A Simplified Method for Correction of Polydispersities From Gel Permeation Chromatography

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Synopsis

A simple method is presented for correction of polydispersity obtained by gel permeation chromatography. The method proposed utilizes well-characterized polystyrene standards for both instrument calibration and construction of a correction curve which is then used for calculation of weight-average and number-average molecular weights and polydispersity of samples to be characterized.

INTRODUCTION

Gel permeation chromatography (GPC) is a new analytical tool which makes use of polymer molecular weights feasible for quality control. Manufacturers and converters of polymers involved in both polymerization and extrusion can now, due to the speed of GPC analysis, utilize molecular weights for material control.

The principles and operation of the gel permeation chromatograph have been well defined by Cazes[1] where the generally accepted method of calculation of weight-average and number-average molecular weights is given in detail. Utilizing this method, the molecular weight averages calculated from the raw chromatograms can be significantly different from the absolute molecular weight averages obtained by classical techniques. These differences are caused by instrumental spreading or band broadening.[2,3]

The two major causes of band broadening have been attributed to axial dispersion and skewing of the chromatogram.[4] Band broadening, which varies with changes in operating conditions and aging of columns, does not allow today's chromatograms to be directly compared with those made at an earlier date unless they have been corrected for broadening. Comparison of results from two different gel permeation chromatographs is also limited by this instrumental spreading which varies from one instrument to the other. Several methods for correction of these effects have been reported in the literature,[3,5,6] but all require the use of complex computer programs.

It is the purpose of this paper to offer a simplified method for GPC correction utilizing simple hand calculations which will give reasonably good agreement with results obtained by classical methods of analysis.

EXPERIMENTAL

A Waters Associates Model 200 gel permeation chromatograph was used for our study.   The instrument was operated at 25 ± 1°C with tetrahydrofuran at a flow rate of 1 ml/min, with the degasser set at 55°C.   All samples at 0.1% concentration, were injected for 120 sec by a Waters automatic sample injection system.   Calibration and calculations were carried out as described by Cazes,[1] plotting peak Å versus elution volume.

Two column sets were used for our study.   The first set consisted of four columns having porosity designations of 10^6, 10^5, 10^4, and 10^3Å.   This set had been in constant use for 20 months and was now showing excessive broadening characteristics.   The second column set, consisting of six columns designated 10^6, 10^5, $2–10^4$, 10^3, and 10^2 Å, was recently installed and in use for two weeks prior to this study.   The two additional columns were added in an attempt to improve resolution of this general-purpose column set.   The 10^6 Å column in our second column set is designated by Waters as "greater than 10^6," while the 10^6 column in the first set is designated "10^6".

RESULTS AND DISCUSSION

When a sample injection is made into a GPC, under ideal conditions, a monodispersed material elutes as a Gaussian function (Fig. 1).   If conditions are other than ideal, which is usually the case, the effects of zone broadening are seen (Fig. 2).

When molecular weights are calculated from a raw chromatogram and the results are compared to those obtained by classical methods, the weight-average molecular weight ($\bar{M}_w$) by GPC agrees reasonably well with light-
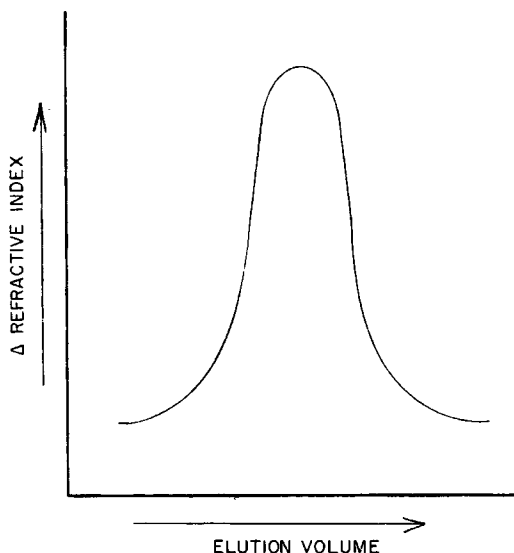

Fig. 1. Idealized chromatogram showing elution of species as a Gaussian function.
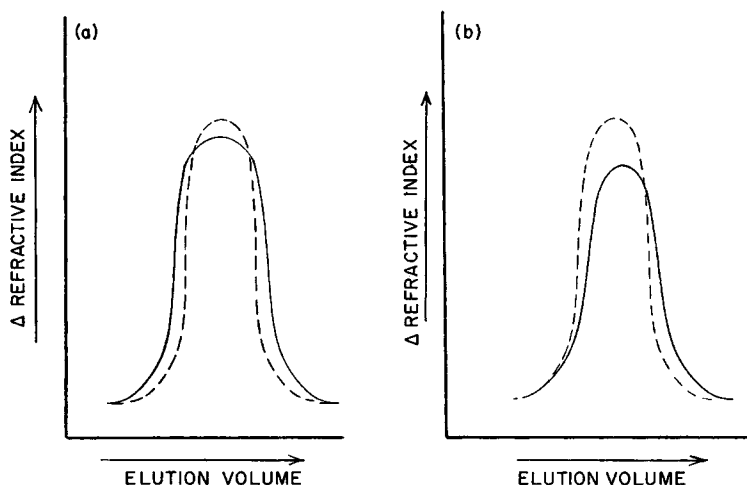
Fig. 2. Comparison of ideal (dashed line) vs. experimental (solid line) chromatogram showing (a) axial dispersion effect; (b) skewing effect.

scattering values over the effective range of the column set, while number-average molecular weight $(\bar{M}_n)$ values are invariably lower than those obtained by osmometry.

Hamielec and Balke[7,8] have shown that while both $\bar{M}_w$ and $\bar{M}_n$ are lowered by skewing, axial dispersion raises $\bar{M}_w$ but further lowers $\bar{M}_n$. Skewing is also found to generally increase with molecular weight of the sample, linearity of the calibration curve, and sample concentration, particularly at higher molecular weights.

These effects are seen to be reconfirmed in our work during the calibration procedure. The various polystyrene standards were run, and a calibration curve was drawn by plotting the peak molecular weight versus elution volume for each. When this calibration curve is used to calculate $\bar{M}_w$ for

TABLE I
Correction of Polydispersity (ΔP) Using Column Set 10^6, 10^5, 10^4, 10^3 Å, Calculated from Original Calibration Curve

|	Supplier values			Experimental values			
Standard	$\bar{M}_w$	$P(t)$		$\bar{M}_w$	P	ΔP	EV[a]
244 Å	10,300	1.06		11,170	1.17	0.11	31.48
480 Å	19,850	1.04		19,612	1.20	0.16	30.44
1220 Å	51,000	1.02		48,945	1.34	0.32	28.85
2360 Å	98,200	1.02		91,262	1.41	0.39	28.00
4000 Å	173,000	1.06		148,716	1.61	0.55	27.27
9800 Å	411,000	1.05		375,180	3.19	2.04	25.90
20,200 Å	867,000	1.12		724,152	5.92	4.80	25.16
NBS 705	179,000	1.05		179,309	1.73	0.68	27.00
NBS 706	257,900	1.88		254,902	3.70	1.82	26.70

[a] Elution volume, 1 count = 5 ml.
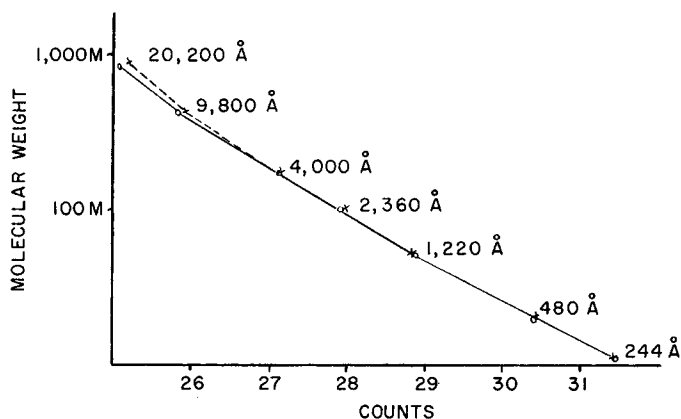
Fig. 3. Typical calibration curve for column set consisting of 10^6, 10^5, 10^4, 10^3 Å porosity. Dashed line indicates corrected curve.

the standards, all values are close to those reported by the suppliers, except the 9800 and 20,200 Å standards. The $\bar{M}_w$ for these standards is lower than reported. This is most readily seen with column set #1. Material eluting at the high end of the calibration curve, where it is not linear, is not properly resolved and calculated, thereby giving a lower molecular weight than is actually present.

There are two ways to correct for this behavior; either the calibration curve can be made more linear by proper choice of additional columns, as with column set #2, or mathematical correction can be applied to the calibration curve. In order to mathematically correct the calibration curve, it is absolutely necessary to have reliable calibration standards. Utilizing these standards, the molecular weights at the various elution volumes on the calibration curve can be adjusted to give the known $\bar{M}_w$ when the standards are calculated. In Figure 3, the solid line is the calibration curve obtained

TABLE II
Correction of Polydispersity (ΔP) Using Column Set 10^6, 10^5, 10^4, 10^3 Å, Calculated from Corrected Calibration Curve

Supplier values			Experimental values			
Standard	$\bar{M}_w$	$P(t)$	$\bar{M}_w$	P	ΔP	EV[a]
244 Å	10,300	1.06	10,974	1.17	0.11	31.48
480 Å	19,850	1.04	19,468	1.21	0.17	30.44
1220 Å	51,000	1.02	49,819	1.36	0.34	28.85
2360 Å	98,200	1.02	94,680	1.43	0.41	28.00
4000 Å	173,000	1.06	156,557	1.71	0.65	27.27
9800 Å	411,000	1.05	404,667	3.39	2.34	25.90
20,200 Å	867,000	1.12	790,370	6.41	5.29	25.16
NBS 705	179,000	1.05	183,952	1.73	0.68	27.00
NBS 706	257,900	1.88	273,588	3.94	1.84	26.70

[a] Elution volume, 1 count = 5 ml.

from the original GPC data. The dashed line is the mathematically corrected portion of the calibration curve. It can be seen that the amount of correction necessary increases with increasing molecular weight (see Tables I and II). Utilizing column set #2 (Table III), the correction necessary is

TABLE III

Correction of Polydispersity (ΔP) Using Column Set 10^6, 10^5, 2-10^4, 10^3, 10^2 Å, Calculated and Corrected for Broadening

	Supplier values			Calculated GPC values			Corrected GPC values	
Standard	$\bar{M}_w$	$P(t)$	$\bar{M}_w$	P	ΔP	P	ΔP
244 Å	10,300	1.06	11,037	1.09	0.03	1.05	$-.01$
480 Å	19,850	1.04	19,247	1.08	0.04	1.02	$-.02$
1220 Å	51,000	1.02	47,599	1.12	0.10	1.01	-0.01
2360 Å	98,200	1.02	94,973	1.21	0.19	1.01	-0.01
4000 Å	173,000	1.06	163,105	1.27	0.21	0.97	-0.09
9800 Å	411,000	1.05	407,805	1.83	0.78	1.08	$+0.03$
20,200 Å	867,000	1.12	791,664	2.51	1.39	1.06	-0.06
NBS 705	179,000	1.05	182,948	1.43	0.38	1.07	$+0.02$
NBS 706	257,900	1.88	284,607	2.90	1.02	2.37	$+0.49$

significantly reduced. Results consistent with these have been previously reported by Smith and Feldman.[9]

The correction procedure proposed in this paper utilizes these facts, accepting the $\bar{M}_w$ as calculated from the calibration curve (adjusted where necessary) and correcting only the $\bar{M}_n$ and the polydispersity.

CORRECTION PROCEDURE

Well-characterized polystyrene standards obtained from Waters Associates were injected into the GPC. (Our work is based on the assumption that the $\bar{M}_w$ and $\bar{M}_n$ values for these standards are correct. If more reliable standards are available, they can be similarly utilized in this procedure.) The peak molecular weights of these standards were plotted against their peak elution volumes, giving a typical calibration curve (Fig. 3). The chromatogram of each standard was then treated as a regular sample, and the calibration curve was used to calculate weight-average molecular weight, number-average molecular weight, and polydispersity for each. We then subtracted the polydispersity $P(t)$ reported by the supplier from the polydispersity P obtained from our calculation of the chromatogram and got a ΔP, or polydispersity correction value (see Table II). (If we plot ΔP versus weight-average molecular weight, we obtain a linear function over the effective range of our column set, Figure 4.)

We now have a plot of weight-average molecular weight against ΔP, or polydispersity correction value. When an unknown sample is run, the $\bar{M}_w$, $\bar{M}_n$, and polydispersity are calculated from the calibration curve. The $\bar{M}_w$
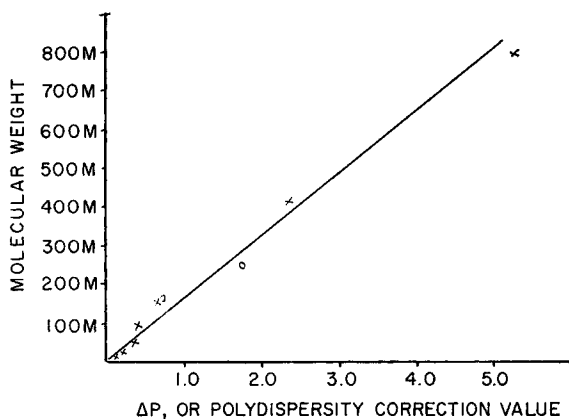
Fig. 4. Typical correction curve drawn for column set consisting of 10^6, 10^5, 10^4, and 10^3 Å porosity: (X) Water standards; (O) NBS standards.

value is then used with the correction curve to find the ΔP, or correction value. Utilizing this ΔP we can now recalculate and correct our number-average molecular weight and the polydispersity. Table IV shows a tabulation of the standards calculated and corrected for instrumental broadening.

TABLE IV
Correction of Polydispersity (ΔP) Using Column Set 10^6, 10^5, 10^4, 10^3 Å, Calculated and Corrected for Broadening

Supplier values			Experimental values		
Standard	$\bar{M}_w$	$P(t)$	$\bar{M}_w$	P	ΔP
244 Å	10,300	1.06	10,974	1.24	0.18
480 Å	19,850	1.04	19,468	1.23	0.19
1220 Å	51,000	1.02	49,819	1.20	0.18
2360 Å	98,200	1.02	94,680	1.01	0.01
4000 Å	173,000	1.06	156,557	0.93	−0.13
9800 Å	411,000	1.05	404,667	1.13	0.08
20,200 Å	867,000	1.12	790,370	1.88	0.76
NBS 705	179,000	1.05	183,952	1.05	0.00
NBS 706	257,900	1.88	273,588	2.46	0.58

CONCLUSIONS

A simple method is presented for correction of polydispersity obtained by GPC. Utilization of this correction method enables results to be compared to those previously obtained on a single instrument or those obtained on different instruments. The correction procedure has been simplified so that it can be used with a minimum of mathematical calculations.

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