JOURNAL OF APPLIED POLYMER SCIENCE VOL. 15, PP. 1607-1622 (1971)

Solution of Tung's Axial Dispersion Equation by Numerical Techniques

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Synopsis

Numerical methods for the solution of Tung's axial dispersion equation have been developed and comprehensively evaluated. These methods are general and can be applied where the instrumental spreading function is unsymmetrical and nonuniform. Computation times required are comparable to those of the method of Chang and Huang being about 10 sec per case on the CDC6400 computer. Memory requirements are minimal and this should permit their use with minicomputers for data acquisition and processing.

INTRODUCTION

In gel permeation chromatography, the elimination of axial dispersion from the permeation process is almost impossible experimentally. Therefore, the GPC elution curve must be corrected for axial dispersion to obtain true molecular weight distribution and molecular weight averages.

When axial dispersion is taken into account, the GPC response $F(v)$ to an input sample $W(y)$ is given by the following integral equation after Tung:[1]

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

where $G(v,y)$ is called the instrumental spreading function and accounts for the total axial dispersion. It is the response for a unit input of a monodispersed polymer sample. Often, the function G has been approximated by a Gaussian distribution:

$$G(v,y) = (h/\pi)^{1/2} \exp\{-h(v-y)^2\}. \tag{2}$$

The above simple analytical form of G permits various analytical treatments of eq. (1) for example, Fourier transformation. Several methods have been proposed by Tung,[1-4] Pierce and Armonas,[5] and Hamielec and Ray[6] to obtain $W(y)$ or its moments from a knowledge of $F(v)$. A correction for nonsymmetrical axial dispersion has been attempted by Hess and Kratz,[7] Smith,[8] Pickett et al.,[9] Balke and Hamielec,[10] and Provder and Rosen.[11] Recently, Chang and Huang[12] developed a very effective search method for obtaining $W(y)$. This method assumes a symmetrical and uniform G function. Uniform G is one whose shape parameters ($\mu_2,\mu_3, \ldots$) are independent of y and can be expressed as $G(v - y)$. However, these methods have certain limitations. These are associated with nonuniform spreading functions, large resolution corrections, narrow chromatograms, and excessive computer storage and computation time.

In the present investigation, we have developed new iterative methods which overcome many of the aforementioned difficulties. We have chosen the method proposed by Chang and Huang (second-order method) as a most promising one for the numerical solution of Tung's axial dispersion equation and compared its performance with our iterative methods. The method of Chang and Huang has been shown[12] to give excellent recoveries of $W(y)$, and it has the added advantages of small computation time and storage. The disadvantage is its limitation to symmetrical instrumental spreading functions.

THEORY

The development of our iterative methods will be given in chronological order, first the development of our method 1, followed by method 2.

Method 1

In order to simplify the formulation, we denote eq. (1) by

$$F(v) = \mathbf{G}\{W(y)\} \tag{3}$$

where $\mathbf{G}\{\ \}$ is the integration operator. Instead of attempting the approach of developing an inverse operation such that $\mathbf{G}^{-1}\{F\} = W$, let us operate with $\mathbf{G}\{\ \}$ on F and take the difference from F itself:

$$\Delta F_1 = F - \mathbf{G}\{F\}. \tag{4}$$

Repeat the above for ΔF_1:

$$\Delta F_2 = \Delta F_1 - \mathbf{G}\{\Delta F_1\}. \tag{5}$$

Figures 1 and 2 illustrate the operations given by eqs. (4) and (5). For the ith operation we have

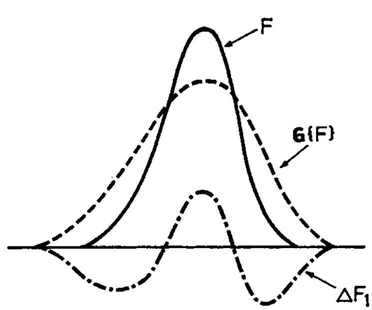


Fig. 1. $\Delta F_1 = F - \mathbf{G}[\mathrm{F}]$.

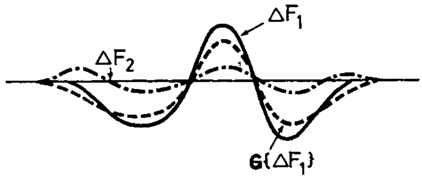


Fig. 2. $\Delta F_2 = \Delta F - \mathbf{G}[\Delta F_1]$.

$$\Delta F_i = \Delta F_{i-1} - \mathbf{G}\{\Delta F_{i-1}\}. \tag{6}$$

Now, sum up eq. (6) from $i = 1$ to N, denoting F by ΔF_0 for convenience:

$$F = \sum_{i=0}^{N-1} \mathbf{G}\{\Delta F_i\} + \Delta F_N \tag{7}$$

When the instrumental spreading is linear, i.e., by doubling an input the output is doubled, the order of summation and **G**-operation is interchangeable:

$$\sum_{i=0}^{N} \mathbf{G}\{\Delta F_i\} = \mathbf{G}\{\sum_{i=0}^{N} \Delta F_i\}. \tag{8}$$

Therefore it follows that

$$F = \mathbf{G}\{\sum_{i=0}^{N-1} \Delta F_i\} + \Delta F_N. \tag{9}$$

Now, by defining

$$W_i = \sum_{i=0}^{i} \Delta F_i \tag{10}$$

we obtain

$$F = \mathbf{G}\{W_{N-1}\} + \Delta F_N. \tag{11}$$

This equation indicates that W_∞ can be the solution for eq. (1) if ΔF_N converges uniformly to zero as $N \rightarrow \infty$.

It should be noted that the above operation may result in a $W(y)$ with small negative values when the iteration is stopped at a certain stage. To overcome this difficulty, the iterative procedure is changed to use the height ratio of F and F_i rather than their difference. This is now described under method 2.

Method 2

This method uses the fact that any GPC response F always has a broader distribution than the input distribution W. Hence, if a distribution F_i is broader than F, the assumed W_i must be sharpened to give a response closer to F. Using W_i and F_i, we introduce the $(i + 1)$th guess as follows:

$$W'_{i+1} = \left(\frac{F}{F_i}\right) W_i \tag{12}$$

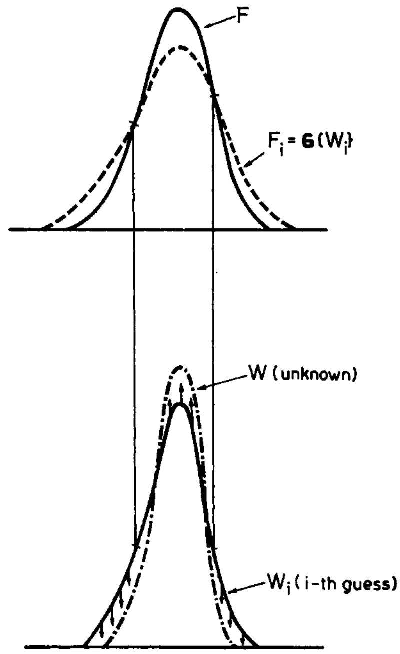


Fig. 3. Direction of correction by method 2.

This is equivalent to giving a correction ΔW_i on W_i such that

$$\Delta W_i = \left(\frac{F - F_i}{F_i}\right) W_i \tag{13}$$

$$W'_{i+1} = W_i + \Delta W_i. \tag{14}$$

It is necessary to normalize W'_{i+1}:

$$W_{i+1} = \mathbf{N}\{W'_{i+1}\} \tag{15}$$

where $\mathbf{N}\{\ \}$ is an integration operator normalizing with respect to area. The initial guess W_1 was started from F itself. Figure 3 illustrates the operation.

The above correction can never yield a negative value in W_{i+1}; however, it is possible that $(F - F_i)$ may not converge to zero in some cases.

EVALUATION OF METHODS 1 AND 2 AND COMPARISON WITH THE METHOD OF CHANG AND HUANG

Experimental GPC chromatograms with a precisely known instrumental spreading function are not available. Since it is essential to use an exact form of $G(v,y)$ to evaluate correction methods, synthesized $F(v)$ curves were used. The evaluation routine is illustrated in Figure 4.

Six different $F(v)$ were synthesized from two kinds of hypothetical $W(y)$, one having three peaks and another having two peaks and a shoulder. This latter one was used by Chang and Huang for their evaluation. The approximate shape of these $W(y)$ and $F(v)$ curves are shown in the first two rows of Table I. A Gaussian and a skewed shape was employed as examples of instrumental spreading functions.

Starting from a known set of $F(v)$ and $G(v,y)$, the $W(y)$ were recovered by method 1, method 2, and by the method of Chang and Huang. Table I

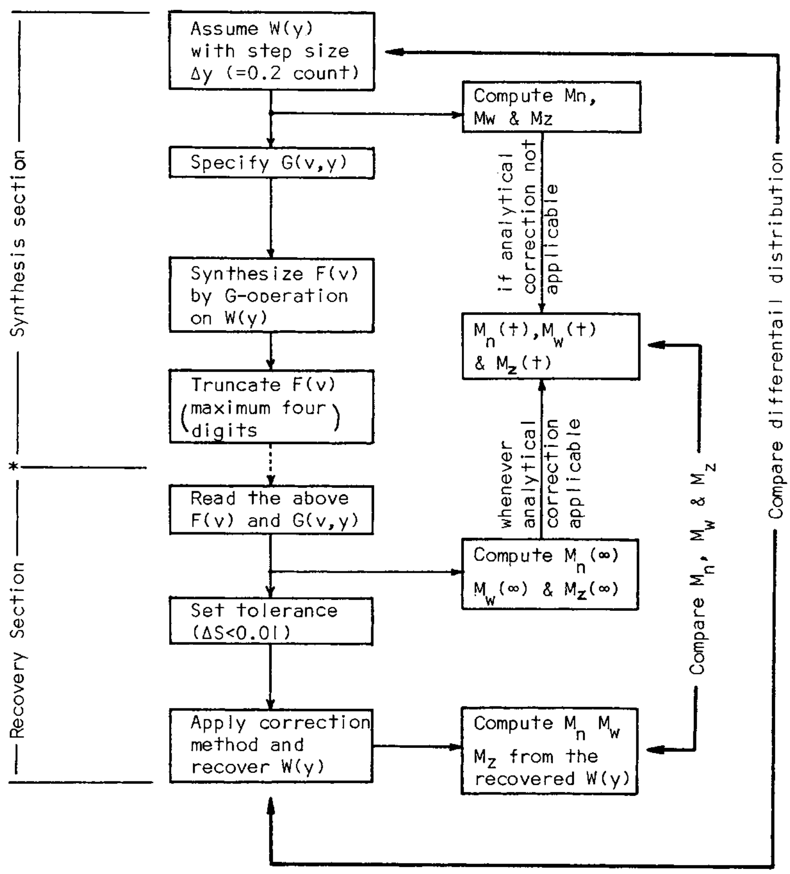


Fig. 4. Evaluation routine.

summarizes the comparison of corrected M_n, M_w, and M_z by each of the methods.

The heights of the synthesized $F(v)$ were truncated before use. The maximum number of figures used was four. In later evaluations, the last figure in the above was truncated, i.e., $F(v)$ had three significant figures at most. Table II lists this latter $F(v)$ for Gaussian spreading with $h = 0.5$. The recoveries from the less accurate $F(v)$ are compared with the first case. The figures in parentheses in Table I show corrected M_n, M_w, and M_z values for the less accurate $F(v)$.

TABLE I
Comparisons of Average Molecular Weights

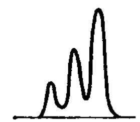
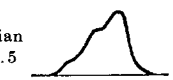
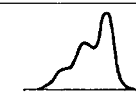
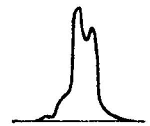
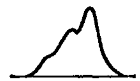
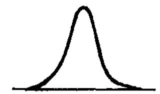
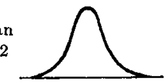
Original $W(y)$	3-Peak $W(y)$						$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$
							3.20	15.0	52.5
Starting set of $G(v,y)$ and $F(v)$	Case 1A Gaussian $h = 0.5$ 			Case 1B Gaussian $h = 0.2$ 			Case 1C Gaussian variable h (0.5–1.5) 		
Uncorrected ave. mol. wt.	$M_n(\infty) \times 10^{-3}$	$M_w(\infty) \times 10^{-3}$	$M_z(\infty) \times 10^{-3}$	$M_n(\infty) \times 10^{-3}$	$M_w(\infty) \times 10^{-3}$	$M_z(\infty) \times 10^{-3}$	$M_n(\infty) \times 10^{-3}$	$M_w(\infty) \times 10^{-3}$	$M_z(\infty) \times 10^{-3}$
	2.71	17.6	85.2	2.12	22.5	169.5	2.97	17.1	8.30
	(2.74)	(17.2)	(78.4)	(2.17)	(21.6)	(140.8)	(2.98)	(16.8)	(77.8)
Corrected ave. mol. wt.	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$
Method 1	3.19	14.9	54.7	3.10	15.0	23,321	3.20	14.9	51.4
	(3.28)	(15.0)	(31.2)	(2.75)	(16.9)	(62,667)	(3.21)	(14.9)	(54.1)
Method 2	3.18	15.1	53.7	3.13	15.5	59.7	3.21	15.3	55.3
	(3.18)	(15.0)	(52.7)	(3.15)[a]	(15.8)[a]	(60.2)[a]	(3.21)	(15.2)	(54.0)
Method of Chang and Huang	3.08	15.8	96.0	3.04	16.2	125.6		Not applicable	
	(3.09)	(15.5)	(95.8)	(3.03)[a]	(16.4)[a]	(159.1)[a]			
Analytical (or true)	3.20	14.9	51.8	3.21	14.9	48.9		Not applicable	
	(3.23)	(14.6)	(47.7)	(3.28)	(14.3)	(40.6)			

TABLE I (*continued*)

Original $W(y)$	3-Peak $W(y)$			Chang and Huang's $W(y)$ 			$M_n \times 10^{-3}$ 237	$M_w \times 10^{-3}$ 603	$M_z \times 10^{-3}$ 2,043
Starting set of $G(v,y)$ and $F(v)$	Case 1D general shape $h = 0.5$ $\mu_3 = 1.0$ 			Case 2A Gaussian $h = 0.5$ 			Case 2B Gaussian $h = 0.2$ 		
Uncorrected ave. mol. wt.	$M_n(\infty) \times 10^{-3}$	$M_w(\infty) \times 10^{-3}$	$M_z(\infty) \times 10^{-3}$	$M_n(\infty) \times 10^{-3}$	$M_w(\infty) \times 10^{-3}$	$M_z(\infty) \times 10^{-3}$	$M_n(\infty) \times 10^{-3}$	$M_w(\infty) \times 10^{-3}$	$M_z(\infty) \times 10^{-3}$
	2.65	17.8	79.2	201	710	3,267	158	896	5,574
	(2.69)	(17.4)	(75.1)	(214)	(675)	(2,486)	(172)	(821)	(3,594)
Corrected ave. mol. wt.	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$
Method 1	3.20	15.9	27,663	238	599	622	227	595	69,269
	(3.17)	(15.5)	(16,049)	(254)	(574)	(2,206)	(284)	(492)	(201,750)
Method 2	3.16	14.9	55.0	235	613	2,382	233	614	2,919
	(3.16)[a]	(14.7)[a]	(53.7)[a]	(242)	(586)	(1,864)	(243)[a]	(592)[a]	(2,667)[a]
Method of Chang and Huang		Not applicable		213	635	4,291	220	653	3,165
				(221)[a]	(623)[a]	(2,800)[a]	(228)[a]	(611)[a]	(2,503)[a]
Analytical (or true)	3.23	15.5	60.0	238	601	1,987	239	592	1,608
	(3.27)	(15.3)	(56.9)	(252)	(572)	(1,512)	(260)	(543)	(1,037)

[a] Did not satisfy $\Delta S < 0.01$.

TABLE II
Numerical Values of $F(v)$ Used in Case 1A and Case 2A[a]

Case 1A				Case 2A			
V	$F(v)$	V	$F(v)$	V	$F(v)$	V	$F(v)$
23.0	0	30.0	120	16.0	0	23.0	93
23.2	0	30.2	121	16.2	0	23.2	98
23.4	0	30.4	120	16.4	0	23.4	101
23.6	1	30.6	120	16.6	0	23.6	102
23.8	1	30.8	121	16.8	0	23.8	103
24.0	2	31.0	122	17.0	0	24.0	102
24.2	3	31.2	125	17.2	1	24.2	100
24.4	5	31.4	131	17.4	1	24.4	96
24.6	7	31.6	137	17.6	1	24.6	92
24.8	10	31.8	145	17.8	2	24.8	87
25.0	14	32.0	153	18.0	2	25.0	81
25.2	18	32.2	160	18.2	2	25.2	74
25.4	22	32.4	165	18.4	3	25.4	67
25.6	27	32.6	168	18.6	4	25.6	60
25.8	32	32.8	168	18.8	4	25.8	52
26.0	38	33.0	164	19.0	5	26.0	45
26.2	43	33.2	156	19.2	6	26.2	38
26.4	47	33.4	145	19.4	7	26.4	32
26.6	51	33.6	132	19.6	8	26.6	27
26.8	54	33.8	117	19.8	10	26.8	22
27.0	57	34.0	101	20.0	12	27.0	18
27.2	59	34.2	84	20.2	14	27.2	14
27.4	61	34.4	69	20.4	17	27.4	12
27.6	63	34.6	55	20.6	20	27.6	9
27.8	65	34.8	42	20.8	24	27.8	8
28.0	69	35.0	32	21.0	29	28.0	6
28.2	73	35.2	23	21.2	34	28.2	5
28.4	79	35.4	17	21.4	39	28.4	4
28.6	85	35.6	11	21.6	46	28.6	3
28.8	92	35.8	8	21.8	53	28.8	3
29.0	99	36.0	5	22.0	60	29.0	2
29.2	106	36.2	3	22.2	67	29.2	2
29.4	112	36.4	2	22.4	75	29.4	1
29.6	116	36.6	1	22.6	82	29.6	1
29.8	119	36.8	0	22.8	88	29.8	1
						30.0	0

[a] Retention volume v in counts and $F(v)$ not normalized.

A linear calibration curve, $\log_{10} M = (46.0 - v)/4.0$, was used to obtain $M_n(t)$, $M_w(t)$, and $M_z(t)$ analytically from uncorrected values $M_n(\infty)$, $M_w(\infty)$, and $M_z(\infty)$. A step size of 0.2 count was used for all the examples shown in Table I. This step is sufficient to obtain M_z to $\pm 0.5\%$ for the present examples. When the analytical solution is not applicable, M_n, M_w, and M_z directly computed from the assumed $W(y)$ are considered true values. The differences between molecular weight averages obtained using the analytical solution and $W(y)$ directly are mainly due to errors in synthesis and truncation of $F(v)$. When the resolution factor h is large, these differences are not significant.

The iteration in each of the correction methods was carried out until the following tolerance was satisfied:

$$\Delta S = \int_0^\infty |F(v) - F_i(v)| dv \leq 0.01.$$

This corresponds to the area difference between the two chromatograms of less than 1% of the total area under $F(v)$. In the case where repeated iterations failed to decrease ΔS but rather gave an oscillation in ΔS without satisfying the tolerance, the iteration was stopped when the first minimum in ΔS was obtained.

Cases 1A and 2A: Gaussian Spreading Functionwith h = 0.5

These are examples of a symmetrical and uniform instrumental spreading function. For a resolution factor of h = 0.5, the corrections to M_n, M_w, and M_z are about 15%, 20%, and 60%, respectively.

The recovered $W(y)$ curves for case 1A by the three methods are compared with the original $W(y)$ in Figure 5. All the methods gave a good

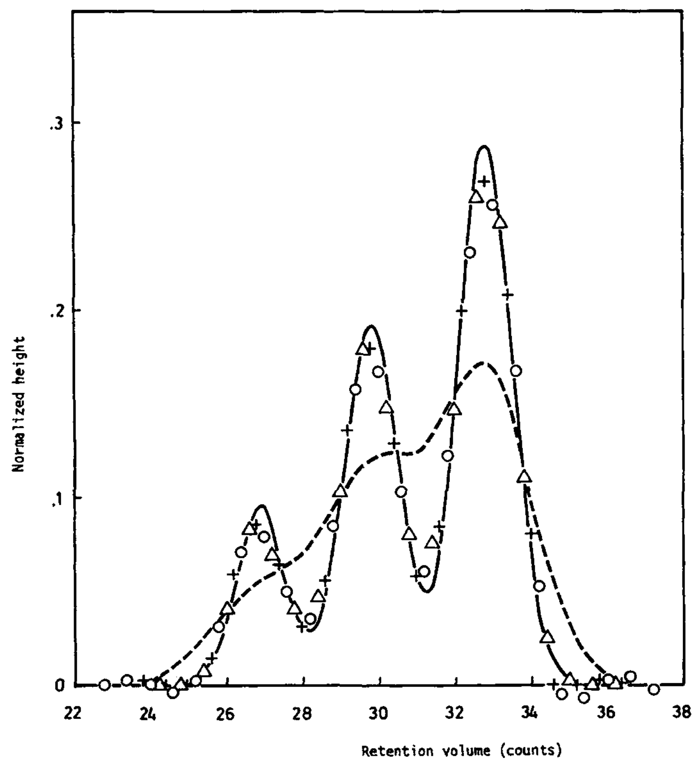


Fig. 5. Recovery of $W(y)$, case 1A (h = 0.5): (——) original $W(y)$; (- - -) $F(v)$; (O) method 1; (Δ) method 2; (+) method of Chang and Huang.

smooth recovery except for somewhat blunt peaks and small fluctuations at both ends of the chromatogram.

Method 1 and method 2 gave corrected M_n and M_w to within $\pm 2\%$ of their true values, and the method of Chang and Huang gave them to within $\pm 5\%$. As for corrected M_z, the first two methods gave $\sim 5\%$ larger values than the true one while the latter method gave an $\sim 80\%$ error.

Reduction of the accuracy in reading $F(v)$ to a maximum of three figures still resulted in a good recovery of the original $W(y)$ values similar to those shown in Figure 5. The errors in corrected M_n and M_w also remained about

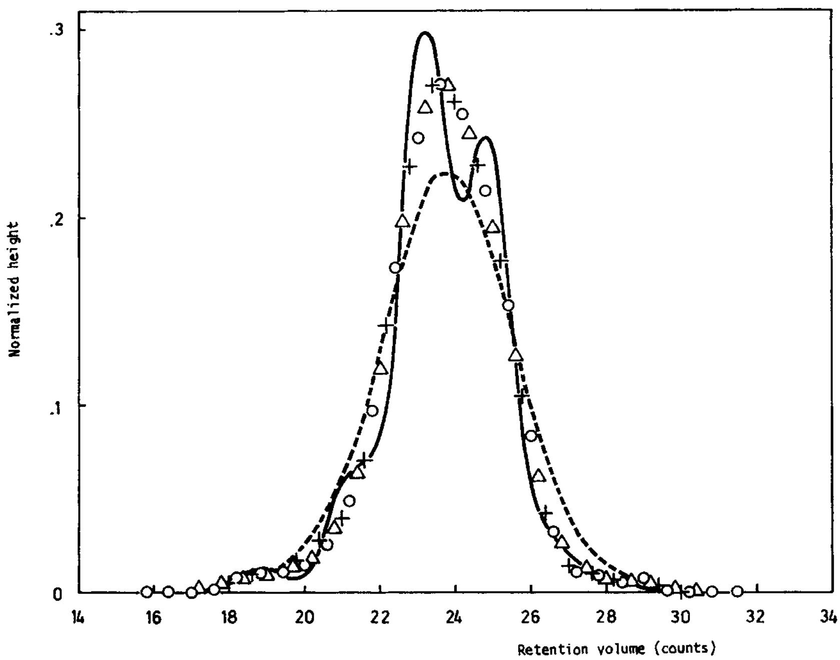


Fig. 6. Recovery of $W(y)$, case 2A ($h = 0.5$): (——) original $W(y)$; (- - -) $F(v)$; (O) method 1; (Δ) method 2; (+) method of Chang and Huang.

the same as before. However, the error in the corrected M_z increased to $\sim 35\%$ for method 1, to $\sim 10\%$ for method 2, and to $\sim 100\%$ for the method of Chang and Huang.

Figure 6 shows the comparison of the recoveries for case 2A. Neither of the methods could recover a $W(y)$ with two peaks. Increased number of iterations with a smaller tolerance ($\Delta S \leq 0.0025$) resulted in slightly better recoveries, with the second peak recovered as a shoulder in all three methods. The reduction of the step size for the whole evaluation routine from 0.2 to 0.1 count did not give any significant improvement. The values of the corrected M_n and M_w were still within $\pm 2\%$. The method of Chang and Huang gave these to within $\pm 10\%$. The corrected M_z, however, differed significantly from the true value. The best M_z obtained was $\sim 20\%$ in error; this was by method 2. When $F(v)$ was truncated still further by one figure, all three methods gave oscillations in the main portion of the recovered $W(y)$. The method of Chang and Huang gave an oscillation in the value of ΔS from the beginning and could not satisfy the tolerance despite their data smoothing process before the iteration procedure. However, once more the corrected M_n and M_w of the three methods are reasonable even though the recovered $W(y)$ appears to be significantly different from the true $W(y)$.

Cases 1B and 2B: Gaussian Spreading Functionwith $h = 0.2$

A set of GPC columns having a Gaussian spreading function with an h value as low as 0.2 may be considered unsatisfactory. However, if the slope of the molecular weight calibration curve is small, this column set may give satisfactory separations. The use of a small resolution factor provides a much more difficult test for any numerical method of recovering $W(y)$.

Recovered $W(y)$ for case 1B is shown in Figure 7. Although the recoveries were smooth and the peaks were shown to exist, the recovery of $W(y)$ as a

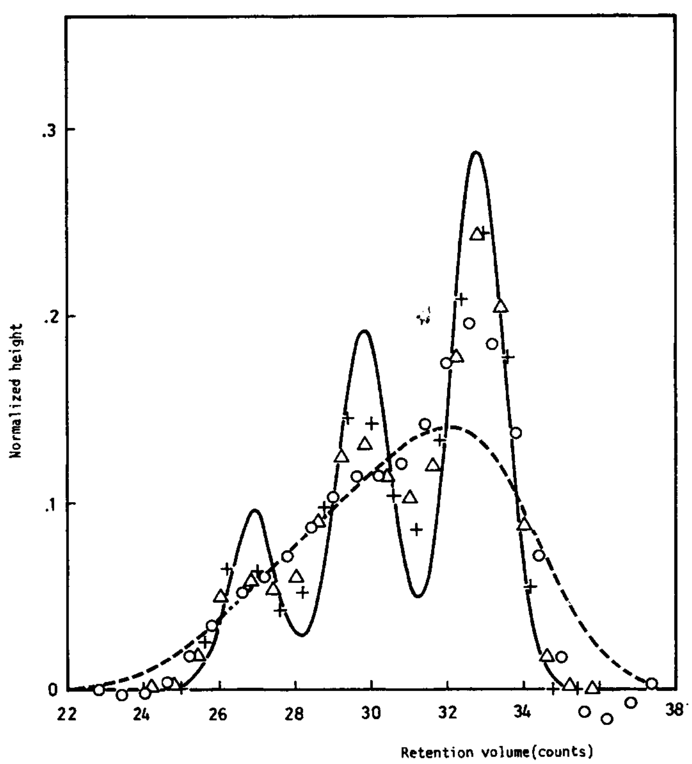


Fig. 7. Recovery of $W(y)$, case 1B ($h = 0.2$): (——) original $W(y)$, (- - -) $F(v)$; (O) method 1; (Δ) method 2; (+) method of Chang and Huang.

whole was rather poor. The method of Chang and Huang gave a slightly better recovery than the other two methods; however, this advantage was lost when corrected M_n and M_w were compared. Methods 1 and 2 gave smaller errors in $M_n(\sim 3\%)$ and $M_w(\sim 5\%)$. Only method 2 gave M_z within a $\sim 20\%$ error. A significant improvement was observed in the recovered $W(y)$ by all three methods when the iteration was continued until a smaller tolerance $\Delta S \leq 0.0025$ was satisfied. The magnitude of recovered peaks in this case was much closer to the original ones.

The recoveries for case 2B were about the same as for case 2A. No significant difference in the three methods were observed. Two peaks were not detected in the recovered $W(y)$, since with a higher resolution ($h = 0.5$), neither method could show their existence. Methods 1 and 2 again gave smaller errors in $M_n(\sim 3\%)$ and $M_w(\sim 5\%)$ than the method of Chang and Huang. It can be seen that the recovered M_z by method 1 is out of the ball park for both cases 1B and 2B. Method 2 gave the smallest errors in M_z for both cases.

Only method 1 could reach $\Delta S \leq 0.01$ when the accuracy in reading $F(v)$ was reduced one digit. But corrected M_n and M_w by this method were not

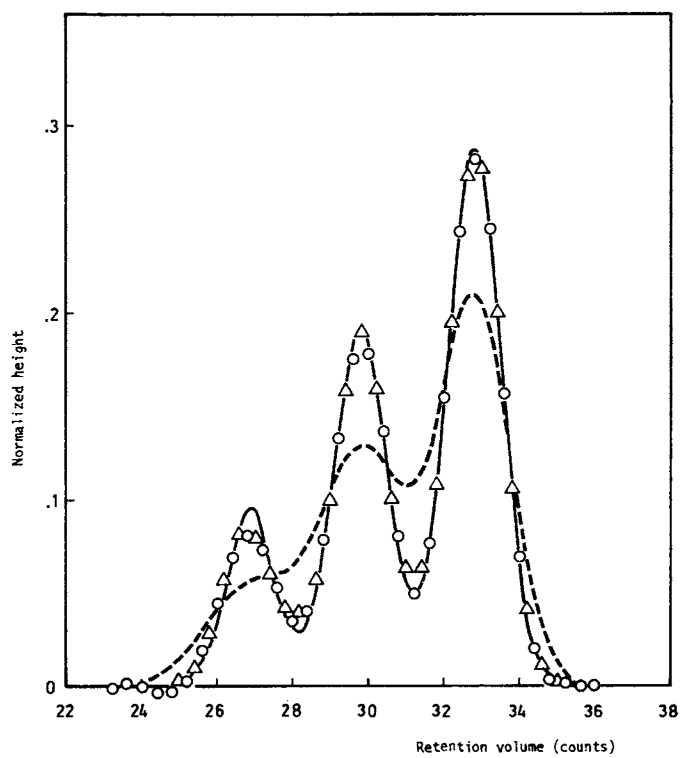


Fig. 8. Recovery of $W(y)$, case 1C (avriable h): (——) original $W(y$; (- - -) $F(v)$; (O) method 1; (Δ) method 2.

any better than those of the other two methods in this instance. Oscillations in the recovered $W(y)$ were found for all three methods.

Case 1C: Gaussian Spreading Function with Variable *h*.

This is an example of an instrumental spreading function which is symmetrical but nonuniform. For the case of nonuniform G, neither the analytical solution nor the method of Chang and Huang apply. The change of h with respect to input species was given by the following quadratic equation:

$$h = 4.879 - 0.373y + 0.008y^2 \tag{16}$$

This gives h values from 0.5 to 1.5 in the retention volume range of the given $F(v)$. Uncorrected M_n, M_w, and M_z show about 10, 20, and 60% deviation from their true values in this example.

Good recoveries of $W(y)$ by both method 1 and method 2 can be seen in Figure 8. Corrected M_n and M_w differ only by $\sim$2% from the true ones, and M_z differs by $\sim$5%. A reduction of the reading accuracy of $F(v)$ did not affect the recovery of $W(y)$ and the corrected molecular weight averages.

Case 1D: General Instrumental Spreading Function[11,10] with $h = 0.5$ and $\mu_3 = 1.0$

This gives an example of a nonsymmetrical, uniform spreading function. Only the two shape parameters h and μ_3 were used with the remaining ones set equal to zero. The combination of $h = 0.5$ and $\mu_3 = 1.0$ gives a spreading function significantly skewed toward higher retention volumes. Because the two-parameter expression in the general spreading function is essentially a cubic function, small negative values appear at about 2.5 counts from its peak position. These negative portions were set to zero, and the shape was normalized for use in the $F(v)$ synthesis and with the correction methods. Deviation of uncorrected M_n, M_w, and M_z from the true values were nearly the same as with case 1A where a Gaussian spreading function with $h = 0.5$ was used.

Figure 9 compares the recovered $W(y)$ with the original one. The shape recovered seems slightly poorer than for case 1A, with the recovered peaks sharper than the true ones. Corrected M_n and M_w had errors within $\pm$5%. Corrected M_z by method 1 was again out of the ball park, while method 2 gave a reasonable value ($\sim$10% error). When the $F(v)$ reading was reduced in accuracy by one digit, both methods gave oscillations in the main portion of the recovered $W(y)$. Again, the corrected molecular weight averages seemed equally good as those obtained from a more accurate $F(v)$.

Computation Time

Computation times required for method 1, method 2, and the method of Chang and Huang are compared in Table III for four cases. It was found

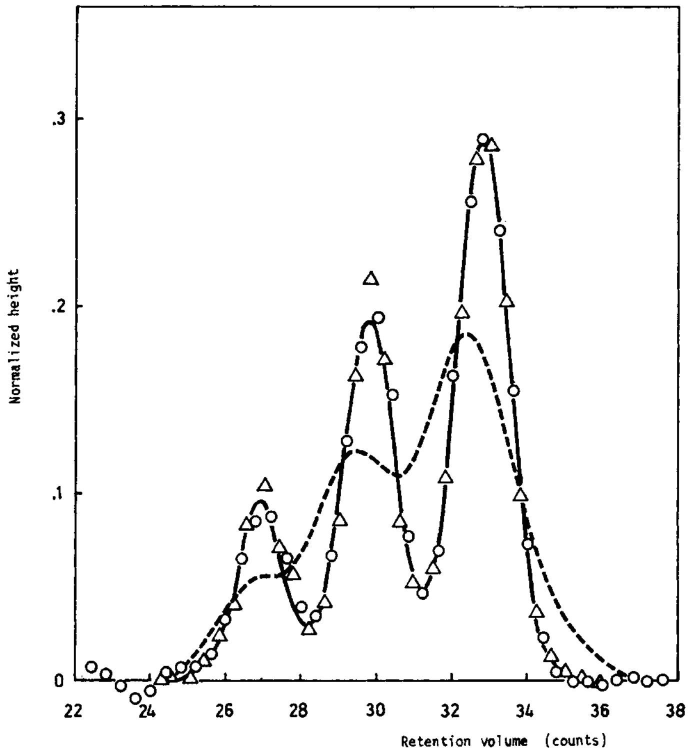


Fig. 9. Recovery of $W(y)$, case 1D ($h = 0.5$, $\mu_3 = 1.0$): (——) original $W(y)$; (- - -) $F(v)$; (○) method 1; (△) method 2.

that the method of Chang and Huang and method 2 are approximately the same, while method 1 required more time due to its **G**-operation beyond the retention volume range of $F(v)$. Fifty more zero data points on $F(v)$ were added to both ends of the chromatogram in the last case to enable iterative **G**-operations. In each of the methods, the most time-consuming part is the multitude of **G**-operations necessary. However, the number of iterations to reach the specified tolerance does not directly represent the computation time because of the differences in operation in each of the methods. The present tolerance $\Delta S \leq 0.01$ was found similar to the one recommended

TABLE III
Comparisons of Computation Time and Number of Iterations[a]

	Case 1A	Case 1B	Case 2A	Case 2B
Method 1	14.9 (14)	17.5 (12)	10.5 (5)	15.8 (10)
Method 2	9.6 (17)	21.5 (47)	7.3 (6)	9.3 (10)
Method of Chang and Huang	7.2 (3)	18.0 (17)	7.0 (2)	6.7 (2)

[a] CDC6400 Computer, with time in seconds. First value in columns shows time in seconds; value in parentheses is the number of iteration to reach $\Delta S < 0.01$.

by Chang and Huang. This appeared reasonable in recovering $W(y)$ and correcting M_n, M_w, and M_z for a resolution factor h higher than 0.5; however, it may be necessary to reduce it at lower resolution to obtain good recoveries for differential distributions.

The digital computer used for all of the calculations in this paper was the CDC6400.

CONCLUSIONS

Two numerical methods of solving Tung's axial dispersion equation have been developed and evaluated. A simultaneous evaluation of the method of Chang and Huang was made. At the time of this investigation, their method appeared to be the most promising one available in the literature. For all six different GPC responses investigated, none of the methods adequately recovered all of the corrected differential distributions. However, the present method 1 and method 2 appear to work as well as the method of Chang and Huang where their method is applicable. Our two methods have wider applicability than the method of Chang and Huang. Since method 2 ensures positive $W(y)$ and requires relatively shorter computation times than method 1, method 2 is recommended for the recovery of corrected differential distributions. However, the uniform convergence of ΔS to zero by method 1 is a very desirable feature.

A computer program, deck, and listing in FORTRAN IV will be provided upon request. There is a \$50.00 service charge. Communications should be sent to one of the authors (A. E. H.).

Nomenclature

$F(v)$	GPC output chromatogram
$F_1(v)$	$\mathbf{G}\{F(y)\}$
$\Delta F_0(v)$	$F(v)$
$\Delta F_i(v)$	$\Delta F_{i-1}(v) - \mathbf{G}\{\Delta F_{i-1}(y)\}$
$G(v,y)$	instrumental spreading function
$\mathbf{G}\{\ \}$	integral operator given by eq. (1)
$\mathbf{N}\{\ \}$	normalizing operator with respect to area
ΔS	area surrounded by two chromatograms F and F_i, $\int_0^\infty \lvert F(v) - F_i(v)\rvert dv$
$W(y)$	molecular weight distribution in terms of molecular species y (retention volume)
$W_i(y)$	ith guess for $W(y)$
h,μ_3	spreading parameters
v,y	retention volume

The authors wish to thank Imperial Oil Company Limited, Toronto, Canada, and Nalco Chemical Company, Chicago, for financial support for this investigation.

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Received January 8, 1971
Revised February 25, 1971