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Analysis of Free Oxirane and 1,4-Dioxane Contents in the Ethoxylated Surface-Active Compounds by Means of Gas Chromatography with Headspace Sample Injection

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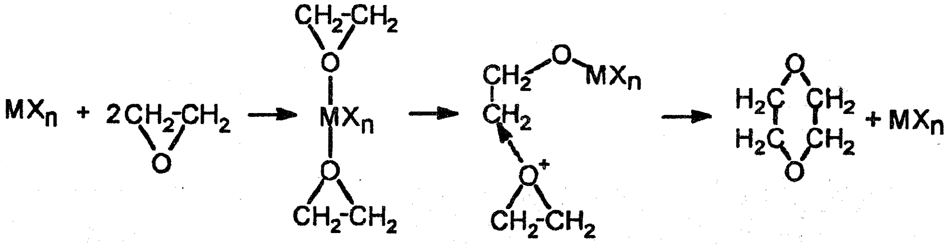
A quantitative analysis of oxirane and 1,4-dioxane contents in ethoxylated alcohols and amines was carried out using gas chromatography with headspace sample injection. Trace amounts of oxirane were determined using absolute calibration method, whereas those of 1,4-dioxane were found by addition of the component to be determined. The ethoxylates of alcohols and amines analyzed contained from 1 to 140 $\mu g\ g^{-1}$ of oxirane and from 2 to 100 $\mu g\ g^{-1}$ of 1,4-dioxane. With oxirane concentrations of more than 3 $\mu g\ g^{-1}$ in an ethoxylated sample, the relative standard deviation was between 0.8% and 3%. With 1,4-dioxane concentrations of more than 5 $\mu g\ g^{-1}$, the relative standard deviation was from 0.8% to 2.6%. The detection limit was 1 $\mu g\ g^{-1}$ for oxirane and 2 $\mu g\ g^{-1}$ for 1,4-dioxane.

Zastosowano technikę chromatografii gazowej z dozowaniem próbki metodą headspace do oznaczania zawartości oksiranu i 1,4-dioksanu. Śladowe ilości oksiranu oznaczano metodą kalibracji bezwzględnej, podczas gdy zawartość 1,4-dioksanu oznaczano dodając oznaczany składnik. Analizowane oksyetylaty alkoholi i alkiloamin zawierały od 1 do 140 $\mu g\ g^{-1}$ oksiranu i od 2 do 100 $\mu g\ g^{-1}$ 1,4-dioksanu. Przy stężeniu oksiranu w analizowanej próbce powyżej 3 $\mu g\ g^{-1}$ względne odchylenie standardowe zmienia się w zakresie od 0.8% do 3%. Przy stężeniu 1,4-dioksanu powyżej 5 $\mu g\ g^{-1}$ względne odchylenie standardowe wynosi 0.8–2,6%. Granica detekcji wynosi 1 $\mu g\ g^{-1}$ dla oksiranu i 2 $\mu g\ g^{-1}$ dla 1,4-dioksanu.

Ethoxylated surface-active compounds find numerous outlets as washing and/or rinsing agents as well as in the production of cosmetics [1–3]. These compounds are formed in the ethoxylation reactions wherein a hydrophobic parent substance (alcohol, amine) is treated with oxirane (ethylene oxide – EO). The quality of the final products is mostly dependent on oxirane and 1,4-dioxane contents. The content of 1,4-dioxane, formed in accordance with the following equation



depends mainly upon the catalyst MX_n used for ethoxylation [4,5]. MX_n usually means metal salt or hydroxide.

The presence of 1,4-dioxane and EO in the final products is important since they are toxic. Also, a carcinogenic effect of 1,4-dioxane on skin was found [6–9]. Hence, the allowable concentrations for these impurities have been set at very low levels (5 $\mu g\ g^{-1}$ for 1,4-dioxane and 10 $\mu g\ g^{-1}$ for ethylene oxide, respectively) [10,11].

The papers published earlier provide few methods for the determination of ethylene oxide and 1,4-dioxane in ethoxylated surface active agents.

Stafford and coworkers [12] have developed a method for the determination of 1,4-dioxane in ethoxylated surfactants using two chromatographic columns of different polarity. Black *et al.* [13] have extracted 1,4-dioxane from cosmetics followed by its determination by gas chromatography. Another paper [14] reports a method for the determination of 1,4-dioxane utilizing gas chromatography coupled with mass spectrometry (GC–MS) and special internal standards. 1,4-Dioxane in cosmetics can be determined by a rapid high-performance liquid chromatographic procedure [15]. Apart from extraction and adsorption based methods, a method applying gas chromatography headspace (HS–GC) analysis of ethylene oxide has been developed [16].

The HS–GC procedure comprises heating a sample to be analysed in a closed vial, at constant temperature and over a specified period of time. After reaching the equilibrium between the liquid and gaseous phases, some volume of the latter is collected and passed to the chromatographic column [17].

The aim of this work is to present a procedure which permits to determine contents of 1,4-dioxane and oxirane in ethoxylated alcohols and/or amines using the combination of the headspace technique and gas chromatography.

EXPERIMENTAL

Standard substances, materials, apparatus

Oxirane (Refinery in Płock, Poland), 1,4-dioxane and *N,N*-dimethylformamide (DMF) (POCh, Gliwice, Poland). The purity of the compounds was 99%.

Gas chromatograph (Perkin–Elmer), series 8700, with flame ionisation detector and capillary column (Permaphase PEG from Perkin–Elmer), 50 m, 0.32 mm, 0.4 μm.

Headspace unit (Perkin–Elmer), type HS-40, injection vials 22 ml capacity, seals/membranes PTFE, and aluminium caps.

Conditions for chromatographic determinations

Temperature of the column was programmed: within 55–110°C it was raised at the rate of 8°C min^{-1} with the initial isothermal conditions taking 3 min, while within 110–210°C it was raised at the rate of 30°C min^{-1}. Temperature of the injector was 230°C and temperature of the detector was 280°C. The carrier gas (hydrogen) stream was split at the ratio 1:30.

Conditions for the headspace unit

Time for thermostatic conditions for ethoxylated alcohols and amines: 30 min; temperature of the thermostat 80°C, temperature of the needle 110°C, temperature of the transfer capillary 120°C, injection time 0.1 min.

Preparation of standard solutions

1 g of 1,4-dioxane was placed in a 100 ml glass flask and diluted with DMF to the volumetric mark. This solution was used to prepare solutions containing from 20 to 5000 μg of 1,4-dioxane in 1 ml.

In order to prepare oxirane standard solutions in DMF, 20 ml of DMF was placed in a 22 ml injection vial with a seal and cap. The vial was weighed. Then 1 ml of EO was added, the vial was quickly closed with the seal and cap, and it was weighed again. This basic solution was diluted with DMF to those containing from 10 to 1400 μg of EO in 1 ml.

Samples were weighed with the accuracy of 0.00002. The volumes were measured with the accuracy of 0.2 μl.

Quantitative analysis of oxirane

The absolute calibration method was employed for quantitative determinations. Calibration curve was obtained for the contents of 1–140 μg g^{-1} oxirane for ethoxylated alcohols and ethoxylated amines. 1 g sample of ethoxylated alcohol or ethoxylated amine was placed in a test vial and 100 μl of DMF was added. The vial was closed tight and its content mixed thoroughly. Then it was placed in the thermostat of the headspace unit. The same material was sampled and analysed three times. Oxirane content was calculated on the basis of peak area obtained and the calibration curve developed earlier. Ethoxylates used to prepare standards contained below 1 μg g^{-1} of oxirane.

Quantitative analysis of 1,4-dioxane

1 g sample of ethoxylated alcohols C_{12-14} or ethoxylated amines C_{12-14} was placed in each of two injection vials. To one of them 100 μl of DMF was then added while other was supplemented with 100 μl of a suitable solution containing increased 1,4-dioxane concentration. The 1,4-dioxane content in the sample tested was calculated from the formula:

$$x_{1,4\text{-dioxane}} = mA/(B-A) \tag{1}$$

in which $x_{1,4\text{-dioxane}}$ denotes content of 1,4-dioxane in the sample (μg g^{-1}), m – weight of 1,4-dioxane added to the sample (μg g^{-1}), A – peak area for 1,4-dioxane (per 1 g of total sample) in the sample tested, B – peak area for 1,4-dioxane (per 1 g of total sample) in the sample with increased dioxane content.

Determination of 1,4-dioxane partition coefficient

1,4-Dioxane partition coefficients in ethoxylated alcohols and ethoxylated amines were determined at 40, 60, 80 and 100°C. For each temperature, 5 empty injection vials were prepared and 5 vials containing 1 ml of ethoxylated alcohol or ethoxylated amine each. To each series of vials, from 1 to 5 μl of

1,4-dioxane were added, the vials were closed tight and their contents analysed with the use of HS–GC. The value of partition coefficient, K, was calculated from the formula:

$$K = \frac{A_C V_V - A_S V_g}{A_S V_S} \tag{2}$$

where K denoted partition coefficient for 1,4-dioxane in ethoxylated alcohols or amines, V_v – volume of an injection vial (ml), V_g – volume of gas phase (ml), V_s – volume of liquid phase (ml), A_c – peak area for 1,4-dioxane in a vial without ethoxylate and A_s – peak area for 1,4-dioxane in a vial containing ethoxylated matter.

The mean value was calculated for the finding from each series of 5 tests.

RESULTS AND DISCUSSION

As a result of this examination, optimum conditions were found for analysis of trace amounts of oxirane and 1,4-dioxane in ethoxylated alcohols and amines by gas chromatography with sample injection by the headspace technique.

Chromatographic separation of impurities contained in the ethoxylates was achieved on a capillary column coated with Permaphase PEG (Fig. 1). The retention index found is 519 for oxirane and 1066 for 1,4-dioxane.

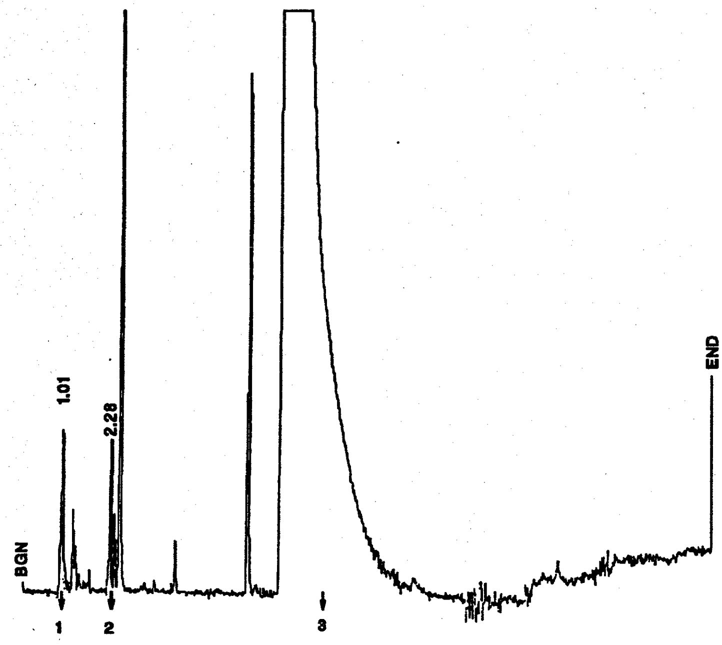


Figure 1. Chromatogram of the gas phase over the sample of C_{12-14} alcohol ethoxylate: 1 – oxirane 5.5 $\mu g\ g^{-1}$, 2 – 1,4-dioxane 8.4 $\mu g\ g^{-1}$, 3 – DMF

Partition coefficients for 1,4-dioxane were determined experimentaly in ethoxylates at different temperatures (Table 1). They decrease as the temperature rises. This means that the higher the temperature, the more 1,4-dioxane is passed into the gas phase. As a result, the elevation of the thermostating temperature of an ethoxylate sample is accompanied by and increase in the 1,4-dioxane peak area. However, partition coefficient does not depend upon the ethoxylate because similar values were obtained for ethoxylated alcohols and alkylamines. This effect can be explained by low volatility of ethoxylates which remain completely in the liquid phase and their similar polarities caused by the presence of similar polyoxyethylene chains. It suggests also that the interactions between nitrogen and oxygen atoms, respectively, of ethoxylated alkylamine and alcohol with 1,4-dioxane molecule are similar or relatively weak in comparison with the effects of the whole polyoxyethylene chains having free terminal hydroxyl groups. Thus, the effect of ethoxylates of low volatility on volatile 1,4-dioxane is negligible.

Table 1. Partition coefficient for 1,4-dioxane in ethoxylated alcohols and ethoxylated amines

Temperature, °C	Partition coefficient *K*
40	410
60	335
80	135
100	115

Figure 2 shows the dependence of 1,4-dioxane peak area on the thermostating time of the sample, using various thermostating temperatures. After 20–30 min the equilibrium is achieved between the gas and liquid phases of ethoxylated alcohols or amines.

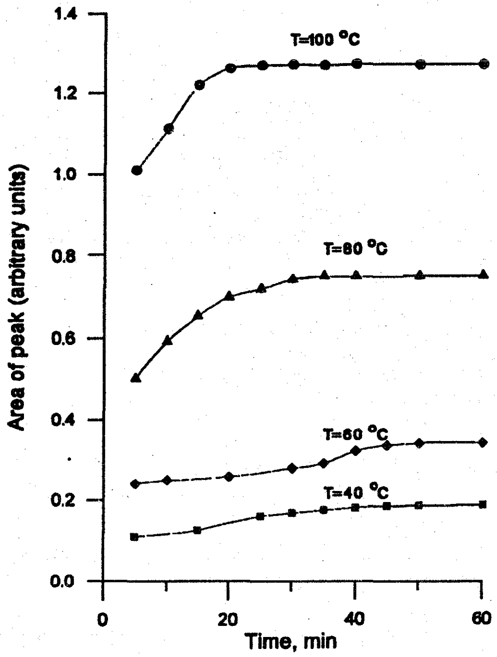


Figure 2. Effect of thermostating time on peak area of 1,4-dioxane; content of 1,4-dioxane in the sample – 94 μg g^{-1}

The effect of the sample volume on the oxirane content in the gas phase was studied. Simulation calculations were performed for two partition coefficient K values that were previously found from the following formula:

$$C_g = C_sV_s/[V_s(K-1) + V_{HS}] \qquad (3)$$

where C_g denotes 1,4-dioxane concentration in the gas phase (μg g^{-1}), C_s – 1,4-dioxane concentration in the liquid sample (μg g^{-1}), V_s – volume of the sample (ml) and V_{HS} – volume of the vial (ml).

The results of these calculations are the curves shown in Fig. 3; it is shown that, for $K = 410$, increasing the volume of the sample of ethoxylate under examination has no effect on 1,4-dioxane content in the sample gas phase. For $K = 130$ and effect of the sample volume is observed only for $V_s < 6$ ml.

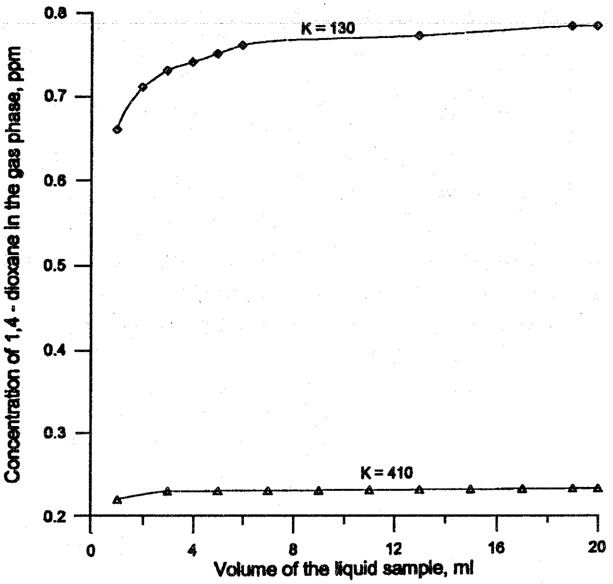


Figure 3. Effect of the ethoxylate sample volume on 1,4-dioxane content in the gas phase

Trace amounts of oxirane were found with the use of the calibration curve plotted for concentrations from 1 to 140 μg g^{-1} of oxirane in ethoxylated alcohols or ethoxylated amines (Fig. 4). Correlation coefficient, r, for the curve expressed by the equation: $y = 0.416x - 0.083$ is 0.998.

Statistical evaluation of the presented method was performed by calculating the confidence interval of an arithmetic mean on the basis of Student's test. The results obtained are shown in Tables 2–5.

For oxirane concentrations of about 1 μg g^{-1} in the sample, the value of relative standard deviation, S_r, is about 13%; for higher oxirane concentrations it is between 0.8% and 3%. It does not depend on the surfactant studied, *i.e.* ethoxylated alcohols or ethoxylated amines.

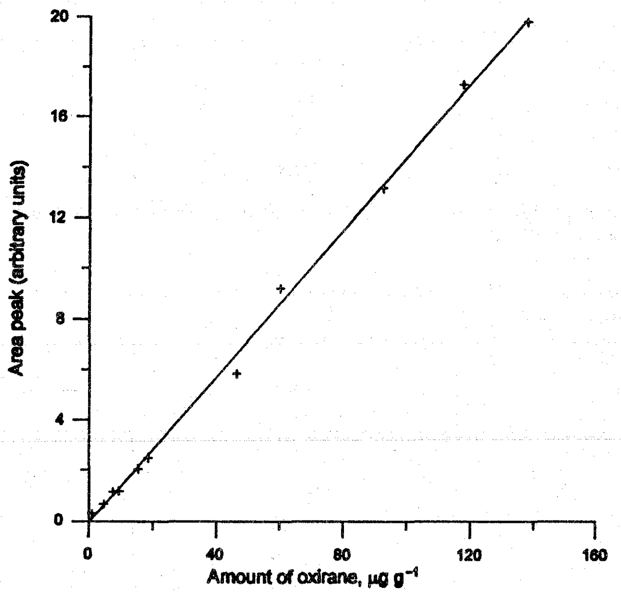


Figure 4. Calibration curve for 1–140 μg g^{-1} of oxirane concentrations in ethoxylated alcohols and amines (thermostating time 30 min, temperature 80°C, injection time 0.1 min)

Table 2. Statistical evaluation of oxirane determination in ethoxylated alcohols (calibration curve, number of analyzed samples $n = 4$)

Amount of oxirane μg g^{-1}	S_r	$S_0\, t/\sqrt{n}$ $P = 0.95, f = 3$
1.5	0.120	0.3
4.0	0.032	0.2
10.5	0.025	0.4
18.5	0.020	0.6
51.0	0.015	1.2
90.5	0.012	1.7
135.0	0.008	1.7

S_0 – standard deviation, $t(P,f)$ – Student's test, P – probability, f – number of degrees of freedom ($f = n - 1$), S_r – relative standard deviation.

Table 3. Statistical evalustion of 1,4-dioxane determination in ethoxylated alcohols (1,4-dioxane addition, number of analyzed samples $n = 4$)

Amount of 1,4-dioxane μg g^{-1}	S_r	$S_0\, t/\sqrt{n}$ $P = 0.95, f = 3$
1.8	0.110	0.3
6.5	0.022	0.2
9.5	0.020	0.3

Table 3. (continuation)

18.5	0.014	0.4
36.0	0.012	0.7
60.5	0.010	1.0
94.0	0.008	1.2

S_0 – standard deviation, $t(P,f)$ – Student's test, P – probability, f – number of degrees of freedom ($f = n - 1$), S_r – relative standard deviation.

Table 4. Statistical evaluation of oxirane content in ethoxylated amines (calibration curve, number of analyzed samples $n = 4$)

Amount of oxirane µg g^{-1}	S_r	$S_0\, t/\sqrt{n}$ $P = 0.95, f = 3$
1.5	0.131	0.4
3.5	0.039	0.4
9.2	0.027	0.5
17.9	0.023	1.1
49.3	0.017	1.7
95.1	0.017	2.6
138.0	0.009	4.5

S_0 – standard deviation, $t(P,f)$ – Student's test, P – probability, f – number of degrees of freedom ($f = n - 1$), S_r – relative standard deviation.

Table 5. Statistical evaluation of 1,4-dioxane content in ethoxylated amines (1,4-dioxane addition, number of analyzed samples $n = 4$)

Amount of oxirane µg g^{-1}	S_r	$S_0\, t/\sqrt{n}$ $P = 0.95, f = 3$
6.3	0.026	0.3
10.5	0.025	0.4
22.5	0.015	0.5
41.3	0.014	0.9
60.5	0.011	1.0
96.5	0.010	1.5

S_0 – standard deviation, $t(P,f)$ – Student's test, P – probability, f – number of degrees of freedom ($f = n - 1$), S_r – relative standard deviation.

A quantitative analysis of 1,4-dioxane in ethoxylated alcohols and amines was carried out by addition of the component to be determined. For 1,4-dioxane concentrations of about 2 µg g^{-1} relative standard deviation is approximately 11%, for higher concentrations of 1,4-dioxane it is between 0.8% and 2.6%. The lower limit of detection experimentally found was 1 µg g^{-1} for oxirane and 2 µg g^{-1} for 1,4-dioxane. Based on the results, optimum conditions were specified for quantitative analysis of oxirane and 1,4-dioxane in ethoxylated samples of alcohols or amines. Owing to the headspace sample injection technique employed, it was possible to determine the volatile impurities in high-boiling ethoxylates fast and with good accuracy, and without preliminary separation of the sample into individual fractions. This study demonstrates that the procedure described can be successfully used for the determination of residual oxirane and 1,4-dioxane in ethoxylated alcohols and amines.

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