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Comparison of Different Techniques of Correcting for Band Broadening in GPC

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Summary

A qualitative description is presented for two types of gel permeation chromatography (GPC) band broadening. One is symmetrical or Gaussian band broadening; the other is unsymmetrical or skewed band broadening. The effects of band broadening on chromatogram interpretation are discussed.

Available methods of correcting the GPC molecular weight distribution (MWD) for the effects of symmetrical and unsymmetrical band broadening are discussed and compared. For symmetrical band broadening, Tung's original polynomial expansion method is generally adequate. Tung's newer methods look promising for both symmetrical and unsymmetrical band broadening, but they require further evaluation. For unsymmetrical band broadening, the method of Balke and Hamielec looks most promising for unimodal MWD's, but it requires further evaluation with more complex MWD's. Except for the latter method, the corrected MWD's for all methods had inconsistent oscillations when resolution was low or skewing was significant. Since these oscillations are probably caused by noise in the chromatogram or inaccuracies in reading chromatogram heights, they could be minimized by improving chromatogram accuracy and by using correction techniques that include adequate data smoothing.

1. INTRODUCTION

This paper compares techniques for interpretation of GPC chromatograms for linear homopolymers. The techniques compared here are those which attempt to correct for the effects of band broadening (also called zone broadening, peak broadening, instrument spreading, im-

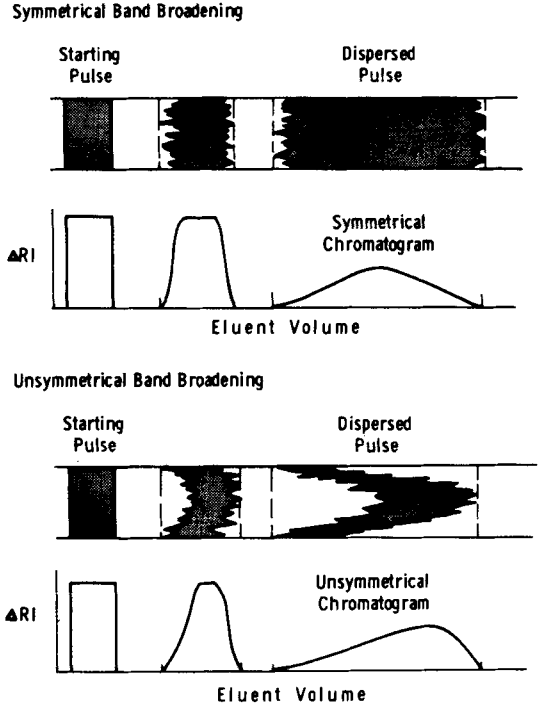

FIG. 1. Effect of axial dispersion and velocity profile on GPC band broadening.

perfect resolution, and axial dispersion). This correction is necessary if absolute molecular weight distributions (MWD's) are desired.

For linear homopolymers there appear to be at least two corrections that must be made, both involving axial dispersion. The GPC chromatogram for a monodisperse polymer may be Gaussian (symmetrical) with respect to eluent volume under certain operating conditions, or it may be highly unsymmetrical, with skewing towards higher eluent volumes and lower molecular weights. Symmetrical and unsymmetrical chromatograms are illustrated in Fig. 1. Symmetrical band broadening is caused by axial dispersion whereas unsymmetrical band broadening or skewing is usually attributed to the effect of velocity profile and radial dispersion on axial dispersion (*1*, *2*). The skewing phenomenon is particularly important for relatively viscous, high molecular weight polymer solutions, where radial dispersion is small due to the small

diffusion coefficients of the polymer molecules. Under these circumstances, velocity profiles can greatly increase axial dispersion and cause unsymmetrical chromatograms.

The effect of symmetrical axial dispersion is to lower the calculated GPC number-average molecular weight, $\bar{M}_n$, and raise the calculated weight-molecular weight, $\bar{M}_w$. The effect of unsymmetrical axial dispersion is to lower both $\bar{M}_n$ and $\bar{M}_w$.

For GPC operation where the chromatograms of narrow standards are Gaussian, methods of chromatogram interpretation are well developed (*3–5*). However, when chromatograms of narrow standards are unsymmetrical, techniques of interpretation are not nearly so well developed (*6–8*). This paper compares the available methods that correct for symmetrical and unsymmetrical band broadening. These are methods by Tung (*3, 9*), Smith (*10*), Hess and Kratz (*11*), Pickett, Cantow, and Johnson (*12*), and Balke and Hamielec (*8*).

2. BASIS FOR THE MATHEMATICAL CORRECTION OF GPC BAND BROADENING

Before comparing the various methods of chromatogram interpretation, it would be instructive to consider the behavior of a pulse of monodisperse polymer solution as it progresses through the GPC columns and the chromatograms resulting therefrom. This will help to illustrate the basis of interpretation for polydisperse samples used by the various methods compared here.

Figure 1 illustrates the two types of undesirable GPC band broadening for an input pulse of monodisperse polymer solution. Symmetrical band broadening is caused by eddy and molecular diffusivity at the leading and trailing edges of the pulse. This type of flow has been referred to as dispersed plug flow (*13*). Its effect is the same on both edges of the pulse and causes symmetrical broadening and dilution of the pulse with a resulting symmetrical chromatogram.

Unsymmetrical band broadening is caused by an interaction between a nonuniform velocity profile and eddy and molecular diffusivity, as illustrated in Fig. 1. Since the pulse velocity ranges from almost zero near the wall to a maximum at the tube center, the resulting chromatogram is skewed toward higher elution volumes. This tailing toward higher elution volumes is more pronounced for higher molecular weight polymers because the larger molecules diffuse more slowly

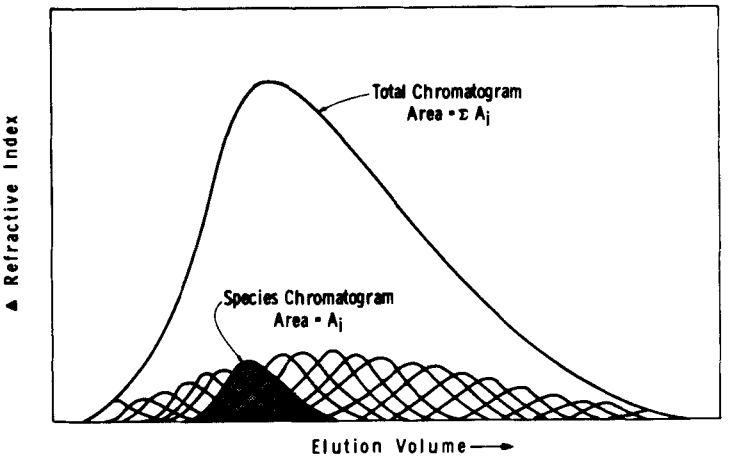

FIG. 2. Species contributions to the total chromatogram.

away from the wall toward regions of lower concentration and higher flow velocity.

For the case where we have band broadening, Fig. 2 illustrates what we might observe if we could "see" the individual molecular species that contribute to the overall chromatogram. To obtain a molecular weight distribution, we would simply measure the amount (i.e., area) of each species present and divide by the total amount. Since we cannot see or measure the amounts of individual species present, these amounts must be calculated from the overall, measured chromatogram. Since more than one species contributes to the chromatogram height at a particular elution volume, the calculation of species amounts is not straightforward. To convert a chromatogram into a molecular weight distribution, each of the techniques compared here must assume a shape for the single molecular species and calibrate for the parameters that define the single species shape. Each method also requires a calibration of molecular weight versus elution volume. From the assumed shape for the single species, the measured height at a particular elution volume can be expressed in terms of the unknown amounts of species contributing at that point. In principle, if n unknown species are present, the MWD can be calculated by reading n heights off the chromatogram to give n equations in n unknowns. The methods of chromatogram interpretation compared here differ only in the techniques they use to solve for the unknown species amounts from measured chromatogram heights.

3. METHODS BY TUNG

3.1. Development

Tung was one of the first to develop methods to correct for band broadening (*3*). In his early development he assumed that the chromatograms of single species in a polydisperse polymer were Gaussian (symmetrical). The Gaussian-shaped chromatogram $F(v)$ was represented by

$$F(v) = A\sqrt{h/\pi}\exp[-h(v - v_0)^2] \tag{1}$$

where v is eluent volume, v_0 is the eluent volume at the peak of the curve, A is a constant related to the area and weight of polymer injected, and h is the resolution factor [$= \frac{1}{2}(\text{variance})^2$].

For a multicomponent polymer system with n species, the chromatogram height $F(v)$ is the sum of the height contributions of the individual species, i.e.,

$$F(v) = \sum_{i=1}^{n} A_i\sqrt{h_i/\pi}\exp[-h_i(v - v_{0i})^2] \tag{2}$$

If the number of species is large, a continuous distribution function $W(y)$ can be used to denote the abundance of components in the mixture. The chromatogram can then be represented by

$$F(v) = \int_{v_a}^{v_b} W(y)\sqrt{h/\pi}\exp[-h(v - y)^2]\,dy \tag{3}$$

where v_a is the initial eluent volume and v_b is the final eluent volume of the chromatogram.

Equation (3) was proposed by Tung (*3*) for the purpose of GPC chromatogram interpretation. It is generally referred to as his integral dispersion equation and is used to solve for species amounts from measured chromatogram heights.

In his early work (*3*) Tung developed two methods of solving his integral dispersion equation to obtain a chromatogram corrected for band broadening. One method used the Gaussian quadrature formula and linear programming. This method has not been extensively evaluated. Tung found that it gave satisfactory results but required excessive computation time (*9*). The other method used a polynomial expansion technique. It has been evaluated for a wide range of GPC operating conditions (*6*, *7*).

The polynomial expansion method assumes that the resolution factor

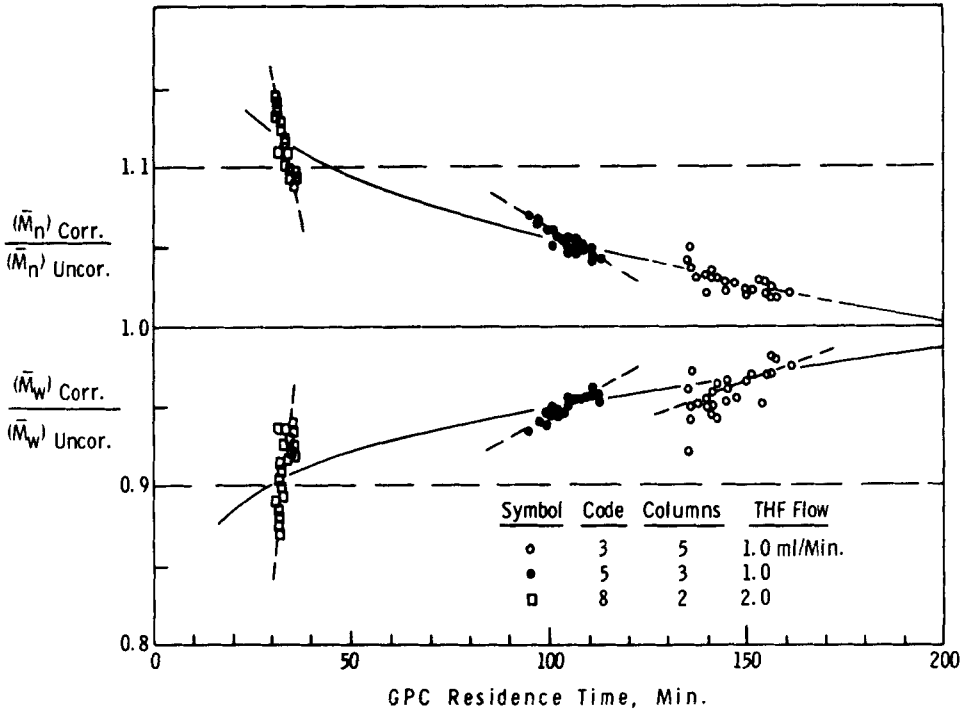

FIG. 3. Ratio of corrected to uncorrected molecular-weight averages as a function of GPC residence time and column combination for Tung's polynomial expansion method. Gaussian band broadening assumed.

h is constant over the elution volume range of a chromatogram and that the band broadening due to dispersion can be represented by a Gaussian distribution function. The method solves for the resolution corrected chromatogram $W(y)$ by using a polynomial representation for $F(v)$ and $W(y)$ and performing the integration in Eq. (3). A predetermined resolution factor is used in the solution.

3.2. Evaluation of Tung's Polynomial Expansion Method

In the evaluation of this and other methods by Duerksen and Hamielec (*6*, *7*), polystyrene samples covering a wide range of molecular weights were analyzed over a wide range of resolutions. Different resolutions were obtained by varying GPC flow rate and column combinations. To be truly effective a correction method should give the

same corrected MWD for the same sample analyzed at several widely different resolutions.

For Tung's polynomial expansion method, molecular weight averages for the same sample run at different resolutions agreed well when band broadening was Gaussian or nearly so (*6*). In general, this was true for low molecular weights (less than 100,000) and flow rates of 1.0 and 3.0 ml/min. At higher molecular weights or a flow rate of 2.0 ml/min, skewing was significant and agreement between molecular weight averages was poor. The averages with skewing present were lower than when no skewing was present.

The effect of assuming Gaussian band broadening and correcting for it is to raise the calculated $\bar{M}_n$ and lower the calculated $\bar{M}_w$ relative to the uncorrected values. This is illustrated in Fig. 3 for a range of GPC residence times and three different column combinations (*6*).

The effect of assuming Gaussian band broadening when it is actually skewed toward higher elution volume and lower molecular weight is illustrated in Fig. 4. The actual skewed single species area is represented by a Gaussian (symmetrical) area (dashed lines) having the same moments about the peak elution volume, v_0. The area between the skewed shape and Gaussian shape on both sides of v_0 is, therefore, regarded as a contribution from lower molecular weight material than is really the case. The net effect is to calculate a lower $\bar{M}_n$ and $\bar{M}_w$ than the true values and an MWD skewed toward lower molecular

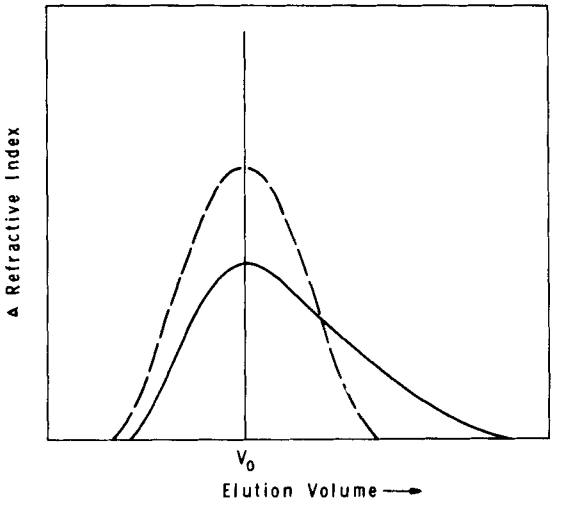

FIG. 4. Skewed vs Gaussian single species shapes.

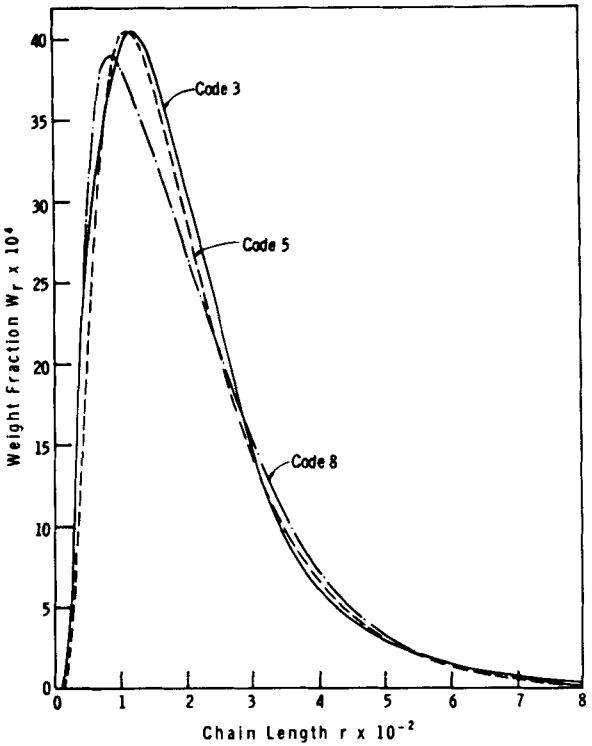

FIG. 5. Typical MWD's for a low molecular weight polystyrene corrected by Tung's polynomial expansion method.

weight. This predicted behavior agrees with the observed behavior (*6*, *14*).

Figure 5 illustrates MWD's calculated by Tung's polynomial expansion method for a low molecular weight sample. Three column combinations were used (*7*), and the resolution corrections were relatively small (less than 10% on the averages). Agreement was good between Column Codes 3 and 5, which had nearly Gaussian band broadening at this molecular weight level. Column Code 8, however, had slightly skewed band broadening; this has resulted in an MWD skewed toward lower molecular weight relative to the Codes 5 and 3 MWD's.

Figure 6 illustrates MWD's calculated for a high molecular weight broad MWD sample. The resolution factors were around 1.0 counts^{-2} for Code 6 and 0.5 for Codes 11 and 12, resulting in a relatively large resolution correction. Skewing for narrow standards for Code 6 was

significant, and for Codes 11 and 12 it was extremely severe, with tailing extending out to the monomer elution volume. The resulting MWD's for the broad samples for Codes 11 and 12 in Fig. 6 were skewed toward lower molecular weight relative to Code 6. In addition, large inconsistent oscillations are observed at low molecular weights for Codes 11 and 12. Tung has pointed out (*9*) that these oscillations can be caused by chromatogram noise and by differences between the assumed and actual single species shape when the resolution correction is large. Codes 11 and 12 had significant chromatogram noise and large resolution corrections.

3.3. Other Methods for Solving Tung's Integral Dispersion Equation

Other methods for solving Tung's integral dispersion equation have recently been developed (*9*, *15*, *16*).

A method by Pierce and Armonas (*15*) is based on the use of Fourier transforms. Since it treats the chromatogram a point at a time, a variation in h can be handled by using a different h at each elution volume considered. The method also requires short computation time. However, from noise in the chromatogram, it is possible to generate oscillations in the corrected chromatogram in taking derivatives at a

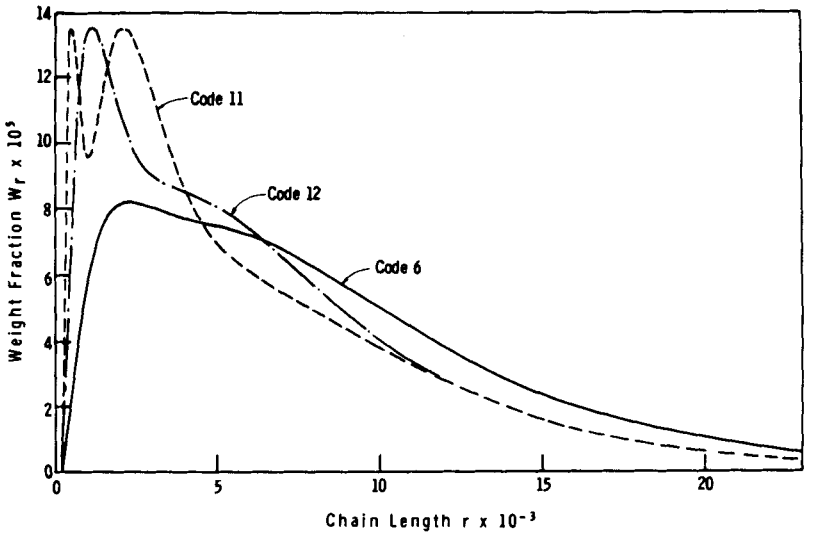

FIG. 6. Typical MWD's for a high molecular weight polystyrene corrected by Tung's polynomial expansion method.

point on the chromatogram (*17*). Tung also points out (*9*) that for large dispersion corrections the use of derivatives at a point gives inaccurate results. Aldhouse and Stanford (*16*) have proposed a similar point-to-point approach using a Taylor's expansion method. Since derivatives of the chromatogram are also required for their solution, the deficiencies of the method of Pierce and Armonas should still be present.

Tung has proposed two new methods of solving his integral dispersion equation (*9*, *18*): a Fourier analysis method and a polynomial method. These compare very favorably with the above-mentioned methods.

Both of Tung's methods are simple and require little computation time. In addition, the polynomial method is less likely to generate oscillations due to the smoothing characteristics of its least squares fitting. The Fourier analysis method can use unsymmetrical functions to correct for skewed band broadening. Further testing and evaluation are required to determine how well this method can correct for unsymmetrical band broadening.

4. METHOD OF SMITH

4.1. Development

To solve for unknown species amounts from measured chromatogram heights, Smith (*10*) proposed an equation which is equivalent to Eq. (2) in Tung's development. In Smith's notation the chromatogram height at elution volume v_0 is

$$f(v_0) = \cdots + \frac{K_{-1}}{\sqrt{2\pi\sigma_{-1}}} \exp\left[\frac{-(v_0 - v_{-1})^2}{2\sigma_{-1}}\right] + \frac{K_0}{\sqrt{2\pi\sigma_0}} + \frac{K_1}{\sqrt{2\pi\sigma_1}} \exp\left[\frac{-(v_0 - v_1)^2}{2\sigma_1}\right] + \cdots \quad (4)$$

where K_j is a factor proportional to the concentration of the jth molecular species. The K_j's are comparable to Tung's A_i's in Eq. (2), and the σ's are related to Tung's h by $h = \frac{1}{2}\sigma^2$. Solution of the K_j's yields the MWD.

Smith assumed that the K_j's were proportional to the chromatogram height at v_j, i.e.,

$$K_j = k_j f(v_j) \quad (5)$$

By considering the polymer sample to consist of a finite number of species n, and by assuming that the proportionality constants k_j are

the same for all species contributing to chromatogram height $f(v_j)$ at elution volume v_j, Smith was able to rewrite Eq. (4) as

$$f(v_j) = k_j \sum_{i=0}^{n} (h_i/\pi)^{1/2} f(v_i) \{\exp [-h_i(v_j - v_i)^2]\} \quad (6)$$

A set of n equations in n unknown k_j's is obtained; one equation for each chromatogram height read. The assumption of the same k_j's for all species contributing at v_j allows the equations in k_j to be solved consecutively rather than simultaneously. This amounts to a point-to-point solution for species amounts and permits the use of a different resolution factor h for each elution volume used.

The k_j values range from zero at each end of the chromatogram to a maximum value at or near the peak elution volume. However, the assumption that the k_j's are the same for all species contributing at v_j is still quite accurate since only those species relatively close to v_j will contribute, and the variation in their k_j's is relatively small.

Smith later modified his method to eliminate the above assumption (*7*). The initial set of calculated k values is used to calculate the chromatogram height at each elution volume v_i using Eq. (6) and the calculated $(k_j)_i$ for each species i. If these calculated heights do not agree with the observed heights, each k is adjusted by the ratio of the observed to calculated height. This calculation is repeated until the desired agreement between observed and calculated heights is obtained.

Smith's modified method also compared the area under the chromatogram and the sum of the area contributions of the assumed species. If the ratio of the calculated to observed area was less than 1, it was necessary to assume more species (i.e., read more heights off the chromatogram). If the ratio was greater than 1, the resolution factors were assumed to be too small. They were increased according to the ratio of the areas and all calculations were repeated.

4.2. Evaluation of Smith's Method

Molecular weight averages by Smith's method using a Gaussian single species shape agreed well with averages by Tung's method (*6*, *14*), even though a variable h was used in Smith's method. The Gaussian shape was inadequate when skewing of narrow standards was significant.

A log normal single species shape gave higher corrected molecular weight averages than did the Gaussian shape. When skewing was significant, the averages for the log normal shape also agreed better

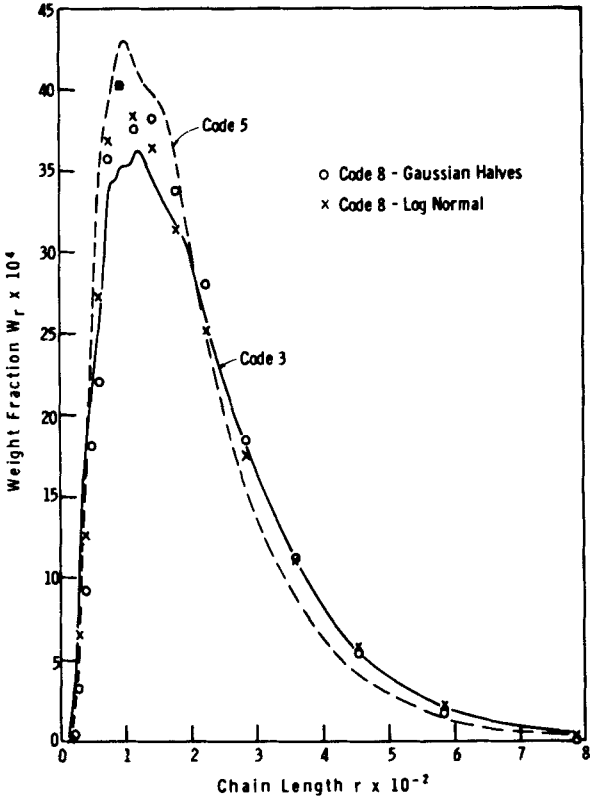

FIG. 7. Typical MWD's for a low molecular weight polystyrene corrected by Smith's method.

with averages calculated at conditions where the single species shape was Gaussian (*6,14*). It has been shown (*14*) that the unsymmetrical log normal shape raises both the number- and weight-average molecular weights relative to the uncorrected values. This behavior is directionally correct for correction of skewed band broadening.

A single species shape made up of two Gaussian halves, each with its own h, did not account for skewed band broadening as well as the log normal shape did (*14*). Using Gaussian halves, the weight-average molecular weights were significantly lower than those calculated with the log normal shape (*14*). The Gaussian halves did not correct sufficiently for skewing.

Typical MWD's for a low molecular weight polystyrene sample

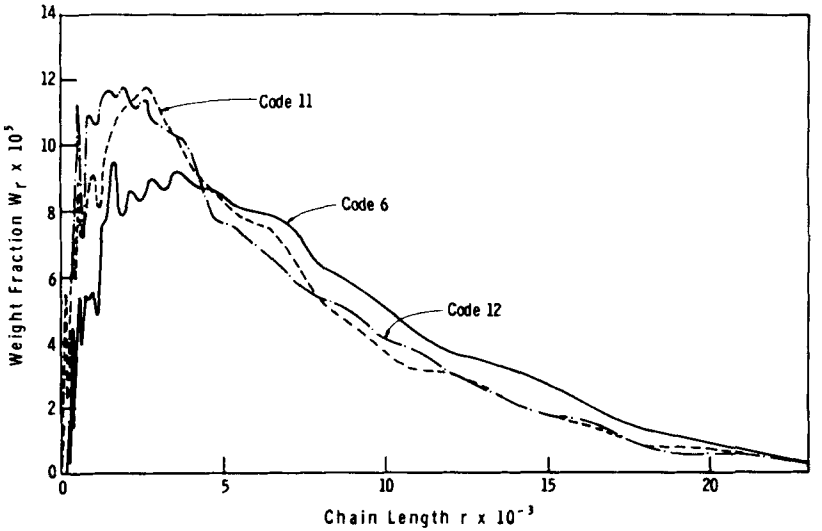

FIG. 8. Typical MWD's for a high molecular weight polystyrene corrected by Smith's method.

($\bar{M}_n = 14{,}000$) are shown in Fig. 7. Agreement between different column combinations is quite good except for small oscillations.

Typical MWD's for a high molecular weight sample ($\bar{M}_n = 400{,}000$) are shown in Fig. 8. These were calculated using a single species shape made up of unequal Gaussian halves. There are large deviations among the MWD's and large oscillations in each MWD. The oscillations may be caused by noise in the chromatogram. The deviations among the MWD's again show that the Gaussian halves did not adequately represent the effect of skewing.

5. THE METHOD OF HESS AND KRATZ

To solve for unknown species amounts from measured chromatogram heights, the method of Hess and Kratz (*11*) approximates the chromatogram by a set of linear algebraic equations which are solved simultaneously by matrix inversion to give species amounts. A sample of broad MWD is considered to consist of a finite number n of "pure" solutes. At least n heights are read off the chromatogram giving n equations in n unknowns, similar in form to Eq. (2). The method is based upon a dispersion model for a packed bed and requires experimental measurement of the single species dispersion coefficient E over the molecular weight range of interest.

Since the dispersion model predicts an unsymmetrical shape for the single species chromatogram (*11*, *13*), it can be used to account for skewing. The predicted shape becomes more skewed as the dispersion coefficient E increases, ranging from almost symmetrical at very low E to very skewed at high E. The experimentally determined value of E has been observed to increase as elution volume decreases (*6*, *14*), corresponding to increased skewing with increased molecular weight.

A very limited evaluation of this method has been made (*6*). For most chromatograms, the solution for species amounts was unsuccessful because the matrix of coefficients for the unknowns was ill conditioned. The successful solutions agreed reasonably well with results by Tung's polynomial expansion method (*6*) for the case of symmetrical band broadening. Tung has pointed out (*9*) that the unsymmetrical shape predicted by the dispersion model of Hess and Kratz could be used in his new Fourier analysis method to account for skewed band broadening. Further evaluation is necessary to determine the adequacy of the dispersion model in accounting for skewed band broadening.

6. THE METHOD OF PICKETT, CANTOW, AND JOHNSON

To solve for unknown species amounts from measured chromatogram heights, the method of Pickett, Cantow, and Johnson expresses the chromatogram or concentration curve as the weighted sum of the normalized concentration curves of its constituent species or fractions (*12*). This equation is similar in form to Eq. (2) in Tung's development. However, the method does not assume a specific shape for the chromatogram of a single species as the previously discussed methods do. Instead, it uses the observable shapes of narrow distribution polymer standards of known MWD to represent the constituent species or fractions. The reshaping principle of the method says that if the chromatogram can be represented as a weighted sum of normalized fractions, the reshaped chromatogram (i.e., the chromatogram corrected for band broadening) is represented by the same weighted sum of the reshaped fractions. The method uses a least squares technique to find the weighting factors that fit the sum of the fractions to the measured chromatogram.

Pickett, Cantow, and Johnson tested their method using two mathematically generated chromatograms (*12*). The method was able to resolve the chromatogram into its constituent fractions if a sufficient number of chromatogram points was used.

The method was also tested on an experimental chromatogram ob-

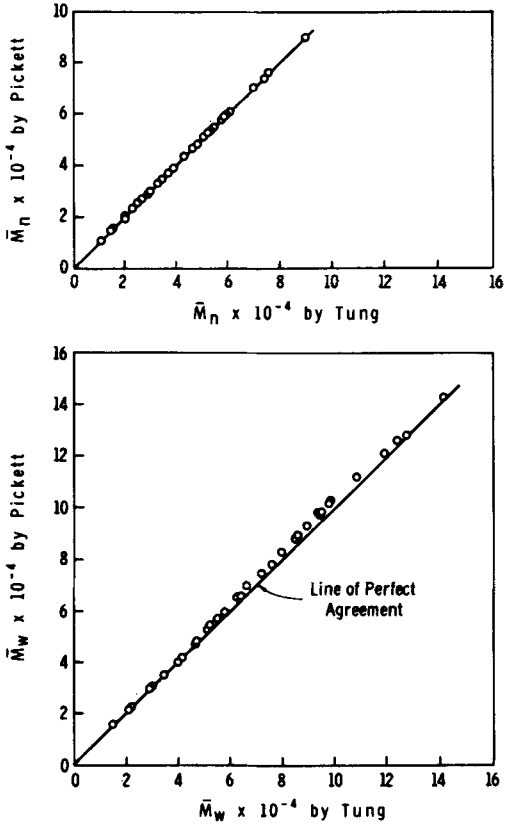

FIG. 9. Comparison of Code 5 molecular weight averages. Method of Pickett, Cantow, and Johnson vs the method of Tung.

tained from a sample consisting of equal amounts by weight of three low molecular weight polystyrene standards (*12*). The chromatogram was unimodal with no shoulders. The chromatograms of the three components were also added mathematically to give an expected chromatogram that was indistinguishable from the measured chromatogram, except for a slight shift in elution volume. The method resolved the synthesized chromatogram exactly into its three components. The measured chromatogram was resolved into three components, but these did not agree with the constituent components, either in proportion or elution volume. This was attributed to the slight shift in elution volume.

An evaluation of the method was also made by Duerksen and

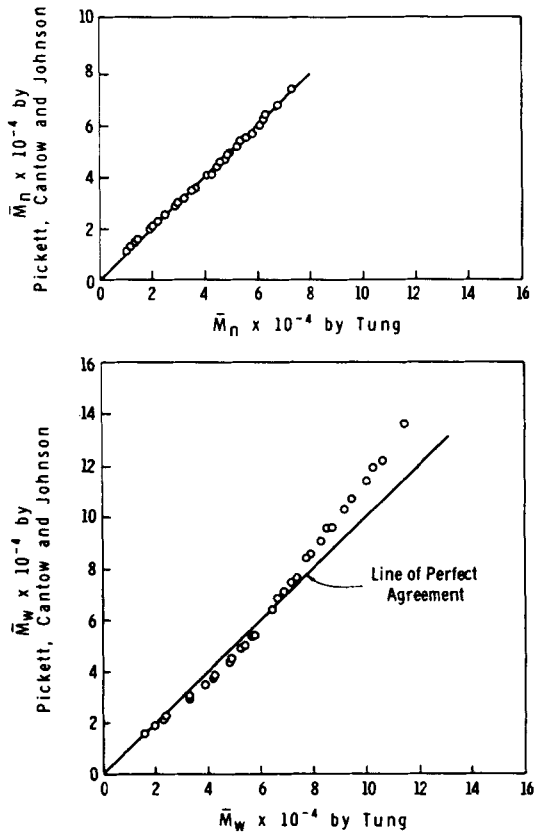

FIG. 10. Comparison of Code 8 molecular weight averages. Method of Pickett, Cantow, and Johnson vs the method of Tung.

Hamielec (*6, 7, 14*) who used broad distribution polystyrene samples. Code 5 standard chromatograms were nearly Gaussian; Code 8 standard chromatograms were significantly skewed. The $\bar{M}_n$ results showed reasonable agreement, but the Code 8 $\bar{M}_w$'s were generally slightly lower than the Code 5 values (*14*).

Figures 9 and 10 compare Codes 5 and 8 molecular weight averages for the method of Pickett et al. with Tung's polynomial expansion method. The Code 5 results show reasonable agreement over the entire molecular weight range. The Code 8 results show reasonable agreement in $\bar{M}_n$ but poor agreement in $\bar{M}_w$. The poor agreement in $\bar{M}_w$ is due to nonlinearities in the calibration curve and skewing effects. These

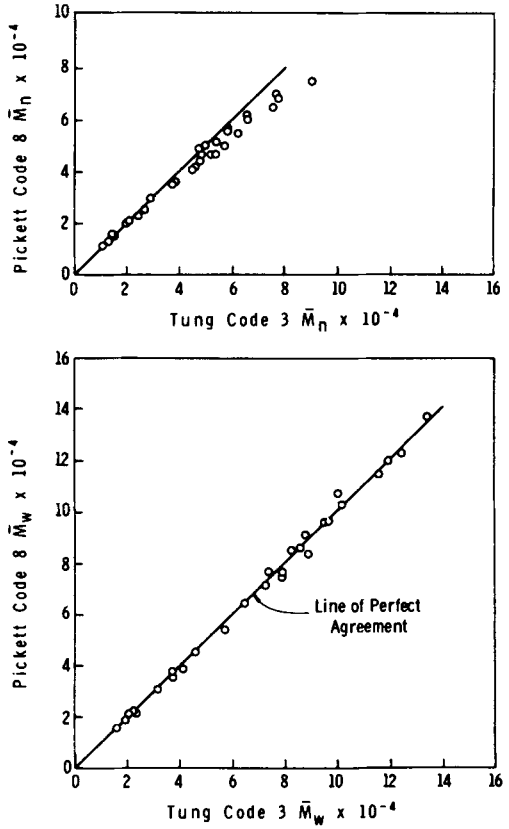

FIG. 11. Comparison of molecular weight averages. Method of Pickett, Cantow, and Johnson for Code 8 vs the method of Tung for Code 3.

effects were accounted for in the method of Pickett et al. but not in Tung's method.

If the method of Pickett et al. successfully accounts for the effect of skewing on molecular weight averages, its Code 8 averages should agree with the Code 3 averages by Tung's polynomial expansion method, since Code 3 standard chromatograms were Gaussian. These results are compared in Fig. 11. Except for the upper $\bar{M}_n$ range, reasonable agreement is indicated, certainly much better than was observed for similar comparisons with the previously discussed methods (*14*).

Typical MWD's for the same sample run on Codes 5 and 8 are compared in Fig. 12. Even though the molecular weight averages from Codes 5 and 8 were in good agreement, the MWD's differed signif-

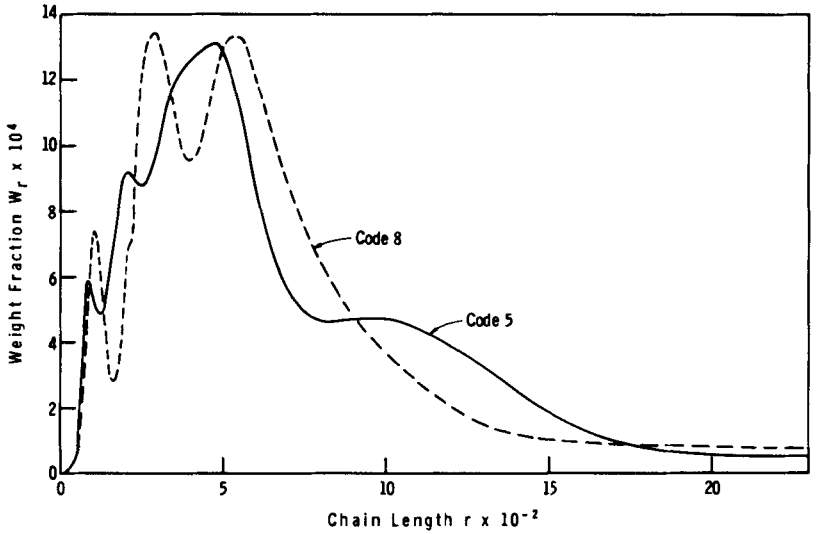

FIG. 12. Typical MWD for a polystyrene corrected by the method of Pickett, Cantow, and Johnson.

icantly in detail. Large inconsistent oscillations were observed in many of the MWD's for Codes 5 and 8, even at low molecular weights. Since the method was able to resolve synthetic chromatograms (*12*) without introducing oscillations, they appear to be caused by noise or inaccuracies in reading the chromatogram. Since detailed knowledge of the MWD may be required to correlate with physical properties of polymers, any artificial oscillations must be eliminated to make the methods of chromatogram interpretation completely effective.

7. THE METHOD OF BALKE AND HAMIELEC

Balke and Hamielec (*8*) have recently proposed a method that corrects separately for symmetrical and skewed band broadening and avoids oscillations in corrected MWD's. The method requires three GPC calibrations:

1. Molecular weight versus elution volume using narrow standards.
2. Resolution factor h versus elution volume to correct for symmetrical band broadening (narrow or broad standards can be used).
3. Skewing factor sk versus elution volume for skewed band broadening (narrow or broad standards can be used).

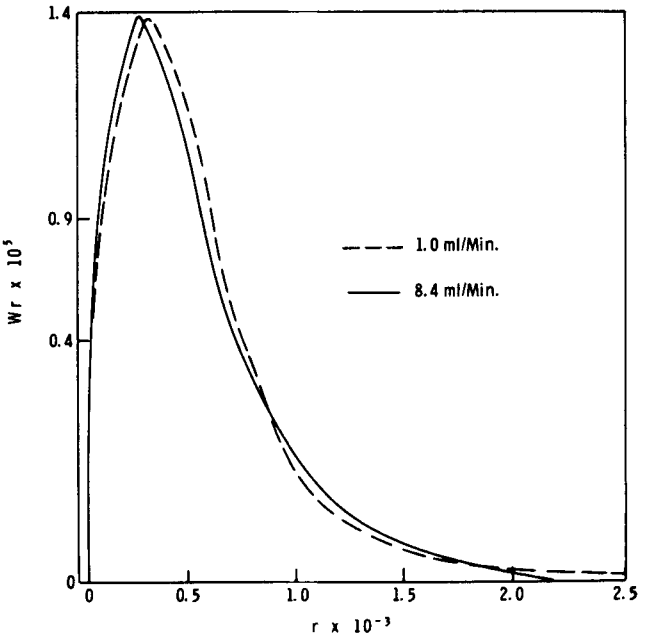

FIG. 13. Comparison of MWD's corrected by the method of Balke and Hamielec and Tung's polynomial expansion method.

Techniques for calibrating for h and sk without using reverse flow are described in the literature (*8, 17*).

When the above calibrations have been made, corrected molecular weight averages for an unknown sample can be calculated from the following equations

$$M_n(h,sk) = M_n(\infty)\left[1 + \frac{sk}{2}\right]\exp(+A/h) \tag{7}$$

$$M_w(h,sk) = M_w(\infty)\left[1 + \frac{sk}{2}\right]\exp(-A/h) \tag{8}$$

where $M_n(h,sk)$ and $M_w(h,sk)$ are the number- and weight-average molecular weights corrected for symmetrical band broadening with h and for skewing from the Gaussian shape with sk. $M_n(\infty)$ and $M_w(\infty)$ are the averages calculated from the chromatogram assuming perfect resolution (no band broadening). $A = (2.303/2C_2)^2$, where C_2 is the slope of the molecular weight calibration curve.

The corrected molecular weight averages are then used to find an

effective linear calibration curve, which is used with the raw chromatogram to calculate a corrected MWD. The corrected MWD will have the correct number- and weight-average molecular weights, but there is no guarantee that higher molecular weight averages will be accurate (*17*). Because the raw chromatogram, rather than a corrected chromatogram, is used to calculate the MWD, any chromatogram noise or reading inaccuracies are less likely to be magnified into artificial oscillations.

Figure 13 shows a comparison of two corrected MWD's for the same sample (*8*). The MWD obtained at 1.0 ml/min flow rate was calculated using Tung's polynomial expansion method (*3*). At this flow rate, the standard chromatograms were close to Gaussian. The MWD obtained at 8.4 ml/min was calculated using the method of Balke and Hamielec (*8*). Although skewing was significant at this high flow rate and the correction for band broadening was large, the MWD agrees very well with the MWD at 1.0 ml/min and does not have any inconsistent oscillations. A more severe test of the method of Balke and Hamielec would be obtained by treating a high flow rate chromatogram for a known mixture with a multimodal MWD to see if the method can resolve the peaks and give the correct MWD.

8. CONCLUSIONS

Tung's original polynomial expansion method works well when the chromatograms of single species are Gaussian. However, when they are skewed, and when the correction for band broadening is large, the corrected molecular weight averages are too low and the MWD's exhibit inconsistent oscillations. Two more recent methods by Tung are computationally faster and more accurate than his original polynomial expansion method. They also allow variable resolution factors. One of these also allows the use of a nonsymmetrical single species shape. Further evaluation of these more recent methods is required.

The method of Smith uses a log normal shape or two Gaussian halves for the single species to account for skewing. Although these work better than the Gaussian shape, they have proven to be inadequate to completely account for skewing. Inconsistent oscillations in the corrected MWD's were observed when skewing was significant and corrections were large.

The method of Hess and Kratz is based upon a dispersion model which predicts a nonsymmetrical single species shape. This method has not been properly evaluated due to computational difficulties with the matrix inversion technique for solving for species amounts.

The method of Pickett, Cantow, and Johnson uses observable shapes for narrow standards to represent the single species shapes. This method appears to account reasonably well for the effects of skewing on molecular weight averages. However, many MWD's exhibit inconsistent oscillations.

The method of Balke and Hamielec corrects separately for symmetrical band broadening and for skewing. The GPC is calibrated for molecular weight, resolution factor, and skewing factor using standards. Corrected molecular weight averages are first found and these are used to find an effective molecular weight calibration curve with which to calculate the corrected MWD from the raw chromatogram. This method appears to adequately account for skewed band broadening and does not generate inconsistent oscillations in the MWD. Further evaluation is necessary for more complex MWD's.

The inconsistent oscillations in the MWD's observed with most of the methods appear to be caused by GPC noise and limited accuracy in reading trace heights, rather than by the mathematical techniques involved. If this is the case, these oscillations might be eliminated by reducing instrument noise, improving the accuracy of height readings, and by smoothing the height readings before calculation. Further work is required in this area.

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