

Statistical Moments of Elution Bands and Their Application in Gel Permeation Chromatography of Polydisperse Macromolecules

MIROSLAV KUBÍN, *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia*

Synopsis

Equations have been derived that relate the statistical moments of uncorrected and spreading-corrected chromatograms for a general form of the spreading function in gel permeation chromatography of polydisperse macromolecules. The first moment (centroid) of the chromatogram is shown to be directly given by the centroid, $\ln M^*$, of a suitably defined molecular weight distribution function of the polydisperse sample, regardless of the position of the calibration dependence, provided it is linear. Both the molecular weight M^* associated with the centroid of the chromatogram and its second central moment (variance) are but little sensitive to the shape of sample molecular weight distribution and can be easily calculated from the polydispersity index M_w/M_n , at least for polymers of a not excessively broad distribution. The derived relations are shown to find application in the calibration of GPC columns by means of characterized, polydisperse standards and in the separation of independent contributions to peak width which originate in sample polydispersity and in band broadening processes in the column. Improved column- and packing performance criteria are also proposed.

INTRODUCTION

For a correct interpretation of data in gel permeation chromatography (GPC) it is in many instances desirable to know how the basic characteristics of the molecular weight distribution (MWD) of the studied polydisperse sample (mode, centroid, width, asymmetry, etc.) influence the shape of the recorder trace (sometimes also of the spreading-corrected chromatogram). Thus, when nearly monodisperse fractions of the polymer to be studied are not available for calibration purposes, one has to resort to secondary calibration standards of appreciable polydispersity; the molecular weight M_{GPC} corresponding to the elution volume at the peak maximum has been shown¹ to depend on the type of MWD of the standard ($M_{\text{GPC}} = (M_n \cdot M_w)^{1/2}$ for the logarithmic normal, $M_{\text{GPC}} = M_w$ for the Schulz-Zimm distribution, etc., where M_n is the number-average and M_w the weight-average molecular weight). It is also often necessary to separate the independent contributions to the peak width that stem from the sample polydispersity and, on the other hand, from the kinetic phenomena in the chromatographic column, e.g., in the calibration of spreading,^{2,3} verification of the governing mechanism of peak broadening,⁴⁻⁷ characterization of the separation efficiency of individual columns or packings,⁸⁻¹² etc.

In this paper it is shown how the moment analysis of elution bands can help to solve these and similar problems. First, general relations are derived

between the respective statistical moments of the actual (uncorrected) recorder trace, of the spreading-corrected chromatogram, and of the spreading function in its general form. Next, an equation is presented that connects the molecular weight M^* , corresponding to the elution volume of the centroid of chromatogram, with the centroid of a suitably defined MWD of the polymer sample. Using several examples of two-parameter model distribution curves it is shown that—in contrast to the quantity M_{GPC} —the molecular weight M^* can be unequivocally determined from the number- and weight-average molecular weight of the sample, at least for polymers with moderately broad distributions.

Finally, the second and third central moments of the spreading-corrected chromatogram are shown to be related to the corresponding central moments of MWD. Again, on the basis of several model distributions it is demonstrated that, for polymers which are not excessively polydisperse, the relationship for the second moment is not very sensitive to the actual shape of MWD and can be employed in predicting the effect of sample polydispersity on the width of its chromatogram.

THEORETICAL

Moments of Uncorrected and Corrected Chromatograms

If we define the corrected chromatogram w (i.e., a chromatogram which would have been observed in the absence of spreading) by the equation

$$w(v) dv = -f_w(M) dM \quad (1)$$

where v is the elution volume and $f_w(M)$, the mass distribution function of molecular weight, is defined in such a manner that the product $f_w(M) dM$ gives the mass fraction of the polymer having molecular weight between M and $M + dM$, the connection between the experimentally observed, uncorrected chromatogram $g(v)$ and the spreading-corrected function w is given by the Tung integral equation¹³

$$g(v) = \int_{v_a}^{v_b} G(v,y)w(y) dy \quad (2)$$

$G(v,y)$ is the so-called spreading function and represents the response—as a function of the elution volume v —of the chromatograph to an infinitesimally short injection of a strictly monodisperse fraction having the retention volume y . We shall assume throughout this paper that all functions in eq. (2) are normalized, i.e.,

$$\int_{v_a}^{v_b} g(v) dv = \int_{v_a}^{v_b} w(v) dv = \int_{v_a}^{v_b} G(v,y) dv = 1 \quad (3)$$

and the integration limits in eqs. (2) and (3) cover the whole range of elution volume; where no confusion can arise, the integration limits will be omitted in the following derivation.

Without serious loss of generality, we may assume that the parameter y in the spreading function is identical with its first statistical moment, i.e.,

$$\int vG(v,y) dv = y \quad (4)$$

{It can be easily deduced that this is true if $G(v, y)$ is Gaussian even with nonuniform (i.e., elution-volume dependent) spreading. The so-called exponentially modified Gaussian spreading function^{14,15} is usually written in the form

$$G_e(v, y') = \frac{1}{\tau\sigma\sqrt{2\pi}} \int_0^\infty \exp\left[-\left(\frac{v - y' - v'}{\sigma\sqrt{2}}\right)^2 - \frac{v'}{\tau}\right] dv' \quad (5)$$

and its first moment is

$$\int vG_e(v, y') dv = y' + \tau$$

However, if we introduce $y = y' + \tau$ into eq. (5), the spreading function

$$G_e(v, y) = \frac{1}{\tau\sigma\sqrt{2\pi}} \int_0^\infty \exp\left[-\left(\frac{v - y + \tau - v'}{\sigma\sqrt{2}}\right)^2 - \frac{v'}{\tau}\right] dv' \quad (6)$$

satisfies requirement (4).}

Let us denote the first moments about zero of the functions appearing in eq. (2) by

$$\mu'_1 = \int vg(v) dv \quad (7a)$$

$$\nu'_1 = \int vw(v) dv \quad (7b)$$

$$\gamma'_1 = \int vG(v, y) dv \equiv y \quad (7c)$$

and the corresponding higher central moments by

$$\mu_k = \int (v - \mu'_1)^k g(v) dv \quad (8a)$$

$$\nu_k = \int (v - \nu'_1)^k w(v) dv \quad (8b)$$

$$\gamma_k = \int (v - y)^k G(v, y) dv \quad (8c)$$

Using eqs. (2), (3), and (4) we may write for μ'_1

$$\mu'_1 = \int v dv \int G(v, y)w(y) dy = \int w(y) dy \int vG(v, y) dv$$

or

$$\mu'_1 = \int yw(y) dy = v'_1 \quad (9)$$

Thus, we see that the respective centroids of the corrected and uncorrected chromatogram are equal for a very broad class of spreading functions that satisfy eq. (4).

For the second moment we have from eq. (2)

$$\mu_2 = \int (v - \mu'_1)^2 g(v) dv = \int (v - \mu'_1)^2 dv \int G(v, y) w(y) dy$$

and this can be written, using eq. (9), as

$$\begin{aligned} \mu_2 &= \int [(v - y) + (y - v'_1)]^2 dv \int G(v, y) w(y) dy \\ &= \int w(y) dy \int (v - y)^2 G(v, y) dv + \int G(v, y) dv \int (y - v'_1)^2 w(y) dy \\ &\quad + 2 \int (v - y) G(v, y) dv \int (y - v'_1) w(y) dy \end{aligned}$$

The last term obviously vanishes; hence, in view of eqs. (3) and (8) we have thus derived the general result

$$\mu_2 = \gamma_2 + v_2 \quad (10)$$

an equation found previously^{2,3} to be valid for a special case of the Gaussian spreading function.

In a completely analogous manner we find for the higher central moments the relations

$$\mu_3 = \gamma_3 + v_3 \quad (11)$$

$$\mu_4 = \gamma_4 + v_4 + 6v_2\gamma_2 = \gamma_4 + v_4 + 6\gamma_2(\mu_2 - \gamma_2) \quad (12)$$

Moments of Chromatogram and MWD

The results derived so far are quite general and do not require any simplifying assumptions except the rather weak one in eq. (4). In the following we shall assume for the sake of simplicity that the calibration dependence of the column is linear,

$$\ln M = A - Bv \quad (13)$$

We now want to derive the relationships between the moments of the corrected chromatogram and those of the molecular weight distribution. Let us first examine the molecular weight M^* that corresponds to the first statistical moment of the chromatogram, $\mu'_1 \equiv v'_1$. We have from eq. (13)

$$v'_1 = (A/B) - (1/B) \ln M^* \quad (14)$$

On the other hand, from its definition we can write for ν'_1

$$\nu'_1 = \int \nu w(\nu) d\nu = \int [(A/B) - (1/B) \ln M] w(\nu) d\nu$$

By virtue of eq. (1) this assumes the form

$$\nu'_1 = (A/B) \int_0^\infty f_w(M) dM - (1/B) \int_0^\infty \ln M f_w(M) dM$$

or

$$\nu'_1 = (A/B) - (1/B) \int_0^\infty \ln M f_w(M) dM \quad (15)$$

as f_w , being a distribution, must be normalized. Comparing eqs. (14) and (15), we deduce immediately that

$$\ln M^* = \int_0^\infty \ln M f_w(M) dM \quad (16)$$

(It will be shown below that the integral in the last equation exists for practically important distributions.)

This result can be given a more lucid interpretation in terms of a distribution function f_L with $\ln M$ as a new random variable; with f_L defined by

$$f_L(\ln M) d(\ln M) = f_w(M) dM \quad (17)$$

eq. (16) takes the form

$$\ln M^* = \int_{-\infty}^{\infty} \xi f_L(\xi) d\xi \quad (18)$$

Accordingly, $\ln M^*$ is the first moment of the distribution f_L .

The integral in eq. (16) can be evaluated analytically for several two-parameter functions (see, e.g., Ref. 16) often used in modeling the molecular weight distributions of polymeric materials, viz., the Schulz-Zimm (SZ) distribution:

$$f_{sz}(M) = \frac{a^{b+1}}{\Gamma(b+1)} M^b \exp(-aM), \quad a, b > 0 \quad (19)$$

where

$$(1/b) = M_w/M_n - 1 \quad (19')$$

the logarithmic normal (LN) distribution

$$f_{LN}(M) = \frac{1}{\vartheta\sqrt{\pi}} \frac{1}{M} \exp \left[- \left(\frac{1}{\vartheta} \ln \frac{M}{M_0} \right)^2 \right], \quad M_0, \vartheta > 0 \quad (20)$$

where

$$\vartheta^2 = 2 \ln (M_w/M_n) \quad (20')$$

and the Rosin-Rammler-Tung (RR) function

$$f_{RR}(M) = npM^{n-1} \exp(-pM^n), \quad p > 0, \quad n > 1 \quad (21)$$

where

$$M_w/M_n = \Gamma(1 + 1/n) \cdot \Gamma(1 - 1/n) = (\pi/n)/\sin(\pi/n) \quad (21')$$

As shown in the Appendix, the results have the form

$$\ln M_{SZ}^* = \ln M_n + \psi(b + 1) - \ln b \quad (22)$$

where $\psi(x) = d \ln \Gamma(x)/dx$,

$$\ln M_{LN}^* = \ln M_n + \vartheta^2/4 \quad (23)$$

and

$$\ln M_{RR}^* = \ln M_n - C/n + \ln \Gamma(1 - 1/n) \quad (24)$$

where $C = 0.577216 \dots$ is Euler's constant.

For the central moments ν_k we can similarly write by virtue of eqs. (13) and (14)

$$\nu_k = (1/B)^k \int_0^\infty [\ln(M^*/M)]^k f_w(M) dM \quad (25)$$

or, again utilizing the distribution f_L ,

$$\nu_k = (1/B)^k \int_{-\infty}^\infty (\ln M^* - \ln M)^k f_L(\ln M) d \ln M$$

which, in view of eq. (18), assumes the simple form

$$\nu_k = (-B)^{-k} \mu_k^{(L)} \quad (26)$$

where $\mu_k^{(L)}$ is the k th central moment of the distribution f_L ,

$$\mu_k^{(L)} = \int_{-\infty}^\infty [\xi - \ln M^*]^k f_L(\xi) d\xi \quad (27)$$

and $B > 0$ is the slope of the linear calibration dependence (13).

Expressions for the second and third central moment ν_2 and ν_3 can again be derived in a closed form by evaluating the integral in eq. (25) for the three above-mentioned model distributions (see the Appendix); thus,

$$B^2\nu_{2,SZ} = \psi'(b + 1) \quad (28)$$

where $\psi'(x) = d\psi/dx$,

$$B^2\nu_{2,LN} = \vartheta^2/2 \quad (29)$$

$$B^2\nu_{2,RR} = (\pi^2/6)n^{-2} \quad (30)$$

and finally

$$B^3\nu_{3,SZ} = \psi(b + 1) \cdot \psi'(b + 1) - \psi''(b + 1) \quad (31)$$

$$B^3\nu_{3,LN} = 0 \quad (32)$$

$$B^3\nu_{3,RR} = -\psi''(1)/n^3 \cong 2.4041n^{-3} \quad (33)$$

DISCUSSION

The assertion that the respective centroids of the uncorrected and corrected chromatogram are equal represents a useful result per se. No such statement can be made about the elution volume at the peak maximum, as follows from the mere fact that for unimodal chromatograms consisting of two strongly overlapping peaks efficient correction procedures can reveal a bimodal character of the corrected chromatogram.^{17,18} Even here, however, eq. (9) remains valid and can be used, e.g., in checking the accuracy of various methods devised to solve the Tung integral equation. The main importance of eq. (9) in the present context lies in that it enables the general relationships (10)–(12) between the central moments to be established. Prior to turning our attention to the utility of these equations, we shall examine the moments of the corrected chromatogram and their relation to the character of sample MWD.

First Moment

It follows from eqs. (16) and (17) that the molecular weight M^* corresponding to the first moment of the chromatogram is independent of the constants A and B , which define the position of the molecular weight calibration dependence, provided that it is linear (cf. Ref. 19). This is a very important result which can be utilized, for example, when a column set is to be calibrated by means of characterized, polydisperse polymer standards: If the quantity M^* can be determined from known characteristics of the given standard (a problem to be discussed below), one point on the sought calibration dependence is obtained for each standard by plotting $\ln M^*$ against the experimentally accessible quantity μ'_1 . If need be, the calibration established in this manner can be further improved by the iteration procedure described earlier.³

Equations (22)–(24) show that, for the three model distributions investigated, $\ln M^*$ depends on the number-average molecular weight and on that parameter of the respective distribution which is connected with its width $M_w/M_n \equiv P$ —see eqs. (19'), (20'), and (21'). Accordingly, M^* can be always determined from the characteristics M_n and M_w .

The right-hand sides of eqs. (22)–(24) may be expanded in powers of $(P - 1)$, where $P = M_w/M_n$; thus

$$\ln(M_{SZ}^*/M_n) \cong (1/2)(P - 1) - (1/12)(P - 1)^2 + (1/120)(P - 1)^4 - \dots$$

$$\ln(M_{LN}^*/M_n) \cong (1/2)(P - 1) - (1/4)(P - 1)^2 + (1/6)(P - 1)^3 - \dots$$

$$\ln(M_{RR}^*/M_n) \cong (1/2)(P - 1) + 0.1899(P - 1)^{3/2} - 0.2204(P - 1)^2 + \dots$$

where the leading terms are identical, indicating that for reasonably small values of P the three functions must be similar. This is confirmed by Figure 1, where the ratio M^*/M_n calculated for the three model distributions from eqs. (22)–(24) is plotted as a function of the polydispersity index P ; we see that, at least in the region of moderately broad distributions ($P \leq 1.8$), the three functions can be approximated by a single master curve. (In fact, the dependences for the SZ and RR functions run close together up to the largest values of P , whereas the curve for the LN distribution begins to deviate downwards near $P \sim 2$.) By means of polynomial regression of the data in Figure 1 in the region $P \leq 1.8$, the equation of the master curve has been therefore derived in the form

$$\ln(M^*/M_n) = (1/2)(P - 1) + 0.0157(P - 1)^2 - 0.1438(P - 1)^3 \quad (34)$$

and it is also plotted as a full line in Figure 1.

The advantages of using, for a polydisperse polymer, the centroid of the chromatogram with the associated molecular weight M^* instead of the elution volume at the peak maximum and the value M_{GPC} are clearly revealed in Table I, which summarizes the relevant data for the Schulz-Zimm

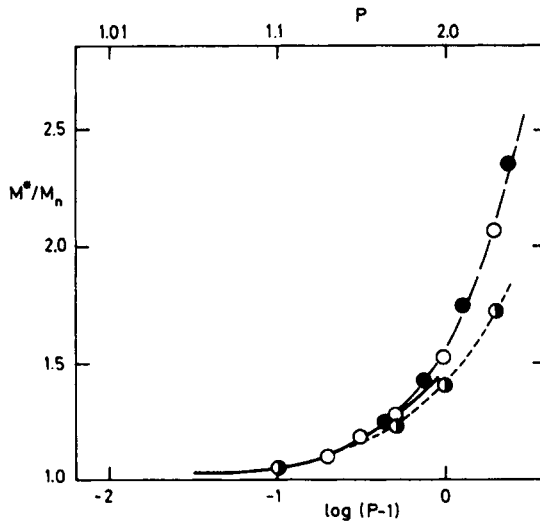


Fig. 1. Molecular weight, M^* , corresponding to the first moment of chromatogram, as a function of sample polydispersity $P \equiv M_w/M_n$: (○) Schulz-Zimm distribution [eq. (22)]; (○) logarithmic normal distribution [eq. (23)]; (●) Rosin-Rammler-Tung distribution [eq. (24)]; full line is the master curve calculated from eq. (34).

TABLE I
Comparison of M_{GPC} and M^* for Schulz-Zimm and Logarithmic Normal Distributions of Different Polydispersity ($M_n = 10^5$)

Parameter	$P - 1$				
	0.1	0.2	0.3	0.5	0.8
$M_{\text{GPC,SZ}} \times 10^{-5}$ ^a	1.1	1.2	1.3	1.5	1.8
$M_{\text{GPC,LN}} \times 10^{-5}$ ^a	1.049	1.095	1.140	1.225	1.342
$M_{\text{SZ}}^* \times 10^{-5}$	1.05	1.102	1.153	1.258	1.418
$M_{\text{LN}}^* \times 10^{-5}$	1.049	1.095	1.140	1.225	1.342
$M_r^* \times 10^{-5}$ ^b	1.051	1.105	1.159	1.266	1.400
$M_t^* \times 10^{-5}$ ^c	1.051	1.105	1.162	1.284	1.492
$[M_{\text{GPC,SZ}}/M_{\text{GPC,LN}} - 1] 100$ (%)	4.9	9.5	14	22.5	34.2
$[M_{\text{SZ}}^*/M_{\text{LN}}^* - 1] 100$ (%)	0.09	0.6	1.1	2.7	5.7
$[M_{\text{SZ}}^*/M_r^* - 1] 100$ (%)	0.12	0.28	0.52	0.6	1.3
$[M_{\text{LN}}^*/M_r^* - 1] 100$ (%)	-0.2	-0.9	-1.6	-3.2	-4.1
$[M_t^*/M_r^* - 1] 100$ (%)	0	0	0.3	1.4	6.6

^a $M_{\text{GPC,SZ}} = M_w$, $M_{\text{GPC,LN}} = (M_n \cdot M_w)^{1/2}$.

^b A value calculated from the regression equation (34).

^c From the series in Eq. (34) truncated after the first term, $M_t^* = M_n \exp [1/2(P - 1)]$.

and logarithmic normal distributions. The quantity M^* is manifestly much less sensitive to the shape of MWD, and the differences between the values calculated for the two model functions remain well within the limits of experimental error of GPC for polydispersities below $P = 1.8$; even the simplified version of eq. (34), truncated after the first term, seems to yield reasonably accurate values of M^* . On the other hand, the deviations of the values of M_{GPC} between the two distributions become quite large for $P > 1.3$.

If the molecular weight distribution of a calibration standard is known (this situation arises, e.g., when GPC columns are to be calibrated by dextran standards produced by Pharmacia Fine Chemicals, Uppsala, Sweden), the required value of M^* can be easily calculated from eq. (18).

Second Moment

Figure 2 shows the dependence of the product B^2v_2 on P as obtained from eqs. (28)–(30). Again, it is true that for moderately broad distributions (say $P \leq 2$) the points lie sufficiently close together to justify an approximate master curve to be plotted through the data. The full line corresponds to the regression equation

$$B^2v_2 \cong (P - 1) - (1/2)(P - 1)^2 + 0.1464(P - 1)^3 \quad (35)$$

calculated from the points that lie below $P = 2$; the two leading terms common to the series expansions of the formulae (28) and (29) in powers of $(P - 1)$ have been retained in this expression.

Equation (35) in combination with the formula (10) can be now used for calibration of the peak broadening using direct-flow (as opposed to reverse-flow²⁰) chromatograms of polymers with known values of $P \equiv M_w/M_n$,

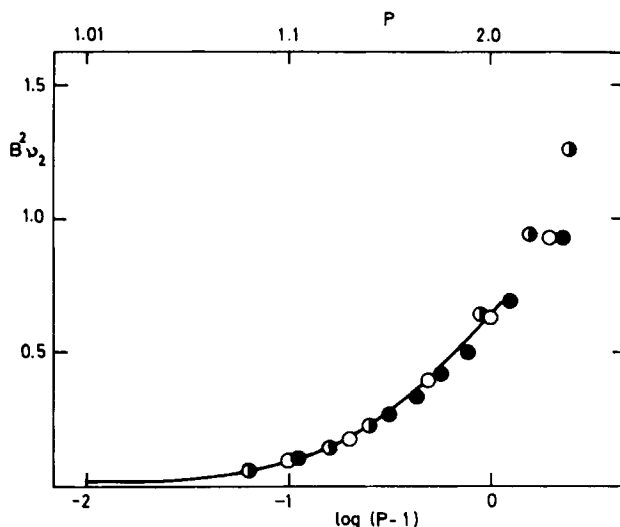


Fig. 2. Second moment v_2 as a function of sample polydispersity $P \equiv M_w/M_n$. Notation as in Figure 1; full line is the master curve calculated from eq. (35).

provided that their distribution is not excessively broad. Thus, the variance of the spreading function at the elution volume of the peak centroid is calculated from

$$\gamma_2 = \mu_2 - (1/B^2)[(P-1) - (1/2)(P-1)^2 + 0.1464(P-1)^3]$$

where the second central moment μ_2 of the experimental chromatogram is easily accessible and B is the slope of the molecular weight calibration dependence, which must be known in advance (if it is curvilinear, the local slope at $v = \mu_1'$ can be used^{3,21}).

Other instances where it is necessary to calculate the contribution of polydispersity to chromatogram width include studies of mass transfer in the mobile and stationary phases⁶⁻⁹ or accurate determination of the polydispersity index for narrow-distribution polymers by means of GPC⁶ or recycle GPC.²² Here it is usually assumed^{7-9,22} that the distribution of the studied polymer obeys the logarithmic normal function because of the simplicity of formula (29), probably first noticed by Tung.¹³ The results presented here indicate that this approximation is valid not only for the nearly monodisperse primary calibration standards but with reasonable accuracy also for polydisperse polymers. Knox and McLennan²³ analyzed theoretically the contribution of polydispersity to the width of GPC bands, assuming the sample distribution to be Gaussian, and derived the formula (written in the present notation)

$$B^2 v_2 = (P-1)(1 + \alpha)$$

where $\alpha \cong (11/4)(P-1) + (137/12)(P-1)^2 + \dots$. In order to be able to characterize the polydispersity by the simplest parameter $P = M_w/M_n$, these authors, however, assumed the number distribution $f_n(M)$ to be Gaussian

$[f_n(M) dM$ gives the *mole* fraction of the polymer having molecular weight between M and $M + dM$] and mistakenly inserted f_n instead of f_w into eq. (1). (This is incorrect because the response of all detectors is proportional to mass—and not to amount-of-substance—concentration in the eluate.) In addition, the difference between M_n and M^* was also neglected in their derivation. It is, however, possible, utilizing the known relation between f_n and f_w

$$f_w(M) = (M/M_n)f_n(M)$$

to derive²⁴ the correct formula for ν_2 on the assumption that $f_n(M)$ is Gaussian; the result reads

$$B^2\nu_2 = (P - 1)(1 - \alpha^*) \quad (36)$$

where

$$\alpha^* = (1/2)(P - 1) + (4/3)(P - 1)^2 + \dots \quad (36')$$

As a consequence of the change of sign in the correction term α^* , the net result is that the Knox–McLennan formula somewhat overestimates the effect of polydispersity. The error is, however, rather small for samples having P close to unity studied in Ref. 6 (3.4% at $P = 1.01$, 11% at $P = 1.03$) and becomes appreciable (48%) only at $P = 1.1$, where the Gaussian model breaks down anyway²⁴ because an infinite series needed in the derivation begins to diverge at $P \simeq 1.11$.

Yau et al.¹⁰ proposed to characterize the performance of chromatographic columns and packings in GPC by means of the specific resolution,

$$R_{sp} = 0.576/(B \cdot \sigma) \quad (37)$$

and the packing resolution factor,

$$R_{sp}^* = 0.576/(\sigma \cdot B\sqrt{L}) = R_{sp}/\sqrt{L} \quad (38)$$

where B is again the slope in eq. (13), σ is the standard deviation of chromatogram of some narrow-distribution polymer ($\sigma = \sqrt{\mu_2}$ in our notation), and L is the column length. Physically, R_{sp} is the chromatographic resolution of the column for a pair of polymers that differ by a factor of 10 in their molecular weight (cf. Refs. 10 and 11), and the packing resolution factor is R_{sp} normalized to unit column length. However, it has been repeatedly stressed that even with the best available polymer fractions the contribution of their polydispersity to the total peak width can be appreciable^{6-9,23} so that the performance criteria as defined above can vary considerably from sample to sample not only as a result of molecular weight dependence of the separation efficiency, but merely due to the varying quality of standards employed in their determination. Clearly, modified criteria are needed that are free from this undesirable variation; on the basis of the above results, corrected column- and packing performance cri-

teria can be defined as

$$R_{\text{sp,cor}} = 0.576/(B\sqrt{\gamma_2}) \quad (39)$$

and

$$R_{\text{sp,cor}}^* = R_{\text{sp,cor}}/\sqrt{L} \quad (40)$$

where γ_2 is the variance of the spreading function which, as follows from its definition, satisfies the above requirement. From eqs. (10) and (35) we have

$$\begin{aligned} R_{\text{sp,cor}} &= 0.576/(B\sqrt{\mu_2 - \nu_2}) \\ &= 0.576/[B\sqrt{\mu_2 - (1/B^2) F(P-1)}] \end{aligned}$$

where $F(P-1) = (P-1) - (1/2)(P-1)^2 + \dots$ is the right-hand side of eq. (35). In view of formula (37) this can be rewritten as

$$R_{\text{sp,cor}} = [1/R_{\text{sp}}^2 - F(P-1)/0.576^2]^{-1/2} \quad (41)$$

The effect of this correction may be seen from the data collected in Table II. It is important to note that the correction of the quantity R_{sp} for sample polydispersity is the more significant, the higher the actual separation efficiency of the column; this is understandable since highly efficient columns will have small γ_2 and the term ν_2 that reflects the polydispersity will dominate in the expression (10) for the actual peak width. When the corrected performance criteria are to be calculated from eq. (41), it is important that the peak variance be determined accurately, preferably by an integration of the whole chromatogram according to eq. (8a). In fact, when the correction according to eq. (41) was attempted with some data taken from the literature,^{8,12} physically impossible values were obtained, indicating that the method used by the authors in the determination of μ_2 (i.e.,

TABLE II
Column Performance Criterion and Its Correction for Sample Polydispersity

Total column length (cm)	Packing	Polystyrene molecular weight	R_{sp}	$R_{\text{sp,cor}}$
Data from Ref. 10				
488	Styragel	97,000	1.27	1.34
488	Porasil	97,000	1.56	1.69
200	Vit-X	97,000	0.97	1.00
120	μ Styragel	97,000	1.14	1.18
100	Lichrospher	97,000	2.50	3.20
60	PSM silica	97,000	2.72	3.71
Data from Ref. 11				
25	Lichrospher 500	51,000	1.6	1.92
25	PSM 800	51,000	2.15	3.23
25	Lichrospher 1000	97,000	2.05	2.38
10	PSM 1500	97,000	1.90	2.16

from the peak width at half height) can seriously underestimate the actual second moment because then the tailing and skewing at both extreme ends of the chromatogram are not properly accounted for.

Third Moment

It has been shown above that the dependences of ν_1 and ν_2 on the polydispersity index are not very sensitive to the actual shape of MWD of the investigated polymer, unless its width is excessively large. In contrast to this finding, the skew of the corrected chromatogram as measured by its third moment ν_3 is appreciably different for the three model distributions. As can be easily verified from eqs. (28)–(33), the skew parameter $\gamma_s = \nu_3/\nu_2^{3/2}$ is zero for the logarithmic normal distribution, constant (independent of P) and positive for the Rosin–Rammler–Tung function ($\gamma_{s,RR} \cong 1.14$), and positive and P -dependent for the Schulz–Zimm distribution, where, for $P = 1.5, 1.8, 2.0$, and 3 , $\gamma_{s,SZ}$ equals $2.1, 1.5, 1.31$, and 0.96 , respectively.

This has serious consequences for the determination of the actual shape of the spreading function $G(v,y)$, if its possible inherent skew is to be taken into account. In several papers^{25–28} procedures have been proposed for the determination of the parameters of a generalized, asymmetric spreading function which is assumed in these instances in a special form, either according to eq. (5) as in Ref. 28 or as a truncated Gram–Charlier series.^{25–27} As follows from eq. (11) the third moment of the uncorrected chromatogram (which alone is experimentally available) is given as a sum of the third moment of the spreading function, γ_3 (the quantity to be determined), and of the third moment of the corrected chromatogram, ν_3 , which can be, however, very different, depending on the shape of sample MWD.

It therefore seems that attempts to evaluate the asymmetry of the actual spreading function of the given system of GPC columns, based on the measured skew of experimental chromatograms, are hardly justified unless the shape of the molecular weight distribution of the calibration standard(s) is accurately known.

APPENDIX

For the Schulz–Zimm distribution we have to evaluate

$$\ln M_{SZ}^* = \int_0^\infty \ln M \frac{a^{b+1}}{\Gamma(b+1)} M^b \exp(-aM) dM$$

Using the integral (Ref. 29, formula 4.352/1)

$$\int_0^\infty \ln x x^{\nu-1} e^{-\mu x} dx = \frac{\Gamma(\nu)}{\mu^\nu} [\psi(\nu) - \ln \mu], \quad \mu, \nu > 0 \quad (42)$$

we see that

$$\ln M_{SZ}^* = \psi(b+1) - \ln a$$

and eq. (22) in the text follows directly because $a = b/M_n$ (cf. Ref. 16).

For the RR function we need the integral

$$\ln M_{RR}^* = \int_0^\infty \ln M \cdot n \cdot p \cdot M^{n-1} \exp(-pM^n) dM$$

Substituting $m = M^n$, $dM = (1/M^{n-1}) dm$, we have

$$\ln M_{RR}^* = (p/n) \int_0^\infty \ln m \exp(-pm) dm$$

Formula 4.331/1 in Ref. 29 states that

$$\int_0^\infty e^{-\mu x} \ln x dx = -(1/\mu)(C + \ln \mu) \quad (43)$$

so that

$$\ln M_{RR}^* = -(1/n)(C + \ln p)$$

but for the RR distribution (cf. Ref. 16)

$$\ln M_n = -(1/n) \ln p - \ln \Gamma(1 - 1/n)$$

and eq. (24) follows.

For the LN distribution it is known¹³ that both the uncorrected and corrected chromatogram is Gaussian with mean M_0 ; accordingly,

$$\ln M_{LN}^* = \ln M_0 \quad (44)$$

and eq. (23) is shown to be valid because (cf. Ref. 16)

$$M_n = M_0 \exp(-\vartheta^2/4)$$

In order to derive the relations for ν_2 and ν_3 in the case of the SZ function, we have to evaluate

$$\int_0^\infty [\ln M_{SZ}^* - \ln M]^k \frac{a^{b+1}}{\Gamma(b+1)} M^b \exp(-aM) dM$$

for $k = 2$ and $k = 3$.

Expanding the expression in brackets and utilizing eq. (42) and the integrals

$$\int_0^\infty (\ln x)^2 x^{\nu-1} e^{-\mu x} dx = \frac{\Gamma(\nu)}{\mu^\nu} \{[\psi(\nu) - \ln \mu]^2 + \psi'(\nu)\}, \quad \mu, \nu > 0$$

(Ref. 29, formula 4.358/2) and

$$\int_0^\infty (\ln x)^3 x^{\nu-1} e^{-\mu x} dx = \frac{\Gamma(\nu)}{\mu^\nu} \{[\psi(\nu) - \ln \mu]^3 + [2\psi(\nu) - 3 \ln \mu] \psi'(\nu) - 2\psi''(\nu)\}, \quad \mu, \nu > 0$$

(Ref. 29, formula 4.358/3), we obtain after a straightforward algebra eqs. (28) and (31) in the text.

In a completely analogous manner for the case of the RR distribution we can make use of eq. (43) and of the integrals

$$\int_0^{\infty} e^{-\mu x} (\ln x)^2 dx = (1/\mu)[\pi^2/6 + (C + \ln \mu)^2], \quad \mu > 0$$

(Ref. 29, formula 4.335/1) and

$$\int_0^{\infty} e^{-\mu x} (\ln x)^3 dx = -(1/\mu)[(C + \ln \mu)^3 + (\pi^2/2)(C + \ln \mu) - \psi''(1)], \quad \mu > 0$$

(Ref. 29, formula 4.335/3) in proving the validity of eqs. (30) and (33).

For $v_{2,LN}$ we have

$$B^2 v_{2,LN} = \int_0^{\infty} [\ln(M_0/M)]^2 \frac{1}{\vartheta M \sqrt{\pi}} \exp\left[-\left(\frac{1}{\vartheta} \ln \frac{M}{M_0}\right)^2\right] dM$$

By substituting $(1/\vartheta)\ln(M/M_0) = x$, $(1/\vartheta M) dM = dx$, we obtain

$$B^2 v_{2,LN} = (1/\sqrt{\pi}) \int_{-\infty}^{\infty} \vartheta^2 x^2 e^{-x^2} dx = \vartheta^2/2$$

in agreement with eq. (29).

Finally, the third moment v_3 is obviously zero for the LN distribution because the chromatogram is in this case Gaussian.¹³

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