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Gel Permeation Chromatography Method for GPC System Definition and Performance Evaluation

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Synopsis

A practical method for the overall performance evaluation of a GPC system (columns) is described. System performance is defined as the ability of the system to give experimental $\bar{M}_n$ and $\bar{M}_w$ values (uncorrected for instrumental spreading and other distorting factors) which agree with the theoretical values, and it is expressed as the per cent deviation between the theoretical and experimental values. The method consists of running blends of monodispersed polystyrene standards of known compositions through the GPC system to be evaluated. From the resulting chromatograms, their $\bar{M}_n$ and $\bar{M}_w$ values are calculated (experimental). The theoretical $\bar{M}_n$ and $\bar{M}_w$ values of the same standards are also calculated from the formulas

$$\bar{M}_n = \frac{\Sigma M_i N_i}{\Sigma N_i} \text{ and } \bar{M}_w = \frac{\Sigma M_i^2 N_i}{\Sigma M_i N_i}$$

on the basis of their composition. By plotting the per cent difference of the experimental values from the theoretical values versus the theoretical values on a semilog scale, the overall performance of the GPC system under investigation is pictorially depicted. Results indicate that performance under experimental conditions can vary significantly from system to system. Results also indicate that performance of a system can be improved and optimized by proper column selection and system modifications.

INTRODUCTION

The accurate conversion of a gel permeation chromatogram to a quantitative molecular weight distribution (MWD) and average molecular weight ($\bar{M}_n$, $\bar{M}_w$) results has been, and still remains, one of the major problems facing GPC (gel permeation chromatography).

From the beginning, instrumental spreading or zone broadening,[1–5] which in turn was attributed to skewing and axial dispersion,[6] has been considered as the major obstacle for such a direct conversion. For example, the usual raw GPC output or gel permeation chromatogram does not exclusively represent the molecular weight distribution of the polymeric material under study, but a convolution of the instrumental spreading function and the molecular weight distribution function of the sample. A correction for the instrumental spreading

calibration curve(s). Several methods for correction of instrumental spreading have been proposed;[7-16] and although all of them are similar in principle and objective, the approach to the problem varies and so do some of the conclusions drawn.

The problem was first considered by Tung[17] who defined and expressed it mathematically with the well-known Tung's Integral Formula. The instrumental spreading function in the formula is characterized by the column Gaussian spreading constant h (proportional to the variance of the band) and a skewing factor k which was proposed later by Balke and Hamielec.[16] Hess and Kratz,[18] who carried out similar studies, consider the problem of axial dispersion. Their approach consists of evaluating the instrumental spreading function from the void function and the instrumental dispersion coefficient of each molecular species and correcting for it by computer deconvolution techniques. Still other workers,[19] in carrying out similar studies, take into account the continuous change in the shape of the chromatographic band for each individual species (SCBIS) due to molecular weight. A more aggressive investigation of the problem followed the proposition of the Tung's Integral Fomula. With the establishment of the formula, different approaches to its solution appeared in the literature. Tung himself[7] presented a treatment in which he allows for a nonlinear GPC calibration curve and possible variation of the resolution factor h with the elution volume. Duerksen and Hamielec[15] in their treatment assume h constant, along with a linear GPC calibration curve. Smit, Hoogervorst, and Staverman[20] in their method assume h to be dependent on elution volume and consider irrelevant if the GPC calibration curve is linear or not. Based on the approach used, some of the conclusions drawn by different workers vary also; i.e., Tung concludes that dispersion exerts an asymmetrical influence on the molecular weight averages. For example, it lowers the value of $\bar{M}_n$ and leaves the value of $\bar{M}_w$ practically unchanged. A similar effect is recognized in the results reported by Pickett, Cantow, and Johnson.[9] Hamielec and Ray predict a symmetrical increase and decrease of the $\bar{M}_n$ and $\bar{M}_w$ values, respectively, only as functions of the calibration parameters and resolution factor h and not depended on the broadness of the distribution curve. Balke and Hamielec,[16] in accounting for symmetrical axial dispersion and skewing, show that while both $\bar{M}_w$ and $\bar{M}_n$ are lowered by skewing, axial dispersion raises $\bar{M}_w$, but further lowers $\bar{M}_n$. They further show that skewing increases with molecular weight of the sample, linearity of the calibration curve, and concentration of the sample.

With all different approaches, propositions, and considerations mentioned above, plus the complex mathematics involved in making GPC corrections, it is easy to explain the "uncertain" state of development quantitative GPC is found today. Results obtained from investigations described here indicate that a more accurate and systematic study of the variables affecting GPC results can be accomplished by first properly defining the performance of the GPC system used to carry out such studies. Proper GPC system definition and performance evaluation is missing from GPC studies reported to date; the reason is evidently due to the unavailability of the proper method for carrying out such an evaluafunction is, therefore, necessary before the corrected chromatogram can be converted to molecular weight distribution and averages by the use of proper tion. The method described here seems to fill this need without resorting to complex mathematics.

EXPERIMENTAL

Materials and Equipment

Three Waters Associates gel permeation chromatographs were used in these studies, two GPC-200 models and one GPC/ALC 301 model. One of the GPC 200 models was equipped with two sets of columns. Each instrument is identified with its set(s) of columns in Table I. GPC styrogel columns used were also supplied by Water Associates, Framingham, Massachusetts. Column sets I, II, and III used in the GPC 200 models were made up of 4 ft × ⅜ in. columns, while column set IV, used in the GPC/ALC 301 model, was made up of 3 ft × ⅜ in. columns.

Column sequence in each column set with their packing exclusion limit is also given in Table I. Polystyrene monodispersed standards used for the preparation of the standard blends are given in Table II. Tetrahydrofuran (THF), GPC grade, was used as solvent and as carrier.

TABLE I
GPC Instruments, Column Banks, Column Sequence in Each Column Set, and Individual Column Exclusion Limits

Column set	GPC no.	Exclusion limit of each column, Å				
		First	Second	Third	Fourth	Fifth
I	GPC 200A	10,000,000	1,000,000	30,000	8,000	—
II	GPC 200B	20,000	700	700	250	—
III	GPC 200B	400,000	30,000	8,000	500	60
IV	GPC/ALC 301	100,000	10,000	1,350	90	65

TABLE II
Polystyrene Standards with Their $\bar{M}_n$, $\bar{M}_w$, and D Values

Polystyrene standard		$\bar{M}_n$	$\bar{M}_w$	D
PS-1	1.99×10^6	1.78×10^6	2.14×10^6	1.20
PS-2	1.80×10^6	1.71×10^6	1.89×10^6	1.11
PS-3	6.70×10^5	6.38×10^5	7.02×10^5	1.10
PS-4	4.98×10^5	4.04×10^5	5.07×10^5	1.25
PS-5	1.71×10^5	1.64×10^5	1.73×10^5	1.05
PS-6	8.30×10^5	7.73×10^5	8.67×10^5	1.12
PS-7	4.02×10^5	3.92×10^5	4.11×10^5	1.05
PS-8	9.72×10^4	9.62×10^4	9.82×10^4	1.02
PS-9	5.00×10^4	4.90×10^4	5.10×10^4	1.04
PS-10	2.03×10^4	2.03×10^4	2.04×10^4	1.01
PS-11	1.97×10^4	1.96×10^4	1.98×10^4	1.01
PS-12	1.00×10^4	9.70×10^3	1.03×10^4	1.06
PS-13	1.03×10^4	1.03×10^4	1.03×10^4	1.00
PS-14	4.80×10^3	4.60×10^3	5.00×10^3	1.09
PS-15	3.60×10^3	3.53×10^3	3.67×10^3	1.04
PS-16	2.10×10^3	2.05×10^3	2.15×10^3	1.05
PS-17	9.00×10^2	8.92×10^2	9.08×10^2	1.02
PS-18	6.00×10^2	5.63×10^2	6.37×10^2	1.13
PS-19	2.10×10^2	2.10×10^2	2.10×10^2	1.00
PS-20	1.04×10^2	1.04×10^2	1.04×10^2	1.00

TABLE III
Monodispersed Polystyrene Standard Blends with Their Per Cent Composition

Blend no.	Single std. no.	% by weight	Blend no.	Single std. no.	% by weight	Blend no.	Single std. no.	% by weight
1	PS-2	50.00		PS-8	19.64	26	PS-7	41.10
	PS-4	50.00		PS-12	20.04		PS-17	20.63
				PS-14	20.24		PS-20	38.26
2	PS-5	50.00		PS-17	19.44			
	PS-2	50.00				27	PS-7	40.92
			15	PS-2	50.00		PS-17	21.40
3	PS-8	32.93		PS-8	25.00		PS-20	37.93
	PS-4	33.74		PS-18	25.00			
	PS-2	33.34				28	PS-2	50.00
			16	PS-14	56.00		PS-8	25.00
4	PS-9	50.00		PS-17	44.00		PS-18	25.00
	PS-3	50.00						
			17	PS-12	33.33	29	PS-13	75.00
5	PS-10	50.00		PS-14	33.33		PS-20	25.00
	PS-3	50.00		PS-17	33.33			
						30	PS-10	8.33
6	PS-11	50.00	18	PS-14	50.00		PS-13	8.33
	PS-6	50.00		PS-17	50.00		PS-15	16.67
							PS-16	16.67
7	PS-2	26.60					PS-18	25.00
	PS-4	26.00	19	PS-14	52.00		PS-19	25.00
	PS-8	25.40		PS-17	48.00			
	PS-13	22.00				31	PS-10	5.56
			20	PS-8	20.00		PS-13	5.56
8	PS-6	50.00		PS-11	20.00		PS-15	11.12
	PS-11	50.00		PS-12	20.00		PS-16	11.12
				PS-16	20.00		PS-18	33.34
9	PS-1	25.00		PS-20	20.00		PS-19	33.34
	PS-5	25.00						
	PS-11	25.00	21	PS-2	20.00	32	PS-10	1.40
	PS-14	25.00		PS-8	20.00		PS-13	1.40
				PS-12	20.00		PS-15	6.94
10	PS-6	70.00		PS-17	20.00		PS-16	6.94
	PS-16	30.00		PS-20	20.00		PS-18	41.66
							PS-19	41.66
11	PS-6	71.30	22	PS-8	25.00			
	PS-16	28.70		PS-12	25.00	33	PS-10	2.05
				PS-17	25.00		PS-13	2.05
12	PS-2	16.60		PS-20	25.00		PS-15	6.85
	PS-4	17.00	23	PS-8	50.00		PS-16	6.85
	PS-8	17.10		PS-12	25.00		PS-18	41.10
	PS-12	15.90		PS-17	25.00		PS-19	41.10
	PS-14	16.70						
	PS-17	16.70				34	PS-10	0.76
			24	PS-8	41.18		PS-13	0.76
13	PS-1	30.00		PS-12	29.41		PS-15	3.79
	PS-5	25.00		PS-17	29.41		PS-16	3.79
	PS-11	25.00					PS-18	45.45
	PS-14	20.00	25	PS-2	41.75		PS-19	45.45
				PS-12	19.53			
14	PS-4	20.64		PS-20	38.72	35	PS-10	0.58

TABLE III (*Continued*)

Blend no.	Single std. no.	% by weight	Blend no.	Single std. no.	% by weight	Blend no.	Single std. no.	% by weight
	PS-13	0.58		PS-19	5.55		PS-4	30.00
	PS-15	2.91					PS-8	40.00
	PS-16	2.91	40	PS-10	41.67			
	PS-18	46.51		PS-12	41.67	46	PS-2	40.00
	PS-19	46.51		PS-15	6.94		PS-4	30.00
				PS-16	6.94		PS-8	30.00
36	PS-10	0.47		PS-18	1.39			
	PS-13	0.47		PS-19	1.39	47	PS-2	20.00
	PS-15	2.36					PS-4	80.00
	PS-16	2.36	41	PS-10	45.45			
	PS-18	47.17		PS-13	45.45	48	PS-2	25.00
	PS-19	47.17		PS-15	3.79		PS-4	75.00
				PS-16	3.79			
37	PS-10	0.47		PS-18	0.76	49	PS-8	66.66
	PS-13	0.47		PS-19	0.76		PS-11	22.22
	PS-15	2.35					PS-12	11.12
	PS-16	2.36	42	PS-10	75.47			
	PS-18	18.86		PS-13	18.87	50	PS-10	25.24
	PS-19	75.47		PS-15	2.35		PS-13	28.04
				PS-16	2.35		PS-15	18.69
38	PS-10	12.50		PS-18	0.48		PS-16	18.69
	PS-13	12.50		PS-19	0.48		PS-18	9.34
	PS-15	25.00						
	PS-16	25.00	43	PS-8	9.09	51	PS-14	38.00
	PS-18	12.50		PS-10	60.61		PS-17	62.00
	PS-19	12.50		PS-12	30.30			
						52	PS-10	12.50
39	PS-10	33.33	44	PS-2	20.00		PS-13	8.34
	PS-13	33.33		PS-4	20.00		PS-15	16.67
	PS-15	11.10		PS-8	60.00		PS-16	16.67
	PS-16	11.10					PS-18	25.00
	PS-18	5.55	45	PS-2	30.00		PS-19	20.84

Procedure

A series of polystyrene standard blends were prepared by weighing the proper amount of each standard separately and then mixing all of them together to make up the particular blend. The weight of each standard used in each blend was equal to the percentage of the overall weight of the blend (before put into solution) given in Table III. The blends were dissolved in THF to give 0.5% overall solutions. The resulting solutions were chromatographed as such or further diluted to as low as 0.1% before use, as needed. The extent of dilution depended on the differential refractometer response by the different components of each blend. Experimental conditions used are as follows: solvent flow rate, 1 ml/minute; count size, 5 ml/5 min; temperature, 25° ± 1°C.

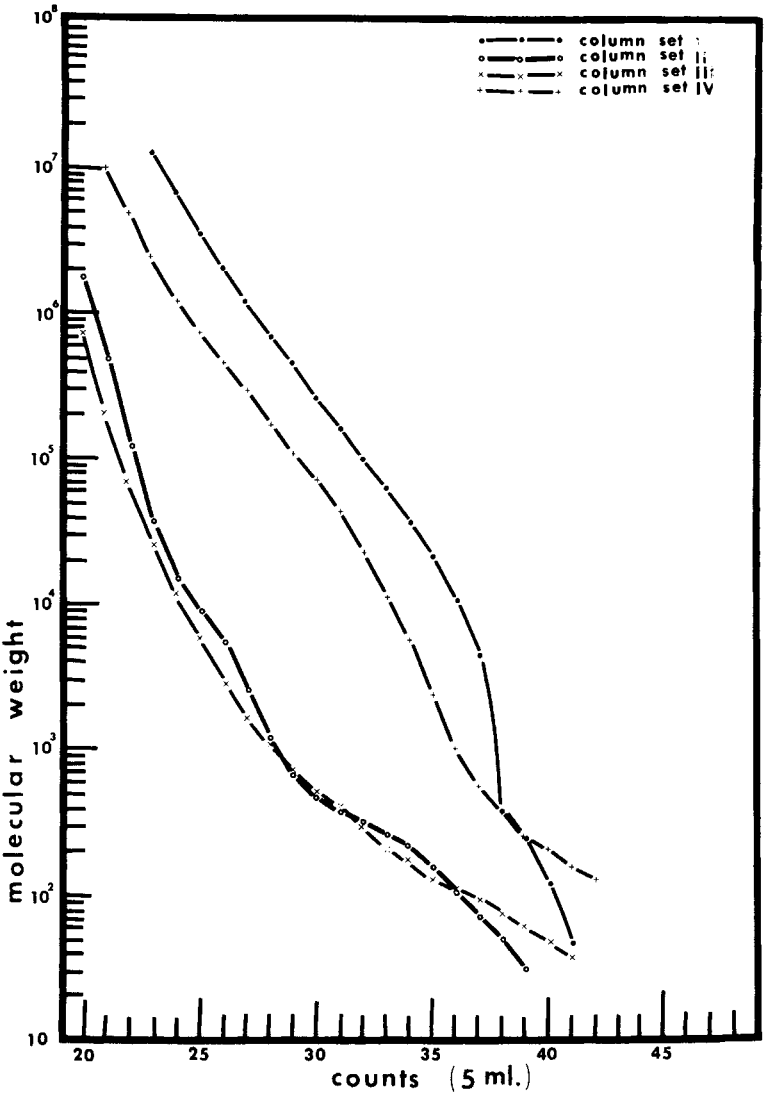

Fig. 1. Calibration curves for the GPC systems (column sets) I, II, III, and IV.

The four GPC systems (GPC column sets) were calibrated according to the accepted standard procedure; calibration curves obtained (by plotting log molecular weight of standard versus its peak position (in counts) are shown in Figure 1. Data from these calibration curves were incorporated into the computer programs used for the calculations. The solution of each standard blend listed in Table III was chromatographed at least in triplicate with each set of columns. Solutions of single polystyrene standards (the same used in preparing the blends) were used for the calibration of all four sets of columns.

Calculations

The GPC chromatograms which resulted from the chromatographying of the different standard blend solutions were used for the calculation of the $\bar{M}_n$ and $\bar{M}_w$ values for each blend, thus obtaining four sets of values (one for each set of

TABLE IV
Theoretical and Experimental $\bar{M}_w$ Values

Blend no.	Theoretical $\bar{M}_w$	Experimental $\bar{M}_w$ values			
		I	II	III	IV
1	1.15×10^6	1.01×10^6	7.32×10^5	8.38×10^5	1.00×10^6
2	9.82×10^5	7.06×10^5	5.38×10^5	6.00×10^5	7.26×10^5
3	8.00×10^5	6.80×10^5	5.55×10^5	5.61×10^5	7.67×10^5
4	3.75×10^5	3.83×10^5	3.07×10^5	2.77×10^5	3.31×10^5
5	3.60×10^5	3.95×10^5	3.15×10^5	2.99×10^5	4.43×10^5
6	4.44×10^5	4.89×10^5	3.90×10^5	3.12×10^5	3.73×10^5
7	6.34×10^5	5.48×10^5	5.95×10^5	4.46×10^5	7.43×10^5
8	4.44×10^5	4.08×10^5	2.91×10^5	3.42×10^5	4.69×10^5
9	5.84×10^5	4.38×10^5	3.91×10^5	3.62×10^5	5.06×10^5
10	6.07×10^5	5.60×10^5	5.19×10^5	4.02×10^5	5.71×10^5
11	6.07×10^5	5.59×10^5	5.15×10^5	5.71×10^5	6.98×10^5
12	4.03×10^5	3.86×10^5	3.05×10^5	3.02×10^5	3.47×10^5
13	3.46×10^5	4.19×10^5	3.37×10^5	3.27×10^5	3.67×10^5
14	1.27×10^5	1.56×10^5	1.15×10^5	11.5×10^5	1.56×10^5
15	9.20×10^5	7.11×10^5	2.97×10^5	5.75×10^5	9.94×10^5
16	3.20×10^3	4.98×10^3	5.43×10^3	3.30×10^3	2.91×10^3
17	5.40×10^3	7.43×10^3	8.81×10^3	4.90×10^3	6.22×10^3
18	2.95×10^3	4.22×10^3	4.49×10^3	2.51×10^3	2.12×10^3
19	3.04×10^3	4.92×10^3	4.39×10^3	2.63×10^3	3.22×10^3
20	2.60×10^4	3.20×10^4	3.07×10^4	2.89×10^4	3.08×10^4
21	3.80×10^5	3.49×10^5	3.33×10^5	3.31×10^5	3.68×10^5
22	2.74×10^4	2.66×10^4	3.75×10^4	2.52×10^4	2.55×10^4
23	5.19×10^4	7.32×10^4	4.46×10^4	4.78×10^4	5.50×10^4
24	4.37×10^4	5.51×10^4	5.47×10^4	4.11×10^4	4.19×10^4
25	7.49×10^5	6.25×10^5	4.70×10^5	5.24×10^5	6.96×10^5
26	1.69×10^5	2.47×10^5	1.88×10^5	1.74×10^5	1.74×10^5
27	1.68×10^5	2.32×10^5	1.80×10^5	1.52×10^5	1.83×10^5
28	9.20×10^5	7.08×10^5	5.70×10^5	6.16×10^5	7.90×10^5
29	7.75×10^3	10.63×10^3	11.65×10^3	6.35×10^3	7.91×10^3
30	3.89×10^3	6.03×10^3	5.34×10^3	4.25×10^3	4.40×10^3
31	2.68×10^3	4.30×10^3	4.32×10^3	3.11×10^3	3.09×10^3
32	1.20×10^3	2.29×10^3	1.99×10^3	1.44×10^3	1.35×10^3
33	1.40×10^3	2.71×10^3	2.17×10^3	1.63×10^3	1.43×10^3
34	8.48×10^2	15.45×10^2	13.66×10^2	12.04×10^2	7.70×10^2
35	7.49×10^2	15.23×10^2	12.07×10^2	9.89×10^2	8.78×10^2
36	6.88×10^2	16.56×10^2	10.77×10^2	10.39×10^2	6.18×10^2
37	5.67×10^2	14.66×10^2	9.66×10^2	8.28×10^2	4.99×10^2
38	5.49×10^3	7.97×10^3	8.22×10^3	6.98×10^3	5.34×10^3
39	1.09×10^4	1.34×10^4	1.60×10^4	1.19×10^4	1.29×10^4
40	1.32×10^4	1.73×10^4	1.81×10^4	1.27×10^4	1.42×10^4
41	1.44×10^4	1.57×10^4	1.73×10^4	1.14×10^4	1.40×10^4
42	1.75×10^4	2.26×10^4	2.35×10^4	1.71×10^4	2.01×10^4
43	2.13×10^4	2.58×10^4	2.55×10^4	2.43×10^4	2.58×10^4
44	5.18×10^5	5.61×10^5	3.95×10^5	4.29×10^5	6.20×10^5
45	7.28×10^5	4.80×10^5	3.05×10^5	6.20×10^5	7.88×10^5
46	8.98×10^5	5.85×10^5	4.25×10^5	7.79×10^5	10.26×10^5
47	7.64×10^5	5.03×10^5	5.80×10^5	4.64×10^5	6.18×10^5
48	8.27×10^5	7.54×10^5	3.45×10^5	7.51×10^5	9.53×10^5
49	7.25×10^4	4.50×10^4	8.85×10^4	8.10×10^4	6.58×10^4
50	9.12×10^3	12.78×10^3	12.47×10^3	9.59×10^3	8.45×10^3
51	2.46×10^3	3.74×10^3	3.80×10^3	2.66×10^3	2.25×10^3
52	4.61×10^3	6.69×10^3	7.39×10^3	4.98×10^3	4.28×10^3

TABLE V
Theoretical and Experimental $\overline{M}_n$ Values

Blend no.	Theoretical $\overline{M}_n$	Experimental $\overline{M}_n$ values			
		I	II	III	IV
1	6.46×10^5	3.79×10^5	1.87×10^5	2.34×10^5	4.84×10^5
2	2.98×10^5	2.61×10^5	1.03×10^5	1.58×10^5	2.32×10^5
3	2.24×10^5	2.05×10^5	$.98 \times 10^5$	1.64×10^5	1.28×10^5
4	9.12×10^4	9.39×10^4	5.68×10^4	6.22×10^4	6.60×10^4
5	3.98×10^4	4.31×10^4	3.50×10^4	2.90×10^4	4.21×10^4
6	3.83×10^4	4.55×10^4	2.93×10^4	3.49×10^4	2.95×10^4
7	4.03×10^4	5.35×10^4	3.87×10^4	2.94×10^4	4.27×10^4
8	3.13×10^5	2.25×10^5	1.37×10^5	1.82×10^5	3.38×10^5
9	1.45×10^4	1.91×10^4	1.60×10^4	1.31×10^4	1.32×10^4
10	6.79×10^3	4.47×10^3	5.07×10^3	4.43×10^3	4.25×10^3
11	7.25×10^3	6.09×10^3	6.15×10^3	5.65×10^3	4.36×10^3
12	4.13×10^3	3.27×10^3	3.94×10^3	3.10×10^3	3.46×10^3
13	1.73×10^4	2.13×10^4	1.74×10^4	1.18×10^4	1.26×10^4
14	3.51×10^3	2.74×10^3	3.08×10^3	2.60×10^3	2.24×10^3
15	2.23×10^3	1.33×10^3	1.94×10^3	1.35×10^3	1.54×10^3
16	1.63×10^3	1.17×10^3	1.76×10^3	1.18×10^3	1.25×10^3
17	2.08×10^3	1.48×10^3	1.87×10^3	1.63×10^3	2.24×10^3
18	1.50×10^3	1.27×10^3	1.45×10^3	1.18×10^3	1.25×10^3
19	1.54×10^3	1.42×10^3	1.40×10^3	1.37×10^3	$.94 \times 10^3$
20	4.87×10^2	4.61×10^2	4.71×10^2	4.62×10^2	4.62×10^2
21	4.61×10^2	5.14×10^2	5.31×10^2	5.59×10^2	3.86×10^2
22	3.69×10^2	3.17×10^2	3.57×10^2	4.50×10^2	3.58×10^2
23	3.21×10^3	2.73×10^3	2.25×10^3	1.86×10^3	3.07×10^3
24	2.74×10^3	1.95×10^3	2.68×10^3	2.52×10^3	2.16×10^3
25	2.67×10^2	2.52×10^2	2.75×10^2	3.13×10^2	2.88×10^2
26	2.56×10^2	2.95×10^2	3.18×10^2	3.30×10^2	2.82×10^2
27	2.59×10^2	2.65×10^2	2.80×10^2	2.74×10^2	2.48×10^2
28	2.24×10^3	1.83×10^3	1.59×10^3	1.84×10^3	1.97×10^3
29	4.04×10^2	4.21×10^2	5.21×10^2	3.87×10^2	4.31×10^2
30	5.64×10^2	5.35×10^2	6.95×10^2	6.02×10^2	5.08×10^2
31	4.41×10^2	3.92×10^2	4.69×10^2	4.94×10^2	3.31×10^2
32	3.60×10^2	3.31×10^2	4.37×10^2	3.77×10^2	3.28×10^2
33	3.63×10^2	3.75×10^2	4.06×10^2	4.14×10^2	4.17×10^2
34	3.33×10^2	3.03×10^2	3.76×10^2	4.27×10^2	4.06×10^2
35	3.26×10^2	3.75×10^2	3.33×10^2	3.16×10^2	3.47×10^2
36	3.22×10^2	3.35×10^2	4.10×10^2	3.67×10^2	2.42×10^2
37	2.53×10^2	2.74×10^2	2.89×10^2	2.83×10^2	3.06×10^2
38	9.73×10^2	8.36×10^2	10.02×10^2	8.59×10^2	7.75×10^2
39	2.02×10^3	1.59×10^3	2.08×10^3	1.42×10^3	1.82×10^3
40	4.81×10^3	2.83×10^3	4.07×10^3	4.18×10^3	4.52×10^3
41	6.91×10^3	3.59×10^3	4.41×10^3	3.93×10^3	5.46×10^3
42	9.60×10^3	11.35×10^3	9.20×10^3	8.12×10^3	8.53×10^3
43	1.28×10^4	1.43×10^4	1.39×10^4	0.90×10^4	1.03×10^4
44	1.46×10^5	1.66×10^5	1.04×10^5	1.18×10^5	1.15×10^5
45	1.97×10^5	1.69×10^5	1.16×10^5	1.39×10^5	1.65×10^5
46	2.45×10^5	2.68×10^5	1.55×10^5	2.05×10^5	2.23×10^5
47	4.75×10^5	4.19×10^5	2.23×10^5	3.47×10^5	4.33×10^5
48	5.01×10^5	3.65×10^5	3.74×10^5	2.80×10^5	4.28×10^5
49	3.36×10^4	4.03×10^4	3.60×10^4	2.96×10^4	2.76×10^4
50	2.88×10^3	1.78×10^3	2.85×10^3	2.52×10^3	3.63×10^3
51	1.28×10^3	1.01×10^3	1.20×10^3	0.96×10^3	1.22×10^3
52	6.34×10^2	5.44×10^2	7.04×10^2	5.96×10^2	4.79×10^2

columns) for each blend. Calculations were carried out according to Cazes.[22] The baseline and count height measurements for each chromatogram were carried out manually. Actual calculations were carried out by computer. The results obtained (experimental values) are listed in Tables IV and V. The corresponding theoretical $\bar{M}_n$ and $\bar{M}_w$ values for each standard blend were calculated by the use of formulas (1) and (2), respectively:

$$\bar{M}_n = \frac{\Sigma M_i N_i}{\Sigma N_i} \tag{1}$$

$$\bar{M}_w = \frac{\Sigma M_i{}^2 N_i}{\Sigma M_i N_i} \tag{2}$$

M_i in formula (1) was substituted by the $\bar{M}_n$ values of each of the polystyrene monodispersed standards used in each blend. M_i in formula (2) was substituted by the $\bar{M}_w$ values of the same polystyrene standards used in the same blend. ($\bar{M}_n$ and $\bar{M}_w$ values of individual polystyrene standards used are listed in Table II.) N_i values used in formulas (1) and (2) were obtained by dividing the fraction weight in grams of each polystyrene standard in the blend by its corresponding first molecular moment. After the experimental and theoretical $\bar{M}_n$ and $\bar{M}_w$ values of each blend were determined, their per cent difference was calculated by formula (3):

$$\% \text{ difference} = \frac{\text{theoretical value} - \text{experimental value}}{\text{theoretical value}} 100 \tag{3}$$

It must be noted that when the per cent difference is calculated, the theoretical values are considered the correct ones; and, as a result, the experimental values are subtracted from the theoretical values. If an experimental value is larger than a corresponding theoretical value, a negative per cent difference value is obtained, and vice versa. The per cent difference of the experimental values from the theoretical values versus the theoretical values is shown in Figures 2 and 3.

RESULTS AND DISCUSSION

From the theoretical point of view, the behavior of a single-component solute zone in GPC can be fully characterized by two phenomenologic parameters:[23] (1) the partition coefficient which determines the average rate of solute transport within the column(s) and reflects the degree of gel pores penetration by the solute molecules, and (2) the axial dispersion coefficient (equivalent plate height) which describes spreading of the solute zone on the column(s) under specified operating conditions. For noninteracting multicomponent systems (like the ones studied here), the behavior of solute zones is determined by the values of the above parameters for each species plus the weight fraction of each species in the sample blend. Considering these two parameters for the four GPC systems (column sets studied here) and knowing that all sample blends, as well as operating conditions used, were the same for all four systems, differences in $\bar{M}_n$ and $\bar{M}_w$ values depicted in Figures 2 and 3, respectively, can only be indirectly attributed to basic differences in the GPC systems themselves (mainly the column sets and probably, partly, the components of the instruments involved such as detectors, column connecting tubing, etc.).

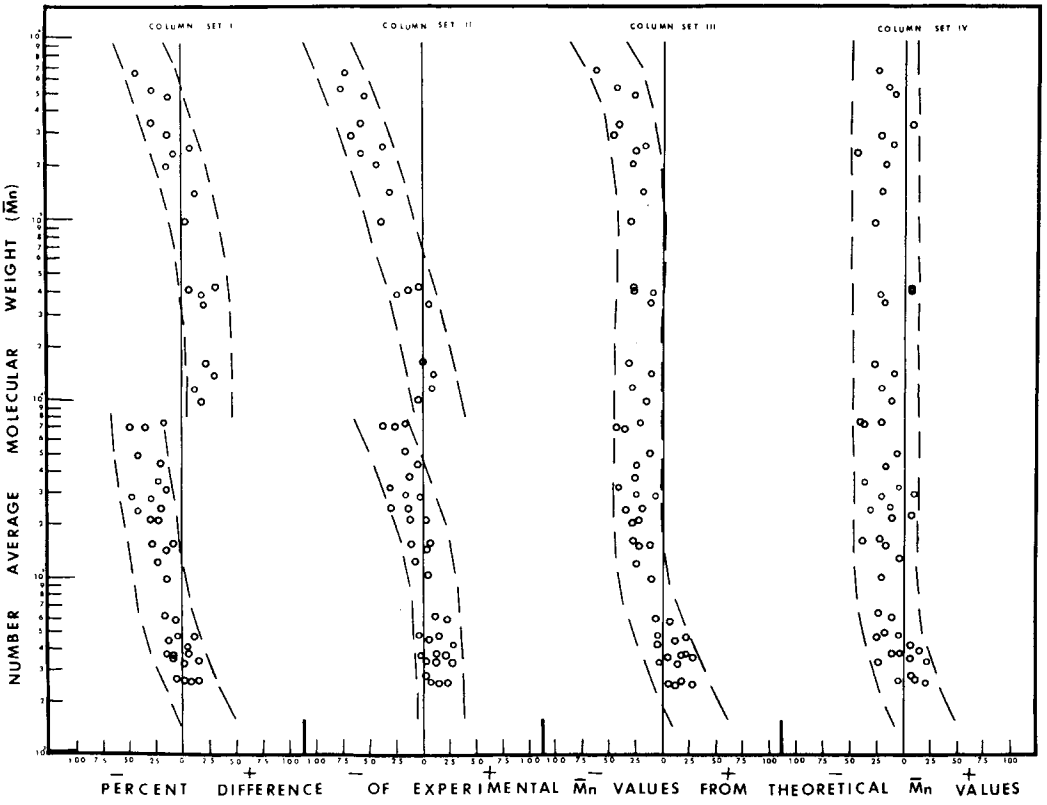

Fig. 2. Per cent difference of the experimental $\bar{M}_n$ values from the theoretical $\bar{M}_n$ values vs. the theoretical $\bar{M}_n$ values for the GPC systems (column sets) I, II, III, and IV.

Since the overall chromatogram of a polydispersed (composite) sample represents a superposition of the chromatograms of the individual monodispersed standards or species making up the sample, and since the chromatogram of each individual species is described by a Gaussian[2] function, these differences in column sets are responsible for the deviations (in degree and direction) of the chromatograms of the individual species from their theoretical Gaussian shape curves. In turn, the cumulative differences of the chromatograms of the individual species in each composite sample are responsible for the deviations of the experimental $\bar{M}_n$ and $\bar{M}_w$ values from the corresponding theoretical (calculated from formulas) $\bar{M}_n$ and $\bar{M}_w$ values depicted in Figures 2 and 3. By examining the results in Figures 2 and 3, the following observations can be made:

1. Reproducibility of uncorrected (for instrumental spreading) GPC results is estimated at ±25%. This reproducibility decreases to as much as ±50% when different samples with close $\bar{M}_n$ and $\bar{M}_w$ values are compared. The uncorrected $\bar{M}_n$ and $\bar{M}_w$ values of a sample can differ from the corrected or theoretical values from zero to as much as ±175%, depending on the size of these values and the GPC system used to obtain them. (The per cent coefficient of variation (% CV) of data discussed here was found by statistical evaluation to range between 3% and 9%.) It must be noted that no special effort was made to obtain exceptionally accurate results in these studies.

2. Comparing results obtained by the four different GPC systems, the per cent

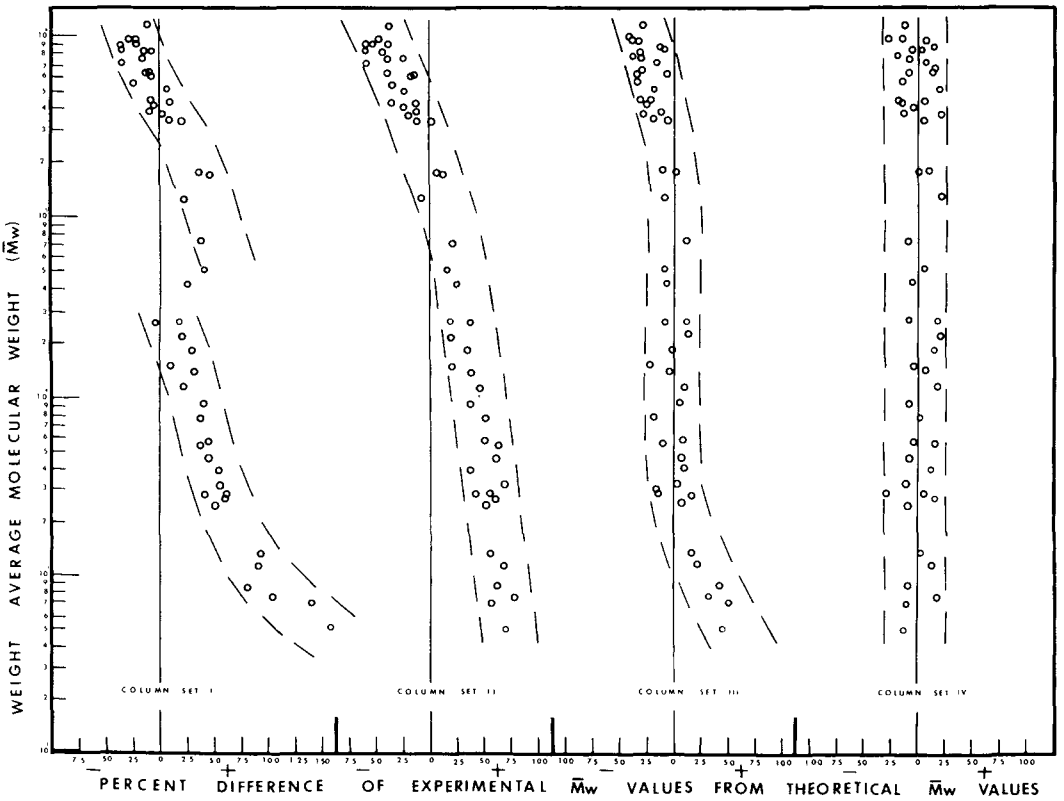

Fig. 3. Per cent difference of the experimental $\bar{M}_w$ values from the theoretical $\bar{M}_w$ values vs. the theoretical $\bar{M}_w$ values for the GPC systems (column sets) I, II, III, and IV.

deviation of the experimental from the theoretical values decreases in degree and increases in uniformity as we go from column set I to column set IV. This deviation is especially drastic and unusual for values obtained with column sets I and II. These two column sets happen to be made up of individual columns with the larger differences in exclusion limits and pore size distribution as compared to column sets III and IV. The "gapping" or "discontinuity" effect resulting from these two sets of columns could be attributed to the "gapping" or "discontinuity" of the exclusion limits of the columns in the column sets. Considering column set I, for example, the exclusion limit goes from 1,000,000 Å to 30,000 Å (i.e., column(s) in the 100,000 Å exclusion limit range are missing). In column set II, similarly, the exclusion limit goes from 20,000 Å to 700 Å (i.e., column(s) in the 1,000 Å to 10,000 Å exclusion limit range are missing). This discontinuity in column porosity exclusion limits or effect is not present in column sets III and IV. The pore size distribution and porosity exclusion limits for the columns making up these two sets of columns are more uniform, and this could account for the smaller per cent deviation and the greater uniformity in deviation of the results.

Comparing $\bar{M}_n$ values obtained with column sets III and IV (Fig. 2), it can be noticed that $\bar{M}_n$ values obtained with column set III deviate more to the left from the zero per cent deviation line than the $\bar{M}_n$ values obtained with column set IV. This could be attributed to the fact that porosity exclusion limits for columns

in column set IV are consistently lower than those making up column set III (see Table I). This could, in turn, be associated with the degree of pore penetration by the different molecular species in the various sample blends.

Although the above correlations are only empirical, the proposed method for GPC system evaluation accomplishes two things. First, it gives an overall qualitative and quantitative picture of the performance of a GPC system under specific operating conditions. In practice, this is what the GPC worker needs to know in order to properly interpret his results. Second, the method suggests that further investigations of factors affecting GPC system performance and which have already been evaluated in a piecemeal fashion should be reevaluated in the light of the overall performance of a GPC system. GPC column arrangement in a column set, according to porosity exclusion limit, has recently been investigated,[24] for example, and it is concluded that a random column arrangement is preferred over the descending (most accepted) and ascending order. The conclusion, however, is made only on the basis of variance between results obtained with different column arrangements.

From the above results, it is evident that lower per cent variance in results obtained from a column set does not necessarily indicate the best column arrangement, although such an arrangement would tend to eliminate or minimize the column "gapping effect" mentioned above. One aspect of GPC column arrangement which has not been thoroughly investigated is the effect of column "discontinuity" or "gapping" of porosity exclusion limits, i.e., the effect of using GPC columns of drastically different exclusion limits in series. Many cases in the literature have been noted in which investigations were carried out under such conditions without any mention or suspicion of the drastic effect this could have on the GPC results.

Throughout these studies, $\bar{M}_n$ and $\bar{M}_w$ values of monodispersed and blends of monodispersed polystyrene standards are discussed and compared. In evaluating these results, the reader should remember that the accuracy of some of these values is limited, i.e., it is well known that there is no way to accurately determine $\bar{M}_n$ above 500,000. Also, in calculating molecular moments by the use of the formula

$$\bar{M}^* = \frac{\Sigma N_i M_i{}^b}{\Sigma N_i M_i (b-1)}$$

the accuracy decreases as b increases from 1 to 2, etc. One advantage in these studies is that data and results are evaluated in a comparative way which tends to cancel out some of the inaccuracies.

Comparison of results in Figures 2 and 3 and the shape of the calibration curves in Figure 1 (prepared from points corresponding to 5-ml counts on the original calibration curves and used in the computer programs), from which these results were calculated, shows that calibration curve linearity is not necessarily required for best GPC system performance.

Recommendations

Recent interlaboratory statistical studies carried out by two groups[25,26] for the purpose of evaluating the accuracy and reproducibility of the GPC method as an analytical tool show the method to be less than reliable. One group[25] de-

clared the method as unfit to be used for quality control and specification analyses. The other group[26] reported over 100% variance in the results obtained by the participating laboratories. Both studies were carefully planned and closely controlled, except for the GPC systems used for which no detailed description or evaluations are given. It was assumed that the performance of all systems is more or less the same, and mostly all differences in performance are eliminated after calibration with the same standards and according to the same accepted calibration procedure. As is shown above, this assumption is not necessarily true, and this seems to be the reason for the large variances in the statistical evaluation results.

On the basis of the above investigations, the author recommends the following steps to be taken for the increase in reliability and confidence in gel permeation chromatography as an analytical tool.

1. **Standardization of GPC Columns.** A standard set of GPC columns made up of a set number of individual columns of specific size and packed with packings of set porosity exclusion limits should be established for universal use, preferably by the ASTM Committee on GPC. The standard column set should either cover all size molecules presently studied by this technique, or more than one standard column set should be established, each covering a certain range of molecular weights.

2. **Standardization of Calibration Procedure for the GPC System.** A GPC system used in any GPC study should be calibrated according to a two-step procedure which should involve: (a) a column performance evaluation test as described here, and (b) a final calibration procedure which should include, besides the presently accepted (log molecular weight versus standard peak position in counts) method, a working or corrected calibration curve as described by Baker.[27] The standard blends to be used for the GPC system evaluation should be specified for common use. Established polydispersed standards could also be used instead for this purpose. In such a case, the calculation of the theoretical $\bar{M}_n$ and $\bar{M}_w$ values should be eliminated in the procedure since these values will be furnished with the standards. If from step a the performance of the system is unacceptable, changes in the system should be made for acceptable performance before calibration step b is attempted.

Why the Above Recommendations

From the work described here, it is evident that instrumental spreading, and other factors affecting GPC results, are very much associated with the performance of the GPC system used. This should be expected since GPC is an exclusion-type chromatography and depends on molecular size distribution. As a result, the separation should be more dependent on the physicochemical properties of the column set involved. In fact, GPC can roughly be compared to a "reverse type" sieve particle size analysis. Just like in a sieve analysis the particle size distribution results for a sample is very much dependent on the number and sequence of sieves as well as the mesh of screens used, similarly, GPC results should depend on the number, sequence, and porosity exclusion limits of columns used. In the second case, the number of columns involved is even more critical because the chromatographing time is limited by the physical properties of the columns and the solvent flow rate. This limitation is eliminated

in the first case by extending the sifting time until complete separation is accomplished.

The calibration procedure presently being used is analytically incorrect. In calibrating any type of instrument, the calibration procedure is usually similar to the analytical procedure except that standards used in the calibration are replaced by the unknown samples. According to the accepted GPC calibration procedure, the calibration curve is constructed by plotting log molecular weight of the individual standards used versus their peak position in counts. When an unknown sample is analyzed, however, the area under the chromatogram is also considered in calculating the results. The construction of corrected calibration curves during calibration step b, suggested above, is to take care of this omission or abnormality. This step in reality corrects for polydispersities of the individual polystyrene standards for the particular GPC system.[27] Whitehouse,[28] by using narrow and board molecular weight distribution standards to generate Benoit's[29] universal calibration curve, demonstrates that the universal calibration is universal only if dispersities of the standards used are taken into account.

References

1. R. N. Kelley and F. W. Billmeyer, *Anal. Chem.*, **41**, 824 (1969).
2. R. N. Kelley and F. W. Billmeyer, *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, **15**, A157 (1970).
3. A. C. Ouano and J. A. Biesenberger, *J. Appl. Polym. Sci.*, **14**, 471 (1970).
4. A. C. Ouano and J. A. Biesenberger, *J. Appl. Polym. Sci.*, **14**, 483 (1970).
5. F. W. Billmeyer, G. W. Johnson, and R. N. Kelley, *J. Chromatogr.*, **34**, 316 (1968).
6. J. H. Duerksen, paper presented at the National ACS Meeting, Houston, Texas, February 22-27, 1970.
7. L. H. Tung, *J. Appl. Polym. Sci.*, **10**, 1271 (1966).
8. E. Rosen and T. Provder, 9th International Seminar on Gel Permeation Chromatography Preprints, Miami Beach, Florida, October 1970.
9. H. E. Pickett, M. J. Cantow, and J. F. Johnson, *J. Polym. Sci. C*, **21**, 67 (1968).
10. W. N. Smith, *J. Appl. Polym. Sci.*, **11**, 639 (1967).
11. P. E. Pierce and J. E. Armonas, *J. Polym. Sci. C*, **21**, 23 (1968).
12. T. E. Aldhouse and D. M. Stanford, 5th International Seminar on Gel Permeation Chromatography Preprints, London, May 1968.
13. T. Ishige, S. Lee, and A. Hamielec, 9th International Gel Permeation Chromatography Preprints, Miami, Florida, October 1970.
14. T. Vladimiroff, 9th International Seminar on Gel Permeation Chromatography Preprints, Miami, Florida, October 1970.
15. J. H. Duerksen and A. E. Hamielec, *J. Polym. Sci. C*, **21**, 83 (1968).
16. S. T. Balke and A. E. Hamielec, *J. Appl. Polym. Sci.*, **13**, 1381 (1969).
17. L. H. Tung, *J. Appl. Polym. Sci.*, **10**, 375 (1966).
18. M. Hess and R. F. Kratz, *J. Polym. Sci. A-2*, **4**, 731 (1966).
19. D. D. Novikov, N. G. Taganov, G. V. Korovina, and S. G. Entelis, *J. Chromatogr.*, **53**, 117 (1970).
20. J. A. M. Smit, C. J. P. Hoogervorst, and A. J. Staverman, *J. Appl. Polym. Sci.*, **15**, 1479 (1971).
21. A. E. Hamielec and W. H. Ray, *J. Appl. Polym. Sci.*, **13**, 1319 (1969).
22. J. Cazes, *J. Chem. Educ.*, **43**, (A576, A625), July–Aug. (1966).
23. H. R. Halvorson and G. K. Ackers, *J. Polym. Sci. A-2*, **9**, 245 (1971).
24. P. M. James and A. C. Ouano, *J. Appl. Polym. Sci.*, **17**, 1455 (1973).
25. H. E. Adams, E. Ahad, M. S. Chang, D. B. Davis, D. M. French, H. J. Hyer, R. D. Law, R. J. J. Simkins, J. E. Stuchbury, and M. Trembley, *J. Appl. Polym. Sci.*, **17**, 269 (1973).

26. ASTM Committee D-20.70.04, Gel Permeation Chromatography Minutes, Atlantic City, New Jersey, June 30, 1971.
27. J. R. Baker, *J. Appl. Polym. Sci.*, **15**, 411 (1971).
28. B. A. Whitehouse, *Macromolecules*, **4** (4), July–Aug. (1971).
29. H. Benoit, P. Rempp, and Z. Grubisic, *Polym. Lett.*, **5**, 753 (1967).

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