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Correction for Axial Dispersion in Gel Permeation Chromatography with a Detector of Molecular Masses

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Summary

Procedures suggested for data correction of a concentration detector in gel permeation chromatography for axial dispersion may be used in data correction of a detector of molecular masses, e.g., viscometer or light scattering cell. The procedure is demonstrated using model chromatograms calculated for two polymers of different polydispersity obeying the Schulz-Zimm distribution function. A procedure is outlined for determination of the spreading factor h by comparing molecular masses calculated from data obtained by both detectors with values provided by the calibration dependence of the column.

Introduction

The problem of correction of chromatograms obtained by gel permeation chromatography (GPC) for axial dispersion has been satisfactorily solved from the mathematical standpoint. If, however, a second detector intended for the molecular mass determination of the polymer fraction which leaves the column is attached in series with the concentration detector, the situation becomes more involved. The second detector may be either a viscometer or a light scattering cell. Lately, both detectors have been miniaturized (OUANO 1972, 1976; LETOT et al. 1980; CAEL et al. 1981) in order to make them compatible with small-size columns now used in high-speed GPC.

If correction for axial dispersion is performed in such arrangement, semiempirical procedures are employed (SCHEINERT 1977), or the resulting quantities are corrected, e.g., constants of the Mark-Houwink equation determined by means of an on-line viscometer (LETOT et al. 1980).

In an exact correction of data provided by the detector of molecular masses and concentration detector for longitudinal spreading, a system of two integral equations must be solved. Although, in principle, the solution of an integral equation can be transposed to that of a system of linear equations, for the detector of molecular masses such procedure does not yield satisfactory results (NAKANO, GOTO 1975). Attempts at its improvement render it too complicated (BERGER 1978).

We try to show that the record made by both detectors may be corrected by employing the same methods as those originally developed only for corrections of records made by the concentration detector. A model calculation using the Pierce and Armonas method is demonstrated (PIERCE, ARMONAS 1968).

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Theory

The relationship between a chromatogram unaffected by spreading, W (corrected chromatogram) and an experimentally accessible spread chromatogram F, can be described in terms of a relation (TUNG 1966)

$$F(V) = \int_{V_1}^{V_2} W(y) \times G(V,y)\, dy \qquad (1)$$

where V and y are the elution volumes, V_1, V_2 are the limiting values of V, G(V,y) is a spreading function usually expressed as

$$G(V,y) = \frac{h}{\pi} \times \exp\left[-h(V-y)^2\right] \qquad (2)$$

and h is the spreading factor.

The corrected molecular mass M and uncorrected $\bar{M}$ values are related by (KOTAKA 1977; BERGER 1978)

$$\bar{M}^a(V) = \frac{\int_{V_1}^{V_2} M^a(y) \times W(y) \times G(V,y)\, dy}{F(V)} \qquad (3)$$

where a is the exponent of the Mark-Houwink equation for the viscometric detector and a=1 for a detector measuring the mass average molecular masses (light scattering).

The left-hand sides of Eq (1) and (3) contain experimentally accessible quantities, while the corrected quantities W(y) and M(y) must be obtained by solving these equations. If the so-called calibration dependence is known for the polymer under study (the dependence of spreading on the elution volume, i.e. on molecular mass of the polymer is neglected in the following), the corrected molecular mass values M(y) calculated using the detector data should coincide with those calculated by employing the calibration dependence.

Stimulated by H.Benoit, T.Kotaka (KOTAKA 1977) investigated the relationship between functions log $\bar{M}(V)$ and log M(y). Using a computer, he generated the unspread ("corrected") data of both detectors assuming a logarithmicnormal distribution and linear calibration dependence. Spreading was simulated by means of Eqs (1) and (3). He showed that the function log $\bar{M}(V)$ was curved and rotated anticlockwise compared with the straight dependence log M(y). This finding was also confirmed experimentally (GALLOT et al. 1972).

These findings are illustrated by Fig.1 which shows results of model calculations described in the following paragraph. One can see that using the calibration dependence (d), a single correct distribution curve (g) is obtained from the corrected chromatogram (a). On the contrary, the spread (uncorrected) (c) chromatogram yields two distribution curves: if the calibration dependence (d) is used in the evaluation, a wider curve (h) is obtained; if, on the other hand, the evaluation is carried out using molecular masses calculated from uncorrected detector

data (curve(e)), the distribution curve (f), is narrower. The Figure also shows corrected functions the calculation of which is described in the following paragraph. These functions involve the corrected chromatogram (c) calculated from curve (b) and values of the function log M (the result of the suggested correction procedure) represented by points near the calibration dependence (d).

The change in the shape of the function log M is due to spreading. Since both the experimental log $\bar{M}(V)$ and the calibration dependence of the column log M(y) are known, it is possible, basically, by comparing both functions, to determine the magnitude of correction, i.e., the spreading factor h. Obviously, this factor is adequately chosen if the correction causes such rotation and regressive deformation of the function log $\bar{M}(V)$ that in an ideal case it coincides with the function log M(y), i.e. with the known calibration dependence of the colum system.

Let us now concentrate on the correction itself. For further procedure, Eq.(3) is suitably written as

$$\bar{M}^a(V)xF(V) = \int_{V_1}^{V_2} M^a(y)xW(y)xG(V,y)\,dy \qquad (4)$$

Let it be denoted in this equation

$$\bar{M}^a(V)xF(V) = \bar{E}_2(V)\ ,\ M^a(y)xW(y) = E_2(y) \qquad (5a)$$

Similarly, in Eq.(1) let it be denoted

$$F(V) = \bar{E}_1(V)\ ,\quad W(y) = E_1(y) \qquad (5b)$$

The system of Eqs (1) and (4) can then read

$$\bar{E}_i(V) = \int_{V_1}^{V_2} E_i(y)xG(V,y)\,dy \qquad (6)$$

For i = 1,2, two equations are obtained, the solution of which makes possible correction of data of both detectors independently, i.e. using experimentally available quantities $\bar{E}_i(V)$ to calculate the corrected values $E_i(y)$. The kernel of both equations is identical; consequently, they may be solved employing any of numerical methods suggested for the solution of Tung's equation (1). For i = 1, we obtain W(y), for i = 2 we obtain W(y) x $M^a(y)$. The ratio of these functions is the required corrected molecular mass (od its power $M^a(y)$).

Let us discuss quantities provided by both detectors. The quantities $E_1(y)$ and $\bar{E}_1(V)$ may have the meaning of the height of the chromatogram, of a mass fraction in the corresponding volume unit (after normalization) or of concentration, because the respective proportionality constant which is easy to determine (GALLOT et al. 1972) in Eq.(6) may be factored out in front of the integration sign and used to reduce the equation. In the further procedure, however, these quantities are suitably regarded as the corrected and uncorrected concentrations respectively.

With the quantities $E_2(y)$ and $\bar{E}_2(V)$ the situation is somewhat more complicated. Viscosity measurements give us directly

the relative viscosity, η_{rel}, as the ratio of the flow times of the eluent and pure solvent, or the specific viscosity $\eta_{sp}=\eta_{rel}-1$. From the definition equations

$$\lim_{c\to 0} \frac{\eta sp}{c} = [\eta] = KxM^a \qquad (7)$$

in which K and a are constants of the Mark-Houwink equation and c is concentration, it is easy to obtain for low concentration

$$\eta_{sp} = KxcxM^a \qquad (c\to 0) \qquad (8)$$

Hence, the product cxM^a proportional to $F(V)x\bar{M}^a(V) = \bar{E}_2(V)$ is identical with η_{sp} but for the proportionality constant, if extrapolation to zero concentration is disregarded. Evaluation of data provided by the viscometric molecular mass detector with extrapolation to infinite dilution by means of the one-point expression (SOLOMON and CIUTA 1962) is dealt with in a forthcoming paper (NETOPILÍK et al. 1982).

Similarly, the equation for light scattering

$$\lim_{\substack{c\to 0\\ \Theta\to 0}} \frac{K'xc}{R_\Theta} = \frac{1}{\bar{M}} \qquad (9)$$

where Θ is the angle of measurement, R_Θ is the Rayleigh ratio and K' is a constant, gives for small angles and low concentrations

$$R_\Theta = K'xcxM \qquad (c\to 0,\ \Theta\to 0) \qquad (10)$$

It can be seen that quantities available directly by experiment and determined both viscometrically and using the scattering cell may be expressed as the product of concentration and molecular mass (raised to power by the exponent a in viscosimetry) and thus employed as the initial functions (left-hand sides of Eq.(4)) in the correction for axial dispersion; Eqs (6) may be solved by using an arbitrary method originally suggested only for correction of the concentration record.

If the correction method requires a normalized chromatogram, both functions must be multiplied by the respective normalization constants prior to its application, and after correction the resulting functions must again be divided by these constants.

Results and Discussion

Model calculations were carried out for two polymers differing in the width of the dis tribution curve. The results of the first calculation are plotted in Fig.1. (The Figure has been described in greater detail in the preceding paragraph) and summarized in Table 1; the results of the second calculation are given in Table 2.

The calculation is based on the gamma distribution, called the Schulz-Zimm distribution function (SCHULZ 1939; ZIMM 1948), referred to below as f(M). From a general relation between the corrected chromatogram and distribution function of the polymer

$$W(y).dy = -f(MxdM \qquad (11)$$

TABLE 1

Molecular mass averages calculated using the correction procedure. Column h contains spreading factor values used in the correction. The value h = 0.35 was used in the simulation of spreading, h =0.273 is the result of the iterative procedure. Indication is given in column M whether the molecular masses were calculated using calibration ("cal") or determined from the respective detector data.

Nr	h	M	$M_n.10^{-4}$	$M_w.10^{-4}$	$M_z.10^{-4}$	M_w/M_n
	Unspread chromatogram					
1		cal	5.000	6.000	7.000	1.200
	Spread chromatogram, h = 0.35					
2		cal	4.671	6.423	8.580	1.375
3		det	5.422	5.998	6.521	1.106
	Corrected chromatogram					
4	0.350	cal	4.907	6.039	7.252	1.231
5	0.350	det	5.064	5.967	6.815	1.178
6	0.273	cal	4.965	5.962	6.998	1.201
7	0.273	det	4.939	5.973	6.962	1.209

TABLE 2

Model calculation for a polymer with wider distribution. Spreading was simulated also using the spreading factor h=0.35; h=0.262 is the result of the iterative procedure. For the meaning of indices cf.Table 1.

Nr	h	M	$M_n.10^{-4}$	$M_w.10^{-4}$	$M_z.10^{-4}$	M_w/M_n
	Calculated corrected					
1		cal	2.000	6.000	10.000	3.000
	Spread chromatogram, h = 0.35					
2		cal	1.872	6.425	12.282	3.431
3		det	2.279	5.999	9.074	2.632
	Corrected chromatogram					
4	0.350	cal	1.956	5.941	10.149	3.037
5	0.350	det	1.967	5.890	9.700	2.994
6	0.262	cal	1.985	5.813	9.633	2.928
7	0.262	det	1.989	5.859	9.984	3.135

we obtain a relation suitable for the construction of a model chromatogram

$$W(y) = \ln 10 \times f(M) \times \frac{1}{M} \times B \qquad (12)$$

where

$$B = \frac{d \log_{10} M}{dy} \qquad (13)$$

is the slope of the calibration dependence

$$\log_{10} M = A + Bxy \qquad (14a)$$

By using these relations, both chromatograms and the corresponding records of the molecular mass detector were generated. The calibration constants chosen in both cases were

$$A = 12.802, \qquad B = -0.1345 \qquad (14b)$$

The corresponding average molecular masses are given in the Tables in the first row.

Spreading was simulated using Eqs (1) and (4). Thus, the product $F(V)x\bar{M}^a(V) = \bar{E}_2(V)$ was calculated directly (with $a = 1$). The spreading factor was $h = 0.35$, integration was performed by using Simpson's rule. The respective average molecular masses calculated by means of the calibration dependence (14) are given in the Tables in the second row (denoted with "cal" in the column "M"). Averages calculated from the detector data are in row 3 (denoted with "det").

The "experimental" data thus calculated were corrected by solving Eqs (6) by means of the method (PIERCE,ARMONAS 1968). First, the correction was carried out using the spreading factor $h = 0.35$, employed before in the simulation of spreading. This corresponds to a situation where, for the given column system, the spreading factor was experimentally determined in advance. The calculated average molecular masses are given in the Tables in rows 4 and 5.

If the spreading factor is not for the given column system, it may be determined using data of both detectors and assuming a know calibration dependence $\log M = f(y)$. It is assumed that for all polymer fractions used in the determination of h this calibration dependence must be satisfied, or in other words, that the polymer must not, e.g., be branched. Obviously, the spreading factor will be determined correctly if the dependence $\log M = f(y)$ calculated from corrected detector data is identified with the calibration dependence of the column determined in advance. In this case the molecular mass averages calculated from calibration and from the detector data do not differ from each other. Hence, the spreading factor may, e.g., be determined by the following procedures:

a) As a criterion, we choose a comparison of the dependence $\log M = f(y)$ calculated from the corrected detector data (index "det") with the experimentally determined calibration dependence (index "cal"). A minimum of the integral

$$\int_{V_1}^{V_2} (\log M(y,h)_{det} - \log M(y)_{cal})^2 \, dy$$

must be sought as a function of the spreading factor h.

b) Another possibility consists in a comparison between the slopes of the calculated and experimental dependences in some appropriately chosen point, e.g., for the elution volume corresponding to the maximum of the chromatogram. In the simplest case of a linear calibration dependence (14a), this procedure is reduced to a search for the zero point of the function $D(h) = B_{det}(h) - B$, where $B_{det}(h)$ is the slope of the calibration dependence calculated from the detector data corrected with the given value h, and B is the slope of the calibration dependence (14a).

c) Another possibility consists in a search for the zero point of the expression

$$1 - \frac{(M_w/M_n)_{cal}}{(M_w/M_n)_{det}}$$

depending on h. Both brackets contain values calculated from the corrected data; indices determine the mode of evaluation. Instead of $(M_w/M_n)_{cal}$, values determined by an independent measurement can be employed, thus determining simultaneously calibration and the spreading factor.

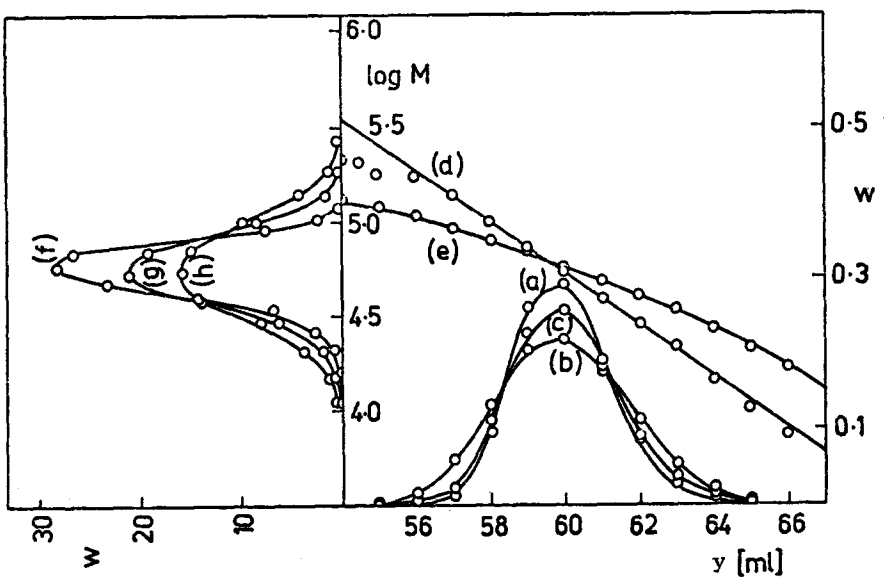

Fig.1. Results of the first calculation (cf.Table 1). Below to the right is the calculated corrected "unspread" chromatogram (a), spread ("experimental") chromatogram (b) corrected "experimental" chromatogram (c). The straight line (d) is the calibration dependence of the column, curve (e) is the dependence log $\bar{M}(V)$ calculated using Eq.(3). Points in the surroundings of straight line (d) are corrected values of the function log M. To the left are the distribution functions: the initial distribution (g), wider distribution (h), distribution calculated from experimental data by means of calibration (d) and narrower experimental distribution (f) calculated only using "detector data". Corrected dependences are a result of the iterative procedure (h=0.273).

Both the chromatograms and distribution functions have been normalized; hence, the coordinate w corresponds to the probability density of the occurrence of the polymer molecule.

In this study, model calculations were carried out with a search for the zero point of the function $D(h) = B_{det}(h) - B$. The spreading factor was determined by the regula falsi method using the expression

$$h_{k+1} = h_k - D_k x \quad \frac{h_{k-1} - h_k}{D_{k-1} - D_k} \qquad (15)$$

where k is the number of iteration. The resulting spreading factors for both model calculations are given in Tables 1 and 2. The model calculation demonstrates the possibility of data correction of both GPC detectors for axial dispersion by employing the same method. If the calibration dependence of the column is known, the iterative procedure allows us to determine the spreading factor value determined in model calculations differed somewhat from used in the simulation of spreading due to the approximative character of the calculation.

In the calculation for a polymer with narrow distribution ($M_w/M_n = 1.2$), the molecular mass averages calculated from data corrected by the iterative procedure agree well with values originally introduced into the procedure. If, on the other hand, the data were corrected by using the spreading factor employed before in the simulation of spreading, the agreement between the calculated molecular mass averages and the original ones was poorer.

For a polymer with a wider distribution curve ($M_w/M_n = 3.0$), the iterative procedure gave a value of the spreading factor approximately identical with that in the preceding case. The agreement between the corrected molecular mass averages and the original ones was somewhat poorer than in the preceding case, but still very good for both values of the spreading factor.

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