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## GAS CHROMATOGRAPHIC ANALYSIS OF ADIPIC ACID-, DIOL- AND TRIOL-BASED POLYESTERS

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### SUMMARY

A gas chromatographic (GC) method is proposed for the quantitative evaluation of polycondensation products of adipic acid, diols (mono-, di-ethylene glycol, 1,4-butanediol) and triols (glycerol, 1,1,1-trimethylolpropane). It comprises alkaline saponification of polyesters followed by acidification or neutralization and GC analysis with flame ionization detection. By means of a single stationary phase, either diols or adipic acid are eluted avoiding, for the acid, the usual and often critical methyl ester derivatization; a second stationary phase is used for triols, if they are present. The whole procedure, including saponification and GC analysis, is very fast, the retention times of the components being in the range 5-10 min. The accuracy of the method, as evaluated by NMR spectroscopy, and its precision are satisfactory.

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### INTRODUCTION

Aliphatic, saturated, relatively low-molecular-weight polyesters, obtained by polycondensation of dicarboxylic acids and diols (in some instances with small percentages of triols), are important in the polymer industry, owing to their extensive use as plasticizers and polyurethane intermediates. The chemical nature of the reactants employed and their molar ratio determine, to a large extent, the chemical and physical properties of the plasticizers or intermediates and, therefore, of the final polyurethane. Thus, the development of fast and simple analytical procedures for the identification and quantitative evaluation of polycondensed reactants is desirable. As for other polyesters, the aim is achieved by complete hydrolytic decomposition of the polymer, followed by the analysis of the resulting reactants.

Gas chromatography (GC) is the most frequently used analytical technique for the alcoholic fraction, the procedures used being those, for instance, reported in refs. 1 and 2, and also for the acidic fraction, by means of a previous carboxylic acid derivatization to more volatile compounds (generally methyl esters). A very large bibliography and exhaustive general reviews are available on this topic<sup>3</sup>. In the derivatization step the methods involved are, for instance, transesterification with methanolic lithium methoxide or sodium methoxide, esterification of liberated acids with diazomethane, methanol-boron trifluoride or *n*-propanol-boron trifluoride re-

agents<sup>4,5</sup>. Trimethylsilyl derivatives for polyols and for mono- and dibasic acids have also been reported<sup>5</sup>.

More recently, the problem has been examined using <sup>13</sup>C NMR spectroscopy which allows homopolyester mixtures to be distinguished from copolyesters, and hence the evaluation of the composition and microstructure as well as the length of the homogeneous block sequences<sup>6</sup>.

Our work is devoted to some types of commercial polyesters resulting from the polycondensation of adipic acid (AA) and one or more of the diols monoethylene glycol (MEG), diethylene glycol (DEG), 1,4-butanediol (BD) and, in some instances, containing low amounts of triols such as glycerol (GLY) and 1,1,1-trimethylolpropane (TMP). The method developed consists of alkaline saponification of the sample followed by acidification or neutralization, and GC analysis using flame ionization detection. The derivatization steps are eliminated in this procedure by the use of a porous polymer stationary phase which elutes and resolves the liberated reactants, either diols or adipic acid. Moreover, by analyzing the original unsaponified sample with the same GC method, the free diol concentration can be determined and hence the correct ponderal ratio between the bound diols in the polyesters.

## EXPERIMENTAL

### *Apparatus*

A Carlo Erba Model 2350 gas chromatograph with flame ionization detector was employed. It was equipped with a device for direct sample injection and with a Speedomax (Leeds and Northrup) potentiometric recorder (1–2.5 mV full scale). Two columns were used: A, for the diols listed and adipic acid, glass column, 70 × 0.4 cm I.D., packed with Chromosorb 101 (60–80 mesh) (Johns-Manville); B, for triols only, glass column 100 × 0.4 cm I.D., packed with 5% Carbowax 20M liquid phase (Union Carbide) on Diatoport S (80–100 mesh) (F & M Scientific).

### *Chemicals*

Adipic acid, monoethylene glycol, diethylene glycol, glycerol, acetone, methylene chloride, sodium or potassium hydroxide were analytical grade reagents from Carlo Erba (Milan, Italy), 1,4-butanediol, analytical grade, from Fluka (Buchs, Switzerland) and 1,1,1-trimethylolpropane, analytical grade, from EGA Chemie (Steinheim, F.R.G.).

### *Sample and standard preparation*

*AA-, MEG- and/or DEG-based samples.* About 1 g of the polyester sample was accurately weighed into a flask and 20 ml of a 1 M aqueous solution of NaOH or KOH were added. The mixture was heated under reflux with vigorous stirring until completion of polyester saponification as indicated by the formation of a clear solution. The latter was acidified with concentrated hydrochloric acid to pH 1, then quantitatively transferred to a calibrated flask (100 ml) and solubilized and brought to volume with acetone. If low amounts of GLY or TMP are bound to the polyester chains, no change in saponification procedure is needed, but it might be necessary to increase the amount of the sample in order to obtain the desired sensitivity.

*AA-, BD-, MEG- and/or DEG-based samples.* Since BD undergoes rapid con-

version into tetrahydrofuran in an acidic medium<sup>7</sup> (but is stable in neutral media), two distinct saponification procedures are needed for this type of polyester. The first procedure, for AA determination, is identical to that previously described; the second one, for all kinds of diols (including BD), differs only in the final stage, which is neutralization to pH 7 instead of acidification to pH 1.

*Samples for free diols determination.* About 5 g of sample were accurately weighed into a calibrated flask (100 ml) and 70 ml of methylene chloride were added. The mixture was stirred until completely solubilized and then brought to volume with the same solvent.

*Standard solutions.* Calibrated standard solutions of each reactant (or of a mixture of several reactants) were prepared in acetone or methylene chloride, at concentrations depending on the specific analytical requirements.

### GC analysis

*AA determination.* Column A was thermostatted at 250°C and the injection block at 300°C. The helium carrier gas flow-rate was adjusted to about 50 ml/min, the detector optimized and 2  $\mu$ l of the sample and 2  $\mu$ l of the standard solution were injected, three times consecutively. A typical chromatogram is shown in Fig. 1.

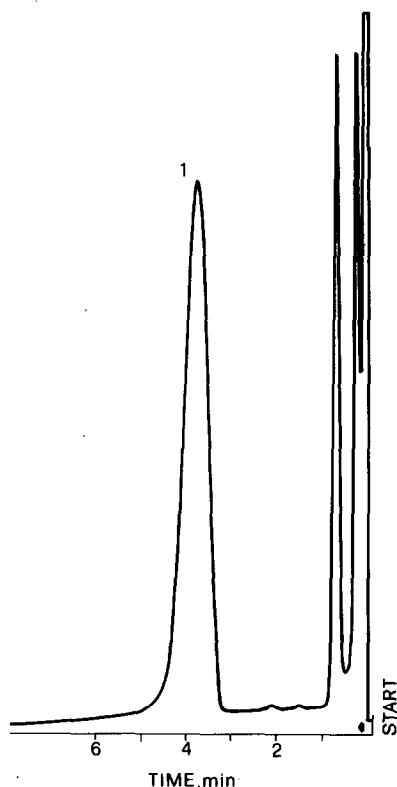


Fig. 1. Chromatogram of underivatized adipic acid (1) from a saponified polyester sample. For conditions see text.

The reactant concentrations were evaluated by the external standard method.

*Diols determination.* Column A was thermostatted at 200°C, and the injection block at 250°C. The analysis was then performed as above (Fig. 2).

*Triols determination.* Column B was thermostatted at 200°C and the injection block at 250°C. The carrier gas flow-rate was adjusted to about 30 ml/min and then the above procedure was followed (Fig. 3).

## RESULTS AND DISCUSSION

As is shown by Figs. 1 (AA), 2 (diols) and 3 (triols), the peaks of the monomeric components are symmetrical, without any "tailing", are well resolved from each other and from the solvent and have reproducible retention times in the range 5–10 min. Therefore reliable qualitative and quantitative determinations can be performed in this way. Since the chromatographic elution times are very short and the sample saponification step generally requires only a few minutes, the total analysis time is reduced in comparison with traditional procedures. The proposed method is also suitable for rapid analytical control.

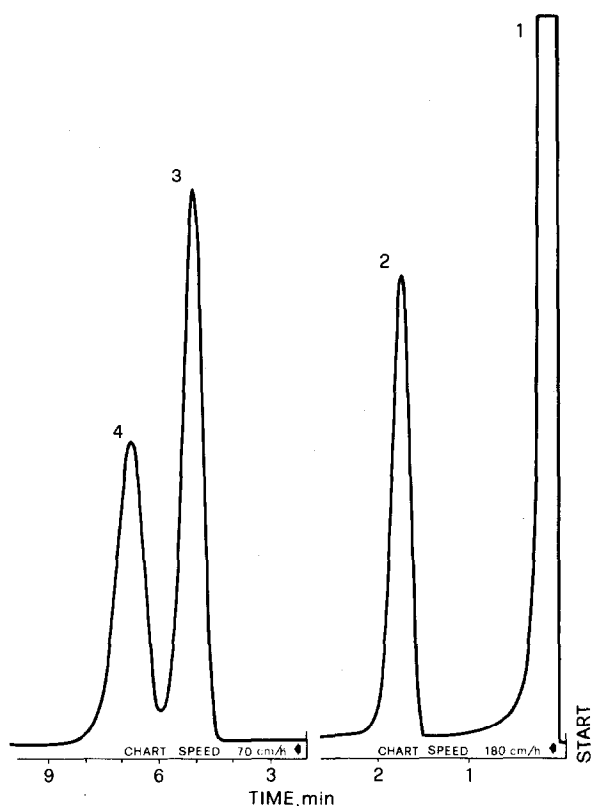


Fig. 2. Chromatogram of a mixture of diols. Peaks: 1 = solvent; 2 = monoethylene glycol; 3 = 1,4-butanediol; 4 = diethylene glycol. For conditions see text.

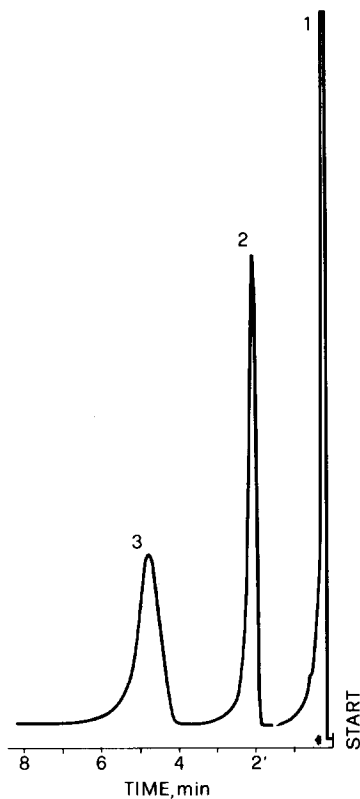


Fig. 3. Chromatogram of a mixture of triols. Peaks: 1 = solvent; 2 = glycerol; 3 = trimethylolpropane.

### Sensitivity

Under the standard conditions described, a sensitivity of 0.02% by weight (of the polyester sample) for triols (GLY and TMP) and 0.01% by weight for each of the free diols is attained. However, this can be improved by use of larger amounts of sample.

### Precision

The reproducibility of the method is satisfactory, estimated standard deviations,  $s$ , being 0.32 for AA at a concentration of 48% by weight and 0.21 for diols, *e.g.* BD, at 20% by weight.

### Accuracy

To evaluate the accuracy of the whole procedure, a set of polyester samples (some commercial products, others synthesized in the laboratory) were analyzed either by this procedure or by an NMR spectroscopic method which was directly applied to the unmodified polyesters, *i.e.*, without any saponification or hydrolysis<sup>8</sup>. The monomeric compositions obtained, shown in Table I, are in good agreement taking into account the different, wholly independent procedures and analytical techniques. Thus the reliability of the proposed method is confirmed.

TABLE I

QUANTITATIVE COMPOSITION (mol %) OF COMMERCIAL AND EXPERIMENTAL POLYESTER SAMPLES AS DETERMINED BY GC (THIS METHOD) AND  $^{13}\text{C}$  NMR SPECTROSCOPY

Sample	AA		MEG		DEG		BD	
	GC	NMR	GC	NMR	GC	NMR	GC	NMR
1	48.9	48.9	21.7	21.1	—	—	29.4	30.0
2	50.1	49.7	31.2	29.3	—	—	18.7	21.0
3	50.2	48.9	21.8	22.2	28.0	28.9	—	—
4	49.8	51.8	31.1	26.0	19.1	22.2	—	—
5	48.3	47.8	8.3	8.1	—	—	43.4	44.1
6	50.3	49.0	12.5	14.2	—	—	37.2	36.8
7	48.3	47.0	39.8	39.8	—	—	11.9	13.2
8	47.9	47.1	36.5	35.5	—	—	15.6	17.4

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