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Calibration of Instrumental Spreading for GPC

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Synopsis

The proper use of the method for correcting instrumental spreading in GPC requires a precise calibration of the spreading characteristics of the instrument. Heretofore, such a calibration could be obtained only through the tedious reverse-flow experiments. A more rapid method of calibrating instrumental spreading is presented in this work. This method uses the leading halves of the chromatograms of several standard polystyrene samples. These chromatograms are normally used in the calibration of molecular weight; additional experimental steps are therefore not required. The calculation of the instrumental spreading characteristics from these chromatograms is also relatively simple. The instrumental spreading characteristics were found to depend on the elution volume but not on the nature of the polymer. Thus, calibration results from using polystyrene standards can be used to treat chromatograms for other polymers. For the present GPC instrument, the spreading was found to reach a maximum at an elution volume near 400,000 in polystyrene molecular weight. The existence of this maximum is in agreement with observations made by other investigators and is an indication that diffusion in the mobile phase is not an important contribution to instrumental spreading. The problem of skewing or tailing is discussed. Indication of skewing was observed for one of the higher molecular weight polystyrene samples but the extent of skewing was not severe at the present flow rate of 2 ml/min.

Introduction

In GPC the relation between the experimental chromatogram, $f(v)$, and the chromatogram after the correction for instrumental spreading, $w(y)$, is given by the integral equation

$$f(v) = \int_{-\infty}^{\infty} w(y)g(v - y)dy \tag{1}$$

where both v and y represent the elution volume or counts and the function $g(v - y)$ represents the overall instrumental spreading.[1] In order to solve for $w(y)$, the spreading function $g(v - y)$ must be known for the instrument under the prevailing operating conditions. Hess and Kratz[2] assumed that a number of narrow-distribution polystyrene samples are monodisperse and calculated the spreading functions from the chromatograms of these samples. Pickett, Cantow, and Johnson[3] estimated the polydispersity of some narrow-distribution polymer fractions and used these estimated values as the bases for their calibration of instrumental spreading. Tung, Moore,

and Knight,[4] using a reverse-flow method, calibrated their GPC instrument for the system of polyethylene in trichlorobenzene. Only the reverse-flow method gives an absolute calibration of instrumental spreading, but the method is tedious to use. Hendrickson[5] determined the polydispersity of several narrow-distribution polystyrene samples by the reverse-flow method and proposed to use these samples as standards for future calibration of instrumental spreading. In the present work this same approach was used. Our standard samples, however, covered a wider range of molecular weight and are readily available from commercial sources. Our results will therefore provide a better basis for accurate and rapid calibration of instrumental spreading in GPC.

FORM OF THE INSTRUMENTAL SPREADING FUNCTION

The concept of instrumental spreading (zone broadening) for conventional chromatography has been applied to treat the spreading in GPC.[6-8] The total instrumental spreading is thought to have come from several sources: (a) the spreading caused by mixing outside the packed columns, (b) the spreading caused by mixing (diffusional and convective) in the mobile phase within the packed columns, and (c) the spreading caused by the process of the transfer of solute between the mobile and stationary phases in the columns.

The effect of (a) has been shown to be small.[9] The effects of (b) and (c) have been shown to give Gaussian spreading for conventional chromatography.[10] However, if the columns are overloaded or if the exchange of solute between the phases is slow, tailing can occur and the spreading function will become skewed. This skewed spreading has also been deduced from the theory of fluid flow through packed beds by Hess and Kratz.[2]

Experimentally, low molecular weight compounds have been observed to give Gaussian or nearly Gaussian spreading in GPC. For high molecular weight species, the shape of the spreading function cannot be observed directly as there are no truly monodisperse high molecular weight polymer samples available as yet. It is indisputable that skewing does occur for very high molecular weight species,[11] particularly at fast flow rates. The shapes of the chromatograms of the high molecular weight narrow-distribution polystyrene samples, however, cannot be used to estimate the extent of skewing, nor can they even be used to judge whether skewing does occur at all. These samples were prepared by anionic polymerization. In the preparation of high molecular weight samples by anionic polymerization, it is difficult to avoid premature termination by impurities and chain transfer reaction. Both mechanisms[12,13] produce a low molecular weight tail in the distribution, which is difficult to distinguish from the skewing for instrumental spreading. In fact, low molecular weight fractions have been isolated from one of the high molecular weight samples[14] used in this work. Assuming an incorrect degree of skewing sometimes introduces larger

errors than using the simpler Gaussian distribution as an approximation for all molecular weight species. This view has been shared by many workers.[3,15,16] Tung, Moore, and Knight[4] have further demonstrated that Gaussian spreading is a good approximation up to a molecular weight of 460,000 for polyethylene. In this work, the Gaussian distribution is therefore assumed; thus

$$g(v - y) = (h/\sqrt{\pi})e^{-h^2(v-y)^2} \tag{2}$$

where h is a parameter describing the width of the spreading and is related to the standard deviation, σ, of the Gaussian distribution by

$$h = 1/\sigma\sqrt{2}. \tag{3}$$

EXPERIMENTAL

The reverse-flow method for calibrating instrumental spreading has been described before.[4] A Waters' Model 200 GPC unit fitted with a flow reversal valve was used. The nominal porosities of the columns are: 10^6, 10^5, 5×10^4, 10^4, 3×10^3, and 8×10^2 Å. The polystyrene samples were purchased from Pressure Chemical Company of Pittsburgh, Pa. They are listed in Table I.

In addition to the above samples, a styrene dimer, a narrow-distribution polybutadiene sample, and a poly(vinyl-chloride) fraction were used. The concentration of the styrene-containing samples in the elution stream was analyzed by an ultraviolet light absorption photometer. The volume of the solution cell for the photometer was 0.07 ml. The original Waters' differential refractometer of the GPC instrument was used for the two non-styrene samples. The ultraviolet light absorption system was insensitive to the impurities in the solvent and the chromatograms of the reverse-flow experiments were therefore free from interferences. The sample solutions were nonetheless carefully degassed before use.

Other experimental conditions were: flow rate, 2 ml/min; solvent, THF; temperature, 24°C; sample concentrations, 0.16% for all except the two highest molecular weight samples, for which the concentration was 0.08%; and sample injection time, 30 sec.

TABLE I
Standard Polystyrene Samples

Samples	Molecular weight[a]
8a	10,300
2a	19,800
7a	51,000
1a	160,000
3a	411,000
6a	860,000
14a	1,800,000

[a] Determined by Pressure Chemical Co.

RESULTS OF THE REVERSE-FLOW EXPERIMENTS

The parameter h in eq. (2) was calculated from the reverse-flow chromatograms by the least-squares regression. Except for the two highest molecular weight polystyrene samples, the fit of the Gaussian distribution to the

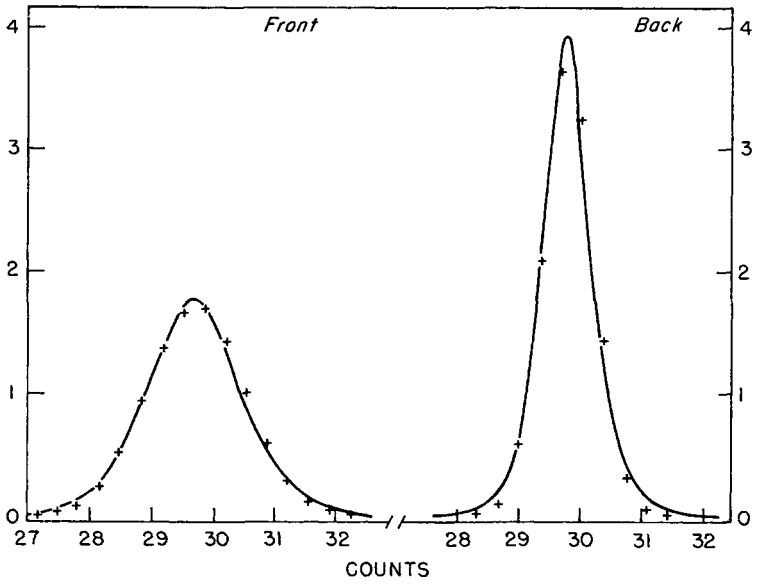

Fig. 1. Gaussian fit of the reverse-flow chromatograms for sample 14a: (+) points represent Gaussian fit; (−) experimental chromatogram.

chromatograms was excellent. Figure 1 shows the fit for sample 14a, the highest molecular weight polystyrene. Even in this highest molecular weight sample the fit is reasonable. Two determinations were made for

TABLE II
The Instrumental Spreading Parameter h

Sample	Peak count	h		
		front	back	overall
14a	29.82	0.888	1.679	1.110
6a	31.02	0.753	1.490	0.951
3a	33.12	0.770	1.042	0.876
Polybutadiene	33.76	0.814	1.040	0.907
1a	35.73	0.872	1.071	0.956
PVC Fraction	38.13	0.978	1.006	0.992
7a	39.02	1.027	1.078	1.052
2a	42.11	1.136	1.067	1.100
8a	43.92	1.225	1.173	1.198
Styrene dimer	54.41	(straight-through run)		1.689

each sample, one for the front half of the columns and one for the back half of the columns. The overall h is calculated by the relation

$$h_{\text{overall}} = \sqrt{2}/\sqrt{(1/h^2_{\text{front}}) + (1/h^2_{\text{back}})}. \quad (4)$$

Table II shows the h values calculated. The overall h values were plotted in Figure 2 as functions of elution counts.

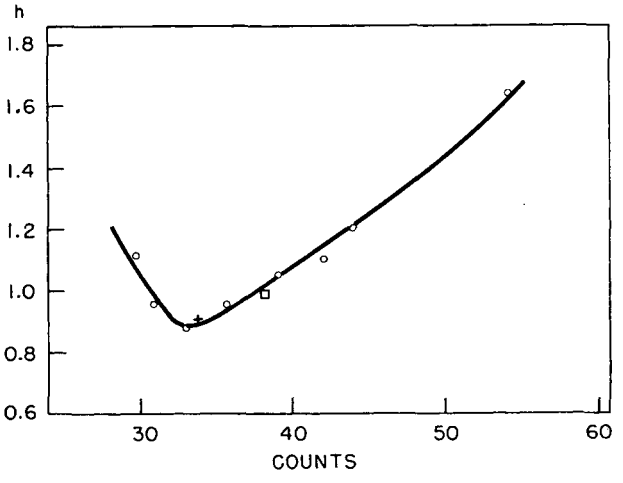

Fig. 2. The variation of the parameter h with elution counts: (O) styrene polymers; (+) polybutadiene; (□) PVC.

PROCEDURES FOR CALIBRATING INSTRUMENTAL SPREADING FROM THE CHROMATOGRAMS OF STANDARD SAMPLES

Using the parameter h given in Table II, we may calculate the polydispersities of the standard samples from their regular straight-through chromatograms. These polydispersities in turn can be used to calibrate the instrumental spreading characteristics of GPC without the tedious reverse-flow experiments. Hendrickson[5] outlined such a procedure in which he measured the width of the chromatograms for the standard samples. He then subtracted from the width the contribution of instrumental spreading determined by the reverse-flow experiments. The net width was converted into a decade span on a molecular weight scale. A more rigorous method of representing the polydispersity in terms of the ratio of weight- to number-average molecular weight has been proposed by Hamielec and Ray.[17] Section A below describes the application of their method to our problem. Hamielec and Ray, however, used an assumption of linear molecular weight calibration (the relation between the logarithm of molecular weight and elution volume or count). Such an assumption prevents the maximum utilization of the experimental precision of GPC. In section B we propose still another method using direct curve fitting. This last method, we believe, is more accurate.

A. Calibration using the M_w/M_n ratios of the Standard Samples

Hamielec and Ray[17] have shown that if the molecular weight calibration is linear, then, regardless of the complexity of the distribution of the sample, there is the relation

$$M_w/M_n = (M_w/M_n)_h \exp(-D^2/2h^2) \tag{5}$$

where M_w/M_n is the weight- to number-average molecular weight ratio of the sample, and $(M_w/M_n)_h$ is the same ratio calculated directly from the uncorrected chromatogram. The instrumental spreading is assumed to be

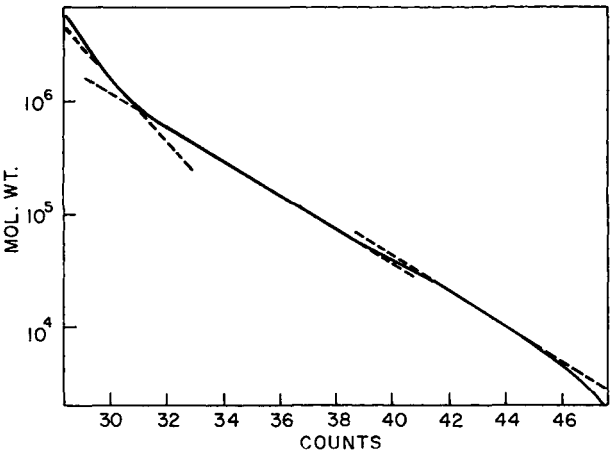

Fig. 3. The molecular weight calibration for the present GPC unit.

Gaussian, with, a constant h. The parameter D is calculated from the linear molecular weight calibration which may be expressed by the equation

$$\ln M = C - Dv \tag{6}$$

The molecular weight calibration of the present GPC unit is shown in Figure 3. The three dash lines in the figure were the linear relations used to calculate the values of D and $(M_w/M_n)_h$ in Table III.

TABLE III
The Polydispersity of the Standard Polystyrene Samples
Calculated by the Method of Hamielec and Ray[17]

Sample	Mol wt	D	h	$(M_w/M_n)_h$	M_w/M_n
14a	1,800,000	0.6324	1.110	2.451	2.084
6a	860,000	0.3525	0.951	1.160	1.083
3a	411,000	0.3525	0.876	1.136	1.048
1a	160,000	0.3525	0.956	1.090	1.018
7a	51,000	0.3525	1.052	1.090	1.031
2a	19,800	0.3611	1.100	1.109	1.051
8a	10,300	0.3611	1.198	1.112	1.063

For an unknown GPC unit, the $(M_w/M_n)_h$ ratios are calculated from chromatograms of the standard samples using the molecular weight calibration for that unit. Then, with the corresponding M_w/M_n ratios listed in the last column of Table III and eq. (5), the h values for the unknown unit can be calculated.

The M_w/M_n ratios listed in Table III, however, are subject to the errors involved in selecting the straight lines from the essentially nonlinear molecular weight calibration. Such a nonlinear relation is not unique for the present GPC unit. In fact, it is a characteristic for any column or column combination unless it is used within a very small range of molecular weight. Because of the exponential relation in eq. (5), any errors in D and $(M_w/M_n)_h$ will be magnified in the final values of h. Consequently, the second significant digit of h may be in doubt.

B. Calibration by Curve Fitting of Chromatograms

The shapes of the chromatograms for the standard samples are usually skewed and non-Gaussian. To overcome the difficulty of fitting a Gaussian distribution to non-Gaussian curves, we propose to use only the leading halves of the peaks. Let v_p represent the elution volume at the peak of the chromatogram $f(v)$ for a standard sample. The Gaussian distribution can be written as

$$f(v) = \frac{h_c}{\sqrt{\pi}} \exp\ [-h_c^2(v - v_p)^2] \tag{7}$$

where h_c is the parameter describing the breadth of the leading half of the observed chromatogram for a standard sample. Least-squares regression can be used to calculate h_c using points on the leading half of the chromatogram [$f(v)$ and v up to $v = v_p$]. The fit of the Gaussian distribution to the leading halves of the seven chromatograms for the standard samples is shown in Figure 4. In Table IV the calculated values of h_c are listed.

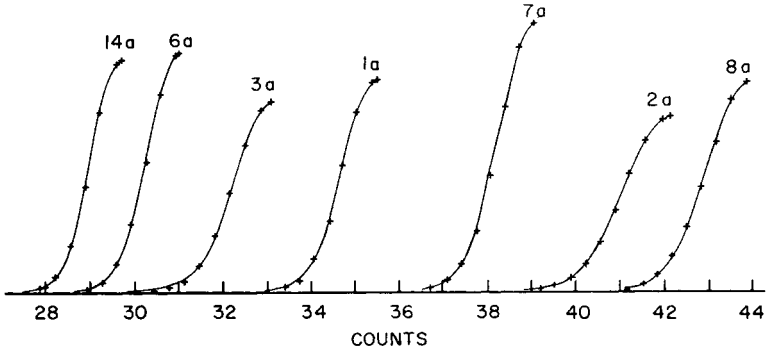

Fig. 4. Gaussian fit of the leading halves of the regular chromatograms of the seven standard polystyrene samples: (+) points represent Gaussian fit; (−) experimental chromatogram.

For samples 14a, 3a, and 1a the differences between h and the corresponding h_c are less than 1.5%, which is believed to be the experimental error. The high molecular weight halves of the distributions for these three samples are therefore extremely narrow. For sample 6a, h_c is significantly larger than h, implying that the chromatogram is narrower than the instrumental spreading. This seemingly paradoxical result may be attributed to the skewing of instrumental spreading and will be discussed in more detail later. Nevertheless, it is evident that the high molecular weight half of the distribution for sample 6a is also very narrow. In calibrating an unknown GPC unit, we may therefore treat the leading halves of the distributions of these four high molecular weight samples as essentially monodisperse distributions and let h_c be taken as the corresponding instrumental spreading parameter h.

TABLE IV
Chromatogram Characteristics of Standard Polystyrene Samples

Sample	Mol wt	Peak count	h	h_c	h_s
14a	1,800,000	29.82	1.110	1.122	—
6a	860,000	31.02	0.951	1.056	—
3a	411,000	33.12	0.876	0.879	—
1a	160,000	35.73	0.956	0.966	—
7a	51,000	39.02	1.052	0.924	1.938
2a	19,800	42.11	1.100	0.725	0.964
8a	10,300	43.92	1.198	0.781	1.031

For the three lower molecular weight samples, h_c in Table IV is significantly smaller than the corresponding h; hence their molecular weight distributions must be considered in calibrating unknown GPC units. Since the leading halves of their chromatograms can be fitted by a Gaussian distribution, the corrected chromatograms, $w(v)$, for these samples must also be nearly Gaussian. We can write

$$w(v) = \frac{h_s}{\sqrt{\pi}} \exp\ [-h_s^2(v - v_p)^2]. \tag{8}$$

The parameters h_s listed in Table IV were calculated from h, h_c, and the relation

$$\frac{1}{h_c^2} = \frac{1}{h_s^2} + \frac{1}{h^2}. \tag{9}$$

Knowing h_s, by virtue of eq. (8) we knew the leading half of the corrected chromatogram $w(v)$. We then used the molecular weight calibration in Figure 3 to convert $w(v)$ to the logarithmic molecular weight distribution, $W_L(\log M)$ listed in Table V.

TABLE V
High Molecular Weight Halves of the Log Molecular Weight Distributions

Sample 8a		Sample 2a		Sample 7a	
Mol wt	$W_L(\log M)$	Mol wt	$W_L(\log M)$	Mol wt	$W_L(\log M)$
10,300	3.3564	19,800	3.7961	51,000	7.7966
10,945	3.3192	20,894	3.7401	52,336	7.7095
11,619	3.1307	22,036	3.5024	53,717	7.0967
12,322	2.8144	23,230	3.1184	55,147	6.2138
13,054	2.4095	24,479	2.6409	56,627	5.1758
13,814	1.9630	25,783	2.1277	58,159	4.1015
14,602	1.5209	27,145	1.6310	59,747	3.0925
15,420	1.1200	28,566	1.1895	61,391	2.2188
16,268	0.7836	30,050	0.8251	63,093	1.5149
17,148	0.5207	31,597	0.5442	64,856	0.9843
18,062	0.3286	33,213	0.3411	66,681	0.6088
19,012	0.1970	34,900	0.2031	68,571	0.3583
20,001	0.1122	36,666	0.1148	70,526	0.2008
21,032	0.0607	38,518	0.0616	72,548	0.1071
22,105	0.0312	40,464	0.0314	74,639	0.0544
23,224	0.0153	42,517	0.0151	76,799	0.0263
24,390	0.0071	44,689	0.0069	79,030	0.0121
25,605	0.0031	46,995	0.0030	81,333	0.0053
26,870	0.0013	49,451	0.0012	83,709	0.0022
28,188	0.0005	52,073	0.0005	86,158	0.0009

The log molecular weight distribution, $W_L(\log M)$, is related to the conventional molecular weight distribution $W(M)$ by

$$W_L(\log M) = \frac{M}{2.3026} W(M) \tag{10}$$

and to the corrected chromatograms by

$$w(v) = W_L(\log M)(d \log M/dv). \tag{11}$$

The term $(d \log M/dv)$ is the derivative of the molecular weight calibration curve. When the molecular weight calibration is linear, then $(d \log M/dv) = -D/2.3026$.

In calibrating an unknown GPC unit, the sequence of the calculation is reversed. From the distribution in Table V, eq. (11), and the molecular weight calibration of the new GPC unit, one can calculate the corrected chromatogram $w(v)$. Then by the least-squares regression, h_s for the $w(v)$ chromatogram can be calculated. The h_c parameter can be calculated from the straight-through chromatogram of the standard sample. Finally, from eq. (9) one can calculate h. All these steps are simple and rapid on a digital computer.

The values in Table V were carried to the fifth digit because they were based on smoothed data. Our experimental precision was accurate only to the third digit.

DISCUSSION

The Instrumental Spreading Parameter *h*

The curve in Figure 2 shows that for the present GPC unit, h has a minimum at a molecular weight of approximately 400,000 on a polystyrene scale. Hendrickson[5] observed that the extent of spreading for species too large to penetrate the gels was approximately the same as that for the solutes of very low molecular weights. The spreading became large only for the partially penetrating species. The existence of a minimum for h is in agreement with his observation. Data in Table II show that the minimum for h occurred at a higher molecular weight for the front half of the columns, which were packed with gels of higher porosity. This again agrees with Hendrickson's observation that only partially penetrating solutes give the larger spreading. Consequently, diffusion in the mobile phase cannot be an important factor for instrumental spreading in GPC.

Table II and Figure 2 show that the spreading for polybutadiene and PVC correlates well with the spreading for polystyrene. For the nonstyrene samples the Waters' differential refractometer was used to analyze the polymer concentration in the effluent. The microcell in the differential refractometer contributed a slightly lesser amount of spreading than the cell in the ultraviolet absorption photometer. On the other hand, we were not able to eliminate completely the interference from impurities to the reverse-flow chromatograms of the nonstyrene samples. The interference from impurities such as dissolved air and water caused a small dip at the tip of these chromatograms. The dips broadened the chromatograms slightly. The above two contributions to spreading are estimated to be small and are compensating. We may therefore conclude that the instrumental spreading is essentially independent of the chemical structure of the polymer and h values calculated from polystyrene standard samples can be used for treating chromatograms for other polymers.

The Polydispersities of the Standard Polystyrene Samples

In anionic polymerization[12] it is well known that the ideal Poisson distribution is best approached when the products are of medium molecular weights. Broader distributions are usually obtained for both high and low molecular weight samples. The variation of M_w/M_n for the present polystyrene samples as shown in Table III is in agreement with such a trend. The M_w/M_n ratios for the highest and the lowest molecular weight samples, may be misleading. The chromatogram of each of the two samples covers a range of molecular weight where the calibration is obviously nonlinear. For sample 14a, the molecular weight calibration used was the line that conformed to the steeper part of the nonlinear curve. The actual chromatogram extended into regions of gentler slopes. The M_w/M_n ratio given in Table III is therefore larger than the true value. For sample 8a, the converse is true and the M_w/M_n ratio is too small. The distributions

listed in Table V, on the other hand, were obtained by using the entire nonlinear molecular weight calibration curve and they are therefore more reliable.

Skewing in Instrumental Spreading

We showed earlier that for sample 6a the chromatogram was narrower than the instrumental spreading. This paradoxical observation may reflect skewing in instrumental spreading. An analysis for such a case is given below.

A skewed instrumental spreading function can in general be represented by

$$g(v - y) = A\phi(v - y) \exp [-p^2(v - y)^2] \tag{12}$$

where A is the reciprocal of the normalization factor and ϕ is a polynomial containing terms some of which are in odd powers of $(v - y)$. For the purpose of illustration we use a simple third power ϕ function and write

$$g(v - y) = (p/\sqrt{\pi})[a(v - y)^3 + 1] \exp [-p^2(v - y)^2]. \tag{13}$$

We assume that the column is packed with gels of uniform porosity and is twice as long as the one for which the spreading function is given by eq. (13). If an ideal pulse of monodisperse sample is injected, then the shape of the concentration zone at the midpoint of the column is given by

$$w_f(v) = (p/\sqrt{\pi})[a(v - v_0)^3 + 1] \exp [-p^2(v - v_0)^2]. \tag{14}$$

If the flow is allowed to progress in the same direction, the zone at the exit of the column is

$$f_f(v) = \int_{-\infty}^{\infty} w_f(y)g(v - y)dy. \tag{15}$$

If we let $z = (v - v_0)/2$, eq. (15) after integration becomes

$$f_f(v) = (p/\sqrt{2\pi})[1 + ao(z) - a^2E(z)] \exp (-2p^2z^2) \tag{16}$$

where $E(z)$ contains only even-power terms of z and $o(z)$ contains only odd-power terms of z:

$$E(z) = 15/64p^6 - 9z^2/16p^4 + 3z^4/4p^2 - z^6 \tag{17}$$

$$o(z) = 2 + 3z/2p^2 \tag{18}$$

If the flow is reversed at the midpoint of the column, then the zone, after being eluted back to the entrance, is

$$f_r(v) = \int_{-\infty}^{\infty} w_r(y)g(v - y)dy. \tag{19}$$

The function w_r is the mirror image of w_f:

$$w_r(v) = (p/\sqrt{\pi})[a(v_0 - v)^3 + 1] \exp [-p^2(v_0 - v)^2] \tag{20}$$

Integration of eq. (19) gives

$$f_r(v) = (p/\sqrt{2\pi})[1 - a^2E(z)] \exp(-2p^2z^2). \quad (21)$$

Equation (21) is symmetrical as it contains only terms of even power of z. Furthermore, the coefficient a must be substantially smaller than 1 in order for eq. (13) to represent a realistic spreading function—a function containing no significantly large negative values. Hence, the second term in the bracket in eq. (21) is negligible and $f_r(v)$ is essentially Gaussian with an h parameter equal to $p/\sqrt{2}$. The same Gaussian expression is found in the equation for $f_f(v)$, but the odd-power terms are not negligible, as they have a coefficient a instead of a^2. These odd-power terms make the leading half of $f_f(v)$ sharper than the Gaussian expression with h of $p/\sqrt{2}$. Thus, the curve-fitting method should give a higher value for h, as in the case for sample 6a. To further illustrate the situation, we substituted 1 for p and 0.2 for a and calculated functions $w_f(v)$, $f_r(v)$, and $f_f(v)$ from eqs. (14), (16), and (21). They are shown in Figure 5. Using $f_r(v)$ as a reverse-flow chromatogram, we obtained an h value of 0.7066, which is very close to the value of $1/\sqrt{2}$, or 0.7071. By curve fitting to the leading half of $f_f(v)$ we obtained an h value of 0.7622. This difference is in the same order as that between h and h_c for sample 6a.

Balk and Hamielec[11] observed that the skewing in instrumental spreading increased with increasing molecular weight up to a limit, and at very high molecular weight they found the skewing to be less severe. The agreement of h and h_c in Table IV for sample 14a suggests also a drop in skewing for the very high molecular weight sample. Nonetheless, we cannot rule out the possibility that such an agreement may be fortuitous. The leading half of the distribution for this sample may not be very narrow, but its chromatogram may have been sharpened by skewing. The two compensating effects may produce the agreement observed.

The current 10% error in h at high molecular weight will, however, introduce a much smaller error in the final corrected chromatograms. At a slower flow rate than the present 2 ml/min, the error in h is expected to be still less. The assumption of Gaussian spreading function, therefore, is

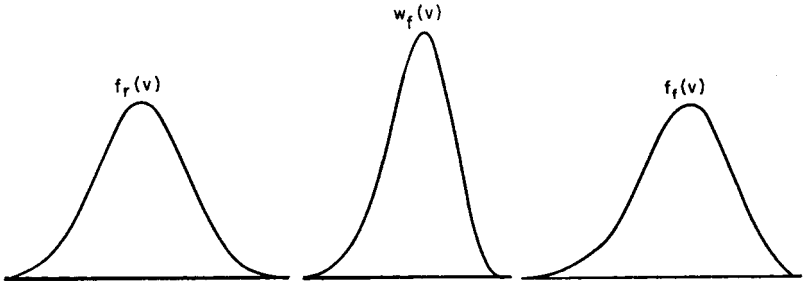

Fig. 5. The functions $w_f(v)$, $f_r(v)$, and $f_f(v)$.

not causing serious errors even at the high molecular weight end of the chromatograms.

CONCLUSIONS

The curve-fitting method described in the present work for calibrating GPC instrumental spreading is a practical one as it uses the same chromatograms that are required for the calibration of molecular weight. No additional experimental steps are needed. The calculation involves only standard methods of regression, which are simple and rapid on a computer. Furthermore, the calibration obtained through the use of standard polystyrene samples can be used to treat chromatograms for other polymers.

The assumption of a Gaussian spreading function may cause some small errors at the high molecular weight end of the chromatogram. Nevertheless, until an experimental method is developed for determining the extent of skewing in the spreading, such errors are unavoidable.

The present results on instrumental spreading support the belief that the spreading caused by diffusion in the mobile phase is unimportant in GPC.

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