

Določitev vrednosti površinske aktivnosti - p-Toluensulfonil izocyanat (TSI) metoda in potenciometrična titracija s tetrabutylammonijevim hidroksidom

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

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

Agents de surface - Détermination de l'indice d'hydroxyle - Méthode au p-toluenesulfonylisocyanate (TSI) et dosage potentiométrique avec l'hydroxyde de tétrabutylammonium

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English Version

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
potentiométrique avec l'hydroxyde de tétrabutylammonium

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

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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of an identical text or by endorsement, at the latest by May 2007, and conflicting national standards shall be withdrawn at the latest by May 2007.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.

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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*

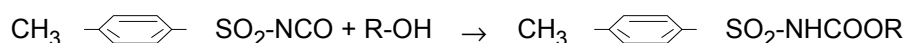
number of milligrams of potassium hydroxide corresponding to the hydroxyl groups in 1 g of material

4 Principle

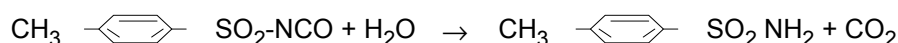
A known mass of test sample is reacted with an excess of p-toluenesulfonyl isocyanate to form an acidic carbamate. Water is added to convert un-reacted isocyanate to sulfonamide followed by direct potentiometric titration of the acidic carbamate with tetra-n-butyl ammonium hydroxide in non-aqueous medium.

The reactions occurring are as follows:

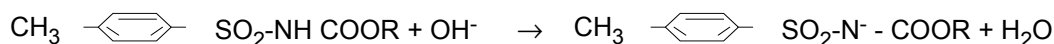
a) formation of acidic carbamate;



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, $c([\text{CH}_3(\text{CH}_2)_3]_4\text{NOH}) = 0,1 \text{ mol/l}$ (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. Solvotrode¹⁾), 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):

$$c = \frac{m_0 \times 1000}{M \times V} \quad (1)$$

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.

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):

$$m = \frac{40}{(OHV)_E} \quad (2)$$

where

$(OHV)_E$ 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 ($10 \pm 0,1$) 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.