Chem. Anal. (Warsaw), **41**, 959 (1996)

Analysis of Ethylene Glycol Traces in Ethoxylated Alcohols by Means of Gas Chromatography with Headspace Sample Injection

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Key words: ethylene glycol, ethoxylated alcohols, gas chromatography, headspace sample injection

A metod was developed for the analysis of trace amounts of toxic ethylene glycol in ethoxylated alcohols which employed capillary gas chromatography with headspace sample injection. A sample was held at the constant temperature of 130°C over 60 minutes and the gas phase was subjected to analysis in the DB-17 capillary column. The relative standard deviation for P = 95% was 18% for ethylene glycol concentration of about 10 μg g^{-1}, and fell to 0.9% when the concentration rised. The limit of detection was 10 μg g^{-1}.

Opracowano metodę oznaczania śladowych ilości glikolu etylenowego w oksyetylenowanych alkoholach wykorzystując kapilarną chromatografię gazową w połączeniu z techniką dozowania headspace. Próbki są termostatowane w temperaturze 130°C przez 60 min, następnie faza gazowa znad roztworu próbki analizowana jest na kolumnie kapilarnej DB-17. Względne odchylenie standardowe dla P = 95% wynosi 18% dla stężenia glikolu etylenowego około 10 μg g^{-1} i maleje do 0.9%, gdy stężenie rośnie. Granica wykrywalności wynosi 10 μg g^{-1}.

Ethoxylated alcohols find numerous applications in washing and cleaning agents as well as in cosmetics [1,2]. It is important that these products should not contain any toxic substances. Not only oxirane and 1,4-dioxane but also monoethylene glycol (EG-1) is found as a toxic impurity in ethoxylated surface-active compounds [3–6].

Polyethylene glycols, including GE-1, are formed in the addition reaction of oxirane and water:

$$H_2O + n\underset{\diagdown O \diagup}{CH_2—CH_2} \rightarrow HO(CH_2—CH_2O)_nH$$

Water molecules responsible for the reaction initiation are usually introduced in trace amounts together with the ethoxylated raw material or they can result from dehydration [7,8].

Since monoethylene glycol is regarded toxic to blood vessels and protoplasm and it exerts narcotic action on human organism, its content in the ethoxylation products should be kept as low as possible [9–11]. From available literature data, its maximum allowable concentration should not exceed 50 ppm [12]. Hence, there is a need to develop a method for the analysis of its trace amounts in ethoxylated surfactants.

No references were found in literature for the analytical method of determining trace amounts of monoethylene glycol in ethoxylated alcohols. The methods employed so far could determine quantitatively total polyethylene glycols in ethoxylated surface active products.

In this paper a method was developed for the analysis of traces of monoethylene glycol, which employs a combination of gas chromatography with the headspace sample injection technique (HS-GC). The method is based on heating up a sample and holding it at constant temperature over some specific time in a closed vial. After achieving thermodynamic equilibrium between gas and liquid phase, some volume of gas phase undergoes GC analysis [13]. Thus, the work follows our previous paper in which the analysis of trace amounts of oxirane and 1,4-dioxane was presented [14].

EXPERIMENTAL

Standard substances, materials, apparatus

Ethylene glycol (Merc), undecanol (Aldrich) and ethoxylated alcohols C_{12-14} (ICSO, Kędzierzyn-Kole, Poland).

Gas chromatograph (Perkin–Elmer), series 8700, with flame ionisation detector and headspace units (Perkin–Elmer), type HS-40, capilary column DB-17 (J & W Scientific) 30 m, 0.32 mm, 0.5 μm, max. operating temperature 300°C, injection vials 22 ml capacity, Al/Silicone seal membranes, aluminium caps, 100 and 1000 μl micro pipettes and measuring flask.

Conditions for chromatographic determinations

Temperature of the DB-17 column was programmed within 50–100°C with the rate of 8°C min^{-1} with the initial isothermal conditions taking 3 min, while within 100–250°C it was raised at the rate of 30°C min^{-1}. Temperature of the injector was 190°C and temperature of the detector was 350°C. The carrier gas (hydrogen) stream was split at the ratio of 1:30. The carrier gas pressure was 56 kPa.

Conditions for the headspace units

Time for thermostatic conditions: 60 min in case of ethoxylated alcohols; temperature of the thermostat 130°C, temperature of the needle 150°C, temperature of the transfer capillary 160°C, injection time 0.08 min.

Preparation of standard solutions

1 g of ethylene glycol was placed in a 100 ml glass flask and diluted with undecanol to the volumetric mark. This stock solution was then used to prepare solutions containing from 100 to 5000 μl of ethylene glycol in 1 ml standard solution.

Quantitative analysis

A 1 g sample of ethoxylated alcohol was placed in each of two injection vials. To one of them 100 μl 1-undecanol was added while the other was supplemented with 100 μl of a suitable solution containing increased ethylene glycol concentration. The ethylene glycol content in the sample tested was calculated from the formula:

$$X_{(EG-1)} = m \times A/(B - A)$$

in which $X_{(EG-1)}$ denotes concentration of ethylene glycol in the sample (μg g^{-1}), m – mass of ethylene glycol added to the sample (μg g^{-1}), A – peak area for ethylene glycol (per 1 g of total sample) in the sample tested and B – peak area for ethylene glycol (per 1 g of total sample) in the sample with increased ethylene glycol content.

Determination of ethylene glycol partition coefficient

Ethylene glycol partition coefficient in ethoxylated alcohols were determined at 100, 110, 120, 130 and 140°C. For each temperature, 5 empty injection vials were prepared and 5 bottles/vials containing 1 ml of ethoxylated alcohol each. To each series of vials, from 1 to 5 μl of ethylene glycol was added, the vials were closed tightly and their contents analyzed with the use of HS-GC. The value of partition coefficient, K, was calculated from the formula [15]:

$$K = (A_C V_V - A_S V_g)/(A_S V_S)$$

in which K denotes partition coefficient for ethylene glycol in ethoxylated alcohols, 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 ethylene glycol in a vial with no ethoxylate and A_S - peak area for ethylene glycol in a vial containing ethoxylated matter.

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

RESULTS AND DISCUSSION

The determining of trace amounts of ethylene glycol in alcohols ethoxylates needs its separation from ethoxylate homologues, other by-products including 1,4-dioxane, unreacted oxirane and polyoxyethylene glycols, and from a selected component used as a diluent. Initial trials permitted to select undecanol as the diluent and appriopriate chromatographic parameters for ethylene glycol separation (Fig. 1).

Partition coefficient, K, for ethylene glycol was determinated experimentally in ethoxylated alcohols at different temperatures of sample thermostat-heating (Table 1). It decreases as the temperature rises. This means that the higher the temperature of thermostat heating, the more ethylene glycol is in the gas phase. However, the effect significantly weakens above 130°C. Hence, the temperature 130°C was selected to thermostate the samples. Elevation of the thermostating temperature of an ethoxylate

sample is accompanied by an increase in the ethylene glycol peak area (Table 1). For ethylene glycol to attain a thermodynamic equilibrium between the gas and liquid phases of ethoxylated alcohols, it is neccessary to find an appriopriate time of thermostating. Fig. 2 shows the dependence of monoethylene glycol peak area on the thermostating time at various temperatures. After 60 min the equilibrium is achieved between gas and liquid phases.

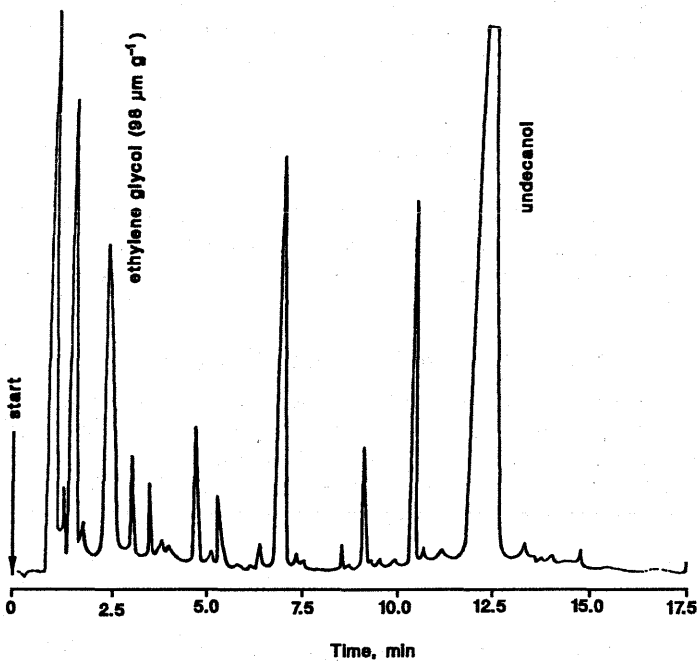

Figure 1. Chromatogram of the gas phase over the sample of C_{12-14} alcohol ethoxylate: 1 – ethylene glycol, 98 μg g^{-1}, 2 – undecanol

Table 1. Partition coefficient for ethylene glycol in ethoxylated alcohols

Temperature, °C	Relative peak area	Partition coefficient *K*
100	0.45	1800
110	0.96	1300
120	1.57	850
130	2.17	600
140	2.36	510

Statistical evaluation of the method above was performed by calculating the confidence level of an arithmetic mean on the basis of *t*-Student distribution. The results obtained are shown in Table 2. A quantitative analysis of ethylene glycol was carried out by addition of the component to be determined. For ethylene glycol concentration of about 10 μg g^{-1} relative standard deviation is approximately 18%;

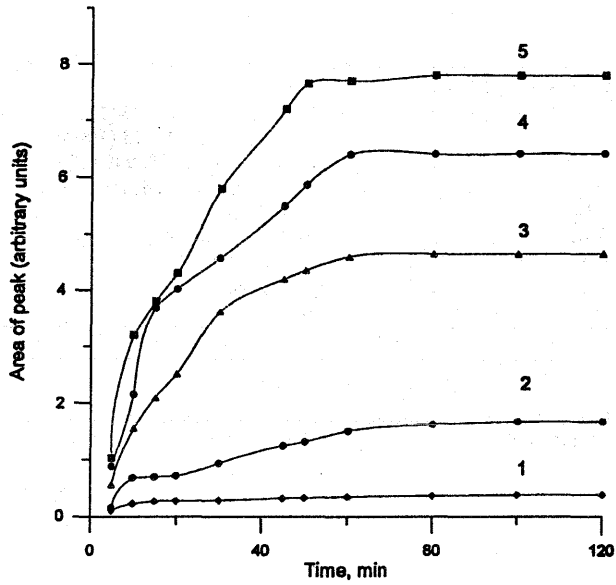

Figure 2. Effect of thermostating time on peak area of ethylene glycol; content of ethylene glycol in the sample – 98 μg g^{-1}

for higher concentrations it is between 0.9 and 11%. The limit of detection was experimentally found to be 10 μg g^{-1}.

This study demonstrates that the procedure described can be successfully used for the determination of ethylene glycol in ethoxylated alcohols.

Table 2. Statistical evaluation of ethylene glycol in ethoxylated alcohols ($n = 4$)

Amount of ethylene glycol, μg g^{-1}	S_r	$S_0 \times t/\sqrt{n}$ $P = 0.95$ $f = 3$
10	0.180	1.1
25	0.110	1.2
44.5	0.090	1.5
64.5	0.050	2.2
98.0	0.030	3.1
180.5	0.011	5.6
256.5	0.009	8.2

S_0 – standard deviation, $t(P,f)$ – test t-Student, P – probability, f – number of degrees of freedom ($f = n - 1$), S_r – relative standard deviation.

Acknowledgment

The work was supported by Polish Scientific Research Committe (KBN) grant No 7 S2 03007.

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Received February 1996
Accepted July 1996