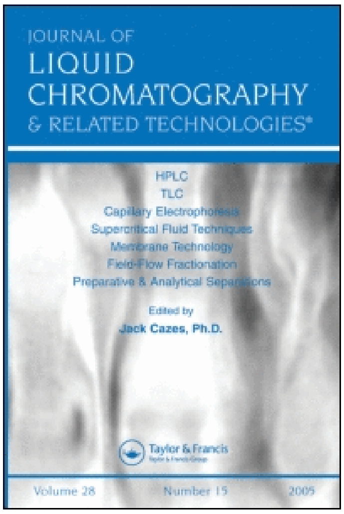

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Optimization of GPC Experiments as an Effective Means of Significantly Enhancing the Resolution of Multicolumn Sets to be Used for Analyzing Specific Polymer Systems

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OPTIMIZATION OF GPC EXPERIMENTS AS AN EFFECTIVE MEANS OF SIGNIFICANTLY ENHANCING THE RESOLUTION OF MULTICOLUMN SETS TO BE USED FOR ANALYZING SPECIFIC POLYMER SYSTEMS

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ABSTRACT

Problems concerning GPC band spreading effects and their elimination were discussed, reference being also made to particular requirements to be met in the case of copolymer studies. GPC analysis optimization experiments were performed in order to minimize instrumental spreading for a multicolumn set operated in carbon tetrachloride. Results of experiments carried out at mobile phase flow rates of 1.0 , 0.3 and 0.1 cm^3/min for narrow MWD solutes were used to compute the values of the degree of polydispersity and other MWD obtainable parameters determining the extent of spreading minimization attained. The GPC data generated for runs conducted at the lowest flow rate employed were shown to have been rendered sufficiently accurate for the raw chromatograms to represent the polymers being analyzed without the need of performing mathematical corrections for imperfect GPC resolution.

INTRODUCTION

Gel permeation chromatography (GPC) is today a widely recognized method of determining the molecular weight distribution (MWD) of polymers. In this technique of instrumental analysis,the solvent flowing inside the GPC column set used constitutes the mobile phase to which is introduced a polymer solution forming a narrow rectangular band at the beginning of analysis. In the course of its migration in the column that band is gradually broadened as a result of processes taking place both inside the columns themselves and in the remaining elements of the chromatographic system(1,2).

Consequently,the MWD curves obtained for polydisperse polymer samples are generally too broad and somewhat skewed because the experimental chromatogram constitutes a composite picture of not only the MWD, but also of the superimposed instrumental spreading effects occurring in the chromatographic columns.

Distortion of experimental chromatograms due to the fact that the band broadening process interferes with the integrity of MWD information reflected by the GPC elution profile,is known to be highly detrimental to chromatographic resolution. Column dispersion effects are thus clearly the main source of errors in the quantitative interpretation of GPC analysis results leading to the determination of polymer molecular weights and MWDs(1-3).

To ensure accuracy and precision of experimental MWD information,the spreading effects resulting from specific features of individual experiments should be removed from the chromatograms,so as to be able to extract from them the desired intrinsic MWD characteristics of the analyzed polymer.

Since the magnitude of GPC peak dispersion effects depends on the rate of the mass transfer process occurring between the mobile phase(solvent) and the stationary phase(solvent trapped inside the pores of column packing),these phenomena are hence determined by such difficult to measure and control factors as pore structure and pore size distribution,microscopic flow irregularities in the packed chromatographic columns , as well as by solvent viscosity and flow rate,polymer sample concentration,and other extracolumn effects(4-6).

As a result,mathematical methods of correcting chromatograms for imperfect resolution require the application of suitable experimental calibration procedures that are by no means trivial to perform , as discussed briefly later on.

And that is the reason why the question of running GPC experiments in conditions making possible a significant minimization of instrumental spreading is of great importance as far as obtaining more accurate and correct MWD information from GPC analyses is concerned.

This trend is reflected by pertinent studies carried out to date on that problem(7-9). As a matter of fact,even though the findings relating to,for instance, resolution enhancement by decreasing solvent flow rate are admittedly not new(10),the problem of improving GPC separation efficiency by optimizing the chromatographic system operating variables continues to receive constant attention,as exemplified by a recent paper of Cooper(11).

The foregoing considerations had induced us to undertake an experimental study aimed at minimizing peak dispersion effects for a column set to be used in our investigations of random copolymers by multiple detector GPC technique. The importance of correcting for imperfect resolution also the chromatograms of polymers for which there is no unique relationship between their size in solution and molecular weight has been indicated in a recent review article(12).

The experiments were performed in carbon tetrachloride,selected as the mobile phase on the basis of its compatibility with one of the solute detectors,the use of the IR flow-through detector employed being limited to solvents transparent at the absorption wavelengths monitored in order to determine copolymer composition variations with respect to molecular weight(13-15).

In view of the relatively high viscosity of carbon tetrachloride(1.0 Cp at 20°C),its choice as GPC solvent constituted in our case an evident compromise between the attainable level of resolution and the amount of information to be obtained from the chromatograms , since solvent viscosity is a factor influencing directly the rate of solute permeation into the pores and hence controlling column dispersion(4-6).

Another aspect of the present work is concerned with the fact of its having been carried out using conventional GPC columns and packings(particle diameter 35 µm) known to yield significantly greater column dispersion effects than those produced by short columns with microparticulate packings(16).

In these conditions it seemed all the more worthwhile to perform the present GPC resolution enhancement study,as the expensive modern microparticulate packings requiring the use of costly high-pressure pumping equipment are not within everybody's reach.

EXPERIMENTAL

Apparatus and Operating Variables

The chromatographic analyses were performed using a Model 200 gel permeation chromatograph (maker:Waters Associates Inc.)equipped with a set of five conventional-type GPC columns(122 mm long;internal dia.0.95 mm) packed with Styragel and Poragel gels with particle diameter of 35 µm and pore sizes of: 10nm, 10^2nm, 10^3nm, $3x10^4$nm and 10^5nm. The Waters Associates R-400 series deflection-type differential refractometer and the Wilks Instruments MIRAN 1A infrared spectrometer were the solute detectors used.

Narrow molecular weight distribution(NMWD)polystyrene standards supplied by Waters Associates Inc.were used in the present work. Freshly distilled carbon tetrachloride(supplier:Polish Chemical Reagents POCh, Gliwice)was the GPC solvent employed.
The GPC experiments were conducted in an air-conditioned laboratory inside which a constant temperature of 21°C ± 1°C was maintained.

As a considerable increase of chromatographic resolution may be attained by reducing solvent flow rate(7,9) ,it was decided to investigate thoroughly the effect of mobile phase flow rate on separation efficiency for a chromatographic system set up for a copolymer study,as already indicated in the introductory section, The experiments were therefore run at the following flow rates:1.0 , 0.3 and 0.1 cm^3/min.

The multicolumn set was selected in such a way as to ensure the linearity of the GPC calibration curve in the molecular weight range of interest,which is in turn known to improve both resolution and accuracy of molecular weights calculated from experimental chromatograms (9,17,18). In order to improve the accuracy of GPC measurements at the low solvent flow rates applied,a suitably modified siphon was used to minimize solvent losses by evaporation(19). The retention volume of chromatographic peaks was determined by calculating the position of the first moment of the peak, known from theory to be independent of flow rate(2,6).

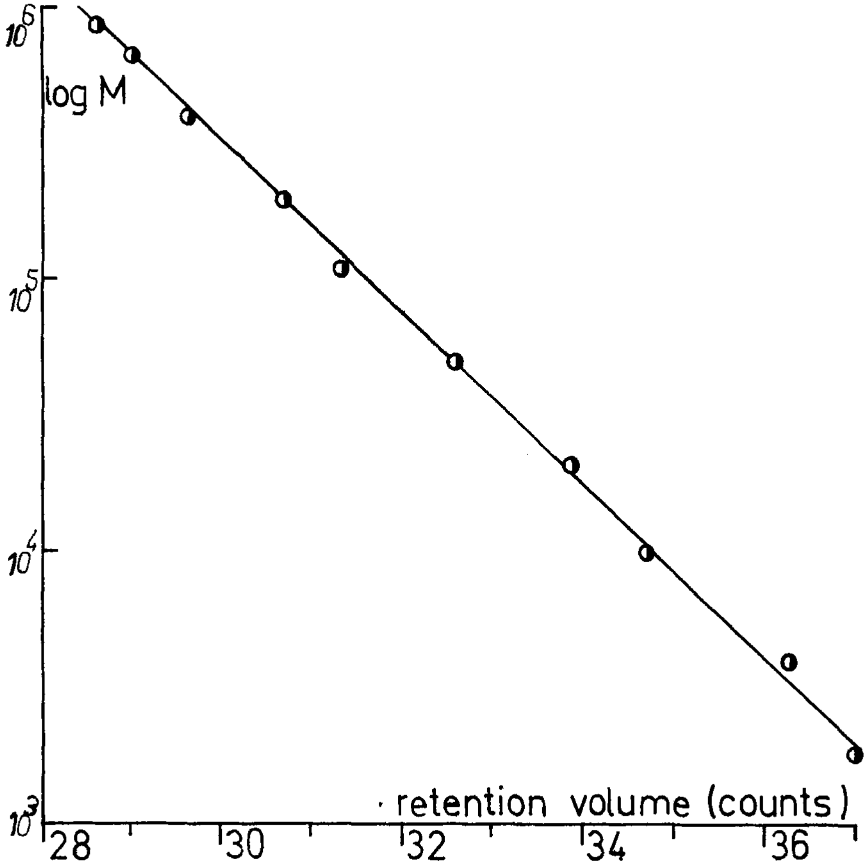

FIGURE 1 The linear calibration dependence obtained for the set of five conventional GPC columns used in the present work - column pore sizes: 10nm , 10^2nm , 10^3nm, $3x10^4$nm, and 10^5nm; GPC solvent:CCl_4 at 25^oC; solvent flow rate: 0.1 cm^3/min .

Optimization of GPC Analyses

The percentage deviation of the degree of polydispersity of NMWD polystyrene standards,determined experimentally from uncorrected chromatograms$(M_w/M_n)_u$, from the "true" polydispersity value quoted for those standards by their supplier $(M_w/M_n)_t$ was selected as a convenient criterion for estimating the effect of GPC solvent (CCl_4) flow rate on the separation efficiency of the multicolumn set employed.

This deviation, expressed overleaf as $\Delta(M_w/M_n)\%$, makes it possible to determine readily the attained resolution enhancement of the chromatographic system investigated, as the values of $(M_w/M_n)_u$ obtained from experimental chromatograms should be equal to their true values $(M_w/M_n)_t$ when the state of infinite resolution has been reached(20).

$$\Delta(M_w/M_n)\% = 100 \times \left[\frac{(M_w/M_n)_u - (M_w/M_n)_t}{(M_w/M_n)_t} \right] \qquad (1)$$

Additional criteria of assessing the attained extent of system resolution increase included the determination of the symmetrical spreading correction factor Λ (21) from uncorrected chromatograms recorded at the three solvent flow rates studied, and also the corresponding values of the specific resolution factor R_s, constituting a general measure of system efficiency(22). The symmetrical correction factor is given by the following relation (when $\Lambda \leqslant 1.05$ spreading effects can be neglected):

$$\Lambda = 0.5 \left[\frac{M_n(t)}{M_n(u)} + \frac{M_w(u)}{M_w(t)} \right] \qquad (2)$$

where :

$M_n(t)$, $M_w(t)$ - true values of the number and weight average molecular weights of the NMWD polystyrene standards

$M_n(u)$, $M_w(u)$ - values of the number and weight average molecular weights of the NMWD polystyrene standards computed from uncorrected chromatograms.

The specific resolution factor R_s was determined for the solvent flow rates studied using the relation given by Bly (22).

$$R_s = \frac{(V_2 - V_1)}{2(\sigma_1/d_1 + \sigma_2/d_2)\cdot\log(M_1/M_2)} \qquad (3)$$

where :

V_1, V_2 - retention volumes for standards with molecular weights M_1 and M_2 ,

σ_1, σ_2 - standard deviation of Gaussian peaks determined from experimental chromatograms of the NMWD samples and expressed in counts ,

d_1, d_2 - polydispersities of the NMWD samples "1" and "2", i.e. $(M_w/M_n)_t$

RESULTS AND DISCUSSION

Chromatographic analyses of a series of NMWD standards were carried out in conditions specified in the experimental section. The linear GPC calibration relationships found for the individual carbon tetrachloride flow rates studied were then used to determine the values of the optimization parameter $\Delta(M_w/M_n)\%$ and the molecular weights of the NMWD polystyrene standards analyzed. Computations were performed according to a program similar to that of Pickett et al (23)

The values of the degree of polydispersity $(M_w/M_n)_u$ and of the optimization parameter $\Delta(M_w/M_n)\%$ calculated from raw chromatograms obtained for the NMWD polystyrene samples at the different flow rates studied, are listed in table 1.

The values of the optimization parameter $\Delta(M_w/M_n)\%$ computed for the three different flow rates investigated were plotted as a function of molecular weight of the NMWD polystyrene samples (Figure 2).

TABLE 1

Values of the Degree of Polydispersity (M_w/M_n) and of the Optimization Parameter $\Delta(M_w/M_n)\%$ Computed from Uncorrected Chromatograms of the NMWD Samples Analyzed at the GPC Flow Rates Studied (CCl_4 at 25°C, Flow Rates - 1.0, 0.3 and 0.1 cm^3/min)

Sample	Standard M_w	$(M_w/M_n)_t$	$(M_w/M_n)_u$			$\Delta(M_w/M_n)\%$		
			1.0	0.3	0.1	1.0	0.3	0.1
1.	867,000	1.122	2.082	1.406	1.313	85.56	25.31	17.02
2.	390,000	1.098		1.228	1.170		11.83	6.55
3.	200,000	1.036	1.370	1.164	1.107	32.23	12.35	6.85
4.	111,000	1.045	1.354		1.104	29.56		5.64
5.	50,000	1.041			1.095			5.18
6.	20,800	1.04	1.268	1.131	1.089	21.92	8.75	4.71
7.	10,000	1.041	1.254	1.144	1.122	20.46	9.9	7.78
8.	4,000	1.103	1.280	1.190	1.127	16.04	7.88	2.17
9.	2,100	1.12	1.513	1.282	1.184	34.82	14.46	5.71

N.B. The true values of the degree of polydispersity quoted in table 1 for samples 4, 8 and 9 are those reported for them by Ambler (24).

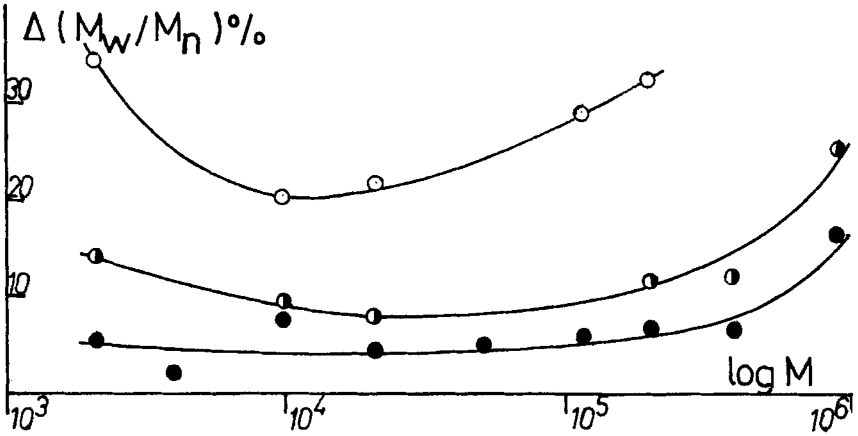

FIGURE 2 The experimental dependence of the optimization parameter M_w/M_n % on molecular weight, found for the different solvent flow rates investigated - CCl_4 at 25°C ; solvent flow rates: 1.0 cm^3/min - ○ , 0.3 cm^3/min - ◑ , 0.1 cm^3/min - ● .

The data listed in table 1 and depicted in figure 2 show clearly that for the lowest flow rate studied (0.1 cm^3/min) there has occurred a considerable reduction of the percentage deviation of the values of the degree of polydispersity determined from raw chromatograms $(M_w/M_n)_u$ from the true degree of polydispersity $(M_w/M_n)_t$ of the NMWD polystyrene standards chromatographed. The significant augmentation of GPC band broadening effects with molecular weight to be observed for the individual flow rates studied is in agreement with pertinent theoretical predictions(4-6, 25,26). Results of MWD analyses obtained for the NMWD samples studied were then utilized to determine the values of the GPC symmetrical spreading correction factor Λ (eqn.2) reflecting the band broadening effects present at the solvent flow rates investigated(21).

Values of the specific resolution factor R_s(22), constituting a qualitative indication of the overall separation efficiency of the chromatographic system, were also determined for the molecular weight range of interest. The obtained values of Λ and R_s were listed in tables 2 and 3.

It can be seen from table 2 that the experimental values of the correction factor Λ, calculated for the NMWD polymer samples studied at the GPC solvent flow rate of 0.1 cm^3/min, are less than 1.05 in the molecular weight range of interest.

This means that instrumental spreading effects have been minimized to such an extent that they may be neglected when interpreting GPC analysis results(8,21). That finding thus confirmed the conclusion drawn from the data listed in table 1 and figure 2, the results of R_s determinations indicating unequivocally the enhancement of overall separation efficiency.

Numerical values of the number(M_n) and weight(M_w) average molecular weights calculated for several NMWD polystyrene standards from chromatograms uncorrected for instrumental spreading effects are compared in table 4 with the corresponding M_n and M_w values quoted for those standards by their supplier.

The results listed in table 4 confirm the validity of observations already made, the improvement in the values of the number average molecular weights of the NMWD samples investigated becoming evident with the reduction of solvent flow rate.
The attained improvement of the accuracy of the numerical values of the number and weight average molecular weights is to be regarded as most satisfactory in the experimental conditions employed. It should be remembered that, in addition to GPC band broadening

TABLE 2

Values of the Symmetrical Spreading Correction Factor Λ Calculated for GPC Data Generated for the NMWD Samples at the Solvent Flow Rates Studied (CCl_4 at 25°C)

Sample	Spreading Correction Factor		
M_w	0.1 cm^3/min	0.3 cm^3/min	1.0 cm^3/min
390,000	1.033	1.058	
200,000	1.036	1.061	1.158
111,000	1.05		1.164
20,800	1.027	1.045	1.10
10,000	1.04	1.05	1.09
2,100	1.049	1.09	1.19

TABLE 3

Values of the Specific Resolution Factor R_s Determined at the Solvent Flow Rates Investigated (CCl_4 at 25°C)

Pairs of Standards	Specific Resolution Factor R_s		
M_{w1} , M_{w2}	0.1 cm^3/min	0.3 cm^3/min	1.0 cm^3/min
867,000 - 200,000	1.37	1.23	0.87
867,000 - 20,800	1.45	1.26	1.06
200,000 - 20,800	1.90	1.53	1.27
200,000 - 10,000	1.68	1.52	1.21
20,800 - 2,100	1.80	1.64	1.32
10,000 - 2,100	1.84	1.66	1.31

TABLE 4

Values of Number and Weight Average Molecular Weights of the NMWD Standards Computed from Raw Experimental Chromatograms Recorded at the GPC Solvent Flow Rates Studied (CCl_4 at 25°C).

Mol.wts.of	GPC Solvent Flow Rate (cm^3/min)		
Standards	0.1	0.3	1.0
773,000	668,000	671,000	478,000
867,000	877,000	944,000	995,000
355,000	353,000	330,000	
390,000	413,500	405,500	
111,000	108,500		93,700
111,000	119,700		127,000
20,200	18,100	20,400	17,700
20,800	19,700	23,100	22,500
1,950	1,870	1,850	1,530
2,100	2,200	2,370	2,320

effects,other sources of error are also to be reckoned with,e.g.errors involved with the choice of correct chromatogram baseline,or those committed when taking readings of chromatogram heights in the chromatographic data treatment stage (3,27) .

The practical value of the experimental approach to GPC resolution optimization carried out to obtain more accurate MWD information may be best appreciated by considering briefly the main problems involved in the general mathematical approach to the elimination of band broadening effects.

The mathematical correction of GPC chromatograms for imperfect resolution requires the determination of the relation between the experimental chromatogram

$F(v)$ of the investigated polymer sample and the molecular weight distribution function $W(M)$ that would be obtained in the absence of column dispersion processes described by the instrumental spreading function $G(v,M)$. It is to be emphasized that the relation between these three functions, given by Tung in the form of the below quoted, familiar convolution integral equation (4) for GPC band broadening, implies that the spreading of a component is not affected by its own concentration and concentrations of other components in solution.

$$F(v) = \int_0^\infty W(M)\ G(v,M)\ dM \qquad (4)$$

where: M - molecular weight, v - retention volume, $G(v,M)$ - normalized instrumental spreading function, $F(v)$, $W(M)$ - experimental and spreading corrected chromatograms, respectively.

Extraction of the function $W(M)$ representing the corrected chromatogram requires the selection of the correct spreading function and the determination of numerical values of its parameters.

Numerous methods of solving the equation (4) with respect to $W(M)$ for a known spreading function have been presented in the literature (29,30), most of them tacitly relying on the assumption that the chromatogram of a polymer sample is a linear superposition of individual chromatograms corresponding to all components of the polymer investigated. Since the elution of each species is known to depend somewhat on the concentration of all other species present, the above assumption may not be explicitly correct over certain concentration and molecular weight ranges (32,33).

Moreover, the spreading function $G(v,M)$ parameters are known to depend on the columns used and on the sizes of polymer molecules. They are also determined

by operating conditions,exhibiting a certain dependence on flow rate and polymer concentration(33).
The concentration dependence has not been yet elucidated adequately,and therefore spreading function treatments have been generally confined to the region of low concentrations in which concentration effects, and specifically species interactions,are sufficiently small to be neglected.

In the case of copolymers it is obviously necessary to exercise caution as far as the question of the absence of specific interactions is concerned (34). Should such interactions prove significant,it would be indeed difficult to maintain that the resolution factor(h) is really independent of polymer type, as asserted by Tung and Runyon in their treatment of the instrumental spreading problem(35).

It therefore becomes all the more important in the case of copolymers to ensure the attainment of an optimum overall resolution efficiency of the chromatographic system by appropriately optimizing experimental conditions.

The importance of such an approach to the minimization of GPC band broadening effects is further supported by the fact that the problem of choosing the correct spreading function has not yet been solved. In addition to the most often employed Gaussian model of the spreading function G(v,M) proposed by Tung et al.(36),numerous attempts have been made to apply more general,asymmetrical spreading functions with a larger number of parameters(37-42).
The main difficulty encountered in this connection is due to the fact that the accuracy of both absolute and GPC techniques of measuring average molecular weights of polymers is insufficient to determine accu-

rately the parameters of the more complex GPC spreading functions (1,42).

It should be pointed out that the application of calibration standards whose molecular weights are known with an accuracy of ± 5 % has been thought until recently to be sufficient for determining the parameters of the spreading function characteristic for a given chromatographic system. That belief has been nevertheless contradicted by numerous literature data (1,37,43). The practical determination of the spreading function suffers chiefly from the lack of good experimental methods of obtaining the values of the number average molecular weight (M_n) over a wide range of molecular weights, so that the commercially available polymer standards have insufficiently accurate M_n values assigned to them (43).

Significance of the above fact should be realized fully when attempting to determine the spreading correction factor (h) either by the extremely tedious reverse-flow experiment (1,35,36) or by computational methods, such as those of Hamielec and Ray (44) or Balke and Hamielec (45).

CONCLUDING REMARKS

In general, it has become widely accepted that the quantitative interpretation of GPC data for the purpose of obtaining correct polymer molecular weight averages requires the application of rather elaborate data treatment procedures in order to deconvolute band broadening effects from experimental chromatograms. Such an attitude among GPC users does tend to limit the number of those who venture beyond the scope of routine GPC data interpretation, even though the correction of raw chromatograms for those effects is well known to be indispensable for NMWD samples(36) and,as indicated by Kotaka and Donkai(46),the omission of band broadening correction may sometimes lead to serious errors also in the case of broad MWD polymer samples.In this situation,the present band broadening minimization study indicates clearly the immense practical value of GPC analysis optimization as an effective means of obtaining more correct and accurate MWD information.

In our case the choice of column length and packing porosity combination together with the application of a low solvent flow rate (0.1 cm^3/min)was found to result in a significant minimization of GPC spreading effects. The resultant increase of chromatographic system resolution was shown to produce such an improvement of the accuracy of GPC analyses that,in comparison with their true values,the values of average molecular weights of NMWD polymer samples computed from raw experimental chromatograms were found to be well within limits of experimental error(3,27).

It is to be further emphasized that the present study was effected for a chromatographic system operating in conditions generally considered as unfavourable to maximum resolution requirements,i.e.conventional type GPC packings with particle diameters of 35 µm and the viscous carbon tetrachloride as GPC solvent were employed.

At the same time,the increase of analysis time resulting from the application of low GPC solvent flow rate in the case of conventional column packings is thought to be offset entirely by the fact that more accurate GPC data are obtained without the necessity of resorting to the complex mathematical methods of eliminating GPC instrumental spreading effects.

Under these circumstances, the effectiveness of the optimization study reported herein is therefore all the more gratifying, and its results should prove particularly encouraging to those who wish to extract the maximum amount of information from their GPC experiments, but do not have access to modern microparticulate packings or special computer systems.

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