The Instrument Spreading Correction in GPC. III. The General Shape Function Using Singular Value Decomposition with a Nonlinear Calibration Curve*

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Synopsis

The Gram-Charlier series was suggested as an empirical instrument spreading function in the first paper (part I) of this series. In the second paper (part II) of this series, the Fourier transform method was used together with the suggested series to solve Tung's integral equation. In this paper, an alternate method for solving Tung's equation is proposed which eliminates some of the limitations of the Fourier transform method. In the approach used in this study, Tung's integral equation is approximated by a set of linear equations. Since no unique least-squares solution can be computed, a closely related problem whose solution closely approximates the original problem is formulated and solved using singular value decomposition. By avoiding the use of the smallest singular values and forcing the equality of the areas of the corrected and the uncorrected chromatograms, an approximate solution to the original problem is obtained in which the oscillations inherently present due to the ill-posed nature of the problem are filtered out. The performance of the method with the experimental data given in Part II is indicated.

INTRODUCTION

In the first paper (part I) of this series,[1] the Gram-Charlier series was suggested as an empirical instrument spreading function and used in conjunction with a linear calibration curve to find an analytical solution to Tung's equation by the method of molecular weight averages. The corrected number- and weight-average molecular weights obtained from the analytical solution were used in conjunction with the hydrodynamic volume concept to obtain a calibration curve corrected for instrument spreading. The corrected calibration curve was used along with the raw chromatogram to obtain the corrected differential molecular weight distribution curve.

In the second paper (part II) of this series,[2] this function was used in Tung's equation to correct the raw retention volume chromatogram, $F(v)$, to a corrected chromatogram, $W(v)$. From $W(v)$, true number- and weight-average molecular weights could be calculated. Tung's equation was

solved by the Fourier transform method, and a nonlinear calibration curve, the form of which was suggested by Yau and Malone,[3] was used.

The Fourier transform method, though relatively fast and small in computer storage requirements, had two major problems. The first problem was the inconsistent manner in which the volume dependence of the instrumental spreading function, $G(v - y)$, was taken into account. Although $G(v - y)$ is a function of volume, the procedure assumed it to be independent of volume for ease of mathematical manipulation during the transformations between volume and frequency (k) space, but then used the functional dependence of $G(v - y)$ on v in the evaluation of the transformed instrument spreading function G(k). The second problem occurred when using the method on actual experimental data. Due to the generation of slowly undulating oscillations in k space, there was considerable doubt as to how far in k space F(k) should be generated. If k_{max} values (the largest value of k at which F(k) is determined) were too small, information would be lost. If k_{max} values were too large, spurious information would be introduced. In part II, k_{max} was estimated semiempirically.

In order to avoid these difficulties, Tung's integral equation is approximated by a set of linear algebraic equations. A closely related problem is then formulated and solved using singular value decomposition in order to avoid the oscillations introduced due to the ill-posed mathematical nature of the problem. The use of singular value decomposition in the solution of integral equations was suggested by Golub and Kahan[4] and applied by Hanson.[5]

The method here may be considered a minimization method as classified by Tung.[6] As expected, it suffers from relatively large computer storage requirements and long computation time. However, it overcomes the difficulties encountered in the Fourier transform method.

TUNG'S INTEGRAL EQUATION

Tung's equation has the form of a convolution integral equation and relates the normalized raw retention volume chromatogram, F(v), to the corrected normalized retention volume chromatogram, W(y), and the instrument spreading function $G(v - y)$ by means of the following equation:

$$F(v) = \int_{-\infty}^{\infty} G(v - y) W(y) dy. \tag{1}$$

The instrument spreading function indicated in part II is

$$G(v - y) = \frac{1}{\sqrt{2\pi\mu_2}} \exp\left[-\frac{(v - y)^2}{2\mu_2}\right]$$

$$\times \left\{1 + \frac{A_3}{3!} H_3\left[\frac{v - y}{\sqrt{\mu_2}}\right] + \frac{A_4}{4!} H_4\left[\frac{v - y}{\sqrt{\mu_2}}\right]\right\}, \tag{2}$$

where A_3 and A_4 are skewing and flatness parameters defined by the equations

$$A_3 = \frac{\mu_3}{\mu_2^{3/2}} \tag{3}$$

$$A_4 = \frac{\mu_4}{\mu_2^2} - 3 \tag{4}$$

and $H_n\left[(v - y)/\sqrt{\mu_2}\right]$ are the Hermite polynomials as defined in Table I. The parameters μ_2, μ_3, and μ_4 are in general a function of the volume y.   As pointed out by Vladimiroff[7] the μ values in eq. (2) were incorrectly[8] considered as a function of v in part II.

TABLE I
Hermite Polynomials

$H_0(x) = 1$
$H_1(x) = x$
$H_2(x) = x^2 - 1$
$H_3(x) = x^3 - 3x$
$H_4(x) = x^4 - 6x^2 + 3$

As indicated by Tung,[6] the integral in eq. (1) may be approximated using m data points of the raw chromatogram by a set of simultaneous linear algebraic equations of the following form:

$$F(v_i) = \sum_{j=1}^{n-1} G(v_i - y_j)W(y_j)\Delta y_j \qquad i = 1, 2, . \ m. \tag{5}$$

If $n - 1$ increments of Δy are used together with the trapezoidal rule, eq. (5) becomes

$$F(v_i) = \frac{\Delta y}{2} [G(v_i - y_1)W(y_1) + 2G(v_i - y_2)W(y_2)$$

$$+ \ldots G(v_i - y_n)W(y_n)] \qquad i = 1, 2 \ldots m. \tag{6}$$

Rearranging yields

$$G(v_i - y_1)W(y_1) + 2G(v_i - y_2)W(y_2) + \ldots G(v_i - y_n)W(y_n) = \frac{2F(v_i)}{\Delta y}$$

$$i = 1, 2, \ldots m. \tag{7}$$

Since the coefficients $G(v - y)$ are known, this represents m equations in n unknowns.   When the $G(v - y)$ function is evaluated for use in eq. (5), the variation of $\mu_2, \mu_3,$ and μ_4 with y may be included.   Generally, m is selected to be greater than n, and an attempt is made to solve eq. (7) in a least-squares sense.   The value selected for n depends on the accuracy and smoothness of the W(y) function desired.   Generally, about 10 points per count is adequate.   The range of W(y) is taken to be the same as that of $F(v)$.

PROBLEM DEFINITION

As pointed out by Duerksen,[9] previous workers who have attempted the solution to eq. (1) by approximating the integral with a set of linear equations have all encountered great difficulty in solution due to ill-conditioning of the resulting matrix. Hanson and Lawson[10] discuss linear least-squares problems in considerable detail and show how singular value decomposition can be used to generate the singular values of the matrix which can then be used for analysis.

Upon letting A be the $m \times n$ matrix arising from eq. (7), X be the desired solution vector W(y), and **B** be the right-hand side vector of eq. (7) there results

$$AX = B. \tag{8}$$

Generally, there will be more data points than points at which a solution is desired. Thus, $m > n$. If the rank of A is equal to n, then there is a unique solution. However, if the rank of A is less than n, then the solution is not unique and an additional criterion is needed to make it unique. This additional criterion is generally taken as the minimum length solution which then can be found from the pseudoinverse[4] of A.

From a practical point of view, however, this procedure requires a definition of which of the singular values are zero and which are not. This is a very difficult task, indeed, especially when there are many small closely spaced singular values. As a result, some additional criterion is needed to

TABLE II
Relationships[a] Between the Moments About. the Mean (μ) of $F(v)$ and $W(v)$

Moment,	Relationship
Zero	area of unnormalized $W(v)$ = area of unnormalined $F(v)$
First	mean of W(u) = mean of $F(v)$
Second[b]	$m_2{}^* = m_2 - \displaystyle\int_{-\infty}^{\infty} \mu_2(y)W(y)dy$
Third	$m_3{}^* = m_3 - \displaystyle\int_{-\infty}^{\infty} \mu_3(y)W(y)dy - 3\int_{-\infty}^{\infty} \mu_2(y)yW(y)dy$
	$\qquad\qquad + 3\mu\displaystyle\int_{-\infty}^{\infty} \mu_2(y)W(y)dy$
Fourth	$m_4{}^* = m_4 - \displaystyle\int_{-\infty}^{\infty} \mu_4(y)W(y)dy - 6\int_{-\infty}^{\infty} \mu_2(y)y^2W(y)dy$
	$\qquad\qquad + 12\mu\displaystyle\int_{-\infty}^{\infty} \mu_2(y)yW(y)dy - 6\mu^2\int_{-\infty}^{\infty} \mu_2(y)W(y)dy$

*Note: $\mu_n(y) = \displaystyle\int_{-\infty}^{\infty} (v - y)^n G(v \quad y)dv, \; n = 2,3,4.$

[b] $m_i{}^*$ refers to $W(v)$, m_i refers to $F(v)$.

select a reasonable solution. A choice may be made from a number of theoretical relationshlps that exist between F(v) and W(v).

By multiplying both sides of eq. (1) by v^n, where $n = 0, 1, 2, 3, 4$ and integrating over c, there results

$$\int_{-\infty}^{\infty} v^n F(v) dv = \underset{-\infty}{\overset{\infty}{\mathrm{S}}} v^n \underset{-\infty}{\overset{\infty}{\mathrm{S}}} G(v - y) W(y) dy dv$$

$$n = 0, 1, 2, 3, 4. \quad (9)$$

Integrating out for each n, the relationships given in Table II result. When the parameters μ_2, μ_3, and μ_4 are constants, the relationships reduce to those given in part II.

If the trapezoidal rule is used to approximate the equal area constraint, then (since the normalized area must equal 1) there results

$$1 = \frac{\Delta y}{2} [W(y_1) + 2W(y_2) + . W(y_n)]. \quad (10)$$

CLOSELY RELATED PROBLEM

The solution of eq. (8) subject to the linear constraints of Table II may be approached in a number of ways. For example, it may be formulated as a quadratic programming problem, since in addition to the equality constraints it is known that the solution must be everywhere nonnegative:

$$x_i = W(y_i) > 0. \quad (11)$$

Marquardt[11] has recently pointed out that when $A^T A$ is poorly conditioned (small eigenvalues), then the least-squares solution to eq. (8) does not necessarily lead to an acceptable solution. He discusses two approaches to solving this problem and compares their properties: (a) the ridge estimation method of Hoer1 and Kennard and (b) generalized inverse estimators. Both approaches can be used to develop generally different but adequate solutions.

In this paper, however, the procedure outlined by Golub[12] has been followed. We seek to find a solution of minimum length which satisfied the constraint that

$$\|AX - B\| = \alpha > \text{minimum} = \text{least-squares solution.} \quad (12)$$

To do this we seek to minimize Φ, where

$$\Phi = \|X\|^2 + \frac{1}{\lambda} [(B - AX)^T (B - AX) - a^{"}] \quad (13)$$

and λ is a Lagrangian multiplier. The solution will lie on a sum-of-squares contour, α^2, which in general will be greater than the least-squares solution which is the low point in the sum-of-squares space. Differentiating with respect to x_i and setting the derivatives equal to zero results in

$$(A^T A + \lambda I) X = A^T B. \quad (14)$$

If is of interest to note that this is exactly the ridge analysis equation of Hoer1 and Kennard discussed by Marquardt.[11]

Everything in eq. (14) is known, except λ. If λ were assumed, however, and $A^T A$ and $A^T B$ were computed, then a linear set of equations would have to be solved to obtain X. This has two disadvantages, however. First, the $A^T A$ calculation, especially if A is large, can lead to considerable errors. Secondly, there is a requirement to save $A^T A$, so extra storage is needed. To avoid these problems, we take the singular value decomposition[10] of A:

$$A = U_{(m \times n)} S_{(n \times n)} V^T{}_{(n \times n)}. \tag{15}$$

The matrices U and V are both orthonormal, and the S matrix is a diagonal matrix of scalars which are the singular values of A. (The singular values of A are the nonnegative square roots of the eigenvalues of $A^T A$.) Since U and V are orthonormal.

$$V^T V = \mathrm{I}, \tag{16}$$

and

$$U^T U = I,. \tag{17}$$

Upon substitution of eq. (15) into eq. (14), there results

$$(S + \lambda S^{-1})Z = \mathrm{c} \tag{18}$$

where

$$Z = V^T X \tag{19}$$

and

$$C = U^T B. \tag{20}$$

Since the matrices are all diagonal, eq. (18) may be written in component form as

$$z_i = \frac{s_i c_i}{\lambda + s_i{}^2}. \tag{21}$$

Once z_i is determined, then the solution from eq. (19) is given by

$$\mathrm{x} = \mathrm{vz}. \tag{22}$$

Since the solution vector X obtained in eq. (22) depends on the choice of λ, a value of λ is searched for until the solution vector satisfies the constraint, eq. (10). The value of λ determines the contour α^2 on which the solution lies.

The procedure to find a solution in the sense of eq. (18) to eq. (8) subject to eq. (10) can be summarized as follows:

a. Given m data points, v_i and $F(v_i)$, from the raw chromatogram, set up a set of m equations in n unknown points $W(y_j)$, $j = 1, 2, \ldots n$ with m $\geq n$.

b.   Estimate λ. When $\lambda = 0$ a least squares solution is found.   When $\lambda \rightarrow \infty$, $z_i \rightarrow 0$, and the solution $\| X \|$ goes to 0.

c. Perform a singular value decomposition of A.   This gives U, S, and V.

d.   Calculate z_i from eq. (21) and then X from eq. (22).   If any $x_i < 0$, set $x_i = 0$.   Also eliminate any tails by setting them to 0.   These sometime occur at the edges of the chromatogram.

e. See if X satisfies eq. (10). If it does, the procedure is completed. If not, reestimate λ and return to step d.

The final result yields X and the value of λ.

RESULTS

Analytical   Data

In order to test the above procedures, a function suggested by Tung[13] and studied in part II was used:

$$F(v) = \frac{0.325H}{\sqrt{\pi[(0.325)^2 + H^2]}} \left\{ 0.6 \exp\left[- \frac{(0.325)^2 H^2 (v - 25)^2}{(0.325)^2 + H^2} \right. \right.$$

$$\left. \left. + 0.4 \exp\left[- \frac{(0.325)^2 H^2 (v - 31)^2}{(0.325)^2 + H^2} \right] \right\} \quad (23)$$

where

$$H = \frac{1}{\sqrt{2\mu_2}}. \quad (24)$$
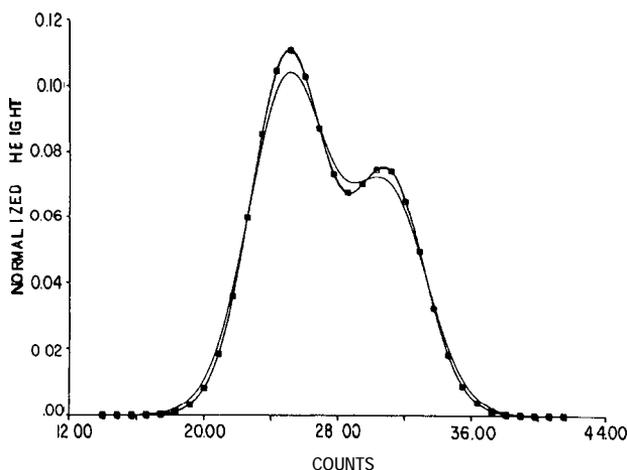
Fig. 1. Test function $H = 0.8$: (—) $F(v)$; (—□—) $W(v)$; (-A-) theory $W(v)$.

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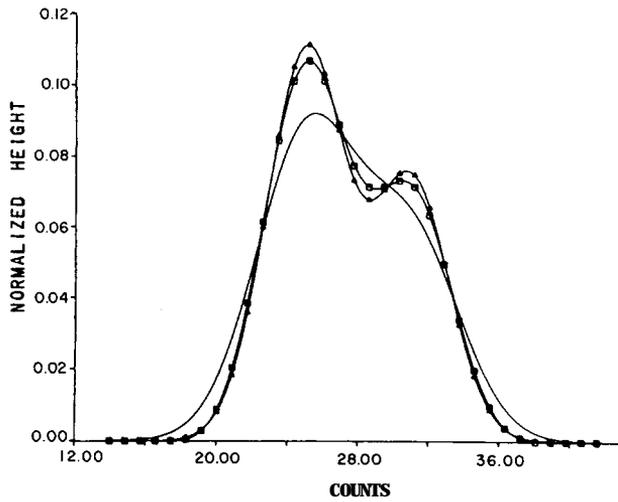
Fig. 2. Test function $H = 0.4$: (—) $F(v)$; (-•-) $W(v)$; (-A-) theory $W(v)$.

The corrected chromatogram is

$$W(v) = \frac{0.325}{\sqrt{\pi}} \{0.6 \ \exp\left[-(0.325)^2(v-25)^2\right]$$

$$+ \ 0.4 \ \exp[-(0.325)^2(v-31)^2]\}. \quad (25)$$

$F(v)$ was generated over the range $14 \leq v \leq 42$ with $\Delta v = 0.1$. Due to storage limitations, however, when more than 99 points were available, 99

TABLE III
Results for Analytical Test Function Eq. (23)

Statistic	$H = 0.8$	$H = 0.6$	$H = 0.4$
s_{max}	0.694375×10^1	0.692089×10^1	0.685971×10^1
s_{min}	0.144872×10^{-5}	0.286682×10^{-7}	0.506216×10^{-7}
Rows of A	99	99	99
Columns of A	99	99	99
λ	0.316594×10^{-2}	0.172493×10^{-2}	0.369109×10^{-1}
Area, $F(v)$	0.99999×10^0	0.99999×10^0	0.99995×10^0
Area, $W(v)$	0.99994×10^0	0.99994×10^0	0.99991×100
Mean, $F(v)$	0.27400×10^2	0.27400×10^2	0.27400×10^2
Mean, $W(v)$	0.27400×10^2	0.27400×10^2	0.27399×102
$m_2, F(v)$	0.14155×10^2	0.14762×10^2	0.16491×102
m_2^*, theory	0.13373×102	$0.13373 \times 10"$	$0.13373 \times 10"$
$m_2^*, W(v)$	0.13376×10^2	0.13377×102	0.13453×102
$m_3, F(v)$	0.10369×10^2	0.10373×10^2	$0.10382 \ X \ 10^2$
m_3^*, theory	0.10369×10^2	0.10369×10^2	0.10369×10^2
$m_3^*, W(v)$	0.10371×10^2	0.10369×10^2	0.10381×10^2
$m_4, F(v)$	0.46418×10^3	0.51677×10^3	0.67792×103
m_4^*, theory	$0.39960 X \ 10^3$	$0.39960 X \ 10^3$	$0.39960 X \ 10^3$
$m_4^*, W(v)$	0.39939×10^3	0.39815×10^3	0.40028×103
Time, sec	133	117	105

equally spaced points in y were computed by interpolation.   For $H = 0.4, 0.6$ and $H = 0.8$, the results are shown in Table III.   Figures 1 and 2 are plots for the cases $H = 0.8$ and $H = 0.4$.   The   theoretical   relationships   between the moments indicated in Table II are also shown in Table III.   (Note, however, μ values are not functions of volume.)   The times, in seconds, are for an IBM 360/65 computer under MVT.   The singular value decomposition was carried out in single precision using the code of Golub and Reinsch[14] as translated into FORTRAN by Hanson.   (R. J. Hanson kindly supplied a copy of the routine.)

   As H goes from 0.8 down to 0.4 ($\mu_2 = 0.782$ to $\mu_2 = 3.12$), it is evident from Table III and the plots that there is somewhat of a degradation in the answers.   As H decreases, the largest singular value $(s)_{max}$ remains essentially the same, but the smallest singular value (s_{min}) decreases considerably. This increasing ill-conditioning appears to limit the accuracy of the numerical results obtained.

Experimental   Data

   The instrumental spreading correction procedure was tested on the same experimental data as reported in part II.   Table IV gives the values derived in part II for the variation of μ_2, μ_3, and μ_4 with volume. In addition, the parameters of the Yau-Malone calibration curve used are also given.

   Table V gives the results of the five test samples, and Figures 3 to 7 give the corresponding plots.   Note that the values of s_{min} given in Table IV are above the value of s_{min} (about $s_{min} = 10^{-7}$) at which numerical problems may begin to be encountered as indicated in the tests of the analytical function.
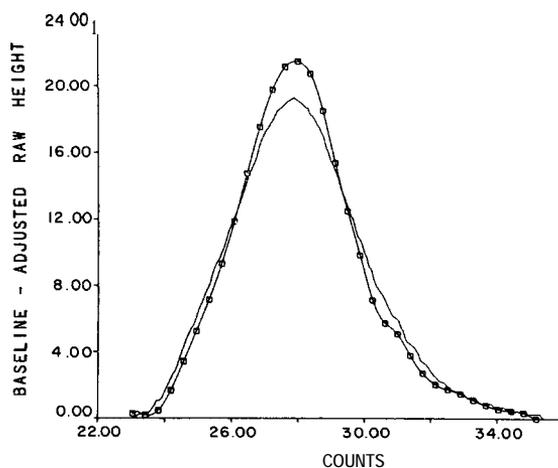
Fig. 3. Uncorrected and corrected chromatogram for sample 181-186: (—) F(v); (—□—) W (v).
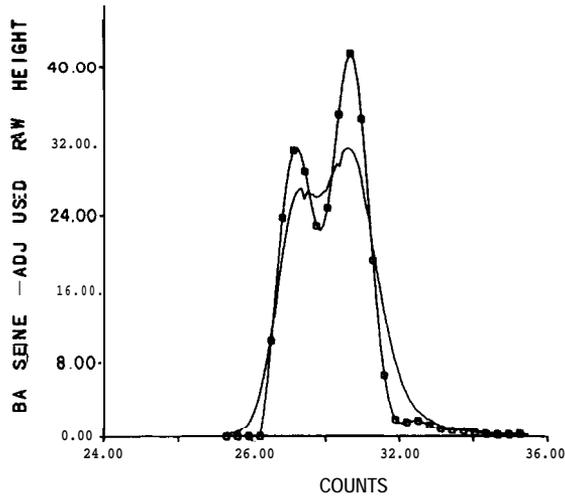
Fig. 4. Uncorrected and corrected chromatogram for sample 196-302-l: (—) F(v); (- • -) $W(v)$.

TABLE IV
Calibration Values for Polystyrene Samples

Volume (5 ml/count)	μ_2	μ_3	μ_4
2 3	0.825	0.970	19.1
2 4	0.950	0.695	19.0
2 3	1.05	0.270	17.1
2 6	1.05	0.160	13.2
2 7	0.927	0.047	8.15
2s	0. 730	0.00	4.32
2 9	0.593	0.0145	2.22
3 0	0.465	0.0346	1.15
3 1	0.397	-0.0750	0.706
3 2	0.370	-0.213	0.550
33	0.425	-0.500	0.650
84	0.510	-0.890	0.859
3 3	0 5 50	-1.18	0.966
3 6	0.595	—1.52	1.10
3 7	0. 580	-1.63	1.01

Yau Malone Curve

$$v = A + B \left\{ \frac{1}{\sqrt{\pi} \, \psi} \, [1 - \exp(-\psi^2)] + \operatorname{erfc}\,(\psi) \right\}$$

$$\psi = \frac{M^D}{C}$$

Values of Yau-Malone Parameters

A = 20.154
B = 22.645
C = 19.337
D = 0.27977

TABLE V
Results for Experimental Test Samples

Statistic	181-183	196-302-1	196-305-1	196-306-1	196-308-1
s_{max}	0.205367×10^2	0.210596×10^2	0.217707×10^2	0.226447×10^2	0.214169×10^2
s_{min}	0.888266×10^{-7}	0.106676×10^{-5}	0.118629×10^{-5}	0.142631×10^{-5}	0.127180×10^{-5}
λ	0.162833×10^1	0.137125×10^2	0.623109×10^1	0.211529×10^2	0.162403×10^2
Unnormalized area, F(v)	92.937	88.431	83.884	91.594	87.440
Unnormalized area, W'(v)	92.937	88.438	85.877	91.597	87.434
Mean, F(v)	28.119	30.239	32.436	31.467	30.654
Mean, W'(v)	28.090	30.172	32.397	31.397	30.575
Predicted m_2[a]	3.2842	0.74357	1.0007	1.0128	1.6709
Calculated m_2[b]	3.5375	0.96013	1.1051	1.1947	1.9230
Predicted m_3*	4.6890	1.02119	-0.27539	1.4765	2.5079
Calculated m_3*	3.3336	0.66598	-0.58955	1.3268	2.1730
Predicted m_4*	31.372	1.3127	1.5039	2.7180	5.8086
Calculated m_4*	43.234	4.4316	3.5339	4.8652	11.024
$10^{-3}\bar{M}_n(\infty)$	130.59	68.735	25.667	38.571	51.167
$10^{-3}\bar{M}_w(\infty)$	373.318	88.042	34.248	51.513	78.378
$P(\infty), F(v)$	2.86	1.28	1.33	1.34	1.53
$10^{-3}\bar{M}_n(t)_w$[c]	139.494	72.491	27.029	40.646	54.025
$10^{-3}\bar{M}_w(t)_w$	353.922	88.358	33.846	51.911	79.401
$P(t)_w$	2.54	1.22	1.26	1.27	1.47
$P(t)$[d]	1.889	1.15	1.20	1.21	1.42
Time, sec	110	76	56	60	74

[a] Values of right-hand side of equations of Table II.
[b] Calculated from W(v).
[c] All the statistics with a subscipt w were calculated from $W(v)$.
[d] Taken from experimental values given in part II.
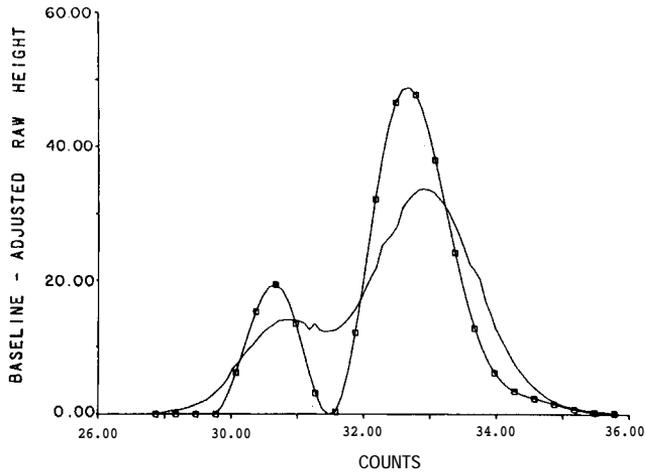
Fig. 5. Uncorrected and corrected chromatogram for sample 196–305-1: (—) F(v); (—□—) $W(v)$.
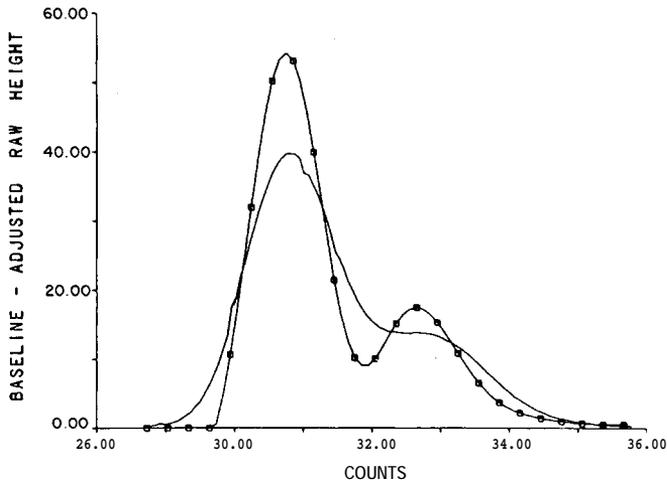
Fig. 6. Uncorrected and corrected chromatogram for sanple 196-806-l; (---) F(v); (- - a -) $W(v)$.

Some discrepancies appear in the $P(\infty)$ values between Table V and Table VIII of part II. This is due to the fact that smoothing was performed on the data in part II at the edges of the chromatogram, while in this study no smoothing was performed.

A study of the results of the statistical calculations given in Table V indicates that the calculated chromatogram, W(v), is consistently too '(broad," i.e., m_2^* and m_4^* calculated from $W(v)$ are always too large when compared to the calculated values obtained from the equations of Table II. This may be due to the sensitivity of the calculation of the moments to the mean.
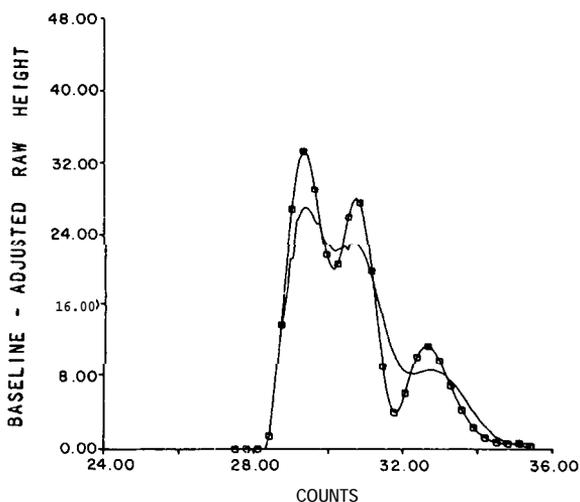
Fig. 7. Uncorrected and corrected chromatogram for sample 196-308-l: (——) $F(v)$; (—□—) $W(v)$.

Attempting to match means or second moments by means of the relationships of Table II met with no better success than the area matching.

The reason for the differences between the calculated and measured molecular weights is not clear. It is suggested that this may be due to a shift in the calibration curve over the extended period of time that the data were taken.

DISCUSSION OF RESULTS

From the studies conducted in this paper and those in part II,[2] some comparisons can be drawn between the Fourier transform method and methods which approximate Tung's integral equation by a set of linear equations.

As indicated in part II,[2] the major computational difficulty with the Fourier transform method was that it was difficult to know how far out in k space F(k) should be generated. Smoothing $F(v)$ at the edges seemed to have little effect on damping the oscillations of F(k). Experiments in which the value of k_{max} was varied to match the areas of $F(v)$ and $W(v)$ were not successful. Recently, Vladimiroff,[15] in suggesting the use of the fast Fourier transform, indicated that mathematical filtration and smoothing operations can be performed on the transform of the experimental chromatogram. He did not apply his method to experimental data, however.

With these facts in mind the two methods might be compared in the following ways :

Constancy of $G(v \quad y)$

In the Fourier transform method, $G(v - y)$ is assumed independent of volume during the transformations between v and k space, but its depen-
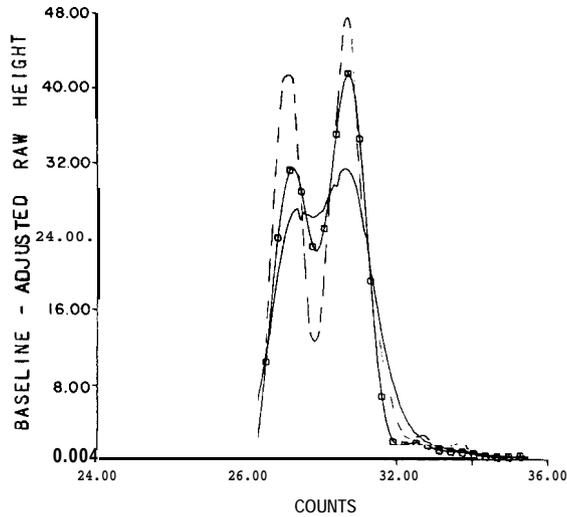
Fig. 8. Comparison of uncorrected chromatogram with corrected chromatograms obtained from linear equation method and Fourier transform method for sample 196-302-1: (-) F(u); (-•o-) $W(v)$ from linear equation method; (- ▬ -) $W(v)$ from Fourier transform method.
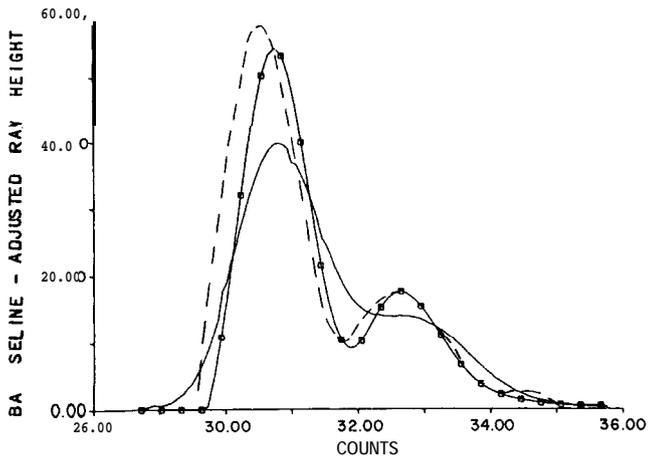
Fig. 9. Comparison of uncorrected chromatogram with corrected chromatograms obtained from linear equation method and Fourier transform method for sample 196306 1: (—) F(v); (-•O--) $W(v)$ from linear equation method; (- ▬ -) $W(v)$ from Fourier transform method.

dence on volume is considered when $G(k)$ is evaluated. In the linear equation method, this inconsistent treatment is not required. Vladimiroff[15] and Tung,[13] however, have suggested that this may not be important, especially if $G(v - y)$ is just a very weak function of volume. Some insight into this problem can perhaps be gained by an examination of Figures 8 and 9

in which the Fourier transform solution from part II[2] has been plotted on Figures 4 and 5. Table IV shows how much μ_2, μ_3, and μ_4 vary over the range of these chromatograms. As can be seen, the variation between the two solutions would not be excessive if the area of the chromatogram obtained from the Fourier transform method is renormalized to that of the observed chromatogram by arbitrarily dividing each data point by the ratio of the area of the corrected chromatogram obtained from the Fourier transform method to that obtained from the observed chromatogram. Even then, the Fourier transform method would be useful only for routine correction of the $\bar{M}_n$ and $\bar{M}_w$ averages. For more involved calculations, such as using a theoretical polymer chain-branching model in conjunction with the corrected chromatograms[16,17] or using data obtained from the corrected chromatogram for the determination of kinetic polymerization parameters,[18-20] the Fourier transform method of solution would be inadequate due to slight shifts in peak retention volume to lower retention volumes, as shown in Figures 8 and 9. The linear equation method of solution would be preferred because of its accuracy and reliability.

Computer Storage Requirements

If one wishes to obtain a reasonably smooth $W(v)$ using linear equations, then about S to 10 points per count should probably be used. In general, this leads to large computer storage requirements which the Fourier transform method generally avoids. For cruder W(v), about 5 points per count, the computer storage requirements tend to be more competitive.

Time

The large amount of time required to find the singular values in the linear equation method generally penalizes the method over the Fourier transform method. As implemented here and in part II,[2] this generally meant that the linear equation method required 5 to 10 times longer computation time than the Fourier transform method.

CONCLUSIONS

The most accurate and reliable method for calculating the instrumental spreading correction appears to be the linear equation method. A number of methods can probably be used for solution, but they must recognize the ill-posed nature of the problem. One pays for it, however, in computer time and storage requirements. If a filtering method for the Fourier transform method can be devised, however, similar to the one suggested in this paper for linear equations which resolves the k_{max} problem, it indeed may be made more attractive. However, the linear equation method would still be the preferred method n-here $G(v - y)$ is a moderate to strong function of retention volume.

Nomenclature[a]

A	$m \times n$ matrix whose elements are $G(v_i - y_j)$; $i = 1, 2, \ldots$ m; $j = 1, 2, . \, . \, n$
B	the right hand side vector of eq. (7) whose elements are $2F(v_i)/\Delta y$, $i = 1, 2, \ldots$ m
C	vector defined by eq. (20)
I_n	n $\times$ n identity matrix
S	$n \times n$ diagonal matrix of singular values of A
T	superscript in A^T, U^T and V^T indicating transpose
U	$m \times$ n matrix consisting of n orthonormalized eigenvectors associated with n largest eigenvalues of AA^T.
V	$n \times$ n matrix consisting of the orthonormalized eigenvectors of A^TA.
X	the solution vector of eq. (8) whose elements are $W(y_j)$, $j = 1, 2, . \, . \, n$
Z	vector defined by eq. (21)
$\|X\|$	Euclidean norm equal to $\sqrt{x_1{}^2 + x_2{}^2 + . \, . \, x_n{}^2}$
Δy_j	jth increment of retention volume
λ	Lagrangian multiplier
Φ	function to be minimized

[a] Symbols and notation found in the text and not defined here have been previously described in parts I and II.

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