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GEL PERMEATION CHROMATOGRAPHY ANALYSIS
OF PLASTICIZER BLENDS

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SUMMARY

Plasticizer blends and components were analyzed using the technique of gel permeation chromatography. A technique is described for the identification of the plasticizer components and a method is given for obtaining the relative weight percent of each component in the blend.

INTRODUCTION

Gel permeation chromatography (GPC) permits size separations of polymers¹⁻⁴. This technique has been applied to the separations of small molecules and low-molecular-weight polymers⁵⁻⁹. Blends of monomeric and polymeric plasticizers were separated by GPC. The components present in the blends were identified by comparing their peak elution volumes with those of known plasticizer standards. Relative weight percentage determinations of each component were obtained through a comparison of peak elution deflections.

EXPERIMENTAL

The blends and components were analyzed with a Waters Associates gel permeation chromatograph, Model 200. The gel permeation chromatograph operated at ambient temperature using tetrahydrofuran (THF) for the solvent with a flow rate of 1 ml/min. The samples were injected using an automatic sample injection system at a maximum weight concentration of 0.25 % in THF. The separations were performed with two Styragel column banks of 10⁵, 10⁴, 10³, 60 and 100, 100, 60, and 60 Å porosities. The columns were checked for adsorption of polar molecules by injecting organic acids to detect any distortion in the chromatograms¹⁰. The 10⁵, 10⁴, 10³, and 60 Å porosity column bank was calibrated using polystyrene standards supplied by Waters Associates for evaluation of the polymer component. The criteria for the selection of the ester, epoxy, and polyester components for investigation were their plasticizing functionality, commercial supply, and price.

Peak elution volumes of known standards were obtained (Fig. 1) and related to their molecular weight or chain length (Tables I and II). Elution volume reproducibility was checked with two plasticizers as shown in Table III. Since some components

had similar elution volumes, the 100, 100, 60, and 60 Å porosity column bank was used to enhance the separation of the low-molecular-weight components. The separating efficiency was evaluated using a blend of 2 esters as shown in Fig. 2. However, since the separation was not significantly improved, the 10^5 , 10^4 , 10^3 , and 60 Å porosity column bank was used in all subsequent work. Further, the use of this latter column bank system permits the determination of weight average chain length (\bar{A}_w), number average chain length (\bar{A}_n), and peak elution volume of a polyester. The polyester's polydispersity (Table II) was narrow enough to relate peak elution volume to chain length.

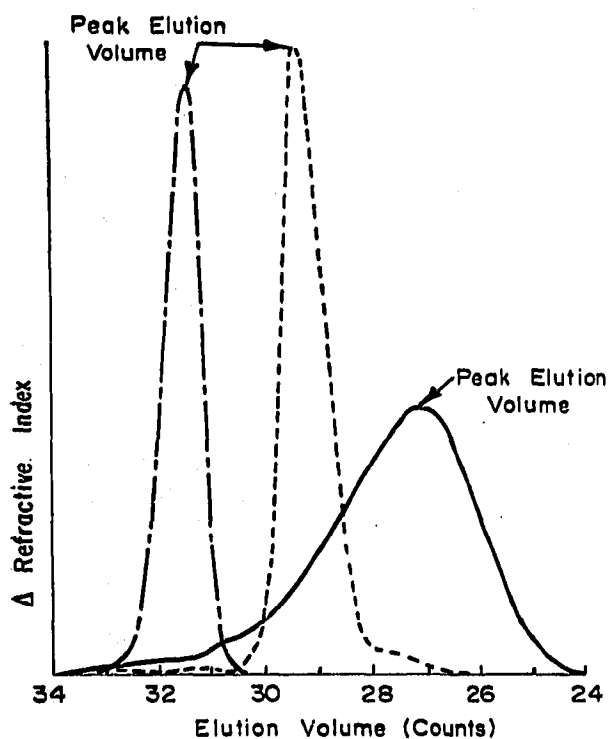


Fig. 1. Peak elution volume. Columns: 10^5 , 10^4 , 10^3 , and 60 Å. Solvent: THF. Temperature: ambient. Concentration: 0.10 g/100 g solution for ester and epoxy; 0.25 g/100 g solution for polyester. —, Polyester; - · - · -, ester; - - - -, epoxy.

Analysis of the polyester component shows low-molecular-weight material eluting in the elution volume range of the epoxy and ester standards as shown in Fig. 3. Very few polyesters of the large number analyzed exhibited large deflections in the overlapping area; therefore, it was possible to detect additional esters and/or epoxies as a result of deviation from the normal polyester distribution curve (Fig. 4).

A correlation was sought between the relative amount of each plasticizer component and peak deflection heights through an analysis of known mixtures. Table IV shows the results of the study.

DISCUSSION

The chromatograms of the esters exhibited symmetrical distributions, except for tributyl citrate which gave two peaks. The presence of monomeric plasticizers in

TABLE I

PEAK ELUTION VOLUMES AND MOLECULAR WEIGHTS OF STANDARDS

<i>Standards</i>	<i>Molecular weight^a</i>	<i>Peak elution volume (counts)</i>
Dimethyl phthalate	194	34.50
Dibutyl phthalate	278	32.67
Butyl benzyl phthalate	312	32.67
Butyl cyclohexyl phthalate	304	32.86
Diphenyl phthalate	318	32.75
Diethyl phthalate	390	31.68
Diisooctyl phthalate	391	31.67
Dinonyl phthalate	419	31.50
Dinonyl <i>n</i> -decyl phthalate	419	31.42
Diisodecyl phthalate	446	31.25
Diundecyl phthalate	474	31.00
Ditridecyl phthalate	530	30.75
Triethyl trimellitate	546	30.69
<i>n</i> -Octyl <i>n</i> -decyl trimellitate	582	30.33
Diethyl adipate	370	31.50
Didecyl adipate	426	31.25
Diisodecyl adipate	426	31.00
Diethyl azelate	413	31.00
Tributyl citrate	360	31.58 and 32.92
Dibutyl sebacate	314	31.83
Diethyl sebacate	426	31.00
Tricresyl phosphate	368	32.41
Epoxidized tallate	530	31.02
Epoxidized soybean oil	1000	29.31
Epoxidized linseed oil	1120	29.04

^a *Modern Plastics Encyclopedia 1967*, Vol. 44, No. 1A, 1966, McGraw-Hill, New York, N.Y.

TABLE II

PEAK ELUTION VOLUMES AND MOLECULAR PARAMETERS OF POLYESTER STANDARDS

<i>Standards</i>	\bar{A}_w	\bar{A}_n	\bar{A}_w/\bar{A}_n	<i>Peak elution volume</i>
Polyester No. 1	47.7	37.2	1.28	29.31
Polyester No. 2	78.3	54.1	1.45	28.15
Polyester No. 3	117	70.8	1.65	27.23
Polyester No. 4	131	78.1	1.68	27.08
Polyester No. 5	152	71.3	2.13	26.62
Polyester No. 6	184	116	1.59	26.54
Polyester No. 7	294	146	2.01	25.77

TABLE III

PEAK ELUTION VOLUME REPRODUCIBILITY

<i>Compound</i>	<i>Peak elution volumes</i>
Diethyl phthalate	31.83, 31.65, 31.67, 31.68, and 31.68
Triethyl trimellitate	30.75, 30.69, and 30.69

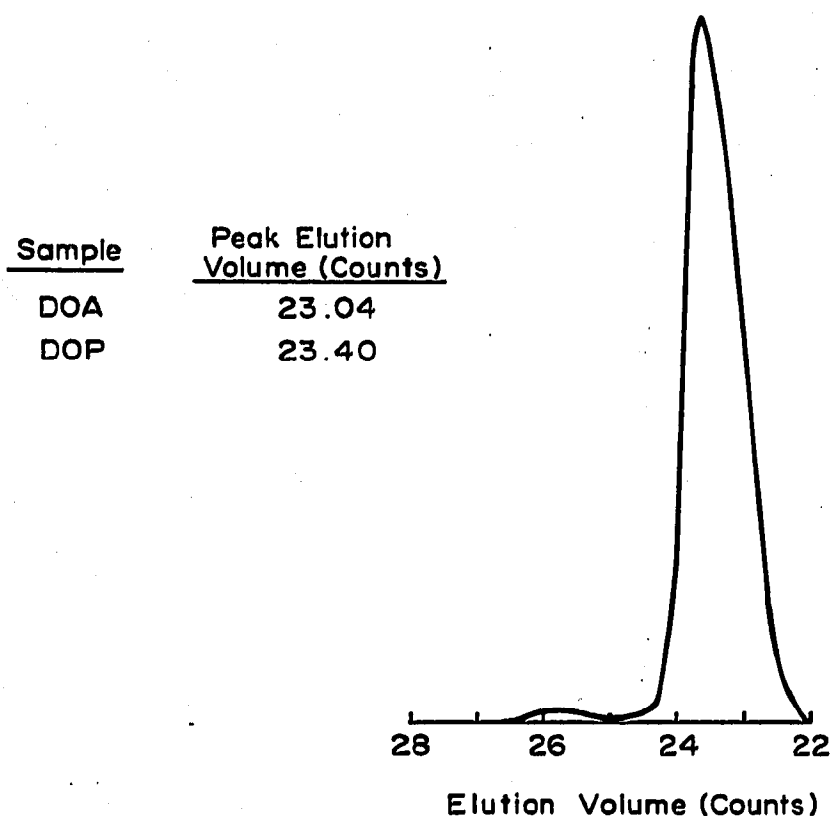


Fig. 2. Column separating efficiency. Column: 100, 100, 60, and 60 Å. Solvent: THF. Temperature: ambient. Concentration: 0.125 g/100 g solution. Sample: dioctyladipate (DOA)/dioctyl phthalate (DOP).

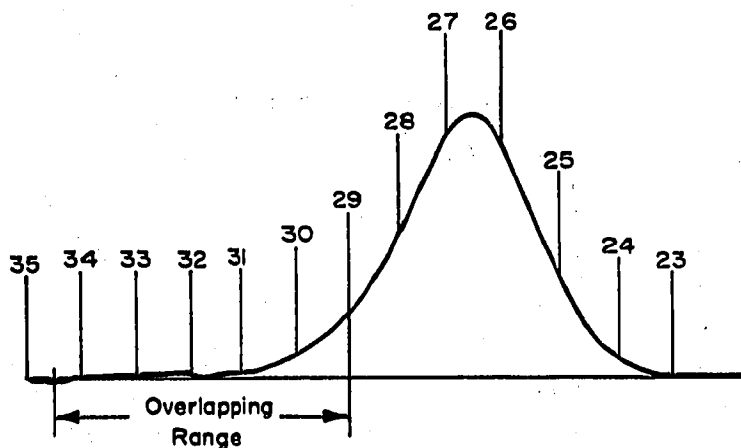


Fig. 3. Polyester elution range. Column: 10⁵, 10⁴, 10³ and 60 Å. Solvent: THF. Temperature: ambient. Concentration: 0.25 g/100 g solution.

a blend was readily discernible due to the characteristic sharpness of their distribution curves. However, their chemical identification by GPC is difficult since esters of different chemical families have similar elution volumes, as shown in Fig. 5. The data in Table III show that small variations occur in elution volumes which lead to further difficulties in identifying components. These variations arise from aging of columns,

solvent pressure changes, and solvent flow changes. Such variations were corrected by injecting a known standard with the blends, and the standard's elution volume was then compared with elution volumes previously obtained.

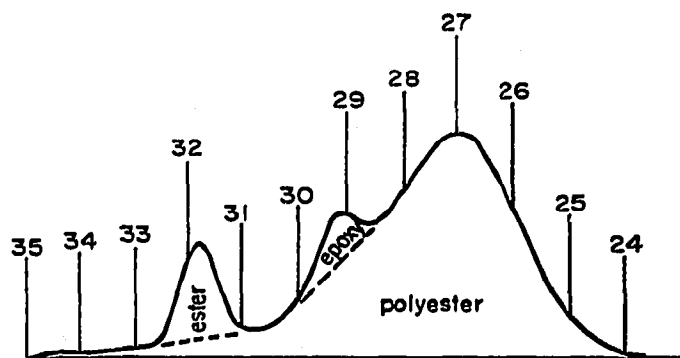


Fig. 4. Chromatograph of plasticizer blend. Column: 10^5 , 10^4 , 10^3 , and 60 Å. Solvent: THF. Temperature: ambient. Concentration: 0.25 g/100 g solution.

TABLE IV

QUANTITATIVE ANALYSIS OF BLENDS

Blend	Column	Known weight percentage	Experimental weight percentage
Polyester	10^5 , 10^4 , 10^3	89	77
Diisodecyl phthalate	and 60 Å	4	10
Epoxidized linseed oil		7	13
Polyester	10^5 , 10^4 , 10^3	93	87
Epoxidized linseed oil	and 60 Å	7	13
Polyester	10^5 , 10^4 , 10^3	85	63
Diisodecyl phthalate	and 60 Å	8	25
Epoxidized linseed oil		7	12
Polyester	10^5 , 10^4 , 10^3	85	62
Diocetyl phthalate	and 60 Å	8	12
Epoxidized linseed oil		7	26
Diocetyl adipate	100, 100, 60	50	No separation
Diocetyl phthalate	and 60 Å	50	
Diocetyl adipate	100, 100, 60	50	No separation
Diisodecyl phthalate	and 60 Å	50	
Diisodecyl phthalate	100, 100, 60	50	45
Epoxidized linseed oil	and 60 Å	50	55
Diocetyl phthalate	100, 100, 60	50	42
Epoxidized linseed oil	and 60 Å	50	58

Fig. 2 shows that identification of the ester by GPC is not unequivocal, but many esters can be eliminated by comparison of peak elution volumes as shown in Table I. The remaining possibilities can be further narrowed through the consideration of the application and cost of the plasticizer blend. Finally, the suspected components can be subjected to the classical analytical method for identification.

The higher-molecular-weight epoxy components were easy to separate from the

esters, but they also eluted in the elution range of the polyester component as shown in Fig. 4. Recognition of this component was relatively easy in a blend, and the identification was not difficult as the only three epoxidized materials considered had widely different elution volumes.

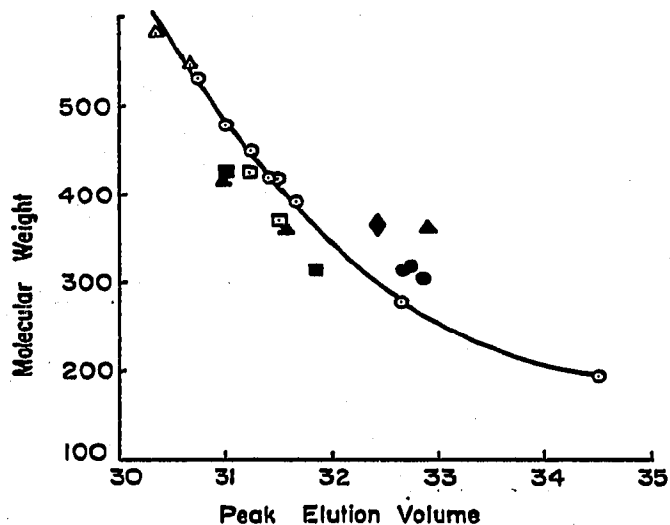


Fig. 5. Peak elution volume. ○, Aliphatic phthalates; ●, aromatic and cyclic phthalates; △, trimellitates; ▲, citrates; □, adipates; ■, sebacates; ◆, phosphate.

The polyester component exhibits a distribution curve typical of most polymers. The \bar{M}_w and \bar{M}_n of the polyester, taken from Table II and supplemented with chemical identification, can help in the identification of the particular polyester.

Attempts to obtain relative amounts of each component in a blend were not successful using the method of peak height deflection (Table IV). This discrepancy is due to a combination of factors which include differences in refractive index of each component, determination of a base line, and the preparation of a blend on a weight basis instead of a molar basis.

CONCLUSION

The gel permeation chromatograph was used to separate and aid in the identification of esters, epoxies and low-molecular-weight polyesters in plasticizer blends through a comparison of elution volumes with elution volumes of known standard components. To test the validity of the procedure, known blends were prepared and analyzed by GPC. Attempts were made to obtain relative amounts of each component by comparing elution heights of the component.

GPC is useful in the separation of plasticizer blends and yields information which helps the analytical chemist in the characterization of the plasticizer. Furthermore, the technique makes it possible for the chemist to eliminate certain combinations from consideration and alerts him to the presence of blends and minor components.

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