SLOVENSKI STANDARD
SIST EN 12582:1999

01-oktober-1999

Površinsko aktivne snovi - Določevanje polietilen glikola glede na molsko maso v neionskih površinsko aktivnih snoveh (kondenzati EO) s HPLC/ELSD

Surface active agents - Determination of the polyethylene glycol content according to molar mass in non-ionic surface active agents (ethoxylated) by HPLC/ELSD

Grenzflächenaktive Stoffe - Bestimmung des Gesamtgehaltes an Polyethylenglycol in nichtionischen grenzflächenaktiven Stoffen (Ethoxylaten) nach molarer Masse mittels HPLC/ELSD

Agents de surface - Détermination de la teneur en polyéthylene glycol en relation avec leur masse molaire dans les agents de surface non ioniques (condensats d'oxyde d'éthylene) par CLHP/DEDL

Ta slovenski standard je istoveten z: **EN 12582:1999**

ICS:

71.100.40 Površinsko aktivna sredstva Surface active agents

SIST EN 12582:1999 **en**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 12582

March 1999

ICS

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

English version

Surface active agents - Determination of the polyethylene glycol content according to molar mass in non-ionic surface active agents (ethoxylated) by HPLC/ELSD

Agents de surface - Détermination de la teneur en polyéthylène glycol en relation avec leur masse molaire dans les agents de surface non ioniques (condensats d'oxyde d'éthylène) par CLHP/DEDL

Grenzflächenaktive Stoffe - Bestimmung des Gesamtgehaltes an Polyethylenglycol in nichtionischen grenzflächenaktiven Stoffen (Ethoxylaten) nach molarer Masse mittels HPLC/ELSD

This European Standard was approved by CEN on 13 February 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

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 September 1999, and conflicting national standards shall be withdrawn at the latest by September 1999.

Annex A is 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 polyethylene glycol (PEG) content in 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 is applicable to all ethoxylated products soluble in methanol or methanol/water mixture.

This method applies to PEG concentrations as mass fraction greater than or equal to 0,1 %.

The method is not applicable to PEG whose molar mass is lower than 400 g/mol. Monomeric ethylene glycol, diethylene glycol, triethylene glycol and glycerol are not detected.

NOTE Evaporative light scattering detector (ELSD) is convenient for routine methods.

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 5725-2:1994, *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.*

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

3 Principle

Polyethylene glycol is separated from the polyethoxylated surface active agents by means of reversed phase liquid chromatography. In this process PEG is eluted in the first minutes while the non-ionic surface active agents are retarded. Evaporative Light Scattering Detector (ELSD) does not detect volatile materials such as the sample solvent; interferences with the PEG peak are limited.

The sample is dissolved in an 80/20 (V/V) mixture of methanol/water or in another methanol/water mixture to obtain a clear solution. A portion of the sample solution is then analysed by high performance liquid chromatography (HPLC).

Quantification of PEG content is achieved by external calibration with PEG molar mass equal to 1000 g/mol.

4 Reagents

All reagents shall be of a recognized analytical grade if not listed in ISO 6353-2 and the water used shall conform to grade 3 in accordance with EN ISO 3696.

4.1 Polyethylene glycol with molar mass of 1000 g/mol, gel permeation chromatography (GPC) grade.

4.2 Methanol: HPLC grade, filtered before use with filter unit (5.5).

4.3 Water : HPLC grade, filtered before use with filter unit (5.5).

4.4 Helium gas, chromatography grade, for degassing eluent.

4.5 Nitrogen or air, dry and without dust.

4.6 Mobile phase, either :

a) 80/20 (V/V) mixture of methanol and water ;

or

b) Methanol.

5 Apparatus

Ordinary laboratory apparatus and glassware with the following.

5.1 HPLC unit equipped with gradient pump.

5.2 Evaporative Light Scattering Detector (ELSD).

5.3 Chromatography column: Octadecyl C18 bonded phase silica gel ; 5 µm ; 250 mm length and 4,6 mm internal diameter.

5.4 Data logger/plotter capable of recording and displaying the chromatographic peak area.

5.5 Filter unit for solvent (0,45 µm).

5.6 Syringes 10 ml.

6 Sampling

6.1 Preparation of the test sample

Prepare and store the test sample in accordance with ISO 607.

6.2 Preparation of test solutions

Weigh, to the nearest 0,1 mg, the test sample mass given in table 1 for the expected PEG content into a 25 ml volumetric flask. Fill to the mark with the mobile phase (4.6.a) or other suitable mixture of methanol/water and dissolve to obtain a clear solution. If necessary, filter through 0,45 µm filter unit.

Table 1

Expected PEG %	Sample mass for 25 ml solution
< 0,1	> 2,5[a)]
0,1 to 2	2,5
2 to 5	1
5 to 10	0,5
10 to 25	0,2

[a)] But not exceeding the sample solubility limits

7 Procedure

7.1 Apparatus settings

Set the HPLC unit according to the following conditions :

7.1.1 Gradient

a) t = 0 min 0 % methanol (4.6.b) ;

b) t = 6 min 0 % methanol (4.6.b);

c) t = 7 min 100 % methanol (4.6.b);

d) t = 30 min 100 % methanol (4.6.b);

e) t = 35 min 0 % methanol (4.6.b).

NOTE Going from mobile phase (4.6.a) to mobile phase (4.6.b) is done in order to elute the ethoxylated products more rapidly.

7.1.2 Flow rate : 1,0 ml/min.

7.1.3 Temperature : Room temperature.

7.1.4 Injection volume : 20 µl.

7.1.5 Detector : Evaporative Light Scattering Detector ELSD

Optimize the working conditions, depending on the apparatus in use and the physical parameters (nebulisation temperature and working pressure).

7.2 Calibration

7.2.1 Preparation of calibration solutions

Weigh, to the nearest 0,1 mg, 0,025 g, 0,05 g, 0,1 g and 0,2 g of polyethylene glycol (PEG 1000) (4.1) each into 100 ml volumetric flasks, dissolve in the mobile phase (4.6.a) and make up to the mark. These solutions respectively correspond to 0,25 %, 0,5 %, 1 % and 2 % of PEG in a test sample of 2,5 g in 25 ml of mobile phase.

NOTE Calibration curves with PEG 400, 1 500 and 2 000 give similar results to PEG 1 000. Curve shifts are observed from PEG 4 000, 6 000 and 8 000. For PEG 10 000, the calibration curve is not linear.

Mix the solution thoroughly. If necessary, filter through a 0,45 µm filter unit.

7.2.2 Calibration curve

Analyse, at least twice, calibration solutions prepared in 7.2.1, in accordance with the chromatographic conditions given in 7.1.

Construct a graph : log of peak area (y-axis) versus log PEG weight in 25 ml (x-axis) and draw a calibration curve.

7.3 Determination

Take the test solution as prepared in 6.2 and carry out the analysis in accordance with the chromatographic conditions given in 7.1.

Typical chromatograms are shown in figure A.1 and A.2.

NOTE In this "reversed phase HPLC" method, polyethylene glycol elute quickly in the first minutes, in only one peak. When the molar mass distribution of PEG is large, it is possible to observe several peaks or shoulders corresponding to different molar masses of PEG.

Sum the peak areas of the chromatogram corresponding to PEG.

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 as mass fraction in percent as follows :

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

where :

m_0 is the mass of sample to be analysed (6.2), in grams ;

m is the mass of PEG determined by means of the calibration curve, in grams.

9 Precision

9.1 Repeatability

The absolute difference between two single test results obtained under repeatability conditions according to ISO 5725-2 shall not be greater than 0,3 % (mass fraction), with a probability of 95 %.

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.

Results of an interlaboratory test carried out in accordance with ISO 5725-2 are given in annex A.

9.2 Reproducibility

The absolute difference between two single test results obtained under reproducibility conditions according to ISO 5725-2 shall not be greater than 1,7 % (mass fraction) with a probability of 95 %.

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.

Results of an interlaboratory test carried out in accordance with ISO 5725-2 are given in annex A.

10 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 results with their units (see clause 8) ;

d) room temperature for each liquid chromatographic determination and all information about ELSD detector ;

e) details of any operations not specified in this European Standard or in the International 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)

Interlaboratory test results

The interlaboratory test results were obtained in the framework of CESIO activity in 1993.

Sample 1 - Branched chain alcohol ethoxylate (near 5 EO)

Laboratory	Number of single values	Mean value	Standard deviation
1	2	1,0	0
2	3	1,06	0,038
3	2	0,84	0,014
4	2	0,95	0,071
5	2	1,10	0,035
6	2	0,75	0,028
7	5	0,92	0,019
8	2	0,92	0,014
9	---	---	---
10	2	0,92	0
11	3	1,04	0,022
12	3	0,95	0,026
13	6	1,08	0,072
14	4	0,64	0,021
15	6	0,80	0,023

Number of laboratories retained after elimination outliers	14
Number of outliers (laboratories)	1
Number of accepted results	41
Mean value (g/100 g sample)	0,95
Repeatability standard deviation s_r (g/100 g sample)	0,0393
Repeatability limit : $r = 2,8\ s_r$ (g/100 g sample)	0,110
Repeatability relative standard deviation (%)	4,14 %
Reproducibility standard deviation s_R (g/100 g sample)	0,1444
Reproducibility limit : $R = 2,8\ s_R$ (g/100 g sample)	0,404
Reproducibility relative standard deviation (%)	15,2 %