

Resolution Correction for Molecular Weight Averages from GPC

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Synopsis

The method of Hamielec and Ray for correcting GPC molecular averages is discussed. It is shown that this method can be combined with the resolution index concept of Smith and Feldman to provide a simple accurate correction method. Practical application of the method to four different column combinations is discussed. Three of the combinations are typical Styragel column combinations, and they are very similar in their correction requirements. The fourth combination employed less gel with resultant higher flow rates and much shorter residence times. It required a larger correction factor, but even so, only a 17% correction to the weight-average or number-average molecular weight was required.

INTRODUCTION

The GPC trace for a polymer provides a relationship $F'(v)$ between polymer concentration and elution volume v . In turn, the elution volume can be related to a molecular weight by means of a calibration curve. However, the problem of obtaining the true molecular weight distribution from $F'(v)$ is complicated by the fact that each increment of elution volume contains a finite range of molecular weights. This is a result of the spreading of each molecular weight species of polymer in passing through the GPC instrument.

Many methods have been proposed to correct for this spreading, but none of them is being used to any appreciable extent.¹ One method, however, provides a very simple and apparently quite accurate method of correcting molecular weight averages. It is based on the suggestion of Hamielec and Ray.² We show herein how their suggestion can be combined with the resolution index³ to obtain a molecular weight correction factor. This can be used to obtain number-average, weight-average, and viscosity-average molecular weights which have been corrected for GPC spreading.

While the basic theoretical development has already been presented by Hamielec and Ray, we develop it again here along somewhat different lines to provide a background for commenting on the effects of some of the assumptions.

THEORETICAL

For a particular polymer sample, the GPC provides the curve $F'(v)$. Each elution volume v can be related to a molecular weight M by means of a calibration curve. It is the usual practice to use polystyrene standard samples for this. In the ideal case of no overlapping of individual molecular weight species, $F'(v)$ and the calibration curve can be combined to give an average molecular weight. Even with real columns, such a molecular weight average is useful though it is not a true average. Consequently, we will distinguish it with a subscript ∞ , i.e., assuming infinite resolution. By way of example with a linear calibration curve, we have as an approximation

$$(\bar{M}_w)_\infty \cong \Sigma F'(v) M \Delta v / \Sigma F'(v) \Delta v \quad (1)$$

where M is obtained from the corresponding elution volume by means of the calibration curve. In the case of nonlinear calibration curves, the calculation is more complicated.⁴ However, in any case, $F'(v)$ and the calibration curve provide all the information needed to calculate these averages. Thus, the limit on the possible accuracy of $(\bar{M}_w)_\infty$ is determined solely by the limits on the accuracy of the GPC curve and the calibration curve.

The three molecular weight averages most likely to be desired are \bar{M}_n , \bar{M}_w , and \bar{M}_v . For our subsequent discussion, it is convenient to use the variable x defined by

$$x = \ln M \quad (2)$$

so that the molecular weight distribution of a polymer sample is given by $W(x)$. Then, the molecular weight averages are

$$\bar{M}_n = 1 / \int_{-\infty}^{\infty} W(x) e^{-x} dx \quad (3)$$

$$\bar{M}_w = \int_{-\infty}^{\infty} W(x) e^x dx \quad (4)$$

$$\bar{M}_v = \left(\int_{-\infty}^{\infty} W(x) e^{\alpha x} dx \right)^{1/\alpha} \quad (5)$$

In the last equation, α is the exponent in the $[\eta]$ - M relation. Thus, all the averages can be expressed as simple functions of bilateral Laplace transforms of the form

$$\bar{W}(s) = \int_{-\infty}^{\infty} W(x) e^{-sx} dx$$

where $\bar{W}(s)$ is a bilateral Laplace transform of $W(x)$. Thus,

$$\bar{M}_n = 1/\bar{W}(1) \quad (6)$$

$$\bar{M}_w = \bar{W}(-1) \quad (7)$$

and

$$\bar{M}_v = (\bar{W}(-\alpha))^{1/\alpha}. \quad (8)$$

Similarly, if $F'(v)$ is converted to $F(x)$ by means of the calibration curve,

$$(\bar{M}_n)_\infty = 1/\bar{F}(1) \quad (9)$$

$$(\bar{M}_w)_\infty = \bar{F}(-1) \quad (10)$$

and

$$(\bar{M}_v)_\infty = (F(-\alpha))^{1/\alpha}. \quad (11)$$

Equations (6) to (11) involve no approximations or assumptions but depend solely on definitions.

We now consider the relations between the bilateral transforms of $F(x)$ and $W(x)$. The GPC spreading of individual molecular weight species can be approximated by

$$F(x) = \int_{-\infty}^{\infty} W(x) G(x-y) dy \quad (12)$$

where $G(x-y)$ is the spreading function. It is written as a function which is independent of molecular weight because that is the only type that can be easily handled in a rigorous manner by this method. In the practical situations which we have investigated (see Application section), this condition is satisfactorily met. The right-hand side of eq. (12) is what mathematicians have called the convolution of the functions $W(x)$ and $G(x)$. It is known that the Laplace transform of a convolution is the product of the Laplace transforms of the two functions. Hence

$$\bar{F}(s) = \bar{W}(s) \bar{G}(s) \quad (13)$$

which leads to

$$\bar{M}_n = (\bar{M}_n)_\infty \bar{G}(1) \quad (14)$$

$$\bar{M}_w = (\bar{M}_w)_\infty / \bar{G}(-1) \quad (15)$$

and

$$\bar{M}_v = (\bar{M}_v)_\infty / (\bar{G}(-\alpha))^{1/\alpha}. \quad (16)$$

The utility of these depends on our ability to evaluate the Laplace transforms of the spreading functions. If $G(x-y)$ is molecular weight dependent, the transforms are also molecular weight dependent. But in the absence of such dependence, precise values for the transforms can be obtained. This provides the means of obtaining true values of the molecular weight averages from the values obtained directly from the GPC curve assuming infinite resolution.

Some simplifications are of practical importance. If $G(x)$ is a symmetrical function, it is evident from the definition of the bilateral Laplace transform that

$$\bar{G}(1) = \bar{G}(-1) \quad (\text{symmetrical } G). \quad (17)$$

For a properly operating GPC system, the spreading is sufficiently symmetrical to justify the use of eq. (17); however, under certain abnormal circumstances, this may not be true. Combining eqs. (14), (15), and (17) gives

$$\bar{G}(1) = \bar{G}(-1) = \sqrt{\frac{(\bar{M}_w)_\infty / (\bar{M}_n)_\infty}{\bar{M}_w / \bar{M}_n}} \quad (\text{symmetrical } G). \quad (18)$$

Thus, $\bar{G}(1)$ can be obtained experimentally from the GPC curve for a polymer of known polydispersity, \bar{M}_w / \bar{M}_n .

An alternate method of obtaining $\bar{G}(1)$ makes use of the resolution index.³ This index may be thought of as the ratio of the molecular weights corresponding to the extremities of the GPC width at half maximum for a very narrow distribution polymer. This method makes use of information normally easily available from the calibration determination. Assume

$$G(x-y) = A \exp \{ - (x-y)^2 / \lambda \} \quad (19)$$

where A is a normalizing constant chosen for convenience to give $\int_{-\infty}^{\infty} G(x) dx = 1$, and λ characterizes the extent of spreading. Then,

$$\lambda = (\ln RI)^2 / 4 \ln 2 \quad (20)$$

where RI is the resolution index. Then,

$$\bar{G}(1) = \bar{G}(-1) = e^{\lambda/4} = \exp \{ (\ln RI)^2 / 16 \ln 2 \} \quad (\text{Gaussian } G). \quad (21)$$

Similarly,

$$(\bar{G}(-\alpha))^{1/\alpha} = (\bar{G}(1))^\alpha = \exp \{ \alpha (\ln RI)^2 / 16 \ln 2 \} \quad (\text{Gaussian } G). \quad (22)$$

Thus, with a Gaussian spreading function, all of the spreading function transforms needed for use in eqs. (14), (15), and (16) are simply related so it is only necessary to experimentally evaluate one, say, $\bar{G}(1)$. For convenience, this useful quantity may be called a molecular weight correction factor.

APPLICATION TO TYPICAL COLUMNS

The molecular weight correction factors have been determined for four column combinations. Three of the combinations are typical assemblies of standard commercial Styragel columns, and the other is a special high-speed column prepared in our own laboratories. Descriptive information on the columns and operating conditions are given in Table I.

TABLE I
Description of Column Combinations

Type of Styragel, Å	10 ⁶ , 10 ⁵ , 10 ⁴ , 10 ³			10 ⁵ , 10 ⁴ , 10 ³
Ratio	1:1:1:1			2:1:1
Total gel volume, ml	220			130
Combination	I	II	III	IV ^a
Solvent ^b	THF	<i>o</i> -DCB	THF	THF
Temperature	R.T.	130°C	R.T.	R.T.
Flow rate, ml/min	2	2	2	6

^a Gel contained in Chromatronix LC-1/2-43 glass column, 1/2 in. inside diameter, 43 in. long.

^b THF is tetrahydrofuran; *o*-DCB is ortho-dichlorobenzene.

The principal spreading information obtained on these column combinations is presented as the resolution indexes given in Table II. The resolution indexes given in the table were obtained by single measurements on the GPC curves of the standard polystyrene samples used in establishing the calibration curves. The measurements were based on a useful suggestion made by Tung and Runyon.⁵ They observed that most of the ionic polystyrenes used as GPC standards have a molecular weight distribution that cuts off sharply above a certain molecular weight. Thus, the GPC curve on the high molecular weight side is determined largely by the spreading of the columns and is not appreciably perturbed by the molecular weight distribution of the standard. This suggests basing the resolution index on a measurement of the distance from the perpendicular at the peak to the high molecular weight edge of the GPC curve at the middistance between base line and maximum. It is evident from the values given in Table II that all four column combinations have a broad molecular weight range in which the resolution index is substantially constant. These data experi-

TABLE II
Resolution Indexes for GPC Column Combinations in Current Use

Polystyrene standard	Resolution index			
	I	II	III	IV ^a
5,000	0.59			
10,000	0.40	0.36	0.37	
19,800	0.37	0.38		0.27
51,000	0.41	0.40		0.26
97,200	0.41	0.38	0.36	0.28
173,000	0.38	0.40		0.29
200,000			0.36	
411,000	0.36	0.40		0.25
867,000	0.40	0.38	0.35	0.27
1,800,000	0.28	0.30		
2,600,000			0.36	

^a Combinations described in Table I.

mentally define the region in which use of a molecular weight-independent spreading function G is justified.

Equation (18) provides a means of determining the molecular weight correction factor $\bar{G}(1)$ without using the resolution index. The values of $\bar{G}(1)$ calculated from eq. (18) are compared with those calculated from eq. (21) in Table III. Good agreement is obtained. Equation (18) requires only the restriction on G that it be symmetrical. Thus, the Gaussian approximation appears satisfactory.

TABLE III
Comparison of Methods for Evaluating $\bar{G}(1)$

Polystyrene standard	98,200	200,000	867,000
Resolution index (RI)	0.36	0.36	0.35
	$\bar{G}(1)$		
$\exp \left\{ \frac{(\ln RI)^2}{16 \ln 2} \right\}$ (eq. (21))	1.10	1.10	1.11
$\sqrt{\frac{(\bar{M}_w)_\infty / (\bar{M}_n)_\infty}{\bar{M}_w / \bar{M}_n}}$ (eq. (18))	1.12	1.10	1.11

The molecular weight correction factors $\bar{G}(1)$ for the four column combinations studied are given in Table IV. These values together with the known range of applicability are based on the resolution indexes of Table III. The three combinations which consist of four standard Styragel columns all have about the same correction factors. The glass column has a larger correction factor, probably due to the smaller amount of Styragel.

TABLE IV
Molecular Weight Correction Factors

	I	II	III	IV
$\bar{G}(1)$	1.08	1.08	1.10	1.17
Range of applicability	10^4 to 10^6	10^4 to 10^6	10^4 to 2.6×10^6	2×10^4 to 10^6

DISCUSSION

The molecular weight correction factor obtained from the resolution index should be very useful for applying spreading corrections to the molecular weight averages of interest. These factors are easily obtainable from the data normally available from the GPC calibration with polystyrene. It appears that the approximations required are satisfactory for normally operating GPC columns. The molecular weight correction factor $\bar{G}(1)$ should be a useful parameter for characterizing the important operational characteristics of a GPC instrument. In particular, it determines how effective the molecular weight fractionation is.

The three typical combinations of columns (I, II, and III) which we have studied show little variation in the correction factors (see Table IV). Thus, the Styragel columns may be fairly uniform in this characteristic, when they are operating properly.

The special column, combination IV of Table I, had much less total gel in it than the others, and the geometry was such that a much more rapid flow rate could be obtained with moderate pressure. This, of course, makes it possible to analyse a sample in a much shorter time. The penalty is reduced resolution, as indicated by the larger molecular weight correction factor $\bar{G}(1)$, given in Table IV. However, the correction factor is still not large. Thus, either the number-average or weight-average molecular weight obtained directly from the GPC curve requires only a 17% correction to give the true value corrected for spreading.

References

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