SLOVENSKI STANDARD
SIST EN 12974:2001

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Površinsko aktivne snovi - Določanje 1,4-dioksana v alkil-etoksi-sulfatnih proizvodih z GLC/metodo vzorčenja v plinski fazi

Surface active agents - Determination of the 1,4-dioxane content in alkyl-ethoxy-sulfate products by GLC/head space procedure

Grenzflächenaktive Stoffe - Bestimmung des Gehaltes von 1,4-Dioxan in Alkylethoxysulfatprodukten durch ein GLC/Head-Space-Verfahren

Agents de surface - Détermination de la teneur en 1,4-dioxane dans les alkylsulfates éthoxylés par CGL/Espace de tete

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English version

Surface active agents - Determination of the 1,4-dioxane content in alkyl-ethoxy-sulfate products by GLC/head space procedure

Agents de surface - Détermination de la teneur en 1,4-dioxane dans les alkylsulfates éthoxylés par CGL/Espace de tête

Grenzflächenaktive Stoffe - Bestimmung des Gehaltes von 1,4-Dioxan in Alkylethoxysulfatprodukten durch ein GLC/Head-Space-Verfahren

This European Standard was approved by CEN on 27 October 1999.

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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.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

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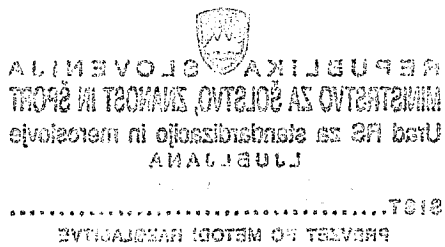

Foreword

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of an identical text or by endorsement, at the latest by June 2000, and conflicting national standards shall be withdrawn at the latest by June 2000.

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.

Annex A is informative.

1 Scope

This European Standard specifies a gas-liquid chromatography GLC/head space method for the determination of the 1,4-dioxane content in alkyl-ethoxy-sulfate products.

The method is applicable to samples containing 1,4-dioxane in the range from 5 mg/kg to 100 mg/kg.

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, *Surface active agents and detergents – Methods of sample division.*

3 Principle

The sample is weighed into a head space vial and a calibration solution/solvent 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 analyzed by temperature programmed GLC. Flame ionization detection and 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 EN ISO 3696.

4.1 1,4-dioxane, purity 98 g/100 g minimum (density 1,03 g/ml at 20 °C).

4.2 4-methyl-1,3-dioxane, purity 98 g/100 g minimum (density 0,98 g/ml at 20 °C).

4.3 N,N-dimethylacetamide (DMA). The suitability of this reagent shall be confirmed by analysing an 1 ml aliquot portion in accordance with clause 8. It shall be free from peaks which interfere with 1,4-dioxane and 4-methyl-1,3-dioxane.

NOTE HPLC grade DMA is suitable.

4.4 Carrier gas, nitrogen or helium.

5 Apparatus

Ordinary laboratory apparatus and following.

5.1 Chromatograph, with the items specified in 5.2 to 5.5.

5.2 Capillary column, capable of the separation characteristics shown in Figure 1.

NOTE A 50 m x 0,53 mm ID fused silica capillary column (film thickness: 5,0 µm) with 5 % phenyl silicone and 95 % methyl silicone stationary phase is advisable.

5.3 Flame ionization detector.

5.4 Head space sampling unit, complete with 20 ml crimped top glass vials, suitable for head space GLC apparatus.

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

5.6 Sealing plears, for the vials.

5.7 Electronic integrator.

5.8 Volumetric flasks, 50 ml and 100 ml capacity.

5.9 Gas tight syringes, 1 ml ± 0,001 ml capacity.

5.10 Analytical balance, accurate to 0,1 mg.

6 Calibration

6.1 Preparation of calibration solutions

6.1.1 Calibration solution A

Add approximately 40 ml of DMA (4.3) to a 50 ml volumetric flask (5.8). Weigh 400 mg ± 1 mg 4-methyl-1,3-dioxane (4.2). Make up to volume with DMA and thoroughly homogenize. Quantitatively dilute 0,5 ml of this solution to 100 ml with DMA.

The final solution A contains 40 µg/ml 4-methyl-1,3-dioxane.

6.1.2 Calibration solution B

Add approximately 40 ml of DMA (4.3) to a 50 ml volumetric flask (5.8). Weigh 200 mg ± 1 mg of 1,4-dioxane (4.1) and 400 mg ± 1 mg of 4-methyl-1,3-dioxane (4.2). Make up to volume with DMA and thoroughly homogenize. Quantitatively dilute 0,5 ml of this solution to 100 ml with DMA.

The final solution B contains 20 µg/ml of 1,4-dioxane and 40 µg/ml of 4-methyl-1,3-dioxane.

6.1.3 Calibration solution C

Add approximately 40 ml of DMA (4.3) to a 50 ml volumetric flask (5.8). Weigh 400 mg ± 1 mg of 1,4-dioxane(4.1) and 400 mg ± 1 mg of 4-methyl-1,3-dioxane (4.2). Make up to volume with DMA and thoroughly homogenize. Quantitatively dilute 0,5 ml of this solution to 100 ml with DMA.

The final solution C contains 40 µg/ml of 1,4-dioxane and 40 µg/ml of 4-methyl-1,3-dioxane.

6.1.4 Calibration solution D

Add approximately 40 ml of DMA (4.3) to a 50 ml volumetric flask (5.8). Weigh 1000 mg ± 1 mg of 1,4-dioxane (4.1) and 400 mg ± 1 mg of 4-methyl-1,3-dioxane (4.2). Make up to volume with DMA and thoroughly homogenize. Quantitatively dilute 0,5 ml of this solution to 100 ml with DMA.

The final solution D contains 100 µg/ml of 1,4-dioxane and 40 µg/ml of 4-methyl-1,3-dioxane.

6.1.5 Calibration solution E

Add approximately 40 ml of DMA (4.3) to a 50 ml volumetric flask (5.8). Weigh 2 000 mg ± 1 mg of 1,4-dioxane (4.1) and 400 mg ± 1 mg of 4-methyl-1,3-dioxane (4.2). Make up to volume with DMA and thoroughly homogenize. Quantitatively dilute 0,5 ml of this solution to 100 ml with DMA.

The final solution E contains 200 µg/ml of 1,4-dioxane and 40 µg/ml of 4-methyl-1,3-dioxane.

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 sample solutions

7.2.1 Internal standard procedure

For test samples of known response factor and internal standard calibration factor as determined in 8.2, use the following procedure.

Add 2 g ± 0,01 g of test sample (7.1) to a head space sample vial. Using the 1 ml gas tight syringe (5.9), add 1 ml ± 0,01 ml of calibration solution A (6.1.1). Seal immediately with septum and crimped top (5.5) and homogenize thoroughly by shaking vigorously.

7.2.2 Standard addition procedure

7.2.2.1 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 7.2.2.2. For samples expected to have a content of 1,4-dioxane from 20 mg/kg to 100 mg/kg, use the procedure described in 7.2.2.3.

7.2.2.2 Using the 1 ml gas tight syringe (5.9), add the following to each of the three vials :

a) 1 ml ± 0,01 ml of calibration solution A (6.1.1) to the first vial. Seal immediately with septum and crimp top (5.5) and homogenize by shaking vigorously.

b) 1 ml ± 0,01 ml of calibration solution B (6.1.2) to the second vial. Seal immediately with septum and crimped top (5.5) and homogenize thoroughly by shaking vigorously.

This solution contains 10 mg/kg of added 1,4-dioxane.

c) 1 ml ± 0,01 ml of calibration solution C (6.1.3) to the third vial. Seal immediately with septum and crimped top (5.5) and homogenize thoroughly by shaking vigorously.

This solution contains 20 mg/kg of added 1,4-dioxane.

7.2.2.3 Using the 1 ml gas tight syringe (5.9), add the following to each of the three vials:

a) 1 ml ± 0,01 ml of calibration solution A (6.1.1) to the first vial. Seal immediately with septum and crimped top (5.5) and homogenize thoroughly by shaking vigorously.

b) 1 ml ± 0,01 ml of calibration solution D (6.1.4) to the second vial. Seal immediately with septum and crimped top (5.5) and homogenize thoroughly by shaking vigorously.

This solution contains 50 mg/kg of added 1,4-dioxane.

c) 1 ml ± 0,01 ml of calibration solution E (6.1.5) to the third vial. Seal immediately with septum and crimped top (5.5) and homogenize thoroughly by shaking vigorously.

This solution contains 100 mg/kg of added 1,4-dioxane.

8 Procedure

8.1 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 NOTE in 5.2:

a) injection temperature 200 °C;

b) column settings as follows:

1) initial temperature 60 °C held for 3 min;

2) intial program rate of 4 °C/min to an intermediate temperature of 80 °C;

3) a final program rate of 30 °C/min to a final temperature of 300 °C; and

4) maintain the final temperature for 5 min.

c) carrier gas flow rate of 10 ml/min; and

d) detector temperature 325 °C.

The head space sampling conditions shall be optimized in accordance with the instrument suppliers recommendations. The test sample bath temperature shall be 70 °C and the equilibrium time shall be 30 min.

8.2 Relative response factor

Determine the 1,4-dioxane content of the test sample using the standard addition procedure according to 8.3.2. Calculate the result in milligrams per kilogram as specified in 10.2.

Calculate the relative response factor, F_d, from the following equation:

$$F_d = \frac{A_i \cdot C_d}{A_d \cdot C_i} \qquad (1)$$

where

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

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

C_d is the content of 1,4-dioxane in the sample, in milligrams per kilogram;

C_i is the content of 4-methyl-1,3-dioxane in the sample, i.e. 20 mg/kg.

8.3 Determination

8.3.1 Internal standard procedure

Prepare a sample blend as specified in 7.2.1. Introduce the sample vial into the head space sampling unit (5.4) and analyse in accordance with the chromatographic conditions given in 8.1.

A typical chromatogram is shown in Figure 1.