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Size exclusion chromatography of polymers with molar mass detection. Computer simulation study on instrumental broadening biases and proposed correction method

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Abstract

This theoretical work evaluates the errors in average molecular weights due to instrumental broadening when a size exclusion chromatograph is fitted with ideal on-line $\bar{M}_n$ or $\bar{M}_w$ sensors, and a correction method is proposed to compensate for such errors. The basic assumptions are that linear homopolymers are analyzed, and that the instrumental broadening is uniform. It was verified that an ideal molar mass detector systematically underestimates the polydispersity and that such bias may be simply obtained from the spreading function polydispersity. The correction method uses an estimate of the instantaneous polydispersity. Such function can be directly obtained from the spreading function alone, since it is proven to be little dependent on the shape of the analyzed MWD. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Size exclusion chromatography (SEC) is the main analytical technique for measuring the molecular weight distribution (MWD) of a polymer [1–5]. When chromatographically-simple polymers are analyzed in an ideal size exclusion chromatograph with perfect resolution, then uniform or monodisperse fractions are instantaneously present in the detector cells, and fractionation occurs on a strict molecular weight basis. Under such ideal conditions, a simple concentration or mass detector (e.g. a differential refractometer, DR) would provide an undistorted or 'correct' mass chromatogram. To obtain the MWD, an independent molecular weight calibration is required and/or an on-line molar mass detector must be used. If uniform or monodisperse standards of the analyzed polymer were available, then impulsive or 'delta' chromatograms would be obtained under perfect resolution and a unique molecular weight calibration would be determined.

Unfortunately, perfect fractionation according to hydrodynamic volume is impossible due to instrumental broadening (IB) and secondary fractionation mechanisms. The main cause of IB is axial diffusion in the fractionation columns; while other minor sources include column end-fitting effects, finite injection volume, finite detection cell volume, and flow profiles in the capillaries. Secondary mechanisms are the consequence of interactions between the sample, the solvent, and the column packing [6]; however, they will not be further considered here.

For chromatographically complex polymers (i.e. copolymers, polymer blends, branched homopolymers, etc.), a variety of molecular weights and compositions coexists in the detector cell, even under perfect resolution. This problem will not be considered here, but an excellent investigation on the errors introduced in global $\bar{M}_n$'s when a combination of DR and LS detectors are employed has recently appeared [7]. That publication, however, does not include the effects of IB. For this reason, it is totally complementary of the present article.

This work theoretically investigates the effect of IB in SEC under the following idealized conditions: (a) linear homopolymers are analyzed; (b) perfectly accurate mass- and molar-mass detectors are employed; (c) a uniform spreading function is adopted; (d) the breadth of the mass chromatogram more than doubles the breadth of the spreading function; and (e) from (hypothetical) monodisperse standards, a linear calibration is obtained, even in the presence of IB.

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Two recent works have considered the computer simulation of chromatograms when molar mass detectors are employed and when a Wesslau or a Schulz–Flory MWD are analyzed [8,9]. Assuming perfect resolution and a linear calibration, it is concluded that in the case of a Wesslau distribution, all three chromatograms corresponding to the mass, the viscosity and the LS detectors are Gaussian symmetrical of equal variance, but of different peak positions (the LS signal is followed by the viscosity signal, and it in turn by the mass signal). The shift between the chromatograms is a function of the sample polydispersity and of the calibration curve slope. In the case of the Schulz–Flory distribution, the three chromatograms have similar and skewed shapes; and again expressions have also been developed that relate the shifts between the peak maxima with the sample polidispersity and the calibration curve slope. When a Gaussian band broadening is admitted and a Wesslau distribution are analyzed, then the calibrations $\log \bar{M}_n(V)$ and $\log \bar{M}_w(V)$ that can be obtained from molar mass detectors are also linear and parallel to each other, but rotated counterclockwise with respect to the perfect resolution case around the average of the concentration distribution. At the chromatogram tails, the calibrations become undetermined due to the large numerical errors involved in the calculations [9].

Light scattering (LS) detectors are normally fitted before DRs. To compensate for the time lag between the two sensors with simultaneous possible distortions in the capillary and the DR cell, a correction for this secondary (or terminal) shift and broadening has been proposed [8,10,11]. In this work, only the IB produced in the fractionation columns is of interest, and secondary broadening effects will not be further discussed.

Several arguments against the necessity of correcting for IB have been suggested, e.g. (i) IB is negligible in modern high-resolution columns; (ii) with molar mass detectors, 'true' molecular weight averages are obtained independently of IB, since at each retention volume an estimate of the instantaneous average molecular weight is detected; and (iii) accuracy in SEC is relatively poor (considering the discrepancies obtained in most round-robin tests), and therefore other more important sources of error should be preferably attacked. Such arguments are not generally valid, however. For example, argument (i) is inapplicable when a narrow-distributed polymer is analyzed, when 'sharp' details of the MWD are required, and/or when column resolution is poor (i.e. for steep calibration curves). As it will become clearer in this work, argument (ii) is strictly valid only for the specific average molecular weight whose instantaneous value is being detected, but it cannot be generalized to the other averages. Lastly, even though other more important sources of error may be present, IB is unavoidable. For this reason, it should be taken into consideration in a truly quantitative analysis.

For linear homopolymers and simple concentration detectors, the IB process is normally modeled through Tung's equation [12]:

$$G(V) = \int_0^\infty g(V, V_0) G^c(V_0)\, dV_0 \tag{1}$$

where $G(V)$ is the measured (mass) chromatogram; $G^c(V)$ is the corrected or 'true' chromatogram; $g(V, V_0)$ is the (in general a nonuniform) spreading function; and V_0 is a dummy integration variable that represents the average retention volume of each individual $g(V)$ function.

As a consequence of IB, a variety of molecular weights simultaneously coexist in the detector cell, even when linear homopolymers are analyzed. For this reason, several instantaneous molecular weight averages can be measured according to the employed detection system. For example, if an ideal LS detector is used in combination with an ideal DR, then an instantaneous weight-average molecular weight $\bar{M}_w(V)$ would be obtained, that represents:

$$\bar{M}_w(V) = \sum_i M_i(V) G_i(V) / \sum_i G_i(V) \tag{2}$$

where i is the number of molecular weight classes present in the detector cell; and G_i is the mass of molecules with molecular weight M_i. Similarly, if an ideal number-average molecular weight detector were available, then the following instantaneous number-average molecular weight $\bar{M}_n(V)$ would be obtained:

$$\bar{M}_n(V) = \sum_i G_i(V) / \sum_i \frac{G_i(V)}{M_i(V)} \tag{3}$$

In both cases, $G(V) = \sum_i G_i(V)$ represents the instantaneous mass, and $G = \int_0^\infty G(V)\, d(V)$ is the total sample mass.

From $\bar{M}_w(V)$ and $\bar{M}_n(V)$, the 'calibrations' $\log \bar{M}_w(V)$ and $\log \bar{M}_n(V)$ can be directly obtained. Such calibrations depend not only on the spreading function, but also on the sample MWD. For this reason, they cannot in principle be applied to homopolymers of the same chemical nature but of a different MWD.

Even in the presence of IB, a unique calibration $\log M(V)$ would still be obtained from strictly uniform calibration standards. For example, if symmetrical chromatograms were produced from such standards, then it is reasonable to assume that the retention volumes of their peak maxima should coincide with the retention volumes of the hypothetical impulsive chromatograms obtained under perfect resolution.

In the simpler case of mass detectors and linear homopolymers, the correction methods that compensate for IB have been classified as 'phenomenological' and 'analytical' [13]. Phenomenological methods typically involve two steps. In the first step, Eq. (1) is inverted or deconvoluted to find $G^c(V)$ from the knowledge of $G(V)$ and $g(V, V_0)$. In the second step, a molecular weight calibration is used, and the 'correct' MWD and averages are obtained. The ill-conditioned nature of the deconvolution operation causes that inversion methods are difficult to adjust, often produce

oscillatory or unstable solutions, and furthermore, such solutions also depend on the algorithm adjustment [14]. Analytical correction methods have been developed for linear calibrations and uniform or non-uniform spreading functions [15]. These methods simultaneously transform retention volumes into molecular weights and correct for IB in a single step. For example, references [8,15–17] have developed the idea of rotating the linear calibration counterclockwise at some intermediate retention volume, as a way of narrowing the molecular weight range of $G(V)$. Such techniques have the advantage of producing stable and non-oscillatory solutions, but are not generally applicable, however. As mentioned before, a linear 'rotated' calibration is only valid for a Wesslau distribution; and even in this particular case, it will be shown below that a non-linearity appears at the chromatogram tails.

It is a well-known experimental fact that a combination of DR and LS detectors underestimates the global polydispersity $\bar{M}_w/\bar{M}_n$ [10,18–20]. Even though this effect has been attributed to IB, no clear ways of compensating for this bias have as yet been published.

In what follows, a SEC experiment involving the use of ideal detectors is numerically simulated, with the aim of quantifying the biases in average molecular weights introduced by IB. Then, a correction method to compensate for such biases is developed. In all computer simulations, the calculations were performed with the maximum possible accuracy, in order to highlight the subtle biases that in theory appear in SEC data treatment. However, the average molecular weights and polydispersities are presented with only three significant figures. Unlike previous studies [8,9], the present approach is not restricted to any particular chromatogram shape. For this reason, an analytical continuous treatment cannot be applied here.

2. Base Numerical Example

Consider the simulation of a typical SEC experiment involving the analysis of a linear polystyrene sample. The main idealization is that (in conjunction with a mass or concentration detector), two molar mass sensors provide perfect estimates of $\bar{M}_n(V)$ and $\bar{M}_w(V)$. For $\bar{M}_n(V)$, it has been proven that such measurement is possible [21–23]. In the case of $\bar{M}_w(V)$, LS detectors are insensitive at low molecular weights, and large measurement errors are produced at the chromatogram tails. However, none of such errors will be contemplated here. The reason for this is that we wish to determine and compensate for the rather minor biases that appear as a consequence of IB.

The following functions (that correspond to an ideal chromatograph with perfect resolution) are assumed to be a priori known: (i) the true or 'correct' chromatogram $G^c(V)$ of Fig. 1(a); and (ii) the linear calibration $\log M(V)$ of Fig. 1(b). The bimodal chromatogram $G^c(V)$ results from the addition of two Gaussian distributions of the same

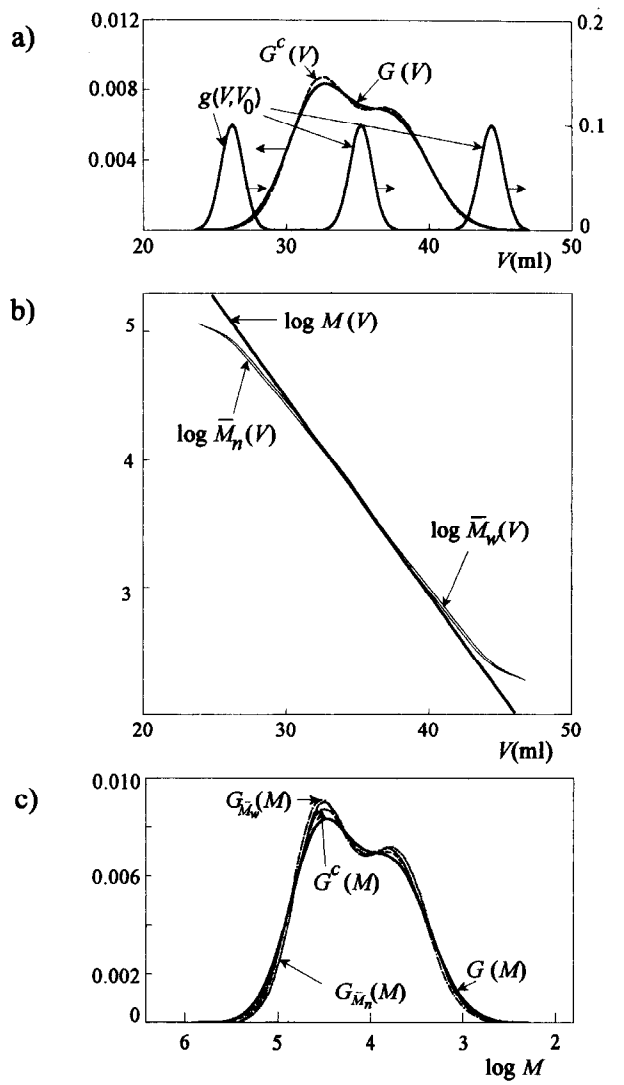

Fig. 1. Base Numerical Example. (a) 'Correct' chromatogram, $G^c(V)$; three samples of the uniform spreading function, $g(V, V_0)$; and resulting 'measured' mass chromatogram, $G(V)$. (b) 'Base' linear calibration obtained from uniform standards, $\log M(V)$; *ad hoc* calibration $\log \bar{M}_n(V)$, obtained from $G(V)$ and $\bar{M}_n(V)$; and calibration $\log \bar{M}_w(V)$, obtained from $G(V)$ and $\bar{M}_w(V)$. (c) 'Correct' MWD, $G^c(\log M)$; broadened MWD obtained from the mass chromatogram and the linear calibration, $G(\log M)$; MWD obtained from $G(V)$ and $\bar{M}_n(V)$, $G_{\bar{M}_n}(M)$; and MWD obtained from a $G(V)$ and $\bar{M}_w(V)$, $G_{M_w}(M)$

area: one of mean 32.2 ml and variance 4 ml^2, and the other of mean 37.4 ml and variance 5.76 ml^2. Strictly speaking, $G^c(V)$ is discrete, with 92 non-zero points taken at regular elution volume intervals ($\Delta = 0.2$ ml). Each point of $G^c(V)$ represents a truly monodisperse fraction, and therefore only 92 molecular weight classes constitute our theoretical sample. The molecular weight range of $G^c(V)$ results is 461–292 000 g/mol. The calibration responds to the function: $\log M = -0.15389V + 9.496885$.

From $G^c(V)$ and $\log M(V)$, the correct MWD $G^c(\log M)$ of Fig. 1(c) was obtained and the resulting average values are presented in the second row of Table 1. Throughout this work, MWDs with horizontal axes representing $\log M$ are

Table 1
Base Numerical Example. Molecular weight averages and polydispersities corresponding to: (a) the 'true' MWD; (b) a broadened MWD obtained from the mass chromatogram and the linear calibration; (c) a biased MWD obtained from a combination of mass- and $\bar{M}_n(V)$ measurements; (d) a biased MWD obtained from a combination of mass- and $\bar{M}_w(V)$ measurements; (e) $\bar{M}_n$ as in (c), but with $\bar{M}_w$ calculated from an estimate of $\bar{M}_w(V)$; and (f) $\bar{M}_w$ as in (d), but with $\bar{M}_n$ calculated from an estimate of $\bar{M}_n(V)$

	MWD	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Polydispersity error[a] (%)
(a)	$G^c(M)$	**6820**	**26 100**	**3.83**	–
(b)	$G(M)$	6560	27 200	4.15	8.19
(c)	$G_{\bar{M}_n}(M)$	**6820**	24 400	3.57	– 6.82
(d)	$G_{\bar{M}_w}(M)$	7330	**26 100**	3.57	– 6.97
(e)	$G_{\bar{M}_n}(M)$; $G_{\bar{M}_{w,approx.}}(M)$	**6820**	26 300	3.86	0.63
(f)	$G_{\bar{M}_{n,approx.}}(M)$; $G_{\bar{M}_w}(M)$	6790	**26 100**	3.85	0.43

'True' values are indicated in bold type
[a][(estimate − 3.83)/3.83] × 100

shown. For this reason, all abscissas in Figs. 1–6 (that represent either retention volumes or molecular weights) are interchangeable. Logarithmic axes were chosen to represent MWDs to minimize the deformation of such curves with respect to the mass chromatograms. For any given molecular weight range, the areas under the 'continuous' MWDs are representative of the sample mass fraction within that range. When a linear calibration is employed, evenly-spaced points along retention volume also result in evenly-spaced points along molecular weights, and therefore no height corrections are required. For unevenly-spaced points along log $M(V)$, moderate height corrections are necessary; but the resulting deformations are considerably less significant than if linear molecular weight axes had been adopted.

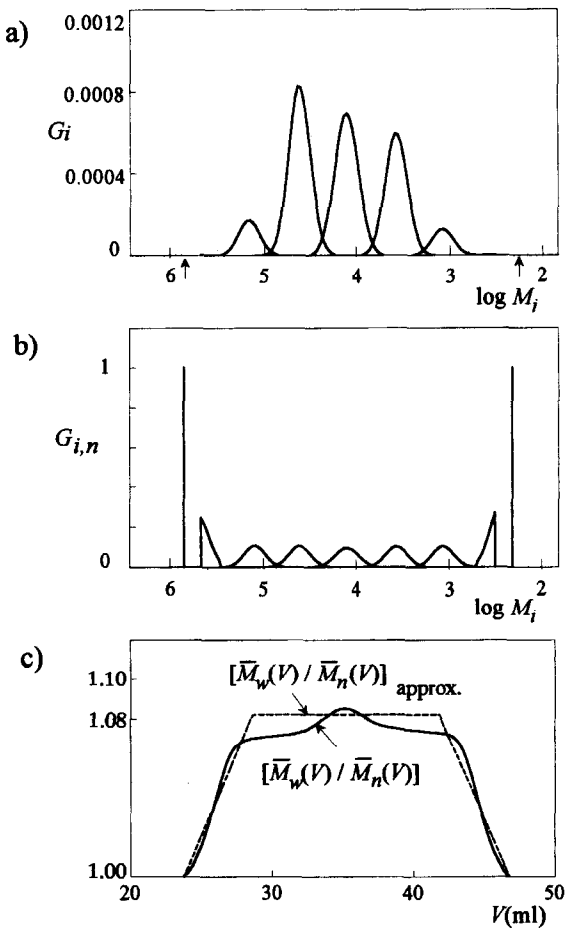

Fig. 2. Base Numerical Example. (a) Several instantaneous MWDs $G_i(\log M_i)$, obtained at different retention volumes. The arrows indicate that negligibly-sized distributions are present at the chromatogram tails. (b) Normalized instantaneous MWDs, $G_{i,n}(\log M_i)$, showing that they tend to uniform distributions at the chromatogram ends. (c) Instantaneous polydispersity $\bar{M}_w(V)/\bar{M}_n(V)$, and approximate instantaneous polydispersity assuming a rectangular mass chromatogram, $[\bar{M}_w(V)/\bar{M}_n(V)]_{approx.}$

In Fig. 1(a), only three individual $g(V)$ functions of $g(V, V_0)$ (with their maxima chosen at the first, the last, and an intermediate point of $G^c(V)$), are represented. Each $g(V)$ function has a mean at the different chromatogram points, a variance of 0.64 ml^2, and 25 non-zero points.

By direct application of Eq. (1), the broadened or 'measured' mass chromatogram $G(V)$ of Fig. 1(a) is obtained. Such a chromatogram has 92 + 25 − 1 = 116 non-zero points. If the linear calibration log $M(V)$ is directly applied to evaluate a (broadened) MWD from $G(V)$, then $G(\log M)$ of Fig. 1(c) is obtained; its corresponding averages are presented in the third row of Table 1. As expected, $\bar{M}_n$ is underestimated, while $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ are both overestimated.

Instead of directly applying Eq. (1), $G(V)$ may also be calculated from the areas under the curves of the instantaneous MWDs. To find any such distributions, note first that a maximum of 25 different $g(V)$ functions (and therefore a maximum of 25 different molecular weight classes) effectively contribute towards any instantaneous MWD. If at each retention volume, the individual contributions in mass G_i and in molecular weight M_i are stored, then the instantaneous MWDs of Fig. 2(a) can be obtained. In Fig. 2(b), the same distributions are represented, but with a normalized vertical axis. Note from Fig. 2(a,b) that (even though with negligibly low masses), the first and last points of $G(V)$ are strictly monodisperse. At the mid-section of $G(V)$, a fixed number of 25 molecular classes is present in the detection cell and the instantaneous distributions are approximately symmetrical. At the chromatogram tails,

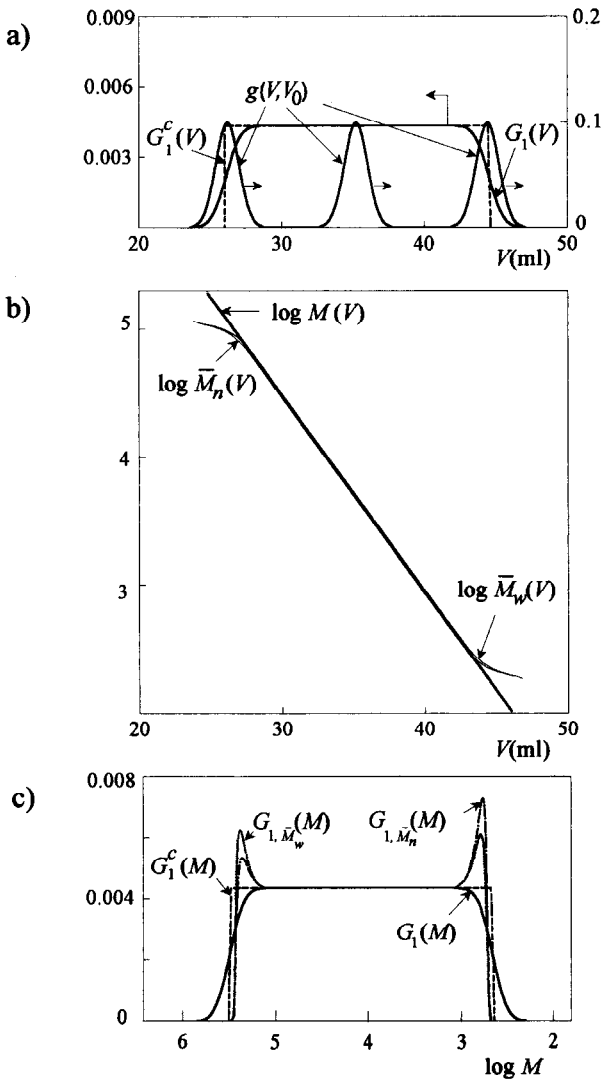

Fig. 3. The 'Rectangular' Example. (a) 'Correct' chromatogram, $G^c(V)$; three samples of the uniform spreading function, $g(V, V_0)$; and resulting 'measured' mass chromatogram, $G(V)$. (b) 'Base' linear calibration obtained from uniform standards, $\log M(V)$; *ad hoc* calibration $\log \bar{M}_n(V)$, obtained from $G(V)$ and $\bar{M}_n(V)$; and calibration $\log \bar{M}_w(V)$, obtained from $G(V)$ and $\bar{M}_{w(V)}$. (c) 'Correct' MWD, $G^c(\log M)$; broadened MWD obtained from the mass chromatogram and the linear calibration, $G(\log M)$; MWD obtained from $G(V)$ and $\bar{M}_n(V)$, $G_{\bar{M}_n}(M)$; and MWD obtained from a $G(V)$ and $\bar{M}_w(V)$, $G_{\bar{M}_w}(M)$

however, skewed and narrower instantaneous MWDs are observed.

From the instantaneous MWDs, $\bar{M}_n(V)$ and $\bar{M}_w(V)$ can be calculated. On a logarithmic vertical scale, these functions produce the ad hoc calibrations $\log \bar{M}_n(V)$ and $\log \bar{M}_w(V)$ of Fig. 1(b). As expected, $\log \bar{M}_w(V)$ is always above $\log \bar{M}_n(V)$ except at the chromatogram ends, where both curves coincide. At the chromatogram tails, the skewed and narrower instantaneous MWDs determine that the two curves bend toward horizontal lines. From $\bar{M}_n(V)$ and $\bar{M}_w(V)$, the instantaneous polydispersity $\bar{M}_w(V)/\log \bar{M}_n(V)$ of Fig. 2(c) was obtained. As expected, $\bar{M}_w(V)/\bar{M}_n(V)$ is unity at the chromatogram ends.

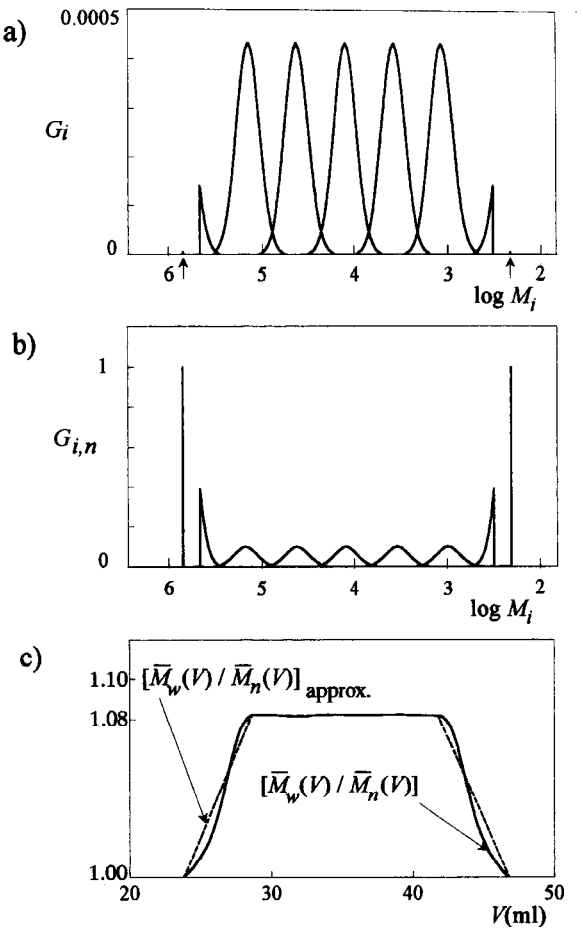

Fig. 4. The 'Rectangular' Example. (a) Several instantaneous MWDs $G_i(\log M_i)$, obtained at different retention volumes. The arrows indicate that negligibly-sized distributions are present at the chromatogram tails. (b) Normalized instantaneous MWDs, $G_{i,n}(\log M_i)$, showing that they tend to uniform distributions at the chromatogram ends. (c) Instantaneous polydispersity $\bar{M}_w(V)/\bar{M}_n(V)$, and approximate instantaneous polydispersity assuming a rectangular mass chromatogram, $[\bar{M}_w(V)/\bar{M}_n(V)]_{approx.}$

From the 'measurements' $G(V)$ and $\bar{M}_n(V)$, the MWD indicated by $G_{\bar{M}_n}(\log M)$ in Fig. 1(c) was obtained. Similarly, from $G(V)$ and $\bar{M}_w(V)$, $G_{\bar{M}_w}(\log M)$ was produced. The moderate non-linearities of $\log M_n(V)$ and $\log M_w(V)$ determine that moderate height corrections were also required for representing such distributions. The average values of $G_{\bar{M}_n}(\log M)$ and $G_{\bar{M}_w}(\log M)$ are given in the fourth and fifth rows of Table 1. For $G_{\bar{M}_n}(\log M)$, the exact $\bar{M}_n$ is obtained while $\bar{M}_w$ is underestimated. For $G_{\bar{M}_w}(\log M)$, $\bar{M}_w$ is accurately determined while $\bar{M}_n$ is overestimated. In both cases, polydispersities below the 'true' value of 3.83 are obtained.

3. Correction method

To illustrate the basis of the proposed technique, two limiting examples will be considered. In Fig. 3, Fig. 4 and Table 2, the Rectangular Example corresponding to chromatogram $G_1^C(V)$ in Fig. 3(a) is presented. In Fig. 5

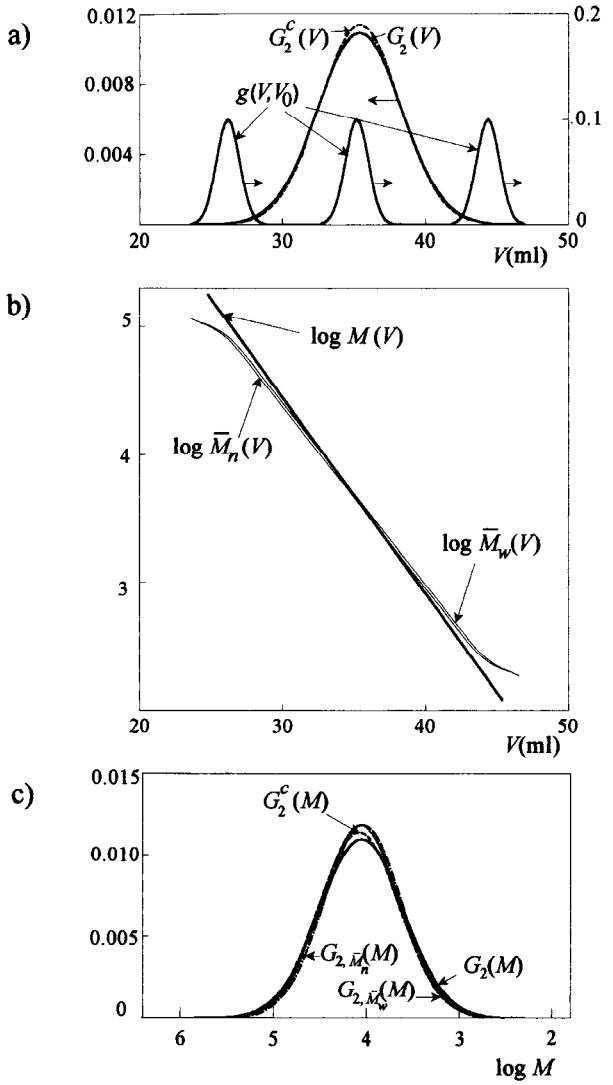

Fig. 5. The Gaussian Example. (a) 'Correct' chromatogram, $G^c(V)$; three samples of the uniform spreading function, $g(V, V_0)$; and resulting 'measured' mass chromatogram, $G(V)$. (b) 'Base' linear calibration obtained from uniform standards, log $M(V)$; *ad hoc* calibration log $\bar{M}_n(V)$, obtained from $G(V)$ and $\bar{M}_n(V)$; and calibration log $\bar{M}_w(V)$, obtained from $G(V)$ and $\bar{M}_w(V)$. (c) 'Correct' MWD, $G^c(\log M)$; broadened MWD obtained from the mass chromatogram and the linear calibration, $G(\log M)$; MWD obtained from $G(V)$ and $\bar{M}_n(V)$, $G_{\bar{M}_n}(M)$; and MWD obtained from a $G(V)$ and $\bar{M}_w(V)$, $G_{\bar{M}_w}(M)$

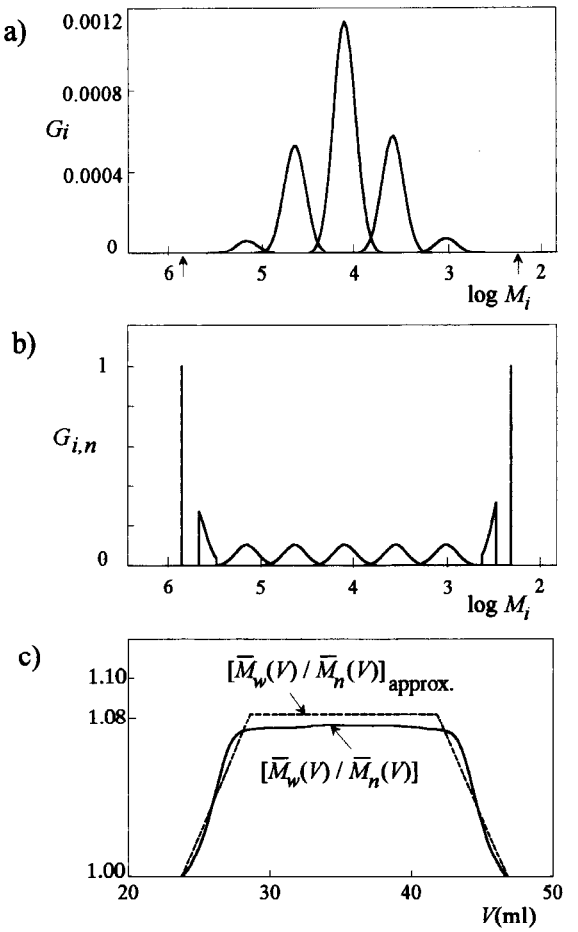

Fig. 6. The Gaussian example. (a) Several instantaneous MWDs $G_i(\log M_i)$, obtained at different retention volumes. The arrows indicate that negligibly-sized distributions are present at the chromatogram tails. (b) Normalized instantaneous MWDs, $G_{i,n}(\log M_i)$, showing that they tend to uniform distributions at the chromatogram ends. (c) Instantaneous polydispersity $\bar{M}_w(V)/\bar{M}_n(V)$, and approximate instantaneous polydispersity assuming a rectangular mass chromatogram, $[\bar{M}_w(V)/\bar{M}_n(V)]_{approx.}$

and Fig. 6 and Table 3, the Gaussian Example of chromatogram $G_2^C(V)$ in Fig. 5(a) is given. $G_2^C(V)$ responds to a Normal distribution of mean 35.4 ml and variance 7.84 ml^2.

In both examples, the same spreading functions, molecular weight ranges, and calibrations of the Base Example in Fig. 1 are readopted. Again, the area under any correct chromatogram or true MWD is $G = 0.4$; while the area under any individual $g(V)$ function is unity. As in the Base Example, the following were calculated: the broadened chromatograms $G_1(V)$ and $G_2(V)$ of Fig. 3(a) and Fig. 5(a); the calibrations log $\bar{M}_n(V)$ and log $\bar{M}_w(V)$ of Fig. 3(b) and Fig. 5(b); the MWDs of Fig. 3(c) and Fig. 5(c); the instantaneous MWDs of Fig. 4(a,b) and Fig. 6 (a,b); and the instantaneous polydispersities of Fig. 4(c) and Fig. 6(c).

Consider first the Rectangular Example. In Fig. 3(b), it can be seen that in the mid-chromatogram section, the calibrations log $\bar{M}_n(V)$ and log $\bar{M}_w(V)$ are both parallel to log $M(V)$. From the MWDs of Fig. 3(c), note that all estimates predict the same (correct) value in the mid-horizontal section, and that all biases are concentrated at the distribution tails. Also, even though the distributions $G_{1,\bar{M}_n}(\log M)$ and $G_{1,\bar{M}_w}(\log M)$ obtained from the molar mass detectors predict the correct limiting molecular weights, artificial overshoots are observed at the distribution tails. From Fig. 4(a) and (b), it is seen that in the mid-chromatogram section all instantaneous MWDs exhibit the same common shape. Furthermore, it can be proven that such shape coincides with the shape of $g(V)$. Each $g(V)$ function represents the chromatogram obtained from a monodisperse sample in the presence of IB. Alternatively, each $g(V)$ function can be thought of as the chromatogram of a hypothetical

Table 2
The Rectangular Example. Molecular weight averages and polydispersities corresponding to: (a) the 'true' MWD; (b) a broadened MWD obtained from the mass chromatogram and the linear calibration; (c) a biased MWD obtained from a combination of mass- and $\bar{M}_n(V)$ measurements; (d) a biased MWD obtained from a combination of mass- and $\bar{M}_w(V)$ measurements; (e) $\bar{M}_n$ as in (c), but with $\bar{M}_w$ calculated from an estimate of $\bar{M}_w(V)$; and (f) $\bar{M}_w$ as in (d), but with $\bar{M}_n$ calculated from an estimate of $\bar{M}_n(V)$

	MWD	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Polydispersity error[a] (%)
(a)	$G^c(M)$	**2910**	**46 300**	**15.9**	–
(b)	$G(M)$	2800	48 100	17.2	8.22
(c)	$G_{\bar{M}_n}(M)$	**2910**	43 400	14.9	− 6.15
(d)	$G_{\bar{M}_w}(M)$	3100	**46 300**	14.9	− 6.13
(e)	$G_{\bar{M}_n}(M)$; $G_{\bar{M}_{w,\text{approx.}}}(M)$	**2910**	46 300	15.9	0.10
(f)	$G_{\bar{M}_{n,\text{approx.}}}(M)$; $G_{\bar{M}_w}(M)$	2910	**46 300**	15.9	− 0.03

'True' values are indicated in bold type
[a][(estimate − 15.9)/15.9] × 100

polydisperse sample obtained under perfect resolution. With perfect resolution, the linear calibration log $M(V)$ is applicable; and therefore the 'calibrations' $\bar{M}_{w,g}(V)$ and $\bar{M}_{n,g}(V)$ corresponding to $g(V)$ can be obtained. In our numerical example, the (fictitious) polydispersity of any $g(V)$ function is $\bar{M}_{w,g}(V)/\bar{M}_{n,g}(V) = \bar{M}_{w,g}/\bar{M}_{n,g} = 1.08$. This value coincides with the instantaneous polydispersity of $G_1(V)$, $\bar{M}_w(V)/\bar{M}_n(V)$ at any of the mid-values. At the chromatogram tails, the instantaneous polydispersity of $G_1(V)$ decreases in a nonlinear fashion, tending to unity at the curve ends (Fig. 4(c)). To understand why $\bar{M}_{w,g}/\bar{M}_{n,g}$ is a constant, note that as $g(V)$ is shifted toward higher retention volumes, $\bar{M}_w(V)$, $\bar{M}_n(V)$, $\bar{M}_{w,g}(V)$ and $\bar{M}_{n,g}(V)$ all decrease at exactly the same rate. (Clearly, this would not have been the case for non-uniform spreading functions and/or for nonlinear 'base' calibrations.)

Consider now the Gaussian Example. As expected from the theoretical work by Jackson and Yau [9], it is verified that (in the mid-chromatogram section) the calibrations log $\bar{M}_n(V)$ and log $\bar{M}_w(V)$ are again both linear and parallel to each other, but now rotated counterclockwise with respect to log $M(V)$ (Fig. 5(b)). The polydispersity function $\bar{M}_w(V)/\bar{M}_n(V)$ is also practically constant in the mid-chromatogram section, but slightly below $\bar{M}_{w,g}/\bar{M}_{n,g}$ (Fig. 6(c)).

To check the effect of the curve discretizations in the previous results, all calculations were repeated, but for a triple number of points; adopting ΔV intervals equal to 1/3 of its original value in all functions. It was verified that the curves obtained were exactly superimposed with those presented in Figs. 1–6, and that the averages, presented in Tables 1–3, also coincided with the shown values, to the last significant figures.

In the three investigated examples, the MWDs differ quite considerably from each other. However, in Fig. 2(c), Fig. 4(c), Fig. 6(c), it can be seen that the three polydispersity functions are all relatively similar; with most of its ordinates below but close to the limiting value $\bar{M}_{w,g}/\bar{M}_{n,g}$. For this reason, it is simple to see that an upper bound for the percentage of error in the global polydispersity is simply given by $[(1 - \bar{M}_{w,g}/\bar{M}_{n,g}) \times 100]$. When an ideal molar mass detector is used, then only one of the estimated averages is biased. Thus, the absolute value of the error in the biased average molecular weight will coincide with that of the polydispersity. In our numerical examples, $\bar{M}_{w,g}/\bar{M}_{n,g} = 1.08$, and therefore an error up to ~ 8% is to be expected in the polydispersity. This may be observed in the last columns of Tables 1–3, where the error in the estimated polydispersity ranges from − 6.13% for the Rectangular Example to − 6.97% for the basic example.

If an approximate instantaneous polydispersity function could be estimated from the spreading function alone, then it would become simple to correct for the molecular weight biases. We here propose to approximate $\bar{M}_w(V)/\bar{M}_n(V)$ with a trapezoidal function that would correspond to a 'rectangular' MWD appearing in the same elution volume range as the measured chromatogram. The following procedure is proposed:

1. the two mid-section limits of $[\bar{M}_w(V)/\bar{M}_n(V)]_{\text{approx.}}$ are determined by adding and substracting the width of $g(V)$ to the high- and to the low-molecular-weight ends of the chromatogram;
2. in the mid-section, adopt a constant $[\bar{M}_w(V)/\bar{M}_n(V)]_{\text{approx.}}$ equal to the 'polydispersity' of $g(V)$, $\bar{M}_{w,g}/\bar{M}_{n,g}$; and
3. for the tails of $[\bar{M}_w(V)/\bar{M}_n(V)]_{\text{approx.}}$, adopt linear variations from the central limit points to unit polydispersity at the chromatogram ends.

From $[\bar{M}_w(V)/\bar{M}_n(V)]_{\text{approx.}}$, the corrected molecular weight averages are then obtained as follows:

1. if $\bar{M}_n(V)$ is measured, calculate the global $\bar{M}_w$ from $\bar{M}_{w,\text{approx.}}(V) = \bar{M}_n(V) \times [\bar{M}_w(V)/\bar{M}_n(V)]_{\text{approx.}}$; and
2. if $\bar{M}_w(V)$ is measured, calculate the global $\bar{M}_n$ from $\bar{M}_{n,\text{approx.}}(V) = \bar{M}_w(V) \times [\bar{M}_w(V)/\bar{M}_n(V)]^{-1}_{\text{approx.}}$.

In Fig. 2(c), Fig. 4(c) and Fig. 6(c), the approximate polydispersity function corresponding to our three examples is presented. By application of the proposed correction method, the results in the last two rows of Tables 1–3 are obtained. Since the polydispersity function was approximated assuming a rectangular distribution, then the best corrections are observed for the Rectangular Example. For

Table 3
The Gaussian Example. Molecular weight averages and polydispersities corresponding to: (a) the 'true' MWD; (b) a broadened MWD obtained from the mass chromatogram and the linear calibration; (c) a biased MWD obtained from a combination of mass- and $\bar{M}_n(V)$ measurements; (d) a biased MWD obtained from a combination of mass- and $\bar{M}_w(V)$ measurements; (e) $\bar{M}_n$ as in (c), but with $\bar{M}_w$ calculated from an estimate of $\bar{M}_w(V)$; and (f) $\bar{M}_w$ as in (d), but with $\bar{M}_n$ calculated from an estimate of $\bar{M}_n(V)$

	MWD	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Polydispersity error[a] (%)
(a)	$G^c(M)$	**6920**	**18 200**	**2.62**	–
(b)	$G(M)$	6650	18 900	2.84	8.19
(c)	$G_{\bar{M}_n}(M)$	**6920**	16 900	2.44	– 6.96
(d)	$G_{\bar{M}_w}(M)$	7440	**18 200**	2.44	– 6.96
(e)	$G_{\bar{M}_n}(M)$; $G_{\bar{M}_{w,approx.}}(M)$	**6920**	18 300	2.64	0.56
(f)	$G_{\bar{M}_{n,approx.}}(M)$; $G_{\bar{M}_w}(M)$	6880	**18 200**	2.64	0.52

'True' values are indicated in bold type
[a][(estimate − 2.62)/2.62] × 100

the Base and the Gaussian Examples, $[\bar{M}_w(V)/\bar{M}_n(V)]_{approx.}$ in general overestimates the real polydispersity function. For this reason, the corrected $\bar{M}_w(V)$ is slightly overestimated, the corrected $\bar{M}_n(V)$ is slightly underestimated, and the corrected polydispersities are both slightly above their true values.

4. Conclusions

Ideal on-line LS detectors produce $\bar{M}_n(V)$ estimations in excess, while ideal $\bar{M}_n(V)$ detectors produce $\bar{M}_w$ estimations in defect. In both cases, this generates an underestimation of the global polydispersity. An upper bound for the biases in the said variables may be simply calculated from the spreading function 'polydispersity' $\bar{M}_{w,g}/\bar{M}_{n,g}$. To compensate for the said biases, a novel correction method was proposed that consists of appropriately shifting the measured instantaneous molecular weight averages using an estimate of the instantaneous polydispersity. The method is numerically robust, because no ill-posed deconvolutions or adjustable parameters are required.

Previous 'analytical' techniques that correct for IB by simply rotating the calibration curve [8,15–17] are strictly applicable to Gaussian mass chromatograms, but cannot be in general adopted. For example, it was verified that for the limiting case of a 'flat' or rectangular chromatograms, $\log \bar{M}_n(V)$ and $\log \bar{M}_w(V)$ both remain parallel to the base linear calibration.

The low sensitivity of the instantaneous polydispersity to the MWD shape determines that a trapezoidal shape for such function can always be adopted. To this effect, the total breadth and the 'polydispersity' of $g(V)$ are required. For typical unimodal chromatograms, the proposed approximation will slightly overestimate the true global polydispersity.

The main limitation of the present approach is that a uniform spreading and a linear 'base' calibration are required. The latter assumption is reasonable, and is in general satisfied, except perhaps for samples containing ultra-high molecular weight material. The former assumption is at present justified by the fact that the determination of nonuniform spreading functions is complicated and still a matter of controversy [14].

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