BRITISH STANDARD

BS EN 13320:2002

Surface active agents — Gas chromatographic trace determination of free ethylene oxide in ethoxylates

The European Standard EN 13320:2002 has the status of a
British Standard

ICS 71.100.40

National foreword

This British Standard is the official English language version of EN 13320:2002.

The UK participation in its preparation was entrusted to Technical Committee CII/34, Methods of test for surface active agents, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

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

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This British Standard, having been prepared under the direction of the Materials and Chemicals Sector Policy and Strategy Committee, was published under the authority of the Standards Policy and Strategy Committee on 28 March 2002

Summary of pages

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EN 13320

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English version

Surface active agents - Gas chromatographic trace determination of free ethylene oxide in ethoxylates

Agents de surface - Détermination de traces d'oxyde d'éthylène libre dans les éthoxylats par chromatographie en phase gazeuse

Grenzflächenaktive Stoffe - Gaschromatographische Spurenbestimmung von freiem Ethylenoxid in Ethoxylaten

This European Standard was approved by CEN on 16 November 2001.

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 Management Centre or to any CEN member.

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EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. EN 13320:2002 E

Contents

Foreword

This document EN 13320 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 2002, and conflicting national standards shall be withdrawn at the latest by August 2002.

The annexes A and B 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, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a test method for the determination of the content of free ethylene oxide in the range from 1 mg/kg to 100 mg/kg in polyglycols, ethoxylates of alcohols and alkylphenols and in fatty acid polyglycol esters.

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 (including amendments).

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

ISO 607, *Surface active agents and detergents – Test methods of sample division*.

3 Principle

The ethoxylates are, after addition of water, analyzed by gas chromatography using a head-space sampling accessory. The free ethylene oxide content is determined by the standard addition test method.

4 Reagents

During the analysis, unless otherwise specified, use only reagents of recognized analytical grade and have been checked in advance as to not interfere with the analytical results.

4.1 **Water** complying with grade 1 as defined in EN ISO 3696.

4.2 **Ethylene oxide**, C_2H_4O, $w(C_2H_4O) \geq 99,5$ %.

4.3 **Ethylene oxide**, C_2H_4O, dissolved in dichloromethane, vials containing 50 mg of ethylene oxide dissolved in 1 ml of dichloromethane.

4.4 **N,N-dimethylformamide**, C_3H_7NO.

5 Apparatus

Ordinary laboratory apparatus and the following.

5.1 **Capillary gas chromatograph**, with flame ionisation detector (FID) and head-space sampling accessory. The apparatus shall be equipped with a split system. The head-space sampling accessory shall be designed such that each head-space bottle can be thermostated for a defined time.

NOTE Since ethylene oxide is easily decomposed by traces of impurities such as acids and transition metals, (catalysed decomposition), a meticulously clean sampling accessory is necessary.

5.2 **Fused silica capillary column**, coating: crosslinked dimethylpolysiloxanes, column length 30 m, internal diameter 0,25 mm, film thickness 1,0 µm.

5.3 **Vials**, closable by means of a septum, 20 ml, suitable for head-space sampling accessory.

5.4 **Septums and aluminium caps**, lined with aluminium or polytetrafluoroethylene (PTFE) for closing the vials.

5.5 **Sealing pliers**, for sealing the caps onto the vials.

5.6 **Integrator or computer**, with appropriate evaluation programme.

5.7 **Analytical balance**, accurate to 0,1 mg.

6 Sampling and preparation of the test sample

6.1 Sampling

The laboratory samples shall be prepared and stored in accordance with ISO 607.

6.2 Test sample

NOTE 1 The test samples can be in liquid, paste or solid form.

For paste-like products, liquefy and homogenize the laboratory samples by gentle warming.

NOTE 2 If the test sample is heated above 50 °C, low results will be obtained.

Do not melt solid products above 50 °C.

7 Procedure

7.1 Preparation of calibration solutions

7.1.1 Standard solutions

Prepare a stock solution of ethylene oxide (EO) (4.2) either by :

a) Difference weighing

Weigh a 200 ml volumetric flask containing about 100 ml of water. Pass about 500 mg of ethylene oxide (4.2) into the water and reweigh. Make up the solution to 200 ml with water. In place of difference weighing, the addition of ethylene oxide (4.2) can be carried out by weighing-in using a cooled syringe, or

b) Using a vial

Dissolve the contents of a vial of ethylene oxide (4.3) in 250 ml of N,N-dimethylformamide (4.4).

NOTE A method of titration of the ethylene oxide stock solution is given in annex B.

Prepare standard solutions with concentrations of $\rho(C_2H_4O)$ = 0,1 g/100 ml and $\rho(C_2H_4O)$ = 0,01 g/100 ml by multistage dilutions with water from the stock solution.

Store the standard solutions in a refrigerator.

7.1.2 Calibration solutions

Prepare calibration solution A as follows :

> Place 2 ml of ethylene oxide standard solution with a concentration of $\rho(C_2H_4O)$ = 0,01 g/100 ml in a 100 ml volumetric flask and make up to the mark with water. 1 ml of this solution contains 2 µg of ethylene oxide.

Prepare calibration solution B as follows :

> Place 1 ml of ethylene oxide standard solution with a concentration of $\rho(C_2H_4O)$ = 0,1 g/100 ml in a 100 ml volumetric flask and make up to the mark with water. 1 ml of this solution contains 10 µg of ethylene oxide.

7.2 Determination

Weigh about 1 g of the test sample (6.2), to the nearest 0,1 mg into each of two vials and add 1 ml of water to each. Close the vials and make sure that they are pressure-tight.

Weigh about 1 g of the test sample (6.2) to the nearest 0,1 mg into each of two further vials and add 1 ml of calibration solution A or B to each. Close the vials and make sure that they are pressure-tight.

For products with a low degree of ethoxylation, solubility problems can be encountered in pure water. In this case, the determination can be carried out using a different solvent such as toluene or N,N-dimethylformamide, provided that it has been shown to give comparable results. The solvent used shall be reported under e) of the test report (see clause 10).

Equilibrate the solutions for 45 min at (70 ± 1) °C.

Inject the solutions and perform the analysis using the following gas chromatographic conditions :

— temperature of the transfer line :	150 °C ;
— thermostating temperature :	70 °C ;
— pressure build-up time :	3 s ;
— injection time :	6 s ;
— analysis time :	45 min.

NOTE 1 GC conditions deviating from those given above may be used provided that a corresponding separation performance is demonstrated.

a) Temperature	
— oven :	50 °C isothermal for 5 min, then from 50 °C to 180 °C at 5 °C/min ;
— detector (FID) :	250 °C.
b) Carrier gas	
— helium :	about 1 ml/min ;
— column pressure :	about 70 kPa (0,7 bar) ;
— split :	about 1 : 40.
c) Hydrogen and air	Optimized for FID ;
d) Evaluation	Using an electronic integrator or computer, with appropriate evaluation programme.

NOTE 2 Unknown constituents of the test sample which are eluted at the same retention time as ethylene oxide can cause systematic errors. Compounds that commonly occur in ethoxylates such as methanol, ethanol, acetaldehyde and 1,4-dioxane are separated from ethylene oxide under the given separation conditions.

8 Calculation and expression of results

The ethylene oxide content, w_j, in micrograms per gram of the test sample, is calculated using the following equations :

$$\overline{A} = \frac{1}{2} \sum_{j=1}^{2} \frac{A_j}{m_j} \tag{1}$$

$$f = \frac{1}{2} \sum_{k=1}^{2} \frac{(B_k / m_k) - \overline{A}}{C_k / m_k} \tag{2}$$

$$w_j = \frac{A_j}{m_j f} \tag{3}$$

where

$\overline{A}$	is the mean peak area of ethylene oxide per unit mass of the original test sample, in millivolts seconds per gram ;
A_i	is the peak area of ethylene oxide in the original test sample in the jth individual determination, in millivolts seconds ;
m_j	is the mass of the original test sample weighed-in for the jth individual determination, in grams ;
j	is the index of the individual determination ;
f	is the mean headspace response factor out of two standard additions, in millivolts seconds per microgram ;
B_k	is the peak area of ethylene oxide in the test sample with the kth standard addition, in millivolts seconds ;
C_k	is the mass of ethylene oxide added to the test sample, in micrograms ;
m_k	is the mass of the original test sample weighed-in for the kth standard addition, in grams ;
k	is the index for the standard addition.

Calculate the result as the mean of w_1 and w_2 to the nearest 0,1 µg/g.

9 Precision

9.1 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.

Typical precision data obtained in a ring test are given in annex A.

9.2 Reproducibility limit

The absolute difference between two 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.

Typical precision data obtained in a ring test are given in annex A.

10 Test report

The information 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 GC conditions used if deviating from those given in 7.2 ;

d) the results calculated according to clause 8 and the test method chosen for evaluation of the results ;

e) 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.

Annex A
(informative)

Ring test results

A.1 Ring tests

The data on repeatability and reproducibility of this test method are the result of an interlaboratory test carried out as follows in 1991 by the German Joint Committee for the Analysis of Surfactants (GAT) :

- test sample A : alkylphenol × 20 moles of EO ;
- test sample B : castor oil × 45 moles of EO.

Each test sample was prepared three times according to 6.2 (test portion of the test sample alone + two standard additions) and analyzed by gas chromatography.

A.2 Selectivity

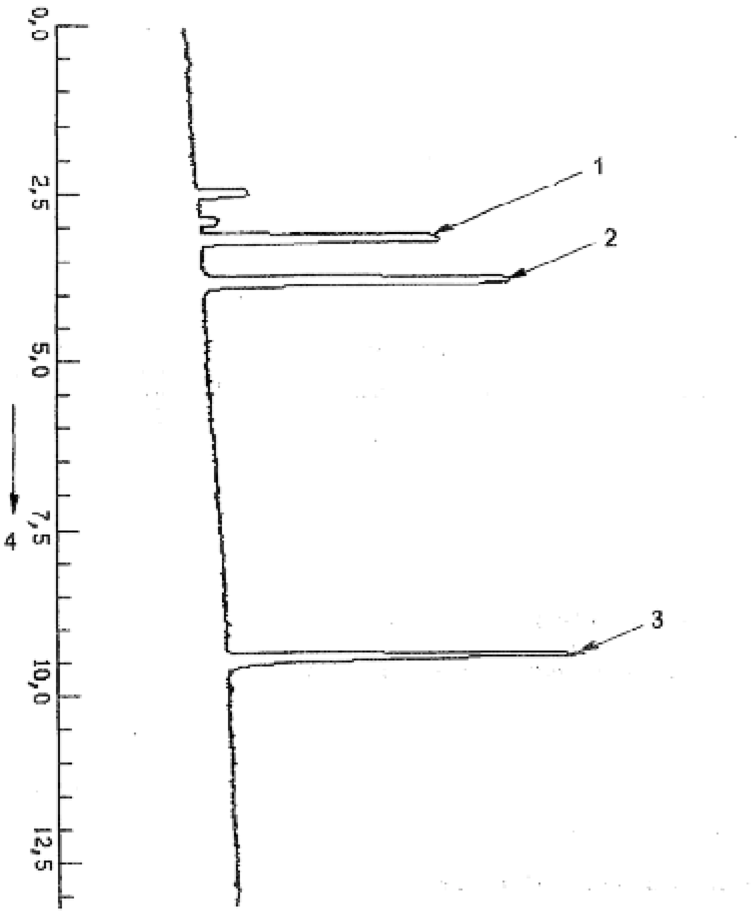
The selectivity of the test method is defined as the ability of the gas-chromatographic system to distinguish ethylene oxide from other interfering components.

The secondary constituents occurring in ethoxylates, e.g. methanol, ethanol, acetaldehyde and 1,4-dioxane, can be separated from ethylene oxide when the specified analytical conditions are used, since they all have a retention time different from ethylene oxide (see Figure A.1). Any methyl formate present can lead to superposition of peaks.

Table A.1

Designation	Sample A	Sample B
Number of participating laboratories	7	7
Number of laboratories retained after eliminating outliers	7	7
Number of individual measurements of all laboratories	43	43
Mean value w (µg/g)	1,76	7,86
Repeatability standard deviation, s_r (µg/g)	0,31	0,68
Repeatability limit, r ($r = 2{,}8 \times s_r$) (µg/g)	0,87	1,90
Repeatability coefficient of variation (%)	17,6	8,7
Reproducibility standard deviation, s_R (µg/g)	0,51	2,32
Reproducibility limit, R ($R = 2{,}8 \times s_R$) (µg/g)	1,43	6,50
Reproducibility coefficient of variation (%)	28,9	29,5

NOTE For practical reasons, some participants in the interlaboratory test deviated in some details from the prescribed procedure.



Key

1 Ethylene oxide
2 Propene oxide
3 1,4-dioxane
4 Time in minutes

Figure A.1 — Example of a chromatogram

Annex B
(informative)

Titration of ethylene oxide stock solution

B.1 Principle

Hydrochloric acid reacts with ethylene oxide in the presence of magnesium chloride (catalyst) to give chloroethanol.

The excess of hydrochloric acid is titrated by ethanolic potassium hydroxide solution potentiometrically.

B.2 Reagents

During the analysis, use only reagents of recognized analytical grade and water complying with grade 3 as defined in EN ISO 3696.

B.2.1 Ethanol, C_2H_6O.

B.2.2 Hydrochloric acid, HCl, ethanolic $c(\mathrm{HCl}) = 0{,}1$ mol/l.

B.2.3 Potassium hydroxide solution, KOH, ethanolic $c(\mathrm{KOH}) = 0{,}1$ mol/l.

B.2.4 Magnesium chloride, hydrate, $MgCl_2 \cdot H_2O$.

B.3 Apparatus

Ordinary laboratory apparatus and the following.

B.3.1 Potentiometric titrating apparatus equipped with a 20 ml plunger burette and stirrer.

B.3.2 Combined glass electrode (for example : Orion 8162 SC 1)).

B.3.3 Magnetic stirrer.

B.3.4 Stoppered flask.

B.3.5 Beaker, 150 ml capacity.

B.3.6 Measuring cylinder, 100 ml capacity.

B.3.7 Analytical balance, accurate to 0,1 mg.

B.4 Sampling

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

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1) Orion 8162 SC is an example of a suitable product available commercially. This information is given for the convenience of users of this standard and does not constitute an endorsement by CEN of this product.

B.5 Procedure

Add 20,0 ml of hydrochloric acid c(HCl) =0,1 mol/l (B.2.2) to 10 ml of a 50 g/100 ml suspension of magnesium chloride (B.2.4) in ethanol (B.2.1) in a stoppered flask (B.3.4). Shake to obtain a saturated solution and leave standing overnight to equilibrate. Weigh 5,00 g of ethylene oxide stock solution (0,25 g/100 ml) into the flask and mix for 10 min. Titrate with potassium hydroxide solution c(KOH) = 0,1 mol/l (B.2.3) determining the end point potentiometrically. Carry out a blank titration, in replacing the stock solutions by water.

B.6 Expression of results

The ethylene oxide content, $w(\mathrm{C_2H_4O})$, expressed as milligrams of ethylene oxide per gram of the stock solution, is given by the following equation :

$$w(\mathrm{C_2H_4O}) = \frac{(V_0 - V_1) \times c \times 4{,}4}{m}$$

where

V_0 is the volume of potassium hydroxide solution (B.2.3) necessary to reach the equivalence point of the volumetric determination with the blank, in millilitres ;

V_1 is the volume of potassium hydroxide solution (B.2.3) necessary to reach the equivalence point of the volumetric determination with the assay, in millilitres ;

c is the numerical value of the concentration of potassium hydroxide solution (B.2.3) ;

m is the mass of ethylene oxide stock solution, in grams.

The result shall be expressed to two decimal digits.

blank

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