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Quantitative Determination of Plasticizers in Polymeric Mixtures by GPC*

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Summary

Organic plasticizers were added to plastics to improve flow and reduce brittleness by lowering the glass transition temperature. The amount of plasticizer added to the base resin determined its efficiency in bringing about these desired changes in properties. Analytical gel permeation chromatography (GPC) was utilized to quantitatively determine the amount of organic plasticizers in poly(styrene) mixtures. The internal standard method was applied to the determination of triethyleneglycoldibenzoate and tricyclohexylcitrate over the concentration range of 5.0 to 30.0 wt-% in poly(styrene). Linear calibration curves and excellent precision between measurements was demonstrated over the concentration range investigated. GPC analysis has the advantage over spectrophotometric techniques in its ability to separate low molecular weight plasticizers from higher molecular weight resins. In addition to the potential of making quantitative measurements from the detected peak, the associated material can be separated from the polymer, collected, and separately analyzed by UV or IR techniques.

INTRODUCTION

Organic plasticizers were added to polymers, primarily amorphous, to improve flow and reduce brittleness by lowering the glass transition temperature. The amount of plasticizer added to the base resin determined its efficiency in bringing about these desired changes in

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properties. Therefore, good quantitative analytical methods are needed to control the amount of plasticizer necessary for optimum materials performance.

Several authors have successfully applied gel permeation chromatography (GPC) to the quantitative measurement of various components in polymers and other mixtures. Mate (*1*) applied GPC to the analysis of oil content in oil-extended elastomers. Larsen (*2, 3*) used the technique to determine butyl cellosolve in copolymer reactions, unreacted trimethylol-propane (TMP) in polyesters, and diphenylmethylsilanol in silicones. Recently, Limpert (*4*) quantitatively measured the amount of asphaltines, solvent distillates, and oils extracted from coal.

Our recent efforts have produced a further quantitative application in GPC analysis. The technique was applied to the quantitative determination of triethyleneglycol dibenzoate and tricyclohexyl citrate plasticizers in poly(styrene) over a 5–30% concentration range.

EXPERIMENTAL

Equipment and Supplies

GPC analyses of the plasticizer–polymer mixtures were carried out using a Waters Associates Model 200 Gel Permeation Chromatograph. The equipment was operated at 40°C, with Eastman tetrahydrofuran as the carrier solvent (flow rate, 1 ml/min). An automatic injection system was used in conjunction with four columns in series; a listing of the column characteristics is given in Table 1.

TABLE 1

Column Characteristics

Designated porosity (Å)	Plate count (plates/ft)
10,000	1230
1,000	1285
250	575
60	900

Materials

Two low molecular-weight plasticizers, tricyclohexyl citrate (TCHC) and triethyleneglycol dibenzoate (TEGDB), were chosen

for this study because of their purity and elution volumes. A high molecular-weight ($\simeq 50K$) poly(styrene) was used to prepare the physical mixtures to insure complete separation of the polymer and plasticizer peaks. Ultra-pure benzil was used as the internal standard because of its long elution time and high purity. Chromatograms of the TCHC, TEGDB, and benzil standard are shown in Figs. 1–3, re-

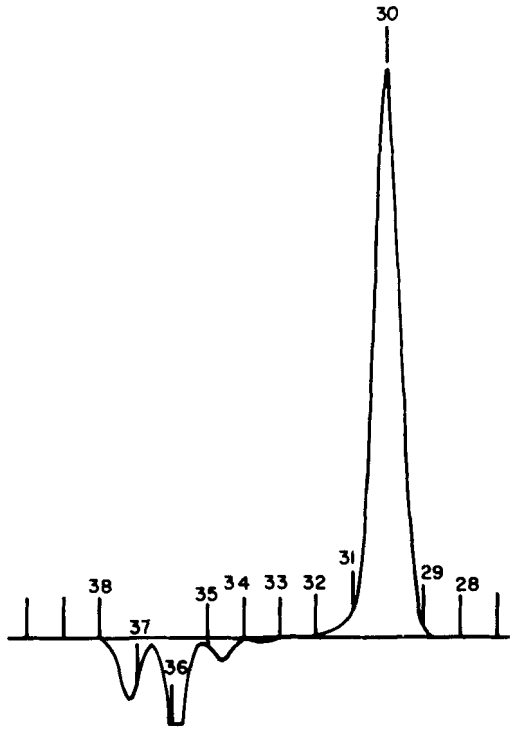

FIG. 1. Chromatogram of TCHC plasticizer.

spectively. The monodispersity of these compounds makes them ideal for quantitative application. Negative peaks at counts 35–37 are associated with dissolved water and air.

Standard Solutions

All standard analytical solutions were prepared by dissolving varying amounts of plasticizer mixed with poly(styrene). The plasticizer concentrations were varied over a range of 5–30% of the total sample

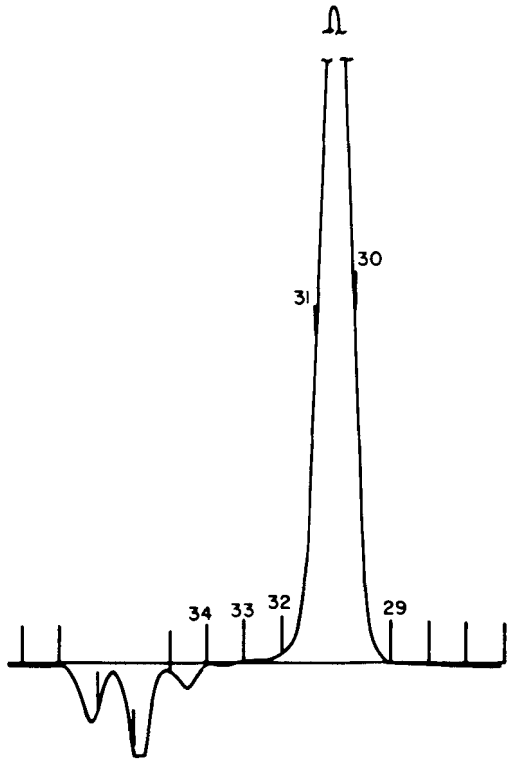

FIG. 2. Chromatogram of TEGDB plasticizer.

weight. Stock solutions were made to minimize weighing errors. The final solution concentrations were 0.5% (500 mg in 100 ml THF).

Analytical Procedures

Each of the standard solutions were analyzed three times to establish the precision of the GPC data. One milliliter of a 1% benzil solution was added to a 10-ml aliquot of each stock solution and prefiltered before injection into the automatic injection system.

Peak area measurements of the plasticizer and internal standard peaks were made using the triangulation method. This method involves the use of the product of peak height and the width at half-height. It is fast and gives reasonable accuracy when the peaks are symmetrical. The heights and widths at half-height were measured as accurately as possible to the nearest hundredth of an inch.

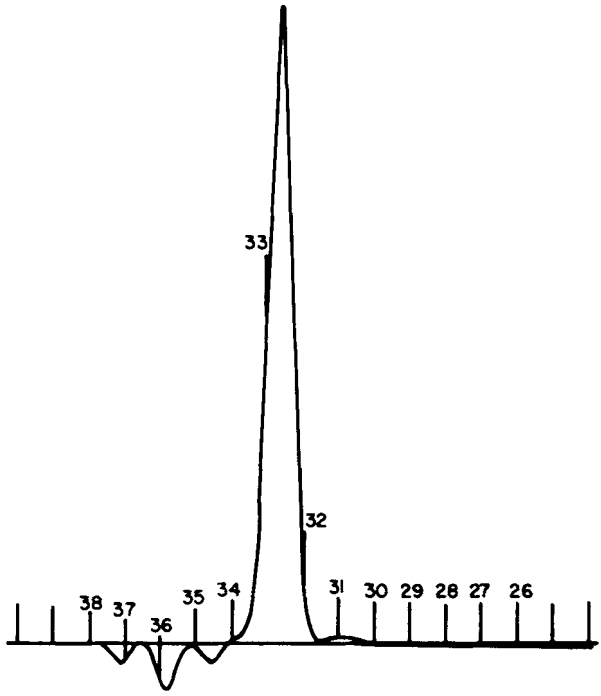

FIG. 3. Chromatogram of benzil standard.

RESULTS AND DISCUSSION

Accurate quantitative chromatographic procedures require a thorough knowledge of the operating characteristics of the detector. Therefore, the refractometer detector system of the GPC was evaluated to determine the linearity of its response within the expected concentration ranges. This was accomplished by analyzing each plasticizer over the range of 5–30% by weight in the polymeric mixture. The results, plotted as weight of plasticizer vs. area of plasticizer peak (Figs. 4 and 5), show that the detector response was linear within the working range, and therefore it was not necessary to apply empirical correction factors.

The internal standard procedure is used extensively in gas chromatography (*5*) to compensate for minor variations in column operation over an extended period of time. This procedure allows for instrumental variations by compensating through the use of an internal stand-

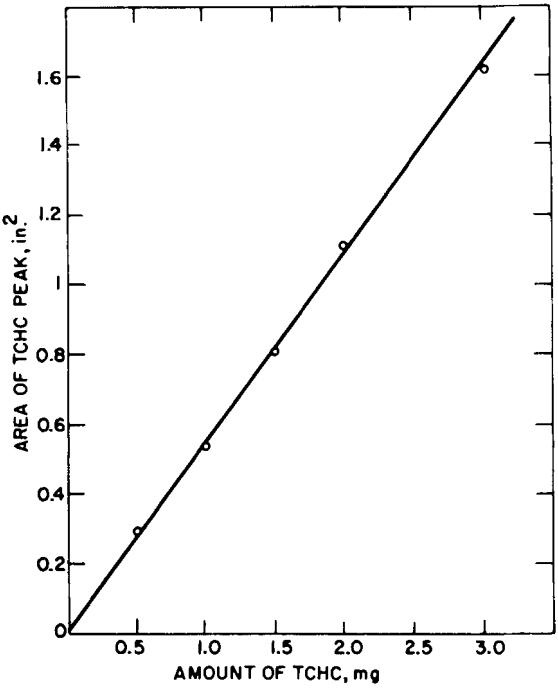

FIG. 4. Effect of TCHC concentration on refractometer response.

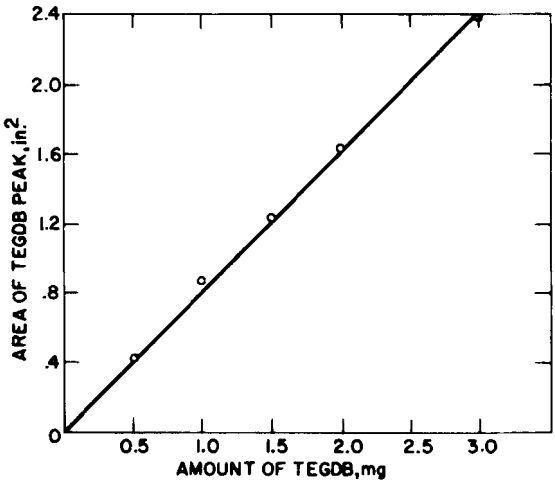

FIG. 5. Effect of TEGDB concentration on refractometer response.

ard. Harvey and Chalkley (*6*) outlined the requirements of an internal standard as follows: (a) yields a completely resolved peak, (b) should be eluted close to component to be measured, and (c) the ratio of peak area to that of the component should be close to unity.

The first two requirements set by Harvey and Chalkley were met by benzil. This organic compound yields a sharp, narrow chromatogram (Fig. 3) and elutes close to both plasticizers studied.

Because of the amount of internal standard added and the refractive index of the plasticizers, the third requirement set by Harvey and Chalkley was deviated from at lower concentrations of plasticizer. However, excellent precision was maintained over the entire range of plasticizer concentration studied. The results of the internal standard measurements for the TCHC and TEGDB plasticizers are summarized in Tables 2 and 3, respectively.

Linear calibration curves (Figs. 6 and 7) were obtained by plotting the ratio, internal standard peak area:plasticizer peak area vs. actual

TABLE 2

Precision of Internal Standard Method for Tricyclohexyl Citrate Plasticizer at Various Concentrations

Solution code	Wt-% TCHC plasticizer added to mixture	Ratio $\frac{\text{TCHC peak}}{\text{Standard peak}}$
A	5.0	0.113
		0.105
		0.114
		Average = 0.1106 ± .0017[a]
B	10.0	0.204
		0.210
		Average = 0.2070
C	15.0	0.297
		0.297
		0.305
		Average = 0.2996 ± .0015
D	20.0	0.414
		0.404
		0.428
		Average = 0.4153 ± .0053
E	30.0	0.572
		0.599
		0.603
		Average = 0.5913 ± .0056

[a] Standard deviation.

TABLE 3

Precision of Internal Standard Method for Triethyleneglycol Dibenzoate Plasticizer at Various Concentrations

Solution code	Wt-% TEGDB plasticizer added to mixture	Ratio $\frac{\text{TEGDB peak}}{\text{Standard peak}}$
F	5.0	0.160
		0.159
		0.160
		Average = 0.1596 ± .0003[a]
G	10.0	0.310
		0.318
		0.313
		Average = 0.3137 ± .0019
H	15.0	0.445
		0.445
		0.443
		Average = 0.4443 ± .0003
I	20.0	0.600
		0.601
		0.598
		Average = 0.5996 ± .0007
J	30.0	0.910
		0.922
		0.895
		Average = 0.9090 ± .0072

[a] Standard deviation.

concentration of plasticizer in the physical mixture. Chromatograms of the physical mixtures containing 20% TEGDB and 30% TCHC in poly(styrene) are shown in Figs. 8 and 9, respectively. The chromatograms demonstrate the excellent separation between the high molecular-weight poly(styrene) and low molecular-weight plasticizers.

The sensitivity of the detector to the compound being studied is important in quantitative GPC. Because the refractive index of the TEGDB component is higher than that of THF, while that of TCHC is closer to THF, one can measure lower concentrations of the TEGDB plasticizer using THF as the carrier solvent.

GPC analysis has an advantage over spectrophotometric techniques in its ability to separate low molecular-weight plasticizers from higher molecular-weight resins. This eliminates spectral interference problems which have to be compensated for in the analysis of mixtures. GPC also offers advantages over other quantitative methods such as

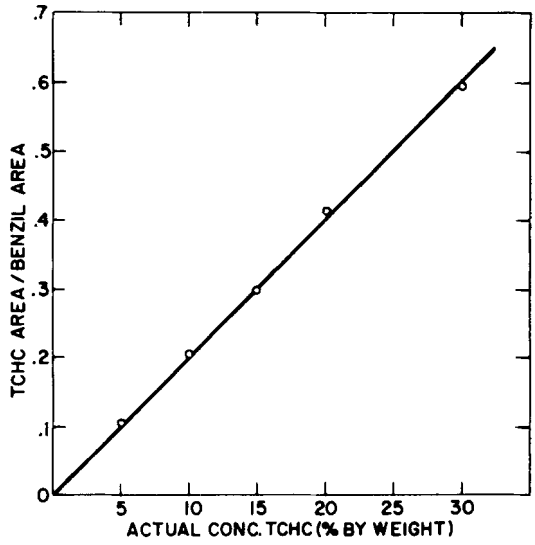

FIG. 6. Calibration curve for per cent TCHC plasticizer using internal standard method.

gas chromatography. First, it eliminates separation of the polymer component before analysis, and second, thermally unstable materials can be analyzed at ambient conditions.

In addition to being able to make quantitative measurements from the detected peak, one can separate the associated material from the polymer and, after collection, analyze it by UV or IR techniques. This is particularly advantageous when one wishes to identify the chemical structure of an unknown plasticizer in a physical mixture.

CONCLUSIONS

Analytical GPC has been successfully applied to the quantitative determination of low molecular-weight organic plasticizers in polymeric mixtures. The internal standard method proved to be the best procedure for this application, as it provides compensation for experimental variations over a long period of time. GPC offers definite advantages over other analytical techniques in its ability to separate high from low molecular-weight materials, and therefore, looks highly promising for quantitative applications to monomers, additives, and catalysts in polymer systems.

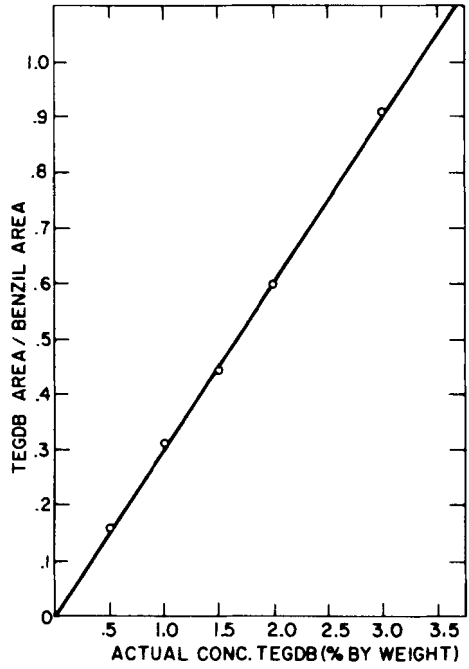

FIG. 7. Calibration curve for per cent TEGDB plasticizer using internal standard method.

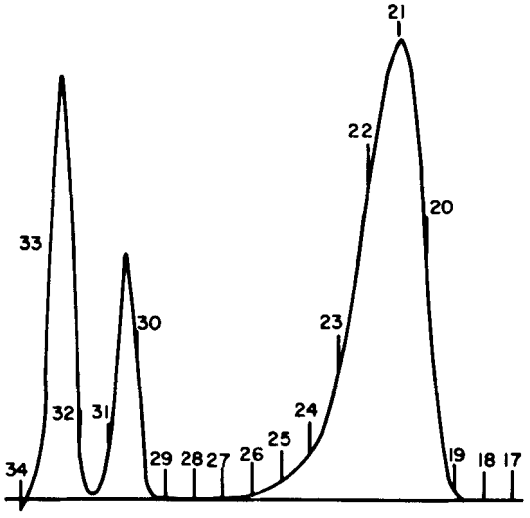

FIG. 8. Chromatogram of 20% TEGDB in physical mixture.

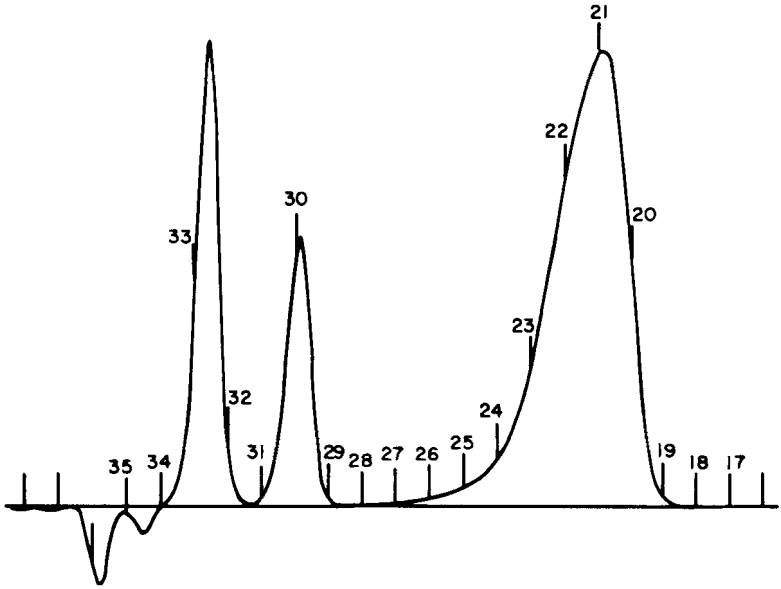

FIG. 9. Chromatogram of 30% TCHC in physical mixture.

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