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SHAPE OF THE CHROMATOGRAPHIC BAND FOR INDIVIDUAL SPECIES AND ITS INFLUENCE ON GEL PERMEATION CHROMATOGRAPHIC RESULTS

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SUMMARY

The determination of the real differential molecular weight distribution requires that the instrumental spreading of the chromatographic band should be taken into account accurately. In other words, the dependence of the instrumental spreading function for an individual substance on the eluent volume should be known under experimental conditions.

Current methods of calculations do not deal with a continuous change in the shape of the chromatographic band for individual species (SCBIS) due to the molecular weight. This may be due to inaccurate differential DMWD results.

The methods of calculating MWD data from GPC involving the continuous change in SCBIS are presented in this work.

In gel permeation chromatography (GPC) the correlation between the raw chromatogram, $f(v)$, and the chromatogram after correction for instrumental spreading, $w(y)$, is given by the integral eqn. 1 which was first suggested by TUNG[1].

$$f(v) = \int_{-\infty}^{\infty} w(y)\, G(v-y)\,dy \qquad (1)$$

v and y are interchangeable and are used to indicate the eluent volume; y is used mainly to indicate the eluent volume as a variable under the integral sign. $G(v-y)$ is a function which determines all types of instrumental spreading.

The real chromatogram represents a superposition of the resulting curves of a finite number of the individual species. It is assumed for the simplicity of calculations that the chromatogram of the individual species is described by a Gaussian function[2]. However, the discrepancy between the average molecular weights calculated upon that assumption and obtained by independent methods indicates the necessity of accounting for the deviation of shape of the chromatographic band for individual species (SCBIS) from the Gaussian curve[3-5].

PROVDER AND ROSEN[4] suggest the following expression to describe the SCBIS:

$$G(v-y) = \Phi(v-y) + \sum_{n=3}^{\infty} (-1)^n \frac{A_n}{n!} \frac{\Phi^{(n)}(v-y)}{(\sqrt{2h})^n} \tag{2}$$

where the first member $\Phi(v-y) = (h/\pi)^{1/2} \exp[-h(v-y)^2]$ is a Gaussian function and the second member takes into account the correction on symmetric and asymmetric deviation from Gaussian shape.

Three parameters (h, A_3 and A_4) have been used which can be determined with calibration standards with three known molecular weight distribution (MWD) characteristics, *e.g.*, M_n, M_w, M_η (M_n is number-average, M_w is weight-average and M_η is viscosity-average molecular weight). Using the experimentally obtained dependences of h, A_3 and A_4 on eluent volume, and the refined HAMIELEC formulas[6], one can obtain average molecular weight for any other polymer sample under the given conditions (*viz.* columns, temperature, solvent, etc.).

It should be noted that this method gives good results for M_n and M_w but does not guarantee the correct values for M_z, M_{z+1} nor the distribution function. This may be due to the fact that linear calibration was assumed as well as the fact that continuous SCBIS change is not taken into account in the range of interest.

In this paper we tried to take into account the continuous change of SCBIS. The following expression is assumed:

$$G(v,y) = \frac{1 + \sum_{i=0}^{\infty} a_i(y)\,(v-y)^i}{1 + \sum_{i=0}^{\infty} a_{2i}(y) \frac{(2i-1)!!}{(2h)^i}} \Phi(v-y) \tag{3}$$

where $\Phi(v-y) = (h/\pi)^{1/2} \exp[-h(v-y)^2]$, y is eluent volume corresponding to maximum on the chromatogram of individual species, v is the chromatogram abscissa, expressed in the eluent volume and $a_i(y)$ is a function characterising the change in SCBIS with the molecular weight of individual species. The expression (3) contains members which depend only on y, that permit variation of the effective half-width and deviation from Gaussian shape according to the experimental conditions.

With eqn. 3 it is possible to obtain an analytical expression of the dependence of SCBIS on eluent volume. It should be noted that the expression is normalised at any fixed y.

Thus, to find MWD it is necessary to determine h and $a_i(y)$, using the set of well-characterised narrow polymer fractions, *i.e.* to carry out the SCBIS calibration under the given experimental conditions.

The SCBIS calibration proceeds in two stages:

(1) By any method described in refs. 3, 5, 7–9, the resolution factor h is obtained for any standard. For further calculation h is taken as constant and equal to the arithmetic mean.

(2) Assuming that in the range of narrow polymer fractions which are used as standards, $a_i(y)$ is constant, $a_i(y)$ can be determined for every standard.

Therefore, formulas from HAMIELEC AND RAY expressions for average molecular weights should be used[10]:

$$M_k(t) = M_k(\infty)\frac{\left(1 + \sum_{i=1}^{i_0} a_i(-1)^i \frac{d^{(i)}}{ds^i}\right) e^{s^2/4h}\Big|_{s=(k-2)D_2}}{\left(1 + \sum_{i=1}^{i_0} a_i(-1)^i \frac{d^{(i)}}{ds^i}\right) e^{s^2/4h}\Big|_{s=(k-1)D_2}} \tag{4}$$

where $M_k(t)$ are average molecular weights, ($k = 1$) corresponds to M_n($k = 2$ to M_w, etc.), and

$$M_k(\infty) = D_1 \frac{\int_{-\infty}^{\infty} f(v)e^{(1-k)D_2 v}\cdot dv}{\int_{-\infty}^{\infty} f(v)e^{(2-k)D_2 v}\cdot dv} \tag{5}$$

D_1 and D_2 are parameters of calibration curve

$$M = D_1 e^{-D_2 v}.$$

i_0 is the number of known average molecular weights (it determines the number of terms in eqn. 3).

Having solved the system (4) with respect to a_i ($i = 1, 2, \ldots m$) for all of the available standards, we obtain the dependence of a_i on eluent volume. This dependence may be approximated for convenience by polynomials of k_0 degree.
Thus,

$$a_i(y) = \sum_{k=0}^{k_0} a_{i,k} y^k. \tag{6}$$

After calibrating SCBIS we may introduce the correction for the instrumental spreading of the polymer chromatogram of any unknown distribution. Thus, we solve eqn. 7, which represents by itself eqn. 1, accounting for eqns. 3 and 6.

$$f(v) = \int_{-\infty}^{\infty} w(y)\frac{1 + \sum_{i=1}^{i_0}\sum_{k=0}^{k_0} a_{i,k} y^k (v-y)^i}{1 + \sum_{i=1}^{I}\sum_{k=0}^{k_0} a_{2i,k} y^k \frac{(2i-1)!!}{(2h)^i}} \Phi(v-y)dy \tag{7}$$

where

$$I = \begin{cases} i_0/2, & \text{if } i_0 \text{ is even} \\ (i_0-1)/2, & \text{if } i_0 \text{ is odd.} \end{cases}$$

The solution of eqn. 7 may be realised by the following scheme: Let us denote

$$H(y) = \frac{w(y)}{1 + \sum_{i=1}^{I}\sum_{k=0}^{k_0} a_{2i,k} y^k \frac{(2i-1)!!}{(2h)^i}}.$$

Represented in eqn 7

$$\Phi(v-y) = (h/\pi)^{1/2} \sum_{m=0}^{m_0} \frac{(-h)^m}{m!} (v-y)^{2m}$$

and regrouping the members we obtain eqn. 8.

$$f(v) = \sum_{j=0}^{2m_0+i_0} v^j \sum_{m=\alpha}^{m_0} \sum_{i=\beta}^{i_0} \sum_{k=0}^{k_0} \sqrt{\frac{h}{\pi}}\, a_{ik} \frac{(-h)^m}{m!} \frac{(2m+i)!(-1)^{2m+i-j}}{j!(2m+i-j)!} \int_{-\infty}^{\infty} y^{2m+i+k-j} H(y)\mathrm{d}y \qquad (8)$$

where

$$\alpha = \begin{cases} \max.\left(0, \dfrac{j-i_0}{2}\right), & \text{if } j-i_0 \text{ is even} \\ \max.\left(0, \dfrac{j-i_0-1}{2}\right), & \text{if } j-i_0 \text{ is odd,} \end{cases}$$

and

$$\beta = \max.(0, j-2m), \qquad \begin{aligned} a_{00} &= 1, \\ a_{0k} &= 0 \text{ for } k = 1, 2, \ldots k_0. \end{aligned}$$

It should be noted that the right hand part of eqn. 8 is the expansion of $f(v)$ of v degrees. Let $f(v)$ be $\sum_{j=0}^{2m_0+i_0} C_j v^j$, and equating coefficients of the same power, we obtain the system of linear algebraic eqn. 9 for the determination:

$$\int_{-\infty}^{\infty} y^n H(y)\mathrm{d}y;$$

$$C_j = \sum_{n=0}^{2m_0+i_0+k_0-j} \sum_{m=\gamma_1}^{\gamma_2} \sum_{i=\eta_1}^{\eta_2} a_{i,\,n+j-2m-i} (h/\pi)^{1/2} \frac{h^m}{m!} \frac{(2m+i)!(-1)^{m+i-j}}{j!(2m+i-j)!} \int_{-\infty}^{\infty} y^n H(y)\mathrm{d}y \qquad (9)$$

where

$$\gamma_1 = \begin{cases} \max.\left(\alpha, \dfrac{n+j-i_0-k_0}{2}\right), & \text{if } n+j-i_0-k_0 \text{ is even,} \\ \max.\left(\alpha, \dfrac{n+j-i_0-k_0-1}{2}\right), & \text{if } n+j-i_0-k_0 \text{ is odd,} \end{cases}$$

$$\gamma_2 = \begin{cases} \min.\left(m_0, \dfrac{n+j}{2}\right), & \text{if } n+j \text{ is even,} \\ \min.\left(m_0, \dfrac{n+j-1}{2}\right), & \text{if } n+j \text{ is odd;} \end{cases}$$

$$\eta_1 = \max.(\beta, n+j-2m-k_0),$$

$$\eta_2 = \min.(i_0, n+j-2m).$$

In eqn. 9 the coefficients at integrals sufficiently decrease with increasing n. It allow one to neglect the integrals with $n > 2m_0 + i_0$.

Thus, we have the system of equations,

$$\int_{-\infty}^{\infty} H(y)y^n dy = A_n, \qquad n = 0, 1, 2 \ldots, 2m_0 + i_0 \tag{10}$$

representing $H(y)$ in the range of Sin

$$H(y) = \sum_{j=1}^{j_0} b_j \operatorname{Sin}\left[j \frac{\pi}{y_k - y_0}(y - y_0)\right] \tag{11}$$

where y_0 and y_k are the beginning and termination of the carrier $w(y)$, respectively.

Substituting (11) into (10) and integrating, we obtain the following system of equations for determining b_j:

$$A_n = \sum_{j=1}^{j_0} b_j \sum_{m=0}^{n} y_0^{n-m} \frac{(y_k - y_0)}{\pi m} \frac{n!}{m!(n-m)!} \times$$

$$\left[\sum_{k=0}^{m} \frac{m!}{(m-k)!} \frac{\pi^{m-k}}{j^{k+1}} \operatorname{Cos}\left(j + \frac{i}{2}k\right)\pi - \frac{m!}{j^{m+1}} \operatorname{Cos}\frac{\pi m}{2}\right] \qquad n = 0, 1, 2, \ldots, j. \tag{12}$$

Now, we solve that system for b_j:

$$w(y) = \left(1 + \sum_{i=1}^{I} \sum_{k=0}^{k_0} a_{2i,k} y^k \frac{(2i-1)!!}{(2h)^i}\right) \sum_{j=1}^{j_0} b_j \operatorname{Sin}\left(j\pi \frac{y - y_0}{y_k - y_0}\right) \tag{13}$$

For the linear calibration ($v = c_1 + c_2 \ln M$) an analytical solution of TUNG's equation can be obtained, taking into account the dependence of SCBIS on molecular weight. For this purpose, the following expression for SCBIS can be employed:

$$G(v,y) = \Phi(v - y) + \sum_{i=3}^{\infty} a_i(y)\Phi^{(i)}(v - y) \tag{14}$$

where $\Phi(v - y) = \sqrt{h/\pi} \exp\left[-h(v - y)^2\right]$, $\Phi^{(i)}(v)$ is the i-th derivative of $\Phi(v)$; $a_i(y)$ and h have the same meaning as in eqn. 3.

The calibration of SCBIS is carried out according to the scheme suggested above. Only eqn. 4 is replaced by the following equation:

$$\frac{M_k(t)}{M_k(\infty)} = \frac{1 + \sum_{i=3}^{\infty} a_i (k-2)^i D_2^i}{1 + \sum_{i=3}^{\infty} a_i (k-1)^i D_2^i} \exp\left[(3 - 2k)\frac{D_2^2}{4h}\right] \tag{15}$$

To make the calculations easier, let us represent $a_i(y)$ in the form of a cubic polynomial

$$a_i(y) = \sum_{k=0}^{3} a_{ik} y^k \tag{16}$$

By substituting eqns. 14 and 16 into TUNG's equation, we obtain:

$$f(v) = \int_{-\infty}^{\infty} w(y)\Phi(v-y)dy + \sum_{i=3}^{i_0}\sum_{k=0}^{3} a_{ik}\int_{-\infty}^{\infty} y^k w(y)\Phi^{(i)}(v-y)dy. \quad (17)$$

(i_0 is the number of known molecular weight averages of the samples used in the calibration of SCBIS plus three).

To solve the above equation we shall use the two-sided Laplace transformation, as suggested by HAMIELEC AND RAY[10].

$$\overline{F}(s) = \overline{w}(s)e^{s^2/4h} + \sum_{i=3}^{i_0}\sum_{k=0}^{3} a_{ik}(-1)^k\overline{w}^{(k)}(s)s^i e^{s^2/4h} \quad (18)$$

or

$$\overline{w}(s) + \sum_{i=3}^{i_0}\sum_{k=0}^{3} a_{ik}(-1)^k\overline{w}^{(k)}(s)s^i = \overline{F}(s)e^{-s^2/4h}, \quad (19)$$

where

$$F(s) = \int_{-\infty}^{\infty} f(v)e^{-sv}dv; \qquad w(s) = \int_{-\infty}^{\infty} w(v)e^{-sv}dv.$$

Here, $\overline{w}^{(k)}(s)$ is the k-th derivative of $\overline{w}(s)$; s is, generally speaking, a complex variable, but from the standpoint of using the formulae obtained we can limit ourselves only to real values of s. Since $w(y)$ is unambiguously determined from the moments (Q_k) of DMWD, and

$$Q(k) = \int_{-\infty}^{\infty} w(y)D_1^{k-1}\exp[(1-k)D_2 y]dy \equiv D_1^{k-1}\overline{w}[(k-1)D_2] \quad (20)$$

the problem of determining $w(y)$ is reduced to the solution of the differential eqn. 18.

Let us represent $\overline{F}(s)$ in the form of a series

$$\overline{F}(s) = \sum_{n=0}^{\infty} b_n s^n \quad (21)$$

b_n in eqn. 21 can be determined from the experimental data using the expressior

$$b_n = \frac{(-1)^n}{n!}\int_{-\infty}^{\infty} v^n f(v)dv \quad (22$$

Since $f(v)$ is bounded in $(-\infty, +\infty)$ and is different from zero in the final interva $[a,b]$, it can be shown using eqn. 22 that the series converges uniformly to $\overline{F}(s)$.

The expansion of $e^{-s^2/4h}$ into a polynomial in s has the form

$$e^{-s^2/4h} = \sum_{m=0}^{\infty}\frac{(-1)^m}{m!(4h)^m}s^{2m} \quad (23$$

and converges uniformly to $\exp(-s^2/4h)$.

Thus, the solution to eqn. 19 can be represented as a series

$$\overline{w}(s) = \sum_{j=0}^{\infty} x_j s^j \tag{24}$$

and converges to $\overline{w}(s)$.

Substituting eqns. 21, 23 and 24 into eqn. 19 and equating terms having the same power of s, we obtain

$$x_n = \sum_{m=0}^{\gamma} \frac{(-1)^m}{m!(4h)^m} b_{n-2m} \text{ (for } n = 0, 1, 2)$$

$$x_n + \sum_{j=\alpha}^{n} x_j \sum_{i=\beta_1}^{\beta_2} (-1)^{i+j-n} a_{i,i+j-n} \frac{j!}{(n-i)!} = \sum_{m=0}^{\gamma} \frac{(-1)^m}{m!(4h)^m} b_{n-2m} \tag{25}$$

(for $n = 3, 4$ etc.)

where

$$\alpha = \text{max. } (0, n - i_0);$$

$$\beta_1 = \text{max. } (3, n - j);$$

$$\beta_2 = \text{min. } (i_0, n, n + 3 - j);$$

$$\gamma = \begin{cases} n/2, & \text{if } n \text{ is even,} \\ (n-1)/2, & \text{if } n \text{ is odd,} \end{cases}$$

or

$$x_0 = b_0;$$

$$x_1 = b_1;$$

$$x_2 = b_2 - \frac{1}{4h} b_0;$$

$$x_n = \frac{1}{\left(1 - a_{33} \dfrac{n!}{(n-3)!}\right)} \times$$

$$\left\{ \sum_{m=0}^{\gamma} \frac{(-1)^m b_{n-2m}}{m!(4h)^m} - \sum_{j=\alpha}^{n-1} x_j \sum_{i=\beta_1}^{\beta_2} (-1)^{i+j-n} a_{i,i+j-n} \frac{j!}{(n-i)!} \right\} \text{ (for } n = 3, 4, 5 \text{ etc).} \tag{26}$$

Let us note that for physical reasons $w(y)$ is bounded and different from zero in the final interval $[c,d]$; since $x_n = [(-1)^n/n!] \int_{-\infty}^{\infty} y^n w(y) dy$, the series $\sum_{n=0}^{\infty} x_n s^n$ converges uniformly to $\overline{w}(s)$.

The determination of $w(y)$ is thus reduced to the determination of the coefficients b_i according to expression 22 and to the solution of system (26) with respect to x_n.

In the same way, expressions for average molecular weights (M_k) can also be obtained:

$$M_k = D_1 \frac{\sum_{n=0}^{\infty} x_n (k-1)^n D_2^n}{\sum_{n=0}^{\infty} x_n (k-2)^n D_2^n} \tag{27}$$

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