696.

5.2 Acetonitrile, with water content < 0,01 % (m/m) (CAS number : 75-05-8).

5.3 Toluene, minimum purity 99 % (m/m) (CAS number : 108-88-3).

5.4 Tetrahydrofurane (THF), minimum purity 99 % (m/m) (CAS number : 109-99-9).

5.5 p-Toluenesulfonyl isocyanate (TSI), minimum purity 96 % (m/m) (CAS number : 4083-64-1).

Maintain a nitrogen pad above this reagent after opening the flask.

5.6 p-Toluenesulfonyl isocyanate (TSI) reagent solution.

Pipette 20 ml of TSI (5.5) into a dry 500 ml volumetric flask half filled with acetonitrile. Make up to the mark with acetonitrile and mix well. This reagent shall be prepared fresh monthly.

5.7 Potassium hydrogen phthalate, primary standard minimum purity 99 %(m/m) dried 2 h at 120 °C (CAS number : 877-24-7).

5.8 Tetra-n-butyl ammonium hydroxide standard volumetric solution, $c([CH_3\ (CH_2)\ _3]\ _4NOH)$ = 0,1 mol/l (CAS number : 2052-49-5). in 2-propanol/methanol.

5.9 Electrolyte: 0,4 mol/l tetraethyl ammonium bromide solution (CAS number : 71-91-0) in ethylene glycol (CAS number:107-21-1).

5.10 Electrolyte: saturated LiCl solution (CAS number : 7447-41-8) in ethanol (CAS number : 64-17-5).

6 Apparatus

Normal laboratory apparatus, and the following.

6.1 Automatic potentiometer, with drift-controlled data acquisition and dynamic titrimetric dosing equipped with an automatic burette assembly and a magnetic stirrer.

6.2 Electrodes: There are two options for the electrodes definition.

6.2.1 Two electrodes system

6.2.1.1 Glass pH electrode.

6.2.1.2 Ag/AgCl double-junction ground joint diaphragm reference electrode, inner and outer chambers filled with 0,4 mol/l solution of tetraethyl ammonium bromide in ethylene glycol (5.9).

or

6.2.2 One electrode system

Combined glass pH electrode for titrations in non aqueous media (e.g. Solvotrode[1]), filled with 0,4 mol/l solution of tetraethyl ammonium bromide in ethylene glycol (5.9).

NOTE For electrode maintenance it is recommended to follow the manufacturer instructions. A saturated lithium chloride solution in ethanol (5.10) can also be used as electrolyte to fill the electrodes.

7 Sampling

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

Samples that are solids at room temperature shall be heated prior to weighing to obtain a clear liquid, at the lowest possible temperature (50 °C to 70 °C) to avoid any undesirable changes in the sample. If higher temperatures are required to melt the sample, for example 110 °C, then the sample shall be removed from the oven as soon as a clear liquid is obtained. After heating, invert the sample container about twenty times to ensure complete homogenisation. Samples that are liquid at room temperature only require inversion mixing.

8 Procedure

8.1 Standardization of tetra-n-butyl ammonium hydroxide standard volumetric solution

Weigh about 0,18 g of dried potassium hydrogen phthalate (5.7) (m_0) to the nearest 0,1 mg into a 100 ml beaker, dissolve it in about 60 ml of freshly boiled water and stir several minutes to ensure complete dissolution.

Carry out a potentiometric titration directly with the tetra-n-butyl ammonium hydroxide standard volumetric solution (5.8).

Record the volume V of the tetra-n-butyl ammonium hydroxide standard volumetric solution (5.8) at the inflection point of the titration curve.

Carry out three to five standardization titrations to obtain a reliable mean value for the 0,1 mol/l tetra-n-butyl ammonium hydroxide concentration (5.8).

Calculate the concentration, c, of the tetra-n-butyl ammonium hydroxide standard volumetric solution (5.8), expressed in moles per litre, using the Equation (1):

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

where

m_0 is the mass of potassium hydrogen phthalate (5.7), in grams;

V is the volume, in millilitres, of the tetra-n-butyl ammonium hydroxide standard volumetric solution (5.8) consumed to the inflection point.

The results shall be given to four decimal places.

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[1] Solvotrode 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 European Standard and does not constitute an endorsement by CEN. Equivalent products may be used if they can be shown to lead to the same results.

8.2 Test portion

Calculate the optimum sample to be weighed, m, expressed in grams, by the Equation (2):

$$m = \frac{40}{(OHV)_{\mathrm{E}}} \qquad (2)$$

where

$(OHV)_{\mathrm{E}}$ is the expected hydroxyl value, in milligrams KOH per sample gram.

For expected hydroxyl values ≤ 2, weigh about 15 g to 20 g of sample as maximum.

8.3 Determination

Weigh the calculated mass of the test portion, m, to the nearest 0,1 mg into a clean and dry 100 ml beaker.

With a measuring cylinder, add 10 ml of acetonitrile (5.2). Add a magnetic stirring bar and stir slowly on a magnetic stirrer until the test portion is dissolved (30 s are usually sufficient).

NOTE 1 Although acetonitrile has been found to dissolve a wide range of product types and should be used where possible, tetrahydrofuran or pentene stabilized chloroform may be used as solvent for products that may be insoluble in acetonitrile (5.2). Alternatively, 3 ml of toluene (5.3) may be used to dissolve a product, followed immediately by addition of 7 ml of acetonitrile (5.2). Superior potentiometric titration curves are obtained in acetonitrile media.

Pipet (10 ± 0,1) ml of TSI reagent (5.6) into the test solution, cover the beaker with a watch glass and stir slowly on the magnetic stirrer for 5 min.

Add 0,5 ml of water to destroy excess of TSI reagent (5.6) and stir for 1 min at slow speed.

Add about 60 ml of THF (5.4) and start the titration with 0,1 mol/l tetra-n-butyl ammonium hydroxide standard volumetric (5.8) solution using the electrodes defined in 6.2.

NOTE 2 A set of titration parameters is given in Annex B for advice.

After titration rinse the electrode(s) to remove residual organic material and next rinse with water and immerse the electrode bulb in water to maintain good hydration of electrode between titrations.

A typical potentiometric titration curve will have two or three inflections as those in Figure C.1.

Record the volume (V_1) at the first potentiometric end point and the volume (V_2) at the second potentiometric end point. Although pH values will not enter into the calculations, record the "apparent" pH values at each of the potentiometric inflection points.

Perform the test solution analysis in duplicate.

9 Calculation and expression of results

The experimental hydroxyl value, OHV, in milligrams of KOH per gram of the test portion, is calculated by the Equation (3):

$$OHV = (V_2 - V_1) \times c \times \frac{56{,}11}{m} \tag{3}$$

where

V_2 is the volume of the tetra-n-butyl ammonium hydroxide standard volumetric solution (5.8) corresponding to the second equivalence point, in millilitres;

V_1 is the volume of the tetra-n-butyl ammonium hydroxide standard volumetric solution (5.8) corresponding to the first equivalence point, in millilitres;

c is the concentration of the tetra-n-butyl ammonium hydroxide standard volumetric solution (5.8), in moles per litre

The results shall be given to one decimal place if the value is above 100 and to two decimal places if the value is below 100.

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.

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.

11 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 15168;

c) the test results;

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)

Interferences

The interferences noted are the following and should be taken into account during the determination:

— primary and secondary amines derivatize quantitatively with the TSI reagent and contribute to the hydroxyl value;

— high levels of water in the test solution can interfere by consuming reagent. The amount of excess TSI reagent prescribed by this test method is quite large, however, so that rather high water levels can be accommodated. Optimum titration curves are obtained, however, when the water content is less than a mass fraction of 1 %;

— any acidic species with a pKa value close to that of the acidic carbamate (formed between TSI and the hydroxyl compound), will contribute to the hydroxyl number and cause high values. Excess base in a product may potentially react with the acidic carbamate to cause low hydroxyl number values. If this test method is to be used for products other than neutral refined products, the analyst should first validate this test method on a case by case basis. For example, an in-process product containing excess acid or base may be analysed using EN 13926, to establish concordance of results with the current TSI test method for that particular matrix. The identities of acidic or basic species contained in-process products are frequently known, so that known addition of these moieties to the product can establish whether or not there is interference exhibited. For example, methane sulfonic acid titrates sufficiently before the acidic carbamate formed between TSI and hydroxyl compound, and therefore does not interfere. At the other extreme, methacrylic acid titrates well after the acidic carbamate of interest and thus causes no interference.

Annex B
(informative)

Titration apparatus settings

The following parameters are the settings for Titroprocessor 726 and Titrinos 716/736/751[2)] and are intended to act as a guideline only (see Table B.1). The titration is carried out with dynamic dosing.

Table B.1 — Instrument settings

Parameter	Value
Measuring point density	1
Dosing rate	30 ml/min
Signal drift	30 mV/min
Equilibration time	5 s
Minimum increment	10 µl
Burette volume/Resolution	20 ml/2 µl
End point criteria	10

NOTE The designations of the parameters correspond to those given by the Titroprocessor 726 and Titrinos 716/736/751.

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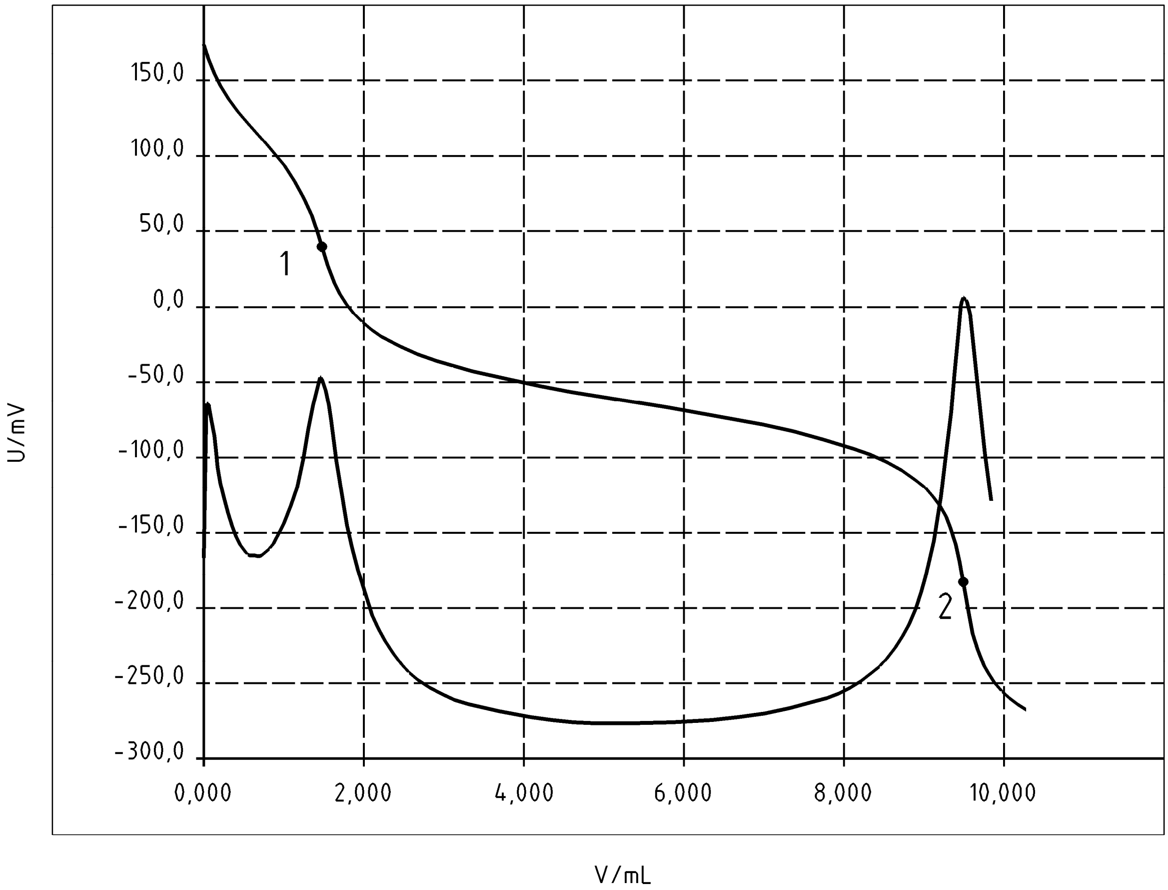
2) Metrohm Titroprocessor 726 and Titrinos 716/36/751 are examples of suitable apparatus commercially available. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the instruments named.

Annex C
(informative)

Example for a typical potentiometric titration curve



Key

1,2 inflection points

Figure C.1 — Example for a typical potentiometric titration curve

The volume to 1 (V_1) is proportional to the acidic species of the greatest strength and is reported to be related with the age of reagent, catalysts present and water in the product. The volume V_1 is usually 0,5 ml to 1,0 ml.

The difference between 2 (V_2) and 1(V_1) is related to the titration of the acidic carbamate of interest formed from the hydroxyl compounds and the TSI reagent. The volume V_2 is usually 5 ml to 10 ml.

A third, less steep and spurious appearing inflection, 3 (V_3), sometimes occurs. Its identity has not been firmly established.

Only V_1 and V_2 are used in the calculation. In acetonitrile medium, V_1 typically occurs at an "apparent" pH of about 5,0 to 5,5, V_2 at a pH of about 9,0 to 9,5 and V_3 at about 11 to 12. If V_2 and V_3 happen to occur rather close together, so that there is some question regarding which one is to be used as V_2 in the calculations, it is advisable to analyse a larger test portion. V_3 will invariably move to higher pH values, further downscale, away from the unmoving V_2 value.

Annex D
(informative)

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

The inter-laboratory test was carried out in 2003 by CESIO (Comité Européen des agents de Surface et de leurs Intermédiaires Organiques)/AISE (International Association for Soaps, Detergents and Maintenance Products) 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 D.1).

Table D.1 — Results of inter-laboratory test

	Allyl EO/PO (MW≈800 g/mol)		EO-Fatty Alcohol (MW≈500 g/mol)		Dodecanol (MW=290 g/mol)	
	EN 13926	EN 15168	EN 13926	EN 15168	EN 13926	EN 15168
Number of participating laboratories	9	8	9	8	9	9
Number of accepted test results	50	48	50	48	47	54
Mean value (mg KOH/g)	69,92	71,22	113,58	114,39	300,73	299,98
Repeatability standard deviation (s_r)	1,862	0,362	2,160	0,321	6,090	1,314
Repeatability coefficient of variation	2,7%	0,5%	1,9%	0,3%	2,0%	0,4%
Repeatability limit (*r*) ($2,8 \times s_r$)	5,22	1,02	6,05	0,90	17,05	3,68
Reproducibility standard deviation (s_R)	3,156	0,631	3,497	0,821	8,598	2,326
Reproducibility coefficient of variation	4,5%	0,9%	3,1%	0,7%	2,9%	0,8%
Reproducibility limit *(R)* ($2,8 \times s_R$)	8,84	1,77	9,79	2,30	24,08	6,51

Bibliography

[1] EN 13926, *Surface active agents — Alkoxylated derivatives — Determination of hydroxyl value — N-methyl imidazole method*

[2] 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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