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Reversed-phase high-performance liquid chromatographic method for the assay of 1,4-dioxane in sulphated polyoxyethylene alcohol surfactants*

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Abstract: A rapid high-performance liquid chromatographic method has been developed for the assay of 1,4-dioxane in ethoxylated fatty alcohol sulphates. After solid-phase extraction using Bakerbond C_{18} cartridges, samples were directly analysed on a LiChrospher CH-8 reversed-phase column with UV detection at 200 nm and an acetonitrile–water eluent. Recovery of 1,4-dioxane from the surfactant matrix was 95.7% in the 40 to 120 μg g^{-1} range. The minimum quantifiable amount was 18 μg g^{-1}. The procedure is simple, reproducible, specific and suitable for routine analyses of commercial surfactants.

Keywords: *Reversed-phase high-performance liquid chromatography; octadecyl-bonded silica cartridges; 1,4-dioxane; sulphated fatty alcohol ethoxylate surfactants.*

Introduction

Sulphated polyoxyethylene fatty alcohols are the most commonly used surfactants in shampoos and bath preparations [1] and are generally contained in skin cleansing gel and lotion formulations [2]. Their advantages over the alcohol sulphates are based on enhanced water solubility, improved foaming quality and reduced irritation to eyes and skin [1, 3].

1,4-Dioxane may be formed during the polymerization of ethylene oxide to produce the polyoxyethylene moiety of the surfactant molecules [4, 5] and also in the sulphation of the ethoxylated alcohols to prepare the sulphated derivatives [6]. 1,4-Dioxane is a carcinogen in rats and mice [7] and it is absorbed through the intact skin of animals [8], hence the need for accurate, precise and rapid techniques for routine analyses of this substance in commercial ethoxylated alcohol sulphate products.

Published methods [6, 9–11] for the assay of dioxane in polyoxyethylated surface-active agents are based on gas chromatography (GC). These procedures, however, have distinct disadvantages such as complex and time-consuming sample preparation [6, 9], specialized and dedicated GC systems [10], unsatisfactory reproducibility [11], extensive calibration [6, 12], frequent changes of the chromatographic column [11] and the high cost of the equipment for the GC–mass spectrometric analysis [11].

Recently the first reversed-phase high-performance liquid chromatographic (RP–HPLC) procedure was developed [13] for the rapid determination of dioxane in cosmetic products. This paper reports the application of this method, with a new solid-phase extraction procedure, to the assay of 1,4-dioxane in commercial sulphated ethoxylated alcohol surfactants.

Experimental

Materials

HPLC-grade 1,4-dioxane, acetonitrile and water were supplied by Farmitalia Carlo Erba (Milan, Italy). Bakerbond C_{18} (BB-C_{18}) cartridges were obtained from J.T. Baker (Phillipsburg, NJ, USA).

Surfactant samples were from commercial suppliers (Texapon samples from Henkel Chimica SpA, Bologna, Italy; Zetesol samples from Zschimmer & Schwarz Italiana SpA, Tricerro, Italy). The nomenclature of the

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CTFA (Cosmetic, Toiletry and Fragrance Association) Cosmetic Ingredient Dictionary [14] has been used throughout.

Chromatography

The HPLC apparatus consisted of a Jasco chromatographic system (Model BIP-I pump, Model GP-A40 solvent programmer and Model UVIDEC-100-V variable-wavelength UV-detector; Jasco, Tokyo, Japan) linked to an injection valve with a 20-μl sample loop (Rheodyne, Cotati, USA) and a chromatographic data processor (Chromatopac C-R3A, Shimadzu, Kyoto, Japan). The detector was set at 200 nm and 0.01 a.u.f.s. Separations were performed according to the method described earlier [13] using a LiChrospher CH-8 column (dp 5-μm, 250 × 4.0 mm i.d.; Merck, Darmstadt, FRG) fitted with a guard column (dp 5-μm, 4 × 4 mm i.d.; Merck) and eluted under gradient conditions at a flow rate of 1.0 ml min^{-1}. Solvent A was acetonitrile–water (5:95, v/v) and solvent B was acetonitrile–water (50:50, v/v). The elution programme was as follows: isocratic elution with 5% solvent B, 95% solvent A for 5 min, then a 2-min linear gradient to 95% solvent B; the mobile phase composition was finally maintained at 95% solvent B for 1 min. Samples were injected 0.5 min after the start of the elution programme. The mobile phase was filtered through type HVLP filters (0.45-μm; Millipore S.A., Molsheim, France) and on-line degassed by a model ERC-3311 automatic solvent degasser (Erma, Tokyo, Japan). Chromatography was carried out at ambient temperature.

Gas chromatographic analyses were performed according to Black *et al.* [5] using a Fractovap 4200 gas chromatograph (Carlo Erba) fitted with a flame ionization detector. The glass column (2.0 m × 4 mm i.d.) was packed with Chromosorb 106 (Alltech, Eke, Belgium). The operating conditions were: column temperature, 210°C; injector port temperature, 230°C; detector temperature, 230°C; carrier gas (nitrogen) flow rate, 40 ml min^{-1}.

The identity of the 1,4-dioxane peak was assigned by co-chromatography with the authentic substance and confirmed by comparison of the gas chromatographic retention time with that of the standard compound.

Peak areas were quantified using the integrator which was calibrated with standard solutions of pure dioxane.

Sample processing

A 1-g amount of the surfactant product was accurately weighed into a 20-ml volumetric flask. Water was added, the sample mixed and then diluted to the mark. A 2.5-ml aliquot of this solution was applied to a pre-conditioned (5 ml of acetonitrile and then 5 ml of water) BB-C_{18} cartridge (sorbent weight, 500 mg) and eluted with 2 ml of acetonitrile–water (10:90, v/v). The latter fraction was directly analysed by RP–HPLC.

Recovery

Dioxane spiking solutions were obtained by quantitative dilution of 1-4 dioxane with water. The test samples were prepared by adding 100-μl aliquots of the spiking solutions, corresponding to 40 and 120 μg g^{-1}, to the surfactant products (1 g). The samples were subjected successively to clean up by BB-C_{18} and determination by HPLC as described above.

Reproducibility

The intra-assay reproducibility was tested by analysing, on 10 different days, 20 μl of the same stock sample preparation from a surfactant product. The inter-assay variability was evaluated by repeated (n = 10) Bakerbond cartridge extractions and HPLC analyses of the same surfactant sample.

Results and Discussion

The inclusion of a BB-C_{18} purification step prior to RP–HPLC analysis was essential for the removal of matrix peaks in the chromatogram of the surfactant extract (not shown) which interfere with the determination of 1,4-dioxane. The octadecyl-bonded silica sorbent efficiently retained dioxane in water and complete desorption (recovery rates >96%) from the cartridge was obtained with the acetonitrile–water (10:90, v/v) eluent. The recovery of dioxane was found to be reproducible between different batches of BB-C_{18}. Moreover multiple samples can be processed simultaneously with specially designed vacuum manifolds.

Figure 1 shows representative chromatograms of a sodium lauryl ether ('laureth') sulphate product (Fig. 1A) and of an undefined blend of fatty alcohol ether sulphates (Fig. 1B) containing 35.6 μg g^{-1} and 113.1 μg g^{-1} of 1,4-dioxane, respectively. Although the actual separation was effected isocratically in about 6

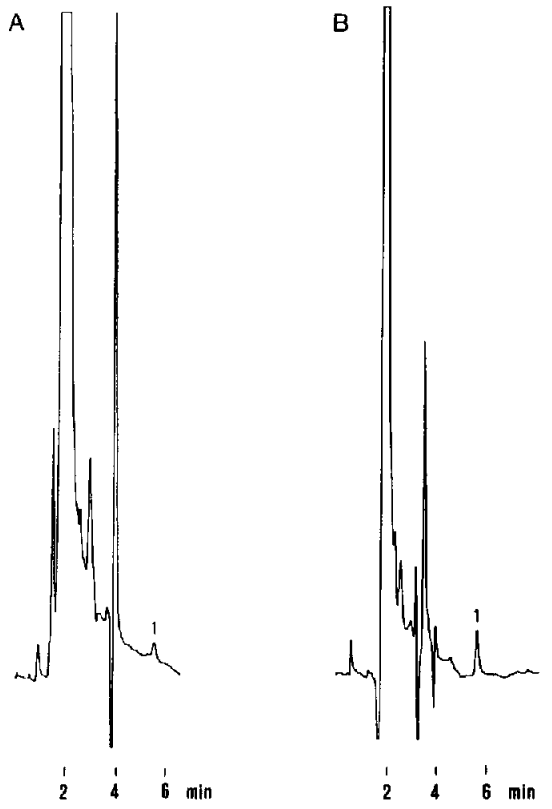

Figure 1
RP–HPLC chromatograms of a sodium laureth sulphate product (A) and of a sample containing an undefined blend of fatty alcohol ether sulphates (B). Operating conditions are described in the text. Peak: 1 = 1,4-dioxane.

min (Fig. 1), a rapid gradient was carried out before the next injection (see the Experimental section) to ensure the elution of strongly retained substances.

A linear correlation was obtained between peak area and concentration of 1,4-dioxane in the range 18–1200 μg g^{-1} (r = 0.999, a = 0.11, b = 0.17). The average recovery of dioxane from surfactant samples was 95.7% ± 3.3 SD (n = 10) in the 40 to 120 μg g^{-1} concentration range. Applying the RP–HPLC procedure to a surfactant product, 1,4-dioxane (35.6 μg g^{-1}) was determined with a relative standard deviation of 3.5% (n = 10) for the intra-assay reproducibility and 6.8% (n = 10) for the inter-assay reproducibility.

The applicability of the method developed in this study to quality control of finished products was demonstrated by assaying commercially available surfactant samples. The results are presented in Table 1.

Virtually identical values (Table 2) were obtained for dioxane when the same surfactant product was analysed by the present RP–HPLC technique or by headspace GC [6]. This indicates that the RP–HPLC procedure is accurate and is not subject to interference from the sample matrix.

In conclusion, the method described here takes less than 20 min to perform and permits the rapid and selective assay of dioxane at the ppm level in sulphated fatty alcohol ethoxylate surfactants. The proposed procedure is less laborious than others reported in the literature; moreover no deterioration of the HPLC column was observed over several weeks of continuous use. Because of the minimal sample preparation, good accuracy and precision the

Table 2
Comparison of amounts of 1,4-dioxane in surfactant products determined by RP–HPLC and headspace GC

Sample	Concentration, μg g^{-1} (mean ± SD, n = 3) RP–HPLC	GC
Texapon K14-SP	41.1 ± 1.6	42.0 ± 3.8
Texapon SBN	113.1 ± 3.1	111.7 ± 9.4

Table 1
Values for the assay of dioxane in sulphated polyoxyethylene surfactants

Compound type*	Trade name	1,4-Dioxane, μg g^{-1} (mean ± SD, n = 5)
Sodium laureth sulphate and sodium myreth sulphate	Zetesol ME/70	270.7 ± 5.3
Sodium laureth sulphate	Zetesol 250	86.9 ± 3.8
Blend of fatty alcohol ether sulphates (undefined)	Texapon SBN	113.1 ± 3.1
Sodium laureth sulphate and sodium myreth sulphate	Texapon K 14-SP	41.1 ± 1.6
Monoethanolamine-laureth sulphate and cocamidopropyl betaine	Zetesol 856 T	316.4 ± 5.6
Ammonium laureth sulphate	Zetesol AP	180.2 ± 4.9
Sodium laureth sulphate	Texapon N70	35.6 ± 2.7
Magnesium laureth sulphate	Texapon MG	44.0 ± 0.7

*Nomenclature according to the CTFA Cosmetic Ingredient Dictionary. "Laureth sulphate" [$CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_nOSO_3Na$] is the nomenclature adopted by the CTFA Cosmetic Ingredient Dictionary [14] for the ethoxylated surfactants which are prepared, as reported in the Introduction, by reacting a fatty alcohol with ethylene oxide to yield a fatty ether (hence the suffix "-eth"). "Myreth" is the corresponding term for myristyl ether.

method is well suited to routine quality control analyses of commercial surfactants.

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