SLOVENSKI STANDARD
SIST EN 12139:1999

01-oktober-1999

Površinsko aktivne snovi - Določanje skupnega deleža polietilen glikola neionskih površinsko aktivnih snovi (kondenzati EO) s HPLC/GPC

Surface active agents - Determination of the total polyethylene glycol content of non-ionic surface active agents (EO adducts) by HPLC/GPC

Grenzflächenaktive Stoffe - Bestimmung des Gesamtgehaltes an Polyethylenglycol von nichtionischen grenzflächenaktiven Stoffen (EO-Addukten) mit HPLC/GPC

Agents de surface - Détermination de la teneur totale en polyéthylene glycol des agents de surface non ioniques (condensats OE) par CLHP/CPG

Ta slovenski standard je istoveten z: **EN 12139:1999**

ICS:

71.100.40 Površinsko aktivna sredstva Surface active agents

SIST EN 12139:1999 **en**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 12139

February 1999

ICS 71.100.40

Descriptors: surfactants, non-ionic surfactants, chemical analysis, determination of content, polyethylene, glycol, condensates, chromatography, high performance liquid chromatography

English version

Surface active agents - Determination of the total polyethylene glycol content of non-ionic surface active agents (EO adducts) by HPLC/GPC

Agents de surface - Détermination de la teneur totale en polyéthylène glycol des agents de surface non ioniques (condensats OE) par CLHP/CPG

Grenzflächenaktive Stoffe - Bestimmung des Gesamtgehaltes an Polyethylenglycol von nichtionischen grenzflächenaktiven Stoffen (EO-Addukten) mit HPLC/GPC

This European Standard was approved by CEN on 25 January 1999.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 12139:1999 E

Foreword

This European Standard 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 August 1999, and conflicting national standards shall be withdrawn at the latest by August 1999.

Annexes A, B, C and D 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, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a method for the determination of the total polyethylene glycol (PEG) content of aromatic and aliphatic non-ionic surface active agents of the type $R-(O-C_2H_4)_{\overline{p}}-OH$, where $\overline{p}$ is the mean ethylene oxide (EO) value. It applies for concentrations of PEG higher than approximately 0,1 g/100 g of the laboratory sample.

The method is applicable up to a degree of ethoxylation of at least 25 for products which are soluble in an 80/20 (V/V) mixture of methanol and water. Long-chain products with a low degree of ethoxylation, such as tallow alcohol[1] 5 E0, are not soluble, and require an amended preliminary treatment.

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.

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696:1987).*

ISO 607:1980, *Surface active agents and detergents - Methods of sample division.*

ISO 6353-2:1983, *Reagents for chemical analysis - Part 2 : Specifications - First series.*

ISO 6353-3:1987, *Reagents for chemical analysis - Part 3 : Specifications - Second series.*

3 Principle

Polyethylene glycol is separated from its monoalkyl ethers by a reverse phase chromatograph column.The use of an additional gel chromatography column (GPC) enables the determination of the molecular mass distribution of the polyethylene glycols in the surface active agent raw material by comparison with PEG calibration PEG standards.

Small amounts of low carboxylic acids, which are often used in industrial processes to neutralise the ethoxylation catalyst, and which interfere with the determination, are removed together with long-chain alkyl polyglycol ethers by means of a special cartridge method. This eliminates potential interference factors and decreases the analysis times.

4 Reagents and materials

During the analysis, unless otherwise stated, use only reagents specified in ISO 6353-2:1983 and ISO 6353-3:1987 if listed there, if not, reagents of recognised analytical grade.

4.1 Methanol, HPLC grade.

4.2 Deionized water, filtered, conforming to the requirements of grade 1 in EN ISO 3696.

4.3 Polyethylene glycol 800, GPC grade.

4.4 Analytical grade anion exchange resin, 100 mesh to 200 mesh, chloride form, total capacity 3,5 milliequivalents/ gram dry resin.

---

[1] CAS Registry Number 99561-04-3

4.5 Reversed phase C18, silica gel bulk material, particle diameter about 40 µm to 60 µm.

4.6 Sodium hydroxide solution, c(NaOH) = 1 mol/l.

4.7 Nitric acid, $c(HNO_3)$ = 1 mol/l.

4.8 Silver nitrate solution, $c(AgNO_3)$ = 1 mol/l.

4.9 Mobile phase, either

a) 80/ 20 (V/V) mixture of methanol/water for samples of the type alkylphenol (e.g. :

i-nonyl phenol 7 EO) or fatty alcohols (e.g. C12/C14 7 EO) with a low degree of ethoxylation ;

or

b) 75/ 25 (V/V) mixture of methanol/water for samples of the type of alkylphenol (e.g. :

i-octyl phenol 25 EO) or fatty alcohols (e.g. C12/C14 25 EO) with a high degree of ethoxylation.

5 Apparatus

Ordinary laboratory apparatus and the following :

5.1 Isocratic HPLC unit, with Refractive Index Detector and column oven.

5.2 Data systems with reintegration facilities for the chromatograms.

5.3 Sample preparation unit for solid phase extraction, such as a vacuum chamber.

5.4 Disposable syringes,10 ml.

5.5 One-mark volumetric flasks 10 ml and 50 ml.

5.6 One-mark pipette 2 ml.

5.7 Piston-type graduated pipette 10 ml.

5.8 Preparative glass chromatography column.

5.9 Special cartridge, prepared as follows :

Convert the ion exchanger (4.4) from chloride to hydroxide form by filling a chromatography column with it and washing it with sodium hydroxide solution (4.6) until no more chloride ions are detected. Wash the exchanger with water and remove from the column.

NOTE The absence of chloride is confirmed when the eluant does not form a precipitate with nitric acid/silver nitrate solution.

Remove the plunger from a 10 ml disposable syringe (5.4), place some cotton wool in the barrel and press down firmly into the end of the barrel with a rod. Add the reserved phase C18 silica gel (see 4.5) up to the 10 ml mark (4,0 g to 4,5 g). Place some cotton wool above the added reserved phase C18 silica gel, press down firmly with the rod, and set the cartridge on the sample preparation unit (5.3). Apply a vacuum and pour the exchanger suspension into the cartridge until about 1 cm is present (see figure B.1). Wash the cartridge by filling it three times with 5 ml methanol, then three times with the mobile phase to be used (4.9). Carry out this washing sequence shortly before the sample is added (see clause 6) to prevent the exchanger drying and cracking.

5.10 Chromatography columns

Prepare two chromatography columns as follows :

a) One column, 250 mm long and 4 mm internal diameter, containing reversed phase C 18 silica gel,5 µm ;

b) One GPC column for aqueous applications, 300 mm long and 7,8 mm internal diameter containing a stationary phase of pore size 120 x 10^{-4} µm, exclusion limit (PEO) 5 x 10^{3} g/mol.

Convert the GPC column for methanol/water using a gradient from 0 % methanol to 80 % methanol over a period of 3 h.

6 Sampling and preparation of the test sample

The laboratory sample shall be prepared and stored in accordance with 5.3 of ISO 607.

Prepare a sample stock solution by weighing 5 g of the laboratory sample to the nearest 0,1 mg, into a 50 ml volumetric flask (5.5) and making up to the mark with the mobile phase (4.9). Place the solution in an ultrasonic bath until it has dissolved completely.

Prepare a test sample by placing a 10 ml volumetric flask in the sample preparation unit (5.3) so that the cannula of the special cartridge (5.9) ends in the neck of the flask. Using an one marked pipette, add 2 ml of the sample stock solution to the special cartridge (5.9). When the sample stock solution has been adsorbed in the cartridge, rinse twice with 4 ml mobile phase (4.9).

NOTE These solvent quantities should be used to ensure efficiency of the cartridge.

Remove the 10 ml volumetric flask from the sample preparation unit and allow it to return to room temperature. Fill to the mark with the mobile phase to be used and transfer it to the automatic sampling vessels or use for direct injection.

7 Procedure

7.1 Apparatus settings

Connect the chromatography columns in series (first : C 18 silica gel column [5.10a] ; second : GPC column [5.10b]).

Set the HPLC unit to the following :

Detector :	RI.	
Flow rate :	1,0 ml/min.	
Temperature :	Column	30 °C.
Injection volume:	100 µl.	

7.2 Calibration

7.2.1 Preparation of calibration solutions

Prepare five calibration solutions using the standard of polyethylene glycol 800 (PEG 800) (4.3) as follows.

Weigh, to the nearest 0,1 mg, five levels of PEG 800 between 15 mg to 80 mg of the PEG (e.g. : 15 mg, 25 mg, 40 mg, 60 mg and 80 mg) into separate 50 ml volumetric flasks and fill to the mark with the mobile phase to be used (4.9). Ensure that the solutions are properly dissolved.

7.2.2 Calibration curve

Analyse each calibration solution, prepared in 7.2.1, at least twice using the chromatographic conditions given in 7.1.

Construct a graph of peak area against PEG mass in calibration solutions and draw a calibration curve.

7.3 Determination of polyethylene glycol content

Carry out at least two analyses on the test sample solution as prepared in clause 6, using the chromatographic conditions given in 7.1.

NOTE Evaluation of the chromatograms is carried out automatically with the help of the available data system by means of the external standard method. Under some circumstances reintegration can be necessary. Analysis times are considerably longer if the sample preparation is not carried out as described in clause 6.

Examples of chromatograms are given in Annex C.

8 Expression of results

Use the calibration curve 7.2.2 to obtain the PEG mass corresponding to the area given by the integrator.

Express the PEG content in percentage by mass as follows :

$$\%\ PEG = \frac{m \times 100}{m_0}$$

where :

m_0 is the mass of sample to be analysed (see clause 6) in grams ;

m is the mass of PEG in the sample determined from the calibration curve (see 7.2.1) in grams.

9 Precision

9.1 Repeatability

The repeatability conditions are conditions where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time.

The absolute difference between two single test results obtained under repeatability conditions shall not be greater than :

- 0,12 g/100 g laboratory sample at a level of 0,67% PEG (See annex A, sample 1) ;
- 0,27 g/100 g laboratory sample at a level of 1,19% PEG (See annex A, sample 2).

NOTE In order to take into account the value of the repeatability standard deviation determined from the ring test for low quantities (in sample 1), the result should be calculated as the mean of five determinations to two decimal digits.

9.2 Reproducibility

The reproducibility conditions are conditions where test results are obtained with the same method on identical test material in different laboratories with different operators using different equipment.

The absolute difference between two single test results obtained under reproducibility conditions shall not be greater than :

- 0,66 g/100 g laboratory sample at a level of 0,67% PEG (see annex A, sample 1) ;
- 0,45 g/100 g laboratory sample at a level of 1,19% PEG (see annex A, sample 2).

10 Test report

The test report shall include at least the following particulars :

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

b) a reference to this European Standard ;

c) the result ;

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