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Note

Determination of total polymer in industrial materials by gel permeation chromatography ("exclusion limit chromatography")

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Methods are often required for the determination of the total polymer content of commercial products which contain a single polymer plus major amounts of relatively low-molecular-weight additives, *e.g.* plasticiser, organic extenders, oils. A number of such methods may be used, *e.g.* infrared spectrophotometry, where suitable selective absorption bands are present, or, more commonly, methods based on separation of the polymer by precipitation followed by determination gravimetrically or by other means. These methods give good results but are time consuming and considerable care must be taken to avoid errors such as solubility losses or occlusion of non-polymeric components.

Gel permeation chromatography (GPC), which separates compounds essentially by molecular size, has been used to separate polymers from low-molecular-weight additives, *e.g.* by Alliet and Pacco[1], for the identification and determination of plasticisers.

However, there appear to be no literature references to the determination of total polymer content in commercial products. The normal broad chromatograms obtained with a large-pore-size column system are suitable for the measurement of molecular weight distribution but total area response is not always easily measured precisely, due to the long-tailing nature of the peaks. By using a column system with small pore size the polymer can be eluted as a single narrow peak at the column exclusion limit. This polymer peak is therefore more easily measured, *e.g.* by peak height or area, whilst retaining the maximum separation from low-molecular-weight materials. This technique ("exclusion limit chromatography") has been applied to the analysis of several commercial materials in this laboratory. The results show a high level of precision and accuracy. Results are shown for three systems, *viz.* polyisobutylenes (PIB) in a propellant pre-mix, a methacrylate polymer-type ashless dispersant in a concentrate in lubricating oil and a nitrocellulose–nitroglycerine–water paste.

EXPERIMENTAL

Apparatus

All work was carried out using a Waters Associates Model 200 gel permeation chromatograph with tetrahydrofuran (THF) as solvent (inhibited with 0.1 % hydro-

quinone) using a flow-rate of 1 ml/min. Solutions of the samples in THF were injected using the normal 2-ml manual injection loop, which was connected to the column system for 5 min to allow complete transfer of the sample. Solvent was degassed at 55°, and columns were used at ambient temperature with the refractometer detector controlled at 30–45°.

Columns were 4 ft. × ⅜ in. O.D. packed with "Styragel" (Waters Ass., Stockport, Great Britain) with the following exclusion limits: (i) PIB, 300 Å; (ii) ashless dispersant, 60 + 100 + 200 + 500 Å; (iii) nitrocellulose–nitroglycerine–water paste, 60 + 100 + 200 + 500 + 5 × 10^6 Å.

Preparation of samples and determination of polymer

PIB. A 0.15% solution of the sample in THF was accurately prepared and allowed to stand overnight to ensure complete dissolution. A calibration standard containing a known similar amount of PIB was prepared in the same way. These solutions were successively injected into the chromatograph at a span of × 1 allowing time for complete elution before injection of the next sample. PIB peak heights were measured and the polymer content calculated by comparison with the standard.

Ashless dispersant. An accurately prepared 0.5% solution of the sample and a calibration solution containing 0.2% of standard polymer were prepared in THF. Each solution was injected into the chromatograph (span ×2). The polymer peak areas were measured by planimeter and the polymer concentration calibrated by comparison with the standard.

The standard polymer used for calibration was obtained by dialysis of a similar concentrate of ashless dispersant in oil.

Nitrocellulose–nitroglycerine–water paste. Two grams of paste were dissolved in 40 ml of THF and further diluted 1:10 to obtain a final solution of 0.5% paste in solvent. A standard analysed paste was treated in the same way. Solutions were injected into the chromatograph with a span setting of ×8. The nitrocellulose polymer peak areas were measured by summing the heights of the chromatogram above the base line at each count interval. One count is 5 ml of elution volume, *i.e.* a 5-min interval at the flow-rate used. The low-molecular-weight nitroglycerine peak height was also measured. The percentages of nitrocellulose and nitroglycerine were calculated by normalisation of the heights or areas after correction for response factors.

RESULTS AND DISCUSSION

Fig. 1 shows the chromatograms obtained and the quantitative results are summarised in Table I.

The PIB determination shows clear separation of the polymer from the low-molecular-weight components which comprise 20% of the sample. The separation on a single GPC column is complete in 45 min. The linearity of response of the refractometer detector was confirmed experimentally. The quantitative results obtained with synthetic mixtures are listed in Table I and show relative standard deviations of 0.6% or better, which shows the high degree of repeatability of the analysis. This is obtained by the use of the high-precision loop injector system. High stability of the chromatograph is essential for results of such high precision and continuous operation of the instrument for 24 h a day is therefore necessary for all the work described in this report. The GPC method of determining PIB in these

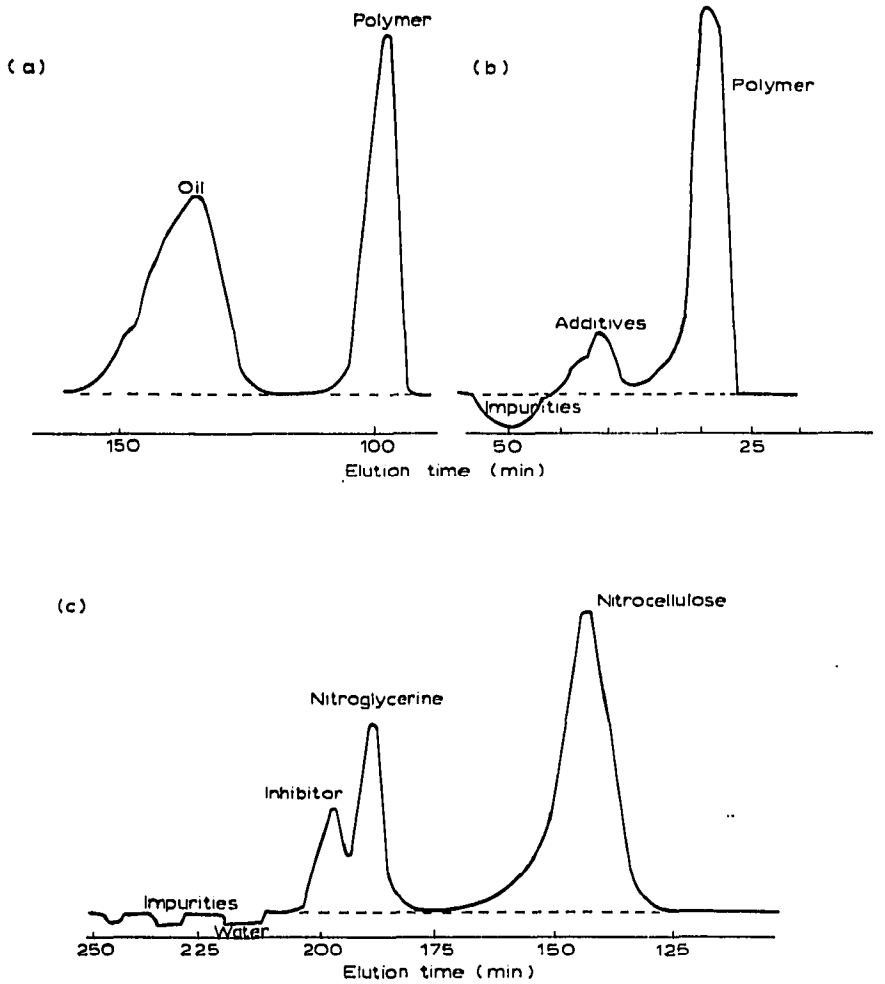

Fig. 1. GPC chromatograms. (a) Ashless dispersant; (b) polyisobutylene; (c) nitrocellulose–nitroglycerine–water paste.

compositions gives a direct measurement of PIB, which is an obvious advantage over older methods, which determined PIB by difference.

Determination of the ashless dispersant presents no problems in using the four-column system described. Calibration requires the use of a standard polymer or an accurately analysed oil–polymer concentrate. In this case dialysis was used to prepare a polymer sample for calibration[2]. The GPC results show good agreement with those obtained by a precipitation method[2].

The nitrocellulose–nitroglycerine–water pastes have previously been examined by quantitatively drying the paste to obtain the water content. Nitroglycerine is extracted by solvent and measured by infrared spectrophotometry. Nitrocellulose is then obtained by difference. The method is therefore lengthy and indirect.

GPC has been used to obtain the nitrocellulose and nitroglycerine contents calculated on the dried material and hence internal normalisation can be used in the calculation. The use of a four-column system (60 + 100 + 200 + 500 Å) gave a

TABLE I

QUANTITATIVE DETERMINATION OF POLYMERS

	Present (%)	*Found (%)*	*Mean found (%)*	*Relative standard deviation (%)*
Polyisobutylene				
Sample 1	80.4*	79.6, 80.1, 79.3 80.4, 80.1, 80.1 80.1, 80.4	80.0	0.4
Sample 2	69.4*	70.4, 69.5, 69.8 70.7, 70.1, 70.1 70.1, 69.5, 69.5	70.0	0.6
Sample 3	90.8*	91.6, 91.6, 91.6 91.6, 91.6	91.6	Nil
Ashless dispersant	34.4**	34.5, 35.3, 35.8	35.2	
Nitrocellulose–nitroglycerine–water pastes				
Sample 1				
% nitroglycerine	35.8***	34.8, 34.8, 34.9 35.1, 35.0	34.9	0.4
% nitrocellulose	64.2***	65.2, 65.2, 65.1 64.9, 65.0	65.1	0.2
Sample 2				
% nitroglycerine	29.4***	28.0, 28.4, 27.9 27.9, 28.2, 28.0	28.1	0.7
% nitrocellulose	70.6***	72.0, 71.6, 72.1 72.1, 71.8, 72.0	71.9	0.3

* Percentage added in synthetic mixture.
** Percentage found by precipitation method.
*** Percentage found by chemical analysis.

noisy maximum to the nitrocellulose peak, which was attributed to a viscosity effect. The addition of the 5×10^6 Å column broadened the nitrocellulose peak and eliminated the noise. Peak heights gave normally acceptable precision (relative standard deviation = $\pm$ 1.1%) but for this particular determination area measurement was found to give improved results. Summation of the polymer peak heights at each count interval gave the very precise results listed in Table I (relative standard deviation = 0.3%).

The general method of exclusion limit chromatography appears by these results to provide a good method for the direct determination of a polymeric ingredient in a wide range of commercial compositions. No prior separation stage is required, the sample merely requiring dissolution in a suitable solvent. The time for the determination depends on the nature of the problem and the precision required, but is mainly instrumental time, and very little operator working time is required.

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