

## DETERMINATION OF DIETHYLENE GLYCOL IN OLIGOMERIC ETHYLENE GLYCOL ESTERS OF SOME AROMATIC DICARBOXYLIC ACIDS

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The new method of determining diethylene glycol is described based on the solvolysis of ester by lithium hydroxide in the ethanolic solution and on the gas chromatography of the resulting reaction mixture. 2% of Versamide 900 on Chromosorb G-AW, DMCS served as the packing of the column and the programmed temperature was used. The standard deviation of the method  $s_{y,x} = 0.56\%$  rel.

In the polyester fibre process based on the ethylene glycol and the terephthalic acid also diethylene glycol (DEG) is formed as a by-product. It originates in both the main stages of the polyester process, *i.e.* in the *trans*-esterification reaction of the dimethyl ester of the terephthalic acid and also other carboxylic acids which are used as the modification agents, and in the successive polycondensation of the mixture of the low-molecular oligomers. The originating diethylene glycol becomes a link of the macromolecular chain and it can never be eliminated from the reaction mixture again. Its presence in the fibre deteriorates both the physical and chemical properties of the product. Therefore, the analytical check of the diethylene glycol content is needed in the run of the whole process. The materials being analysed are not only the monomeric esters dissolved or suspended in the ethylene glycol excess but also the low- and high-molecular oligomers, solid at room temperature.

The generally usable analytical procedure has to make possible a reliable decomposition of the sample at which all the amount of the diethylene glycol present at any form is converted into the solution in some convenient solvent. Further, it has to involve a simple and reliable determination of the released diethylene glycol in the reaction mixture. The survey of the majority of the methods proposed is given in the papers<sup>1,2</sup>. The following reactions are used for the decomposition of the sample: the solvolysis by water<sup>2,3</sup> or by solutions of the strong bases<sup>1,4-7</sup> in convenient solvents, or the *trans*-esterification<sup>8</sup> by methanol or ethanol at temperatures of the boiling point of the mixture under the normal or higher pressure. The amount of diethylene glycol in the reaction mixture prepared is in most cases determined by gas chromatography. The conditions for the gas chromatographic determination of diethylene glycol are to a certain degree affected by the composition of the reaction mixture after the decay of the sample. Therefore, it is impossible to combine any method of the decompositions with any conditions of the gas chromatographic analysis. The polar stationary phases are mostly used, *e.g.*, Carbowax 100000 to 1000000 on Chromosorb<sup>8</sup>, Carbowax 20 M on Chromosorb W-HMDS or Gas-Chrom Z or Aeropak No 30 (*see*<sup>2</sup>), polyethylene glycol 600-2000 on Spherochrom - 1 or Sterchamol<sup>9</sup>, polyethylene glycol adipate on Celit 545 (*see*<sup>10</sup>). The non-polar stationary phases were also

proposed, e.g., polyethylene 6000 on Firebrick<sup>11</sup> or Porapak S<sup>12</sup>. The method of the internal standardization was mostly chosen for the quantitative determination using benzyl alcohol<sup>2</sup>, dimethylether of tetraethylene glycol<sup>7</sup>, 1,4-butane diol<sup>8</sup> or tributyl phosphate<sup>10,11</sup> as the internal standards. According to the principle used, the paper<sup>13</sup> is beyond the set of the described methods. It recommends to dissolve the mixture of the low-molecular oligomers of ethylene glycol terephthalate in pyridine and to convert them by bis(trimethylsilyl) trifluoroacetamide to silyl ethers which are determined by gas chromatography using Silicon OV-101/Chromosob W as a column packing. Because of the operating difficulties and time consuming work the chemical methods<sup>1,3</sup> based on the multistage separation of diethylene glycol released are of limited significance for determining the diethylene glycol content in the reaction mixture after the decomposition.

In the present work the method for the determination of diethylene glycol in the products and intermediates from the polyester fibre process was worked out. It utilizes the solvolysis of the sample by the lithium hydroxide in the ethanol solution at the boiling point of the reaction mixture and at normal pressure, followed by the gas chromatographic determination of diethylene glycol in the liquid reaction mixture.

## EXPERIMENTAL

**Materials.** Ethylene glycol (reagent grade), diethylene glycol (pure), triethylene glycol (pure), 1,5-pentane diol (pure) and lithium hydroxide (reagent grade) were supplied by Lachema, Brno. The purity of glycols was checked by gas chromatography. The 0.3% of diethylene glycol were found in ethylene glycol, triethylene glycol contained traces of ethylene glycol and diethylene glycol and some additional non-identified compounds. The other glycols were found chromatographically pure. An 80% water solution of hydrazine hydrate (pure) was supplied by Xenon, Lodz, Poland. In addition to water it contained two non-identified compounds by gas chromatographic check. The samples of the polyester fibres and polycondensate granules were kindly furnished by Silon Works, the solutions of glycol isophthalate and sodium salt of 5-sulphoisophthalic acid in ethylene glycol solution were prepared in this Institute.

**Calibration solutions I, II and III** were prepared by precise weighing of about 2.8 g of 1,5-pentane diol (PED), 2.5 g of diethylene glycol (DEG) and 21 g of ethylene glycol (EG) respectively always into the 100 ml volumetric flask and making up to the mark by butanol. In order to prepare the calibration standards the solutions *I* and *II* were mixed in such a way that the ratio of the mass concentrations of DEG/PED was approximately 3 : 2.6; 1.5 : 1; 1 : 1; 1 : 2. About 5 g of the solution *III* were always added to obtain the resulting ratio of EG/DEG similar to that found in the reaction mixtures after the decomposition of the polyester samples. The weighed amount of 1,5-pentane diol for the internal standard was chosen to create approximately a comparable concentration as that of diethylene glycol in the analysed solution.

**Apparatus.** The apparatus used for the present study was PYE Heated Dual Flame Ionisation Detector Programmed Chromatograph, Model 64 (Series 104, Cambridge, Great Britain). It was equipped with a recorder 0—1 mV (Honeywell, model Elektronik 194). The column employed was a 170 × 0.4 cm I.D. glass U-tube. Nitrogen was used as the carrier gas at the flow rate approximately of 30 ml/min. The samples were introduced with 10 µl Hamilton microsyringe. The injection port and the detectors were maintained at 170°C and 180°C respectively. The following temperature programme was used: isothermal heating at 50°C for 5 min, linear increase from 50 to 140°C at 1°C/min.

*Column packing.* Versamid 900 (Hewlett-Packard) served as the stationary phase on Chromosorb G-AW, DMCS, of the particle size 80/100 mesh (Johns-Manville). The packing was prepared in the usual manner by dissolving the stationary phase in the mixture of butanol and chloroform 1 : 1 and slurring with the support. It contained 2% of the liquid phase. The packed columns were conditioned for 12 hours at 250°C with the carrier gas flow. The method of the internal standardization was employed for the quantitative determining the diethylene glycol, 1,5-butane diol was found to be the most convenient internal standard.

*Procedure.* Approximately 2 g of the samples of the polycondensate granules, polyester fibres or products of the direct esterification of the sodium salt of 5-sulphophthalic or isophthalic acid with glycol were weighed and transferred into the weighed 50 ml flask. About 5 g of lithium hydroxide and 11 ml of ethanol were added. The mixture was hydrolyzed under reflux for 2 hours. Then the flask containing the mixture was weighed again. The solid part was left to settle down, approximately 2 g were weighed from the liquid part and the known amount of 1,5-butane diol was added. The 10  $\mu$ l sample of this mixture was used for the gas chromatographic analysis.

*Calculations.* The calibration graph was obtained by plotting the ratios of the retentions curves areas of DEG/PED versus the ratios of their weighed amount. The best straight line was calculated by the least square method and the standard deviation  $s_{y,x} = 0.56$ . The weight percentage of diethylene glycol was calculated from the original weight of the sample, from the amount of the internal standard added and from the areas corresponding to diethylene glycol and the internal standard.

## RESULTS AND DISCUSSION

If the whole analytical procedure is to be accomplished by the gas chromatographic determination it is important to avoid liquids containing a larger amount of non-volatile and nonevaporable compounds. This material is deposited not only in the injection port but also in the column inlet and can deteriorate its separation efficiency after a greater number of analyses is carried out. This condition is fulfilled by hydrolyses or *trans*-esterification with ethanol both under a higher pressure and by solvolysis with hydrazine hydrate solution. After such a decomposition the liquid phase of the reaction mixture can contain water, ethanol, ethylene glycol, diethylene glycol, hydrazine and diethyl terephthalate respectively and can easily be separated mechanically from the sediment of the terephthalic acid or hydrazinium terephthalate. By using a solution of sodium methoxide or an alcoholic solution of potassium hydroxide for the solvolysis the elimination of the soluble salts of terephthalic acid is necessary. However, for the total solvolysis of a macromolecular sample by water or ethanol under a higher pressure the period of several hours or several tens of hours is needed.

The solvolysis by the hydrazine hydrate solution is the most rapid procedure. Unfortunately, the reagent in question is difficult to get in the sufficient purity and moreover, is subject to a decomposition reaction. Carrying out the decomposition by the latter method followed by gas-chromatographic determination of diethylene glycol in the reaction mixture according to the paper<sup>5</sup> we received

satisfactory results with one sample of hydrazine hydrate only. The other samples were also suitable for the decomposition but a various amount of nonidentified impurities affected the results of diethylene glycol determination. Making attempts at finding other solvolytic reagents we found that morpholine or its solution in ethanol proved also suitable. Morpholinide of the terephthalic acid or morpholinium terephthalate was soluble in the same limited amount as similar hydrazine compounds. However, little reproducibility of the chromatograms of these reagents and their reaction mixtures was found.

Also the experiments with individual ethanol amines or their mixtures were unsuccessful. A relatively high solubility of their salts with the terephthalic acid and the low volatility of excessive amines disturb the gas chromatographic analysis. The experiments showed good reproducibility for determining the total amount of diethylene glycol in the fine crushed samples of the polyester granules and also in the product (liquids and suspensions) of the esterification of the sodium salts of the 5-sulphoisophthalic and the isophthalic acids with ethylene glycol. The solution of lithium hydroxide in ethanol was found to be a suitable reagent for the solvolysis of all the sample types of various intermediates and products from the polyester fibre production when diethylene glycol is to be determined. As it is evident from the

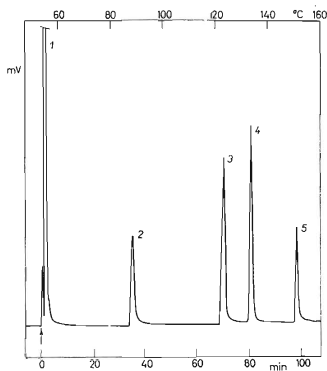


FIG. 1

Separation of the Synthetic Mixture of Glycols Column

170 × 0.4 cm I. D., 2% of Versamide 900 on Chromosorb G-AW, DMCS, 80–100 mesh, N<sub>2</sub> 30 ml/min; the temperature programming is described in the experimental part. 1 Ethanol, 2 ethylene glycol, 3 diethylene glycol, 4 1,5-pentane diol, 5 triethylene glycol.

Table I the saponification of low and also high molecular oligomeric glycol esters of all the aromatic acids investigated proceeds quantitatively at the boiling of the reaction mixture within a short period of time with a minimal excess of a free base. In agreement with the literature the solubility of lithium terephthalate was found to be sufficiently low to eliminate the danger of contamination of the chromatographic column inlet with the solid evaporation residue from the liquid phase as far as the samples of glycol esters of the terephthalic acid are concerned. If glycol esters of the isophthalic or 5-sulphoisophthalic acids are contained in the sample the lithium salts of the released acids are to a limited degree soluble. Also the use of hydrazine hydrate or alcoholic solutions of other alkali hydroxides suffers from similar difficulties.

The column packings recommended for the chromatographic separation of oligomeric ethylene glycols which we tested possessed in most cases a common disadvantageous property. They showed a tailing of the chromatographic fractions which considerably depreciate the chromatographic analysis and it sometimes made the

TABLE I

The Results of the Determination of Diethylene Glycol in Polyethylene Glycol Terephthalate and in the Products of the Esterification of the Isophthalic Acid and the Sodium Salt of the 5-Sulphoisophthalic Acid

*n* Number of measurements,  $\bar{x}$  mean value of six measurements, %, *s* standard deviation, % abs.

Sample	<i>n</i>	$\bar{x}$	<i>s</i>
Tesil 12	6	0.95	0.043
PET Silon 208	6	1.98	0.065
PET Silon 29	5	1.50	0.088
PET Silon 31	2	2.18; 2.12	—
PET Silon 35 <sup>a</sup>	9	1.15	0.03
PET Silon 37	5	1.25	0.064
PET Dynamit Nobel	5	1.63	0.055
A <sup>b</sup>	2	0.95; 1.00	—
B <sup>b</sup>	2	0.44; 0.47	—
C <sup>c</sup>	5	2.80	0.07
D <sup>c</sup>	2	3.15; 3.22	—
E <sup>d</sup>	5	3.37	0.077

<sup>a</sup> After the pressure hydrolysis<sup>3</sup> it was found:  $\bar{x} = 1.31\%$ ,  $s = 0.132$  ( $n = 5$ ), after the solvolysis with hydrazine hydrate<sup>5</sup> it was found:  $\bar{x} = 1.29\%$ ,  $s = 0.28$  ( $n = 5$ ). <sup>b</sup> The reaction mixture after the esterification of the isophthalic acid with glycol. <sup>c</sup> The reaction mixture after the esterification of the sodium salt of the 5-sulphoisophthalic acid with glycol. <sup>d</sup> The reaction mixture after the esterification of the potassium salt of the sulphoterephthalic acid with glycol.

quantitative determination entirely unfeasible. In order to complete the analysis within a reasonable period of time on Porapak S alone or coated with 2% of Tween 80 higher temperatures were necessary than those recommended by the producer. Consequently, as a result there appeared fast degradation of the column packing accompanied with the deterioration of the separation efficiency and cutting its life short. Out of all stationary phases tested, Versamid 900 on Chromosorb G-AW, DMCS was found to be the best. This packing made it possible to operate the column at relatively low temperatures (50–140°C), the retention peaks of all the components remaining sharp and symmetrical. The mild conditions in question protected the stationary phase from a thermal degradation and considerably extended its useful life. Therefore, more than one hundred analyses could be carried out on the same column packing and no change of the separation efficiency was observed. Temperature programming allowed the separation to be completed within a reasonable period of time. As the most convenient internal standard 1,5-pentane diol was found. Fig. 1 shows the separation of the synthetic mixture containing ethylene glycol, diethylene glycol, 1,5-pentane diol and triethylene glycol in the ethanolic solution. The results of the separation of DEG in the products of the esterification of various dicarboxylic acids by glycol are summarized in Table I.

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