SIMPLE AND EFFICIENT METHOD OF ZONE SPREADING CORRECTION IN GEL PERMEATION CHROMATOGRAPHY

S. VOZKA and M. KUBÍN

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6 (Czechoslovakia)

SUMMARY

A method of zone spreading correction in gel permeation chromatography is described that is applicable in the case of a Gaussian-type spreading function. Instead of the integral Tung equation, an equivalent partial differential equation is solved numerically and in this way the necessary calculations are considerably simplified. The method is applied to artificial and real chromatograms and the results are compared with those of some known correction procedures.

INTRODUCTION

The imperfect resolving power of real chromatographic columns, due to zone spreading, distorts the results of gel permeation chromatographic (GPC) analyses of polymers. In order to obtain accurate data on molecular weight distributions and on molecular weight averages, it is therefore imperative to use special correction procedures that partly or completely eliminate the influence of the dispersion in the column.

From the mathematical point of view, the zone spreading correction requires an integral (Tung) equation to be solved by a suitable numerical method. In the literature one can find many different procedures[1-9], but most of them require, with only minor exceptions[10,11], fast computers with large storage space. In this paper, a zone spreading correction procedure is proposed that is very simple and fast, such that the necessary calculations can be carried out, if need be, even with a simple desk calculator.

The procedure is based on the assumption that the spreading function in the Tung equation is Gaussian, a condition which is usually well fulfilled with the highly efficient columns used in modern GPC instruments.

THEORETICAL

The relationship between the original, normalized chromatogram, $f(x)$, and the chromatogram corrected for zone spreading, $w(x)$, is described by the Tung integral equation

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

where x is the elution volume. Its kernel, $K(x,y)$, is usually called the spreading function and represents the elution curve of a monodisperse polymer with a molecular weight corresponding to the elution volume y. In the following discussion we limit ourselves to the case of a Gaussian spreading function, which we shall write as

$$K(x,y) = \sqrt{(h/\pi)} \exp[-h(x-y)^2] \tag{2}$$

The spreading factor, h, is inversely proportional to the extent of sample spreading in a given column.

Firstly, we shall show that under these conditions the integral eqn. 1 represents a solution of a boundary value problem analogous to a certain problem of free diffusion. This equivalent boundary value problem can be stated as follows: Solve

$$D \cdot \frac{\partial^2 f(x,t)}{\partial x^2} = \frac{\partial f(x,t)}{\partial t} \tag{3}$$

subject to the boundary conditions

$$f(x, 0) \quad = w(x) \tag{4}$$

$$f(\infty, t) \quad = 0 \tag{5}$$

$$f(-\infty, t) = 0 \tag{6}$$

[This problem can be given the following physical interpretation: if the concentration of a compound in a one-dimensional space (space coordinate x) has initially the shape $w(x)$, find how the shape has changed by free diffusion proceeding for a time t_d, if the diffusion coefficient, assumed to be constant, is D.]

The solution of this boundary value problem[12] is of the form

$$f(x,t_d) = \frac{1}{2\sqrt{\pi\,Dt_d}} \int_{-\infty}^{\infty} \exp\left[-\frac{(x-y)^2}{4D\,t_d}\right] w(y)\,\mathrm{d}y \tag{7}$$

which is the same as that of the Tung integral eqn. 1 with the kernel given by eqn. 2, provided that we put

$$D\,t_d = 1/4h \tag{8}$$

It follows that the calculation of the corrected chromatogram can be reduced to the determination of the boundary condition $w(x)$ in the problem given by eqns. 3–6, where the function $f(x,t_d)$ is known [it is identical with the actual, uncorrected chromatogram $f(x)$] and the quantity h can be obtained in advance by calibrating the column with a series of narrow fractions, e.g., by the reverse-flow method[13].

In order to obtain the final correction equations in the simplest form, we shall solve this problem by a simple method of finite differences. Its essence rests on using the Taylor expansion to estimate the values of the sought function in points with abscissae that differ by a small increment from those where the values of the func-

tion are known. For the derivatives in the Taylor series we substitute their numerical analogues obtained by approximating the given function by an interpolation polynomial.

This procedure can be repeated in an optional pre-selected number of steps (k), where the function values calculated in step i serve as a basis for a computation of derivatives in step $i + 1$. Starting from the known values of $f(x,t_d)$ (uncorrected chromatogram), we reach the sought function $w(x)$ after k steps. The differential eqn. 3 is instrumental in transforming the derivatives with respect to the coordinate x (only these are experimentally available) into derivatives with respect to t, to be substituted into the Taylor series.

The above principle can be modified in many different ways in order to obtain a more precise solution (e.g., see ref. 14), but all of these procedures require more sophisticated algorithms. In this work we employed only the Taylor series method and a higher precision was obtained by substituting higher-order derivatives.

Taylor expansion of the function $f(x,t)$ in t can be written as

$$f(x,t - \Delta t) = f(x,t) - \Delta t \cdot \frac{\partial f(x,t)}{\partial t} + \frac{\Delta t^2}{2} \cdot \frac{\partial^2 f(x,t)}{\partial t^2} - \frac{\Delta t^3}{6} \cdot \frac{\partial^3 f(x,t)}{\partial t^3} + \cdots \quad (9)$$

assuming that all partial derivatives exist.

Using a notation more suitable for discrete quantities, $i.e.$,

$$f(x_i, t_n) = f_{i,n}, \quad \frac{\partial f(x,t)}{\partial t} \Bigg|_{\substack{x = x_i \\ t = t_n}} = \frac{\partial f_{i,n}}{\partial t} \quad (10)$$

and similarly for higher derivatives, eqn. 9 can be rewritten as

$$f_{i,n-1} = f_{i,n} - \Delta t \cdot \frac{\partial f_{i,n}}{\partial t} + \frac{\Delta t^2}{2} \cdot \frac{\partial^2 f_{i,n}}{\partial t^2} - \frac{\Delta t^3}{6} \cdot \frac{\partial^3 f_{i,n}}{\partial t^3} \cdots \quad (11)$$

It is evident from eqn. 3 that $\partial f_{i,n}/\partial t$ can be directly substituted; further, it holds that

$$D \cdot \frac{\partial^4 f_{i,n}}{\partial x^4} \approx \frac{\partial^3 f_{i,n}}{\partial x^2 \partial t} \quad (12)$$

and also

$$D \cdot \frac{\partial^3 f_{i,n}}{\partial x^2 \partial t} \approx \frac{\partial^2 f_{i,n}}{\partial t^2} \quad (13)$$

so that for the second derivative in t we obtain the relationship

$$D^2 \cdot \frac{\partial^4 f_{i,n}}{\partial x^4} \approx \frac{\partial^2 f_{i,n}}{\partial t^2} \quad (14)$$

Similarly, it holds for the third derivative in t that

$$D^3 \cdot \frac{\partial^6 f_{i,n}}{\partial x^6} \approx \frac{\partial^3 f_{i,n}}{\partial t^3} \quad (15)$$

etc. Substituting now into eqn. 11, we obtain the relationship

$$f_{i,n-1} = f_{i,n} - D\Delta t \cdot \frac{\partial^2 f_{i,n}}{\partial x^2} + \frac{D^2 \Delta t^2}{2} \cdot \frac{\partial^4 f_{i,n}}{\partial x^4} - \frac{D^3 \Delta t^3}{6} \cdot \frac{\partial^6 f_{i,n}}{\partial x^6} + \dots \quad (16)$$

in which we find only derivatives in x and different powers of the product $D\Delta t$. If the calculation is performed in k steps, we can express Δt in terms of t_d:

$$\Delta t = t_d/k \qquad (17)$$

and according to eqn. 8 we obtain for $D\Delta t$

$$D\Delta t = 1/(4kh) \qquad (18)$$

Substituting from eqn. 18 into eqn. 16, we obtain a final equation for calculation of the quantity $f_{i,n-1}$, where all coefficients are numerically accessible. If we now calculate the partial derivatives in x using relationships obtained by approximating the function $f_{i,n}$ by an interpolation polynomial and if we put $r = (4kh\Delta x^2)^{-1}$, we obtain the following equations directly applicable to the calculation of quantities $f_{i,n-1}$:

$$f_{i,n-1} = f_{i,n}(1 + 2r) - r(f_{i-1,n} + f_{i+1,n}) \qquad (19)$$

if the Taylor series is truncated after the term with the first derivative;

$$f_{i,n-1} = f_{i,n}\left(1 + \frac{5}{2}r + 3r^2\right) - \left(f_{i-1,n} + f_{i+1,n}\right)\left(\frac{4}{3}r + 2r^2\right) +$$

$$+ \left(f_{i-2,n} + f_{i+2,n}\right)\left(\frac{1}{12}r + \frac{1}{2}r^2\right) \qquad (20)$$

from the Taylor series with the second derivative; and finally

$$f_{i,n-1} = f_{i,n}\left(1 + \frac{49}{18}r + \frac{14}{3}r^2 + \frac{10}{3}r^3\right) - \left(f_{i-1,n} + f_{i+1,n}\right)\left(\frac{3}{2}r + \frac{13}{4}r^2 + \frac{5}{2}r^3\right) +$$

$$+ \left(f_{i-2,n} + f_{i+2,n}\right)\left(\frac{3}{20}r + r^2 + r^3\right) - \left(f_{i-3,n} + f_{i+3,n}\right)\left(\frac{1}{90}r + \frac{1}{12}r^2 + \frac{1}{6}r^3\right) \qquad (21)$$

for the expansion including the third derivative. In these equations the subscript i corresponds to the values of the elution volume, $i.e.$, to the abscissae of the chromatogram, the subscript n corresponds to the quantity t in such a way that $t = t_d$ for $n = k$ (where k is the chosen number of steps) and $t = 0$ for $n = 0$.

Eqns. 19–21 were derived on the assumption that D in eqn. 3 is constant; this is equivalent ($cf.$, eqn. 8) to the assumption that the spreading factor, h, is independent of the elution volume. It would be possible to solve an equivalent boundary value problem also for the case $D = D(x)$, but the main advantage of the proposed procedure, $viz.$, the simplicity of the final correction equations (eqns. 19–21), would be lost. In correcting the chromatograms where the spreading factor was a function of the

elution volume, we used a procedure common to other known correction methods[4,6,10] varying values of r, calculated from the known relationship $h = h(x)$, were substituted into eqns. 19–21.

EXPERIMENTAL

Chromatograms of poly(methyl methacrylate) and polystyrene were obtained with a Waters Model ALC 100 instrument with four Styragel columns ($5 \cdot 10^6$, $1.5 \cdot 10^5$, $1.5 \cdot 10^4$ and $5 \cdot 10^2$ Å) in series. The flow-rate of solvent (tetrahydrofuran) was 1 ml/min and the detector was a differential refractometer. The calibration graph for polystyrene samples was linear and followed the relationship

$$\log_{10} M = \frac{95.1859 - v}{7.4349} \qquad (22)$$

where v is the elution volume, which throughout this whole paper is expressed in counts (1 count $= 2.40$ ml), and M is the molecular weight. The spreading factor, h, of the Gaussian kernel in the Tung integral equation depended on the elution volume through the second-order polynomial

$$h = -0.93102 + 0.02541 \, v - 0.00007 \, v^2 \qquad (23)$$

RESULTS AND DISCUSSION

In order to verify the efficiency of the proposed correction method, we applied it to artificial chromatograms and also to real chromatograms of poly(methyl methacrylate) and polystyrene. In constructing two artificial chromatograms we used a superposition of two Schulz–Zimm molecular weight distribution functions (chromatogram A) and one Schulz–Zimm distribution function (chromatogram B), in both instances with known molecular weight averages (M_n and M_w). In chromatogram B a very narrow distribution with $M_n = 1.00 \cdot 10^5$ and $M_w = 1.10 \cdot 10^5$ was used; in chromatogram A two narrow Schulz–Zimm molecular weight distributions with parameters $M_n^{(1)} = 4.5 \cdot 10^5$, $M_w^{(1)} = 5.0 \cdot 10^5$, weight fraction $\alpha_1 = 0.6$ and $M_n^{(2)} = 1.35 \cdot 10^6$, $M_w^{(2)} = 1.5 \cdot 10^6$, weight fraction $\alpha_2 = 0.4$ were superimposed, to yield a composite distribution function with

$$M_n = \left[\frac{\alpha_1}{M_n^{(1)}} + \frac{\alpha_2}{M_n^{(2)}} \right]^{-1} = 6.137 \cdot 10^5$$

and

$$M_w = \alpha_2 M_w^{(2)} + \alpha_1 M_w^{(1)} = 9.0 \cdot 10^5$$

From the known course of the initial molecular weight distribution, g(M), a corrected normalized chromatogram $w(v)$ was calculated with the relationship

$$w(v) = -g(M) \cdot M \cdot 2.303 \, (d \log M/dv)$$

The value —0.1345 calculated from the experimental calibration (eqn. 22) was substituted for the derivative in this equation. The uncorrected chromatograms $f(v)$ were then calculated by numerical integration of eqn. 1: in case A a constant spreading factor $h = 0.2$ was used, whereas in case B an elution-volume-dependent h according to eqn. 23 was employed. To adjust the precision of the input data to the precision expected in real chromatograms, the heights of calculated normalized "uncorrected" chromatograms were multiplied by 1000 and rounded off to an even first decimal (which corresponds to a precision of ± 0.2 mm for a chromatogram with a maximum height of about 14 cm).

Preliminary calculations showed that the correction based on the simplest equation (eqn. 19) is inadequate and cannot be used in practice. On the other hand, eqns. 20 and 21 require the numerical calculation of higher derivatives and a low precision in reading the heights of chromatograms (especially at their extreme ends, where the relative error is the highest) can lead to artificial oscillations in the corrected curve. The occurrence of this undesirable effect is minimized if a judiciously selected integral multiple of the true volume count increment, $\Delta v_{calc} = l \Delta v$, with $l = 1,2,3...$, is used in eqns. 20 and 21 instead of Δv itself. The modified equations are then

$$f_{i,n-1} = f_{i,n} \left(1 + \frac{5}{2}r + 3r^2\right) - \left(f_{i-l,n} + f_{i+l,n}\right) \left(\frac{4}{3}r + 2r^2\right) +$$

$$+ \left(f_{i-2l,n} + f_{i+2l,n}\right) \left(\frac{1}{12}r + \frac{1}{2}r^2\right) \qquad (20a)$$

and

$$f_{i,n-1} = f_{i,n} \left(1 + \frac{49}{18}r + \frac{14}{3}r^2 + \frac{10}{3}r^3\right) - \left(f_{i-l,n} + f_{i+l,n}\right) \left(\frac{3}{2}r + \frac{13}{4}r^2 + \frac{5}{2}r^3\right)$$

$$+ \left(f_{i-2l,n} + f_{i+2l,n}\right) \left(\frac{3}{20}r + r^2 + r^3\right) - \left(f_{i-3l,n} + f_{i+3l,n}\right) \left(\frac{1}{90}r + \frac{1}{12}r^2 + \frac{1}{6}r^3\right) \qquad (21a)$$

In view of the lower relative precision in reading the heights at the extreme ends of chromatograms, equations of lower order were used in the actual calculations for abcissae $i = 1$ to $i = 3l$ and $i = N - 3l + 1$ to $i = N$, where N is the total number of experimental points (e.g., in a computer program based on eqn. 21a, eqns. 19 and 20 were used at the extreme ends).

The artificial chromatogram A was used to study the influence of the number of calculating steps (k) and the influence of the quantity Δv_{calc} on the correction efficiency of eqn. 21a. Fig. 1 clearly shows that the correction efficiency increases with the number of iterations (k), although the small improvement in resolution brought about by increasing the number of steps from $k = 5$ to $k = 15$ hardly justifies tripling the computation time.

Even for $k = 1$ (i.e., with a direct, non-iterative application of eqn. 21a) one attains a distinct although by no means perfect resolution of both superimposed peaks.

Fig. 2 shows a significant influence of the diminishing Δv_{calc} on the correction efficiency of eqn. 21a for a constant number of iterations $k = 3$. (However, a further decrease to $\Delta v_{calc} = \Delta v = 0.5$ leads to considerable oscillations of the computed
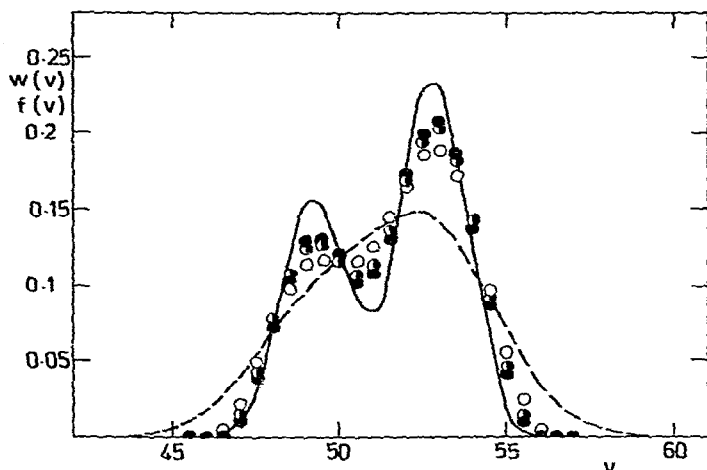
Fig. 1. Influence of the number of iteration steps (k) on the correction efficiency of eqn. 21a applied to artificial chromatogram A. Calculated with $\Delta v_{calc} = 1.5$. Broken line, uncorrected chromatogram $f(v)$; solid line, known course of the corrected chromatogram $w(v)$; $\bigcirc$, $k = 1$; $\circledcirc$, $k = 5$; $\bullet$, $k = 15$.

function w.) It is also evident that even with a moderate number of iterations ($k = 3$), a very good correction efficiency can be achieved. This fact emerges even more clearly from Fig. 3, where the results obtained by applying eqns. 20a and 21a in three iteration steps are compared with a very efficient correction procedure, viz., Method 2 of Ishige et al.[8]. (We have had very useful experience with this algorithm* for some years and accordingly we use it as a standard for comparison purposes.) Fig. 3 also shows a chromatogram corrected according to the method of Pierce and Armonas[10]; this method is comparable with the procedure proposed here in terms of simplicity and rapidity of calculation.
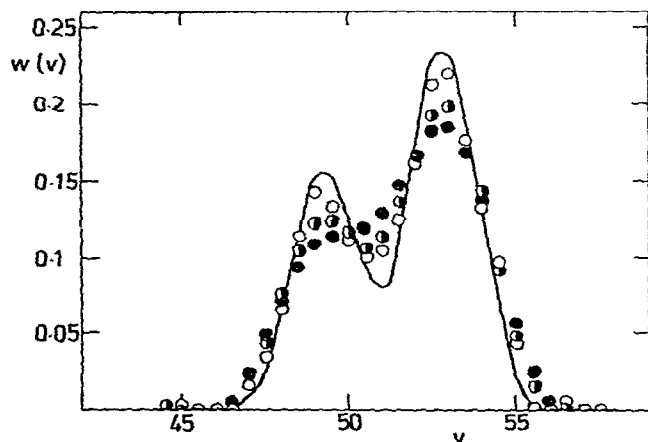

Fig. 2. Influence of the value of Δv_{calc} on the correction efficiency by eqn. 21a applied to the artificial chromatogram A. Calculated with $k = 3$. Curve, original course of $w(v)$; $\bigcirc$, $\Delta v_{calc} = 1$; $\circledcirc$, $\Delta v_{calc} = 1.5$; $\bullet$, $\Delta v_{calc} = 2$.

* The program written in Fortran IV was made available by courtesy of Prof. Hamielec.
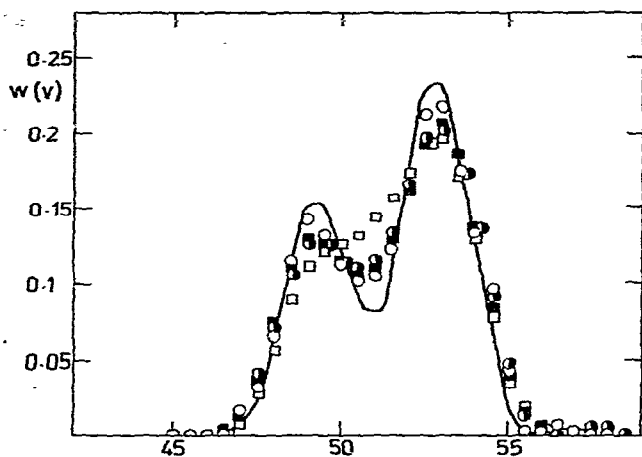
Fig. 3. Comparison of the correction efficiency of different methods applied to the artificial chromatogram A. ○, This work, eqn. 21a, $k = 3$, $\Delta v_{calc} = 1$; ◐, this work, eqn. 20a, $k = 3$, $\Delta v_{calc} = 1$; ■, Ishige et al.[8] (Method 2); □, Pierce and Armonas[10]; curve, original course of $w(v)$.

It follows from the comparison of the curves in Fig. 3 that the efficiency of the simple correction based on the sevenpoint eqn. 21a is comparable with, if not better than, the sophisticated algorithm used by Ishige et al. The correction eqn. 20a also affords good results, whereas the Pierce and Armonas method gives only a slight in-
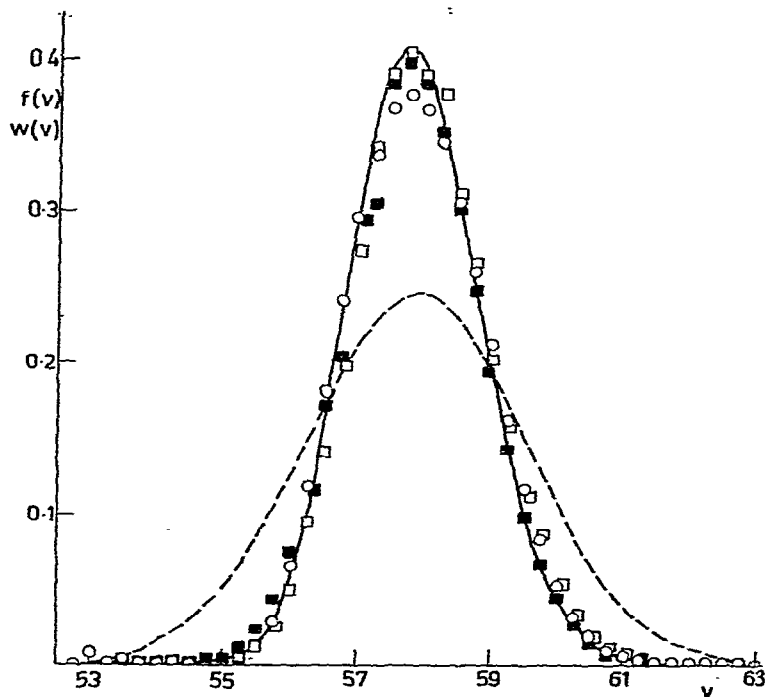

Fig. 4. Corresponding comparison to that in Fig. 3 for the artificial chromatogram B. Notation as in Fig. 3. Broken line, uncorrected chromatogram $f(v)$.

dication of a resolution of both peaks. [In this connection we should mention the interesting finding that our method based on eqns. 20a and 21a works very well with $\Delta v_{calc} = 1$, satisfactorily with $\Delta v_{calc} = 1.5$ and unsatisfactorily with $\Delta v_{calc} = \Delta v = 0.5$, whereas the computer program used by Ishige *et al.* yields good results only in the last instance. With $\Delta v_{calc} = 1$ it iterated very slowly, did not manage to satisfy the prescribed tolerance (0.01) and the final corrected curve closely resembled that obtained by the method of Pierce and Armonas.]

Computer programs for all of the methods were written in Basic and implemented on a Wang 2200 desk-top programmable calculator with 12 kB storage capacity. Net computation times for the correction of chromatogram A in Fig. 3 were: $2\frac{1}{2}$ min. with eqn. 21a, 1 min for the method of Pierce and Armonas, and 83 min for the method of Ishige *et al.*

A corresponding comparison of our method (eqn. 21a) with the procedures of Ishige *et al.* and Pierce and Armonas for the artificial chromatogram B is shown in Fig. 4. In this instance of a unimodal, very narrow molecular weight distribution ($M_n/M_w = 1.1$) all of the methods gave very good results and the calculated curves fitted the original function $w(v)$.

Finally, in Figs. 4 and 5 the proposed correction procedure (eqn. 21a, $\Delta v_{calc} = 1.5$) is compared with the methods of Ishige *et al.* and Pierce and Armonas on real chromatograms obtained with polystyrene and poly(methyl methacrylate); a spread-
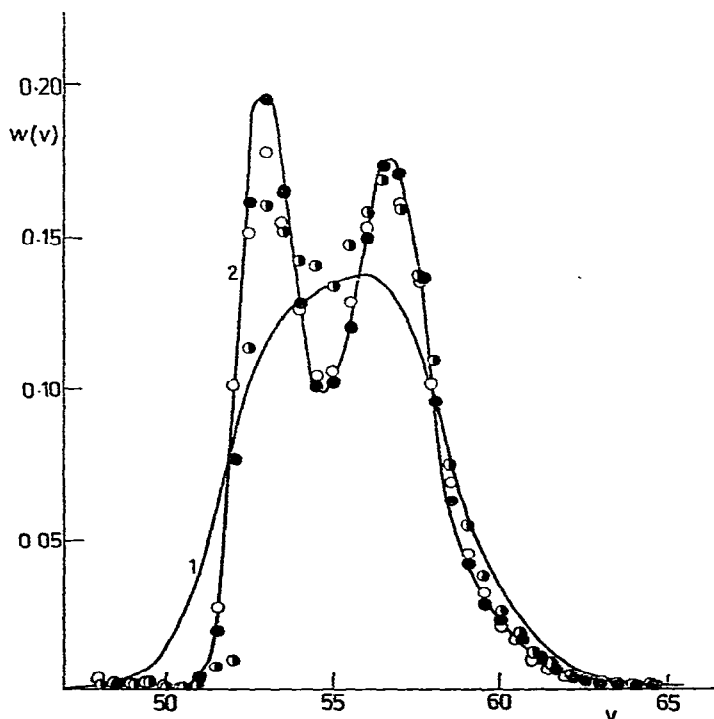

Fig. 5. Comparison of different methods of correction applied to a real chromatogram of polystyrene. 1 = Normalized, uncorrected chromatogram; 2 = Ishige *et al.*[8]; ○, this work, eqn. 21a, $k = 5$, $\Delta v_{calc} = 1.5$; ◑, Pierce and Armonas[10].
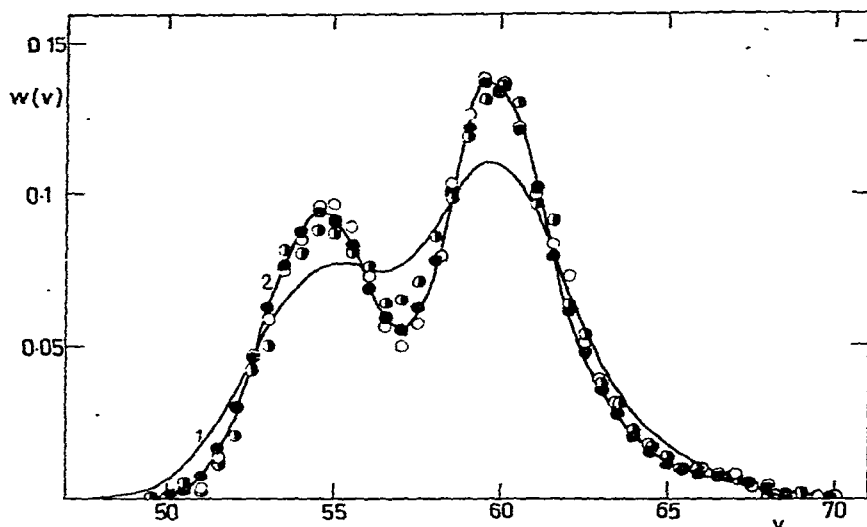
Fig. 6. Corresponding comparison to that in Fig. 5 for a real chromatogram of poly(methyl meth-acrylate). Notation as in Fig. 5.

ing factor, $h(v)$, given by eqn. 23 was used throughout. The chromatogram of the polystyrene sample in Fig. 5 indicates the presence of two strongly superimposed peaks; all three correction methods were able to resolve them. Eqn. 21 and the method of Ishige *et al.* gave again very similar corrected chromatograms; the resolution of the method of Pierce and Armonas was much worse. A very similar situation arises in the correction of a chromatogram of poly(methyl methacrylate) shown in Fig. 6, although in this instance the separation of both peaks is somewhat greater; as a result, even the method of Pierce and Armonas gives a satisfactory result. The net computation times with the Wang 2200 calculator were as follows: (a) for the chromatogram in Fig. 5, *ca.* 1¾ min (Pierce and Armonas), *ca.* 2¼ min (eqn. 21a) and 72 min (Ishige *et al.*); (b) for the chromatogram in Fig. 6, *ca.* 2 min (Pierce and Armonas),

TABLE I

MOLECULAR WEIGHT AVERAGES CALCULATED BY DIFFERENT CORRECTION METHODS FROM CHROMATOGRAMS OF POLYSTYRENE AND POLY(METHYL METH-ACRYLATE)

Method	Sample	$M_n \cdot 10^4$	$M_w \cdot 10^4$	$M_z \cdot 10^4$
Uncorrected	Polystyrene	7.615	14.969	25.115
Pierce and Armonas[10]		7.862	12.594	17.610
Eqn. 21a, $\Delta v_{calc} = 1.5, k = 5$		8.164	13.933	19.850
Ishige *et al.*[8]		8.236	13.867	19.249
Uncorrected	Poly(methyl methacrylate)*	3.536	12.148	30.000
Pierce and Armonas[10]		3.813	10.802	22.872
Eqn. 21a, $\Delta v_{calc} = 1.5, k = 5$		3.742	10.826	21.814
Ishige *et al.*[8]		3.790	11.263	23.565

* Calculated from a calibration graph for polystyrene assuming the validity of the universal calibration according to Grubisic *et al.*[15].

ca. 3 min (eqn. 21a) and 32 min (Ishige *et al.*). Corrected values of number-, weight- and z-averages obtained by the three methods for both real samples are given in Table I.

From the point of view of correction efficiency, eqn. 21a is to be preferred to the simpler eqn. 20a. It is recommended that one should work with $\Delta v_{calc} = 1$, or $\Delta v_{calc} = 1.5$, with a number of iteration steps not greater than $k = 5$. In all of the examples studied, the proposed method of zone spreading correction based on eqn. 21a proved to be equally efficient but much simpler and faster than the method of Ishige *et al.* It is particularly suitable for laboratories with only a small computer with restricted storage capacity; with lower demands on accuracy, eqn. 21a can be used in a single step and the calculation can then be carried out with a simple desk-top calculator. The proposed procedure is limited to the case of a Gaussian kernel in the Tung integral equation, but it is, however, capable of accommodating a variable spreading factor, $h(v)$. The method does not require a fine sub-division of the abscissa in reading the chromatogram heights, which speeds up considerably the processing of a large number of experimental results.

REFERENCES

1 M. Hess and R. F. Kratz, *J. Polym. Sci., Part A-2*, 4 (1966) 731.
2 L. H. Tung, *J. Appl. Polym. Sci.*, 10 (1966) 375.
3 W. N. Smith, *J. Appl. Polym. Sci.*, 11 (1967) 639.
4 L. H. Tung, *J. Appl. Polym. Sci.*, 13 (1969) 775.
5 V. S. Chang and R. Y. M. Huang, *J. Appl. Polym. Sci.*, 13 (1969) 1459.
6 E. M. Rosen and T. Provder, *Separ. Sci.*, 5 (1970) 485.
7 E. M. Rosen and T. Provder, *J. Appl. Polym. Sci.*, 15 (1971) 1687.
8 T. Ishige, S.-I. Lee and A. E. Hamielec, *J. Appl. Polym. Sci.*, 15 (1971) 1607.
9 V. S. Chang and R. Y. M. Huang, *J. Appl. Polym. Sci.*, 16 (1972) 329.
10 P. E. Pierce and J. E. Armonas, *J. Polym. Sci., Part C*, 21 (1968) 23.
11 F. C. Frank, I. M. Ward and T. Williams, *J. Polym. Sci., Part A-2*, 6 (1968) 1357.
12 W. Jost, *Diffusion in Solids, Liquids and Gases*, Academic Press, New York, 1960, p. 33.
13 L. H. Tung, J. C. Moore and G. W. Knight, *J. Appl. Polym. Sci.*, 10 (1966) 1261.
14 D. U. von Rosenberg, *Methods for the Numerical Solution of Partial Differential Equations*, Elsevier, New York, 1969.
15 Z. Grubisic, P. Rempp and H. Benoit, *J. Polym. Sci., Part B*, 5 (1967) 753.