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Surface active agents — Determination of free propylene oxide content in propylene oxide adduct surfactants — GC method

Agents de surface tensioactifs — Détermination de la teneur en oxyde de propylène libre dans les produits d'addition à base d'oxyde de propylène — Méthode de chromatographie en phase gazeuse (GC)

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Foreword

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This document was prepared by Technical Committee ISO/TC 91, *Surface acting agents*.

Surface active agents — Determination of free propylene oxide content in propylene oxide adduct surfactants — GC method

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1 Scope

This document specifies an analytical procedure for the determination of free propylene oxide in surfactants which are synthesized from propylene oxide copolymers.

The method is appropriate for the qualitative and quantitative determination of propylene oxide groups in propylene oxide adducts, polyethers and polyglycol esters by headspace gas chromatography (HS-GC) with a flame ionization detector (FID) based on external procedure. Gas chromatography-mass spectrometry (GC-MS) is used for the confirmatory purposes.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

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

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Principles

The sample is weighed into a headspace vial and the sealed vial is placed in a head space sampling instrument and allowed to reach thermal equilibrium. A portion of the vapour phase is then analysed by temperature programmed gas chromatography (GC). Qualitative detection is determined by retention time of target compounds with FID or by relative abundance ratios of the fragment ions with MSD. Quantification is achieved by external quantification method for GC-FID.

5 Reagents

During the analysis, use only reagents of recognized analytical grade.

5.1 Water, complying with grade 3 in accordance with ISO 3696.

5.2 Certain concentration of propylene oxide stock solution, prepared by either of the following two methods:

a) Propylene oxide, C_3H_6O, with a purity of mass fraction ≥99,7 %, dissolved in acetonitrile, vials containing 1,0 mg of propylene oxide dissolved in 1 ml of acetonitrile.

b) Commercial propylene oxide stock solutions of appropriate concentration if available may also be used to simplify procedure and maintain the accuracy of solution concentration, e.g. 1 000 µg/mL dissolved suitable solvent, or equivalent.

5.3 N, N-dimetylacetamide (DMAC), C_3H_7NO, with a purity ≥99,9 %.

DMAC may be substituted with other solvent which offers affordable safety and convenience. Applicability of the solvent should be evaluated by appropriate validation. Possible substitutes are including, but not limited to the following:

— Dimethyl formamide (DMF);

— Diethyl formamide (DEF);

— Dimethyl sulfoxide (DMSO);

— Diluted water, grade 3 in accordance with ISO 3696

— Sodium chloride, or other salt.

5.4 Nitrogen, to operate the gas chromatograph, with a purity ≥99,998 %.

5.5 Helium, to operate the gas chromatograph-mass spectrometer, with a purity ≥99,999 %.

6 Apparatus

NOTE An instrument or item of apparatus is listed only where it is special or made to a particular specification, usual laboratory glassware and equipment being assumed to be available.

Ordinary laboratory apparatus and the following:

6.1 Analytical balance, with an accuracy of 0,1 mg.

6.2 Capillary gas chromatography system, equipped with flame ionization detector (FID) or mass spectrometry (MSD) and fitted with an automatic headspace sampler.

6.3 Headspace sampling unit.

6.4 Crimped top glass vials, with a capacity of 20 ml or of another size suitable for the particular auto sampler employed, with PTFE-coated butyl rubber septa and crimp-closures.

6.5 Septum and crimped tops, lined with aluminium or PTFE, for closing the vials.

6.6 Sealing pliers, for the vials.

6.7 Vortex mixer, with a fixed speed mode.

6.8 Volumetric flasks, with a capacity of 10 ml, 50 ml and 100 ml.

6.9 Micropipette or micro syringes, with a capacity of 10 µl, 50 µl, 100 µl and 1 ml ± 0,01 ml.

6.10 Capillary chromatographic column, capable of the separation characteristics shown in Figure 2.

The following is an example of a GC column which has been found to be suitable for propylene oxide analysis:

EXAMPLE A fused silica capillary glass or quartz column 30 m long and 0,32 mm in internal diameter the inner surface of which is a capillary column coated with a 1,0 µm thick layer of 6 % cyanopropylphenyl-94 %dimethylpolysiloxane as stationary phases, or equivalent.

7 Preparation of calibration solutions

7.1 Standard solutions

7.1.1 General

Prepare the working solution of propylene oxide either by difference weighing or using a commercial standard vial.

7.1.2 Difference weighing

Weigh a 50 ml volumetric flask containing approx. 40 ml of DMAC (5.3). Add ~50 mg propylene oxide (5.2 a) into the flask and reweigh with a cooled syringe. Fill the flask to the mark with DMAC and mix carefully. By weighing the difference, calculate the actual concentration in mg propylene oxide/ml solution precisely.

7.1.3 Commercial standard vial

Prepare appropriate concentrations of standard solution by multistage dilutions with DMAC (5.3) from the certified propylene oxide stock solutions (5.2 b), that may be purchased from commercial suppliers.

Stored solution in a refrigerator at 4 °C for about 4 weeks.

7.2 Calibration solutions

Prepare the calibration solution as follows:

Add about 8 ml DMAC (5.3) each into seven 10 ml volumetric flasks (6.8). Using a micropipette or micro syringe (6.9), pass a certain amount of propylene oxide working solution (see 7.1) into the volumetric flasks according to Table 1. Make up to volume with DMAC and follow by vortex and oscillation, so that each calibration solution contains 0 µg; 2,5 µg; 5,0 µg; 10,0 µg; 12,5 µg; 25,0 µg; 50,0 µg and 100,0 µg of propylene oxide respectively.

Table 1 — Preparation of calibration solutions

Calibration solution	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Volume of the solution, µl	0,0	25,0	50,0	125,0	250,0	500,0	1 000,0
Make up to volume with DMAC, ml	10	10	10	10	10	10	10
Approximate concentration of propylene oxide[a], (µg/ml)	0	2,5	5,0	12,5	25,0	50,0	100,0

[a] The accurate concentration of propylene oxide in each calibration solution is obtained by the calculation with the mass of propylene oxide.

8 Sampling and preparation of the test sample

8.1 Preparation of the test sample

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

8.2 Determination

Weigh about 1,0 g (accurate to 0,1 mg) of the test sample (8.1) and add it to each of three separate headspace sample vials (6.3). Then, add 5 ml of DMAC (5.3), to each of the vials. Seal each vial, and after 2 min vortexing homogenization, put it in the headspace sampler and conduct the test.

NOTE The above processing procedure is suitable for liquid paste or solid samples while liquefaction and homogenization is necessary for some samples with poor aqueous solubility and low dissolution. In principle, the sample preparation methods for solid substances can be accelerated by gentle warming or by heating the solvent (below 50 °C).

8.3 Qualitative determination

Under the chromatographic and mass spectrometer conditions given below (see Clause 9), identify the propylene oxide based on the retention times. If the retention time of chromatographic peak is consistent with that of standard propylene oxide, the occurrence of selected ions in sample mass spectra is confirmed after the deduction of background, and the relative abundance ratio of detect ion is consistent with that of the standard sample shown in Table 2 and Table 3, the presence of propylene oxide in sample is determined.

Table 2 — Detect ion and relative ion intensities

Analytes	Detect ion (m/z) and relative range of the response %
Propylene oxide	28:58:27:31(100:81:50:31)

Table 3 — Allow relative deviation of relative ion abundance

Allow relative deviation %	Relative ion abundance %
±20	>50
±25	20 to 50
±30	10 to 20
±50	≤10

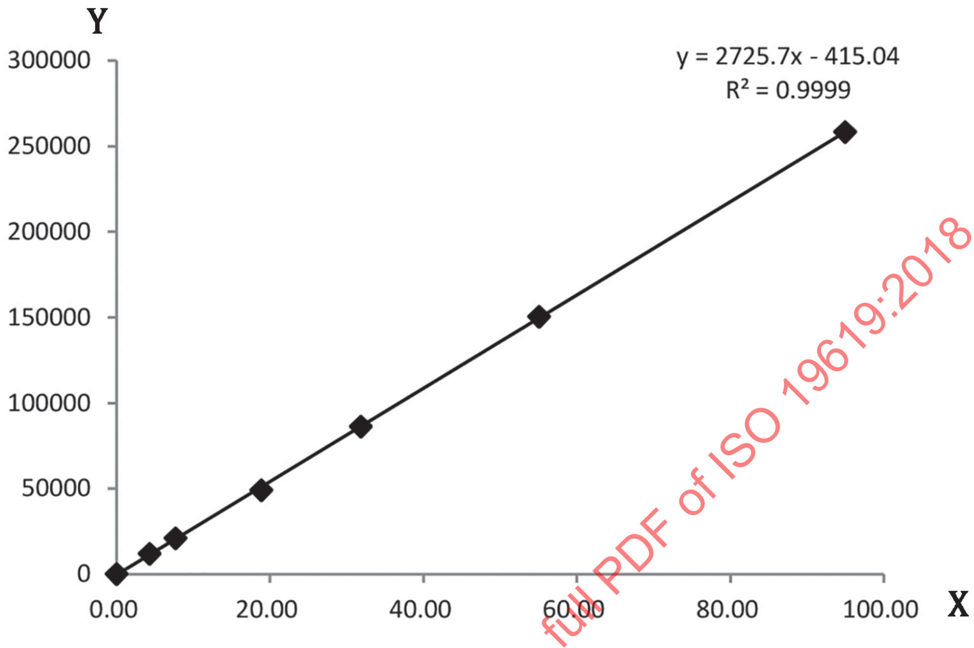
8.4 Quantitative determination

Using the propylene oxide standard solution (7.2), establish a standard calibration curve. Test the samples by headspace chromatography procedure and calculate the analyte level in sample based on the concentration measured according to the corresponding linear regression equations and peak areas.

Prepare a calibration curve by plotting the propylene oxide peak areas on the ordinate (Y-axis) versus content for the propylene oxide component on the abscissa (X-axis). Extrapolate the line to the point where it intercepts the abscissa (see Figure 1). This intersection is the propylene oxide content of the sample.

When calculating the results in accordance with the standard addition procedure, the calibration curve should be rectilinear and the correlation coefficient should be 0,995 or better. The standard deviation of the values at the intercept shall not exceed a 10 % of the mean value. Or else, prepare the new solutions and determine again. If necessary, add 1 or 2 determination points.

According to the content of analyte in test samples, select similar concentration of the calibration working solutions. Appropriate dilution can be made if the expected content of target compounds is high and out of the linear range.



Key

X propylene oxide concentration, µg/ml

Y propylene oxide peak area

Figure 1 — Example of a peak area versus concentration graph for the standard addition procedure

The propylene oxide content, *w*, expressed in milligrams per kilogram and the propylene oxide concentration in the test sample are obtained according to Formula (1):

$$w = \frac{m_i}{m} \quad (1)$$

where

w is the propylene oxide content, in µg/g;

m_i is the mass of propylene oxide measured according to the calibration line, in µg;

m is the mass of test sample, in g.

9 Chromatographic and mass spectrometer conditions

The choice of chromatographic conditions depends on the apparatus in use and can be varied from those given below, provided that suitable separation of the compounds of interest is maintained. The following conditions have been found to be suitable for the column recommended in note in 6.10.

a) injection temperature 230 °C;

b) column settings as follows:

  1) initial temperature: 50 °C held for 5 min;

  2) initial program rate of 10°C/min to an intermediate temperature of 150 °C;
  3) isothermal at 150 °C for 1 min;
  4) a final program rate of 20 °C/min to a final temperature of 220 °C;
  5) maintain the final temperature for 5 min.

c) carrier gas: nitrogen or helium, flow rate of 1,5 ml/min;

d) detector temperature 260 °C;

e) headspace sampling conditions settings as follows:
  1) headspace oven temperature: 70 °C;
  2) sample loop temperature: 90 °C;
  3) sample equilibrium time: 30 min;

f) transfer line temperature 110 °C;

g) injection time 1 min, injection volume 1 ml;

h) splitless or split as a proper ratio shall be applied;

i) Ion source temperature: 230 °C;

j) Quadrupole temperature: 150 °C;

k) Ionization mode: EI;

l) Ionization energy:70 eV;

m) Data acquisition mode: selected ion monitoring(SIM);

10 Evaluation

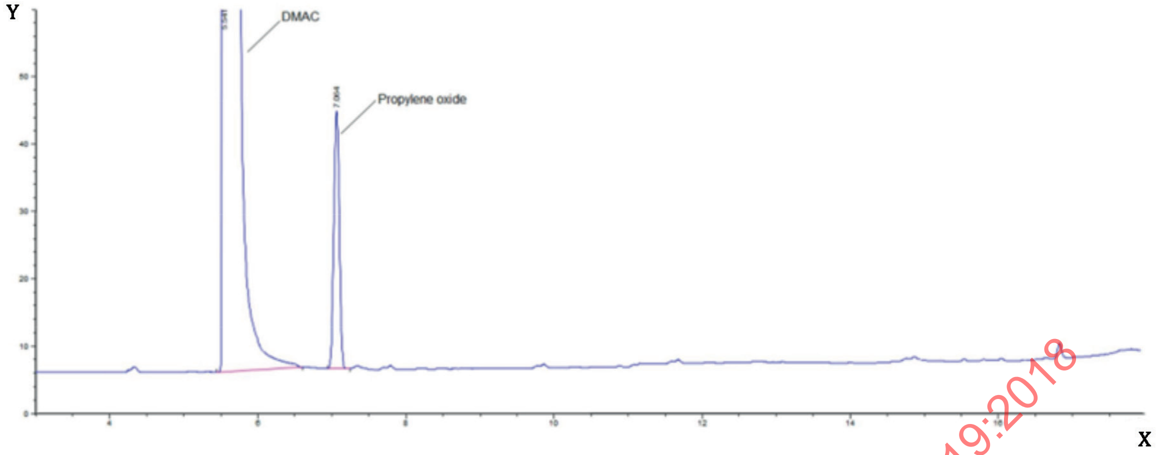
10.1 General

The standard addition method gives more precise data. However, the external standard technique is most commonly used for routine analyses.

For external calibration, a typical LOD value for analyte in test sample with GC-FID is 0,015 µg/g while the LOQ of the method is 0,03 µg/g.

10.2 Identification

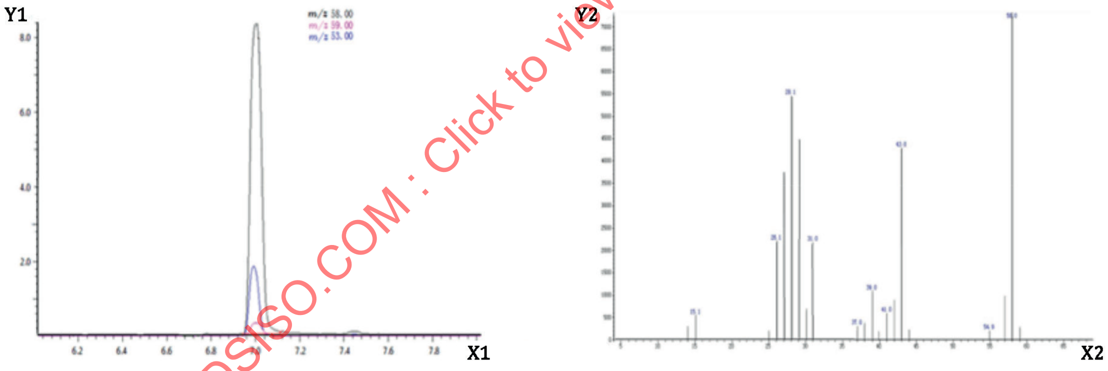
The analysed propylene oxide and the solvents DMAC are identified by comparing the retention times and mass spectra of the sample with those of the references substances. Under selected chromatographic conditions, identify the components of the test sample by reference to Figure 2 and Figure 3.



Key

X retention time, in min
Y peak areas, in kConuts
1 peak of solvent DMAC
2 peak of propylene oxide

Figure 2 — Chromatogram obtained by GC-FID from reference with the conditions mentioned above



SIM chromatogram at *m/z* 58

Mass spectrum of propylene oxide

Key

X1 retention time of propylene oxide, in min
Y1 abundance (× 10,000), in kConuts

X2 *m/z*
Y2 abundance, %

Figure 3 — Chromatogram obtained by GC-MS and image for mass spectrum reference

10.3 Calculation

Determine the area of the propylene oxide peak and calculate the content using the calibration solutions data.

11 Precision

11.1 Repeatability

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.

11.2 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.

12 Test report

The test report shall include the following information:

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

b) the method used;

c) the results obtained and the used determination procedure,

d) the results calculated according to Clause 8 and 9;

e) Any details not specified this method or which are optional, as well as any factor which may have affected the results;

f) Type and date of sampling, reference analyst, notebook reference number, date of the analysis, and date of the report.