BS ISO 16560:2015

BSI Standards Publication

Surface active agents — Determination of polyethylene glycol content in nonionic ethoxylated surfactants — HPLC method

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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.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Surface active agents — Determination of polyethylene glycol content in nonionic ethoxylated surfactants — HPLC method

Agents de surface tensioactifs — Dosage de la teneur en polyéthylène glycol dans les surfactants éthoxylés non ioniques — Méthode par CLHP

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 91, *Surface active agents*.

Introduction

This International Standard was developed based on EN 12582.

INTERNATIONAL STANDARD ISO 16560:2015(E)

Surface active agents — Determination of polyethylene glycol content in nonionic ethoxylated surfactants — HPLC method

1 Scope

This International 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-$(O\text{-}C_2H_4)_n$ OH; where n 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 %. This International Standard 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.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 607, *Surface active agents and detergents — Methods of sample division*

ISO 5725-2, *Accuracy (trueness and precision) measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
polyethylene glycol content
amount of polyethylene glycol, expressed as a percentage by mass, calculated from the calibration curve in accordance with this International Standard

4 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) or charged aerosol detector (CAD) 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 1 000 g/mol.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and the water used shall conform to grade 3 in accordance with ISO 3696.

5.1 Polyethylene glycol, with molar mass of 1 000 g/mol, gel permeation chromatography (GPC) grade.

5.2 Methanol, HPLC grade, filtered before use with filter unit (6.5).

5.3 Water, HPLC grade, filtered before use with filter unit (6.5).

5.4 Helium gas, chromatography grade, for degassing eluent.

5.5 Nitrogen or air, dry, and without dust.

5.6 Mobile phase, either of the following:

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

b) methanol.

6 Apparatus

Ordinary laboratory apparatus and glassware with the following.

6.1 HPLC unit, equipped with gradient pump.

6.2 Evaporative light scattering detector (ELSD), or charged aerosol detector (CAD).

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

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

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

7 Sampling

7.1 Preparation of the test sample

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

7.2 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 100 ml volumetric flask. Fill to the mark with the mobile phase [5.6 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 content, %	Sample mass, g[a]
<0,1	>1
0,1 to 2	1
2 to 5	0,5
5 to 10	0,25
10 to 25	0,1

[a] Sample mass can be adjusted depending on the detector sensitivity.

8 Procedure

8.1 Apparatus settings

Set the HPLC unit according to the following conditions.

8.1.1 Gradient

a) t = 0 min 0 % methanol [5.6 b)];

b) t = 6 min 0 % methanol [5.6 b)];

c) t = 7 min 100 % methanol [5.6 b)];

d) t = 30 min 100 % methanol [5.6 b)];

e) t = 35 min 0 % methanol [5.6 b)].

NOTE Going from mobile phase [5.6 a)] to mobile phase [5.6 b)] is done in order to elute the ethoxylated products more rapidly.

8.1.2 Flow rate: 1,0 ml/min.

8.1.3 Temperature: room temperature.

8.1.4 Injection volume: 20 µl.

8.1.5 Detector: evaporative light scattering detector (ELSD), or charged aerosol detector (CAD).

Optimize the working conditions, depending on the apparatus in use and the physical parameters.

8.2 Calibration

8.2.1 Preparation of calibration solutions

Weigh, to the nearest 0,1 mg, 0,1 g of polyethylene glycol (PEG 1 000) (5.1) into a 100 ml volumetric flask, dissolve with the mobile phase [5.6 a)] and make up to the mark. Quantitatively transfer 1,0 ml, 5,0 ml, 10 ml, 25 ml of this solution each into 100 ml volumetric flasks and make up to the volume with the mobile phase. The concentrations of PEG in these solutions respectively are 0,01 g/l, 0,05 g/l, 0,1 g/l, 0,25 g/l. Mix the solution thoroughly. If necessary, filter through a 0,45 µm filter unit.

NOTE Mass of polyethylene glycol can be adjusted depending on the detector sensitivity.

8.2.2 Calibration curve

Analyse, at least twice, calibration solutions prepared in 8.2.1, in accordance with the chromatographic conditions given in 8.1. Construct a graph: log of peak area (y-axis) versus log PEG weight in 100 ml (x-axis) and draw a calibration curve.

NOTE For ELSD, calibration curves give similar results when molar masses of PEG are less than or equal to 4 000, and curve shift is observed when the molar mass of PEG is greater than 4 000. For CAD, calibration curves give similar results when molar masses of PEG are less than or equal to 10 000, and curve shift is observed when the molar mass of PEG is greater than 10 000.

8.3 Determination

Take the test solution as prepared in 7.2 and carry out the analysis in accordance with the chromatographic conditions given in 8.1. Typical chromatograms are shown in Figure 1 and Figure 2.

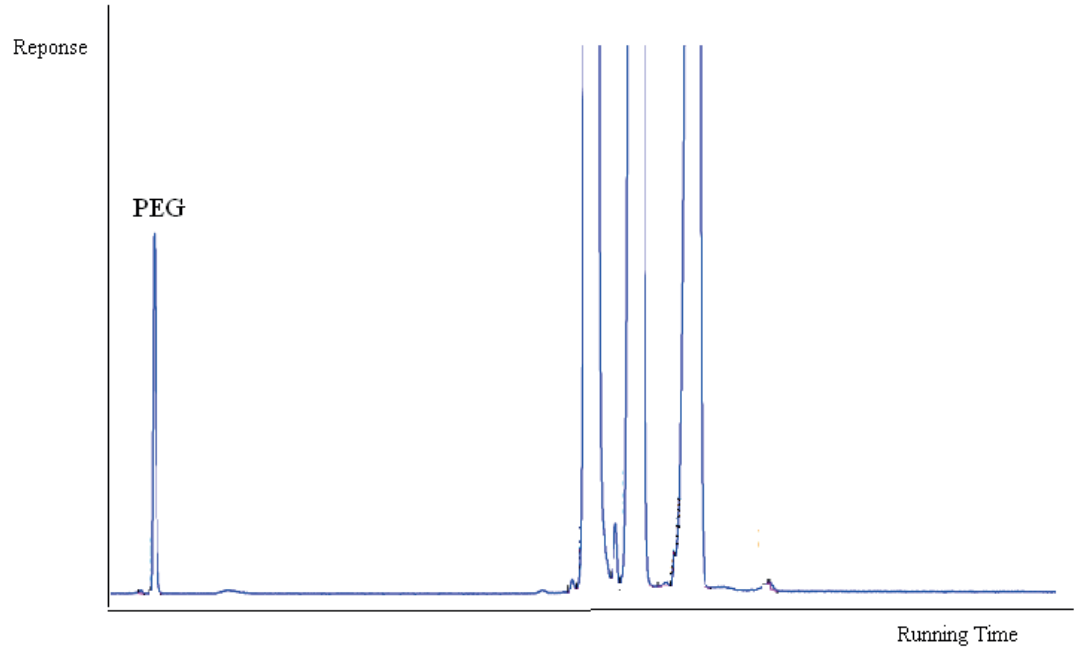

Figure 1 — Chromatogram of fatty alcohol ethoxylate (near 3 EO) by ELSD

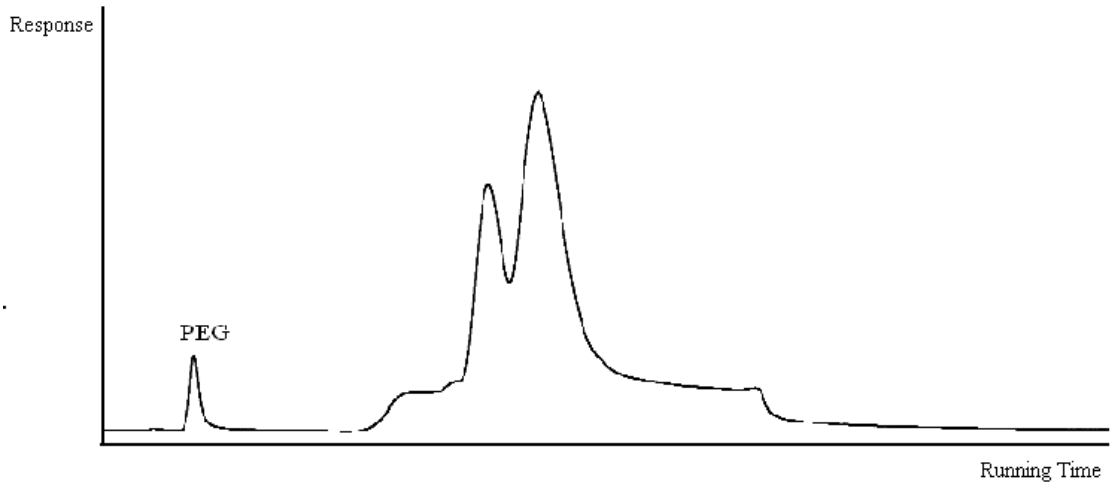

Figure 2 — Chromatogram of fatty alcohol ethoxylate (near 25EO) by CAD

NOTE In this reversed phase HPLC method, polyethylene glycol elutes 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.

9 Expression of results

Use the calibration curve in 8.2.2 to obtain the PEG mass corresponding to the area given by the integrator. Express the PEG content as mass fraction in percent as follows:

$$\text{PEG},\% = \frac{m \times 100}{m_0} \quad (1)$$

where

m_0 is the mass of sample to be analysed (7.2), in grams;

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

10 Precision

10.1 Repeatability

The absolute difference between the results of two determinations carried out simultaneously or in rapid succession by the same operator on the same sample using the same equipment according to ISO 5725-2 shall not be greater than 0,2 % with a probability of 95 %.

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

10.2 Reproducibility

The absolute difference between two results obtained in different laboratories on the same sample according to ISO 5725-2 shall not be greater than 0,8 % with a probability of 95 %.

Results of an interlaboratory test carried out in accordance with ISO 5725-2 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 International Standard, i.e. ISO 16560;

c) the results with their units (see Clause 9);

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

e) details of any operations not specified in this International 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)

Results of interlaboratory tests for fatty alcohol ethoxylate

Table A.1 — Fatty alcohol ethoxylate (near 3 EO)

Laboratory	Number of single values	Mean value (g/100 g sample)	Standard deviation	Detector
1	6	0,36	0,018	ELSD
2	6	0,38	0,002	ELSD
3	6	0,40	0,023	ELSD
4	—	—	—	—
5	6	0,38	0,014	ELSD
6	6	0,39	0,014	CAD
7	6	0,39	0,019	CAD
8	6	0,33	0,018	CAD
9	6	0,34	0,016	CAD
10	6	0,38	0,005	CAD
11	6	0,39	0,006	CAD

Number of laboratories retained after eliminating outliers	11
Number of outliers (laboratories)	1
Number of accepted results	60
Mean value (g/100 g sample)	0,37
Repeatability standard deviation s_r (g/100 g sample)	0,015 0
Repeatability limit: $r = 2{,}83\ s_r$ (g/100 g sample)	0,042 4
Repeatability relative standard deviation (%)	4,05
Reproducibility standard deviation s_R (g/100 g sample)	0,028 6
Reproducibility limit: $R = 2{,}83\ s_R$ (g/100 g sample)	0,080 9
Reproducibility relative standard deviation (%)	7,73

Table A.2 — Fatty alcohol ethoxylate (near 25 EO)

Laboratory	Number of single values	Mean value (g/100 g sample)	Standard deviation	Detector
1	6	3,21	0,064	ELSD
2	6	3,68	0,074	ELSD
3	6	3,30	0,075	ELSD
4	6	3,64	0,087	CAD
5	6	3,50	0,055	CAD
6	6	3,91	0,092	CAD

Number of laboratories retained after eliminating outliers	6
Number of outliers (laboratories)	0
Number of accepted results	36
Mean value (g/100 g sample)	3,54
Repeatability standard deviation s_r (g/100 g sample)	0,076
Repeatability limit: $r = 2{,}83\ s_r$ (g/100 g sample)	0,215
Repeatability relative standard deviation (%)	2,15
Reproducibility standard deviation s_R (g/100 g sample)	0,266
Reproducibility limit: $R = 2{,}83\ s_R$ (g/100 g sample)	0,753
Reproducibility relative standard deviation (%)	7,51

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