

## Dispersion in Gel Permeation Chromatography. A Rapid Numerical Solution to Tung's Integral Equation

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### Synopsis

A rapid iteration method has been developed to correct the molecular weight averages calculated from raw GPC data for dispersion. Though simple in its performance, it covers the general case that the instrumental spreading characteristics (Tung's resolution factor  $h$ ) depend on the elution volume. Moreover, it is irrelevant whether the calibration curve, being the logarithmic plot of the molecular weight versus the elution volume, is linear or not. The method has been applied to a number of well-characterized polystyrene mixtures and yields molecular weight averages which agree with those predicted theoretically. The effect of asymmetry exerted by the dispersion on both molecular weight averages  $\bar{M}_n$  and  $\bar{M}_w$  is also discussed.

### INTRODUCTION

The phenomenon of dispersion in GPC has been described adequately by Tung's integral equation<sup>1</sup>

$$F(v) = \int_{-\infty}^{+\infty} w(y)(h/\pi)^{1/2} \exp\{-h(v-y)^2\} dy \quad (1)$$

where  $F(v)$  represents the observed chromatogram;  $w(y)$ , the corrected chromatogram;  $v$  and  $y$ , the elution volume; and  $h$ , the resolution factor. Equation (1) is valid only if the instrumental spreading can be assumed to be Gaussian;  $w(y)$  is closely related to the differential molecular weight distribution  $w(M)$  by means of the  $\log M$  versus  $v$  relation, i.e., the calibration curve. When  $h$  becomes infinitely large,  $F(v)$  equals  $w(v)$ , and no dispersion is present.

In all those cases where finite values of  $h$  are found, one has to account for the dispersion effect. From the foregoing it is clear that a strictly monodisperse sample should yield a purely Gaussian chromatogram of which the width corresponds to the extent that dispersion has taken place. Instead of letting the flow pass through the columns in one direction, one may also reverse it, say, halfway, and force it to follow the same pathway back. In doing so, one annihilates the separation into molecular sizes. The remaining spreading reflected in the observed chromatogram must then be due to

the dispersion in the apparatus. This so-called reversed-flow technique, first proposed by Tung, Moore, and Knight<sup>2</sup> is particularly useful for distribution with a small, ill-defined heterodispersity.

After Tung had established eq. (1), many approaches appeared in literature to solve the problem of dispersion in GPC. A survey of them has been made by Duerksen and Hamielec.<sup>3</sup> Most authors<sup>4-6</sup> who have taken eq. (1) as a starting point for their treatments assume  $h$  nonvariable with the elution volume. Hamielec and Ray<sup>4</sup> have shown that even an analytical solution of eq. (1) exists if  $h$  is constant and the calibration curve is linear. Their solution predicts a symmetrical increase and decrease of  $\bar{M}_n$  and  $\bar{M}_w$ , respectively, which do not depend on the broadness of the distribution, but which are functions only of a calibration parameter and the resolution factor  $h$ . However, there is no a priori reason to expect that  $\bar{M}_n$  and  $\bar{M}_w$  change symmetrically, for variation of  $h$  with the elution volume has been reported frequently and calibration curves are only linear in a small range. Therefore, one should try to look after a solution which fully accounts for possible variations of  $h$  and which allows of nonlinear calibration curves. Indeed, such a treatment has been given already by Tung<sup>1</sup> (Gaussian quadrature approximation of the integral equation). Other methods which are general in this respect are those of Hess and Kratz<sup>7</sup> and of Picket, Cantow, and Johnson.<sup>8</sup> However, the latter methods, which are completely acceptable because of their general approach, give rise to mathematical complications. These consist in the occurrence of oscillations in the corrected chromatograms involving artificial maxima which cannot be tolerated.

The method under discussion here concurs with the more general approaches. The classical difficulties, met with the inversion of an ill-defined matrix, have been avoided by the application of a rapid iteration procedure. The calculation can be performed as well by hand as by a small computer (computer program in ALGOL 60 available on request).

### THEORETICAL

The method we consider here starts from eq. (1). Suppose we split up the chromatogram in sufficiently small intervals so that the integral may be replaced by a sum to a good approximation. Then, instead of eq. (1), we may write

$$F_i = \sum_{k=1}^N \delta(h_k/\pi)^{1/2} \exp\{-h_k(i-k)^2\delta^2\} w_k \quad (2)$$

where  $F_i$  = the observed chromatogram in cm at the elution volume  $v_i$ ,  $w_k$  = the corrected chromatogram in cm at the elution volume  $v_k$ ,  $N$  = the number of intervals in which the elution range is subdivided,  $\delta$  = the interval or mesh size expressed in counts (1 count = 5 ml), and  $h_k$  = the resolution factor in reciprocal square counts at the elution volume  $v_k$ .

In a more abbreviated form, eq. (2) reads

$$F_i = \sum_{k=1}^N A_{ik} w_k \quad (3)$$

where the meaning of  $A_{ik}$  follows from a confrontation of eq. (3) with eq. (2), or, in matrix notation,

$$F = AW \quad (4a)$$

and in reciprocal form,

$$W = A^{-1}F. \quad (4b)$$

The matrix  $A$  is divided as

$$A = I - B \quad (5)$$

where  $I$  represents the unit matrix, and the original eq. (4b) becomes

$$W = (I - B)^{-1}F. \quad (6)$$

The right-hand side of eq. (6) is then developed in a series according to

$$W = (I + B + B^2 + B^3 + \dots B^n)F. \quad (7a)$$

This series converges if, as  $n$  becomes large,  $B^n$  approaches 0. The criterion of convergence requires that all eigenvalues of the matrix  $B$  must be smaller in absolute value than unity.<sup>9</sup>

Then we replace (7a) by

$$W = F + \sum_{i=1}^n B^i F \quad (7b)$$

and, using the definition of  $R_i$ ,

$$R_i = B^i F \quad (8)$$

we arrive finally at

$$W = F + \sum_{i=1}^n R_i \quad (9)$$

where the matrices  $R_i$  are related to each other by

$$\begin{aligned} R_1 &= BF \\ R_i &= BR_{i-1} \quad (i = 2, 3, \dots n) \end{aligned} \quad (10)$$

The matrices  $R_1, R_2, \dots R_n$  can be consecutively calculated with the use of the prescription, eq. (10). If the  $m^{\text{th}}$  iteration yields a matrix  $R_m$  which lies within the experimental error of matrix  $F$ , the process may be stopped. Equation (9) enables us to calculate the matrix  $W$  and from this, using the calibration data, the differential molecular weight distribution and the molecular weight averages  $\bar{M}_n$  and  $\bar{M}_w$ . As a test of the method, we can regenerate the matrix  $F$  by a simple matrix multiplication according to (4a) and check the found matrix against the experimentally observed matrix.

The crucial point in the method is whether convergence is present in the iteration eq. (10) or not. If only a weak convergence is found, some improvement can be reached by the choice of a larger mesh size.

## EXPERIMENTAL

The measurements were performed on a Water's Model 200 GPC, in which columns had been installed with nominal porosities of  $10^7$ ,  $7 \times 10^5$ ,  $3 \times 10^4$ ,  $10^4$ , and  $3 \times 10^3$  Å. This set of columns works preeminently for molecular weights up to 500,000. The operational conditions were: flow rate, 1 ml/min; solvent, toluene; solute, narrow polystyrene standards of Pressure Chemical Company, Pittsburgh, and Lustrex (the broad commercial polystyrene distributed by Prof H. Benoit); temperature, ambient; sample concentration, 0.2–0.6%; sample injection time, 120 sec; signal amplification,  $4 \times$  or  $8 \times$ .

Pure polystyrene standards were used for calibration. The relation of  $\log M$  to the elution volume  $v$  was approximated by a polynomial of the third degree. The original and recovered molecular weights have been compiled in Table I. For measuring the resolution factor  $h$ , we have followed Tung<sup>2</sup> by applying his reverse-flow technique. Slightly skewed Gaussian chromatograms were observed. For this reason, we have only used the leading halves of the chromatograms for the determination of  $h$ . As can be seen in Table I,  $h$  decreases with decreasing elution volume. In previous observations with the mentioned set of columns, except the  $10^7$  Å column, a distinct minimum was found in the variation of  $h$  with  $v$ . Both behaviors have been reported.<sup>2,10</sup> A quadratic least-squares approximation was used to obtain interpolated values of  $h$ . The goodness of fit is shown in Table I.

TABLE I  
Chromatogram Characteristics of Standard Polystyrene Samples

$v$ , counts	$M$ $\times 10^{-3}$	Code	$M_{\text{calc}}$ $\times 10^3$	$h_{\text{obs}}$ , counts <sup>-2</sup>	$h_{\text{calc}}$ , counts <sup>-2</sup>
46.31	0.600	—	0.529	2.39	2.35
45.01	1.220	—	1.490	2.40	2.12
44.53	2.100	—	2.083	2.00	2.03
41.73	10.300	A	9.977	1.59	1.61
40.14	20.400	B	20.028	1.30	1.36
37.98	51.000	C	48.348	1.14	1.11
36.42	97.200	D	95.582	1.01	0.97
35.37	160.000	E	160.620	0.95	0.87
35.10	200.000	F	185.563	—	0.86
33.70	411.000	—	429.451	0.74	0.76
33.28	498.000	—	571.680	0.72	0.74
32.81	670.000	—	804.629	—	0.71
32.70	860.000	—	874.695	—	0.71
32.12	1800.000	—	1390.493	0.66	0.68

## APPLICATION OF THE METHOD

In order to illustrate the method, we have worked out the Lustrex sample in Table II. Measuring of the chromatogram had been performed with a mesh size of 0.25 count. The observed  $F$  matrix has been placed in the first

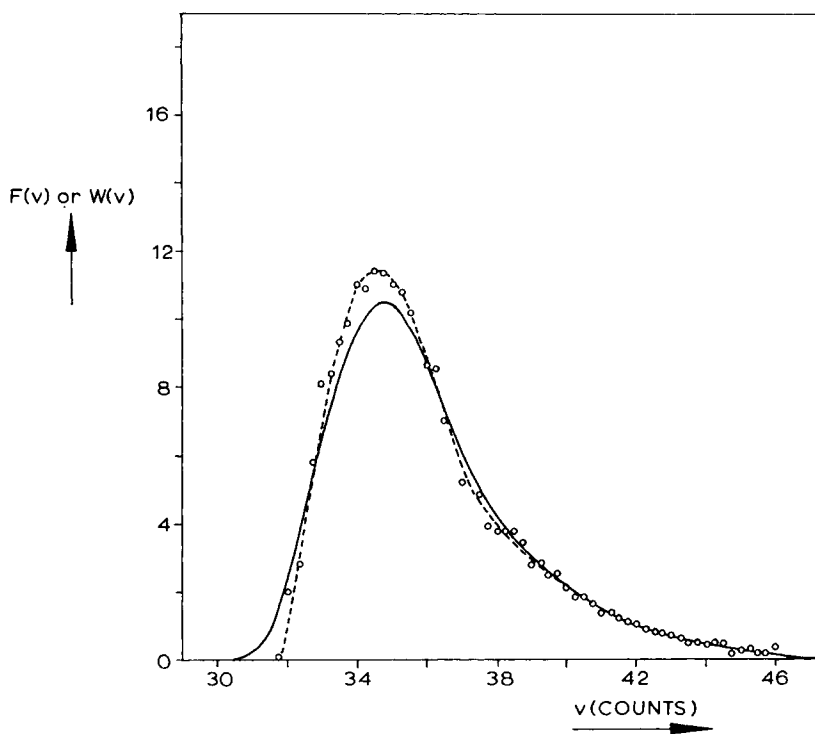


Fig. 1. Corrected and uncorrected chromatograms of a commercial polystyrene (Lustrex): (—) experimental  $F(v)$ ; (---) actual  $W(v)$ ; (O) points obtained from the iteration method; 1 count = 5 ml.

column of Table II. The second column of Table II gives the first correction embodied in the matrix  $R_1$ . The systematic alternation of its negative and positive elements already indicates roughly the shape of the corrected chromatogram (Fig. 1). After each iteration, the matrix  $W$  and also the corresponding  $\bar{M}_n$  and  $\bar{M}_w$  were computed. The first and the last elements of the matrix  $W$  show an oscillatory trend. If one carries the iteration too long, the oscillations propagate over the whole matrix. However, as may be concluded from Table II, the agreement of the regenerated matrix with the observed matrix has been reached before the oscillations become serious. In fact, the first correction determines the dispersion correction for the greater part. The remaining oscillatory points at the beginning and the end of the matrix  $W$  were omitted in the calculations and the figures.

Besides a broad distribution, a number of narrow multimodal distributions were subjected to the iteration method. Here, the mesh size amounted also 0.25 count. Mixtures were composed of equal weight fractions of the constituting solutes being polystyrene standards. The corresponding data have been collected in Table III. Assuming that the standards were perfectly monodisperse, we have computed the theoretical molecular weight averages. The required number of iterations depends on

TABLE II. Data Obtained from the Iteration for the Broad LuStrex Sample

$F$	$R_1$	$W_1$	$W_2$	$W_3$	$W_4$	$W_5$	$W_6$	$W_7$	$F_{calc}$
0.00	-0.22	-0.22	-0.18	-0.08	+0.01	+0.09	+0.14	+0.19	-0.03
0.02	-0.34	-0.32	-0.33	-0.26	-0.19	-0.12	-0.07	-0.03	-0.01
0.10	-0.45	-0.35	-0.43	-0.40	-0.35	-0.29	-0.24	-0.20	+0.06
0.27	-0.55	-0.28	-0.42	-0.43	-0.41	-0.37	-0.32	-0.27	+0.22
0.46	-0.72	-0.26	-0.56	-0.71	-0.81	-0.89	-0.95	-1.01	+0.51
0.85	-0.79	+0.06	-0.32	-0.55	-0.72	-0.87	-0.99	-1.11	+0.95
1.45	-0.75	+0.70	+0.31	+0.07	-0.13	-0.29	-0.43	-0.57	+1.57
2.43	-0.42	+2.01	+1.87	+1.84	+1.85	+1.90	+1.95	+2.02	+2.36
3.29	-0.29	+3.00	+2.87	+2.81	+2.79	+2.78	+2.78	+2.79	+3.28
4.30	-0.08	+4.22	+4.17	+4.16	+4.16	+4.15	+4.15	+4.15	+4.30
5.38	+0.17	+5.55	+5.61	+5.66	+5.70	+5.73	+5.75	+5.77	+5.37
6.55	+0.51	+7.06	+7.32	+7.52	+7.69	+7.84	+7.99	+8.12	+8.42
7.42	+0.58	+8.00	+8.19	+8.28	+8.34	+8.37	+8.40	+8.41	+7.41
8.23	+0.64	+8.87	+9.01	+9.03	+9.00	+8.95	+8.89	+8.83	+8.30
9.02	+0.77	+9.79	+9.96	+10.01	+10.00	+9.98	+9.94	+9.91	+9.06
9.69	+0.88	+10.57	+10.80	+10.89	+10.94	+10.97	+11.00	+11.03	+9.66
10.07	+0.83	+10.90	+11.05	+11.06	+11.04	+11.01	+10.97	+10.94	+10.10
10.38	+0.84	+11.22	+11.39	+11.43	+11.44	+11.45	+11.46	+11.47	+10.37
10.47	+0.78	+11.25	+11.38	+11.41	+11.41	+11.42	+11.43	+11.44	+10.46
10.37	+0.66	+11.03	+11.11	+11.10	+11.08	+11.07	+11.05	+11.04	+10.38
10.15	+0.56	+10.71	+10.77	+10.76	+10.76	+10.75	+10.75	+10.76	+10.15
9.77	+0.42	+10.19	+10.21	+10.19	+10.17	+10.16	+10.15	+10.14	+9.78
9.29	+0.29	+9.58	+9.57	+9.55	+9.54	+9.53	+9.53	+9.52	+9.29
8.70	+0.14	+8.84	+8.78	+8.74	+8.71	+8.68	+8.66	+8.64	+8.72
8.16	+0.10	+8.26	+8.27	+8.31	+8.37	+8.44	+8.51	+8.58	+8.09
7.40	-0.11	+7.29	+7.17	+7.11	+7.07	+7.04	+7.01	+6.98	+7.43
6.80	-0.15	+6.65	+6.58	+6.57	+6.60	+6.62	+6.65	+6.68	+6.77
6.07	-0.32	+5.75	+5.57	+5.47	+5.39	+5.31	+5.24	+5.17	+6.14
5.60	-0.26	+5.34	+5.28	+5.29	+5.31	+5.35	+5.38	+5.42	+5.56
5.08	-0.28	+4.81	+4.75	+4.75	+4.78	+4.80	+4.83	+4.86	+5.05
4.57	-0.33	+4.24	+4.14	+4.09	+4.05	+4.01	+3.97	+3.92	+4.61
4.22	-0.26	+3.96	+3.91	+3.90	+3.89	+3.87	+3.86	+3.84	+4.24
3.92	-0.19	+3.73	+3.73	+3.76	+3.77	+3.79	+3.80	+3.81	+3.91
3.66	-0.12	+3.54	+3.60	+3.66	+3.71	+3.75	+3.79	+3.83	+3.62

3.37	-0.10	+3.27	+3.31	+3.35	+3.37	+3.39	+3.41	+3.43	+3.35
3.06	-0.14	+2.92	+2.91	+2.89	+2.86	+2.82	+2.79	+2.75	+3.10
2.85	-0.09	+2.76	+2.78	+2.79	+2.78	+2.78	+2.78	+2.77	+2.85
2.61	-0.09	+2.52	+2.53	+2.52	+2.51	+2.50	+2.48	+2.47	+2.62
2.42	-0.05	+2.37	+2.40	+2.42	+2.44	+2.46	+2.48	+2.49	+2.40
2.19	-0.07	+2.12	+2.13	+2.13	+2.13	+2.43	+2.13	+2.13	+2.19
1.98	-0.08	+1.90	+1.90	+1.89	+1.87	+1.86	+1.86	+1.85	+1.99
1.81	-0.06	+1.75	+1.76	+1.76	+1.77	+1.78	+1.79	+1.80	+1.80
1.63	-0.07	+1.56	+1.56	+1.56	+1.56	+1.56	+1.56	+1.57	+1.63
1.46	-0.08	+1.38	+1.36	+1.35	+1.33	+1.32	+1.31	+1.29	+1.47
1.34	-0.06	+1.28	+1.28	+1.28	+1.28	+1.29	+1.29	+1.29	+1.34
1.22	-0.05	+1.17	+1.17	+1.17	+1.17	+1.17	+1.17	+1.17	+1.22
1.12	-0.04	+1.08	+1.09	+1.10	+1.10	+1.11	+1.11	+1.12	+1.22
1.02	-0.03	+0.99	+0.99	+0.99	+0.99	+0.99	+0.99	+0.99	+1.02
0.93	-0.03	+0.90	+0.90	+0.90	+0.90	+0.89	+0.89	+0.89	+0.93
0.85	-0.03	+0.82	+0.83	+0.82	+0.82	+0.82	+0.82	+0.82	+0.85
0.78	-0.02	+0.76	+0.77	+0.77	+0.78	+0.78	+0.78	+0.78	+0.78
0.70	-0.02	+0.68	+0.67	+0.67	+0.66	+0.65	+0.65	+0.64	+0.71
0.65	-0.00	+0.65	+0.66	+0.67	+0.68	+0.69	+0.71	+0.72	+0.64
0.57	-0.02	+0.55	+0.55	+0.54	+0.54	+0.54	+0.53	+0.53	+0.57
0.51	-0.02	+0.49	+0.49	+0.48	+0.48	+0.47	+0.47	+0.47	+0.51
0.45	-0.02	+0.43	+0.42	+0.41	+0.40	+0.38	+0.37	+0.36	+0.46
0.42	-0.00	+0.42	+0.43	+0.44	+0.45	+0.46	+0.47	+0.47	+0.41
0.38	+0.01	+0.39	+0.40	+0.42	+0.44	+0.46	+0.48	+0.49	+0.36
0.30	-0.03	+0.27	+0.25	+0.23	+0.22	+0.20	+0.19	+0.17	+0.31
0.27	-0.02	+0.25	+0.24	+0.23	+0.22	+0.22	+0.21	+0.21	+0.27
0.25	-0.00	+0.25	+0.25	+0.25	+0.25	+0.25	+0.26	+0.26	+0.25
0.22	+0.00	+0.22	+0.22	+0.22	+0.22	+0.22	+0.21	+0.21	+0.22
0.19	+0.01	+0.20	+0.21	+0.21	+0.21	+0.21	+0.21	+0.21	+0.19
0.17	+0.03	+0.20	+0.24	+0.27	+0.30	+0.32	+0.35	+0.37	+0.15
0.07	-0.03	+0.04	+0.03	+0.01	+0.00	-0.01	-0.03	-0.04	+0.08
0.02	-0.04	-0.02	-0.04	-0.05	-0.07	-0.08	-0.09	-0.10	+0.03
0.00	-0.03	-0.03	-0.04	-0.05	-0.05	-0.05	-0.05	-0.05	+0.00
$M_w \times 10^{-3} 282$		260	256	255	255	256	256	257	
$M_n \times 10^{-3} 40$		42	42	42	41	41	41	41	

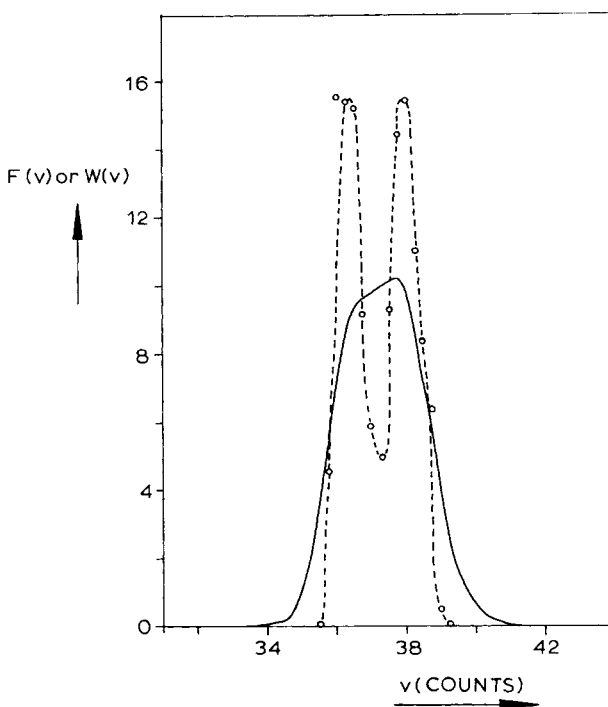


Fig. 2. Corrected and uncorrected chromatograms of a bimodal distribution (code CD): (—) experimental  $F(v)$ ; (---) actual  $W(v)$ ; (O) points obtained from the iteration method; 1 count = 5 ml.

the broadness of the distribution varying from 5 to 25 iterations for the broad Lustrex sample and the small mixture DE, respectively. The results are shown in Figures 2, 3, 4, and 5. It is clearly seen that the right number of peaks appears in each corrected chromatogram. Even the light shoulders in the uncorrected chromatograms in Figures 3 and 4 yield outlined

TABLE III  
Molecular Weight Averages for a Variety of Polystyrenes

Solute	$c_i$ , wt-%	$g_i$ , wt fraction	Uncorrected		Corrected		Predicted	
			$M_w$ $\times 10^{-3}$	$M_n$ $\times 10^{-3}$	$M_w$ $\times 10^{-3}$	$M_n$ $\times 10^{-3}$	$M_w$ $\times 10^{-3}$	$M_n$ $\times 10^{-3}$
Lustrex	0.3	—	282	40	256	41	—	—
Lustrex	0.6	—	287	40	253	44	—	—
Lustrex	0.6	—	279	41	248	42	—	—
Mixture CD	0.6	0.50	73	57	74	63	74	67
Mixture DE	0.6	0.50	130	102	129	114	128	121
Mixture DE	0.6	0.50	146	111	150	125	148	131
Mixture CDF	0.5	0.33	115	74	117	80	116	86
Mixture ABCDF	0.4	0.20	76	25	76	27	76	28
Mixture ABCDF	0.4	0.20	75	24	75	26	76	28



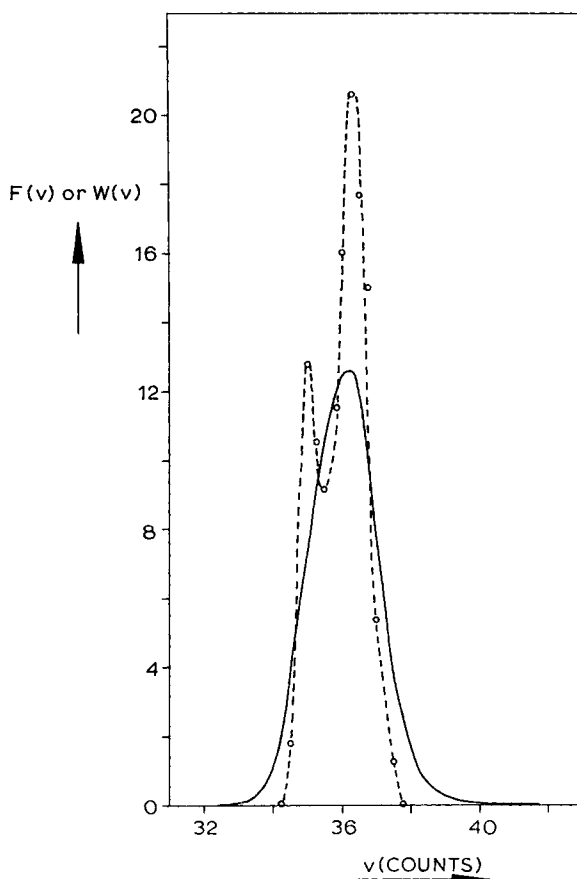


Fig. 3. Corrected and uncorrected chromatograms of a bimodal distribution (code DE): (—) experimental  $F(v)$ ; (---) actual  $W(v)$ ; (O) points obtained from the iteration method; 1 count = 5 ml.

peaks after correction. Moreover, the peak elution volumes agree in all cases with the expected elution volumes, as it should be (cf. Table IV). Finally, Table III shows that the dispersion has no influence at all on  $\bar{M}_w$ , but causes a shift in the value of  $\bar{M}_n$  to the theoretically predicted value; for the Lustrex sample,  $\bar{M}_w$  is shifted and  $\bar{M}_n$  is not. The remaining discrepancy must be ascribed to the assumption of complete monodispersity of the standards, whereas they actually have  $\bar{M}_w/\bar{M}_n$  ratios up to 1.06. The calculations have been repeated with a larger mesh size of 0.5 count. Indeed, nearly the same results were obtained as in the former case.

## DISCUSSION

Comparing the uncorrected data with those which can be theoretically expected, one concludes that the observed dispersion exerts a clearly asymmetrical influence on the actual value of the molecular weight averages.

Concerning the composed mixtures, it may be said that it lowers the value of  $\bar{M}_n$ , whereas it leaves the value of  $\bar{M}_w$  practically unchanged. A similar behavior can be recognized in the results reported by Pickett, Cantow, and Johnson.<sup>8</sup> (See Table IV of ref. 8.) Unfortunately, most computational methods do not lend themselves very well to a perspicuous analysis of the origin of this asymmetrical effect because of the numerical approach of the problem. The analytical methods should be more promising in this respect, but are restricted by severe conditions, not very acceptable from a practical point of view.

In fact, there are three sources to be distinguished which may give rise to asymmetrical effects. They are: (a) a non-Gaussian dispersion in the apparatus; (b) the curvature of the observed chromatogram; and (c) the dependence of the dispersion on the elution volume.

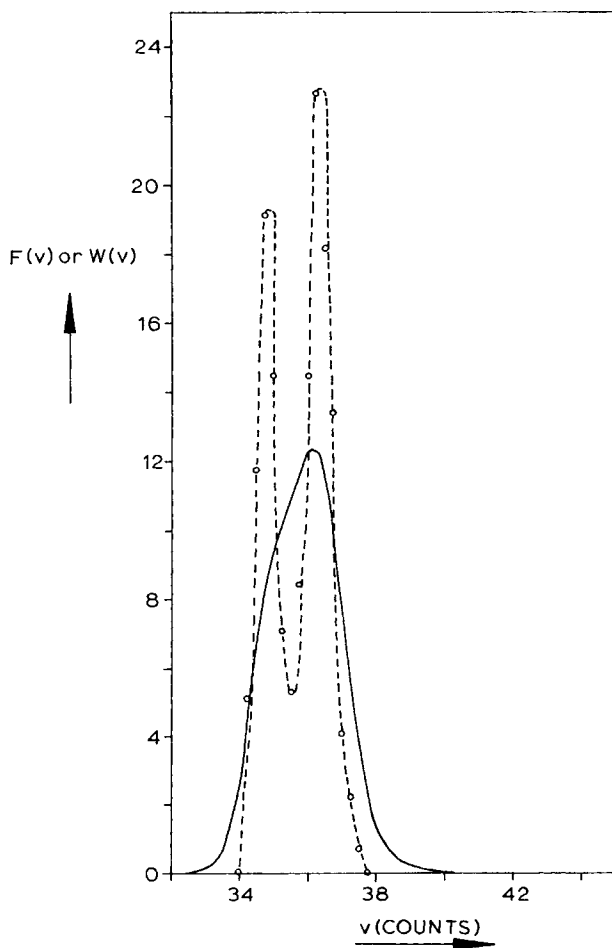


Fig. 4. Corrected and uncorrected chromatograms of a bimodal distribution (code DF): (—) experimental  $F(v)$ ; (---) actual  $W(v)$ ; (O) points obtained from the iteration method; 1 count = 5 ml.

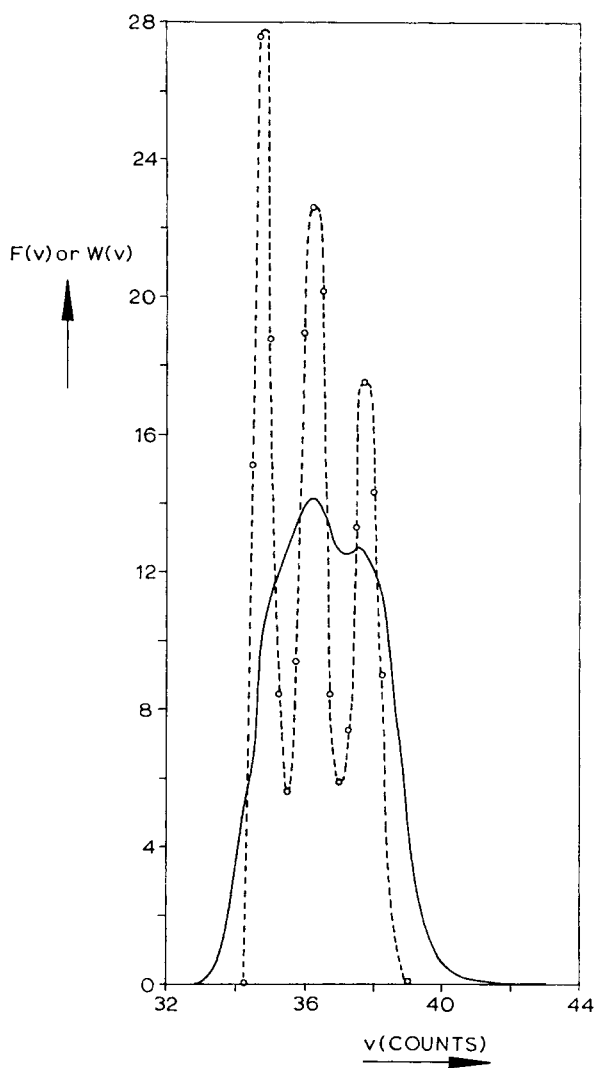


Fig. 5. Corrected and uncorrected chromatograms of a trimodal distribution (code CDF): (—) experimental  $F(v)$ ; (---) actual  $W(v)$ ; (O) points obtained from the iteration method; 1 count = 5 ml.

**Source (a).** The influence of a non-Gaussian dispersion on the evaluation of molecular weight averages has been recently pointed out by Hamielec.<sup>11</sup> He assumes the calibration curve to be linear and implicitly the dispersion characteristics to be independent of the elution volume. His results (formulas 23 and 24) may be recapitulated as

$$\bar{M}_n(h)/\bar{M}_n(\infty) = (1 + \Delta_n)\exp(D_2^2/4h) \quad (11)$$

$$\bar{M}_w(h)/\bar{M}_w(\infty) = (1 + \Delta_w)^{-1}\exp(-D_2^2/4h) \quad (12)$$

TABLE IV  
Comparison of Peak Elution Volumes of Simple and Mixed Polystyrene Standards

Mixture	From calibration		From corrected chromatograms	
	$M$ $\times 10^{-3}$	$V_{\text{peak}}$ , counts	$V_{\text{peak}}$ , counts	$M$ $\times 10^{-3}$
ABCDF	200.0	35.10	34.9	207.3
	97.2	36.42	36.3	101.2
	51.0	37.98	37.9	50.0
	20.4	40.14	40.1 <sup>b</sup>	20.9
	10.3	41.73	41.7 <sup>b</sup>	9.9
CDF	200.0	35.10	34.9	207.3
	97.2	36.42	36.3	101.2
	51.0	37.98	37.7 <sup>b</sup>	53.2
DE	160.0	35.10	35.0	196.1
	97.2	36.42	36.3	101.2
CD	97.2	36.42	36.3	101.2
	51.0	37.98	37.9	50.0
DF	200.0	35.10	34.9	207.3
	97.2	36.42	36.3	101.2

where  $\bar{M}_n(\infty)$  and  $\bar{M}_w(\infty)$  refer to molecular weight averages before correction and  $\bar{M}_n(h)$  and  $\bar{M}_w(h)$ , to the same quantities after correction;  $\Delta_n$  and  $\Delta_w$  are skewing factors accounting for the non-Gaussian shape of the dispersion chromatograms; and  $D_2$  represents the slope of the linear cali-

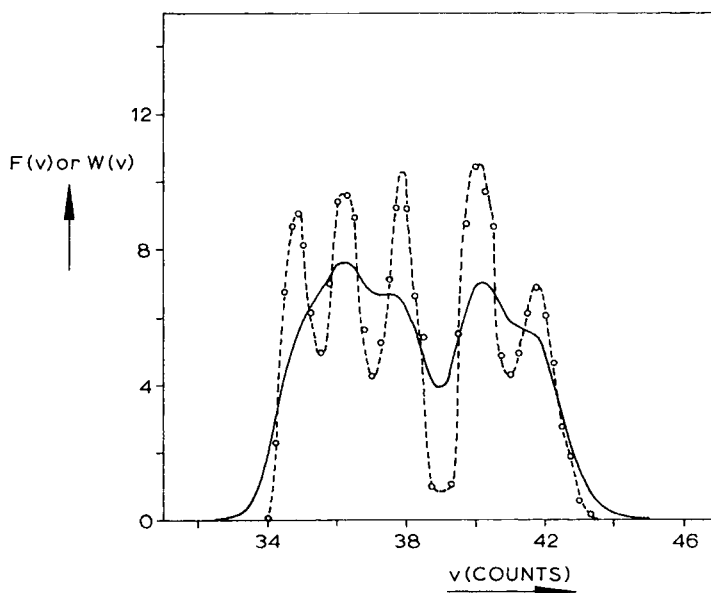


Fig. 6. Corrected and uncorrected chromatograms of a pentamodal distribution (code ABCDF): (—) experimental  $F(v)$ ; (---) actual  $W(v)$ ; (O) points obtained from the iteration method; 1 count = 5 ml.

bration curve. In general,  $0 \leq \Delta_n < 1$  and  $0 \leq \Delta_w < 1$ , where the signs of equality refer to the case of purely Gaussian dispersion in the apparatus. In the latter case, eqs. (11) and (12) reduce to

$$\bar{M}_n(h)/\bar{M}_n(\infty) = \exp(D_2^2/4h) \quad (13)$$

$$M_w(h)/M_w(\infty) = \exp(-D_2^2/4h) \quad (14)$$

suggesting a symmetrical correction for  $\bar{M}_n$  and  $\bar{M}_w$ . However, in the general case, the skewing factors  $\Delta_n$  and  $\Delta_w$  must be accounted for.

From eq. (11) it is seen that the corrected value  $M_n(h)$  is increased over the uncorrected value  $M_n(\infty)$  by the dispersion  $D_2^2/4h$  as well as by the skewness  $\Delta_n$ , whereas from eq. (12) it is seen that  $M_w(h)$  differs less from  $M_w(\infty)$  as the dispersion  $D_2^2/4h$  and the skewness  $\Delta_w$  counteract each other. So, non-Gaussian dispersion may affect  $\bar{M}_n$  more than  $\bar{M}_w$ . Nevertheless, we do not believe that non-Gaussian dispersion was important in the present case, since we have got nearly perfectly Gaussian chromatograms from the reverse-flow experiments. Moreover, our systems have not met the requirements of a constant  $D_2$  and dispersion parameters independent of the elution volume. It must be noted that the dispersion correction, according to the treatment of Hamilec, essentially ignores the broadness of the distribution because it is a function of  $D_2$  and  $h$  only with both parameters supposed to be independent of  $v$  or  $M$ .

**Source (b).** A method which allows nonlinear calibration curves but requires also a constant  $h$  is due to Pierce and Armonas.<sup>5</sup> They approximate the function  $\ln F(y)$  by a quadratic function about a definite point  $v_0$  according to

$$\ln F(y) = \exp\{a - b(y - v_0) - c(y - v_0)^2\} \quad (15)$$

and find finally

$$W(v_0) = \{h/(h - c)\}^{1/2} F(v_0) \exp\{-b^2/4(h - c)\}. \quad (16)$$

From eq. (16) one may conclude that, if the chromatogram shows a flat curvature in a definite point, or rather the first and second derivatives are very small in that point (i.e.,  $b$  and  $c$  are small), the dispersion correction becomes negligible. This phenomenon emerges from Figure 1, where at the low molecular weight side the corrected and uncorrected curves coincide, but where at the high molecular weight side, both curves depart greatly. Consequently,  $\bar{M}_n$  is affected by dispersion to a lesser extent than  $\bar{M}_w$  is.

**Source (c).** If  $h$  is constant, the matrix  $A$  appearing in eq. (4) is symmetrical. If  $h$  varies with the elution volume, the matrix  $A$  has lost its symmetry, and the same can be expected for the dispersion correction derived from it.

## SUMMARY

The iteration described here can be handled as a simple and efficient correction for the occurrence of dispersion in GPC. Its application to some

multimodal distributions clearly shows that resolution in GPC can be improved considerably. The asymmetrical effect of the dispersion on  $\bar{M}_n$  and  $\bar{M}_w$  is reasonably recovered by the method.

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