

Analysis of the Accuracy of Determination of Molar Mass Distribution by the GPC with the On-Line Light-Scattering Detector

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Synopsis

The effect of errors of the concentration (c -) and the light-scattering molar mass (M -) detector in gel permeation chromatography (GPC) on the accuracy of the determination of the molar mass distribution (MMD) was analyzed. Model calculations showed that the reliability of MMD obtained from c -detector data and from a carefully performed calibration dependence is higher than that obtained by combining data of the M - and c -detectors. A criterion of the uncertainty of the MMD determination by the GPC method with the M -detector was suggested, and its dependence on MMD parameters of the analyzed polymer and on the magnitude of injection was investigated.

INTRODUCTION

Along with the development of the gel permeation chromatographic (GPC) method, and particularly with the development and increasing use of the light-scattering molar mass detector (M -detector) based on low-angle laser light scattering (LALLS photometry),¹⁻³ a problem arose regarding the accuracy of the determination of molar mass distribution of the analyzed polymer in such an experimental arrangement. In this connection, a considerable number of papers have been devoted to (a) the investigation of the effect of axial dispersion inside the chromatographic column on the shape of records provided by the differential refractometer or another concentration detector, and by the molar mass detector (viscometer, LALLS photometer); as well as to (b) the calculation corrections of this dispersion.⁴⁻⁹ Deformations of chromatographic records due to zone spreading outside the column and the possibilities of their suspension were also analyzed.¹⁰

In this study, we disregard the MMD distortion due to axial dispersion inside and outside the column, along with some other potential sources of errors in GPC,¹¹ and examine only the accuracy of data obtained by the concentration and molar mass detector, and its effect on the reliability of the resulting molar mass distribution.

THEORETICAL

We have a GPC setup with a differential refractometer and a LALLS photometer as detectors of the concentration and molar mass of the polymer in the eluate, with a negligible distortion of the shape of records of the two detectors due to spreading inside and outside the column.

The polymer concentration in the eluate, c , is measured with an accuracy characterized by the variance, σ_c^2 . The LALLS photometer measures the intensity of light scattered from the polymer solution at such a low angle of observation ($\theta < 6^\circ$) that the excess Rayleigh ratio, ΔR_θ , corresponding to the dissolved polymer, need not be extrapolated to a zero angle of measurement, because $\Delta R_\theta \doteq \Delta R_0$. Under the experimental conditions used, this value is subjected to an experimental error with the variance σ_R^2 .

We try to find a relationship among σ_c^2 and σ_R^2 and σ_M^2 (σ_M^2 is the variance of molar mass values, M , calculated from the data of the differential refractometer and LALLS photometer). Assuming that the errors of both detectors are independent of each other, we have:¹²

$$\sigma_M^2 = \left(\frac{\partial M}{\partial c} \right)_{\Delta R_0}^2 \sigma_c^2 + \left(\frac{\partial M}{\partial \Delta R_0} \right)_c^2 \sigma_R^2 \quad (1)$$

In the graphic representation of MMD, a logarithmic plot is usually employed for the M axis; consequently, $\sigma_{\log M}^2$ is used below, instead of σ_M^2 :

$$\sigma_{\log M}^2 = \left(\frac{1}{2.3M} \right)^2 \sigma_M^2 \quad (2)$$

For light scattering from polymer solutions, the basic equation holds at $\theta = 0$:¹³

$$\frac{Kc}{\Delta R_0} = \frac{1}{M} + 2A_2c \quad (3a)$$

whence for the molar mass M we have:

$$M = \left(\frac{Kc}{\Delta R_0} - 2A_2c \right)^{-1} \quad (3b)$$

K is the optical constant (including also the squared refractive index increment), and A_2 , is the second virial coefficient whose dependence on molar mass may usually be expressed as²:

$$A_2 = aM^{-\alpha} \quad (4)$$

For the partial derivatives in eq. (1), we have, then,

$$\left(\frac{\partial M}{\partial c} \right)_{\Delta R_0} = -\frac{1}{c^2} \left(\frac{K}{\Delta R_0} - 2A_2 \right)^{-1} = -\frac{M}{c} \quad (5)$$

$$\left(\frac{\partial M}{\partial \Delta R_0} \right)_c = \left(\frac{\partial M}{\partial \Delta R_0} \right)_{c, A_2} + \left[\left(\frac{\partial M}{\partial \Delta R_0} \right)_{\Delta R_0, c} \cdot \frac{dA_2}{dM} \left(\frac{\partial M}{\partial \Delta R_0} \right)_c \right] \quad (6a)$$

$$\begin{aligned} \left(\frac{\partial M}{\partial \Delta R_0}\right)_c &= \left(\frac{\partial M}{\partial \Delta R_0}\right)_{C,A_2} \cdot \left[1 - \left(\frac{\partial M}{\partial A_2}\right)_{\Delta R_0,c} \cdot \frac{dA_2}{dM}\right]^{-1} \\ &= \frac{(1 + 2A_2Mc)^2}{Kc(1 + 2\alpha A_2Mc)} \end{aligned} \quad (6b)$$

With respect to low polymer concentrations in the eluate, $2A_2Mc$ is so small that the error introduced into the calculation by the often rather inaccurate values of the parameters a and α [eq. (4)] can be neglected.

By combining eqs. (1), (2), (5), and (6b), we obtain the final relation for the variance of the molar mass logarithm values, $\sigma_{\log M}^2$, calculated from the data of the M- and c-detectors, using eq. (3b).

$$(\sigma_{\log M}^2)_d = \left(\frac{1}{2.3c}\right)^2 \left\{ \left[\frac{(1 + 2A_2Mc)^2}{KM(1 + 2\alpha A_2Mc)} \right]^2 \sigma_R^2 + \sigma_c^2 \right\} \quad (7)$$

The subscript d is used to distinguish the respective value from $(\sigma_{\log M})_c$, which corresponds to the determination of $\log M$ via the concentration detector data and the known calibration dependence.

To estimate the $(\sigma_{\log M}^2)_c$ values, one has to know the reliability of constants of the calibration curve, which for the sake of simplicity is considered in the linear form:

$$\log M = K_1 + K_2V \quad (8)$$

It is assumed that the calibration was performed using n polymer standards with a narrow MMD, and that their molar mass values, M_i ($i = 1, 2, \dots, n$), are known with an error σ_{M_i} which is proportional to M_i . This assumption is based on experience with the light scattering method, which in the range of its optimal applicability yields M values subjected to a constant relative error $(\sigma_M)_{LS}$:

$$\sigma_{M_i} = M_i (\sigma_M)_{LS} \quad (9)$$

Also, the elution volume, V_i , of each calibration standard is determined with a certain error, which is not always negligible. The variance of the elution volumes, σ_V^2 , is small in precise GPC experiments as compared with that in M_i ; for the sake of simplicity, the error of determination of the elution volume will not be considered.

The standard deviation of $\log M$, obtained at the given elution volume V from the calibration dependence,⁸ the constants of which have been calculated by the least-squares method, is determined by:

$$(\sigma_{\log M}^2)_c = \frac{(\sigma_M^2)_{LS}}{2.3^2} \left[\frac{1}{n} + \frac{(V - \sum_{i=1}^n V_i/n)^2}{V_i^2 - \left(\sum_{i=1}^n V_i\right)^2/n} \right] \quad (10)$$

(It should be mentioned here that the error in determination of M or $\log M$ by means of calibration dependence is a random one, due to the randomness of the errors of parameters of the calibration functions. A given calibration, however, introduces a systematic error into further calculations!)

MODEL CALCULATIONS

Using two real and two model MMD, it will be shown how the magnitude of $(\sigma_{\log M})_d$ and $(\sigma_{\log M})_c$ for polymers with various average molar masses and various polydispersities varies with molar mass. Furthermore, the dependence of $(\sigma_{\log M})_d$ on the magnitude of injection for polymers with various MMD will be examined by means of model calculations. The calculations were based on the three following assumptions:

1. The analyzed polymer has a logarithmic-normal (Wesslau's molar mass distribution¹⁴ described by the mass differential distribution function:

$$w(\log M) = (1\sqrt{\beta^2\pi}) \exp[-(1/\beta^2)\log^2(M/M_0)] \quad (11)$$

with the parameters M_0 and $\beta^2 = 2 \log(M_w/M_n)$.

2. The calibration function is linear [eq. (8)], with the constants⁹ $K_1 = 12.8$ and $K_2 = -0.135 \text{ cm}^{-3}$.

3. No axial dispersion is considered, either in the column or beyond.

Under these circumstances, the polymer concentration in the eluate at the elution volume V is:

$$c(V) = -w(\log M) M_0 K_2 \quad (12)$$

where m_0 is the total mass of the injected polymer. For the constants K , α , and a , we used $K = 1.1 \times 10^{-7} \text{ mol cm}^2 \text{ g}^{-2}$ (Ref. 3), $\alpha = 0.227$, $a = 8.4 \times 10^{-3} \text{ mol}^{0.773} \cdot \text{cm}^3 \cdot \text{g}^{-1.773}$ (Ref. 15), which corresponds to polystyrene solutions in toluene.

The σ_c and σ_R values were estimated on the basis of data reported for the level of the instrumental noise. This noise is regarded as a random phenomenon with a normal frequency distribution characterized by the parameters μ and σ^2 . At the same time, the noise level is taken to be 2σ , for which it holds that the probability for the given quantity to be $\mu \pm 2\sigma$ at the given moment is higher than 95%. Spikes on the LALLS photometer are not considered here, because they may to a great extent be suppressed by suitable experimental arrangement, and the residual noise may be eliminated electronically or numerically.

From Ouano's and Kaye's data¹ on the magnitude of noise in a polystyrene-chloroform system ($K = 2.2 \times 10^{-7} \text{ mol} \cdot \text{cm}^2 \cdot \text{g}^{-2}$), we have for the differential refractometer $\sigma_c = 5 \times 10^{-7} \text{ g} \cdot \text{cm}^{-3}$, and for the LALLS photometer $\sigma_R = 7.5 \times 10^{-8} \text{ cm}^{-1}$. The firm Chromatix³ gives for the KMX-6 apparatus as the minimal detectable magnitude of $\Delta R_{0,\min}$ such value of ΔR_0 at which the signal-to-noise ratio is 10. Hence, we have $\sigma_R = 3 \times 10^{-8} \text{ cm}^{-1}$ for the magnitude of noise in the MMD measurement of polystyrene in toluene. Roughly half the σ'_R value compared with the mea-

surement in chloroform corresponds to half the value of the constant ($K = 1.1 \times 10^{-7} \text{ mol}\cdot\text{cm}^2\cdot\text{g}^{-2}$).

At the same time, it is reported^{1,16,17} that the reproducibility of the ΔR_0 measurement by means of the LALLS photometer is 2–2.5%, to which $\sigma_R'' = 1.2 \times 10^{-2} \Delta R_{0,\text{max}}$ is assigned, where $\Delta R_{0,\text{max}}$ is the magnitude of the signal in the maximum of the record of the M-detector.

Obviously, the $\sigma_R' = 7.5 \times 10^{-8}$ or $3 \times 10^{-8} \text{ cm}^{-1}$ values given earlier should be regarded as limiting values which hold at such $\Delta R_{0,\text{max}}$ that the M-detector operates at its maximum sensitivity ($\sigma_R''^2 \cong \sigma_R'^2$). If $\Delta R_{0,\text{max}}$ is so high that $\sigma_R''^2 > \sigma_R'^2$, σ_R'' is the factor determining the experimental error. This means that the higher of the values must be substituted for the variance into eq. (7). In the former case, we will say that the detector operates in the regime of a constant absolute error; in the latter, that we have here a regime of constant relative experimental error.

In order to estimate the $(\sigma_{\log M}^2)_c$ values, one should know $(\sigma_M)_{LS}$ [eq. (9)], the number of standards n used in the calibration, and the respective retention volumes. Let us consider a relatively precise calibration involving six polymeric standards with narrow MMD, the average molar masses of which, $M_{w,i}$ ($i = 1, 2, \dots, 6$), uniformly cover the range of molar masses on the logarithmic scale within two orders of magnitude, e.g., $M_{w,i} = (0.2, 0.5, 1.0, 2.0, 5.0, 10.0) \times 10^5 \text{ g mol}^{-1}$. Let each of these molar masses be determined by an independent method (e.g., by wide-angle light scattering) with an accuracy of 5%,¹³ i.e., $(\sigma_M)_{LS} = 2.5 \times 10^{-2}$. According to eq. (8), the individual molar mass values $M_{w,i}$ have certain corresponding V_i values which, after substitution into eq. (10), yield the dependence of $(\sigma_{\log M}^2)_c$ on the elution volume V and, indirectly by means of eq. (8), also on the molar mass, M :

$$(\sigma_{\log M}^2)_c = \frac{(\sigma_M^2)_{LS}}{(2.3)^2} \left[\frac{1}{6} + \frac{(V - 56.6)^2}{109.1} \right] \quad (13)$$

The model calculations of $(\sigma_{\log M}^2)_d$ and $(\sigma_{\log M}^2)_c$ were carried out for distribution functions¹¹ with various M_0 values determining the position of the maximum and β^2 characterizing the width of distribution, both at a constant injection, m_0 , and at such an injection:

$$m_0 = - \frac{c_{\text{max}}}{[K_2 w(\log M_0)]} \quad (14)$$

which would ensure that the height of the maximum on the concentration detector record, c_{max} , will be the same for all MMD of various widths.

RESULTS AND DISCUSSION

As follows from eq. (7), $(\sigma_{\log M}^2)_d$ is inversely proportional to the polymer concentration in the eluate; i.e., this error influences most strongly the peripheral parts of MMD, particularly in the range of low M values. This statement can be justified by using two reported MMD (Fig. 1) in which

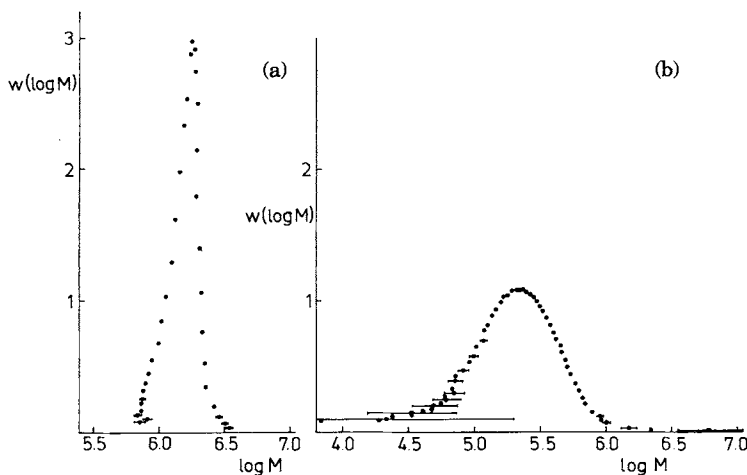


Fig. 1. The distribution function of molar mass, $w(\log M)$, of polystyrene standards: (a) Pressure Chemical Co., $M_w = 1.8 \times 10^6$ g·mol⁻¹, $M_w/M_n = 1.2$, measured in chloroform¹ ($K = 2.2 \times 10^{-7}$ mol·cm²·g⁻², $\alpha = 0.28$, $a = 2.1 \times 10^{-2}$ mol^{0.72}·cm³·g^{-1.72}, $\sigma_R = \sigma_R'' = 1 \times 10^{-7}$ cm⁻¹); (b) NBS-706 $M_w = 257.8 \times 10^3$ g·mol⁻¹, $M_w/M_n = 2.1$, measured in toluene³ ($K = 1.1 \times 10^{-7}$ mol·cm²·g⁻², $\alpha = 0$, $a = A_2 = 4.4 \times 10^{-4}$ mol·cm³·g⁻², $\sigma_R = \sigma_R'' = 1.1 \times 10^{-7}$ cm⁻¹). Horizontal intercepts at chosen points have the length $2(\sigma_{\log M})_d$ [cf. eq. (7)], $\sigma_c = 5 \times 10^{-7}$ g·cm⁻³.

changes in $(\sigma_{\log M})_d$ in the course of distribution are illustrated by horizontal intercepts $(\log M - (\sigma_{\log M})_d, \log M + (\sigma_{\log M})_d)$ plotted at some points.

The comparison of the course of $(\sigma_{\log M})_d$ and $(\sigma_{\log M})_c$ is demonstrated by means of two model distribution functions with the same position of the maximum (i.e., the same M_0 value) and different width (Fig. 2). Both dependences, $(\sigma_{\log M})_d$ and $(\sigma_{\log M})_c$, on $\log M$ are convex, with a minimum near M_0 where $(\sigma_{\log M})_d \approx (\sigma_{\log M})_c < (\sigma_M)_{LS}$. Toward the periphery of MMD, $(\sigma_{\log M})_d$ increases much more quickly than $(\sigma_{\log M})_c$, and even before the concentration of the polymer with a given M becomes negligible, $(\sigma_{\log M})_d$ increases much above $(\sigma_M)_{LS}$. At the same time, the magnitude of $(\sigma_{\log M})_c$ does not exceed $(\sigma_M)_{LS}$ in the whole range of MMD. The hatched area in Figure 2 is part of the area below the distribution curve where $(\sigma_{\log M})_d$ is larger than a certain limit, in our case, $2(\sigma_{\log M})_{LS}$. The size of this area is used as a criterion of uncertainty of the determination of the given distribution and is denoted as C_r . According to definition, always $C_r \leq 1$.

A comparison between the course of $(\sigma_{\log M})_d$ and $(\sigma_{\log M})_c$ shows that the determination of MMD, obtained by using a carefully performed calibration, is more exact than that obtained by combining GPC with the M-detector. A reliable calibration is not always feasible, however.¹⁸ In those cases where calibration standards are not available, e.g., with branched polymers, or with samples having a low content of a high-molar mass fraction, GPC with an on-line M-detector may, under suitable experimental conditions, prove to be of great value. For this reason, we have examined the reliability of MMD determination as a function of the magnitude of injection (Fig. 3) and of the polydispersity of samples (Fig. 4).

If the M-detector operates in the regime of a constant absolute error, then at a given M_0 and β^2 value, C_r decreases steeply with an increasing

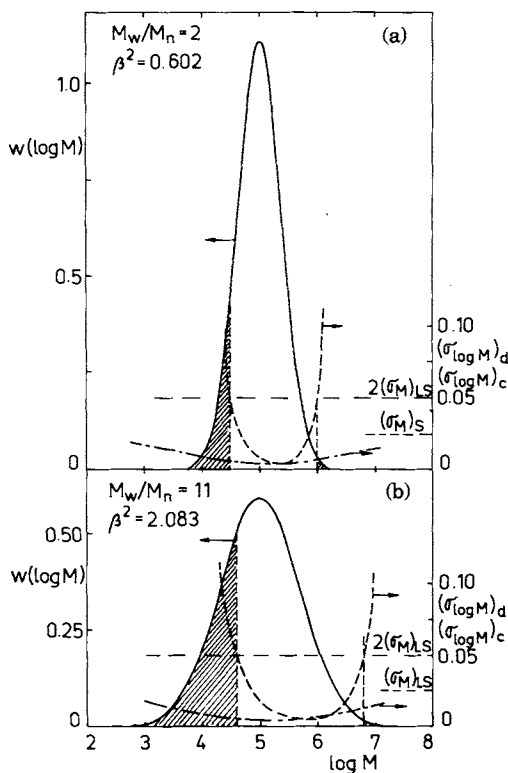


Fig. 2. Model distribution functions $w(\log M)$ (—) and the $(\sigma_{\log M})_d$ (- - -) and $(\sigma_{\log M})_c$ (- · -) dependences on molar mass M : $M_0 = 1 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$, $m_0 = 2 \times 10^{-3} \text{ g}$, $\sigma_c = 5 \times 10^{-7} \text{ g} \cdot \text{cm}^{-3}$, $\sigma_R = 1.2 \times 10^{-2} \Delta R_{0,\text{max}}$. (a) $M_w/M_n = 2$, $C_r = 0.0095$; (b) $M_w/M_n = 11$, $C_r = 0.280$. The ratio of the dashed area to the total area below the distribution curve gives the degree of uncertainty in the determination of the given MMD, C_r .

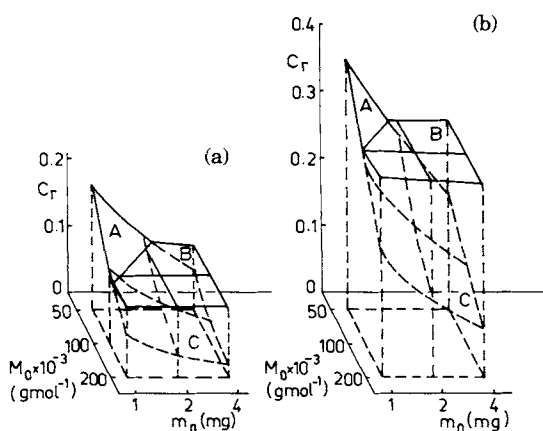


Fig. 3. The dependence of the criterion of the degree of uncertainty of the MMD determination, C_r , on the magnitude of injection and molar mass, M_0 , of a polymer with the polydispersity index $M_w/M_n = 2$ (a), and $M_w/M_n = 11$ (b). Area A: measurement in the regime of constant absolute error; area B: measurement in the regime of constant relative error; area C (dashed): measurement according to Hamielec et al.¹⁹

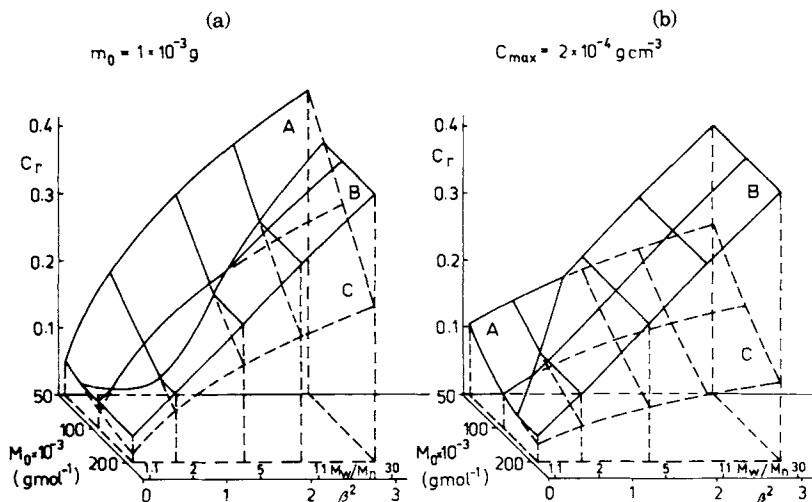


Fig. 4. The dependence of the criterion of the degree of uncertainty of MMD determination, C_r , on the distribution parameters M_0 and β^2 (a) at constant magnitude of injection ($m_0 = 1 \times 10^{-3}$ g) and (b) at constant height of the maximum of the concentration detector ($c_{\max} = 2 \times 10^{-4}$ g cm $^{-3}$). The designations of areas A, B, and C are the same as in Figure 3.

magnitude of injection, m_0 (Fig. 3, area A), being virtually independent of m_0 at an invariable value of the product $m_0 M_0$. In the regime of constant relative error (area B), C_r at a given sample polydispersity is independent both of injection m_0 and of molar mass M_0 .

Hamielc et al.¹⁹ suggested and used a procedure that allows us to reduce the experimental error by switching the sensitivities of the M-detector during the measurement according to the magnitude of its signal. In this procedure, the M-detector operates in the peripheral parts of the chromatogram always in the regime of constant absolute error, irrespective of the magnitude of injection and molecular parameters of the sample. Such experimental arrangement roughly corresponds to the dashed area C in Figure 3, which in principle is a continuation of area A below the level of area B. Clearly, under these circumstances the accuracy of the determined MMD steeply increases (C_r decreases) with increasing $m_0 M_0$. At the same time, C_r increases with increasing width of distribution β^2 or M_w/M_n (cf. Figs. 3a, 3b).

The rise of C_r with increasing width of distribution of the sample can be seen in Figure 4a, which represents the dependence of C_r on M_0 and β^2 at constant injection m_0 ; Figure 4b shows the same dependence at constant height of the maximum on the concentration record, c_{\max} . Whereas the position and shape of area B, which corresponds to measurement in the regime of constant relative error, are the same in both figures and depend neither on m_0 nor on c_{\max} , the dependence of area A (regime of constant absolute error) strongly depends on the magnitude of injection, m_0 , or on the height of the maximum, c_{\max} . The dashed area C confirms the conclusion made in the discussion of Figure 3, namely that by employing the procedure suggested by Hamielc et al.,¹⁹ the accuracy of determination of MMD may be considerably raised in some cases. In any case, however, C_r strongly increases with broadening MMD; only in the regime of constant absolute

error and at constant c_{\max} is this increase slower, because if this condition is to be satisfied, injection m_0 must increase simultaneously with increasing β^2 [eq. (14)].

It can be seen from the comparison between areas A and B in Figures 3 and 4 that, at the given molar mass and polydispersity of the analyzed polymer, it is preferable to use for the analysis such quantity of the sample at which the M-detector might operate already in the regime of constant relative error. At the same time, a further increase of injection is useless (unless the procedure according to Hamielec et al.¹⁹ is employed), because it always raises the danger of the so-called concentration effects.⁸

CONCLUSION

The accuracy of determination of the molar mass distribution by GPC with the LALLS photometer on line is satisfactory in the range near the maximum of the distribution function, where the signal-to-noise ratios of the both detectors are sufficiently high. In the peripheral regions of MMD, and particularly in the range of low molar masses, the error of determination of M steeply increases. Indeed, in this region, MMD is determined more accurately — if this is feasible — by a c-detector and by use of the calibration dependence. On the contrary, in the high-molar-mass range, where the signal of the M-detector is still sufficiently strong, but the polymer concentration is already below the sensitivity limit of the c-detector, it would be possible, in principle, to obtain c values by combining data of the M-detector and the calibration dependence:

$$c = \frac{\Delta R}{KM} \quad (15)$$

(The term containing the second virial coefficient in eq. (3a) can be neglected in this case.)

If no reliable calibration dependence is at one's disposal, then the amount of the polymer used in the analysis should be such as to suppress the concentration effects to the minimum, while at the same time allowing the M-detector to operate in the regime of constant relative error (or to use the procedure according to Hamielec et al.¹⁹). Because the optimal magnitude of injection of the polymer, m_0 , depends on its molar mass and polydispersity, it is advisable, in a careful analysis of an unknown sample, to perform a preliminary experiment (or experiments), and from the estimates of M_0 (or M_w) and M_w/M_n values thus obtained, to optimize the magnitude of injection.

Understandably, the limited sensitivity of detectors and axial dispersion both inside and outside the column are not the only sources of errors in the GPC experiment with the on-line M-detector.¹¹ In addition to errors of purely chromatographic origin (concentration effect and the like), these are predominantly inaccuracies in the determination of the value of constant K and of the instrumental constants of both detectors. The latter two, however, give rise to a systematic, and not random, error.

The problems associated with the limited sensitivity of detectors in a GPC experiment lead, for example, to the considerable and systematically neg-

ative errors in the M_w value of polyethylene standards observed by Grinshpun et al.²⁰ These authors see the source of these errors mainly in the fact that polymer fractions with the highest molar mass, even if present in a refractometrically undetectable concentration, may basically affect the magnitude of M_w . The simplest way to avoid this error is by calculating M_w not from MMD, but directly from the ratio of areas below the curves of the signal of the LALLS photometer and differential refractometer.¹¹ The inaccuracy caused by neglecting the second virial coefficient [eq. (3b)] is certainly lower than the errors observed by Grinshpun et al.²⁰

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References

1. A. C. Ouano and W. Kaye, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1151 (1974).
2. A. C. Ouano, *J. Chromatogr.*, **118**, 303 (1976).
3. "Determination of Molecular Weight Distribution by Combining Low-Angle Light Scattering with Gel Permeation Chromatography," Chromatix Appl. Note LS-2, 1977.
4. L. H. Tung, *J. Appl. Polym. Sci.*, **10**, 375 (1966).
5. A. E. Hamielec and W. R. Ray, *J. Appl. Polym. Sci.*, **13**, 1319 (1969).
6. S. Balce and A. E. Hamielec, *J. Appl. Polym. Sci.*, **13**, 1381 (1969).
7. L. Marais, Z. Gallot, and H. Benoit, *J. Appl. Polym. Sci.*, **21**, 1955 (1977).
8. L. H. Tung and J. C. Moore, in *Fractionation of Synthetic Polymers: Principles and Practices*, L. H. Tung, Ed., Dekker, New York 1977.
9. M. Netopilik, *Polym. Bull.*, **7**, 575 (1982); **10**, 478 (1983).
10. R. Bressau, in *Liquid Chromatography of Polymers and Related Materials II*, J. Cazes and X. Delamare, Eds., Dekker, New York 1980, p. 73.
11. M. Martin, *Chromatographia*, **15**, 426 (1982).
12. J. R. Green and D. Margerison, *Statistical Treatment of Experimental Data*, Elsevier, Amsterdam 1977.
13. J. M. Evans, in *Light Scattering from Polymer Solutions*, M. B. Huglin, Ed., Academic Press, London, 1972.
14. H. Wesslau, *Makromol. Chem.* **20**, 111 (1956).
15. Z. Tuzar, J. Podešva, and O. Procházka, unpublished data.
16. "Measurement of the Absolute Molecular Weight and Molecular Weight Distribution of Polyolefins," KMX-6 Application Note LS-3, Chromatix 1978.
17. Chromatix CMX-100 — Light Scattering Detektor, Operation Manual, Chromatix.
18. M. Kubin, *J. Liq. Chromatogr.*, **7**(S-1), 41 (1984).
19. A. E. Hamielec, A. C. Ouano, and L. L. Nebenzahl, *J. Liq. Chromatogr.*, **1**, 527 (1978).
20. V. Grinshpun, K. F. O'Driscoll, and A. Rudin, *J. Appl. Polym. Sci.*, **29**, 1071 (1984).

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