Headspace Analysis of 1,4-Dioxane in Products Containing Polyethoxylated Surfactants by GC–MS

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Key Words

Gas chromatography-mass spectrometry
Headspace analysis
Polyethoxylated surfactants
1,4-dioxane

Summary

A headspace, gas chromatography-mass spectrometric (GC–MS) method for the identification and quantitation of 1,4-dioxane in polyethoxylated surfactants is described. An isotope dilution method employing 1,4-d^8-dioxane has been used for the quantitation of 1,4-dioxane which is based on the determination of the molecular ion (mass 88) by MS. The detection limit of the method was 0.3 ppm 1,4-dioxane. 82 % of the cosmetic products investigated were found to contain 0.3–96 ppm 1,4-dioxane, and 85 % of the products for dish washing investigated contained 1.8–65 ppm 1,4-dioxane.

Introduction

Polyethoxylated surfactants are commonly used in the formulation of, among others; cosmetics, products for dish washing and autocare. During the production of polyethoxylated detergents by the reaction of fatty alcohols with ethylene oxide, some ehtylene oxide is polymerised to form 1,4-dioxane [1]. Although some 1,4-dioxane may be removed by vacuum stripping, the polyethoxylated surfactants available as raw material for the production of shampoos and so on may be contaminated. It has been estimated that about one-third of emulsion-based cosmetics contain polyethoxylated derivatives contaminated by 1,4-dioxane [2].

1,4-dioxane has been shown to be carcinogenic to animals, and has been considered as a possible carcinogen to humans [3–7]. Furthermore, 1,4-dioxane may also be toxic to liver [8], lungs and kidneys [9] and the central nervous system [10]. According to the EEC directive on cosmetic products, 1,4-dioxane must not be used in their formulation.

Black et al [11] have extracted 1,4-dioxane from cosmetic products followed by its determination by gas chromatography (GC). However, recovery of 1,4-dioxane was found to be only 70–80 %. Levels of 1,4-dioxane in cosmetic products have been determined by Rümenapp and Hild [12] by headspace GC. Other volatile substances in cosmetics, for example perfumes, may, however, interfere. A selective method for the analysis of 1,4-dioxane in chemical products may involve its separation from other components by headspace GC followed by identification by mass spectrometry (MS) and determination of the molecular ion by MS. The present paper describes a headspace GC–MS method employing the above scheme for the determination of 1,4-dioxane in cosmetic products and in products for dish washing. An isotope dilution method using 1,4-d^8-dioxane has been employed for the GC–MS analysis.

Experimental

Chemicals and Glasware

1,4-d^8-dioxane was obtained from Aldrich Chemicals, FRG. Analytical grade 1,4-dioxane and dichloromethane were from E. Merck, FRG. Dichloromethane was distilled before use.

10 ml headspace glass vials and Teflon-coated silicon septa were from Hewlett Packard, USA. The vials and septa were heated at 150 °C for at least 16 h before use. Air-tight syringes for the injection of gases into the GC were from Precision Sampling Corporation, USA. The syringe was prewarmed to 80 °C before use, and cleaned with atmospheric air before reuse.

Samples

76 products including shampoos, hair- and body gels, liquid soap, balms, foam preparations; and 13 dish-washing products were obtained either form a Danish Retail Market or from manufacturers or importers of these products.

Identification

A 1 g sample was weighed in a headspace vial. The vial was closed using a Tefon-coated silicon septum. The

0009-5893/90/3 0441-05 $ 03.00/0

closed vial containing the sample was then heated at 80 °C for 16–18 h. GC–MS screening in the mass range 29–100 of a 0.5 ml gas sample in the headspace vial was performed as described under GC–MS conditions. The identification of 1,4-dioxane was established by comparing the mass spectrum of the sample GC–MS peak, (the retention time of which corresponded with that of standard 1,4-dioxane), with the mass spectrum of 1,4-dioxane in the MS-library.

Preparation of Standards for Quantitation

A sample (shampoo or dish-washing product) which did not contain 1,4-dioxane was used for the preparation of standards. 1 g of sample was weighed accurately in a headspace vial. To this, 25 µl 0.1 % (V/V) 1,4-dioxane and 25 µl 0.1 % (V/V) 1,4-d^8-dioxane were added and the vial closed immediately. Both 1,4-dioxane and 1,4-d^8-dioxane were diluted with dichloromethane. Several headspace vials using the same sample as well as the same diluted 1,4-dioxane and 1,4-d^8-dioxane were prepared at a time because a mean value from 6–8 analyses of a standard was used for the calculation of the 1,4-dioxane content of the samples. The diluted 1,4-dioxane and 1,4-d^8-dioxane should be used as soon as possible (within an hour).

Quantitation

An approximately 1 g sample was weighed accurately in a headspace vial. To this 25 µl dichloromethane and 25 µl 0.1 % (V/V) 1,4-d^8-dioxane (as used for the preparation of standards) were added and the vial closed immediately. After heating the vial for 16–18 h at 80 °C, the headspace GC–MS of the gas(es) in the sample vial was performed in the selective ion (masses 88 and 96) mode as described further. Each sample was analysed in duplicate. Before and after each analysis, the GC–MS of a standard containing 25 µl 0.1 % (V/V) 1,4-dioxane and 25 µl 0.1 % (V/V) 1,4-d^8-dioxane (prepared as above) was performed under the same conditions.

The mass intensities (areas) of masses 88 (molecular ion of 1,4-dioxane) and 96 (molecular ion of 1,4-d^8-dioxane) were measured. The ratio of mass intensities 88 to 96 for the sample (A) and standard (B) were calculated. The 1,4-dioxane in the sample was then calculated from:

$$\text{1,4-dioxane content (ppm)} = \frac{A}{B^*} \times \frac{1}{M} \times 25 \times 1.033 \;{}^{**}$$

where

M = weight of sample (g)

* mean of 6–8 standards (prepared together with sample) was used.

** density of 1,4-dioxane.

GC–MS Conditions

GC Instrument:	Hewlett Packard GC 5890A
GC column:	Supelcowax 10, 60 m x 0.32 mm i.d., df 0.25 µ
Carrier gas:	Helium, 50 ml min^{-1}.
Injector:	Split ratio 1:25, 260 °C. 500 µl sample gas injected with air-tight syringe.
GC-oven temperature program:	2 min at 50 °C, 5 °C min^{-1} to 100 °C. Thereafter 25 °C min^{-1} to 250 °C, 7 min at 250 °C.
MS Instrument:	Finnigan INCOS 50
Interface:	260 °C direct to ion source
Scan descriptor	
for identification:	mass 29.5 – mass 100.5 in 0.411 s
for Quantitation:	mass 87.5 – mass 88.5 in 0.091 s mass 95.5 – mass 96.5 in 0.092 s
Ionization:	70 eV electron impact at 170 °C
MS-library:	National Bureau of standards.

Results and Conclusions

Preliminary experiments were carried out to establish equilibrium conditions for the degassing of 1,4-dioxane from the samples in the headspace vials, the amount of isotopic 1,4-dioxane to be used as internal standard and to establish the linearity of the calibration curve. Headspace vials containing 1 g sample (shampoo or dish-washing product, 1,4-dioxane content approximately 30 ppm) were heated for various times (0–24 h) and headspace GC–MS run. Equilibrium of 1,4-dioxane between the sample and the headspace was achieved after 16 h heating at 80 °C (Figure 1). The calibration curve for 1,4-dioxane, from the analysis of a sample of shampoo spiked with 0–200 ppm 1,4-dioxane, was linear in the concentration range investigated (results not shown). Furthermore, the calibration curves were also linear when 25 µl and 50 µl 0.1 % 1,4-d^8-dioxane were used as internal standard. Therefore, 25 µl 0.1 % 1,4-d^8-dioxane was used as internal standard.

The detection limit for the identification of 1,4-dioxane was approximately 0.3 ppm. The recovery from 2 samples spiked with 50 ppm 1,4-dioxane, was 92 % and 94 %. The relative standard deviation was 9.1 ± 1.1 %, and day to day variation of standards was < 3 %.

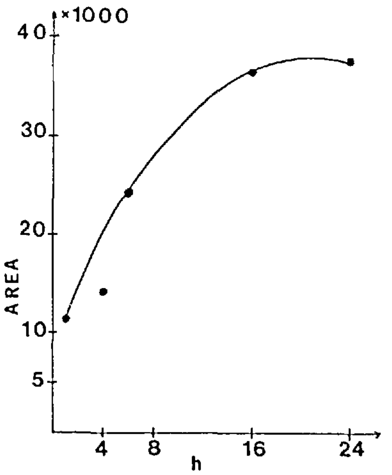

Figure 1

Time dependent degassing of 1,4-dioxane from 1 g sample of shampoo in closed headspace vial at 80 °C.
Abscissa: Mass intensity (area) of mass 88 in GC–MS analysis.
Ordinate: Heating time in hours (h).

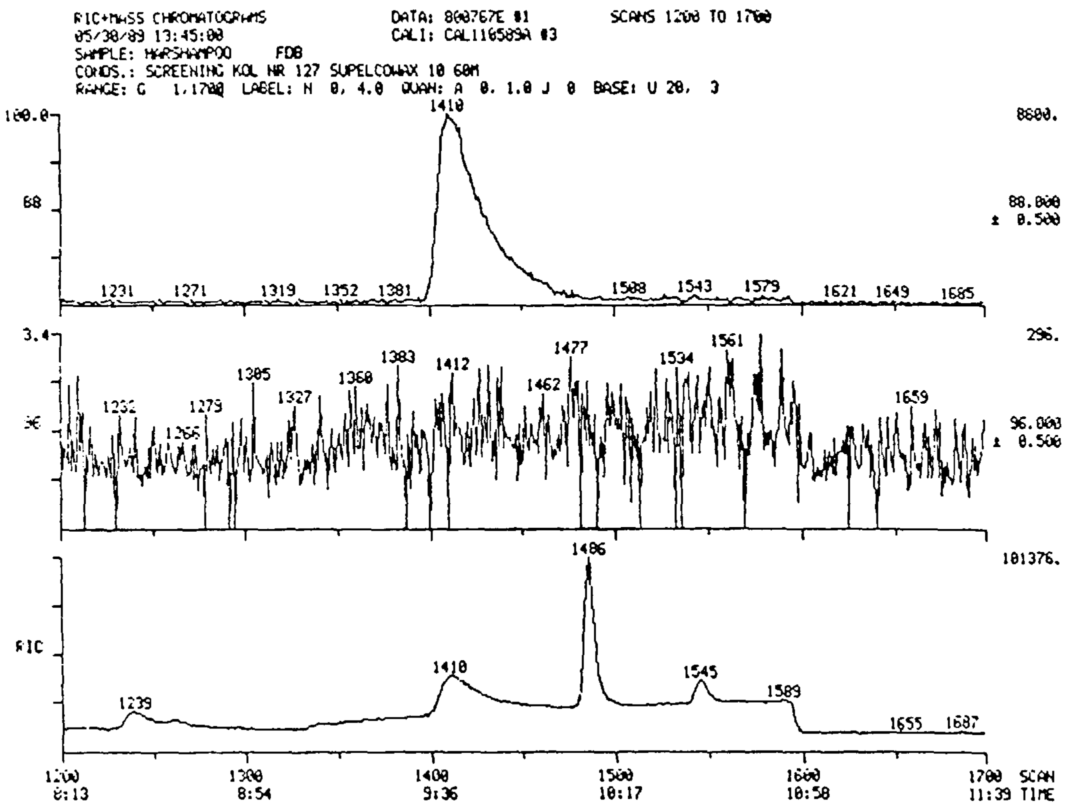

Figure 2a

Screening of 1,4-dioxane in shampoo by GC–MS see Experimental.

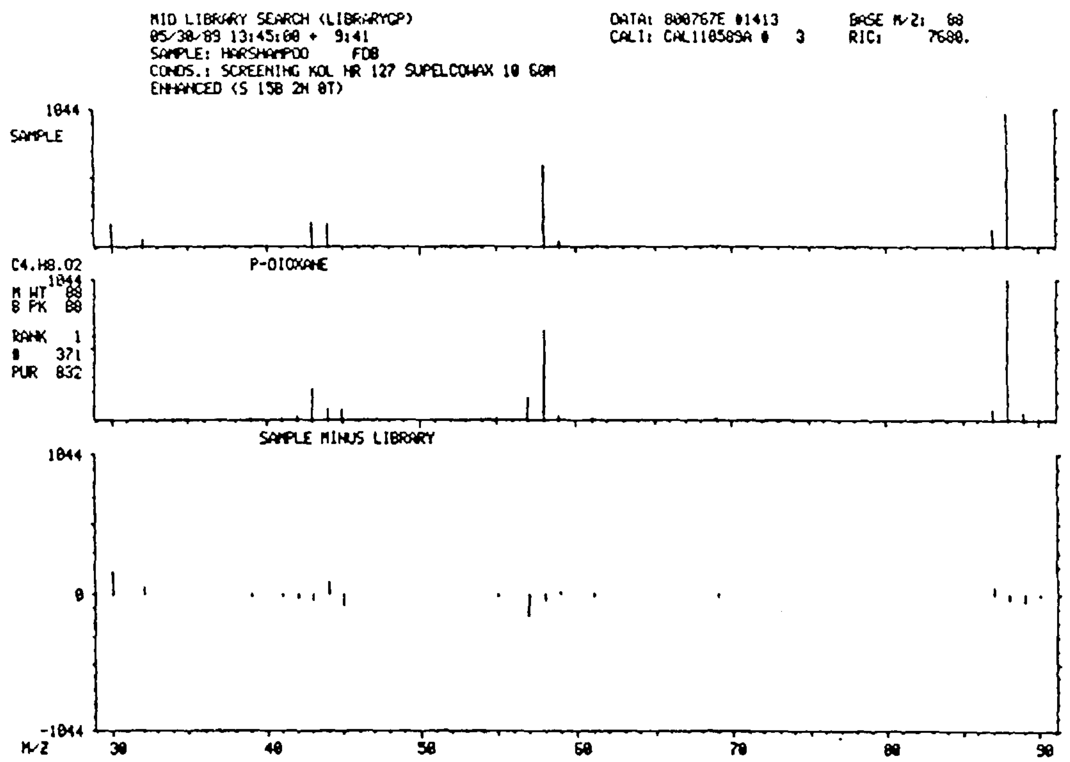

Figure 2b

Comparision of mass-spectrum of Scan no. 1410 (see Fig. 2a) of sample with 1,4-dioxane in the MS-library. Identification established from mass-spectrum and retention time in GC.

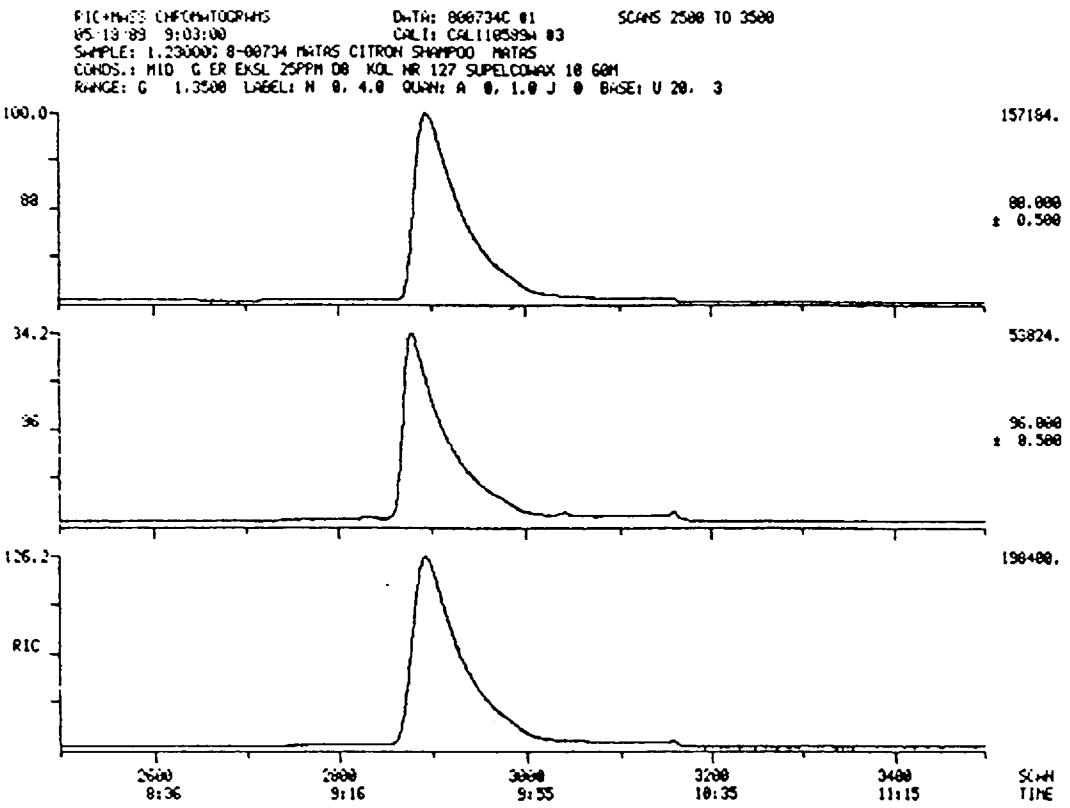

Figure 3

Analysis of shampoo by GC–MS in selective ion monitoring mode for determination of molecular ions masses 88 and 96, resepctively for 1,4-dioxane and 1,4-d^8-dioxane.

Table I. 1,4-dioxane in 76 cosmetic products.

1,4-dioxane content (ppm)	No. of Products	% of total investigated Products
n.d.	12	16
0,3 - 10	22	29
10 - 20	11	15
20 - 50	27	36
50 - 100	4	5

n.d. = not detected.

Table II. 1,4-dioxane in 13 dish washing products.

1,4-dioxane content (ppm)	No. of Products
n.d.	2
0,3 - 10	6
10 - 20	2
20 - 50	2
50 - 100	1

n.d. = not detected.

A typical example of screening for 1,4-dioxane is shown in Figures 2a and 2b, and a GC–MS run in selective ion-monitoring mode for quantitation of masses 88 and 96 is shown in Figure 3.

As described in Table I, 62 (82 %) of the cosmetic products contained 0.3–96 ppm 1,4-dioxane. The distribution of 1,4-dioxane in a number of cosmetic products is also reported in Table I. In Table II, the 1,4-dioxane content of the dish washing products is given; 11 (85 %) of these were shown to contain 1.8–65 ppm 1,4-dioxane.

The present method may be used for the control and supervision of 1,4-dioxane in various types of chemical products containing polyethoxylated derivatives. Furthermore, the method may also be suitable for the quality control of polyethoxylated surfactants.

The 1,4-dioxane content of the samples need not alarm consumers, as the maximum allowable concentration in chemical products is > 500 ppm. Nevertheless, the effect of cumulative doses should not be ignored in workers frequently exposed to polyethoxylated surfactants or products containing polyethoxylated surfactants, for example, workers in cosmetic industries and hair saloons. Regulation of 1,4-dioxane impurity in polyethoxylated surfactants should be considered by national and international authorities.

Acknowledgements

Technical assistance was provided by Miss Pernille Nielsen.

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Received: Feb. 9, 1990
Accepted: Feb. 25, 1990
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