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SIMPLE AND INEXPENSIVE APPLICATION OF STERIC EXCLUSION CHROMATOGRAPHY FOR THE ISOLATION OF LOW-MOLECULAR-WEIGHT ADDITIVES FROM POLYMER SYSTEMS

M. J. SHEPHERD and J. GILBERT

Ministry of Agriculture, Fisheries and Food, Food Science Division, Haldin House, Queen Street, Norwich NR2 4SX (Great Britain)

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SUMMARY

The application of steric exclusion chromatography is described for the isolation of additives from polymers. A simple and inexpensive, gravity-flow system has been evaluated employing Sephadex LH-60 with tetrahydrofuran as eluent, and recoveries have been shown to be quantitative for a range of additives employed in poly(vinyl chloride) formulations, although problems were encountered in the recovery of antioxidants and organotin stabilisers. Maximum column loadings of polymer have been established in order to maximise recovery of additives present at low levels and for the trace analysis of transformation products.

INTRODUCTION

Measurement of low-molecular-weight additives and other species in polymer matrices frequently necessitates a preliminary separation from the polymer. Separations by selective solvent extraction[1,2] or by repeated fractional precipitation[3,4] are unsatisfactory for routine use on the basis of the time and manipulative skills required and the inevitable uncertainty about their efficiency where unidentified components are being studied.

Steric exclusion chromatography (StEC) was initially used for obtaining molecular-weight distributions of polymers but more recently its use has been extended to the measurement of low-molecular-weight components in plastics, for example in the analysis of surface coatings[5–7], monomers and additives[8–11]. The technique has been successfully used for plasticisers which are present in relatively large amounts and have UV-absorbing properties[11]. Additives at low concentrations present more difficulties especially in the case of non-UV-absorbing species. Methods have been developed for 0.3% toluene diisocyanate monomer in urethane adhesives[8], butyl-lithium in polystyrene[9] and methyl acrylate in polyacrylates[10]. One factor limiting the wider use of StEC in plastics analysis has been the detection limit obtainable with the small sample loadings (no more than 50 mg) which can be used on the 9-mm analytical columns of poly(styrene–divinylbenzene) employed. Larger

columns of this material would allow greater loadings but they are expensive to purchase and are difficult to produce satisfactorily in the laboratory.

The present work describes a system based on a column of Sephadex LH-60, which (like LH-20) can be packed satisfactorily in the laboratory and gives an adequate flow-rate under gravity, which avoids the compressibility associated with such gels. Separation mechanisms other than steric exclusion are minimised by the use of tetrahydrofuran as solvent. The method has been applied in the separation of the small molecules from up to 180 mg plastic and no major difficulty is anticipated in increasing the loading to 500 mg. Previous workers have used LH-20 for removing small molecules[12] and macromolecules[13,14] from biological extracts. Resins have been separated on LH-20[15] and Mulder and Buytenhuys[16] have employed LH-20 during preparative scale separations of a range of small organic molecules. The requirement for the present work arose from the concern about migration of minor constituents from plastic packaging into foods. Attention in recent years has centred on the levels of residual monomers (particularly vinyl chloride) in food-grade plastics[17,18], but there has also been some interest in additives (for example heat stabilisers[19,20]) incorporated in the course of manufacture. Surveillance of additives intended for food-contact use on the basis of a positive list has become a legislative requirement in certain countries and this has prompted interest in other minor constituents such as additive transformation products likely to be found in polymer systems used for food packaging. The system described in this paper is suitable for use in both research and routine applications as a simple, inexpensive and rapid system for quantitative isolation of low-molecular-weight constituents of polymers used in food packaging.

EXPERIMENTAL

Materials

Sephadex LH-60 and SR 25/45 columns (45 × 2.5 cm I.D.) with adjustable end pieces were obtained from Pharmacia (Uppsala, Sweden); AnalaR grade tetrahydrofuran (THF), Sudan III (tetrabenzene-β-naphthol), polystyrene, mol. wt. *ca.* 10^5, and AnalaR grade 30% hydrogen peroxide from BDH (Poole, Great Britain), methyl stearate and methyl palmitate from Sigma (London, Great Britain); poly(ethylene glycol), mol.wt. 1540 (PEG 1540) from Koch-Light (Colnbrook, Great Britain); tris(nonylphenyl)phosphite (TNPP, "Phosclere P315") from Akzo Chemie (Liverpool, Great Britain); 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (HMBT, "Tinuvin P") from Ciba Geigy (Basle, Switzerland); epoxidised soya bean oil (ESBO, "Lankroflex GE") from Lankro Chemicals (Manchester, Great Britain); poly(vinyl chloride) (PVC) (Corvic S57/116 base polymer) from ICI Plastics Division (Welwyn Garden City, Great Britain).

THF was redistilled immediately before use. Sudan III was purified by column chromatography on silica gel. ESBO was freed from polymeric material by prior chromatography on LH-60. PVC was purified by reprecipitation with methanol from THF.

Methods

StEC. Sephadex LH-60 swollen in redistilled THF was packed into columns

in the usual manner. Gel column lengths were typically 30–33 cm. After the gel bed had settled, efficiency of packing was checked visually by chromatographing 2 ml of a solution of Sudan III in THF. Columns were repacked if any inhomogeneity of the red band was observed. Flow-rates of up to 6 ml/min were obtained by gravity flow under a head of about 2 m. Flow-rates decreased with use and columns were repacked when less than 1 ml/min was obtainable. Normal sample volume was 2.0 ml, containing 2% PVC plus the desired additive. Samples were applied to the column in the following manner. The solution was dispensed into a test tube and, after stopping the flow of eluent, the solvent inlet was transferred to the tube from the THF reservoir. Elution was restarted and continued until all the sample was syphoned onto the column. The walls of the tube were then washed with 1–2 ml THF and the washings also syphoned onto the column. The eluent stream was again stopped, the solvent inlet replaced in the reservoir and elution continued. When chromatograms were required, 2.5-ml fractions were collected. Alternatively, two bulk fractions were collected, the first containing polymer, the second the additive. With column lengths of 30–33 cm, fraction volumes were standardised at 90 ml and 100 ml, respectively.

The additive fraction was then either evaporated to small volume, transferred to a volumetric flask and made up to the mark with THF, or, if a solvent other than THF was preferable, evaporated to dryness, redissolved in (normally) diethyl ether and again made up to known volume in a volumetric flask. Aliquots were then taken for analysis.

Analyses. (i) Polystyrene and HMBT were assayed by UV spectrophotometry. Wavelengths were chosen so that peak maxima of 1–2 absorbance units were obtained.

(ii) TNPP was oxidised using sulphuric acid and AnalaR 30% hydrogen peroxide (50% hydrogen peroxide gave an unacceptably high reagent blank). Phosphorus in the digest was estimated by the method of Morrison[21].

(iii) ESBO was determined by a modification of the picrate method of Fioriti *et al.*[22,23]. Aliquots (1 ml) of ESBO in diethyl ether, contained in a 25-ml volumetric flask, were mixed with 0.2 ml of a 0.25 *M* solution of picric acid in ethanol and allowed to stand for 24 h. The flasks were made up to the mark with 1% sodium hydroxide in water–ethanol (20:80) and the adsorption at 490 nm measured immediately. A linear calibration curve is obtained for amounts of ESBO up to 1 mg.

(iv) Methyl stearate was estimated by gas chromatography using a Pye GCD chromatograph and a 1.52 m × 4 mm I.D. glass column packed with 3% OV-1 on Diatomite CLQ. Carrier gas (nitrogen) flow-rate was 60 ml/min, oven temperature 220°, detection was by a flame ionisation detector. The dry residue to be determined was dissolved in cyclohexanone, chosen as a non-volatile solvent, containing methyl palmitate as internal standard.

(v) PEG 1540 was determined gravimetrically.

RESULTS AND DISCUSSION

Typical additive levels in polymers, excluding plasticisers, are 0.1 to 1.0% by weight, while transformation products are likely to be present at much lower

concentrations. Thus it is important that the quantity of polymer which is fractionated is kept as high as possible in order to ensure that good detection limits can be achieved for constituents in the low-molecular-weight fraction. A preliminary series of experiments were carried out, therefore, in order to determine the maximum loading of polymer which could be applied to the column whilst retaining complete separation of the small molecules. The chromatograms shown in Fig. 1 were obtained from solutions containing a range of concentrations of polystyrene but similar concentrations of HMBT. Fig. 2 shows the effect of keeping sample concentration constant but varying the volume loaded onto the column.

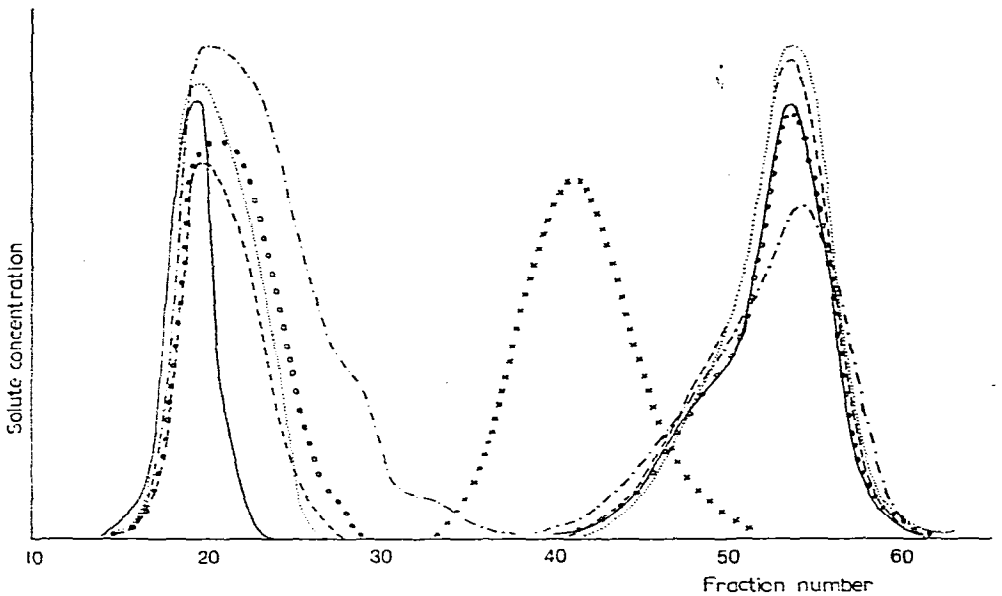

Fig. 1. The effect of polymer concentration upon the separation of polystyrene and HMBT. Sample size 2.0 ml containing polymer at 0.5% (———), 1.0% (· · · · · ·), 2.0% (– – –), 3.0% (o o o) and 5.0% (– · – · –). Fraction volume 2.5 ml. × × × marks the elution profile of PEG 1540.

These results show that up to 180 mg of polymer can be applied to a column of this type without causing any overlap of the polystyrene and HMBT peaks. When an additive of significantly higher molecular weight is present, the separating ability of the column will be reduced. This is shown in Fig. 1 by the elution profile of PEG 1540. The difference in elution volumes between polystyrene and PEG 1540 is only 60% of that between polystyrene and HMBT. Although this sample was not chromatographed as a mixture with polystyrene, it can be predicted that complete separation of the oligoether would be achieved, probably even from as much as 100 mg of high-molecular-weight polymer.

Resolution is obviously dependent upon both sample loading[24] and molecular-weight (more accurately, molecular-size[25]) difference, but it can be seen from Table I that a range of additives, with molecular weights up to 980, can be separated from 40 mg PVC. The discrepancies in recoveries can be ascribed to the difficulty of handling the very dilute additive solutions obtained from the column. Thus the

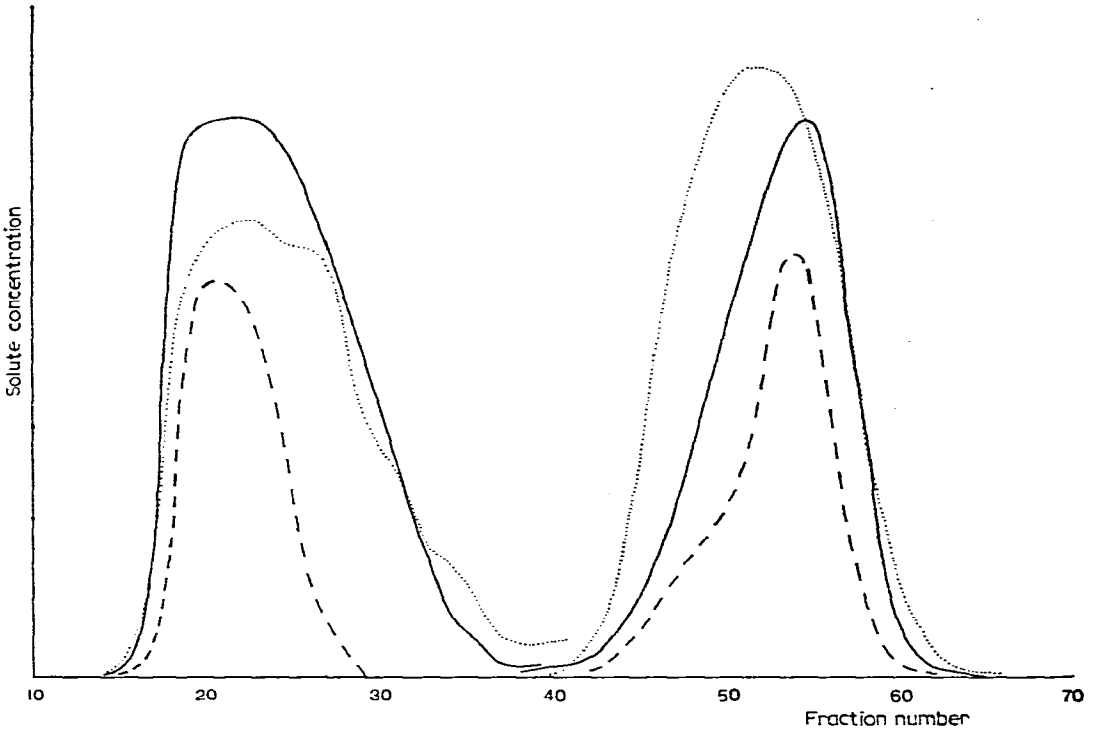

Fig. 2. The effect of sample size upon the resolution of polystyrene and HMBT. Polymer concentration 3.0%. Sample size: — — —, 2.0 ml; · · · · · ·, 4.0 ml; ———, 6.0 ml. Fraction volume 2.5 ml.

TABLE I

RECOVERIES OF ADDITIVES FROM COLUMN

Samples were applied in 2 ml of THF containing 2% PVC except where stated otherwise.

Compound	*Molecular weight*	*% additive in PVC*	*Amount added (mg)*	*Amount found (mg)*
HMBT	225	0.1	0.0400	0.0385
		0.1	0.0400	0.0412
		0.1	0.0400	0.0428
Methyl stearate	298	1.8	0.900	0.826
		1.8	0.900	0.981
		1.8	1.000	1.090
TNPP	691	No added PVC	0.0803	0.0799
			0.0803	0.0835
TNPP	691	0.5	0.248	0.207
		0.5	0.233	0.204
ESBO	690–980	3.6	1.504	1.429
		3.6	1.504	1.504
		3.6	1.504	1.467

analysis of HMBT requires little sample preparation, and the recovery of this compound is most nearly quantitative, despite its addition at the lowest concentration of any of the additives in the table.

The most significant problem encountered during this work was due to the poor stability of THF. Although only THF freshly distilled from copper(I) chloride was used, decomposition products of the solvent were always evident when samples were concentrated from large volumes of THF. It might be possible to reduce the extent of degradation by distilling under nitrogen, but other workers have experienced similar difficulties even when taking all possible precautions[5]. Nevertheless, THF remained the solvent of choice because of its advantages for StEC, its ready solvation of PVC and its low boiling point which facilitates sample concentration for subsequent analysis.

One major class of additives which cannot be isolated by StEC using THF is the antioxidants. Several experiments with 2,6-di-*tert*.-butyl-*p*-cresol (BHT) led to low and erratic recoveries and it was realised that the most probable explanation was that the BHT was being consumed whilst stabilising the solvent. Thus it would be necessary to change solvents in order to separate this type of additive. Problems were similarly encountered with recoveries of organotin stabilisers for PVC. Again, initial experiments indicated low and variable recoveries of the additives. Losses of these compounds by adsorption are well known[26], but no improvement was observed on silanizing all the glassware used, including the column. Attempts to elucidate the cause of this phenomenon are continuing.

For many additives, however, this simple approach to sample preparation is adequate. It is used on a routine basis in this laboratory and applications have included the separation of epoxidised compounds and their chlorohydrin transformation products in the course of an investigation of the fate of epoxide heat stabilisers during the processing of PVC[27] and also studies of the reactions in the PVC system of the stabiliser tris(nonylphenyl)phosphite.

The technique has also been employed for the fractionation of PVC oligomers, using gels with exclusion limits lower than that of Sephadex LH-60. In each of these cases, StEC has enabled the generation of information that would have been impossible to obtain by other means.

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