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Note

A simplified numerical method for correction of polydispersities from gel permeation chromatography

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The problem of instrumental spreading in gel permeation chromatography has been considered in detail in recent years (*e.g.*, ref. 1).

The mathematical expression relating the experimental chromatogram f(v), the true chromatogram w(y) and the function g(v,y) describing the instrumental spreading can be represented by the following equation[2]:

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

where v and y both represent elution volume.

In this discussion we shall assume that g(v,y) is a simple Gaussian distribution:

$$g(v,y) = \frac{h}{\sqrt{\pi}} \exp\left[-h^2 (v-y)^2\right] \tag{2}$$

where h is a parameter describing the width of the spreading. The calibration of instrumental spreading is reduced to the determination of the parameter h in eqn. 2, which can be accomplished by means of the reversed-flow technique[3].

In the theory of integral equations, eqn. 1 is called a "Fredholm equation of the first kind," and its solution can be obtained by expanding the functions that appear in it into Fourier series[4].

It is known that a system of Hermite polynomials, $H_n(t)$, is complete and orthonormal with $\exp(-t^2)$ in $(-\infty, \infty)$. From the physical sense of the function w(y), it follows that

$$\int_{-\infty}^{\infty} y \exp(-y^2)\, w^2(y)\, dy < \infty \tag{3}$$

Therefore, the Fourier series of the function w(y)

$$w(y) = \sum_{n=0}^{\infty} w_n H_n(y) \qquad y \in (-\infty,\infty) \tag{4}$$

where

$$w_n = \frac{1}{2^n n! \sqrt{\pi}} \int_{-\infty}^{\infty} w(y) \exp(-y^2)\, H_n(y)\, dy \tag{5}$$

converges to it in $L_2(-\infty, \infty)$.

Substituting eqns. 2 and 4 into eqn. 1, we obtain

$$f(v) = \sum_{n=0}^{\infty} w_n \frac{h}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp[-h^2(v-y)^2] H_n(y)\, dy \tag{6}$$

Let

$$b_n(v) = \int_{-\infty}^{\infty} \exp[-h^2(v-y)^2] H_n(y)\, dy \tag{7}$$

then eqn. 6 can be rewritten in the form

$$f(v) = \frac{h}{\sqrt{\pi}} \sum_{n=0}^{\infty} w_n b_n(v) \tag{8}$$

It can be shown that the solution of eqn. 1 is unique[5]. The function f(v) is given in tabular form (experimental points) $\{f(v_i), (v_i); i = 0,1,2,3,\ldots, N\}$.

For any point, it is possible to calculate $b_n(v_i)$.

In numerical calculations, the infinite series in eqns. 4 and 8 are replaced by finite partial sums. Thus, eqn. 8 can be rewritten as follows:

$$f(v_i) = \frac{h}{\sqrt{\pi}} \sum_{n=0}^{N} w_n b_n(v_i); \qquad i = 0, 1, 2, \ldots, N \tag{9}$$

If $\det|b_n(v_i)| \neq 0$, then it is possible to determine the coefficients w_n by solving eqn. 9 and consequently the function w(y), given by eqn. 4.

To test the method proposed in this paper, we have performed numerical calculations. There remains the pure mathematical problem of proving how far the inversion used affects the obtained form of w(y).

For this purpose, we accepted the function[6]

$$w(y) = \frac{0.325}{\sqrt{\pi}} \{0.6 \exp[-(0.325)^2 (y-25)^2] + 0.4 \exp[-(0.325)^2 (y-31)^2] \tag{10}$$

with the same parameters as in Tung's paper[6]. In the Gaussian function g(v,y), we accepted the constant value of $h = 0.4$. Using these functions, we evaluated numerically the function f(v). Next, we chose 25 "theoretical" values for $f(v_i)$, $i = 0,1,2,\ldots, 24$. Using these values, we reproduced the function w(y) according to the method described above.

Fig. 1 shows the results of our calculations. The solid line represents the function w(y) from eqn. 10 and the dashed line the reproduced function w(y). It can be concluded that the numerical method used reproduced the form of the function w(y) well.

The method of calculation is very simple and fast, and has been reduced to the following operations:

(1) computation of the $(N+1)$ integrals (eqn. 7);
(2) solution of the linear system (eqn. 9);
(3) calculation of the sum in eqn. 4.

It should be stressed that in the above calculations all of the integrals from eqn. 7 can be fully evaluated analytically.

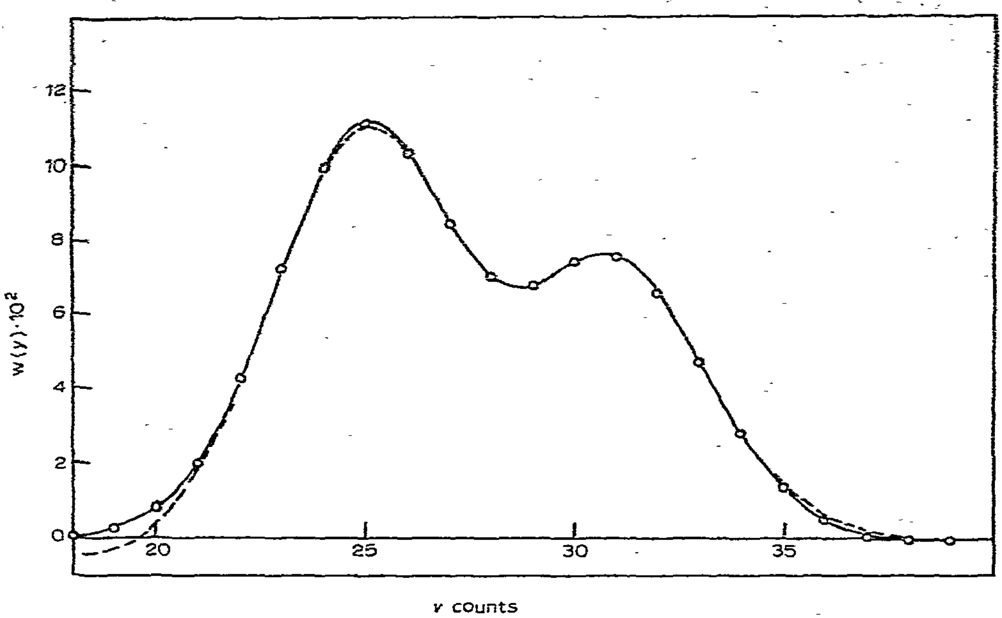

Fig. 1. Relationship between assumed chromatogram w(y) (solid line) and reproduced chromatogram (dashed line).

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