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Mathematical Analysis of Gel Permeation Chromatography Data

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Synopsis

The purpose of this paper is to show how a theoretical molecular weight distribution can be found which would result in a given gel permeation chromatogram. Also, to show how the method can be applied to blending problems where one desires a given molecular weight distribution.

Introduction

Gel permeation chromatography (GPC) is a method for the determination of molecular weight distributions of high polymers developed by Moore.[1] Relative to other standard methods, GPC is quite rapid. However, in many instances the polymer is such that good resolution is obtainable only from columns up to 20 ft. in length with perhaps 20,000 theoretical plates. Elution rates in the order of 1 ml./minute are used. The total time required for analysis is several hours. If shorter columns and higher elution rates are used, one obtains chromatographs in which, at best, only partial separation of species is observable. Nevertheless, this considerably speeds up the analysis and it is desirable that meaningful conclusions be obtainable from these data.

The purpose of this paper is to show how a theoretical molecular weight distribution can be found which would result in a given gel permeation chromatogram and also to show how the method can be applied to blending problems where one desires a given molecular weight distribution.

This method differs from that proposed by Tung[2] in that it does not require the distribution to be a continuum. It does not require smoothing of experimental data as in the method of Hess and Kratz[3] but does at present utilize a symmetrical pattern of axial dispersion. Such a pattern was shown to be useful by Tung et al.[4]

Background

Moore and Hendrickson[5] have shown that narrow molecular weight fractions give GPC curves that are bell-shaped, corresponding closely to the normal or Gaussian distribution function. Each species or narrow fraction is eluted at a given volume characteristic of the column packing,

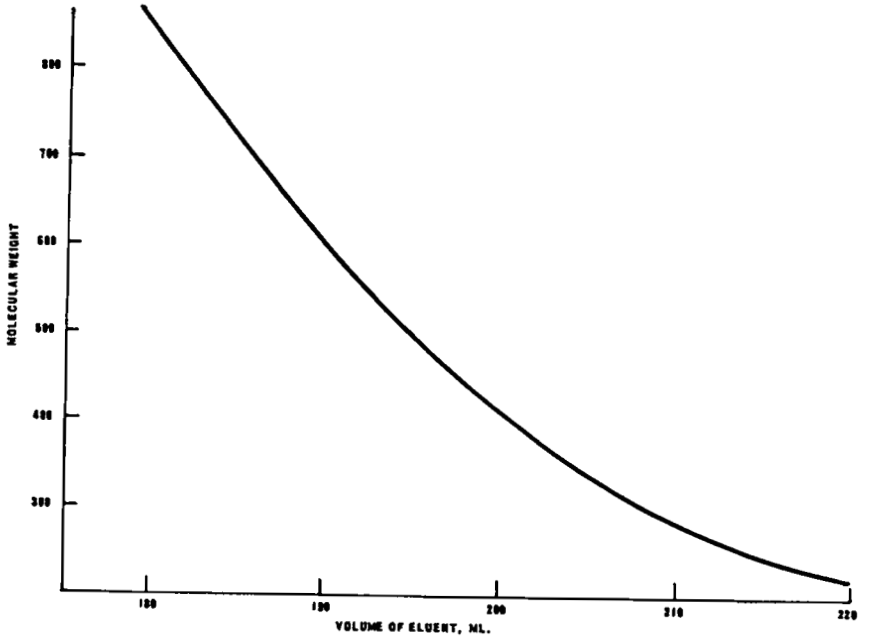

Figure 1.

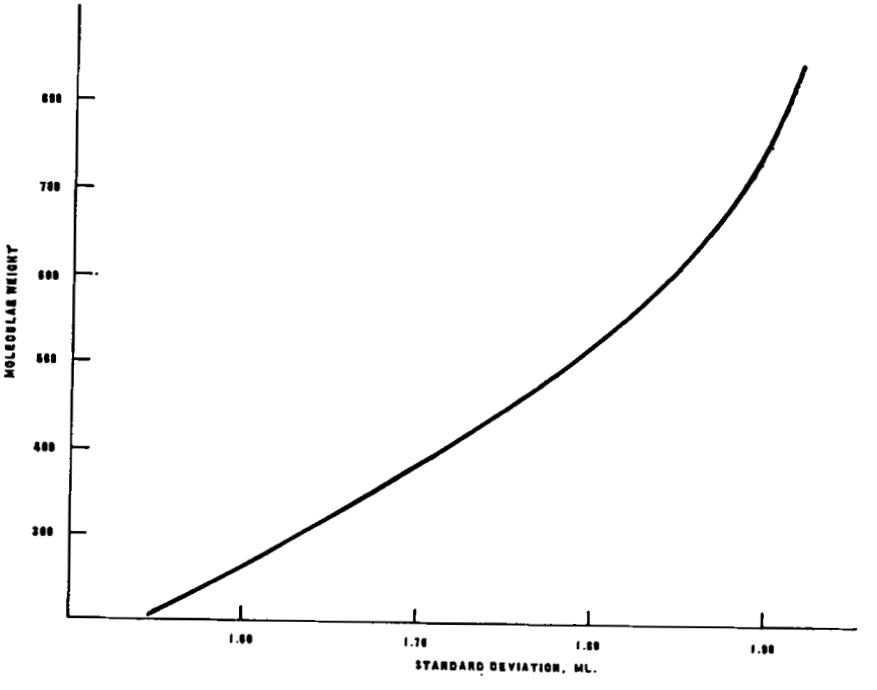

Figure 2.

molecular weight (average), solvent, and operating conditions. They have also found that at moderate loading the peak widths (hence, standard deviations) are independent of the loading. Thus, it is possible to calibrate a column by using samples of known narrow molecular weight distributions, determining the elution volume at the peak and the standard deviation. Techniques for obtaining calibration curves are described by Tung et al.[4] Figures 1 and 2 show calibration curves replotted from the data of Moore and Hendrickson.[5]

Derivation of Equations

After calibration, one can write the equation for a GPC of a narrow molecular weight sample as

$$g(x) = (K/\sqrt{2\pi}\sigma) \exp -\{(x_0^2 - x)^2/2\sigma^2\} \quad (1)$$

where x_0 and σ are obtained from the calibration curves and K is a proportionality constant such that

$$K = g(x_0)\sqrt{2\pi}\sigma$$

Now consider the upper curve of Figure 3 as a typical GPC curve obtained by plotting refractive index versus eluent volume.

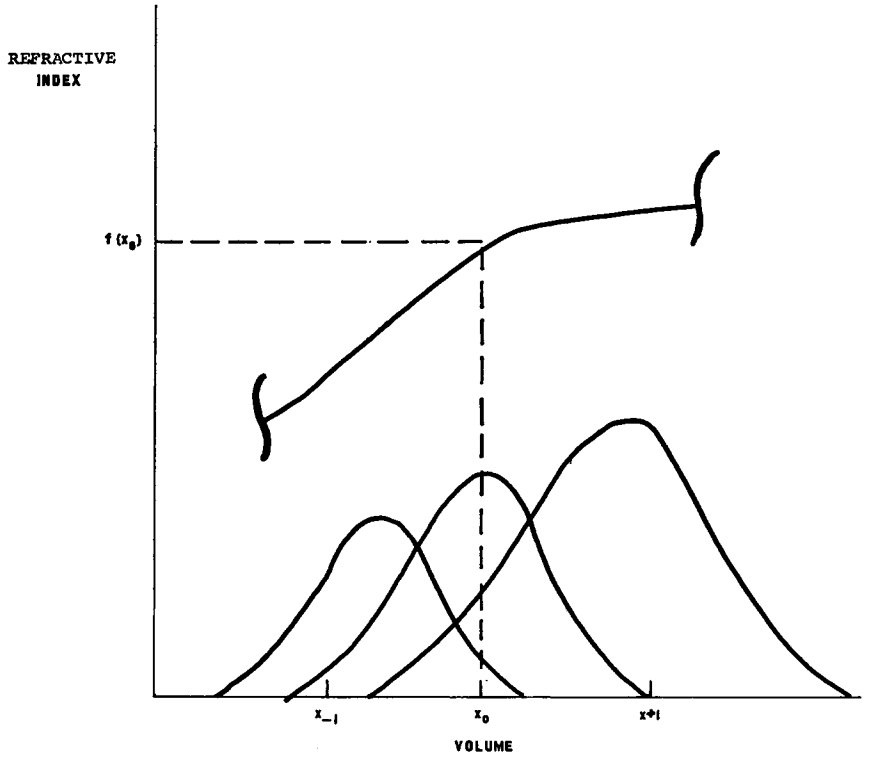

Figure 3.

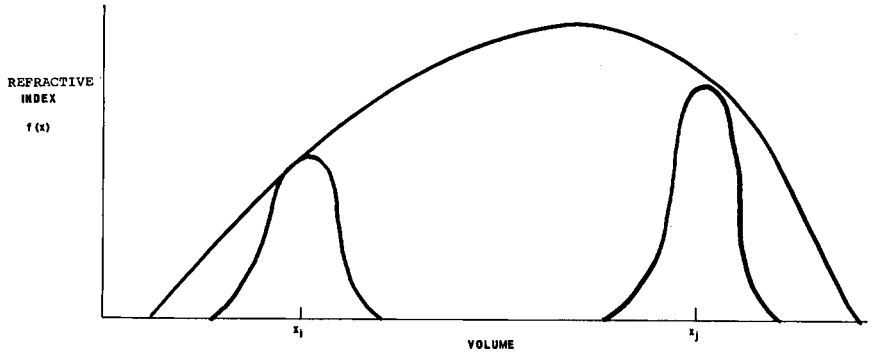

Figure 4.

TABLE I
Gel Permeation Chromatography for Sample No. 1 (Polyglycol P400 Data Base Case)

Vol., ml.	Ht. obs.	Sig.	k	Ht. calc.	Per cent	Cum. per cent	M.W.
180.00	0.00	1.88	0.00	0.00	0.00	0.00	850.0
182.50	0.80	1.88	1.29	0.21	0.12	0.12	773.0
183.60	1.60	1.88	0.00	0.00	0.00	0.12	750.0
184.60	3.10	1.86	2.02	1.34	0.77	0.90	715.0
185.80	5.30	1.86	0.00	0.00	0.00	0.90	690.0
186.90	7.80	1.83	2.33	3.96	2.25	3.16	656.0
188.20	12.00	1.83	0.00	0.00	0.00	3.16	625.0
189.50	16.90	1.80	2.53	9.48	5.30	8.46	598.0
190.80	23.00	1.80	0.00	0.00	0.00	8.46	570.0
192.10	30.10	1.77	2.70	18.32	10.06	18.53	540.0
193.50	37.10	1.77	0.00	0.00	0.00	18.53	510.0
194.80	44.20	1.73	3.20	32.54	17.55	36.08	482.0
196.60	48.20	1.73	0.00	0.00	0.00	36.08	450.0
198.30	54.20	1.69	3.72	47.53	25.02	61.10	424.0
200.30	41.10	1.69	0.00	0.00	0.00	61.10	390.0
202.40	41.30	1.64	3.86	38.64	19.75	80.86	366.0
204.70	23.50	1.64	0.00	0.00	0.00	80.86	333.0
207.10	27.20	1.59	3.98	27.19	13.43	94.29	308.0
210.10	8.00	1.59	0.00	0.00	0.00	94.29	275.0
213.10	12.10	1.51	3.80	12.10	5.70	99.99	250.0
216.00	0.00	1.51	0.00	0.00	0.00	99.99	233.0
230.00	0.00	1.51	0.00	0.00	0.00	99.99	197.0

$\bar{M}_w$:	$0.426E + 03$
$\bar{M}_n$:	$0.403E + 03$
$\bar{M}_v$:	$0.422E + 03$
M_w/K_n:	$0.105E + 01$
$\bar{M}_z$:	$0.449E + 03$
$\bar{M}_{z+1}$	$0.471E + 03$
J:	$0.744E - 08$

Per cent of total weight of sample accounted for: 101.36

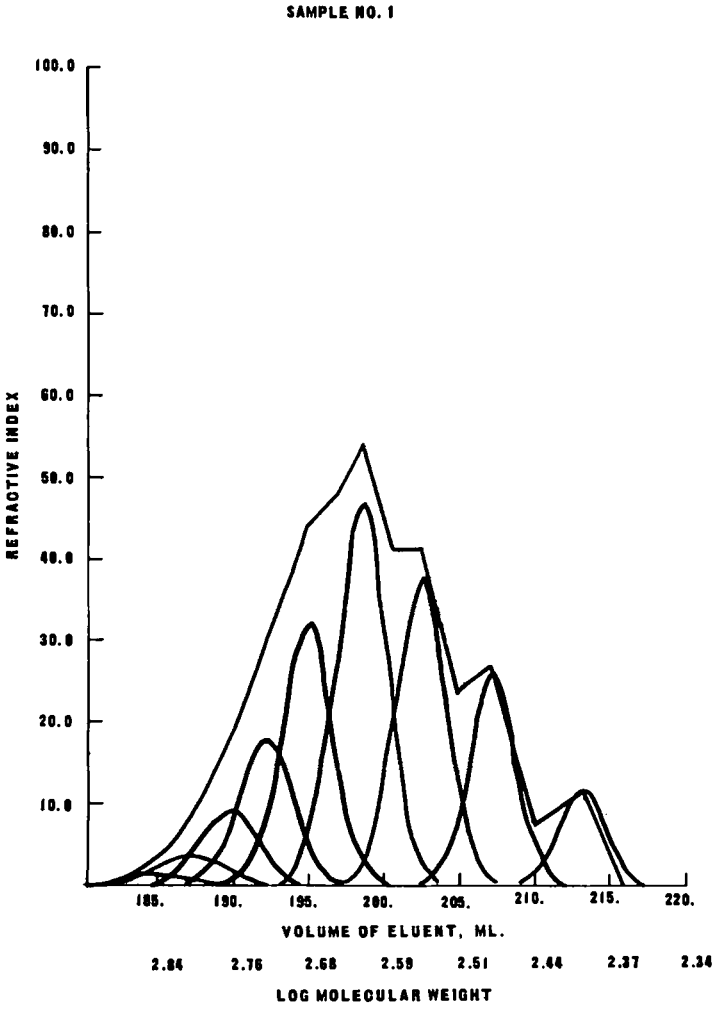

Figure 5.

It is postulated that the concentration of polymer in the eluent at point x_0 is due not only to the particular species eluted at that point but also consists of species having adjacent elution points. We can express this mathematically as

$$f(x_0) = \ldots + \frac{K_{-1}}{\sqrt{2\pi}\sigma_{-1}} \exp -\left\{\frac{(x_0 - x_1)^2}{2\sigma_{-1}^2}\right\} + \frac{K_0}{\sqrt{2\pi}\sigma_0}$$

$$\exp -\left\{\frac{(x_0 - x_1)^2}{2\sigma_0^2}\right\} + \frac{K_1}{\sqrt{2\pi}\sigma_1} \exp -\left\{\frac{(x_0 - x_1)^2}{2\sigma_2^2}\right\} + \ldots \quad (2)$$

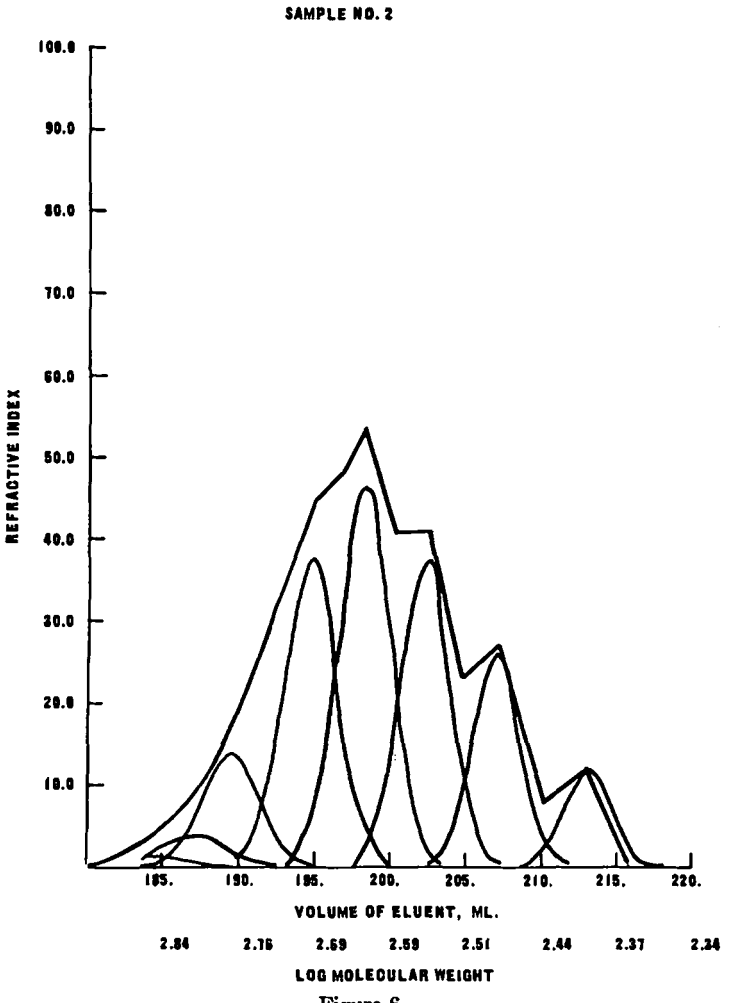

Figure 6.

where K_j is a scaling factor proportional to the concentration of the jth molecular species. K_j is generally unknown but it is reasonable to assume that it is proportional to the refractive index value at x_j, i.e.,

$$K_j = k_j f(x_j) \tag{3}$$

Letting $h = 1/2\sigma^2$ and indexing the molecular species from 0 to n we can rewrite eq. (2) as

$$f(x_j) = k_j f(x_0)(h_0/\pi)^{1/2} \exp -\{h_0(x_j - x_0)^2\} + k_j f(x_1)(h_1/\pi)^{1/2} \exp -\{h_1(x_j - x_1)\} + \ldots + k_j f(x_n)(h_n/\pi)^{1/2} \exp -\{h_n(x_j - x_n)^2\}$$

or

$$f(x_j) = k_j \sum_{i=0}^{n} (h_j/\pi)^{1/2} f(x_i) \exp -\{h_i(x_j - x_i)^2\} \quad (4)$$

k_j is a proportionality constant relating the concentration (refractive index) of molecular species j to the concentration of total polymer in the eluent at point x_j. Since x_j and σ_j can be determined by calibration runs, eq. (4) can be solved for k_j.

Per Cent of Components

The area under a bell-shaped curve centered at x_j, if it is Gaussian, is proportional to its peak height and standard deviation. From eq. (4) we get the peak height $H(x)$ as

$$H(x_j) = k_j f(x_j)(h_j/\pi)^{1/2} \quad (5)$$

TABLE II
Gel Permeation Chromatography for Sample No. 2
(Polyglycol P400 Data with Component Omitted at 192.1 ml.)

Vol. ml.	Ht. obs.	Sig.	k	Ht. calc.	Per cent	Cum. per cent	M.W.
180.00	0.00	1.88	0.00	0.00	0.00	0.00	850.0
182.50	0.80	1.88	1.29	0.21	0.13	0.13	773.0
183.60	1.60	1.88	0.00	0.00	0.00	0.13	750.0
184.60	3.10	1,86	2.02	1.34	0.81	0.94	715.0
185.80	5.30	1.86	0.00	0.00	0.00	0.94	690.0
186.90	7.80	1.83	2.33	3.96	2.35	3.29	656.0
188.20	12.00	1.83	0.00	0.00	0.00	3.29	625.0
189.50	16.90	1.80	3.87	14.49	8.45	11.74	598.0
190.80	23.00	1.80	0.00	0.00	0.00	11.74	570.0
192.10*	30.10	1.77	0.00	0.00	0.00	11.74	540.0
193.50	37.10	1.77	0.00	0.00	0.00	11.74	510.0
194.80	44.20	1.73	3.79	38.45	21.62	33.37	482.0
196.60	48.20	1.73	0.00	0.00	0.00	33.37	450.0
198.30	54.20	1.69	3.72	47.53	26.08	59.45	424.0
200.30	41.10	1.69	0.00	0.00	0.00	59.45	390.0
202.40	41.30	1.64	3.86	38.64	20.59	80.05	366.0
204.70	23.50	1.64	0.00	0.00	0.00	80.05	333.0
207.10	27.20	1.59	3.98	27.19	14.00	94.05	308.0
210.10	8.00	1.59	0.00	0.00	0.00	94.05	275.0
213.10	12.10	1.51	3.80	12.10	5.94	99.99	250.0
216.00	0.00	1.51	0.00	0.00	0.00	99.99	233.0
230.00	0.00	1.51	0.00	0.00	0.00	99.99	197.0

$\bar{M}_w$:	$0.420E + 03$
$\bar{M}_n$:	$0.398E + 03$
$\bar{M}_v$:	$0.417E + 03$
$\bar{M}_w/\bar{M}_n$:	$0.105E + 01$
M_z:	$0.444E + 03$
M_{z+1}	$0.467E + 03$
J:	$0.739E - 08$

Per cent of total weight of sample accounted for: 97.23

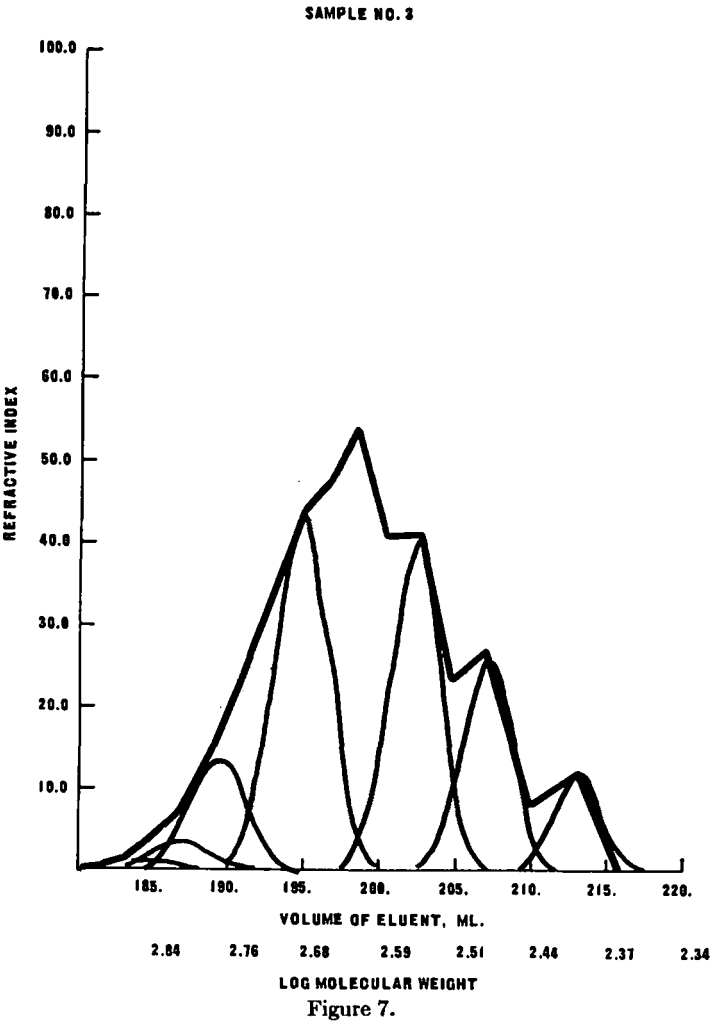

Figure 7.

and its area is

$$A_j = \int_{-\infty}^{\infty} k_j f(x_j)(h_j/\pi)^{1/2} \exp -\{h_j(x_j - x)^2\}dx = k_j f(x_j) \qquad (6)$$

Equation (6) can be solved for each assumed species (or narrow fraction of species). Since the weight of a species (or fraction) is directly proportional to the area A_j, we can find the per cent of a given species by,

$$\text{Per cent of species } j = (A_j/(\Sigma A_j) \times 100 \qquad (7)$$

Check on the Assumed Components

This, of course, is a percentage of total weight of assumed species. It is not necessarily the percentage of species j in the polymer sample. In

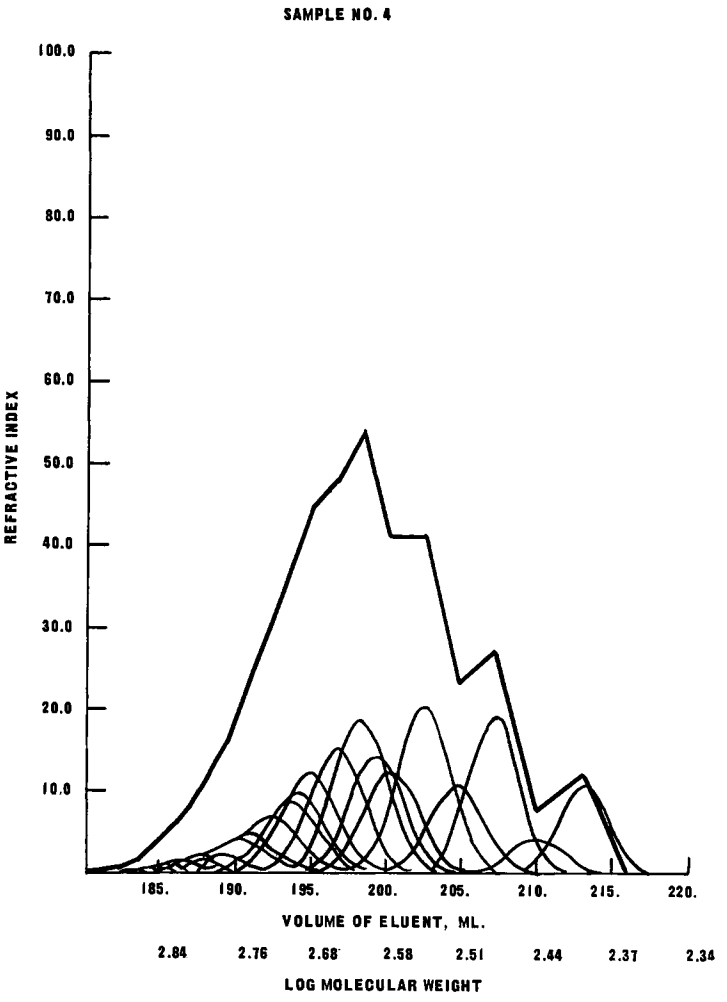

Figure 8.

fact, species j may not even be present. What we have determined is a theoretical composition which would give a GPC coinciding, at each elution volume corresponding to an assumed species, with the GPC we obtained.

We might further illustrate this point with a hypothetical example. In Figure 4, if we assumed that the polymer contained only species x_i and x_j, eqs. (4) and (5) would determine the peak heights of the bell-shaped curves centered at x_i and x_j. A polymer composed of $A_i/(A_i + A_j)$ parts of species i and $A_i/(A_i + A_j)$ parts of species j would give a GPC that would coincide with that of the hypothetical polymer at points $f(x_i)$ and $f(x_j)$ only.

Obviously $A_i + A_j$ will not be equal to the area under the GPC. This is a sure indication that we have assumed too few species. Since we can

TABLE III
Gel permeation Chromatography for Sample No. 3
(Polyglycol P400 Data with Samples Omitted at 192.1 and 198.3 ml.)

Vol., ml.	Ht. obs.	Sig.	k	Ht. calc.	Per cent	Cum. per cent	M.W.
180.00	0.00	1.88	0.00	0.00	0.00	0.00	850.0
182.50	0.80	1.88	1.29	0.21	0.17	0.17	773.0
183.60	1.60	1.88	0.00	0.00	0.00	0.17	750.0
184.60	3.10	1.86	2.02	1.34	1.03	1.20	715.0
185.80	5.30	1.86	0.00	0.00	0.00	1.20	690.0
186.90	7.80	1.83	2.33	3.96	2.99	4.19	656.0
188.20	12.00	1.83	0.00	0.00	0.00	4.19	625.0
189.50	16.90	1.80	3.87	14.49	10.75	14.95	598.0
190.80	23.00	1.80	0.00	0.00	0.00	14.95	570.0
192.10*	30.10	1.77	0.00	0.00	0.00	14.95	540.0
193.50	37.10	1.77	0.00	0.00	0.00	14.95	510.0
194.80	44.20	1.73	4.35	44.20	31.63	46.59	482.0
196.60	48.20	1.73	0.00	0.00	0.00	46.59	450.0
198.30	54.20	1.69	0.00	0.00	0.00	46.59	424.0
200.30	41.10	1.69	0.00	0.00	0.00	46.59	390.0
202.40	41.30	1.64	4.12	41.29	28.01	74.60	366.0
204.70	23.50	1.64	0.00	0.00	0.00	74.60	333.0
207.10	27.20	1.59	3.98	27.19	17.82	92.43	308.0
210.10	8.00	1.59	0.00	0.00	0.00	92.43	275.0
213.10	12.10	1.51	3.80	12.10	7.56	99.99	250.0
216.00	0.00	1.51	0.00	0.00	0.00	99.99	233.0
230.00	0.00	1.51	0.00	0.00	0.00	99.99	197.0

$\bar{M}_w$: 0.421E + 03
$\bar{M}_n$: 0.392 + 03
$\bar{M}_v$: 0.416E + 03
$\bar{M}_w/\bar{M}_n$: 0.107E + 01
$\bar{M}_z$: 0.451E + 03
$\bar{M}_{z+1}$: 0.481E + 03
J: 0.771 − 08

Per cent of total weight of sample accounted for: 76.38

find each A_j by eq. (6) and we can find the approximate area under the GPC by numerical integration, we have a method of determining if we have assumed too few species.

Unfortunately, the comparison of the area under the GPC and ΣA_i will not indicate when we have assumed too many species. (The more species assumed, the closer ΣA_i will be to the area under the GPC.*) However, by eliminating species until ΣA_i becomes less than the area of the GPC we can determine a set of species that is, at least, sufficient to reproduce the actual GPC.

Effect of Calibration Errors

If the σ values are in error, then the area under the bell-shaped curves may not represent the actual weight of the species and if the σ are too

* See next section for exception.

TABLE IV
Gel Permeation Chromatography for Sample No. 4
(Polyglycol P400 Data with Extra Assumed Components)

Vol., ml.	Ht. obs.	Sig.	k	Ht. calc.	Per cent	Cum. per cent	M.W.
180.00	0.00	1.88	0.00	0.00	0.00	0.00	850.0
182.50	0.80	1.88	0.70	0.11	0.07	0.07	773.0
183.60*	1.60	1.88	0.81	0.27	0.16	0.23	750.0
184.60	3.10	1.86	0.99	0.65	0.38	0.61	715.0
185.80*	5.30	1.86	1.03	1.17	0.68	1.29	690.0
186.90	7.80	1.83	0.99	1.68	0.96	2.26	656.0
188.20*	12.00	1.83	0.97	2.53	1.45	3.71	625.0
189.50	16.90	1.80	0.96	3.61	2.03	5.75	598.0
190.00*	19.00	1.79	0.96	4.06	2.27	8.03	580.0
190.80	23.00	1.80	0.99	5.06	2.85	10.88	570.0
192.10*	30.10	1.77	1.05	7.13	3.94	14.83	540.0
193.50	37.10	1.77	1.07	8.95	4.95	19.78	510.0
194.00*	40.00	1.74	1.12	10.26	5.59	25.38	490.0
194.80	44.20	1.73	1.25	12.70	6.90	32.28	482.0
196.60*	48.20	1.73	1.43	15.90	8.63	40.92	450.0
198.30	54.20	1.69	1.50	19.22	10.19	51.11	424.0
199.30*	47.00	1.69	1.34	14.89	7.89	59.00	405.0
200.30*	41.10	1.69	1.32	12.78	6.78	65.78	390.0
202.40	41.30	1.64	2.12	21.29	10.96	76.74	366.0
204.70*	23.50	1.64	1.96	11.16	5.74	82.49	333.0
207.10	27.20	1.59	2.97	20.32	10.10	92.59	308.0
210.10*	8.00	1.59	2.21	4.44	2.21	94.80	275.0
213.10	12.10	1.51	3.44	10.93	5.19	100.00	250.0
216.00	0.00	1.51	0.00	0.00	0.00	100.00	233.0
230.00	0.00	1.51	0.00	0.00	0.00	100.00	197.0

$\bar{M}_w$:	$0.423E + 03$
$\bar{M}_n$:	$0.400E + 03$
$\bar{M}_v$:	$0.419 + 03$
$\bar{M}_w/\bar{M}_n$:	$0.105E + 01$
$\bar{M}_z$:	$0.446E + 03$
$\bar{M}_{z+1}$:	$0.469E + 03$
J:	$0.740E - 08$

Per cent of total weight of sample accounted for: 100.72

large, the contribution of adjacent species to a given species will be overestimated. Also, species near the tails of the GPC will cause the sum of areas, ΣA_j, to be greater than the area under the GPC. If the error in σ is proportional to σ, i.e., $\sigma_{\text{true}} \propto \sigma_{\text{obs}}$, then the apparent areas are proportional to the true areas and the per cent calculated by eq. (7) is correct.

Examples

The necessary calculations for this analysis are best done by computer. Table I (sample 1) shows the output of a computer program written by the author.

TABLE V
Gel Permeation Chromatography for Sample No. 5 (Polyethylene Data Base Case)

Vol., ml.	Ht. obs.	Sig.	k	Ht. calc.	Per cent	Cum. per cent	M.W.
70.00	0.00	2.17	0.00	0.00	0.00	0.00	3,000,000.0
72.50	2.50	2.11	2.80	1.32	0.26	0.26	2,000,000.0
75.00	4.50	2.09	2.75	2.36	0.47	0.74	1,500,000.0
77.50	5.80	2.07	2.39	2.66	0.53	1.27	1,400,000.0
80.00	9.50	2.07	2.67	4.87	0.97	2.24	1,300,000.0
82.50	12.80	2.06	2.62	6.49	1.28	3.53	1,000,000.0
85.00	16.50	2.03	2.62	8.51	1.66	5.19	700,000.0
87.50	20.20	2.01	2.57	10.29	1.99	7.18	600,000.0
90.00	25.50	1.99	2.61	13.31	2.54	9.73	450,000.0
92.50	31.20	1.95	2.62	16.64	3.12	12.86	350,000.0
95.00	36.00	1.94	2.58	19.14	3.56	16.42	280,000.0
97.50	41.80	1.90	2.58	22.66	4.13	20.56	220,000.0
100.00	48.00	1.85	2.56	26.46	4.71	25.28	180,000.0
102.50	54.20	1.84	2.57	30.14	5.34	30.63	140,000.0
105.00	61.00	1.80	2.57	34.73	6.00	36.64	110,000.0
107.50	66.50	1.76	2.56	38.48	6.52	43.16	85,000.0
110.00	72.00	1.71	2.56	43.07	7.07	50.23	65,000.0
112.50	74.20	1.66	2.52	44.91	7.17	57.40	50,000.0
115.00	75.50	1.65	2.54	46.36	7.36	64.77	38,000.0
117.50	73.60	1.65	2.56	45.44	7.22	71.99	27,000.0
120.00	67.50	1.64	2.54	41.65	6.57	78.57	20,000.0
122.50	59.00	1.63	2.53	36.45	5.72	84.29	14,000.0
125.00	49.50	1.62	2.54	30.92	4.82	89.12	10,000.0
127.50	39.50	1.56	2.49	25.18	3.77	92.90	6,200.0
130.00	29.50	1.51	2.45	19.06	2.77	95.68	4,000.0
132.50	23.00	1.45	2.52	15.96	2.22	97.90	2,000.0
135.00	13.60	1.39	2.47	9.58	1.28	99.19	1,100.0
137.50	7.50	1.07	2.07	5.77	0.59	99.79	500.0
140.00	2.50	1.02	2.14	2.09	0.20	99.99	230.0
142.50	0.10	0.97	1.11	.04	0.00	100.00	30.0
145.00	0.00	0.92	0.00	0.00	0.00	100.00	30.0
150.00	0.00	0.92	0.00	0.00	0.00	100.00	30.0

$\bar{M}_w$:	$0.154E + 06$
$\bar{M}_n$:	$0.125E + 05$
$\bar{M}_v$:	$0.116E + 06$
$\bar{M}_w/\bar{M}_n$:	$0.123E + 02$
$\bar{M}_z$:	$0.612E + 06$
$\bar{M}_{z+1}$:	$0.107E + 07$
J:	$0.637E - 04$

Per cent of total weight of sample accounted for: 100.15

The data are taken from Moore and Hendrickson.[5] Columns 1 and 2 are the data of the chromatograph of eluent volume versus refractive index. Columns 3 and 8 are standard deviation and molecular weights as obtained from the calibration curves of Figures 1 and 2. Column 4 gives the k values as calculated by eq. (4); column 5 gives the peak heights of the individual bell-shaped curves as calculated by eq. (5); column 6 gives the

TABLE VI
Gel Permeation Chromatography for Sample No. 6
(Polyethylene Data with Standard Deviation at 77.5 and 135.0 ml.;
Polyethylene Data Base Case)

Vol., ml.	Ht. obs.	Sig.	k	Ht. calc.	Per cent	Cum. per cent	M.W.
70.00	0.00	2.36	0.00	0.00	0.00	0.00	3,000,000.0
72.50	2.50	2.30	2.19	0.95	0.21	0.21	2,000,000.0
75.00	4.50	2.28	2.71	2.13	0.47	0.68	1,500,000.0
77.50	5.80	4.00	2.68	1.55	0.60	1.29	1,400,000.0
80.00	9.50	2.26	2.57	4.31	0.94	2.23	1,300,000.0
82.50	12.80	2.24	2.40	5.49	1.19	3.43	1,000,000.0
85.00	16.50	2.21	2.46	7.32	1.57	5.00	700,000.0
87.50	20.20	2.19	2.44	8.98	1.91	6.92	600,000.0
90.00	25.50	2.17	2.49	11.71	2.47	9.39	450,000.0
92.50	31.20	2.13	2.52	14.75	3.05	12.44	350,000.0
95.00	36.00	2.11	2.49	16.99	3.48	15.93	280,000.0
97.50	41.80	2.07	2.50	20.14	4.05	19.98	220,000.0
100.00	48.00	2.02	2.49	23.65	4.64	24.63	180,000.0
102.50	54.20	2.01	2.51	27.00	5.27	29.90	140,000.0
105.00	61.00	1.96	2.52	31.33	5.96	35.87	110,000.0
107.50	66.50	1.92	2.51	34.75	6.48	42.36	85,000.0
110.00	72.00	1.86	2.52	39.00	7.05	49.41	65,000.0
112.50	74.20	1.81	2.48	40.70	7.16	56.57	50,000.0
115.00	75.50	1.80	2.51	42.13	7.37	63.94	38,000.0
117.50	73.60	1.80	2.53	41.42	7.24	71.19	27,000.0
120.00	67.50	1.79	2.52	37.95	6.60	77.79	20,000.0
122.50	59.00	1.78	2.51	33.22	5.74	83.54	14,000.0
125.00	49.50	1.77	2.50	27.95	4.80	88.35	10,000.0
127.50	39.50	1.70	2.42	22.46	3.71	92.06	6,200.0
130.00	29.50	1.65	2.30	16.43	2.63	94.70	4,000.0
132.50	23.00	1.58	2.51	14.59	2.24	96.94	2,000.0
135.00	13.60	5.00	4.38	4.75	2.31	99.25	1,100.0
137.50	7.50	1.20	2.10	5.25	0.61	99.86	500.0
140.00	2.50	1.11	1.35	1.21	0.13	99.99	230.0
142.50	0.10	1.06	0.91	0.03	0.00	100.00	30.0
145.00	0.00	1.00	0.00	0.00	0.00	100.00	30.0
150.00	0.00	1.00	0.00	0.00	0.00	100.00	30.0

$\bar{M}_w$:	$0.150E + 06$
$\bar{M}_n$:	$0.116E + 05$
$\bar{M}_v$:	$0.110E + 06$
$\bar{M}_w/\bar{M}_n$:	$0.129E + 02$
$\bar{M}_z$:	$0.606 + 06$
$\bar{M}_{z+1}$:	$0.106E + 07$
J:	$0.639E - 04$

Per cent of total weight of sample accounted for: 102.83

percentage of the individual components as determined by eq. (7); and column 8 is the cumulative per cents of column 7.

The weight-average molecular weight, number-average molecular weight, etc. are all calculated by the well-known formulas for these values.

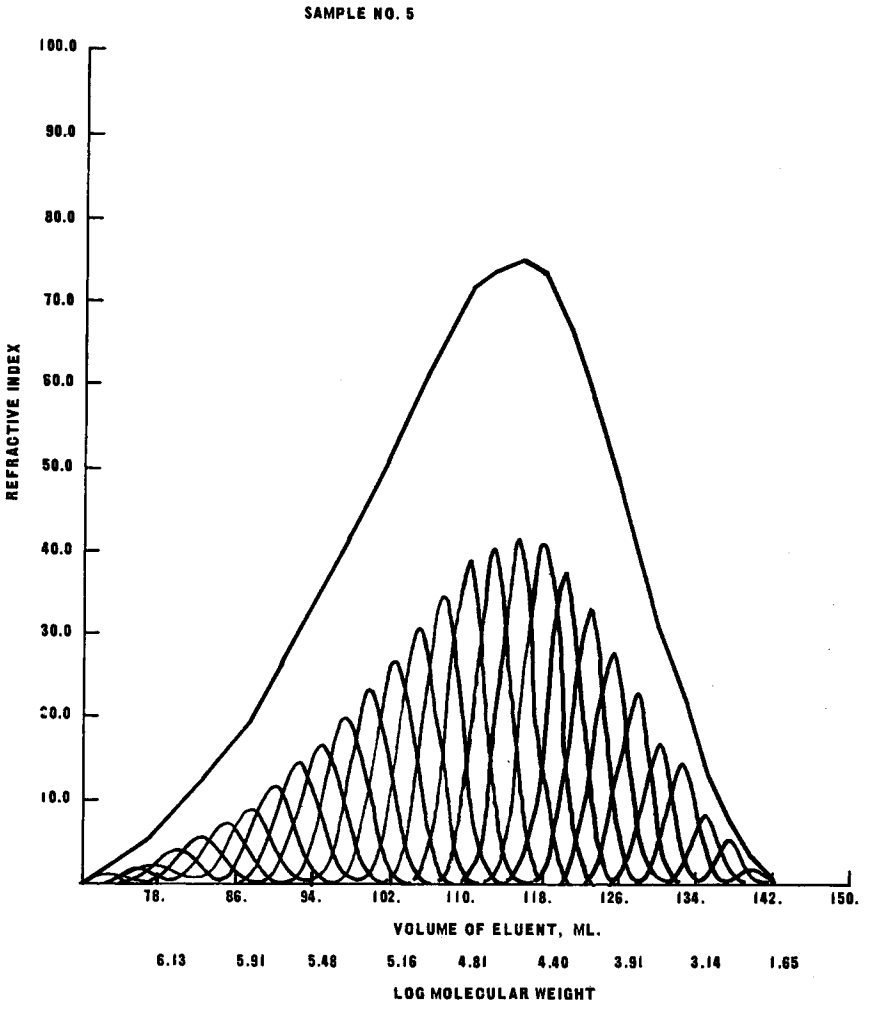

Figure 9.

The last item is the ratio of the sum of the areas of the individual bell-shaped curves to the total area under the GPC.

Figure 5 shows a plot of the chromatograph and the curves representing the individual components. The curves were machine-plotted by using a Calcomp plotter, and the sharp peaks result from the plot being produced by drawing straight lines from point to point of the chromatograph data. The bell-shaped curves were plotted by solving eq. (3) for K and then eq. (1) for 33 values of x. Note that the ordinates of the bell-shaped curves sum to the ordinate of the GPC curve.

Figure 6 and Table II for sample 2 show the effect of assuming no component at 192.1 ml. eluent volume (molecular weight 540). Note the calculated amount of adjacent components has been increased. Although

the sum of the ordinates of the bell-shaped curves equal the ordinate of the GPC at 189.5 and 194.8 ml., they do not at 192.1 ml.

The effect of erroneously assuming too few components is more dramatically shown for sample 3 (Fig. 7, Table III) where the main component is omitted.

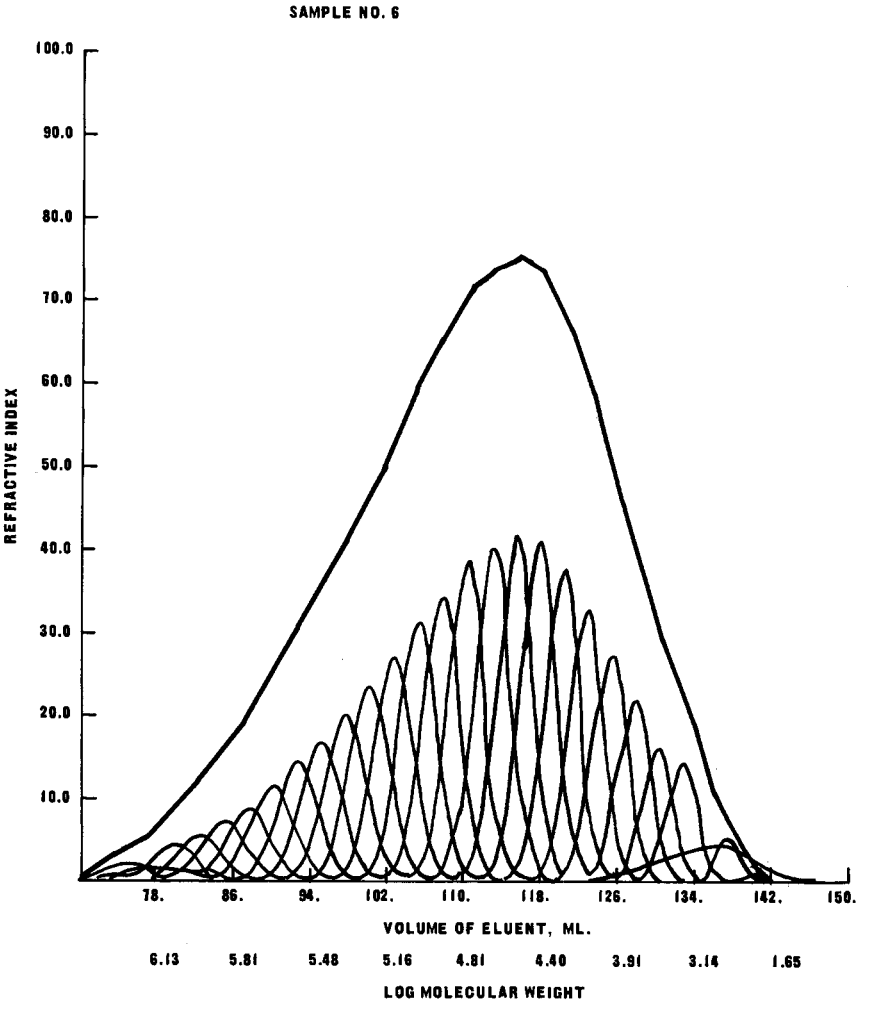

Figure 10.

In sample 4 (Fig. 8, Table IV), extra components (those indicated by an asterisk) were assumed. The calculated quantities of the actual components are decreased to compensate for the presence of the added components.

Figure 9 and Table V show the results of a typical polyethylene GPC (sample 5).

Figure 10 and Table VI (sample 6) show the effect of overestimating the standard deviation of the individual fractions assumed near the tails of the GPC. Part of the area under the individual curves is outside the

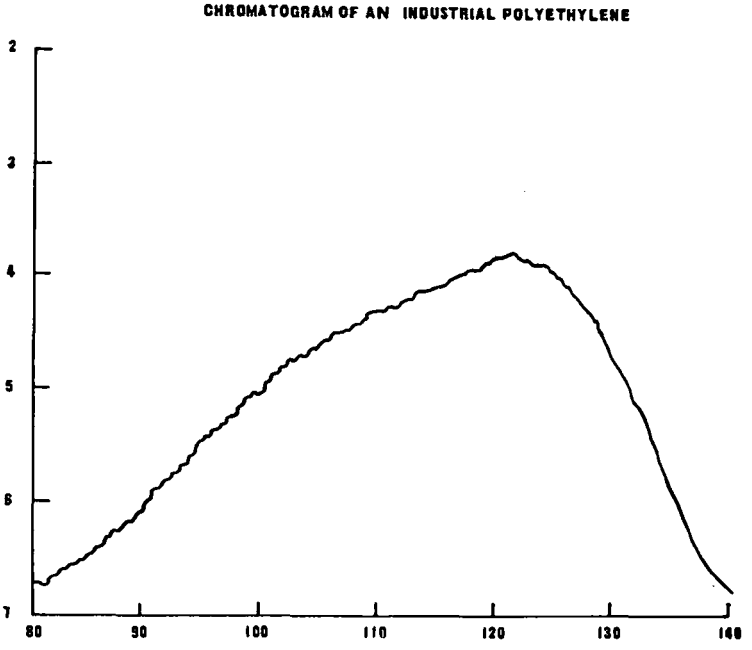

Fig. 11. Chromatogram of an industrial polyethylene.

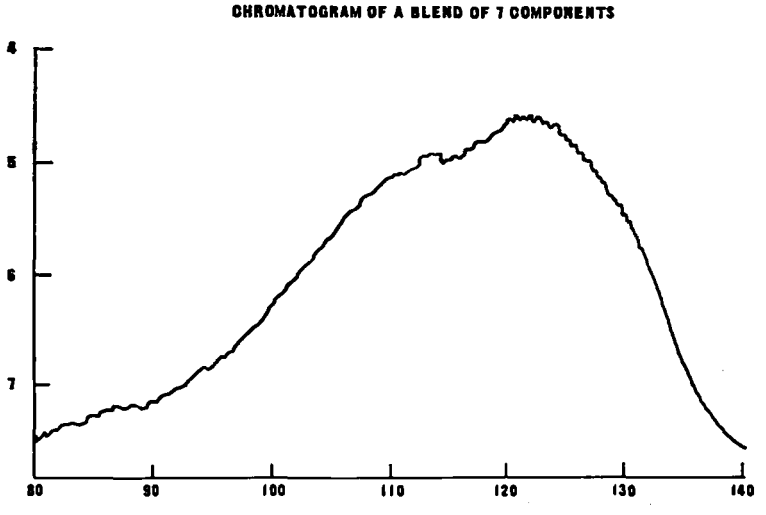

Fig. 12. Chromatogram of a blend of seven components.

curve. Note that the sum of the areas of the individual components now exceeds the area of the GPC.

Blending Applications

Since this method of analysis determines a theoretical composition or molecular weight distribution that would result in a given GPC we can apply the same procedure to blending problems of the following type: Given n batches of polymer, each with its own average molecular weight and standard deviation, can these be blended to give a batch having a specified molecular weight distribution, and if so, what proportions of each should be used?

The answer is easily obtained by specifying the desired molecular weight distribution as if it were a GPC and let the assumed components be all, or part, of the available batches. If the distribution can be obtained (approximated), the analysis will show agreement between the area under the GPC and the sum of areas representing the components. The required percentage of each will also be given.

In most cases, the batches to be blended will not have true Gaussian distributions. If so, then the blending proportions must be considered as approximate only. However, in practice it has been found to give good approximations even if the component distributions are considerably non-normal.

As an example of a blending application, Figure 11 shows the chromatograph of an industrial polyethylene. It was desired to reproduce this polymer by blending other polymers having different molecular weight distributions. The polymers to be blended had average molecular weights and standard distributions as given in Table VII.

TABLE VII
Blending Components

Component no.	Avg. mol. wt.	Std. deviation, ml. of eluent
1	235,000	13.00
2	127,000	14.90
3	100,000	11.50
4	95,000	12.40
5	80,000	11.40
6	14,300	5.90
7	5,300	5.60

Table VIII (sample 745) shows the calculated percentage of the components required to reproduce as near as possible the required chromatogram. Figure 12 shows the chromatogram of the actual blend. The agreement is quite good, considering that some of the components of the industrial polymer were present in relatively small quantities in the blend polymers.

TABLE VIII
Gel Permeation Chromatography for Sample No. 745
(Data for Blending Test, May 25, 1966)

Vol., ml.	Ht. obs.	Sig.	k	Ht. calc.	Per cent	Cum. per cent	M.W.
60.00	0.00	2.38	0.00	0.00	0.00	0.00	3,000,000.0
70.00	4.00	2.36	0.00	0.00	0.00	0.00	3,000,000.0
72.50	7.50	2.30	0.00	0.00	0.00	0.00	2,350,000.0
75.00	5.00	2.28	0.00	0.00	0.00	0.00	1,850,000.0
77.50	5.00	2.26	0.00	0.00	0.00	0.00	1,450,000.0
80.00	6.30	2.26	0.00	0.00	0.00	0.00	1,170,000.0
82.50	7.50	2.24	0.00	0.00	0.00	0.00	930,000.0
85.00	10.50	2.21	0.00	0.00	0.00	0.00	740,000.0
87.50	16.00	2.19	0.00	0.00	0.00	0.00	590,000.0
90.00	22.00	2.17	0.00	0.00	0.00	0.00	475,000.0
92.00	27.00	12.40	0.00	0.00	0.00	0.00	400,000.0
92.50	29.00	2.13	0.00	0.00	0.00	0.00	375,000.0
95.00	36.50	2.11	0.00	0.00	0.00	0.00	300,000.0
97.50	42.00	13.00	5.81	7.49	8.77	8.77	235,000.0
100.00	47.50	2.02	0.00	0.00	0.00	8.77	185,000.0
102.50	54.00	2.01	0.00	0.00	0.00	8.77	145,000.0
103.80	56.00	14.90	6.46	9.69	13.01	21.78	127,000.0
105.00	58.00	1.96	0.00	0.00	0.00	21.78	110,000.0
105.50	59.00	11.50	6.71	13.74	14.24	36.03	100,000.0
106.00	60.00	12.40	6.81	13.15	14.69	50.72	95,000.0
107.50	61.50	1.92	0.00	0.00	0.00	50.72	83,000.0
107.90	62.00	11.40	7.02	15.24	15.65	66.38	80,000.0
110.00	64.50	1.86	0.00	0.00	0.00	66.38	62,500.0
112.50	67.50	1.81	0.00	0.00	0.00	66.38	46,000.0
115.00	70.00	1.80	0.00	0.00	0.00	66.38	38,500.0
117.50	73.50	1.80	0.00	0.00	0.00	66.38	25,000.0
120.00	76.50	1.79	0.00	0.00	0.00	66.38	17,800.0
121.50	75.80	5.90	6.88	35.29	18.76	85.14	14,300.0
122.50	75.00	1.78	0.00	0.00	0.00	85.14	12,300.0
125.00	71.50	1.77	0.00	0.00	0.00	85.14	8,300.0
127.50	64.00	1.70	0.00	0.00	0.00	85.14	5,400.0
128.00	60.00	5.60	6.88	29.43	14.85	100.00	5,300.0
130.00	51.50	1.65	0.00	0.00	0.00	100.00	3,350.0
132.50	39.50	1.58	0.00	0.00	0.00	100.00	1,900.0
135.00	22.50	1.52	0.00	0.00	0.00	100.00	1,000.0
137.50	10.50	1.17	0.00	0.00	0.00	100.00	480.0
140.00	4.50	1.11	0.00	0.00	0.00	100.00	225.0
142.50	2.00	1.06	0.00	0.00	0.00	100.00	100.0
145.00	0.00	1.01	0.00	0.00	0.00	100.00	50.0
147.50	0.00	1.00	0.00	0.00	0.00	100.00	20.0
150.00	0.00	0.00	0.00	0.00	0.00	100.00	10.0
160.00	0.00	0.00	0.00	0.00	0.00	100.00	10.0

$\bar{M}_w$:	$0.813E + 05$
$\bar{M}_n$:	$0.210E + 05$
$\bar{M}_v$:	$0.715 + 05$
$\bar{M}_w/\bar{M}_n$:	$0.386E + 01$
$\bar{M}_z$:	$0.132E + 06$
$\bar{M}_{z+1}$:	$0.163E + 06$

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Résumé

Le but de ce manuscrit est de montrer comment une distribution de poids moléculaire théorique peut être trouvée telle qu'elle résulterait d'un chromatogramme par perméation sur gel. Aussi pour montrer comment la méthode peut être appliquée à des problèmes de mélange où l'on désire obtenir une distribution de poids moléculaire déterminée.

Zusammenfassung

Der Zwerck der vorliegenden Mitteilung ist es, zu zeigen, wie eine theoretische Molekulargewichtsverteilung gefunden werden kann, die einem gegebenen Gelpermeationschromatogramm entspricht. Weiters wird gezeigt, wie diese Methode auf Mischungsprobleme angewendet werden kann, wenn eine gegebene Molekulargewichsverteilung erhalten werden soll.

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