Journal of Chromatography, 218 (1981) 703–713
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,094

ANALYSIS OF ADDITIVES IN PLASTICS BY HIGH-PERFORMANCE SIZE-EXCLUSION CHROMATOGRAPHY

M. J. SHEPHERD* and J. GILBERT
Ministry of Agriculture, Fisheries and Food, Food Science Laboratories, Haldin House, Old Bank of England Court, Queen Street, Norwich NR2 4SX (Great Britain)

SUMMARY

The application of high-performance size-exclusion chromatography is described for the analysis, in plastics, of low-molecular-weight additives and their decomposition products. The limitation on maximum attainable sensitivity of the method due to sample size has been established by an examination of the relationship between column loading and resolution for a simple additive–polymer mixture. The effects of sample volume and concentration are described in terms of peak broadening, and the results are discussed in relation to mechanisms of solute dispersal. The advantages of this type of approach over other techniques for the analysis of non-volatile yet unstable components of plastics are discussed, and the use of the method is illustrated with examples of studies of the fates of phosphite and epoxidised oil stabilisers in heat-treated poly(vinyl chloride) sheets.

INTRODUCTION

Analysis or identification of low-molecular-weight components in plastics is severely restricted by the polymer matrix. *In situ* spectroscopic methods are sometimes possible[1], but it is usually necessary to perform a preliminary separation of the species of interest. This has commonly been achieved by selective solvent extraction or repeated fractional precipitation. Size-exclusion chromatography (SEC —we have now adopted the ASTM recommended term[2] in preference to "steric" exclusion chromatography) offers some advantages as an alternative or complement to the traditional methods, both because of the simplicity of SEC and also the possible uncertainties about the efficiency of selective techniques.

SEC has been used widely for the analysis of surface coatings, but its applications to the separation from polymers of small amounts of low-molecular-weight compounds have been limited. We have reported the use of open-column SEC in the analysis of plastics additives[3], and residual isocyanates in urethane adhesives have been determined by SEC[4] and high-performance SEC (HP-SEC)[5]. Styrene has been quantified in copolymers by HP-SEC[6], and the same authors similarly measured low levels of polychlorinated biphenyls in polystyrene[7]. Other applications of SEC in this area have included the measurement of high levels of plasticiser in polystyrene[8] and of

0021-9673/81/0000–0000/$02.50

oil in extended elastomers[9], whereas qualitative analysis of additives has been performed by stopped-flow SEC with IR detection[10]. Generally, however, only HP-SEC methods permit direct analysis, although the relatively low cost and much higher sample-loading capacity of open-column SEC ensure that this technique will be complementary to, rather than displaced by, HP-SEC.

Our requirement for the analysis of low-molecular-weight compounds in plastics has occurred in the course of work on the possible migration into food of such species from plastic food-packaging materials. Although the major area of concern has been perceived as being due to residual monomers[11–14], other constituents of packaging are also potential migrants. These include many of the additives incorporated into packaging for technological reasons of manufacture and use, and also decomposition products of these additives, residues of ingredients from the polymerisation process and oligomers.

Analysis of such specific migrants in food samples poses formidable problems, and consequently our approach has been that of characterising additive transformation products in the plastic, with the intension of subsequently carrying out migration studies on identified compounds, as exemplified by our studies of the poly(vinyl chloride) (PVC)–epoxidised oil stabiliser system[15–17].

In this paper we describe an evaluation of the column-loading capacity of HP-SEC for the analysis of additives, their degradation products and any other low-molecular-weight compounds present in plastics and give some examples of applications of the method.

EXPERIMENTAL

Materials

PLgel HP-SEC columns (30 × 0.77 cm) packed with 10 μm poly(styrene–divinylbenzene) of pore sizes 50, 100 and 500 Å were obtained from Polymer Laboratories Ltd. (Church Stretton, Salop, Great Britain). Sephadex LH-60 and SR100/25 columns were from Pharmacia (Uppsala, Sweden). The 5-μm Techsphere ODS column (25 × 0.42 cm) was from HPLC Technology Ltd. (Macclesfield, Great Britain).

Polystyrene (PS; molecular weight *ca.* 100,000) was from BDH (Poole, Dorset, Great Britain), and PVC base resin "Corvic S57/116", a bottle-blowing grade of weight-average molecular weight between 75,000 and 100,000 with a *K* value of 56–57, from ICI Plastics Division (Welwyn Garden City, Great Britain). Tris(nonylphenyl) phosphite (TNPP, "Phosclere P315") was from Akzo Chemie (Liverpool, Great Britain) and *p*-nonylphenol (NP) from Pfaltz and Bauer (Stamford, CT, U.S.A.); 2-(2-hydroxy-5-methylphenyl)benzotriazole (HMBT, "Tinuvin P") was from Ciba Geigy (Basle, Switzerland); all solvents were of HPLC grade from Rathburn Chemicals Ltd. (Walkerburn, Great Britain). Glyceryl tri-[1-^{14}C]epoxyoleate (TETO) and its trichlorohydrin were synthesised as before[16]. The PVC and polystyrene were reprecipitated from tetrahydrofuran–methanol when required for HP-SEC standard solutions.

Methods

HP-SEC. The chromatographic system consisted of a model 6000A pump

(Waters Assoc.); Rheodyne 7125 or Altex 210 valve injectors, fitted with 20-μl loops unless otherwise indicated; and a Pye LC-UV detector followed in-line by an Optilab Multiref 902 differential refractometer thermostatically controlled at 30.00 ± 0.01 °C with a Colora WK4 thermocirculator. The following column sets were used:

Set A, 2 × 100 Å PLgel
Set B, 500 Å, 2 × 100 Å, 50 Å PLgel

All HP-SEC was performed in tetrahydrofuran (THF) medium at a flow-rate of 1.0 ml/min except where otherwise stated.

Column-loading experiments. Column set A was used. Series A injections were made by overfill of a 20-μl loop. Series B and C injections were made by partial fill of a 100-μl loop with the exception of injection mode 22, in which the loop was overfilled. The term injection mode is used (with reference to Table I) to describe the particular combination of parameters (sample volume, concentration of PS and loop size) under discussion.

Applications

Phosphite stabiliser analysis. Pressed sheets of PVC incorporating 1.00% of TNPP were prepared in a manner analogous to that reported for epoxidised stabilisers[15]; the sheet thickness was 0.08 cm. Sections of these sheets (5 × 1 × 0.08 cm) were heated in an air-circulating oven at 170°C for various times. The strips were then individually cut into pieces of *ca.* 1 mm^2, and these pieces were randomised before sampling to prepare 2-ml aliquots of 2% solutions in THF. These solutions were analysed by HP-SEC (column set A) at a flow-rate of 1.5 ml/min. Standard solutions of TNPP and NP contained 2% of precipitated PVC. Linear calibration graphs were obtained for 0–5 μg of NP and 0–10 μg of TNPP in 20-μl injections.

Epoxide stabiliser analysis. PVC sheets incorporating 2.92% of [1-^{14}C]-labelled TETO were prepared as before[16], giving material of specific activity 0.864 μCi/g; the sheet thickness was 0.08 cm. Strips (5 × 1 × 0.08 cm) were heated at 170° in an air-circulating oven for 40 min, then cut into pieces of *ca.* 2 mm^2 and randomised. A sample of this polymer (0.305 g) was chromatographed in two portions on a Sephadex LH-60 column (74 × 2.4 cm), with THF as mobile phase, as described previously[16].

The low-molecular-weight fraction from the Sephadex column was evaporated to dryness, the residue was dissolved in 200 μl of THF, and four 20-μl aliquots were separated by HP-SEC on column set B. The combined TETO–chlorohydrin fractions were evaporated, the residue was dissolved in 50 μl of acetonitrile–chloroform (75:25), and 10-μl samples were chromatographed on a Techsphere ODS column. Elution was with the same solvent mixture delivered from a Waters 6000A pump, and detection was by liquid scintillation counting (Beckman LS-100C) of 250-μl aliquots collected directly in vials and mixed with 10.0 ml of a solution (4 g/l) of PPO in toluene.

RESULTS AND DISCUSSION

Sensitivity is generally of considerable importance in this area of analysis, and

TABLE I

COLUMN EFFICIENCIES FOR A LOW-MOLECULAR-WEIGHT PLASTICS ADDITIVE WHEN CO-INJECTED WITH POLYSTYRENE

Injection mode No.	*Concentration of PS (%)*	*Volume injected (μl)*	*Mass of PS injected (μg)*	*Replicate HMBT peak $W_{\frac{1}{2}}$ volumes (ml)*	*Value of N for HMBT peak (calculated* from average $W_{\frac{1}{2}}$)*
*Series A injections***					
1	0	20	0	0.37, 0.37	12,400
2	1	20	200	0.38	11,800
3	2	20	400	0.39, 0.40	10,900
4	3	20	600	0.425	9390
5	4	20	800	0.53	6040
6	5	20	1000	0.65, 0.66, 0.645, 0.66, 0.645, 0.66	3980
7	6	20	1200	0.90	2090
*Series B injections***					
8	2	20	400	0.39, 0.395	11,000
9	3	20	600	0.495	6920
10	4	20	800	0.55, 0.53	5820
11	5	20	1000	0.61, 0.59, 0.62 0.59, 0.61	4650
12	6	20	1200	0.60, 0.625	4520
13	2	10	200	0.37	12,400
***	2	20	400	0.39, 0.395	11,000
14	2	30	600	0.455, 0.445	8380
15	2	40	800	0.495, 0.52	6590
16	2	50	1000	0.565, 0.53, 0.55, 0.52, 0.57	5670
17	2	60	1200	0.645, 0.69	3810
18	2	70	1400	0.71, 0.735	3250
*Series C injections***					
***	5	20	1000	0.61, 0.59, 0.62, 0.59, 0.61	4650
19	3.33	30	1000	0.59, 0.625	4600
20	2.5	40	1000	0.56, 0.615, 0.60	4850
***	2	50	1000	0.565, 0.53, 0.55, 0.52, 0.57	5670
21	1.33	75	1000	0.445, 0.475, 0.47	7900
22	1	100	1000	0.43, 0.44	8970

* Calculated from the equation $N = 5.54\,(L/W_{\frac{1}{2}})^2$.
** See *Methods* for experimental details.
*** These entries duplicated for ease of comparison.

therefore a knowledge of the maximum permissible column loading is essential. Sample size is limited because of peak broadening due to viscosity effects, including viscous fingering[18,20] and restricted diffusion of the low-molecular-weight solutes. Hence, the relationship between column loading and resolution was investigated by injecting solutions containing both PS and the plastics UV-stabiliser HMBT and

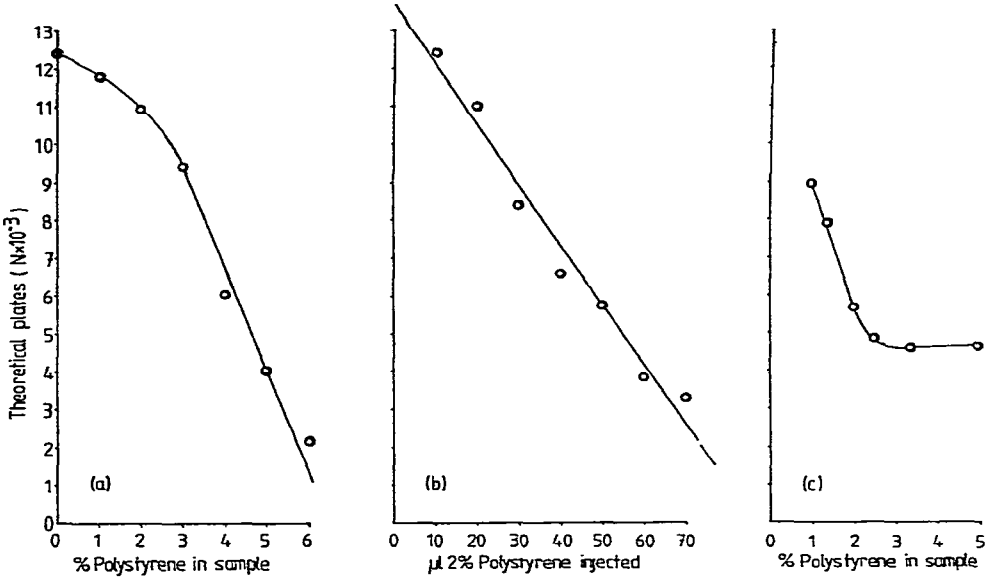

Fig. 1. Effect of sample volume and polymer concentration on chromatographic efficiency of a low-molecular-weight plastics additive when co-injected with polystyrene.

calculating theoretical plate numbers, N, for the additive peak (see *Methods*). The results are given in Table I, and the dependence of N on sample concentration and volume is shown graphically in Fig. 1. This indicates clearly that, when the total mass of injected polymer remains constant, higher efficiency arises from making larger injections of more dilute polymer solutions. This effect is well known in the SEC of polymers[20] and indicates that entrainment of low-molecular-weight additives by macromolecules is the major cause of peak broadening. This conclusion is confirmed by the observation that the retention time of the additive peak decreases progressively when the polymer loading is increased (without simultaneously reducing the concentration of the sample), as can be seen from Fig. 2.

The series C injections show that column efficiency was doubled when the same mass of polymer was injected as a 1% solution rather than as a 5% solution. Ultimately, maximum column loadings will be determined by the desired resolution, but for favourable separations 1 mg or more of polymer can be injected. It is of interest to compare injection modes 22 and 2. These indicate that the increase in injection volume from 20 to 100 µl increases the $W_{\frac{1}{2}}$ value for the peak only by a similar amount. This is the result expected when chromatographing low-molecular-weight solutes by HP-SEC and thus indicates that, in this instance, the polymer is having little or no effect on the chromatography. Therefore, if a column efficiency of, for example, 4000 theoretical plates could be tolerated, which implies a peak half-width of approximately 0.65 ml, injection volumes of up to 300 µl of a 1% polymer solution might be possible.

A comparison of the results from injection modes 1–7 and 8–12 of Table I indicates that there is little difference in column efficiency between the loop-overfill and loop-part-fill techniques of sample injection. Presumably, at the very highest

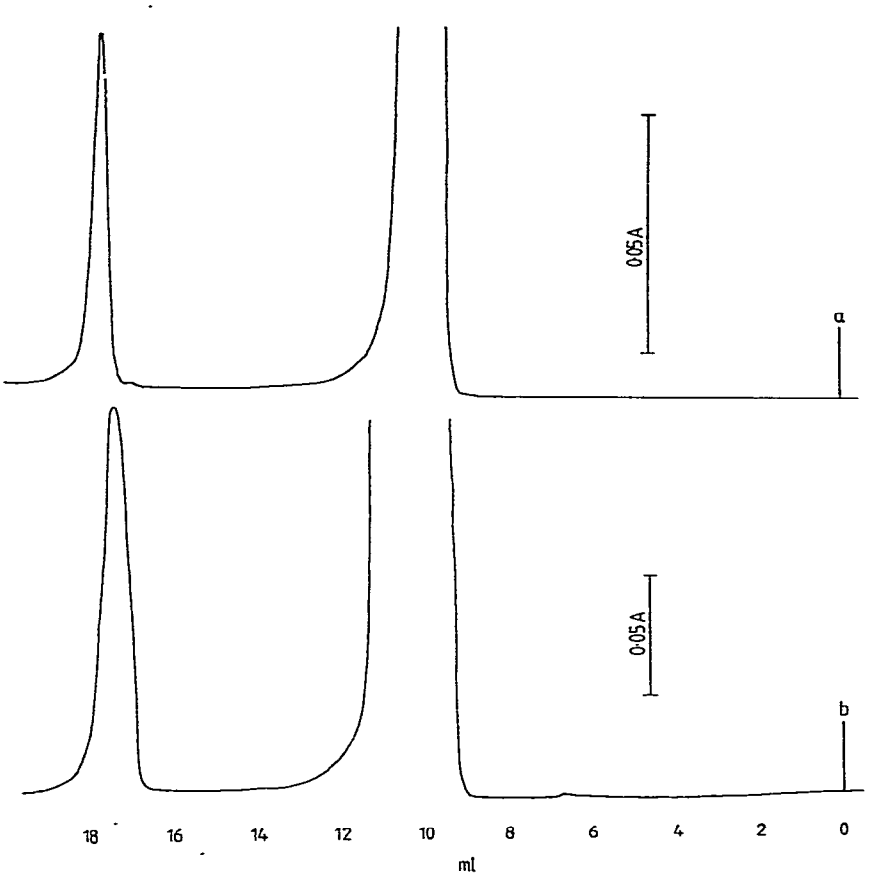

Fig. 2. Typical chromatograms of PS–HMBT mixtures. (a) Injection mode No. 8 (see Table I), UV detection, 0.16 A f.s.d. (b) Injection mode No. 18 (see Table I), UV detection, 0.32 A f.s.d.

polymer concentrations, some mixing is occurring in samples when the latter technique is used. Typical chromatograms from which the data of Table I were calculated are shown in Fig. 2. It can be seen that the major effect of an increase in polymer concentration on the additive peak is to broaden it, leaving the over-all peak profile unaltered. However, the effect of viscous fingering can be seen in the shape of the PS peaks in Fig. 3. Split peaks and other irregular shapes were usual at the higher PS concentrations (3% or more) and were not reproducible. Efficient SEC is dependent on rapid diffusion of solutes, and this too is reduced in viscous samples.

Although axial spreading of samples will occur in the valve loop and valve–column connection, this dispersal mechanism cannot be important. When the column set was removed and 20-μl samples were injected directly into the detector, the trace width for a 6% PS solution was only 2.5 times that for a HMBT solution containing no PS. Thus, in the absence of additional on-column dispersal effects, the peak half-width for the 6% PS sample would have been no more than 150 μl greater than that for the sample containing no polymer. As most of the peak broadening occurs on-column and additive–polymer mixtures may be widely separated by correct choice of columns, the results found here will apply to any set of columns (irrespective of their

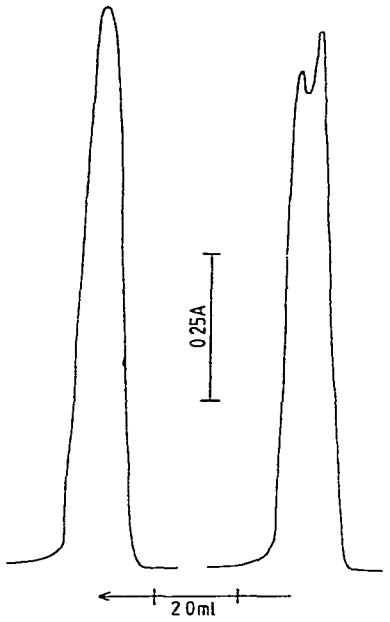

Fig. 3. Replicate PS peak profiles; injection mode No. 4 (see Table I). UV detection, 1.28 A f.s.d.

number) packed with 10-μm particles of porous polymer gels. Those with 5-μm packings will probably perform better, as diffusion distances are shorter and viscous fingering should be reduced.

Hence, it has been shown that HP-SEC can be used to separate low-molecular-weight compounds from relatively large amounts of polymers without serious loss of resolution of the additives. The technique has been in routine use in this laboratory for a number of years, and the following applications illustrate the utility of HP-SEC

TABLE II

DEGRADATION OF TRIS(NONYLPHENYL) PHOSPHITE STABILISER (INCORPORATED IN PVC AT AN INITIAL CONCENTRATION OF 2% w/w) AS MEASURED BY DIRECT HP-SEC ANALYSIS

ND = not detectable (less than 2%).

Sample	*Time sheet heated at 170°C (min)*	*Residual TNPP (%)*	*NP found as % of initial TNPP*	*Total TNPP accounted for (%)*
Coated base resin	–	82.8	–	82.8+
Pressed sheet	0	39.3	18.9	58.2
Pressed sheet	5	4.1	51.8	55.9
Pressed sheet	10	ND	61.5	61.5
Pressed sheet	15	ND	56.5	56.5
Pressed sheet	20	ND	57.8	57.8
Pressed sheet	25	ND	53.7	53.7
Pressed sheet	30	ND	45.3	45.3

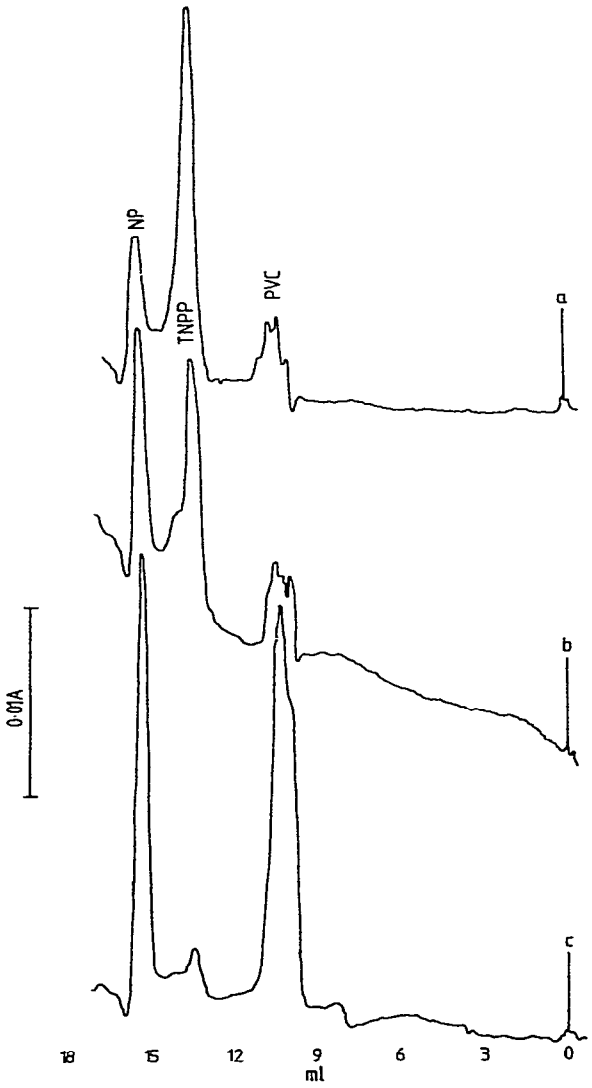

Fig. 4. HP-SEC chromatograms of TNPP-stabilised PVC: (a) Coated base resin powder. (b) Pressed sheet, no additional heat treatment. (c) Pressed sheet after 5 min at 170°C. UV detection, 0.04 A f.s.d. (See *Methods* for experimental details.)

in analysis and also the separation of components for further investigation by other techniques. Although in most instances the molecular-weight information gained has been valuable, it was usually of secondary benefit, the prime use of HP-SEC being as a physical method of separation.

Analysis of phosphite stabilisers

A pre-stabiliser is often added to PVC base resins during manufacture in order

to prevent discolouring of the resin during drying; phosphite esters may be used for this purpose. PVC sheets incorporating 1.0% of a typical stabiliser (TNPP) were analysed for TNPP and its degradation product nonylphenol (NP) after heating at 170° for various times to simulate heat processing during packaging fabrication. HP-SEC was the ideal technique for this analysis, as TNPP is both non-volatile and susceptible to hydrolysis. Thus, a liquid-chromatography method was necessary and it was important that stabiliser residues should be subjected to the minimum of handling. Analysis by HP-SEC required only that the sample be dissolved in THF. The results found are presented in Table II with chromatograms demonstrating progressive loss of TNPP shown in Fig. 4. It can be seen that most of the TNPP was consumed during the 30-sec pressing period and the remainder was lost during the first few minutes of subsequent heat treatment, with consequent formation of chromophores in the polymer (Fig. 4c). However, only about 60% of the additive is accounted for in Table II although there is evidence of partially degraded TNPP in Fig. 4b. which would increase the recovery of additive for the unheated sheet. The chro-

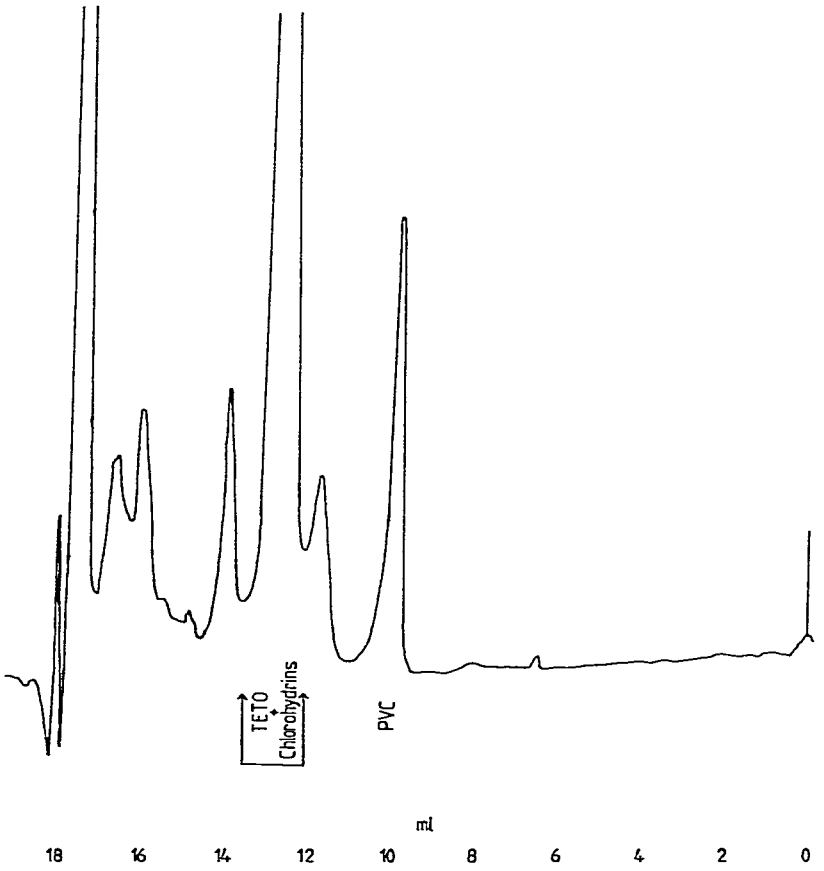

Fig. 5. HP-SEC chromatogram of low-molecular-weight fraction from TETO-stabilised PVC sheet. RI detection, "calibrate" setting. The chlorohydrins + TETO fraction indicated was collected for further analysis (see Fig. 6). (See *Methods* for experimental details.)

matograms in Fig. 4 indicated that no products of significantly lower molecular weight than NP were formed. All peaks later than NP were derived from the solvent. Thus, another advantage of HP-SEC was demonstrated, in that all components of the sample were eluted from the column in a defined time and therefore it can be deduced that the missing stabiliser-degradation products must have been associated with the polymer. The results of Table II were confirmed by both UV and RI studies, and it is unlikely that other products (derived, for example, by benzene ring cleavage) were not detected. However, although the degradation product is described here as NP, derivatives of NP of similar molecular weight would not have been resolved. The suggestion that the additive unaccounted for was lost by binding to the polymer requires confirmation, preferably by radio-tracer experiments.

Analysis of epoxide stabilisers

Epoxidised triglycerides, such as soya bean oil, are frequently used as PVC stabilisers. The use of HP-SEC for the analysis of chlorohydrin transformation products of the model compound glyceryl triepoxyoleate (TETO) has been described[16]. An estimate of total chlorohydrins was obtained by dissolving a sample of plastic in THF and derivatising the mixture with a bulky group. The derivatised chlorohydrins were then well separated from all other components of the mixture and, although partly resolved, could be measured as a group[16]. A complex mixture of chlorohydrins was expected, with various isomers of mono-, di- and tri-substituted TETO possible.

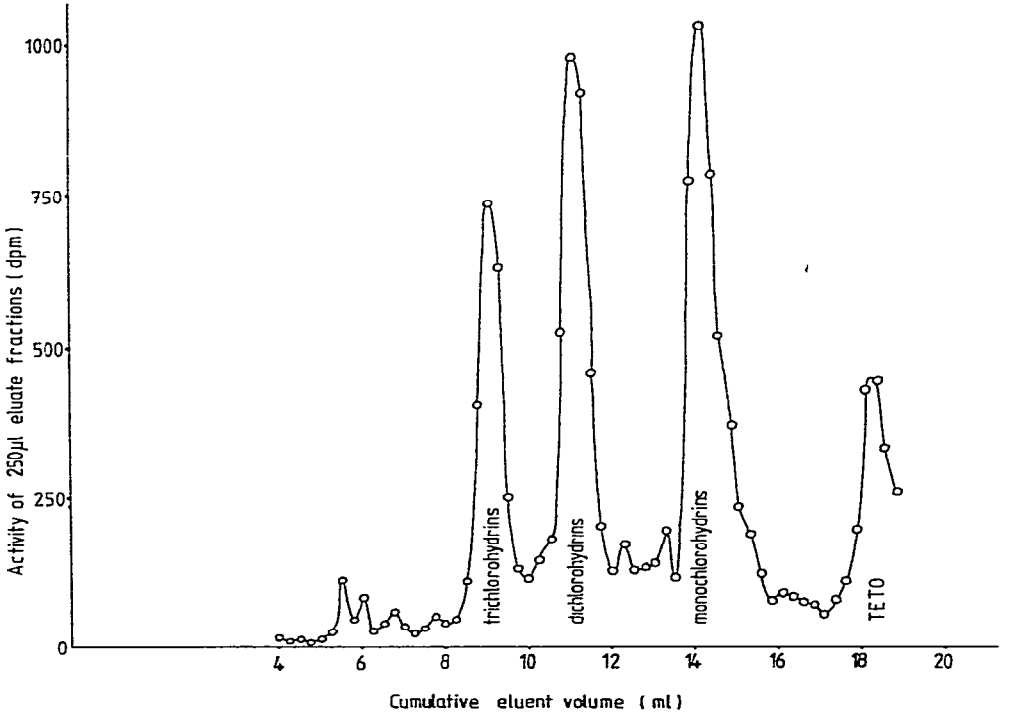

Fig. 6. Reversed-phase HPLC chromatogram of chlorohydrins + TETO fraction (Fig. 5) from TETO-stabilised PVC sheet. Radiochemical detection. (See *Methods* for experimental details.)

With the HP-SEC columns available, these components could not be resolved either from each other or from TETO itself, and recycle HP-SEC yielded only partial separation. Reversed-phase HPLC was suitable for the analysis of chlorohydrin mixtures, but not in the presence of polymer. Thus, SEC was used to separate material for subsequent examination by reversed-phase HPLC. Open-column SEC[3] was performed in order to separate the additive and its transformation products from a 300-mg sample of heat-treated PVC stabilised with [1-^{14}C]-TETO. However, the low-molecular-weight fraction still contained substantial amounts of PVC with molecular weights up to about 2000 (ref. 19). Consequently, HP-SEC was necessary in order to obtain a sample containing essentially only TETO and its derived chlorohydrins, as shown in Fig. 5. The indicated fraction was trapped and analysed by reversed-phase HPLC (see Fig. 6). A combination of chromatographic techniques were used here, but HP-SEC performed an essential function in obtaining a clean sample for reversed-phase HPLC; it is doubtful whether this could have been achieved in any other way.

Analysis of low-molecular-weight compounds in plastics by direct HP-SEC will not be suitable for all applications. Adequate sensitivity will often be a problem, as will the inherently limited resolving power of any SEC technique. Further, solubility limitations (of, for example, polyolefins) can rule out the use of SEC in this area. Nevertheless, for many analyses HP-SEC should be the method of choice because of its unique combination of simplicity and predictability with its additional advantage of generating information about molecular weight.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to ICI Ltd. (Plastics Division) for the gift of PVC base resin, and to Mr. M. Jumani of Southbank Polytechnic, London, and Mr. J. Bygrave for their assistance with the experimental work.

REFERENCES

1 D. A. Wheeler, *Talanta*, 15 (1968) 1315.
2 D. D. Bly, *J. Liquid Chromatogr.*, 3 (1980) 465.
3 M. J. Shepherd and J. Gilbert, *J. Chromatogr.*, 178 (1979) 435.
4 F. Spagnolo and W. M. Malone, *J. Chromatogr. Sci.*, 14 (1976) 52.
5 U. Lotz, *Farbe Lack*, 85 (1979) 172.
6 J. M. Pacco, A. K. Mukherji and D. L. Evans, *Sep. Sci. Technol.*, 13 (1978) 277.
7 J. M. Pacco and A. K. Mukherji, *J. Chromatogr.*, 144 (1977) 113.
8 D. F. Alliet and J. M. Pacco, *Sep. Sci.*, 6 (1971) 153.
9 R. D. Mate and H. S. Lundstrom, *J. Polym. Sci., C*, 21 (1968) 317.
10 F. M. Mirabella, E. M. Barrall and J. F. Johnson, *Polymer*, 17 (1976) 17.
11 L. Rossi, J. Waibel and C. G. vom Bruck, *Food Cosmet. Toxicol.*, 18 (1980) 527.
12 J. Gilbert and J. R. Startin, *Food Chem.*, (1982) in press.
13 J. Gilbert, M. J. Shepherd, J. R. Startin and D. J. McWeeny, *J. Chromatogr.*, 197 (1980) 71.
14 J. Gilbert and J. R. Startin, *J. Chromatogr.*, 205 (1981) 434.
15 J. Gilbert and J. R. Startin, *Eur. Polym. J.*, 16 (1980) 73.
16 M. J. Shepherd and J. Gilbert, *Eur. Polym. J.*, 17 (1981) 285.
17 J. Gilbert, M. J. Shepherd, J. R. Startin and J. Eagles, *Chem. Phys. Lipids*, 28 (1981) 61.
18 J. C. Moore, *Sep. Sci.*, 5 (1970) 723.
19 J. Gilbert, M. J. Shepherd and M. A. Wallwork, *J. Chromatogr.*, 193 (1980) 235.
20 J. Janča, *J. Liquid Chromatogr.*, 4 (1981) 181.