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Surface active agents — Determination of 1,4-dioxan residues in surfactants obtained from epoxyethane by gas chromatography

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National foreword

This British Standard is the UK implementation of ISO 17280:2015.

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 1,4-dioxan residues in surfactants obtained from epoxyethane by gas chromatography

Agents de surface — Détermination de la teneur en résidus de 1,4-dioxane dans les agents tensioactifs obtenus à partir d'époxyéthane par chromatographie en phase gazeuse

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Foreword

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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*.

Surface active agents — Determination of 1,4-dioxan residues in surfactants obtained from epoxyethane by gas chromatography

1 Scope

This International Standard provides a method for the determination of 1,4-dioxane residues in surfactants which are synthesized from epoxyethane, such as alkyl ether sulfates and alcohol ethoxylates.

The method is applicable for samples containing 1,4-dioxane more than 5 mg/kg. For samples containing 1,4-dioxane more than 100 mg/kg, the sample solutions should be diluted to appropriate concentration.

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

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

ISO 5725-2, *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*

3 Principle

The sample is weighed into a head space vial and a calibration solution is added. 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 GC with flame ionization detection. Either an internal standard or standard addition method of quantification are employed.

4 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.

4.1 **1,4-Dioxane,** purity 99,5 % minimum.

4.2 **4-Methyl-1,3-dioxane,** purity 98 % minimum.

4.3 **N, N-dimethylformamide (DMF)**.

DMF may be substituted with other solvent. Applicability of the solvent should be evaluated by appropriate validation. Possible substitutes are including, but not limited to following:

— N, N-dimetylacetamide(DMA);

— Dimethyl sulfoxide (DMSO);

— Diethyl formamide (DEF);

— Formamide.

Diluent shall be free from peaks which interfere 1,4-dioxane and 4-methyl-1,3-dioxane.

4.4 Carrier gas: nitrogen or helium, purity 99,99 % minimum.

5 Apparatus

Ordinary laboratory apparatus and the following.

5.1 Analytical balance, 0,1 mg readability.

5.2 Gas chromatography system, attached with temperature programmed device and flame ionization detector (FID).

5.3 Head space sampling unit

5.4 20 ml crimped top glass vials, sealing pliers and sealing clamp suitable for head space unit.

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

5.6 Sealing pliers, for the vials.

5.7 Capillary column, capable of the separation characteristics shown in **Figure 2**.

NOTE A 30 m × 0,32 mm (id) fused silica capillary column (film thickness: 0,25 µm) with nitroterephthalic acid modified polyethylene glycol stationary phase is advisable.

5.8 Volumetric flasks, 50 ml and 100 ml capacity.

5.9 Gas tight syringes or glass pipettes, 1 ml ± 0,01 ml capacity.

6 Preparation of calibration solutions

6.1 Calibration solution A

Add approximately 40 ml of DMF (4.3) to a 50 ml volumetric flask. Weigh 0,2 g of 1,4-dioxane (4.1) to record the exact mass to obtain the accurate concentration in each calibration solution I. Make up to volume with DMF and thoroughly homogenize. The solution is A.

Prepare each calibration solution I according to Table 1.

Table 1 — preparation of calibration solutions

Calibration solution I	I_1	I_2	I_3	I_4	I_5
Volume of the solution A/ml	0,0	0,5	1,0	2,5	5,0
Make up to volume with DMF/ml	100	100	100	100	100
The approximate concentration of 1,4-dioxane[a]/(µg/ml)	0	20	40	100	200

[a] The accurate concentration of 1,4-dioxane in each calibration solution I is obtained by the calculation with the mass of 1,4-dioxane.

6.2 Calibration solution B

The calibration solution B which contains the calibration solution B_1 and the calibration solution B_2 is used to relative response factor procedure.

a) Add approximately 40 ml of DMF to a 50 ml volumetric flask, weigh 0,4 g of 4-methyl-1,3-dioxane (4.2) to record the exact mass to obtain the accurate concentration in calibration solution C. Make up to volume with DMF and thoroughly homogenize. The solution is C.

b) Add 0,5 ml ± 0,01 ml of this solution C and 1,0 ml ± 0,01 ml of solution A to a 100 ml volumetric flask, make up to volume with DMF and thoroughly homogenize. The solution is B_1. The accurate concentration of 4-methyl-1,3-dioxane and 1,4-dioxane in the final solution B_1 is obtained by the calculation with the mass of 4-methyl-1,3-dioxane and 1,4-dioxane.

c) Add 0,5 ml ± 0,01 ml of this solution C to a 100 ml volumetric flask, make up to volume with DMF and thoroughly homogenize. The solution is B_2. The accurate concentration of 4-methyl-1,3-dioxane in the final solution B_2 is obtained by the calculation with the mass of 4-methyl-1,3-dioxane.

7 Procedure

7.1 Preparation of the test sample

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

7.2 Standard addition procedure

7.2.1 Preparation of test sample solutions

7.2.1.1 Add 2 g ± 0,01 g of test sample (**7.1**) to each of three separate head space sample vials. For samples where the 1,4-dioxane content is expected to be less than 20 mg/kg, use the procedure described in **7.2.1.2**. For samples expected to have a content of 1,4-dioxane from 20 mg/kg to 100 mg/kg, use the procedure described in **7.2.1.3**.

7.2.1.2 Using the 1ml gas tight syringe or glass pipette (**5.9**), add the following to each of the three vials:

a) 1 ml ± 0,01 ml of calibration solution I_1 (6.1) to the first vial. Seal immediately with septum and crimped top (5.5) and homogenize by shaking vigorously.

b) 1 ml ± 0,01 ml of calibration solution I_2 (6.1) to the second vial. Seal immediately with septum and crimped top (5.5) and homogenize by shaking vigorously. The added amount of 1,4-dioxane relative to the test sample content is approximate 10 mg/kg.

c) 1 ml ± 0,01 ml of Calibration solution I_3 (6.1) to the third vial. Seal immediately with septum and crimped top (5.5) and homogenize by shaking vigorously. The added amount of 1,4-dioxane relative to the test sample content is approximate 20 mg/kg.

7.2.1.3 Using the 1 ml gas tight syringe or glass pipette (**5.9**), add the following to each of the three vials:

a) 1 ml ± 0,01 ml of calibration solution I_1 (6.1) to the first vial. Seal immediately with septum and crimped top (5.5) and homogenize by shaking vigorously.

b) 1 ml ± 0,01 ml of calibration solution I_4 (6.1) to the second vial. Seal immediately with septum and crimped top (5.5) and homogenize by shaking vigorously. The added amount of 1,4-dioxane relative to the test sample content is approximate 50 mg/kg.

c) 1 ml ± 0,01 ml of Calibration solution I_5 (6.1) to the third vial. Seal immediately with septum and crimped top (5.5) and homogenize by shaking vigorously. The added amount of 1,4-dioxane relative to the test sample content is approximate 100 mg/kg.

7.2.2 Determination

Analyse each blend as prepared in 7.2.1 by introducing the sample vial into the head space sampling unit (5.4) and analysing in accordance with the chromatographic conditions given in Clause 8.

7.2.3 Expression of results

Construct a graph of peak area (y-axis) versus content (x-axis) for the1,4-dioxane component. Extrapolate the line to the point where it intercepts the x-axis (see Figure 1). This intersection is the 1,4-dioxane content of the sample, c_1, expressed as milligrams per kilogram.

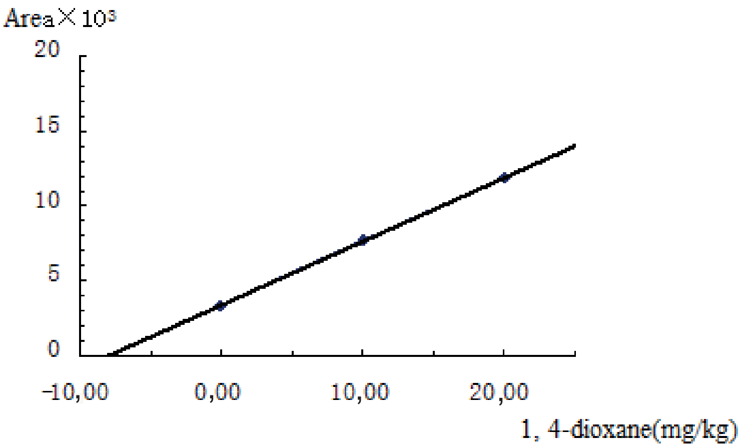


Figure 1 — Example of a peak area versus concentration graph for the standard addition procedure

NOTE When calculating the results in accordance with the standard addition procedure, the relative coefficient r should be above 0,995. Or else, prepare the new solutions and determine again. If necessary, add 1~2 determination points.

7.3 Relative response factor procedure

7.3.1 Determination of relative response factor

Add 2 g ± 0,01 g of sample to a head space sample vial. Using the 1 mL gas tight syringe or glass pipette (5.9), add 1,0 mL ± 0,01 mL of calibration solution B_1 [6.2, b)] to determinate related response factor. Seal immediately with septum and crimped top (5.5) and homogenize thoroughly by shaking vigorously.

Note The sample in this procedure is the same matrix as the test sample, which does not contain1,4-dioxane or contains 1,4-dioxane with known concentration, to ensure the consistency of the gas-liquid equilibrium in the sample vial.

Calculate the relative response factor k from the following Formula (1):

$$k = \frac{A_s c_2}{A_i c_1} \tag{1}$$

where

k is relative response factor;

A_s is the area of 1,4-dioxane, in peak area units;

A_i is the area of 4-methyl-1,3-dioxane, in peak area units;

c_1 is the 1,4-dioxane content in test sample (7.1), in milligrams per kilogram;

c_2 is the 4-methyl-1,3-dioxane content in the sample (i.e. 20 mg/kg), in milligrams per kilogram.

7.3.2 Preparation of test sample solutions

Add 2 g ± 0,01 g of test sample (7.1) to a head space sample vial. Using the 1 mL gas tight syringe or glass pipette (5.9), add 1,0 mL ± 0,01 mL of calibration solution B_2 [6.2, c)]. Seal immediately with septum and crimped top (5.5) and homogenize thoroughly by shaking vigorously.

7.3.3 Determination

Analyse each blend as prepared in 7.3.2 by introduce the sample vial into the head space sampling unit (5.4) and analyse in accordance with the chromatographic conditions given in Clause 8.

7.3.4 Expression of results

The 1,4-dioxane content, c_1, expressed as milligrams per kilogram, is given by the following Formula (2):

$$c_1 = \frac{A_1 c_2}{k A_2} \tag{2}$$

where

A_1 is the area of 1,4-dioxane, in peak area units;

A_2 is the area of 4-methyl-1,3-dioxane, in peak area units;

c_1 is the 1,4-dioxane content in test sample (7.1), in milligrams per kilogram;

c_2 is the 4-methyl-1,3-dioxane content in the sample (i.e. 20 mg/kg), in milligrams per kilogram;

k is the relative response factor.

8 Chromatographic 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 the note in 5.7.

a) injection temperature 250 °C;

b) column settings as follows:

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

    2) initial program rate of 10 °C/min to an intermediate temperature of 90 °C;

  3) a final program rate of 20 °C/min to a final temperature of 220 °C;

  4) maintain the final temperature for 5 min.

c) carrier gas: nitrogen or helium, flow rate of 2,0 ml/min;

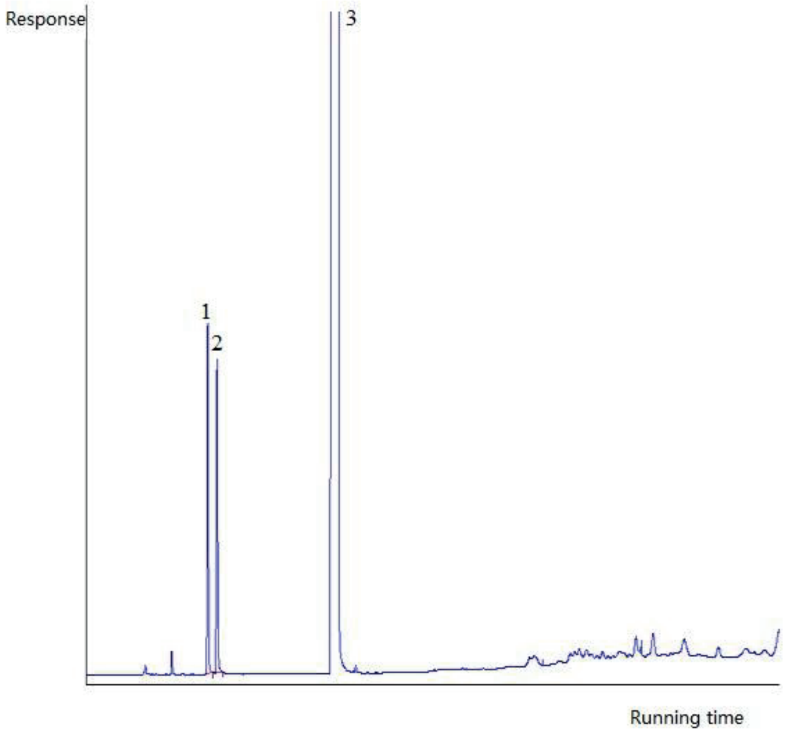
d) detector temperature 260 °C;

e) The head space sampling conditions shall be optimized in accordance with the instrument suppliers recommendations. The headspace oven shall be 85 °C and the equilibrium time shall be 20 min;

f) transfer line temperature 150 °C;

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

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



Key

1 1,4-dioxane
2 4-methyl-1,3-dioxane (internal standard)
3 solvent peak (DMF)

Figure 2 — A typical chromatogram of a test sample

9 Evaluation

9.1 General

Standard addition method gives more precise data. However, the relative response factor procedure is often used for routine quality control.

9.2 Identification

The analysed 1,4-dioxane and 4-methyl-1,3-dioxane and the solvents DMF are identified by comparing the retention times of the sample with those of the references substances. Identify the components of the test sample by reference to Figure 2.

9.3 Calculation

Determine the area of the 1,4-dioxane peak and, if appropriate, the 4-methyl-1,3-dioxane peak using the data.

10 Precision

10.1 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, shall not exceed the repeatability limit (*r*) in more than 5 % of cases.

According to ISO 5725-2, from the data given in Annex A, the relative repeatability limit [computed from the mean of the 1,4-dioxane content in per cent (m/m)] can be expected to be

a) 18 % for contents less than or equal to 20 mg/kg, and

b) 8 % for contents greater than 20 mg/kg.

10.2 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, shall not exceed the reproducibility limit (*R*) in more than 5 % of cases.

According to ISO 5725-2, from the data given in Annex A, the relative reproducibility limit [computed from the mean of the 1,4-dioxane content in per cent (m/m)] can be expected to be 40 %.

11 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) details of any operations not specified in this International Standard, i.e. ISO 17280:2014, or in the standards to which reference is made, and any operations regarded as optional, as well as any incidents likely to have affected the results;

e) type and date of sampling;

f) date of receipt and date of analysis.

Annex A
(informative)

Statistical data from the ring carried out

Table A.1 — Statistical data for standard addition procedure

	Standard addition procedure	
	Sample 1	Sample 2
Number of laboratories eliminating outliers	10	10
Number of outliers (laboratories)	1	1
Number of accepted results	19	19
Content of 1,4-dioxane, in mg/kg	13,2	53,3
Repeatability standard deviation, s_r	0,85	1,50
Repeatability limit r (for P = 95 %)	2,41	4,24
Repeatability relative standard deviation, in %	6,4	2,8
Repeatability limit related to the content of 1,4-dioxane as % (m/m), in %	18,3	8,0
Reproducibility standard deviation, s_R	1,20	7,57
Reproducibility limit, R (for P = 95 %)	3,40	21,4
Reproducibility relative standard deviation, %	9,1	14,2
Reproducibility limit related to the content of 1,4-dioxane as (m/m) %, in %	25,8	40,2

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