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Polymer Reactors and Molecular Weight Distribution. VIII. A Method of Interpreting Skewed GPC Chromatograms

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Synopsis

A new method of interpreting GPC chromatograms which accounts for skewing and symmetrical axial dispersion has been developed. General relationships for a symmetrical axial dispersion correction and for a skewing correction are derived.

The method has been verified experimentally for unimodal chromatograms and linear calibration curves over a wide range of GPC operating conditions, polymer molecular weights and polydispersities. Measurements of h and skewing factors were obtained by a once-through technique. The need for performing reverse flow experiments has been eliminated. Artificial oscillations in the corrected chromatogram due to step size (Method of Pierce-Armonas), and to number of terms in a polynomial expansion (Method of Tung and Method of Smith) are eliminated.

The method has yet to be evaluated for nonlinear calibration curves and multi-modal distributions. However, suggestions for its application in these circumstances are presented.

INTRODUCTION

Molecular weight averages by GPC are often not in agreement with those obtained by absolute measurement and therefore several methods of correcting the GPC molecular weight distribution for imperfect resolution have been proposed. In a recent evaluation by Duerksen and Hamielec,[1] of the Tung Polynomial Expansion Method, Smith's Method, the Method of Hess and Kratz, and the Method of Pickett, Cantow and Johnson, it was found that all of these methods were subject to artificial oscillations in both the corrected chromatogram and the corrected differential distribution. This was particularly evident at low resolution factors (large resolution correction). It is important to eliminate these oscillations for often it is necessary to establish the existence of a real shoulder or peak.

Another outstanding disadvantage of these methods was their failure to adequately account for skewing.[3] Skewing is defined as the shifting of the GPC chromatogram to higher elution volumes relative to the true calibration curve. It is significant at intermediate and at high molecular weights. Its importance will vary from polymer to polymer. When skewing was not

present Tung's method was preferred. Recently Pierce and Armonas[6] presented a method based on a Fourier Transform solution of Tung's Integral Dispersion Equation. This method, like Tung's, assumes a Gaussian shape for the chromatograms of single species. It also does not account for skewing.

In order to evaluate this method[6] and to explore possibilities of using the h factor and linear calibration curve constants to correct GPC chromatograms the following computer programs were developed in this investigation:

(*1*) Linear Calibration Curve Search I
- (*a*) h is assumed infinite
- (*b*) Mn and Mw are read in with the GPC chromatogram heights,
- (*c*) C_1 and C_2 in the relation "$v = C_1 - C_2 \log_{10} M$" are searched for using a Rosenbrock two variable search until the correct Mn and Mw are calculated. The differential distribution yielding this Mn and Mw is also printed out. An evaluation of this program is available.[4]

(*2*) Pierce-Armonas Resolution Correction
A constant, linear or quadratic h factor may be used.

(*3*) Linear Calibration Curve Search II
This is the same as (1) above except that a known h is read in and Pierce-Armonas resolution correction is used with a two variable Rosenbrock search

(*4*) h Factor Search
This is similar to (3) above except that a constant or variable h factor is searched for by using either a Fibonacci Search or a Rosenbrock Search.

In the study which followed a systematic experimental investigation of skewing was made at flow rates as high as 8.4 ml/min and molecular weights up to one million. It was soon evident that some method of correcting for skewing had to be developed before methods which corrected for symmetrical axial dispersion would yield correct results. Even then, artificial oscillations would render these methods of limited use.

A solution to the problem of skewing and of artificial oscillation was accomplished by developing a new method of correction where first the molecular weight averages are obtained and then the differential distribution.

THEORETICAL DEVELOPMENT

From Duerksen and Hamielec's study[1] it was evident that the h factor used in a method which assumed Gaussian shape for the chromatograms of monodisperse standards consistently lowered the Mw and raised the Mn from the infinite resolution values to a degree directly related to the decrease in h. When the ratio of the corrected to the uncorrected Mn and the corrected to the uncorrected Mw was plotted against GPC residence time an almost symmetrical plot resulted (See Fig. 11, Ref. 1). These results sug-

gested the relationships given in eqs. (1) and (2) for both skewed and unskewed chromatograms. The chromatograms of Code 8 in particular had significant skewing.

$$\frac{Mn(h)}{Mn(\infty)} = 1 + k(h) \tag{1}$$

$$\frac{Mw(h)}{Mw(\infty)} = 1 - k(h) \tag{2}$$

where $Mn(\infty)$ is the number-average molecular weight found by assuming perfect resolution. $Mn(h)$ is the number-average molecular weight found assuming symmetrical Gaussian dispersion with resolution factor h. Similar definitions apply to the weight-average molecular weights.

By addition of (1) and (2), a general relation (3) was obtained.

$$\frac{Mn(h)}{Mn(\infty)} + \frac{Mw(h)}{Mw(\infty)} = 2 \tag{3}$$

To test the validity of eqs (1) and (2) for narrow and broad GPC chromatograms over a wide range of molecular weights and resolution factors the Pierce-Armonas solution was used to generate resolution corrected number and weight-average molecular weights. This numerical procedure proved the validity of eqs. (1), (2), and (3). This quickly led to an analytical solution by Hamielec and Ray[5] using a Laplace transformation.

Derivation of the Symmetrical Axial Dispersion Correction

Tung's integral equation is given by:

$$F(v) = \int_{V_a}^{V_b} W(y)(h/\pi)^{1/2} \exp(-h(v - y)^2)dy \tag{4}$$

Also, from the definition of the h corrected molecular weight averages ($Mn(h)$ and $Mw(h)$) and the molecular weight averages ($Mn(\infty)$ and $Mw(\infty)$) of the GPC chromatogram calculated at infinite resolution the following ratios may be written:

$$\frac{Mw(h)}{Mw(\infty)} = \frac{\int_{-\infty}^{\infty} W(v)M(v)dv}{\int_{-\infty}^{\infty} F(v)M(v)dv} \tag{5}$$

$$\frac{Mn(h)}{Mn(\infty)} = \frac{\int_{-\infty}^{\infty} F(v)/M(v)dv}{\int_{-\infty}^{\infty} W(v)/M(v)dv} \tag{6}$$

where $W(v)$ is the corrected chromatogram, $F(v)$, is the observed chromatogram and $M(v)$ is the molecular weight.

If it is then assumed that the GPC calibration curve can be represented by the following equation:

$$M(v) = M = D_1 e^{-D_2 v} \tag{7}$$

where D_1 and D_2 are positive constants and v is the elution volume. Then,

$$v = \frac{1}{D_2} \ln D_1 - \frac{1}{D_2} \ln M \tag{8}$$

Since the conventional calibration curve is

$$v = C_1 - C_2 \log_{10} M \tag{9}$$

then

$$C_1 = \frac{1}{D_2} \ln D_1 \tag{10}$$

and

$$C_2 = \frac{2.303}{D_2} \tag{11}$$

Substituting (7) into (5) gives

$$\frac{Mw(h)}{Mw(\infty)} = \frac{\int_{-\infty}^{\infty} W(v) e^{-D_2 v} \, dv}{\int_{-\infty}^{\infty} F(v) e^{-D_2 v} \, dv} \tag{12}$$

Whose solution by Laplace transform is

$$\frac{Mw(h)}{Mw(\infty)} = e^{-D_2^2/4h} = e^{-A/h} \tag{13}$$

Similarly,

$$\frac{Mn(h)}{Mn(\infty)} = e^{D_2^2/4h} = e^{A/h} \tag{14}$$

where

$$A = \frac{(2.303)^2}{4C_2^2} = \frac{1.326}{C_2^2}$$

It should be noted here that C_2 is the value used in (9) which obtained $Mn(\infty)$ at infinite resolution.

Derivation of the Skewing Correction

If we insist that after resolution correction the molecular weight averages correspond to the absolute values ($Mn(t)$ and $Mw(t)$) then

$$Mn(t) = Mn(h) \tag{15}$$

$$Mw(t) = Mw(h) \tag{16}$$

and

$$Mn(sk) = Mn(\infty) \tag{17}$$

$$Mw(sk) = Mw(\infty) \tag{18}$$

To obtain a criterion for skewing we add (13) and (14):

$$\frac{Mn(t)}{Mn(\infty)} + \frac{Mw(t)}{Mw(\infty)} = e^{A/h} + e^{-A/h} \tag{19}$$

For a skewed chromatogram

$$\frac{Mn(t)}{Mn(\infty)} + \frac{Mw(t)}{Mw(\infty)} \neq e^{A/h} + e^{-A/h} \tag{20}$$

Therefore define the skewing factor sk by:

$$\frac{Mw(t)}{Mw(\infty)} + \frac{Mn(t)}{Mn(\infty)} - (e^{A/h} + e^{-A/h}) = sk \tag{21}$$

Now, since the only difference between the distribution corrected for skewing and that uncorrected, is a change in the calibration curve constants then if we assume the calibration curve to be

$$M(v) = D(1,sk)\, e^{-D(2,sk)v} \tag{22}$$

for the skewing corrected distribution and,

$$M(v) = D(1,t)\, e^{-D(2,t)v} \tag{23}$$

for the uncorrected distribution

$$\frac{Mw(sk)}{Mw(\infty)} = \frac{D(1,sk)\int_{-\infty}^{\infty} F(v)\, e^{-D(2,sk)v}\, dv}{D(1,t)\int_{-\infty}^{\infty} F(v)\, e^{-D(2,t)v}\, dv} \tag{24}$$

where

$$D(1,t) = e^{C(1,t)D(2,t)}$$

$$D(2,t) = \frac{2.303}{C(2,t)}$$

$$D(1,sk) = e^{C(1,sk)D(2,sk)}$$

$$D(2,sk) = \frac{2.303}{C(2,sk)}$$

and where $C(1,t) = C_1$ and $C(2,t) = C_2$ (the true linear calibration curve constants as obtained from peak elution volumes).

Now if we assume that $C(2,sk) = C(2,t)$, that is, that the main purpose of the skewing correction is a change in $C(1,t)$ (i.e., a shifting of the chromatogram to account for skewing) then the integrations are equivalent and

$$\frac{Mw(sk)}{Mw(\infty)} = \frac{D(1,sk)}{D(1,t)}$$

$$= \frac{\exp\,(C(1,sk)D(2,sk))}{e^{C(1,t)D(2,t)}}$$

$$= \exp\,(D(2,t)\,(C(1,sk) - C(1,t))) \tag{25}$$

Similarly

$$\frac{Mn(sk)}{Mn(\infty)} = \frac{Mw(sk)}{Mw(\infty)} \tag{26}$$

Then

$$B = \frac{Mn(sk)}{Mn(\infty)} = \frac{Mw(sk)}{Mw(\infty)} = \exp\,(2.303/C_2\,(C(1,sk) - C(1,t))) \tag{27}$$

$$\frac{2.303}{C_2}\,(C(1,sk) - C(1,t)) = \ln B$$

$$= 2.303 \log_{10} B$$

$$C(1,sk) = C_1 + C_2 \log_{10} B$$

Substituting (15), (16), (17), and (18) into (13) and (14) and dividing through by $Mw(\infty)$ and $Mn(\infty)$, respectively, results in (28) and (29).

$$\frac{Mn(t)}{Mw(\infty)} = Be^{-A/h} \tag{28}$$

$$\frac{Mn(t)}{Mn(\infty)} = Be^{A/h} \tag{29}$$

Add (28) and (29)

$$sk + (e^{-A/h} + e^{A/h}) = B(e^{-A/h} + e^{A/h})$$

$$B = \frac{sk}{(e^{-A/h} + e^{A/h})} + 1 \tag{30}$$

$$C(1,\, sk) = C_1 + C_2 \log_{10} \left\{\frac{sk}{e^{-A/h} + e^{A/h}} + 1\right\} \tag{31}$$

Using Taylor series expansion in (31)

$$C(1,\, sk) \simeq C_1 + C_2 \log_{10} \left(1 + \frac{1}{2}\, sk\right) \tag{32}$$

Determination of *sk* from Standards

sk is determined after injection of narrow or broad standards directly from its definition (eq. (21)).

Determination of h from Standards

In general, from (28), (29), and (30) and using Taylor series approximation:

$$Mw(t) = Mw(\infty)\left(1 + \frac{1}{2}sk\right)e^{-A/h} \tag{33}$$

$$Mn(t) = Mn(\infty)\left(1 + \frac{1}{2}sk\right)e^{A/h} \tag{34}$$

Divide (33) by (34) and let

$$P(\infty) = \frac{Mw(\infty)}{Mn(\infty)} \tag{35}$$

$$P(t) = \frac{Mw(t)}{Mn(t)} \tag{36}$$

Then

$$P(t) = P(\infty)\,e^{-2A/h} \tag{37}$$

$$h = \frac{2A}{\ln P(\infty) - \ln P(t)} \tag{38}$$

or, by making use of the Taylor series expansion of e^x assuming third and larger terms negligible:

$$h = \frac{2.652}{C_2^2}\left(\frac{P(\infty)}{P(\infty) - P(t)}\right) \tag{39}$$

Determination of Corrected Molecular Weight Averages for an Unknown

The equations which apply are similar to (33) and (34):

$$Mw(sk,h) = Mw(\infty)\left(1 + \frac{1}{2}sk\right)e^{-A/h} \tag{40}$$

$$Mn(sk,h) = Mn(\infty)\left(1 + \frac{1}{2}sk\right)e^{A/h} \tag{41}$$

Where $Mw(sk,h)$ and $Mn(sk,h)$ are the corrected weight and number-average molecular weight, respectively.

If sk and h have been determined correctly then

$$Mw(t) = Mw(sk,h) \tag{42}$$

and

$$Mn(t) = Mn(sk,h)$$

EXPERIMENTAL

To study skewing in GPC chromatograms over a range of conditions polystyrene standards and polystyrene samples produced by free radical

TABLE I
Description of GPC Column Combinations[a]

Column combination code no.	No. of columns in series	Maximum rated porosities, straight chain angstroms					Flow rate ml/min	Combination plates/ (ODCB)
		Column 1	Column 2	Column 3	Column 4	Column 5		
8	2	10^5	800	—	—	—	2.0	470
5	3	10^5	10^4	800	—	—	1.0	615
13	3	10^5	10^4	800	—	—	3.0	467
14	3	10^5	10^4	800	—	—	6.0	—
15	3	10^5	10^4	800	—	—	8.4	—
12	5	7×10^6	10^6	10^5	10^4	800	2.0	—
16	5	7×10^6	10^6	10^5	10^4	800	3.0	—

[a] The GPC operating temperature for all column combinations was 24 ± 2°C.

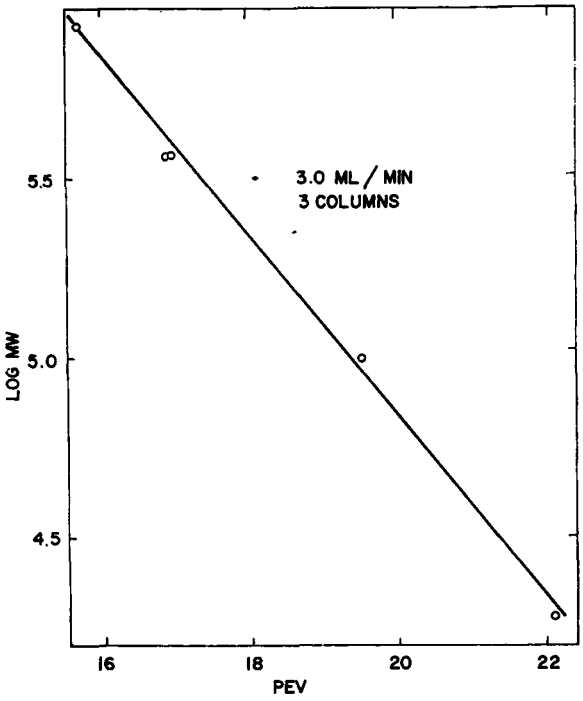


Fig. 1. Code 13 calibration curve.

polymerization ranging as high as one million in molecular weight were analyzed with three different column combinations and five different flow rates as described in Table I. The data used for Codes 8, 5 and 12 as well as the reverse flow results have been previously obtained for other studies by Duerksen and Hamielec.[1]

The GPC was the standard Waters unit Model 100. The solvent was tetrahydrofuran (THF) and the operating temperature was 24 ± 2°C. One ml of solution was injected. For Codes 5, 8 and 12 the concentration was 0.1%. For the other codes the concentration was generally 0.05%. The lower concentrations were made possible by the installation of the Waters R-4 conversion kit. The Waters digital translator was also installed. At flow rates above 2 ml/min reading of the chromatograms was accomplished with the aid of a combined linear and quadratic interpolation

TABLE II
Variation of Eluent Volume/Count with Flow Rate

Flow rate (ml/min)	EV (ml)	Flow rate (ml/min)	EV (ml)
0	4.75	3.0	4.89
1.0	4.77	6.0	5.05
2.0	4.85	8.4	5.17

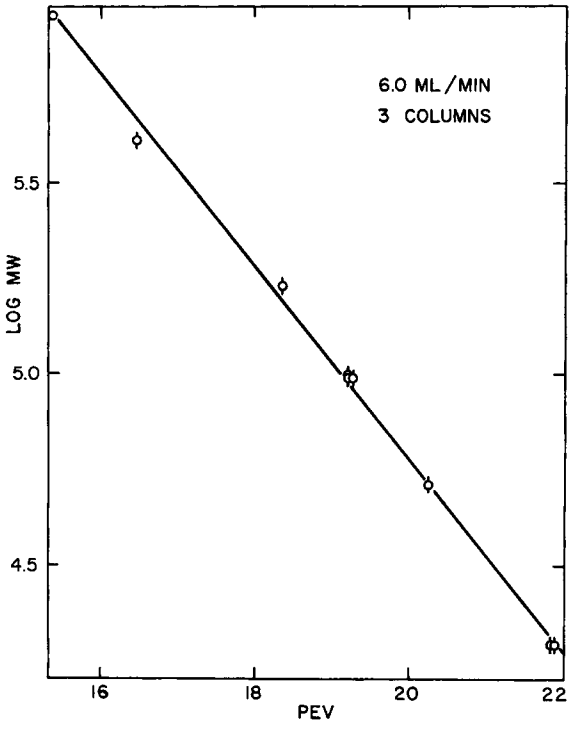


Fig. 2. Code 14 calibration curve.

program since the minimum time increment for height read out on the digital translator was once every 20 sec.

Calibration curves for Codes 13, 14, 15, and 16 are shown in Figures 1, 2, 3, and 4. These were considered linear over the range of interest. The change in elution volume/count with flow rate (Table II) has been taken into account. The calibration curves for the other Codes are shown in previous publications by Duerksen and Hamielec.[1,2]

The maximum pressure obtained was 600 psi with Code 15. No compression of the crosslinked polystyrene gel was evident either in successive chromatograms obtained or in any deviation of pressure variation with increasing flow rate. No leaks in the system resulted from the high pressures.

RESULTS

1. Pierce and Armonas Evaluation

This method was found to be relatively simple to program and flexible enough to easily permit additions such as search programs. In the final version of the program, which we developed, the validity of the solution to Tung's integral equation, could be checked, not only by examination of the areas under the curves and the corrected and regenerated chromatograms

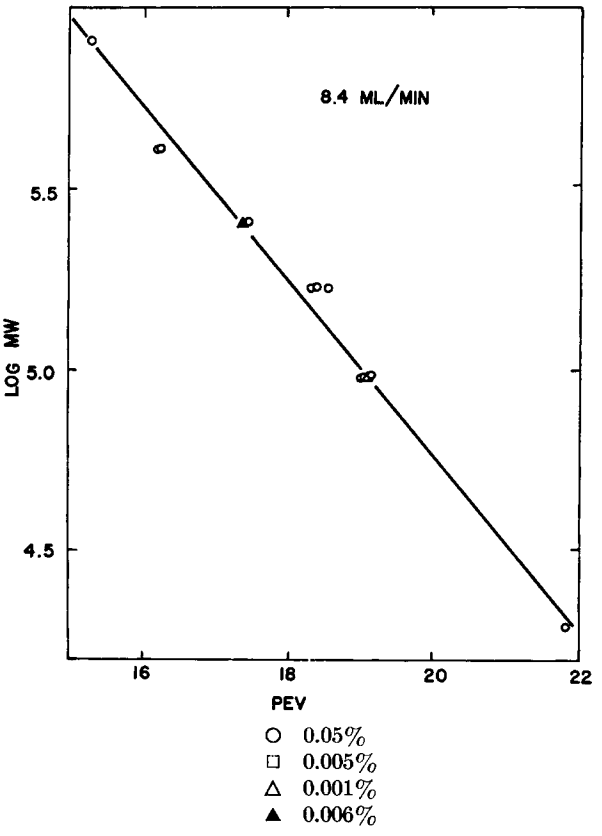


Fig. 3. Code 15 calibration curve.

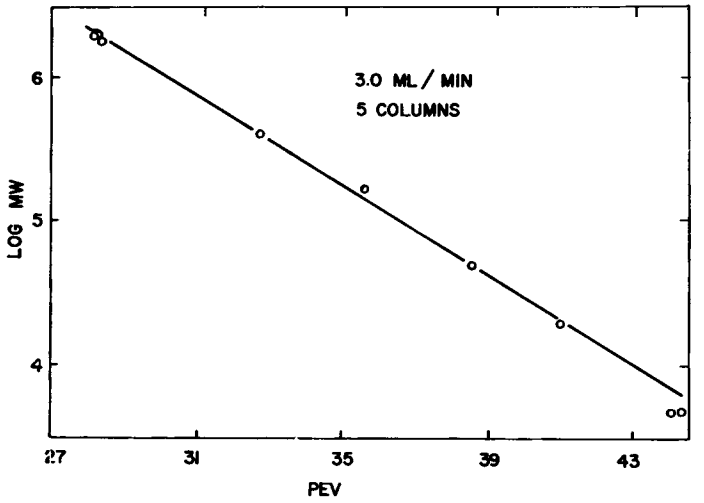


Fig. 4. Code 16 calibration curve.

TABLE III
Mn and *Mw*—Absolute and Infinite Resolution Values

Run	Std	$Mn(t) \times 10^{-4}$	$Mw(t) \times 10^{-4}$	$P(t)$	$Mn(\infty) \times 10^{-4}$	$Mw(\infty) \times 10^{-4}$	$P(\infty)$
Code 8							
08201	108	24.7	26.7	1.08	14.3	21.9	1.53
08202	108	24.7	26.7	1.08	13.7	22.1	1.61
08203	41984	16.4	17.3	1.06	11.0	15.4	1.41
08204	41984	16.4	17.3	1.06	11.2	15.9	1.42
08205	103	11.8	12.5	1.05	9.52	12.6	1.33
08206	103	11.8	12.5	1.05	8.62	12.7	1.49
08207	4A	9.76	9.62	<1.06	7.97	10.7	1.34
08208	7A	5.01	5.05	<1.06	4.55	6.17	1.36
08209	4190039	1.97	1.99	1.01	1.70	2.35	1.38
08210	8A	1.09	1.00	1.06	0.850	1.13	1.33
Code 5							
05108	3A	39.2	39.4	<1.06	33.3	43.0	1.29
05109	3A	39.2	39.4	<1.06	37.9	53.3	1.41
05110	108	24.7	26.7	1.08	23.8	31.4	1.32
05101	108	24.7	26.7	1.08	19.7	25.0	1.26
05112	103	11.8	12.5	1.05	10.0	12.6	1.26
05102	CST30	3.48	6.14	1.76	3.29	6.49	1.97
05113	7A	5.01	5.05	<1.06	4.80	5.46	1.14
05105	CST29	1.48	3.62	2.45	1.41	3.81	2.72
05115	2A	1.98	1.98	<1.06	1.81	2.10	1.16
05116	4190039	1.97	1.99	1.01	1.79	2.08	1.16
05117	4190039	1.97	1.99	1.01	1.80	2.06	1.15
05107	CST31	1.02	1.46	1.42	0.982	1.52	1.55
05118	8A	1.09	1.00	<1.06	0.953	1.11	1.17
05103	8A	1.09	1.00	<1.06	0.975	1.12	1.15

05114	12A	0.207	0.220	<1.10	0.269	0.314	1.17
05120	15A	0.0927	—	<1.10	0.211	0.252	1.20
Code 13							
13301	3A	39.2	39.4	<1.06	22.8	34.7	1.53
13305	3A	39.2	39.4	<1.06	30.1	39.1	1.30
13303	4A	9.76	9.62	<1.06	7.96	9.04	1.14
13307	CST30	3.48	6.14	1.76	3.14	5.75	1.83
13302	4190039	1.97	1.99	1.01	1.82	2.11	1.16
Code 14							
14602	3A	39.2	39.4	<1.06	25.4	38.6	1.52
14604	41984	16.4	17.3	1.06	11.7	15.4	1.31
14611	4A	9.76	9.62	<1.06	7.25	9.34	1.29
14613	4A	9.76	9.62	<1.06	7.20	9.43	1.31
14601	4A	9.76	9.62	<1.06	7.23	9.03	1.25
14605	7A	5.01	5.05	<1.06	4.32	5.18	1.20
14612	CST30	3.48	6.14	1.76	2.95	6.01	2.04
14603	4190039	1.97	1.99	1.01	1.68	2.07	1.23
14616	4190039	1.97	1.99	1.01	1.66	2.05	1.23
Code 15							
158606	3A	39.2	39.4	<1.06	24.1	38.6	1.61
158610	3A	39.2	39.4	<1.06	25.6	39.2	1.53
15811	108	24.7	26.7	1.08	13.5	22.1	1.64
15814	108	24.7	26.7	1.08	14.1	21.4	1.52
158609	41984	16.4	17.3	1.06	11.4	16.1	1.41
15806	41984	16.4	17.3	1.06	10.3	14.2	1.38
15809	41984	16.4	17.3	1.06	10.8	14.7	1.36

(*continued*)

TABLE III (*continued*)

Run	Std	$Mn(t)$ $\times 10^{-4}$	$Mn(t)$ $\times 10^{-4}$	$P(t)$	$Mn(\infty)$ $\times 10^{-4}$	$Mn(\infty)$ $\times 10^{-4}$	$P(\infty)$
158608	4A	9.76	9.62	<1.06	7.35	9.66	1.31
15822	4A	9.76	9.62	<1.06	8.50	10.1	1.19
15817	CST30	3.48	6.14	1.76	3.32	5.71	1.72
15818	CST30	3.48	6.14	1.76	3.23	5.79	1.80
15819	CST30	3.48	6.14	1.76	3.22	5.82	1.81
158607	4190039	1.97	1.99	1.01	1.77	2.30	1.30
Code 12							
12201	G35	19.00	57.00	3.00	7.86	42.5	5.40
12202	COOPA	11.60	30.40	2.62	5.00	23.0	4.60
12203	NBS706	13.65	25.78	1.89	10.9	26.0	2.41
Code 16							
16312	61970	178.	215.	1.20	115.	165.	1.43
16321	14A	161.	170.	1.18	58.3	160.	2.74
16328	41984	16.4	17.3	1.06	13.3	16.1	1.21
16334	7A	5.01	5.05	<1.06	5.14	5.95	1.16
16335	11A	0.52	—	<1.10	0.86	1.00	1.18

as well as the corresponding distributions but, the moments of the respective distributions as well. It was found that the choice of step size was extremely critical, particularly at low resolution factors. Choice of the wrong step size led to oscillations in the corrected chromatograms. A similar result occurred in the Tung program when the wrong choice of the number of terms to be used in the hermite polynomial was made. This deficiency in the Pierce-Armonas program caused the search for h factors to be a difficult if not impossible task. Furthermore, choice of step size was continually in doubt because of the difficulty in ascertaining whether the oscillation removed by a step size change was actually part of the distribution or a mathematical artifact.

It has been concluded in this evaluation that the method of Pierce-Armonas does not satisfactorily eliminate these artificial oscillations. In fact, all methods of resolution correction available in the literature suffer from this deficiency.

It is evident from the results listed in Table III that resolution correction only through Pierce-Armonas, even if successfully carried out, would often not even change the weight average molecular weight in the correct direction since skewing caused an excessively low $Mw(\infty)$ and symmetrical axial dispersion correction would cause a further decrease.

2. The Symmetrical Axial Dispersion Correction

From eqs. (13), (14), (26), (40), and (41)

$$\frac{Mw(sk,h)}{Mw(sk)} = \frac{Mw(h)}{Mw(\infty)} = e^{-A/h} \tag{43}$$

$$\frac{Mn(sk,h)}{Mn(sk)} = \frac{Mn(h)}{Mn(\infty)} = e^{A/h} \tag{44}$$

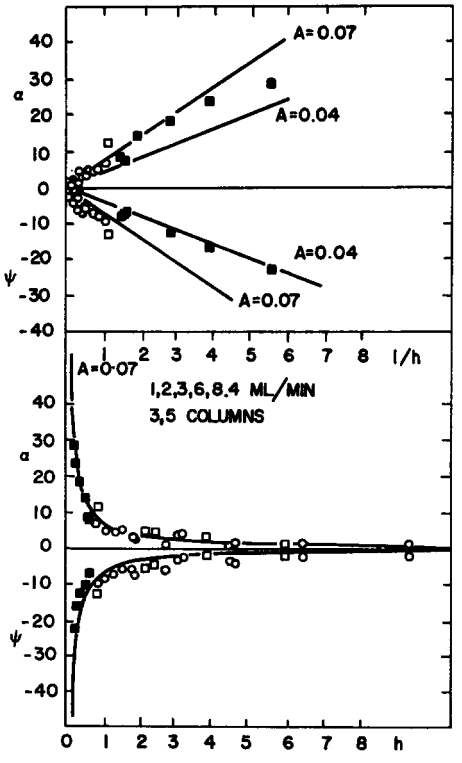
Now using Taylor series expansion and assuming third and higher order terms to be negligible write (43) and (44) as:

$$\frac{Mw(sk,h)}{Mw(sk)} = \frac{Mw(h)}{Mw(\infty)} = 1 - \frac{A}{h} \tag{45}$$

$$\frac{Mn(sk,h)}{Mn(sk)} = \frac{Mn(h)}{Mn(\infty)} = 1 + \frac{A}{h} \tag{46}$$

Thus a plot of these ratios vs. h should result in a hyperbola and vs. $1/h$ should yield a straight line. This agreed very well with experimental data obtained (Fig. 5). Scatter in this figure is entirely attributed to the difficulty in obtaining an accurate solution to Tung's integral equation by any practical method. To obtain these figures, only the best solution resulting from hundreds of trials were accepted. These were chosen by examining the solution checks available in the Pierce-Armonas program. At low h factors (below unity) the standard of solution acceptable was necessarily lower.

In order to examine theoretical values of h more closely, h was calculated by eqs. (45) and (46) with $A = 0.07$ and with A as defined by the theory using $C_2 = C(2,sk)$ and then $C_2 = C(2,t)$. In Table IV the latter two calculations are compared with actual values used in Pierce-Armonas. The



□ $\frac{\text{Mw}}{\text{Mn}} < 3.0$

○ $\frac{\text{Mw}}{\text{Mn}} < 1.1$

■ $\frac{\text{Mw}}{\text{Mn}} < 3$; C2 = 5.72

Mw $< 0.5 \times 10^6$

Fig. 5. α and ψ plotted against $1/h$ and against h where

$$\alpha = \frac{Mn(h) - Mn(\infty)}{Mn(\infty)} \times 100$$

$$= \frac{Mn(sk,h) - Mn(sk)}{Mn(sk)} \times 100$$

$$\psi = \frac{Mw(h) - Mw(\infty)}{Mw(\infty)} \times 100$$

$$= \frac{Mw(sk,h) - Mw(sk)}{Mw(sk)} \times 100$$

TABLE IV
Comparison of Actual and Theoretical h Values

Run	$Mn(t)$ $\times 10^{-4}$	$P(t)$	h actual[a]	$1/h$ actual[a]	$\frac{Mn(sk,h)}{Mn(sk)}$	h_{theory}, eq. (46), $C_2 = C_2$	h_{theory}, eq. (46), $C_2 = C(2,sk)$	$\frac{Mw(sk,h)}{Mw(sk)}$	h_{theory}, eq. (45), $C_2 = C_2$	h_{theory}, eq. (45), $C_2 = C(2,sk)$	Σ[b]
05101	24.7	1.08	3.23	0.309	1.038	2.66	2.66	0.911	3.49	3.49	0.009
05102	3.48	1.76	0.862	1.16	1.121	0.836	0.844	0.871	0.791	0.791	−0.009
05105	1.48	2.45	2.17	0.461	1.046	2.20	2.20	0.945	1.84	1.84	−0.009
05103	1.09	<1.06	6.39	0.157	1.021	4.82	4.82	0.989	9.20	9.20	0.0101
05103	1.09	<1.06	13.32	0.075	1.008	12.65	12.65	0.994	16.86	16.86	0.002
05107	1.02	1.42	2.39	0.419	1.043	2.35	2.37	0.957	2.35	2.37	0.0004
13303	9.76	<1.06	4.48	0.223	1.001	82.3	83.3	0.959	2.00	2.02	−0.04
13307	3.48	1.76	3.80	0.263	1.025	3.29	3.31	0.980	4.11	4.14	0.004
13307	3.48	1.76	5.97	0.167	1.013	6.33	6.38	0.982	4.57	4.60	−0.005
14605	5.01	<1.06	1.10	0.913	1.044	1.87	1.87	0.913	0.947	0.947	−0.04
158606	39.2	<1.06	3.03	0.330	1.039	2.03	2.05	0.964	2.20	2.23	0.003
158606	39.2	<1.06	4.67	0.214	1.011	7.19	7.27	0.956	1.80	1.82	−0.032
158610	39.2	<1.06	2.74	0.365	1.007	11.31	11.49	0.937	1.26	1.28	−0.056
15814	24.7	1.08	9.37	0.107	1.009	8.79	8.89	0.996	19.79	20.02	0.005
158609	16.4	1.06	0.914	1.094	1.067	1.18	1.20	0.903	0.815	0.828	−0.013
15809	16.4	1.06	1.57	0.635	1.046	1.72	1.74	0.940	1.32	1.34	−0.015
15822	9.76	<1.06	1.87	0.535	1.025	3.17	3.18	0.934	1.20	1.20	−0.041
15818	3.48	1.76	11.85	0.084	1.007	11.31	11.34	0.976	3.30	3.30	0.016
12201	19.0	3.00	0.179	5.58	1.283	0.143	0.149	0.778	0.183	0.190	0.062
12201	19.0	3.00	0.255	3.92	1.234	0.172	0.179	0.836	0.247	0.257	0.073
12201	19.0	3.00	0.351	2.85	1.185	0.219	0.228	0.877	0.330	0.343	0.062
12201	19.0	3.00	0.506	1.98	1.144	0.281	0.292	0.896	0.390	0.405	0.039
12203	13.7	1.89	0.617	1.62	1.071	0.571	0.574	0.923	0.526	0.589	−0.004
12203	13.7	1.89	0.650	1.54	1.081	0.500	0.502	0.924	0.533	0.535	0.005
12203	13.7	1.89	0.680	1.47	1.089	0.455	0.457	0.922	0.520	0.523	0.011

[a] "Actual" indicates h values used in Pierce-Armonas solution of Tung's integral equation.
[b] $\Sigma = Mn(sk,h)/Mn(sk) + Mw(sk,h)/Mw(sk) - 2$.

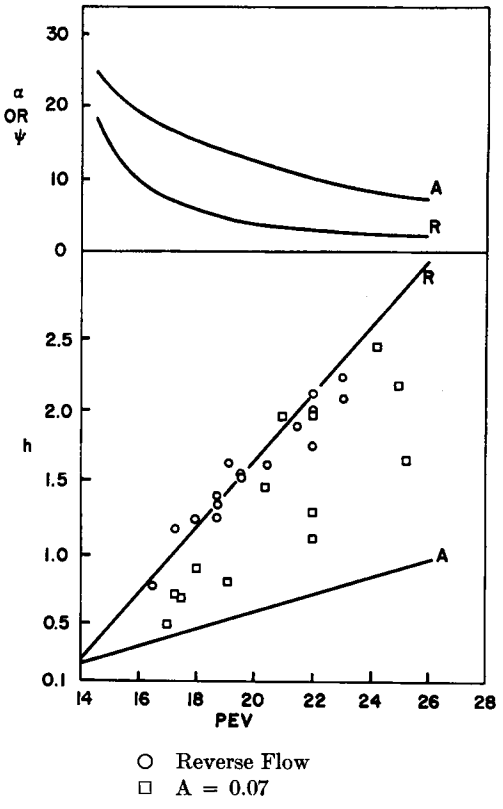


Fig. 6. h vs. PEV. Reverse flow values are compared with those calculated using $A = 0.07$ in eq (39). Significance of scatter of points is indicated in upper plot. It is evident that the difference between the worst line "A" and the reverse flow line "R" is almost constant insofar as percent correction introduced (α and ψ are defined above for Fig. 5).

agreement is excellent considering the error involved in solving Tung's equation. There is no significant difference between calculations using $C(2,sk)$ and those using $C(2,t)$. This was expected since $C(2,sk) \simeq C(2,t)$. Values of h obtained using $A = 0.07$ are slightly different at lower h values for these calibration curves than those calculated using the correct value of A.

Values of h calculated from eq. (39) are compared with those obtained by reverse flow in Table V. Theoretical values are generally lower, significantly so at the lower h values. Values of h calculated from eq. (39) by assuming $A = 0.07$ are plotted with reverse flow values in Figure 6. A worst line "A" is drawn and the significance of the difference in correction resulting compared to the reverse flow line "R" is illustrated in the upper diagram. It is evident that scatter in values of h greater than 1.5 is much less important than scatter at lower values of h. Uncertainty in calculation of h originates in the uncertainty present in the polydispersities. Thus,

broad samples are preferable to narrow in this calculation. Table VI also shows values of h obtained by Fibonacci Search (Program 4). These values were generally too high because the search converged when oscillations occurred in the chromatograms. Values of h for Codes 13, 14, and 15 calculated with $A = 0.07$ are plotted in Figure 7. Again uncertainty in the polydispersity of "monodisperse" standards caused some scatter of data. h values appear quite low at 6 and 8.4 ml/min.

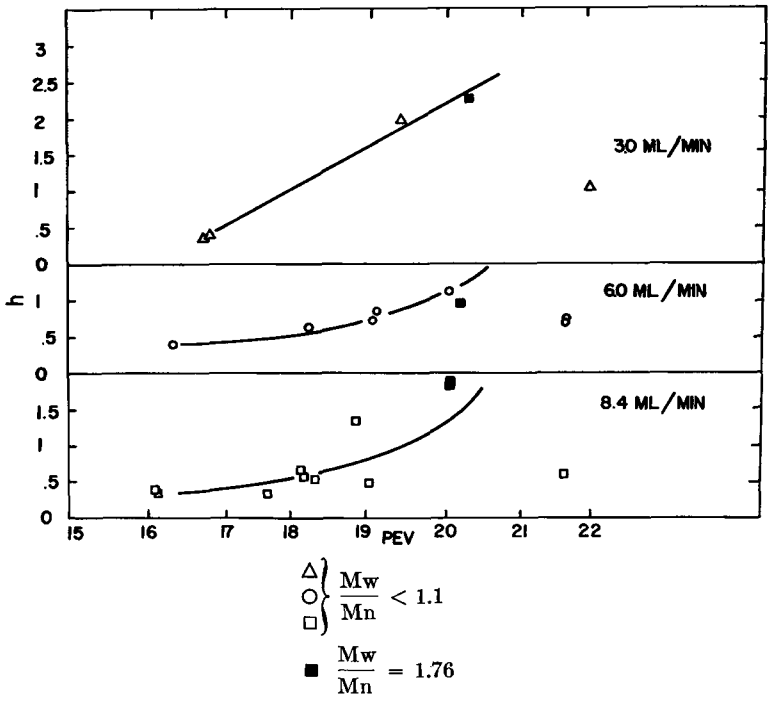


Fig. 7. Codes 13, 14, and 15. h factors calculated using $A = 0.07$ in eq (39).

From these results it was evident that the h factor caused significant correction only at very low values of h ($h < 1$). Even values as low as 0.3 caused only about a 25% correction in the molecular weight averages. This is in great contrast to the power of the skewing correction.

3. The Skewing Correction

According to eqs (27) and (30)

$$\frac{Mn(sk)}{Mn(\infty)} = \frac{Mw(sk)}{Mw(\infty)} = B \simeq 1 + \frac{1}{2} sk \tag{47}$$

In order to test the above relation the molecular weight ratios were plotted vs. sk (Fig. 8).

TABLE V
Comparison of h from Reverse Flow with h from Theory

Run	sk	h_{rev}	$Mn_{h_{rev}} \times 10^{-4}$	$Mw_{h_{rev}} \times 10^{-4}$	h_{theory} Eq. (39)
08201	0.939	1.70	17.8	19.4	1.84
08202	1.005	1.75	17.0	19.7	1.64
08203	0.617	1.88	13.2	13.8	2.18
08204	0.551	1.85	13.8	14.2	2.13
08205	0.287	1.97	10.3	10.5	2.57
08206	0.413	2.02	10.4	11.5	1.83
08207	0.128	2.07	9.32	9.61	2.59
08208	−0.081	2.37	5.26	5.63	2.45
08209	0.002	2.93	1.90	2.17	2.02
08210	−0.823	3.31	0.930	1.05	2.66
05108	0.092	1.03	37.0	38.9	1.13
05109	−0.228	0.96	42.1	48.0	0.815
05110	−0.111	1.14	26.2	28.8	1.11
05101	.321	1.20	21.9	23.2	1.59
05112	.216	1.46	10.9	11.8	1.21
05113	−0.031	1.77	5.07	5.16	2.88
05115	0.034	2.16	1.90	2.00	2.35
05116	0.053	2.16	1.88	1.98	1.56
05117	0.054	2.16	1.89	1.97	1.66
05118	−0.051	2.40	0.995	1.07	2.15
05103	−0.085	2.39	1.02	1.08	2.59
05114	−0.531	2.86	0.280	0.304	3.38
05120	−1.215	2.94	0.218	0.244	2.43
12201	1.75	0.44	8.60	40.2	0.182
12202	1.64	0.65	5.33	22.1	0.190
12203	0.244	0.56	11.6	24.4	0.376

$Mn(\infty)$ and $Mw(\infty)$ were easily obtained from the GPC chromatogram and the true calibration curve sk was obtained for the standards from eq. (21).

In order to obtain $Mn(sk)$ and $Mw(sk)$ the GPC chromatogram with the values of $Mn(t)$ and $Mw(t)$ were read into the linear calibration curve search [Program (1)]. Then values of C_1 and C_2 were searched for

$$\frac{Mn(t)}{Mn(sk)} + \frac{Mw(t)}{Mw(sk)} - 2 = 0 \tag{48}$$

so that (47) above was satisfied, the correct C_1 and C_2 yielded $Mn(sk)$ and $Mw(sk)$ as the values calculated at infinite resolution. Then this C_1 and C_2 were called $C(1,sk)$ and $C(2,sk)$ and were the values of C_1 and C_2 necessary to effect the skewing correction. Values obtained are tabulated in Table VII. Excellent agreement was shown in the plot of molecular weight averages vs. sk (Fig. 8 and Table VIII) and eq (47) was thus corroborated over a wide range of conditions. Figure 8 with the obviously very small change in C_2 necessary to effect skewing correction substantiated the assumption that

TABLE VI
Values of h from Search and from Theory

Run	sk	h (search)	h, eq. (39) $A = 0.07$	h eq. (39), $C_2 = C(2,sk)$	PEV
13301	0.855	1.90	0.388	0.540	16.96
13305	0.310	1.480	0.688	0.892	16.86
13303	0.290	1.70	2.02	2.47	19.55
13307	0.176	3.80	2.59	4.30	20.49
13302	0.023	1.08	1.05	1.32	22.16
14602	0.566	—	0.393	0.545	16.47
14604	0.525	0.943	0.648	0.843	18.32
14611	0.376	1.35	0.720	0.932	19.20
14613	0.376	1.09	0.664	0.863	19.20
14601	0.415	1.14	0.855	1.09	19.25
14605	0.135	1.100	1.15	1.44	20.24
14612	0.201	—	0.950	1.20	20.40
14603	0.128	0.904	0.710	0.917	21.84
14616	0.155	1.40	0.698	0.900	21.86
158606	0.647	2.00	0.342	0.425	16.21
158610	0.536	1.89	0.386	0.468	16.25
15811	1.038	0.80	0.340	0.421	17.45
15814	0.999	—	0.414	0.497	17.40
158609	0.513	0.92	0.484	0.568	18.18
15806	0.810	1.17	0.530	0.619	18.39
15809	0.695	1.50	0.550	0.635	18.26
158608	0.324	0.886	0.656	0.745	19.13
15822	0.101	1.160	1.21	1.317	18.99
15817	0.135	∞	∞	∞	20.38
15819	0.136	∞	5.00	5.209	20.28
158607	−0.024	0.847	0.561	0.680	21.79
16312	0.851	<0.9	0.800	0.388	28.20
16321	1.824	<0.5	0.490	0.306	28.35
16328	0.308	0.346	1.31	0.504	35.59
16334	−0.177	<0.5	1.55	0.725	38.55
16335	−0.875	0.43	1.99	0.922	43.72

skewing correction was mainly the result of a change in C_1 for a linear calibration curve.

Values of sk were calculated for a wide range of samples and plotted against PEV in Figure 9 through 12. Generally sk was found to increase with molecular weight and flow rate. This was expected since both of the latter variables were found to affect skewing. It is evident that two other variables also affect the sk. These are the linearity of the calibration curve and the concentration at higher molecular weights. For a normal calibration curve which is linear at the central portion and which tails up at the high molecular weight end and down at the lower molecular weight end using the linear relation for a sample eluting near either end would cause great changes in $Mn(\infty)$ and $Mw(\infty)$. For a sample eluting at the high molecular weight end less high molecular weight material than was really

TABLE VII
Results of $C(1,sk)$,$C(2,sk)$ Search

Run	$Mn(sk) \times 10^{-4}$	$Mw(sk)$	$P(sk)$	$C(1,sk)$	$C(2,sk)$	$\frac{A}{\left(\frac{2.303}{C_2}\right)^2}\frac{1}{4}$
05101	22.7	29.3	1.29	37.41	3.63	0.101
05102	3.24	6.64	2.05	37.65	3.61	0.102
05105	1.41	3.81	2.70	37.55	3.62	0.101
05103	0.931	1.08	1.16	37.47	3.63	0.101
05107	0.983	1.53	1.56	37.55	3.62	0.101
PEV C_1 and C_2				37.55	3.62	0.101
13301	32.4	49.8	1.54	39.89	3.98	0.0837
13305	34.7	45.3	1.31	39.59	3.99	0.0833
13303	9.03	10.3	1.14	39.57	3.99	0.0833
13307	3.41	6.28	1.84	39.54	4.00	0.0829
13302	1.84	2.13	1.16	39.48	4.01	0.0823
PEV C_1 and C_2				39.46	4.01	0.0823
14602	32.5	49.5	1.52	39.39	3.98	0.0837
14604	14.8	19.5	1.32	39.40	3.98	0.0837
14611	8.54	11.0	1.29	39.32	3.99	0.0833
14613	8.47	11.1	1.31	39.35	4.00	0.0829
14601	8.65	10.8	1.25	39.40	4.00	0.0829
14605	4.61	5.53	1.20	39.26	4.01	0.0823
14612	3.24	6.63	2.05	39.28	4.00	0.0829
14603	1.79	2.20	1.23	39.21	4.01	0.0823
14616	1.79	2.21	1.24	39.26	4.01	0.0823
PEV C_1 and C_2				39.16	4.01	0.0823
158606	31.9	51.1	1.60	39.85	4.07	0.0880
158610	32.4	49.9	1.54	39.73	4.06	0.0804
15811	20.4	33.8	1.66	40.05	4.06	0.0804
15814	21.1	32.2	1.53	40.05	4.07	0.0800
158609	14.3	20.3	1.42	39.74	4.06	0.0804
15806	14.5	20.0	1.38	39.92	4.06	0.0804
15809	14.5	19.9	1.37	39.91	4.07	0.0800
158609	8.46	11.2	1.32	39.64	4.07	0.0800
15822	8.87	10.5	1.18	39.54	4.09	0.0793
15817	3.52	6.07	1.72	39.57	4.09	0.0793
15819	3.45	6.20	1.80	39.54	4.09	0.0793
15818	3.45	6.19	1.79	39.59	4.09	0.0793
158607	1.77	2.30	1.30	39.49	4.09	0.0793
PEV C_1 and C_2				39.49	4.09	0.0793
12201	14.4	83.4	5.78	65.54	5.61	0.0421
12202	8.91	43.5	4.88	65.48	5.61	0.0421
12203	12.3	28.8	2.34	64.70	5.71	0.0407
PEV C_1 and C_2				64.56	5.72	0.0405
16312	164.	235.	1.43	68.89	6.46	0.0318
16321	111.	311.	2.80	70.60	6.44	0.0320
16328	15.3	18.6	1.22	69.46	6.48	0.0316
16334	4.69	5.41	1.15	69.02	6.53	0.0311
16335	0.482	0.564	1.17	67.88	6.60	0.0304
PEV C_1 and C_2				69.23	6.51	0.0312

TABLE VIII
Comparison of B Calculated from SK with Experimental Values of Number and Weight Average Ratios

Run	$M_n(t)$ $\times 10^{-4}$	$P(t)$	$P(\infty)$	SK	B (Calculated)	$P(sk)$	$\frac{Mn(sk)}{Mn(\infty)}$ (Experimental)	$\frac{Mw(sk)}{Mw(\infty)}$ (Experimental)
13301	39.2	<1.06	1.53	0.855	1.428	1.54	1.42	1.44
13305	39.2	<1.06	1.30	0.310	1.155	1.31	1.15	1.16
13303	9.76	<1.06	1.14	0.290	1.145	1.14	1.13	1.14
13307	3.48	1.76	1.83	0.176	1.088	1.84	1.09	1.09
13302	1.97	1.01	1.16	0.023	1.011	1.16	1.01	1.01
14602	39.2	<1.06	1.52	0.566	1.283	1.52	—	—
14604	16.4	1.06	1.31	0.525	1.263	1.32	1.26	1.27
14611	9.76	<1.06	1.29	0.376	1.188	1.29	1.18	1.18
14613	9.76	<1.06	1.31	0.375	1.188	1.31	1.18	1.18
14601	9.76	<1.06	1.25	0.415	1.208	1.25	1.20	1.20
14605	5.01	<1.06	1.20	0.135	1.068	1.20	1.07	1.07
14612	3.48	1.76	2.04	0.201	1.100	2.05	1.10	1.10
14603	1.97	1.01	1.23	0.128	1.064	1.25	1.06	1.06
14616	1.97	1.01	1.23	0.155	1.078	1.24	1.08	1.08
158606	39.2	<1.06	1.61	0.647	1.324	1.60	1.32	1.33
158610	39.2	<1.06	1.53	0.536	1.268	1.54	1.26	1.27
15811	24.7	1.08	1.64	1.03	1.515	1.66	1.51	1.53
15814	24.7	1.08	1.52	0.999	1.500	1.53	1.50	1.50
158609	16.4	1.06	1.41	0.513	1.257	1.42	1.25	1.26
15806	16.4	1.06	1.38	0.810	1.405	1.38	1.41	1.41
15809	16.4	1.06	1.36	0.695	1.348	1.37	1.34	1.35
158608	9.76	<1.06	1.31	0.324	1.162	1.32	1.15	1.16
15822	9.76	<1.06	1.19	0.101	1.050	1.18	1.04	1.04
15817	3.48	1.76	1.72	0.134	1.067	1.72	1.06	1.06
15819	3.48	1.76	1.81	0.136	1.068	1.80	1.07	1.07
15818	3.48	1.76	1.80	0.138	1.069	1.30	1.07	1.07
16312	178.	1.20	1.43	0.850	1.425	1.43	1.42	1.43
16321	161.	1.18	2.74	1.824	1.912	2.80	1.90	1.94
16328	16.4	1.06	1.21	0.307	1.154	1.22	1.15	1.16
12201	19.0	3.00	5.40	1.75	1.875	5.78	1.83	1.96
12202	11.60	2.62	4.60	1.64	1.820	4.88	1.78	1.89
12203	13.7	1.89	2.41	0.244	1.122	2.34	1.15	1.11

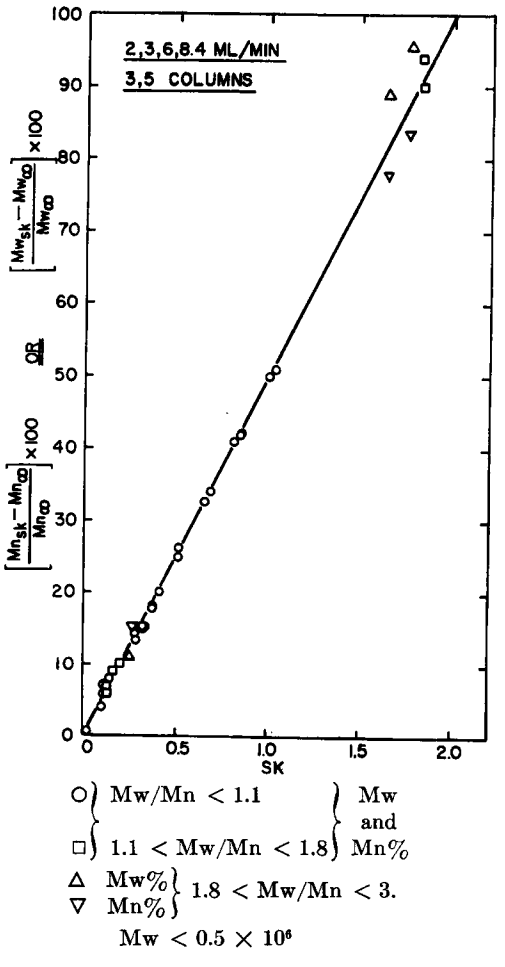


Fig. 8. Test of "$B = 1 + \frac{1}{2}sk$" (eq. (30)) where $B = Mn(sk)/Mn(\infty) = Mw(sk)/Mw(\infty)$. Here the percent change rather than the ratios are plotted against sk.

present would be calculated. This would lower $Mn(\infty)$ and $Mw(\infty)$ and therefore, raise sk. Similarly at the low molecular weight end less lower molecular weight material than was really present would be calculated. This would raise $Mn(\infty)$ and $Mw(\infty)$ and hence lower sk. Higher concentration would be expected to raise sk, particularly at high molecular weights.

In Figures 9 through 12 several plots of sk vs. PEV are presented. The above effects are much in evident. Scatter of data is reasonable except for the data of 8.4 ml/min. In this case accurate reading of narrow GPC chromatograms at such a high flow rate for moment calculations was the primary source of error. It should be noted that only lcc of solution rather than the full sample loop (2cc) was injected in an effort to obtain plug flow rather than a laminar velocity profile. The small error involved in injection time was probably responsible for small differences in concentration and

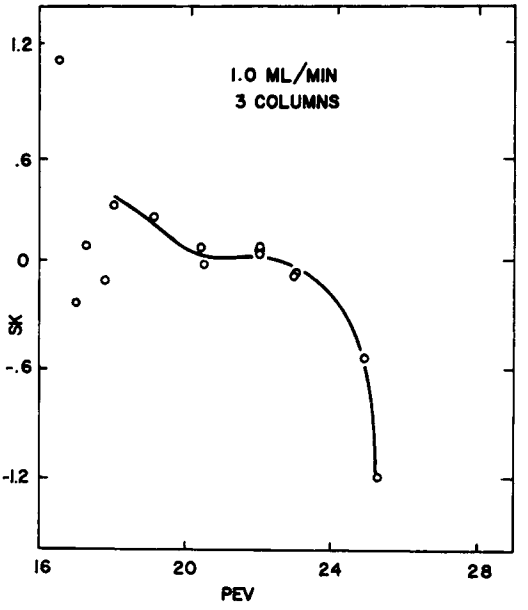


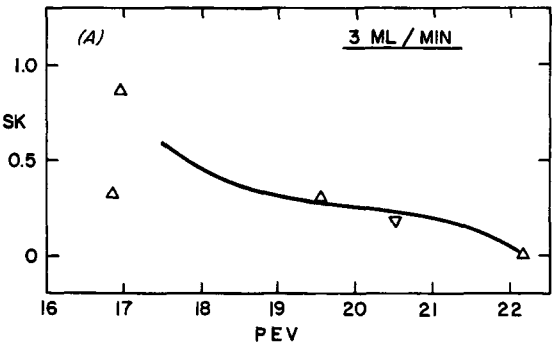
Fig. 9. Code 5; *sk* vs. *PEV*. Negative *sk* appear when the calibration curve drops and scatter is present at the high molecular weight end likely due to concentration effects and/or high molecular weight calibration curve cut-off.

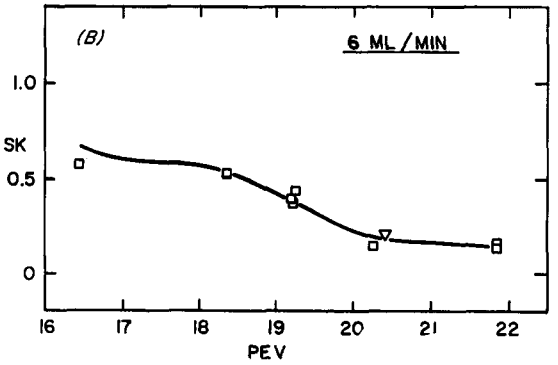
hence significant concentration effect at high molecular weights in the *sk* vs. *PEV* plots.

The most important aspects of these figures is that a correlation was obtained for both broad and narrow standards against peak elution volume.

3.1 Physical Interpretation of Skewing

Skewing is an overloading or concentration effect. When the polymer sample is injected at essentially infinite dilution conditions skewing is negligible. When the amount injected (at constant volume) is increased, two phenomena are observed. Firstly, the calibration curve as measured using peak position shifts towards higher elution volumes. Secondly, the chromatogram shape of monodisperse standards becomes skewed towards the low molecular weight (or high elution volume) end. The calibration curve no longer coincides with mean eluent volume of the standards. Using this chromatogram with the measured calibration curve (based on peak position) gives number and weight average molecular weights which are sometimes both smaller than their true values, as measured by light scattering and osmometry. To correct for this discrepancy one must use an effective calibration curve which more closely coincides with the mean eluent volume. This effective calibration curve should account for skewing of standards. In this paper work with some broad molecular weight standards has shown that the effective calibration curve is the





$\triangle \quad \frac{Mw}{Mn} < 1.10$

$\nabla \quad \frac{Mw}{Mn} = 1.76$

$\square \quad \frac{Mw}{Mn} < 1.10$

$\nabla \quad \frac{Mw}{Mn} < 1.76$

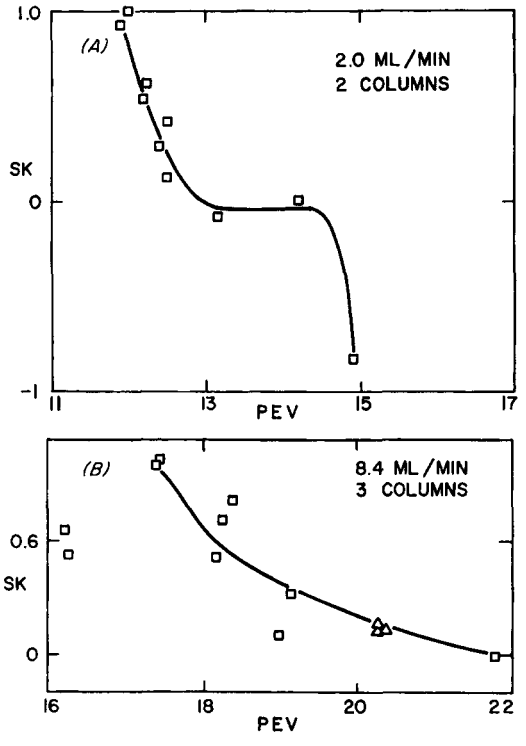
Fig. 10. Codes 13 and 14: *sk* vs. *PEV*.

same as that for the narrow standards. Further work is required to investigate this over a wide range of loadings.

4. Nonlinear Calibration Curves, Broad and Multipeaked Distributions

4.1 Nonlinear Calibration Curves

4.1.1 Symmetrical Axial Dispersion Correction. The chromatogram $W(v)$ corrected for symmetrical axial dispersion can be obtained from $F(v)$ using an effective calibration curve and then the true nonlinear calibration curve. $W(v)$ thus may be calculated using either the search technique [(on $Mn(h)$ and $Mw(h)$] presented in this paper or the methods of Tung or of



□ $\frac{\text{Mw}}{\text{Mn}} < 1.1$

△ $\frac{\text{Mw}}{\text{Mn}} < 1.8$

□ $\frac{\text{Mw}}{\text{Mn}} < 1.1$

Fig. 11. Codes 8 and 15: *sk* vs. *PEV*.

Pierce-Armonas. The former method is recommended for reasons previously mentioned.

4.1.2 Skewing Correction. The derivation of this correction assumes a linear calibration curve. However, assumption of a nonlinear calibration curve would have led to the same result.

For example if eqs. (22) and (23) are replaced by:

$$M(v) = D(1,sk) \exp(-D(2,t)v - D(3,t)v^2 - D(4,t)v^3) \tag{22A}$$

$$M(v) = D(1,t) \exp(-D(2,t)v - D(3,t)v^2 - D(4,t)v^3) \tag{23A}$$

The term after the integral sign in eq. (24) cancel out leaving:

$$B = \frac{Mw(sk)}{Mw(\infty)} = \frac{Mn(sk)}{Mn(\infty)} = \frac{D(1,sk)}{D(1,t)} \tag{26}$$

Therefore, for any calibration curve (for any shaped chromatogram) a change in $D(1, sk)$ will change Mn and Mw by equal percentages in the same direction. By defining the skewing correction in this manner the polydispersity is unchanged. The symmetrical axial dispersion correction alone

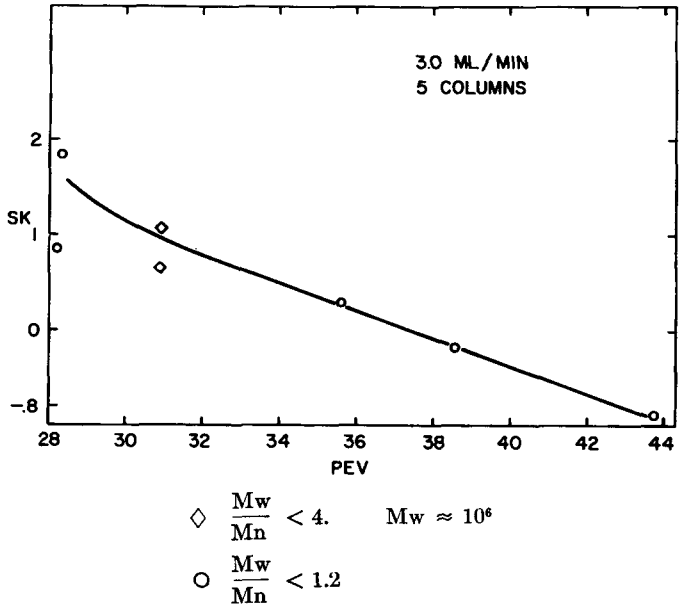


Fig. 12. Code 16: *sk* vs. *PEV*. Two very broad high molecular weight standards correlated well with the narrower standards.

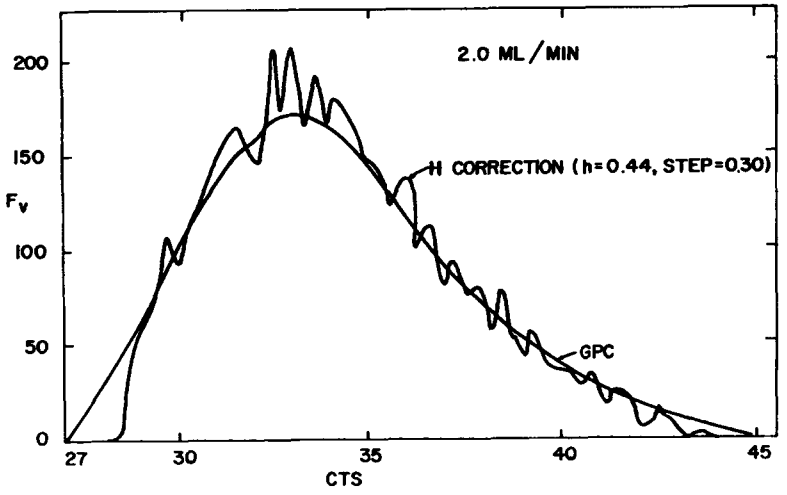


Fig. 13. GPC chromatogram and resolution corrected chromatogram for standard G35 (Run 12201). The low h factor causes incorrect step size to result in severe oscillations in method of Pierce-Armonas.

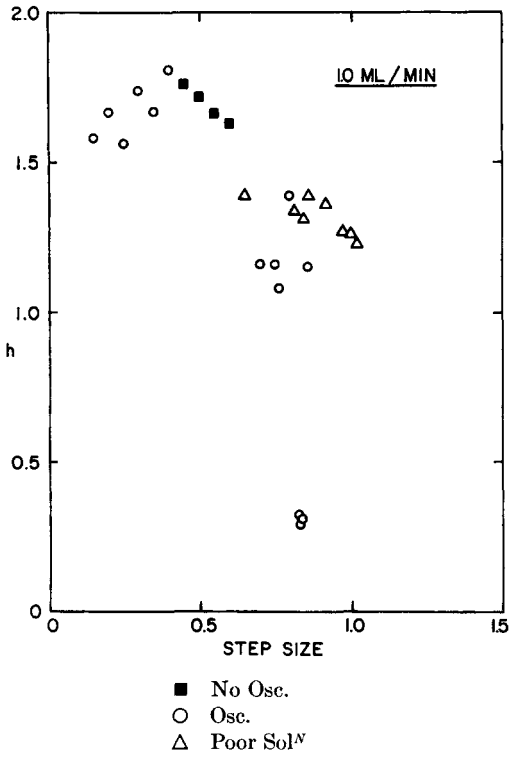


Fig. 14. Variety of h factors obtained by present search program showing dependence on step size.

changes the polydispersity. Then the skewing correction only involves the problem of determining B. Once $W(v)$ is obtained $Mn(h)$ and $Mw(h)$ can be calculated using the true (nonlinear) calibration curve. Then B can be related to known averages as follows:

$$Mw(sk,h) = D(1,sk) \int W(v)\exp\left(-D(2,t)v - D(3,t)v^2 - D(4,t)v^3\right) dV$$

Multiplying both sides by $D(1,t)/D(1,sk)$ and rearrange to obtain:

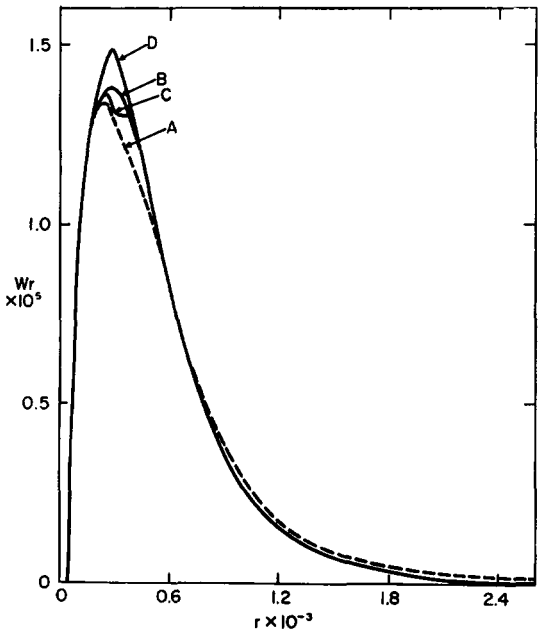
$$B = \frac{D(1,sk)}{D(1,t)} = \frac{Mw(t)}{Mw(h)} \tag{49}$$

where $Mw(t) = Mw(sk,h)$.

A similar expression may be obtained for $Mn(t)$

$$B = \frac{Mn(t)}{Mn(h)} \tag{50}$$

This permits calculation of B from broad or narrow standards.



A 1.0 ml/min
B 3.0 ml/min
C 6.0 ml/min
D 8.4 ml/min

Fig. 15. Codes 5, 13, 14, and 15 uncorrected differential distributions showing increasing skewing with increasing flow rate with the exception of Code 14 which shows a bimodal distribution for this sample.

4.2 Broad and Multipeaked Distributions

4.2.1 Symmetrical Axial Dispersion Correction. If the sample is not unimodal or if it is very broad then a single resolution factor h which normally corresponds to peak elution volume might not be adequate. Then a simple mathematical fractionation of the chromatogram into arbitrary unimodel narrow components, for which single values of h are suitable, may be performed A method of fractionation is presently being developed.

4.2.2 Skewing Correction. This correction may be carried out as described in 4.1.2 for any shape of chromatogram. The problem here is to know what value of B (or sk for a linear calibration curve) to use for an unknown. If skewing is attributed to a viscosity effect it is likely that a correlation of B (or sk) against viscosity of solution injected rather than peak elution volume should be used for a broad or multipeaked distribution. Since B is a parameter which corrects all molecular weights for a certain bulk viscosity only one value of B is used for the entire multipeaked distribution.

A potentially more direct solution to the problem of skewing correction, if applicable, would be to calculate the mean eluent volume for each mono-

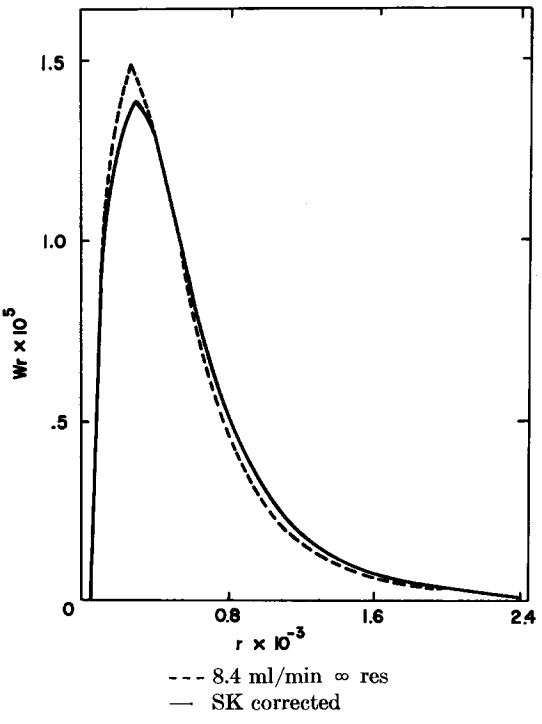


Fig. 16. Skewing correction of a distribution at 8.4 ml/min. Here $h = \infty$ and the *sk* corrected distribution is the true distribution.

disperse sample used in obtaining the calibration curve and to plot the elution volume at this point rather then the peak elution volume. The calibration curve resulting (likely nonlinear) would then incorporate the skewing correction. No further skewing correction would then be necessary if this new calibration curve was considered the true calibration curve. This new approach is presently being evaluated

4.3 Correcting Higher Moments of the Distribution

Hamielec and Ray[5] have developed a general form for correcting any moment of the uncorrected distribution for symmetrical axial dispersion.

$$\frac{Q_k(h)}{Q_k(\infty)} = \left\{\prod_{j=0}^{k-1} \exp\{[3 - 2(k-j)]D_2^2/4h\}\right\} \exp\{-D_2^2/4h\} \quad (51)$$

where $k = 1, 2, 3$.

Here $Q_k(\infty)$ is the uncorrected kth moment and $Q_k(h)$ is the corrected kth moment.

Moments are defined by:

$$Q_k = \sum_{r=1}^{\infty} r^k P_r \quad (52)$$

where P_r is the concentration of polymer molecules (moles/l) and r = chain length.

In terms of the GPC chromatogram:

$$Q_k(\infty) = M_0^{1-k} \int_{-\infty}^{\infty} M(v)^{k-1} F(v)\, dV \tag{53}$$

where M_0 is the monomer molecular weight and $M(v)$ is given by the calibration curve used.

So then, all moments of the uncorrected distribution may be corrected for the effects of symmetrical axial dispersion. Thus, the calibration curve search used to effect the correction may be checked by calculating the moments of the corrected distribution obtained. In addition, the search may now be made for an effective nonlinear calibration curve by using higher moments in the search objective function.

5. Determination of True Linear Calibration Curves from Polydisperse Samples

(A) *No Significant Skewing and Infinite Resolution* ($sk = 0$, $h = \infty$)

A direct calibration curve search can be made. $Mn(t)$, $Mw(t)$ and the GPC chromatogram are read in and the $C_1 - C_2$ search is performed until (49) is satisfied.

$$[Mn(t) - Mn(C1,C2)]^2 + [Mw(t) - Mw(C1,C2)]^2 = 0 \tag{54}$$

	Mn ×10⁻⁵	Mw ×10⁻⁵	Mw/Mn
STD 41900039	0.197	0.199	1.01
A ∞ RES	0.168	0.207	1.23
B SK(=0.128)	0.177	0.217	1.23
C SK+h(=0.90)	0.190	0.200	1.04

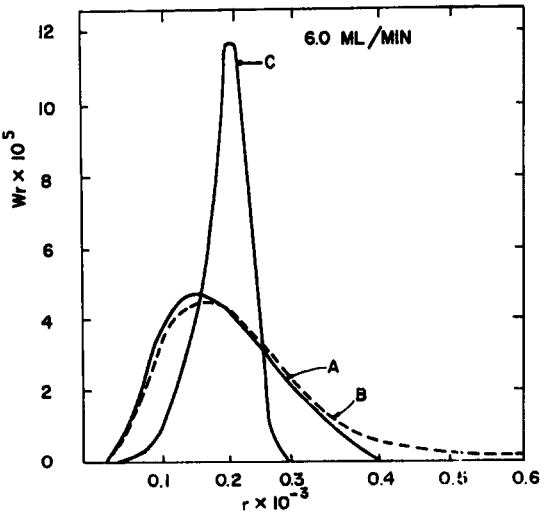


Fig. 17. Low molecular weight standard with low skewing correction but high resolution correction.

(B) No Significant Skewing but Significant Symmetrical Resolution Correction ($sk = 0$, $h < 1.5$)

Procedure is similar to (*A*) except that the objective function (50) is used and h must also be read in.

$$\left[Mn(t) - Mn(C1,C2)\exp\left(+\frac{(2.303)^2}{C_2^2\,4h}\right)\right]^2 + \left[Mw(t) - Mw(C1,C2)\exp\left(-\frac{(2.303)^2}{C_2^2\,4h}\right)\right]^2 = 0 \quad (55)$$

(C) Significant Skewing and Significant Resolution Correction ($sk > 0$, $h < 1.5$)

Procedure is similar to (*A*) except that the objective function (51) is used and both sk and h are read in

$$\left[Mn(t) - Mn(C1,C2)\left(1+\frac{1}{2}sk\right)\left(\exp\frac{(2.303)^2}{C_2^2\,4h}\right)\right]^2 + \left[Mw(t) - Mw(C1,C2)\left(1+\frac{1}{2}sk\right)\left(\exp\frac{-(2.303)^2}{C_2^2\,4h}\right)\right]^2 = 0 \quad (56)$$

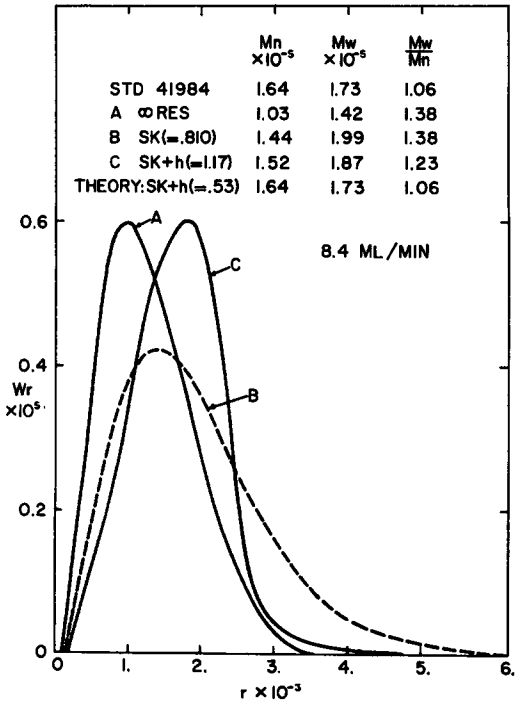


Fig. 18. High molecular weight standard with significant skewing correction and high resolution correction. More resolution correction was required but could not be accomplished because of step size difficulties in the Pierce-Armonas program.

6. Use of the Method in Determining Corrected Molecular Weight Averages for Broad or Narrow Samples

(A) Determining the h and sk versus PEV Plots for GPC Operating Conditions

(*1*) From injections of broad or narrow standards (preferably broad to avoid errors in polydispersity) calculate $Mn(\infty)$ and $Mw(\infty)$ using the true calibration curve. Avoid concentration variations between samples wherever possible.

(*2*) Calculate *sk* from eq. (21).

(*3*) Calculate *h* from eq. (38) or (39) (if the two term Taylor series approximation is valid (i.e., the third and higher order terms are negligible).

(*4*) Plot results for both broad and narrow standards together against peak elution volumes.

(B) Determining the Corrected Molecular Weight Averages for an Unknown

(*1*) Determine *sk* and *h* from *PEV* by reading these values on the previously found *sk* vs. *PEV* and *h* vs. *PEV* plots for the particular GPC operating conditions.

(*2*) Calculate $Mn(sk,h)$ and $Mw(sk,h)$ from eqs. (40) and (41).

7. Use of the Method in Determining Corrected Differential Molecular Weight Distributions

(A) Successive application of sk and h using Pierce-Armonas

This was the initial attempt at determining the differential distribution. It proved to be the least desirable because of the artificial oscillation problem (Figs. 13 and 14). The molecular weight averages obtained are listed in Table IX. Despite its impractical nature this method was useful to illustrate just how the *sk* correction and *h* correction affected the chromatograms (Figs. 15 through 18).

(B) Linear Calibration Curve Search

Since it is known that *h* is related to C_2 and *sk* primarily to C_1 once $Mn(t)$ and $Mw(t)$ or their good estimates $Mn(sk,h)$ and $Mw(sk,h)$ are known then the differential distribution may be obtained by starting with the original C_1 and C_2 and slowly searching, using Program (1) and eq. (51) as the objective function. This, in effect, implements both an *sk* and *h* factor correction on the chromatogram. The probability of more than one set of C_1 and C_2 giving the same Mw and Mn and different distribution is likely remote. In our use of the program we have never encountered an ambiguous distribution although sometimes, as with any search program difficulties in finding the solution were encountered.[4] Since this technique involves no extraneous mathematical operations in calculating the distribution and therefore no step size problems to induce artificial oscillations, very narrow distributions

TABLE IX
Successive Application of *sk* and *h*

Run	*SK*	*h*	*Mn(t)* × 10^{-4}	*Mw(t)* × 10^{-4}	*Mn(∞)* × 10^{-4}	*Mw(∞)* × 10^{-4}	*Mn(sk)* × 10^{-4}	*Mw(slc)* × 10^{-4}	*Mn(sk,h)* × 10^{-4}	*Mw(sk,h)* × 10^{-4}
13307	0.100	1.00	3.48	6.14	3.14	5.74	3.26	5.96	3.59	5.50
13307	0.180	1.00	3.48	6.14	3.14	5.74	3.38	6.20	3.72	5.72
13307	0.150	1.00	3.48	6.14	3.14	5.74	3.34	6.11	3.67	5.64
14612	0.100	1.00	3.48	6.14	2.93	5.96	3.44	6.68	3.54	5.62
14612	0.201	1.00	3.48	6.14	2.93	5.96	3.46	7.04	3.57	5.86
15817	0.100	1.00	3.48	6.14	3.32	5.70	3.49	6.00	3.77	5.48
15817	0.500	1.00	3.48	6.14	3.32	5.70	8.16	27.2	7.15	22.14
15818	0.138	1.00	3.48	6.14	3.32	5.79	3.44	6.16	3.72	5.70
15818	0.100	1.00	3.48	6.14	3.32	5.29	3.38	6.05	3.66	5.60
15819	0.100	1.00	3.48	6.14	3.32	5.83	3.37	6.08	3.67	5.60
15819	0.136	1.00	3.48	6.14	3.32	5.83	3.43	6.18	3.74	5.70
12201	1.750	0.440	19.0	57.0	7.88	42.5	14.6	78.1	16.6	70.0
12201	1.750	0.175	19.0	57.0	7.88	42.5	13.0	68.1	19.7	53.4
12202	1.500	0.161	11.6	30.4	5.00	23.0	8.90	39.6	11.7	26.9
12202	1.641	0.650	11.6	30.4	5.00	22.0	9.04	41.4	9.82	38.6
12203	0.250	0.560	13.7	25.8	5.69	17.8	12.0	28.9	13.4	26.5
12203	0.500	0.650	13.7	25.8	5.69	17.8	13.4	32.5	14.6	29.8

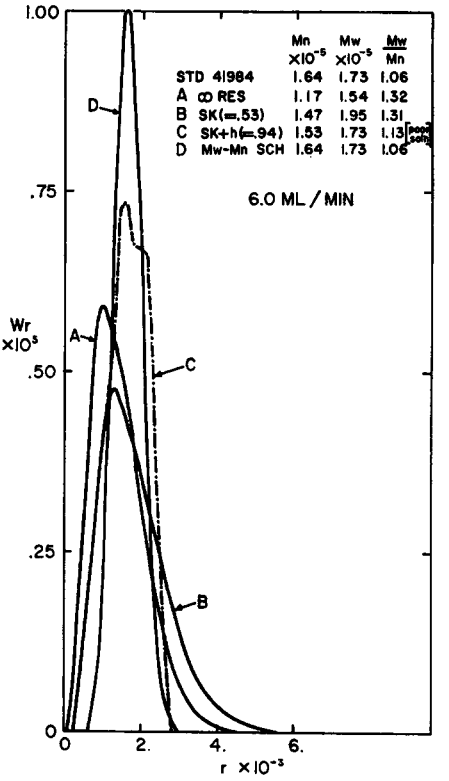


Fig. 19. Successive application of *sk* and *h* corrections compared to the result of a $C_1 - C_2$ search on the true *Mn* and *Mw*. The shoulder on curve *C* is very likely the result of step size difficulty in the Pierce-Armonas program.

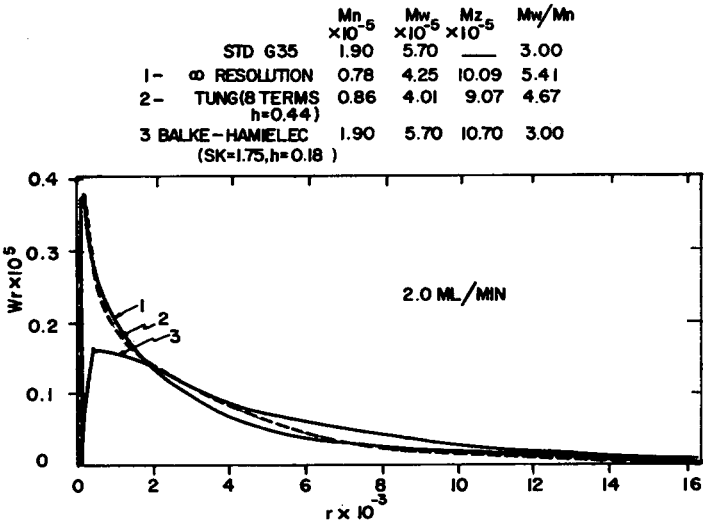


Fig. 20. Result of a $C_1 - C_2$ search compared to Tung resolution correction only.

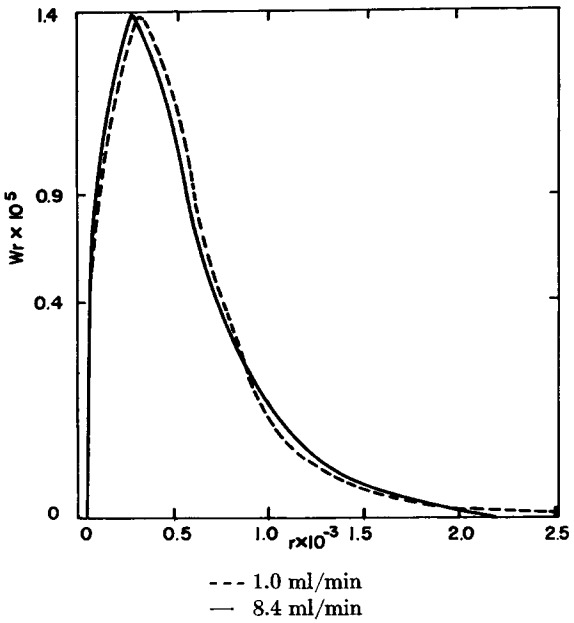


Fig. 21. Comparison of a search corrected 8.4 ml/min distribution with a distribution obtained at 1 ml/min and corrected by using Tungs Hermite polynomial method [$Mw(t) = 6.14 \times 10^4$; $Mn(t) = 3.48 \times 10^4$].

could be obtained without difficulty. Figure 19 shows the narrow distribution obtained by search compared with an attempt to obtain a similar distribution by successive application of sk and h as in (A) above. Figures 20 and 21 show results of this search.

CONCLUSIONS

A new method of interpreting GPC chromatograms which accounts for skewing and symmetrical axial dispersion has been developed. The method has been verified for unimodal chromatograms and linear calibration curves over a variety of GPC operating conditions and polymer molecular weights. In its present form this method can treat sk and h corrections which depend on concentration. This would necessitate the experimental determination of sk and h at a variety of concentration levels. In the present investigation a comprehensive study of concentration effects was not made.

Some of the advantages of this new method are: (*1*) a once through technique may be used to accurately measure the sk and h factors; reverse flow experiments are no longer required, (*2*) both narrow and broad standard may be used to measure the sk and h factors, (*3*) oscillations in the corrected chromatogram due to step size limitations (Method of Pierce-Armonas) and member of terms in a polynomial (Method of Tung, Method of Smith) are eliminated, (*4*) the true molecular weight averages may be easily ob-

tained with a desk calculator, (5) the differential distribution may be obtained rapidly with a small computer.

The principal advantage of this new method is that it seems to allow correct interpretation of skewed GPC chromatograms. This is particularly important for high flow rates (short residence times) and high molecular weights. Application of the method to situations involving nonlinear calibration curves and multi-modal distributions is yet to be evaluated. However, its use in these circumstances is discussed and appears feasible.

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Nomenclature

A	= a constant ($= 1.326/C_2^2$)
C_1,C_2 or $C_1(t),C_2(t)$	= the calibration curve constants determined from the *PEV* of monodisperse standards (the "true" calibration curve) and defined by eq. (9)
$C(1,sk),C(2,sk)$	= the calibration curve constants necessary to effect a skewing correction when used in eq. (9)
D_1,D_2 or $D(1,t),D(2,t)$	= the calibration curve constants determined from the *PEV* of monodisperse standards (the "true" calibration curve) but defined by eq. (7) rather than (9)
$D(1,sk),D(2,sk)$	= the calibration curve constants necessary to effect a skewing correction when used in eq. (7)
$F(v)$	= the function giving the heights of the GPC response (uncorrected chromatogram)
h	= the resolution factor (a measure of curve spreading due to symmetrical axial dispersion[6])
$K(h)$	= a function of resolution factor
M_0	= monomer molecular weight
$M,M(\infty),M(v)$	= molecular weight in the calibration curve obtained from monodisperse standards [eqs. (7), (23)]
$M(sk)$	= molecular weight in the calibration curve used to effect a skewing correction [eq. (22)]
$Mn,Mn(t)$	= the true (absolute) value of number average molecular weight
$Mn(h)$	= the number average molecular weight corrected for symmetrical axial dispersion
$Mn(\infty)$	= the uncorrected number average molecular weight calculated from the GPC response
$Mn(sk)$	= the number average molecular weight corrected for skewing

$Mn(sk,h)$ = the number average molecular weight corrected for both skewing and symmetrical axial dispersion

Mw, $Mw(t)$ = the true (absolute) value of weight average molecular weight

$Mw(h)$ = the weight average molecular weight corrected for symmetrical axial dispersion

$Mw(\infty)$ = the uncorrected weight average molecular weight calculated from the GPC response

$Mw(sk)$ = the weight average molecular weight corrected for skewing

$Mw(sk,h)$ = the weight average molecular weight corrected for both skewing and symmetrical axial dispersion

$P(\infty)$ = the uncorrected polydispersity (eq. (35))

$P(sk)$ = the skewing corrected polydispersity [$= Mw(sk)/Mn(sk)$]

$P(t)$ = the true polydispersity [eq. (36)]

PEV = peak elution volume (in counts)

P_r = concentration of polymer molecules (moles/l)

Q_k = Kth moment of a chromatogram defined by eq. (52)

$Q_k(h)$ = Kth moment of the chromatogram corrected for symmetrical axial dispersion

$Q_k(\infty)$ = Kth moment of the uncorrected chromatogram

r = polymer chain length

SCH = abbreviation for "search"

SK = skewing factor [defined by eq. (21)]

V,v = elution volume

V_a = initial elution volume for sample (low elution count)

V_b = final elution volume for sample (high elution count)

W_r = normalized weight fraction

$W(y)$ = function giving the heights of the chromatogram corrected for symmetrical axial dispersion

y = dummy variable

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