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Mathematical Methods of Correcting Instrumental Spreading in GPC*

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Summary

Various mathematical approaches to correct instrumental spreading in GPC are summarized. The basic equation describing the spreading correction is identical to that used in X-ray diffraction for correcting its instrumental spreading. In GPC, however, artificial oscillation is easily induced in the solution of the basic equation. This difficulty is partially overcome by data smoothing procedures.

INTRODUCTION

Like any other type of chromatography, the GPC chromatogram of a monomeric compound appears as a curve of finite width as shown in Fig. 1. The position of the peak of the curve depends on the molecular weight of the compound; the area under the curve is proportional to the amount of the compound in the total sample; and the width of the curve depends on various band spreading mechanisms in the GPC instrument, both within and without the columns. For a polydispersed sample such as those normally encountered in high polymers, the chromatogram is a composite of the curves of all its components. The total area under the curve is still proportional to the amount of the entire sample but the height of the curve does not reflect the relative abundance of the components at the corresponding elution volumes, as

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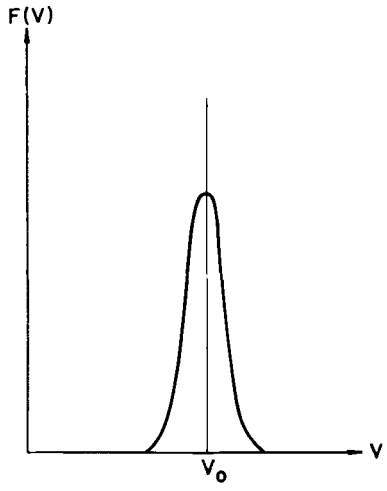

FIG. 1. Chromatogram of a monodisperse sample.

it depends also on the abundance of the neighboring components. At the ends of the chromatograms there are curve portions representing components which do not even exist in the sample. For accurate molecular weight distribution analysis, this overlapping and diffused pat-

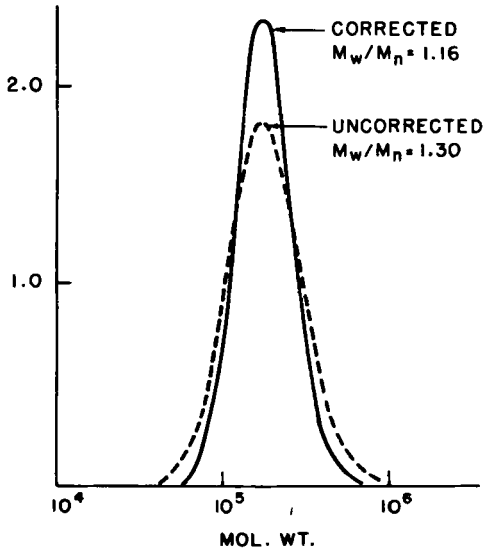

FIG. 2. Comparison of an instrumental spreading corrected distribution with an uncorrected distribution.

tern of the chromatogram must be corrected. Figure 2 shows the difference between a corrected and uncorrected chromatogram.

DERIVATION OF THE CORRECTION EQUATION

Let us assume that for the moment the instrumental spreading function is Gaussian. Thus, the chromatogram of a monomeric compound has the shape of a Gaussian curve. Let $f(v)$ denote the chromatogram as a function of the elution volume (or count) v. For a monomeric compound then

$$f(v) = A(h/\sqrt{\pi}) \exp [-h^2(v - v_0)^2] \quad (1)$$

where v_0 is the elution volume at the peak, h is a parameter related to the width of the Gaussian curve, and A is the total area under the curve. For a multicomponent system

$$f(v) = \sum_i A_i(h_i/\sqrt{\pi}) \exp [-h_i^2(v - v_{0i})^2] \quad (2)$$

The area A_i under the Gaussian curve is proportional to the amount of that component in the sample. Thus, when the number of components in the sample becomes very large we may replace A_i with a continuous function $w(y)$ that has a value at elution volume y proportional to the amount of the component with its peak at y. Equation (2) becomes now

$$f(v) = \int w(y)(h/\sqrt{\pi}) \exp [-h^2(v - y)^2]\, dy \quad (3)$$

The function $w(y)$ is the chromatogram free from the effect of instrumental spreading and therefore the unknown to be solved. If we let $g(v\text{-}y)$ denote the instrumental spreading function in general then

$$f(v) = \int w(y)g(v - y)\, dy \quad (4)$$

Equation (4) has the form of a convolution integral equation and is the same equation that describes the instrumental spreading correction in X-ray diffraction.

METHODS OF SOLUTION

There are apparently three different approaches used by GPC investigators in solving the above integral equation.

1. Solution by Minimization

Aside from the method of steepest descent in the function space used by Chang and Huang (*1*), other methods of minimization as

reported by Hess and Kratz (*2*), by Smith (*3*), by Pickett et al. (*4*), and by the author (*5*) all involved the approximation of eq. (4) by a set of linear algebraic equations in the following form.

$$f(v_j) = \sum_i^n w(y_i)g_j(v_j - y_i)(\Delta y)_i \tag{5}$$

Equation (5) is for the jth equation. For each point on the chromatogram an equation like Eq. (5) can be written. The unknown w function is now represented by n unknown points $w(y_i)$ spaced in suitable intervals $(\Delta y)_i$ apart. The products $g_j(v_j\text{-}y_i)\,(\Delta y)_i$ are known and they are the coefficients for the unknowns $w(y_i)$. The unknowns can be solved by methods of minimization if we read from the chromatogram a total number of points larger than n.

Solution by way of linear algebraic equations has the flexibility of using any form for the g-function. The g-function can be made to vary with elution volume v. These methods, however, generally require large computer storage spaces and often long computation time. The computation for the method of Chang and Huang (*1*) was reported to be fast.

2. Solution by Fourier Transform

This is the approach used by Stokes (*6*) for the case of X-ray diffraction. Pierce and Armonas (*7*) have published an attractive simplification of this approach for GPC. The author (*8*) has also adopted Stoke's method to GPC problems.

The Fourier transforms for the three functions involved in Eq. (4) are:

$$F(k) = (1/\sqrt{2\pi}) \int_{-\infty}^{\infty} f(v)e^{ikv}\,dv \tag{6}$$

$$G(k) = (1/\sqrt{2\pi}) \int_{-\infty}^{\infty} g(v)e^{ikv}\,dv \tag{7}$$

$$W(k) = (1/\sqrt{2\pi}) \int_{-\infty}^{\infty} w(v)e^{ikv}\,dv \tag{8}$$

The limits of integration in Eq. (4) can be extended to $+\infty$ and $-\infty$ even though both $f(v)$ and $w(y)$ have values of zero beyond the ends of the chromatogram. Then according to the Faltung theorem

$$W(k) = (1/\sqrt{2\pi})[F(k)/G(k)] \tag{9}$$

Since $F(k)$ and $G(k)$ can be computed from the given functions,

$W(k)$ is now known. By the following inverse transform we may obtain the corrected chromatogram $w(v)$.

$$w(v) = (1/\sqrt{2\pi}) \int_{-\infty}^{\infty} W(k)e^{-ivk}\, dk \tag{10}$$

The equations involved in this approach imply that a constant g-function with respect to v is required. But this inflexibility can be circumvented by treating the chromatogram one section at a time using the proper g-function for each section.

3. Solution through Polynomial Representation of the Chromatogram

Three published methods used this approach, one by Aldhouse and Stanford (*9*) and two by the author (*5, 8*).

In general, the functions $f(v)$ and $w(y)$ for the chromatograms can be represented by polynomials. If the product of $w(y)$ and $g(v\text{-}y)$ is integrable, then by a comparison of the coefficients of $f(v)$ with those of the polynomial after integration, the coefficients for $w(y)$ may be solved. A convenient polynomial to use is

$$f(v) = \exp\left[-q^2(v - v_0)^2\right] \sum_{i=0}^{n} U_i(v - v_0)^i \tag{11}$$

where q, v_0, and U_i are adjustable parameters and coefficients. Because of the exponential factor, the right-hand side of Eq. (11) ap-

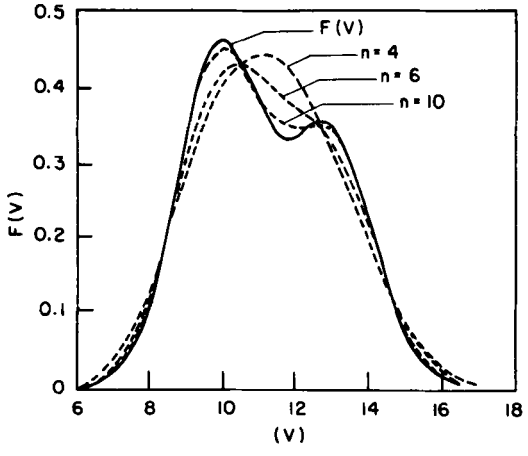

FIG. 3. Fitting of a two-peak distribution by polynomials.

proaches zero when v approaches $+\infty$ and $-\infty$. The fit of Eq. (11) to a chromatogram is not difficult. Figure 3 shows the fit to a complex chromatogram. When n in Eq. (11) is 16, the curve calculated is indistinguishable from the given chromatogram.

In the polynomial approach the form of the g-function is more restrictive. The Gaussian function works well. Some asymmetrical g-function may also be used but it must be integrable when combined with $w(y)$.

Our current correction method uses a fourth-degree polynomial to correlate nine points on the chromatogram at a time. The g-function used is Gaussian. The procedure is repeated with every point on the chromatogram as the center point of the nine-point fit. In this way the h parameter in the Gaussian g-function may be varied with the elution volume. The calculation on a computer for this scheme is extremely fast and uses a relatively small amount of storage spaces.

The methods discussed so far all require high speed digital computers to execute the calculation. Frank, Ward, and Williams (*10*), however, have described a simple method, the calculation for which may be managed by a desk calculator. From the chromatogram they separated one or several Gaussian curves, depending on the number of peaks in the chromatogram. The residual smooth function was left uncorrected. The Gaussian peaks were narrowed by subtracting from them the instrumental spreading which was assumed to be also Gaussian. A similar approach has been used in our laboratory and proved to be very useful for the chromatograms of extremely narrow distribution samples. For these narrow distribution chromatograms the more complex method could be difficult to use because of the problem of oscillation.

THE PROBLEM OF OSCILLATION

Duerksen and Hamielec (*11*) have made a comparison of some of the above-mentioned methods. In all methods examined by them some degree of oscillation induced by the computation was suspected. Figure 4 shows a chromatogram $f(v)$ calculated from a known $w(y)$ function when the instrumental spreading g is relatively broad with respect to w. It can be seen that a small variation in the slope of $f(v)$ will bring about a considerable larger variation in the slope of $w(y)$. This sensitivity of $w(y)$ varies with the breadth of the g-function or the extent of correction. In the limiting case where there is no correction or $g = 1$,

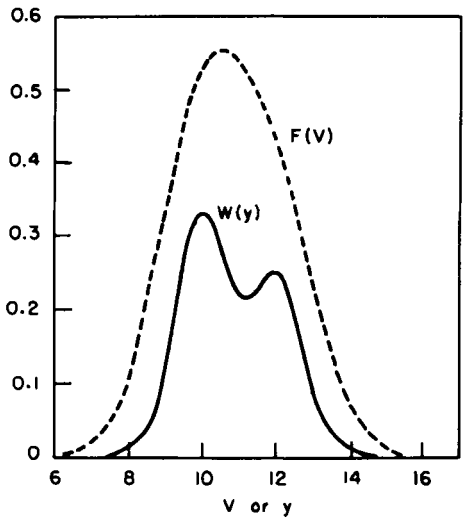

FIG. 4. Relation between corrected chromatogram $W(y)$ and uncorrected chromatogram $F(v)$ when the instrumental correction is large.

$w(y)$ becomes identical to $f(v)$. In any other cases variation of the slope for $f(v)$ is always less than that for $w(y)$. If in experiments $f(v)$ can be determined to a high degree of precision and if the g-function used describes the spreading characteristics extremely accurately, then the solution for $w(y)$ can be obtained with a high degree of confidence regardless of the method used. In reality neither of the conditions can be fulfilled and as a result the uncertainties in $f(v)$ and in $g(v\text{-}y)$ are easily transformed into oscillations in $w(y)$. This problem is more severe when the correction is large or when the sample contains very narrow peaks. It is also more pronounced at the ends of a chromatogram where the $f(v)$ function is even less precisely known. To minimize the fluctuations in the raw data, mathematical correlations are used to smooth out $f(v)$ before calculation. In fact, in many of the above-mentioned methods such a data-smoothing procedure is implicitly or explicitly carried out in the computer program for the method. Whether one method of solution is better than another depends often more on this smoothing procedure than the mathematics involved. If smoothing is too drastically done, then some of the true features of $w(y)$ may be lost; if not enough is accomplished, then oscillations may show up in the solution. It is not unusual that a smoothing procedure is found to be sufficient for one chromatogram but

totally inadequate for another. Such a fact is perhaps the reason why in so short a time so many solutions were proposed for this one problem. No one is apparently completely satisfied with the correction method which he has on hand.

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