A New Method for Correcting Axial Dispersion in GPC

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Synopsis

In this paper, a new method for correcting GPC results in order to take into account the axial dispersion of a given set of columns is proposed. The idea is to evaluate the different average molecular weights and the polydispersity for a given elution volume. In order to do so, one needs only to know the efficiency of the set of columns and the different derivatives at a given point of the chromatogram. Some possible applications of this method are reviewed mainly for the characterization of polydispersity and for the determination of the viscosity law if one uses the universal calibration.

INTRODUCTION

Gel permeation chromatography (GPC) is one of the best tools for the characterization of polymers; it has even been used for a few years as a preparative technique. More recently, the use of an automatic viscometer as second detector has made possible the determination of the instantaneous viscosity at a given elution volume thus making possible a direct measurement of molecular weight if one assumes the validity of universal calibration.

The interpretation of the results is straightforward as long as one does not take into account the axial dispersion. But, unfortunately, this approximation is not always sufficient. For instance, the fractions obtained in preparative GPC are not absolutely monodisperse. Many authors have suggested correction methods based on the deconvolution technique. They are difficult to handle and not very successful.

In this paper, we would like to present an approximation method by which one can evaluate the polydispersity of a fraction eluted at a given elution volume as a function of the molecular weight distribution of the sample and the axial dispersion.

PRINCIPLE OF THE METHOD

According to Tung,[1] the chromatogram of the polymer is the convolution of two distribution functions. One is the distribution $C(V)$ of the polymer as a function of the elution volume V; $C(V)dV$ is the amount of the polymer with an elution volume between V and $V + dV$; and $G(V - V_e)$ is the axial dispersion

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function. It represents the shape of the chromatogram for a monodisperse system with elution volume V_e with normalization at unity of the area between the curve and the elution volume axis.

The chromatogram, then, has the following equation:

$$F(V_e) = \int_0^\infty C(V) \cdot G(V - V_e) dV \tag{1}$$

where $F(V_e)$ is the response of a detector sensitive to the concentration and $\int_0^\infty F(V_e) dV_e$ is the total amount of polymer injected.

The first hypothesis we shall make is to assume that $G(V - V_e)$ is a Gaussian distribution and has the following equation:

$$G(V - V_e) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} \exp\left\{-\frac{(V - V_e)^2}{2\sigma^2}\right\} \tag{2}$$

where σ is the axial dispersion parameter. This assumption is not limiting the generality of our solution, since in practice with an apparatus in good working conditions, the curve obtained for a monodisperse system has always this shape. The parameter σ can depend on the elution volume V_e; it is usually a smooth function of V_e. Therefore, if we limit ourself to a small range of elution volume, we can always neglect its variations.

Another approximation is related to the calibration curve. For the sake of simplicity, we shall deal simultaneously with two cases. In the first case, we assume that one studies only a kind of polymer, i.e., that one uses a calibration curve in $\ln M$ as function of the elution volume V_e. In a small range of elution volume, this curve can always be taken as a straight line with equation

$$V - V_e = a \ln \frac{M}{M_e} \tag{3}$$

where M_e is the molecular weight of the specie eluted at volume V_e.

In other cases, it is better to use the universal calibration and the hydrodynamical volume ϕ to characterize the set of columns. In this case, one will write

$$V - V_e = A \ln \frac{\phi}{\phi_e} \tag{4}$$

If one uses the relation $\phi = [\eta]M$ and if the polymer obeys a viscosity law of the Mark–Houwink type, i.e., $[\eta] = KM^\alpha$, the relation between a and A is evident:

$$A = a(\alpha + 1) \tag{5}$$

Moreover, if the calibration curve is a straight line in a large range of elution volume for M, this will be also the case for ϕ.

Our purpose is to evaluate the different averages of M or ϕ of a fraction eluted at volume V_e. Using for G its Gaussian expression (2), eq. (1) can be written as

$$F(V_e) = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{+\infty} C(V) \exp\left\{-\frac{(V - V_e)^2}{2\sigma^2}\right\} dV \tag{6}$$

Using the calibration curve, it is possible to change the variable and to use, instead

of V, the quantities M or ϕ. The concentration $C(V)\,dV$ is transformed to $C(M)$ dM or $C(\phi)\,d\phi$. They still characterize the polydispersity of the injected sample. One obtains

$$F(V_e) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} C(M) \exp\left\{-\frac{a^2}{2\sigma^2}\ln^2\frac{M}{M_e}\right\} dM \qquad (7)$$

or

$$F(\phi_e) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} C(\phi) \exp\left\{-\frac{A^2}{2\sigma^2}\ln^2\frac{\phi}{\phi_e}\right\} d\phi \qquad (8)$$

$F(V_e)$ is proportional to the total amount of polymer eluted at elution volume V_e. The quantity under the integral is the contribution of polymers with either molecular weight between M and $M + dM$ or ϕ and $\phi + d\phi$. We want now to obtain averages of M and ϕ; they can be defined as

$$M_\beta = \left[\frac{\sum c_i M_i{}^\beta}{\sum c_i}\right]^{1/\beta} \qquad (9)$$

β being respectively equal to 1, -1, and α for the weight-, number-, and viscosimetric-average molecular weights.

We can use the same definitions for ϕ writing

$$\phi_\beta = \left[\frac{\sum c_i \phi_i{}^\beta}{\sum c_i}\right]^{1/\beta} \qquad (10)$$

For instance, with these notations of the viscometer-average hydrodynamical volume, ϕ, β is equal to $\alpha/(\alpha + 1)$.

Going from summation to integration, we define the functions

$$Y(\beta) = \int_0^{+\infty} M^\beta C(M)\, dM \qquad (11)$$

$$Y^*(\beta) = \int_0^{+\infty} \phi^\beta C(\phi)\, d\phi \qquad (12)$$

Thus, the β averages become

$$M_\beta = \left[\frac{Y(\beta)}{Y(0)}\right]^{1/\beta} \qquad (13)$$

$$\phi_\beta = \left[\frac{Y^*(\beta)}{Y^*(0)}\right]^{1/\beta} \qquad (14)$$

These results are independent on the normalcy of both $y(\beta)$ and $Y^*(\beta)$.

EVALUATION OF $Y(\beta)$ AND $Y^*(\beta)$

Under the summation sign, we have the product of two functions; one is sharp peaked, its shape being governed by the efficiency of the column set through the parameter $\tau = \sigma/a$ or $\tau^* = \sigma/A$; the other characterizes the polydispersity of the original sample. Neglecting the axial dispersion is the same as assuming $\sigma = 0$. It seems, therefore, reasonable to try to improve this approximation expanding the integrals as functions of τ or τ^*. This is tedious but straightforward.

We first introduce the new variable $z = \ln M/M_e$ and assume that we have C as function of $\ln M$. We thus obtain

$$Y(\beta) = \int_0^{+\infty} C(z + \ln M_e) \exp\left\{-\frac{1}{2\tau^2} z^2 M_e{}^\beta\right\} dz \tag{15}$$

Then,

$$Y(\beta) = M_e{}^\beta \int_0^{+\infty} C(z + \ln M_e) \left(\frac{M}{M_e}\right)^\beta \exp\left\{-\frac{z^2}{2\tau^2}\right\} dz \tag{16}$$

$$Y(\beta) = M_e{}^\beta \int_0^{+\infty} C(z + \ln M_e) \exp\left\{-\frac{z^2}{2\tau^2} + \beta z\right\} dz \tag{17}$$

We now introduce the new variable:

$$X = z - \tau^2 \beta$$

obtaining

$$Y(\beta) = M_e{}^\beta \exp\left\{\frac{1}{2}\tau^2\beta^2\right\} \int_{-\infty}^{+\infty} C(\ln M_e + X + \beta\tau^2) \exp\left\{-\frac{X^2}{2\tau^2}\right\} dX \tag{18}$$

It is now easy to expand the expression of C in a Taylor series. Each term can be integrated giving the final result

$$Y(\beta) = M_e{}^\beta \exp\left\{\frac{1}{2}\tau^2\beta^2\right\} \sum_0^n \frac{1}{n!} \sum_0^{2k-p} (c^p{}_{2k-p} \tau^{2(p+k)+1}$$
$$\times \prod_1^{2k-1} (2k-1) \sqrt{2\pi}\, \frac{\partial C(\ln M_e)}{\partial(\ln M)^n} \tag{19}$$

where $n = 2k - p$ and the quantities $c^p{}_{2k-p}$ are Newton's expansion coefficients. A similar expression can be written for Y^* replacing M by ϕ and τ by τ^*.

From these results, one obtains the averages M_β and ϕ_β by the general formulas

$$M_\beta = \left[\frac{Y(\beta)}{Y(0)}\right]^{1/\beta} = M_e \exp\left\{\frac{\tau^2\beta}{2}\right\} \left[1 + \tau^2 \frac{C'}{C}\right.$$
$$\left. + \tau^4 \left(\frac{\beta}{2}\frac{C''}{C} + \frac{1}{2}\frac{C'''}{C} - \frac{(\beta-1)}{2}\frac{C'^2}{C^2} - \frac{1}{2}\frac{C'C''}{C^2}\right)\right] \tag{20}$$

$$\phi_\beta = \left[\frac{Y^*(\beta)}{Y(0)}\right]^{1/\beta} = \phi_e \exp\left\{\frac{\tau^{*2}\beta}{2}\right\} \left[1 + \tau^{*2} \frac{C'}{C}\right.$$
$$\left. + \tau^{*4} \left(\frac{\beta}{2}\frac{C''}{C} + \frac{1}{2}\frac{C'''}{C} - \frac{(\beta-1)}{2}\frac{C'^2}{C^2} - \frac{1}{2}\frac{C'C''}{C^2}\right)\right] \tag{21}$$

where we have stopped the expansion after τ^4 or τ^{*4}.

Since the molecular weight M is much more used than the hydrodynamical volume ϕ, we shall first discuss in terms of molecular weight. Putting in eq. (20) $\beta = 1, -1$ and α one obtains the classical averages M_w, M_n, and M_η:

$$M_w = M_e \left[\exp\left\{\frac{\tau^2}{2}\right\}\right] \left[1 + \tau^2 \frac{C'}{C} + \tau^4 \left(\frac{C''}{2C} + \frac{1}{2}\frac{C'''}{C} - \frac{1}{2}\frac{C'C''}{C^2}\right)\right] \tag{22}$$

$$M_\eta = M_e \left[\exp\left\{ \tau^2 \frac{\alpha}{2} \right\} \right] \left[1 + \tau^2 \frac{C'}{C} \right.$$
$$\left. + \tau^4 \left(\frac{\alpha}{2} \frac{C''}{C} + \frac{1}{2} \frac{C'''}{C} - \frac{(\alpha-1)}{2} \frac{C'^2}{C^2} - \frac{C'C''}{2C^2} \right) \right] \quad (23)$$

$$M_n = M_e \left[\exp\left\{ -\frac{\tau^2}{2} \right\} \right] \left[1 + \tau^2 \frac{C'}{C} \right.$$
$$\left. + \tau^4 \left(-\frac{1}{2} \frac{C''}{C} + \frac{1}{2} \frac{C'''}{C} + \frac{C'^2}{C^2} - \frac{C'C''}{2C^2} \right) \right] \quad (24)$$

Then, the polydispersity index is equal to

$$\frac{M_w}{M_n} = \exp\{\tau^2\} \left[1 + \tau^4 \left(\frac{C''}{C} - \frac{C'^2}{C^2} \right) \right] \quad (25)$$

Until now, we have limited our investigation to precise fractions with elution V_e. Since, if one uses preparative GPC or if one uses a viscometric detector of the capillary type, it is usual to collecting fractions eluted between V_1 and V_2, it could be interesting to generalize our formulas to this case.

Formally, it is very simple; one has merely to introduce, instead of $Y(\beta)$ or $Y^*(\beta)$, the function $Z(\beta)$ and $Z^*(\beta)$ defined as

$$Z(\beta) = \int_{V_1}^{V_2} Y(\beta) dV \quad (26)$$

and

$$Z^*(\beta) = \int_{V_1}^{V_2} Y^*(\beta) dV \quad (27)$$

After the same type of calculation as before, the following expression can be obtained for the expansion of $Z(\beta)$:

$$Z(\beta) = \exp\left\{ \frac{1}{2} \tau^2 \beta^2 \right\} \int_{\ln M_1}^{\ln M_2} \exp\{(\beta) \ln M\} \sum_0^n \frac{1}{n!}$$
$$\times \sum_0^{2k-p} c^P{}_{2k-p} \tau^{2(p+k)+1} \prod_1^{2k-1} (2k-1) \sqrt{2\pi} \frac{\partial^n C(\ln M)}{\partial(\ln M)^n} d\ln M \quad (28)$$

Moreover, one can obtain $Z^*(\beta)$ replacing τ and M by τ^* and ϕ.

These expressions could be used with digital computers, but this is a small correction as long as $V_2 - V_1$ is not too large.

CASE OF THE GAUSSIAN DISTRIBUTION

There is an important special case where eq. (6) can be integrated. It occurs when the distribution of $C(\ln M)$ or $C(\ln \phi)$ is Gaussian. This type of distribution is known as the Wesslau distribution:

$$C(\ln M) = \frac{1}{\sqrt{2\pi}} \frac{1}{\gamma} \exp\left\{ -\frac{1}{2\gamma^2} \ln^2 \frac{M}{M_0} \right\} \quad (29)$$

It depends on two parameters: M_0, the maximum frequency molecular weight;

and γ, the width of the distribution. The following relations are well known:

$$M_w = M_0 \exp\left\{+\frac{1}{2}\gamma^2\right\} \tag{30}$$

$$M_\eta = M_0 \exp\left\{\frac{\alpha}{2}\gamma^2\right\} \tag{31}$$

$$M_n = M_0 \exp\left\{-\frac{1}{2}\gamma^2\right\} \tag{32}$$

If the polymer has a Wesslau distribution and obeys the Mark–Houwink relation $[\eta] = KM^\alpha$, we have

$$C(\ln\phi) = \frac{1}{\sqrt{2\pi}}\frac{1}{\gamma^*}\exp\left\{-\frac{1}{2\gamma^{*2}}\ln^2\frac{\phi}{\phi_0}\right\} \tag{33}$$

with

$$\gamma^{*2} = \gamma^2(\alpha+1)^2 \tag{34}$$

With these values, integration of eq. (6) is straightforward, and one obtains

$$Y(\beta) = M_0^\beta \exp\left\{-\frac{(V-V_0)^2}{2\sigma^2}\right\}\exp\left\{\frac{\beta + \dfrac{a(V-V_0)^2}{\sigma^2}}{2\left(\dfrac{a^2}{\sigma^2}+\dfrac{1}{\gamma^2}\right)}\right\} \tag{35}$$

and

$$Y^*(\beta) = \phi_0^\beta \exp\left\{-\frac{V-V_0)^2}{2\sigma^2}\right\}\exp\left\{\frac{\beta + \dfrac{A(V-V_0)^2}{\sigma^2}}{2\left(\dfrac{A^2}{\sigma^2}+\dfrac{1}{\gamma^2}\right)}\right\} \tag{36}$$

where V_0 is the elution volume of the peak of the distribution.

It is obvious that the fractions are Gaussian of the Wesslau type. They are characterized by two parameters: the molecular weight M_{peak} corresponding to M_0 of eq. (29) and the polydispersity index γ'^2:

$$M_{peak} = M_e^{1/1+\tau^2/\gamma^2}M_0^{1/1+\gamma^2/\tau^2} \tag{37}$$

$$\frac{1}{\gamma'^2} = \frac{1}{\gamma^2} + \frac{1}{\tau^2} \tag{38}$$

From these values, M_w and M_n can be easily deduced.

The same is valid for ϕ. Each fraction is Gaussian of the Wesslau type characterized by ϕ peak and $\gamma^{*\prime}$ and we have

$$\phi_p = \phi_{el}^{1/1+\tau^{*2}/\gamma^{*2}}\phi_0^{1/1+\gamma^{*2}/\tau^{*2}} \tag{39}$$

$$\frac{1}{\gamma^{*\prime 2}} = \frac{1}{\gamma^{*2}} + \frac{1}{\tau^{*2}} \tag{40}$$

As in the preceding case, we have tried to see what happens when, instead of an instantaneous fraction, one uses a finite elution volume $V_2 - V_1$.

The calculations are made following exactly the same scheme as in eqs. (26) and (28), and one obtains

$$Z(\beta) = M_0{}^\beta \exp\left\{\frac{1}{2}\beta^2\gamma^2\right\} \int_{u(\beta,V_1)}^{u(\beta,V_2)} \frac{1}{\sqrt{2\pi}} \exp\left\{\frac{-U^2(\beta,V)}{2}\right\} dU \qquad (41)$$

where

$$U(\beta,V) = \frac{1}{\sqrt{\gamma^2 + \tau^2}}\left[\frac{V - V_0}{a} - \beta\gamma^2\right] \qquad (42)$$

The function under the summation sign can be easily integrated between two limits.

The average molecular weights can be deduced:

$$M_w = M_0 \exp\left\{\frac{1}{2}\gamma^2\right\} \frac{E_{V_1}{}^{V_2}(1)}{E_{V_1}{}^{V_2}(0)} \qquad (43)$$

$$M_\eta = M_0 \exp\left\{\frac{\alpha}{2}\gamma^2\right\} \left[\frac{E_{V_1}{}^{V_2}(\alpha)}{E_{V_1}{}^{V_2}(0)}\right]^{1/\alpha} \qquad (44)$$

$$M_n = M_0 \exp\left\{-\frac{1}{2}\gamma^2\right\} \frac{E_{V_1}{}^{V_2}(0)}{E_{V_1}{}^{V_2}(-1)} \qquad (45)$$

$$\frac{M_w}{M_n} = \exp\{\gamma^2\} \frac{E_{V_1}{}^{V_2}(1) \times E_{V_1}{}^{V_2}(-1)}{(E_{V_1}{}^{V_2}(0))^2} \qquad (46)$$

where

$$E_{V_1}{}^{V_2}(\beta) = \int_{u(\beta,V_1)}^{u(\beta,V_2)} \frac{1}{\sqrt{2\pi}} \exp\left\{\frac{-U^2(\beta,V)}{2}\right\} dU \qquad (47)$$

DISCUSSION OF RESULTS

Characterization of the Polydispersity of the Fractions

Looking at the results obtained for a Gaussian chromatogram, one sees that the polydispersity of the fractions is independent of the elution volume. In this case, all fractions are Gaussian (Wesslau-type distribution), and, as we have said, they are characterized by a parameter γ' such as

$$\frac{1}{\gamma'^2} = \frac{1}{\gamma^2} + \frac{1}{\tau^2}$$

From this expression, one sees that all the fractions are rather narrow since the inequality $\gamma'^2 < \tau^2$ is always valid. It means that for all fractions we can write

$$M_w/M_n \leqslant \exp \tau^2$$

This remark can be extended to the general case quite easily. From expression (25), if one neglects terms of the order τ^4 and more, one obtains also fractions of the Gaussian type and constant polydispersity with the equality $M_w/M_n = \exp \tau^2$.

For more careful and precise determination, it can be interesting to see the effect of the coefficient of τ^4. This coefficient can be rewritten as $d^2 \log c/d$

$\log^2 M$. This quantity is a constant for the Wesslau distribution; but since its order of magnitude is small for a good set of columns, we do not pursue its discussion.

Application to Recycling

If one takes the ideal case where the volume dV_e of the fractions is very small, one can see immediately that after n runs in a recycling process,[2] relation (38) becomes

$$\frac{1}{\gamma_n{}^2} = \frac{1}{\gamma^2} + \frac{n}{\tau^2}$$

Therefore, the polydispersity of a fraction is given by the relation

$$\frac{M_w}{M_n} \approx \exp \frac{\tau^2}{n}$$

This means that if instead of one column one uses n identical columns, the efficiency parameter σ/a or σ/A is divided by $\sqrt{n}$; this is quite obvious from the definitions.

This result on the polydispersity of the fractions being quite trivial, since we have shown that GPC with a good machine gives narrow fractions if the efficiency is good, one could question the legitimacy and the utility of this calculation. We want to show now that some more useful results can be obtained if one compares the averages to what we have called M_{e1}.

Relation Between M Elution and the Molecular Weights

It is usual to assume that the molecular weight or the hydrodynamic volume obtained from the elution volume and the calibration curve represents the molecular weight of the sample or its hydrodynamic volume. After our discussions showing the low polydispersity of the fractions, this seems quite justified; but a more careful examination shows that it is not the case and that this correction has to be taken into account for correct evaluation of the data.

It is usual to define M_{peak} as $(M_n M_w)^{1/2}$; it coincides with the maximum of the distribution in the Gaussian case and should not be far from it even if the distribution is not completely Gaussian. From our results, one sees that M_{peak}, M_w, M_η, and M_n differ from M_{e1} by a factor which is first order in τ^2. Therefore, this correction is essential and has to be taken into account. From formulae (22), (23), and (24), one sees that it depends on the sign of the quantity $d \log C/d \log M$. If this quantity is positive, all the averages are larger than M_{e1}; if it is negative, it is the contrary. This can be explained qualitatively very easily, and a similar correction was proposed on a purely empirical basis by Heitz[3] and used by Servotte and De Bruille.[4]

Some remarks have to be made concerning the use of this correction:

1. We do not know the polydispersity curve $c = f(\log M)$; therefore, the estimation of $d \log C/d \log M$ and of the higher terms is theoretically impossible. But, since this is only a correction, it seems justified to use the chromatogram

to evaluate these quantities, since with the actual efficiency of the columns, the difference between the corrected curve and the chromatogram is negligible.

2. We have assumed that τ or τ^* is constant. Since we are making a calculation for each point of the curve, it is very easy to take into account the variations of the efficiency of the columns as function of elution volume, using for τ the definition $\sigma_{V_e}/(dV_e/d \log M)$. In practical cases, this quantity does not vary rapidly with V_e, which justifies completely this procedure.

APPLICATION TO THE CORRECTION OF EXPERIMENTAL RESULTS

Using the correction we have presented here, it is possible to obtain much more precise results.

Determination of Polydispersity

The classical method for the determination of polydispersity consist in dividing the chromatogram in segments of height h_i corresponding to elution volume V_e and molecular weight M_{e_i} and to write

$$M_w = \frac{\sum h_i M_{e_i}}{\sum h_i}$$

for M_w and similar expressions for M_n, $M_\eta \cdots$.

In order to obtain better results, one has to replace M_{e_i} by M_{w_i}, M_{n_i}, M_{η_i}, using formulae (22), (23), and (24). This takes into account axial dispersion and leads to a much better precision. It has to be noted that if τ is constant and if the polymer has a Gaussian distribution, this correction can be made in a much simpler way using the completely integrated equations.

Determination of Viscosity Law of an Unknown Polymer

In this case, one has to use the universal calibration. Experiments made using an additional viscometric detector give

$$V_{e_i}, C_i, [\eta]_i$$

From universal calibration, one obtains ϕ_i. Usually, one calculates the ratio $\phi_i/[\eta]_i$ in order to obtain M_i, but this M_i is an elution molecular weight and not a viscometric-average molecular weight. One has to correct ϕ_i, which is really a $\phi_{i_{e_1}}$, into an average corresponding to viscosity-average molecular weight. This is only possible if one knows the Mark–Houwink coefficient α but, as we have seen, it is possible to use a rough approximation for it since the results are not very sensitive to its real value.

In conclusion, we hope that this new correction method will be useful and improve the precision of gel permeation chromatography as a quantitative analytical tool.

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