SEC–Viscometer Detector Systems. I. Calibration and Determination of Mark–Houwink Constants

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SYNOPSIS

Five different types of calibration curve currently used in size exclusion chromatography–differential viscometer (SEC–DV) systems were identified and their use summarized. A simple method of deriving weighting factors for fitting local intrinsic viscosity calibration curves was shown to greatly improve the precision of calculated molecular weight distributions. The problem of reliably extrapolating the fitted curves to allow for differences in sensitivity among detectors has yet to be examined. With regard to Mark–Houwink constants, a method of fitting data from the SEC–DV system to obtain more statistically sound values was derived. For the data used here, the new method involves fitting a plot of logarithm of the local intrinsic viscosity of the sample vs. logarithm of the universal calibration curve parameter, J_i. Results for the data obtained appeared only slightly more precise than those for the traditional method. However, the new method promises improved reliability. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The widespread use of size exclusion chromatography (SEC)–viscometer detector systems has increased, rather than eliminated, our need to consider two old chromatography topics: calibration and resolution correction. There are several reasons for the increasing importance of these topics. One is that these topics have now expanded: calibration can now refer to correlations of molecular weight or intrinsic viscosity with retention volume; resolution correction can be applied to the differential refractive index (DRI) chromatogram, the whole polymer molecular weight averages, and the local intrinsic viscosities.[1] Another reason is that new uses for the calibration curves are being proposed: for example, they are being utilized in determining interdetector volume.[2–7] Finally, additional complications arise as new variables affect our data: measured local intrinsic viscosity values show high noise levels at the extreme ends of the molecular weight range of the sample and increase uncertainty of the tails of the computed molecular weight distribution; least-squares cubic spline fits to calibration curves have sometimes been used because very high resolution columns caused irregular calibration changes.[4,5]

In this paper, we focus upon calibration and the closely coupled subject of determining Mark–Houwink constants. In Part II, resolution correction and its association with interdetector volume determination are the topics.

THEORY

Calibration Fundamentals

The various types of calibration curves considered in this paper are as follows:

Type I Calibration Curve: Molecular Weight Calibration from Narrow Standards

This is the classical SEC calibration curve determined by correlating logarithm of the peak molecular weight with the peak retention volume for narrow polymer standards.

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Type II Calibration Curve: Intrinsic Viscosity Calibration from Narrow Standards and the Differential Viscometer (DV) Detector

This is a correlation of the logarithm of the intrinsic viscosity of polymer standards vs. retention volume. The intrinsic viscosity is obtained from the DV of the narrow standards using eq. (1):

$$\overline{[\eta]} = \frac{\sum_{i=1}^{n_{dv}} \eta_{sp,i} \Delta v}{m} \tag{1}$$

where $\overline{[\eta]}$ is the whole polymer intrinsic viscosity; $\eta_{sp,i}$, the local specific viscosity at retention volume, v_i, (i.e., the total volume of eluent that has passed through the columns up to that time); n_{dv}, the number of data points in the DV chromatogram; m, the mass of polymer injected; and Δv, the constant retention volume increment.

Type III Calibration Curve: Universal Calibration Curve Derived from Types I and II Calibration Curves

This is a correlation of the logarithm of the size parameter J_i vs. peak retention volume where J_i is the product of the molecular weight (from the Type I calibration curve) and the intrinsic viscosity (from the Type II calibration curve) at each retention volume.

Type IV Calibration Curve: Intrinsic Viscosity Calibration from the DV and DRI Detectors

This is a correlation of the logarithm of the local intrinsic viscosity vs. retention volume. The local intrinsic viscosity (i.e., the intrinsic viscosity at each retention volume, $[\eta]_i$) is obtained from eq. (2):

$$[\eta]_i = \frac{\eta_{sp,i}}{c_i} \tag{2}$$

where c_i, the concentration at retention volume v_i, is obtained from the DRI detector response, W_i, assuming perfect resolution:

$$c_i = \frac{W_i}{\sum_{i=1}^{n_{ri}} W_i \Delta v} m \tag{3}$$

where n_{ri} is the number of data points in the DRI chromatogram.

Equation (3) in terms of the normalized heights of the perfect resolution DRI chromatogram, $W_{N,i}$, is

$$c_i = W_{N,i} m \tag{4}$$

To obtain the $\eta_{sp,i}$ corresponding to each c_i, the interdetector volume must be known.

Type V Calibration Curve: Molecular Weight Calibration from Types III and IV Calibration Curves

This molecular weight calibration curve can be generated for each sample using the values of J_i (from the Type III calibration curve) with the corresponding value of the local intrinsic viscosities measured for the sample, $[\eta]_i$ (i.e., obtained from the Type IV calibration curve):

$$\log M_i = \log J_i - \log[\eta]_i \tag{5}$$

The above calibration curves are used in many ways in SEC interpretation. In this paper, we focus on the following uses:

a. Molecular weight averages. $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ by application of a molecular weight calibration curve to the DRI chromatogram:

$$\overline{M_k} = \frac{\sum_{i=1}^{n_{ri}} W_i M_i^{k-1} \Delta v}{\sum_{i=1}^{n_{ri}} W_i M_i^{k-2} \Delta v} \tag{6}$$

where $\bar{M}_k$ is $\bar{M}_n$ when $k = 1$; $\bar{M}_w$, when $k = 2$, and $\bar{M}_z$, when $k = 3$.

The calibration curve required to specify M_i in eq. (6) can be the classical SEC one (a Type I calibration curve) or one determined via the universal calibration curve and the DV (a Type V calibration curve). If the sample contains branched molecules and the latter source is used, then the calibration curve being used is really a plot of local M_n vs. retention volume[8] and the molecular weight averages from eq. (6) can therefore be in error.

b. Molecular weight distribution. The molecular weight distribution of interest here is a plot of $W_{N,\log M_i}$ vs. $\log M_i$, where $W_{N,\log M_i} \Delta \log M_i$ is the weight fraction of polymer between $\log M_i$ and $\log M_i + \Delta \log M_i$.

The ordinate of the molecular weight distribution, $W_{N,\log Mi}$ can be obtained from the DRI detector response in the usual way:

Table I Results for NBS 706 Polystyrene

Average	True Value	Calculated Using Narrow Standard Molecular Weight Calibration Curve and DRI[a]		Calculated Using Universal Calibration, DV and δ[a]	
		Value ± 100 s/ Mean	% Deviation from True Values	Value ± 100 s/ Mean	% Deviation from True Values
$\bar{M}_n$	123,200	101,000 ± 7.72% (102,200 ± 7.83%)	−18.0 (−17.0)	117,800 ± 7.22%	−12.2
$\bar{M}_w$	275,600	289,600 ± 1.00% (296,600 ± 1.05%)	5.08 (7.62)	269,800 ± 2.19%	−2.10
$\bar{M}_z$	434,800	609,200 ± 2.30% (630,400 ± 4.43%)	40.1 (45.0)	558,300 ± 4.33%	28.4

[a] Values in parentheses are results of using a spline fit to the molecular weight (Type I) calibration curve instead of a polynomial fit.

$$W_{N,\log M_i} = -W_{N,i}\left(\frac{\Delta v}{\Delta \log M}\right) \qquad (7)$$

where $W_{N,i}$ is the normalized DRI response at retention volume v and $\Delta v/\Delta \log M$ is the inverse of the slope of the Type I calibration curve.

When we apply eq. (7) to a branched homopolymer with the calibration curve from the Type

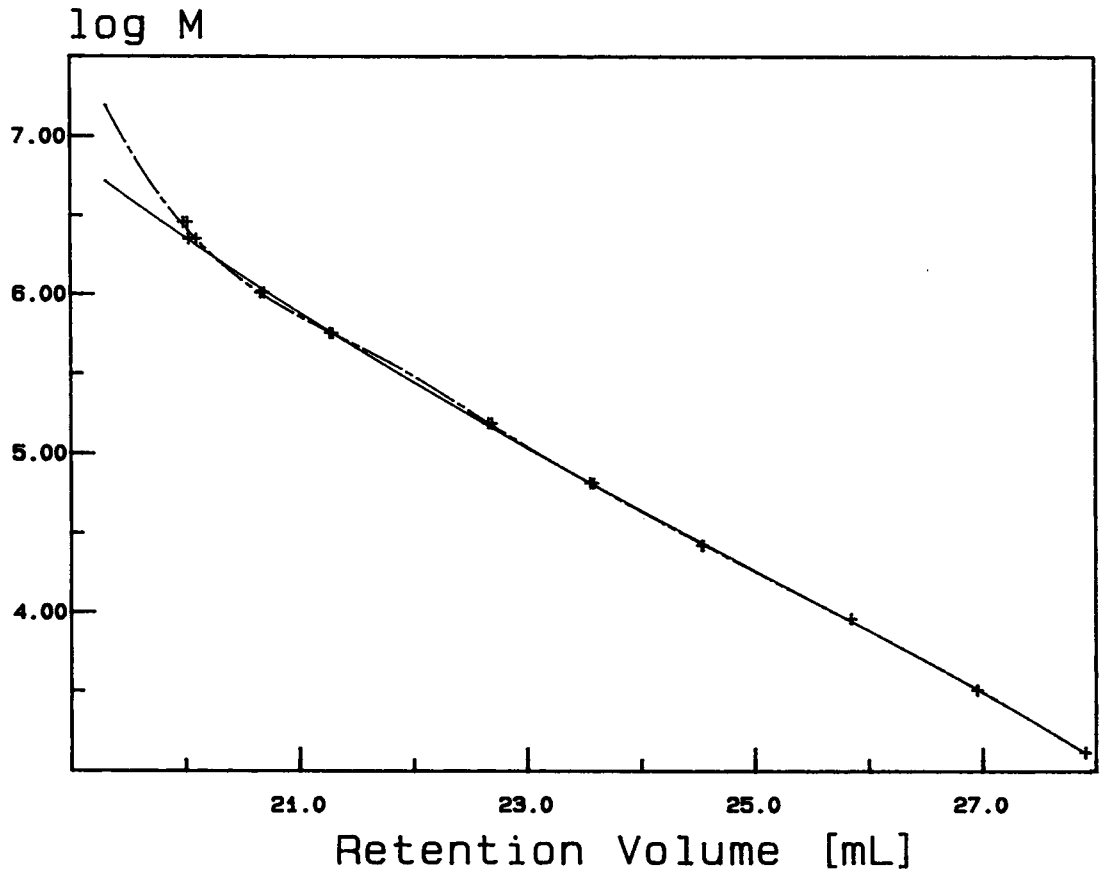

Figure 1 Fit of conventional molecular weight calibration curve obtained from narrow standards (Type I calibration curve) using a fourth-order polynomial (——) and least-square cubic splines (- - -).

V calibration curve, we actually have a plot of $W_{N,\log Mn,i}$ vs. $\log M_{n,i}$, where $W_{N,\log Mn,i}\ \Delta \log M_n$ is the weight fraction of polymer between $\log M_{n,i}$ and $\log M_{n,i} + \Delta \log M_{n,i}$.

c. Mark–Houwink constants. Although difficult to obtain precisely because of their intercorrelation,[9,10] Mark–Houwink constants, K and a, are particularly important when branching analysis must be done.[11] For the SEC–DV system, the constants are conventionally obtained from fitting plots of logarithm of the local intrinsic viscosities of the sample measured using the DV vs. logarithm of molecular weight obtained from a Type V calibration curve [see eq. (5)]. However, this means that the correlation used is $\log[\eta]_i$ vs. $\log J_i - \log[\eta]_i$. Thus, the values of $\log K$ and a are obtained by fitting the following equation:

$$\log[\eta]_i = \log K + a(\log J_i - \log[\eta]_i) \qquad (8)$$

This is obviously a poor equation to be fit by linear regression because linear regression assumes that the error in the values plotted on the abscissa are free of random error while those on the ordinate contain a constant amount of random error. The plot forming the basis for eq. (8) has the ordinate value also as a part of the abscissa value. Also, since $\log[\eta]_i$ of the sample is plotted on both axes, it may be expected that the plot may be distorted if variations in this viscosity are much greater than variations in J_i. Rearranging eq. (8) provides

$$\log[\eta]_i = \left\{\frac{\log K}{1+a}\right\} + \left\{\frac{a}{1+a}\right\}\log J_i \qquad (9)$$

Thus, K and a can be obtained by fitting eq. (9) to a plot of $\log[\eta]$ vs. $\log J$. This assumes constant error in $\log[\eta]$ and negligible error in $\log J$. If there is more error in $\log J_i$, then the reversed plot of $\log J_i$ vs. $\log[\eta]_i$ is required so as to have the quantity with the most error plotted as the ordinate. [Equation (9) would then be rearranged to be explicit in $\log J_i$.]

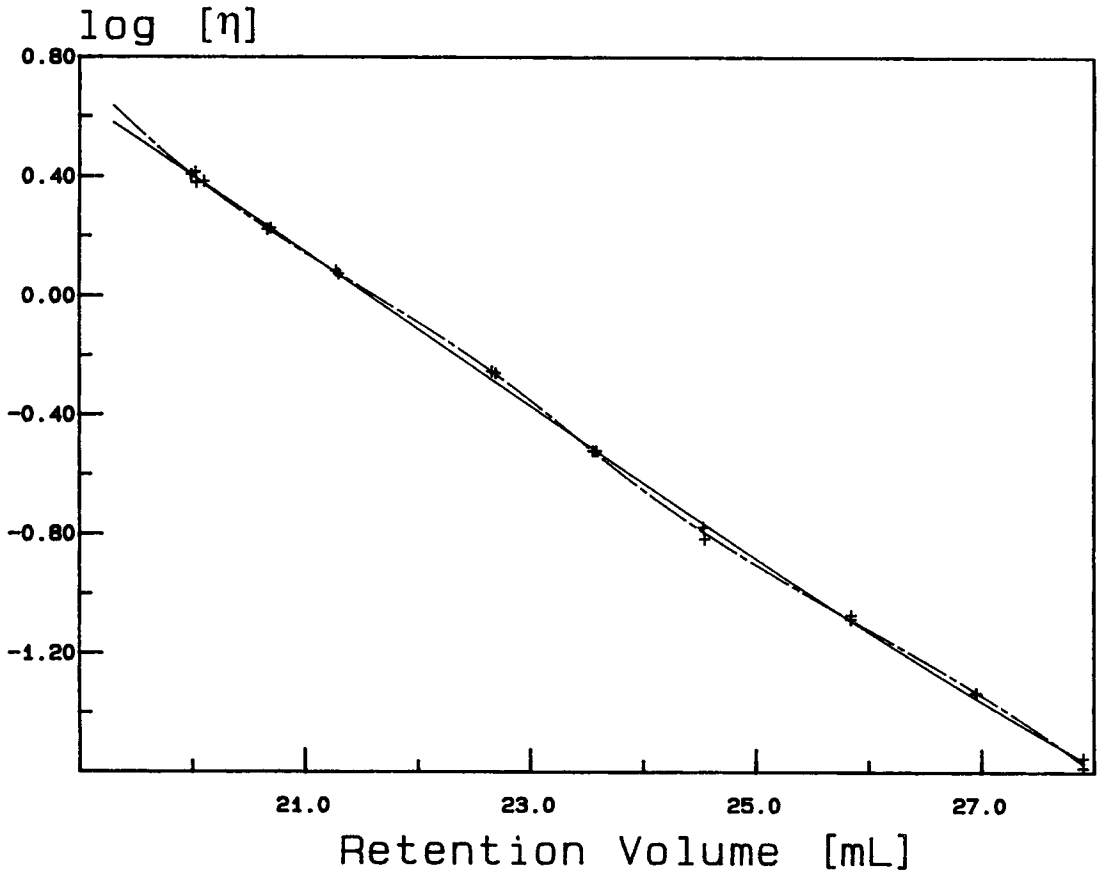

Figure 2 Fit of intrinsic viscosity calibration curve obtained from narrow standards (Type II calibration curve) using a fourth-order polynomial (——) and least-square cubic splines (- - -).

Fitting of Calibration Curves

Fitting of the traditional molecular weight calibration from narrow standards (Type I calibration) is now routinely done. Typically, linear regression is used to fit a polynomial to the data:

$$\log M_i = a_1 + a_2 v_i + a_3 v_i^2 + a_4 v_i^3 + a_5 v_i^4 \quad (10)$$

(Note: Linear regression can fit a curve.[12] The adjective "linear" refers to linearity with respect to the coefficients and not with respect to retention volume.)

Recently, it was found that data points tended to scatter nonrandomly around the fitted line.[2,5,13] This result was attributed to a characteristic of improperly matched pore sizes in mixed-gel columns. Least-square cubic splines were used to more closely fit the data.[4,5] These equations resemble "piecewise polynomials" in that they fit a sequential, selected number of data points at a time with an equation of the form of eq. (10). Splines are computed so that there is a smooth, continuous transition from one piece of the curve to another. Very complex, irregular patterns of data can be fit. In this paper, further examples comparing polynomial and spline fits are shown.

Fitting of calibration curves obtained for individual samples from molecular weight sensitive detectors such as the DV (e.g., the Type IV calibration curve) presents new problems. These data normally show higher noise at either end of the data range corresponding to the tails of the chromatograms. At the same time, there is often considerable interest in defining the molecular weight distribution tails and in elucidating branching at the data extremes.

Some authors prefer to fit a straight line or higher-order polynomial using simple linear regression. Others truncate the data at either end and fit only the smooth central portion. As mentioned above, simple linear regression assumes that the error in the ordinate is a constant. Application of the

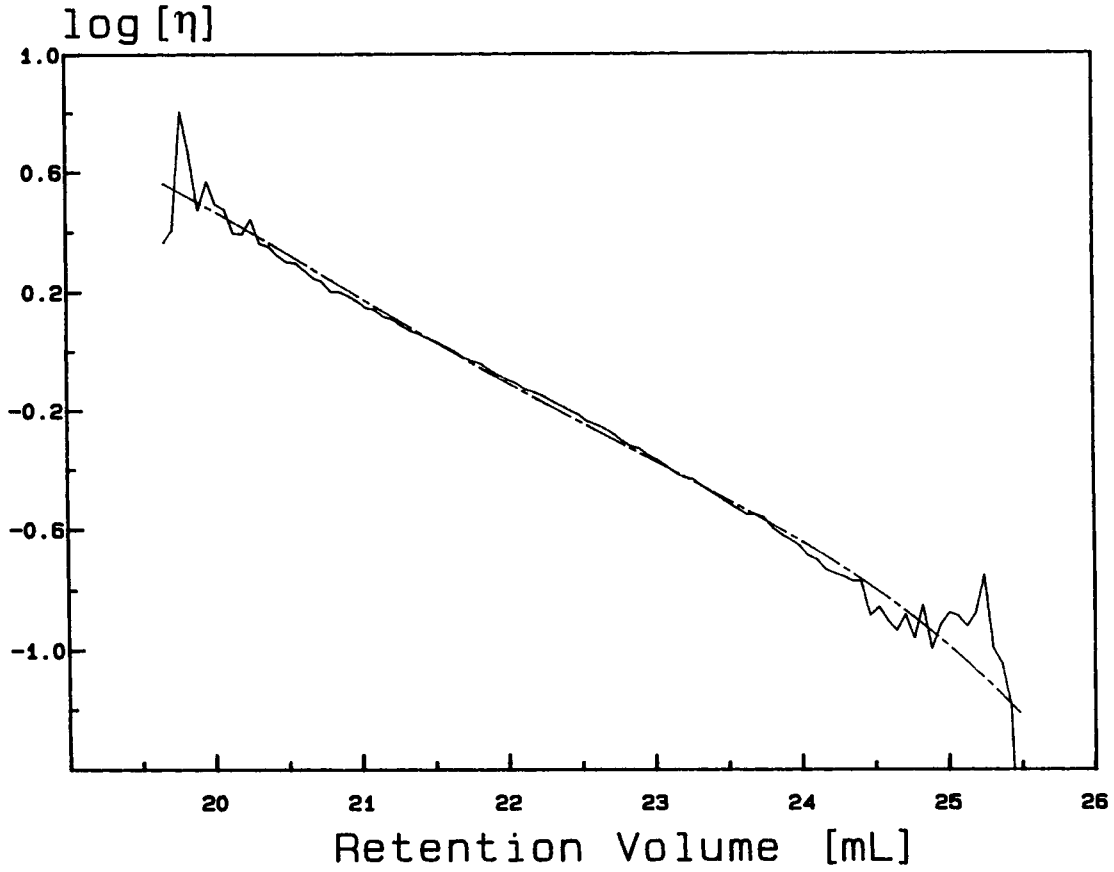

Figure 3 Local intrinsic viscosities of NBS 706 polystyrene measured by the DV (——) vs. retention volume and an unweighted fit of a fourth-order polynomial (- - -) (a Type IV calibration curve).

error propagation equation[1,12,14] can readily show that the error in the ordinate value, $\log[\eta]_i$, is the fractional error and, assuming zero covariance, is given by

$$\frac{s_{[\eta]_i}}{[\eta]_{\text{avg}_i}} = \sqrt{\frac{s^2_{\eta_{\text{sp}_i}}}{\eta^2_{\text{sp,avg}_i}} + \frac{s^2_{c_i}}{c^2_{\text{avg}_i}}} \tag{11}$$

where the s values refer to error standard deviations and the subscript *avg* refers to averaging over the values represented in s. Equation (11) relates the error in specific viscosity and concentration to the error in intrinsic viscosity at each v_i. It shows that if the fractional error (or % error) in specific viscosity and in concentration are constant with retention volume then the fractional error in intrinsic viscosity is also a constant at each v_i.

In fitting a Type IV calibration curve with a fourth-order polynomial similar to eq. (10) except applied to intrinsic viscosity, the computer program minimizes the following expression:

$$O(a_{i,\eta}) = \sum_{i=1}^{n_{dv}} \omega_i \{\log[\eta]_i - \log[\eta]_{i,\text{polynomial}}\}^2 \tag{12}$$

where the subscript "polynomial" indicates the values calculated from the polynomial with coefficients $a_{i,\eta}$. The ω_i are weighting factors that specify the importance of each data point to the fit. A frequently used weighting factor in statistics is

$$\omega_i = \frac{1}{s^2_{\log[\eta]_i}} \tag{13}$$

where

$$s^2_{\log[\eta]_i} = \left[\frac{1}{2.303}\frac{s_{[\eta]_i}}{[\eta]_i}\right]^2 \tag{14}$$

In simple (unweighted) linear regression, the weighting factors are assumed to be all the same value for each data point. They are set equal to unity as an arbitrary constant. From eq. (14), it can be

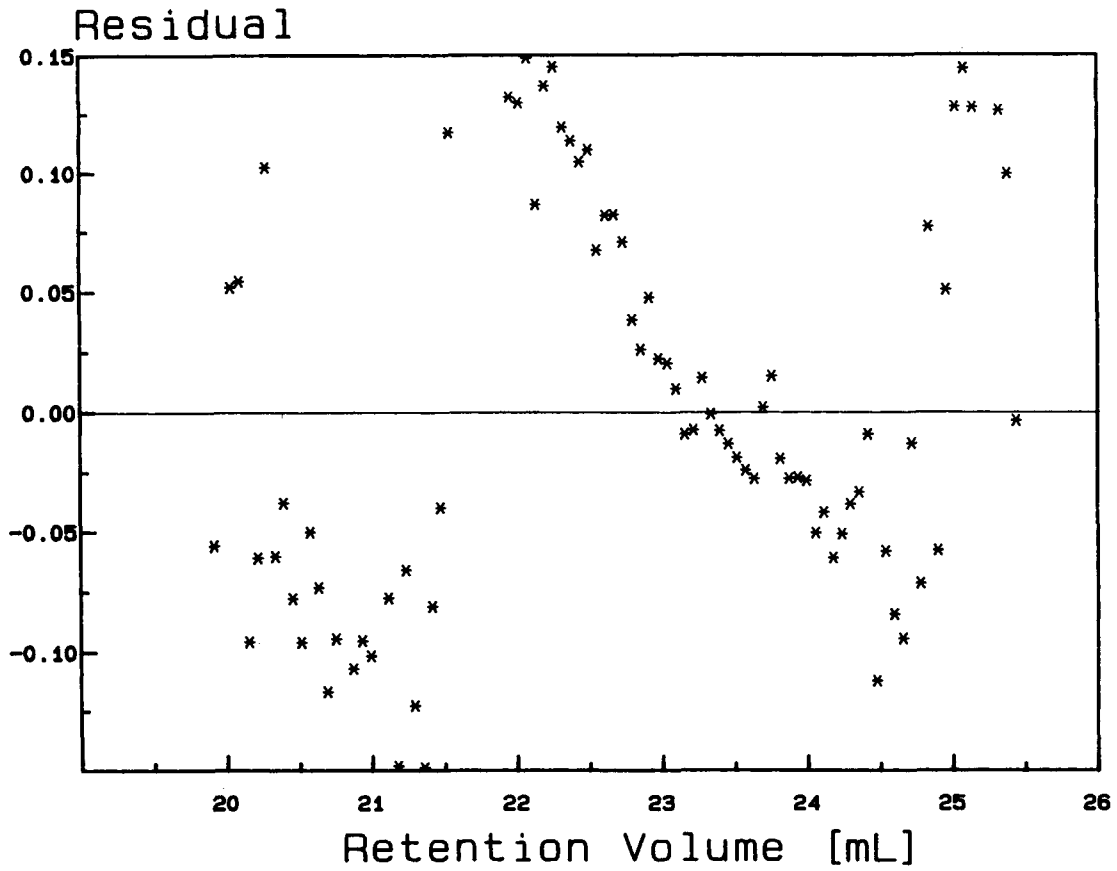

Figure 4 Plot of residuals for intrinsic viscosity vs. retention volume for Figure 3. Residuals are calculated as $(\log[\eta]_i - \log[\eta]_{i,\text{polynomial}})$.

seen that this is only valid if the fractional error in intrinsic viscosity is constant with retention volume. If it is not constant, the error estimate given by eq. (11) can be used to provide the weighting factors. Equation (14) can be used to provide an estimate of the fractional error for the $[\eta]$ needed in eq. (11). This estimate can be checked by direct measurement of the fractional error using replicate measures of $[\eta]_i$:

$$\frac{s_{[\eta]_i}}{[\eta]_{\text{avg}_i}} = \left(\frac{1}{[\eta]_{\text{avg}_i}}\right) \sqrt{\sum_{j=1}^{n_{[\eta]}} \frac{([\eta]_{i,j} - [\eta]_{\text{avg}_i})^2}{n_{[\eta]} - 1}} \quad (15)$$

where $n_{[\eta]}$ is the number of intrinsic viscosity replicated data points at retention volume v_i and the subscript j refers to the replicate considered.

Expected relationships between intrinsic viscosity and molecular weight can provide some guidance as to what form of equation should be used to fit the intrinsic viscosity calibration curve. For example, if a polymer is known to obey the Mark–Houwink equation, then it can readily be shown that the same order polynomial as is used to fit the conventional molecular weight calibration curve should also fit the intrinsic viscosity calibration curve for the sample. One consideration here, however, is that a lower-order polynomial may show less tendency to wind through the data and be more readily extrapolated if the chromatogram includes only a narrow region of the retention volume range. Even more important is the fact that the Mark–Houwink relationship does not necessarily hold over the whole retention volume range.[15]

In this paper, the error in measured local intrinsic viscosities is experimentally determined. Improvements in fitting the intrinsic viscosity calibration curve (the Type IV calibration curve) are sought by using weighted least squares. Emphasis is placed upon devising a procedure for readily estimating weighting factors.

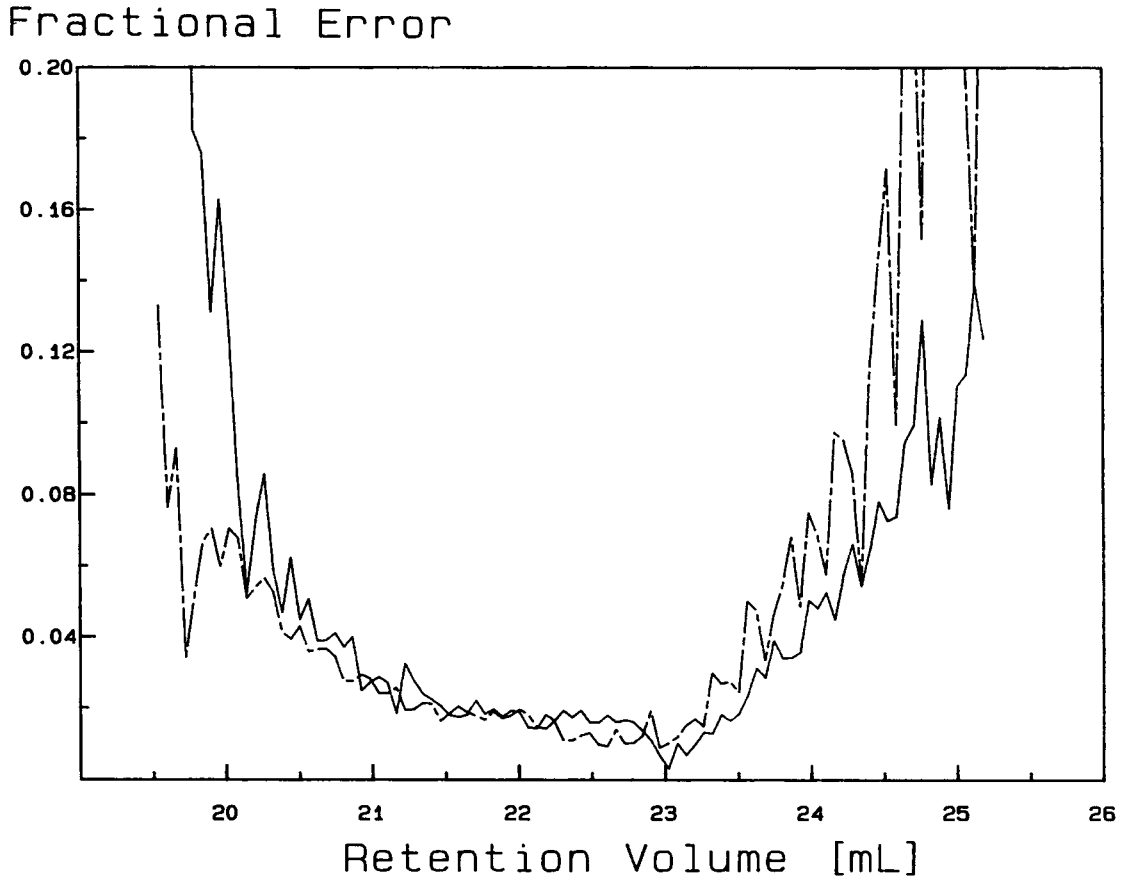

Figure 5 Fractional error at each retention volume for concentration (——) and specific viscosity (- - -) chromatograms. Error standard deviation/(average value at each retention volume) plotted vs. retention volume.

EXPERIMENTAL

Polystyrene standards included NBS 706 (National Bureau of Standards) and PSBR 300K (American Polymer Standards Corp., Ohio) broad molecular weight distribution standards. Also, Polymer Laboratories narrow molecular weight distribution polystyrene standards were used. For polyethylene, NBS 1475 (linear) and NBS 1476 (branched) were analyzed.

A Waters 150C high-temperature size exclusion chromatograph operating at 145°C and utilizing 1,2,4-trichlorobenzene as the mobile phase was used. At the exit of the chromatograph, the flow was split between a differential refractometer and a Model 110 differential viscometer (Viscotek Corp.). Three 20-micron PLgel mixed-bed columns were used. Injection volumes were all 100 μL with injection concentrations of 0.2 wt % for broad molecular weight distribution polymers, 0.05 wt % for narrow standards of 570,000 molecular weight and greater, and 0.1 wt % for other narrow standards. Polystyrene samples were dissolved overnight at room temperature. Polyethylene samples required 3 h at 160°C on a rotator in an oven and an additional 2 h at 145°C in the SEC. Irganox 1010, 0.2 wt %, was added to polyethylene standards as a stabilizer. A distinct solvent impurity peak was found to be useful as a marker for polystyrene standards. Flow correction was generally less than 0.1%.

RESULTS AND DISCUSSION

System Setup

The recently developed "systematic approach" for multidetector SEC was used to establish system parameters. Analysis of NBS 706 using the narrow standard molecular weight calibration curve (the Type I curve) and the DRI trace is shown in Table

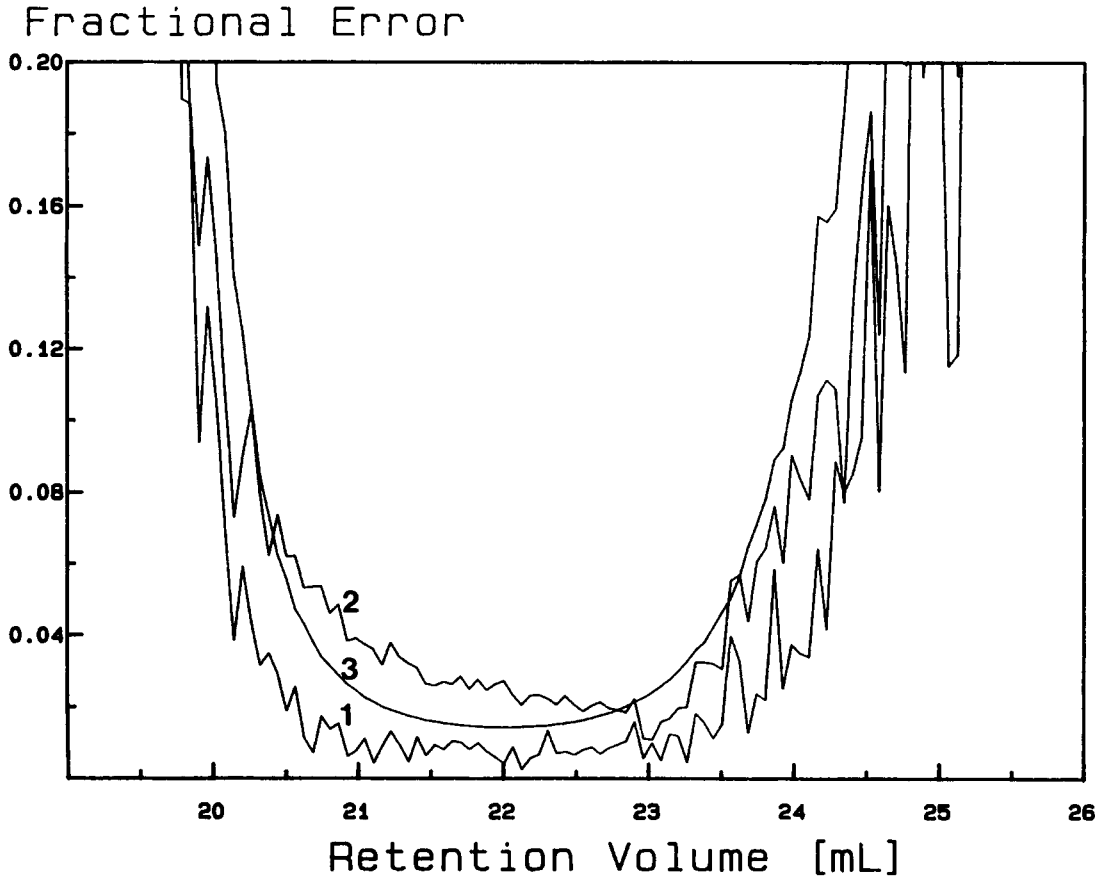

Figure 6 Reproducibility of local intrinsic viscosity values vs. retention volume: (1) determined from five replicates [eq. (15)]; (2) determined by using the data of Figure 5 and eq. (11); (3) determined by using $s^2_{\eta_{sp}}$ of 1.1283×10^{-9} and s_c^2 of 2.9189×10^{-13} [g/mL]^2 in eq. (11).

I. Axial dispersion effects in these 20 micron columns and uncertainty in the calibration curve beyond the highest molecular weight data point were responsible for the low $\bar{M}_n$ value and high $\bar{M}_z$ value, respectively. Table I also shows the sample estimates of the error standard deviation for each value based upon 10 replicates shown as a percent of the mean value.

The PSBR 300K polystyrene standard was used to establish the DPT sensitivity factor for the DV detector. Using a single variable Fibonacci search, it was found that a DPT value of 0.5255 was necessary to match the vendor's value of whole polymer intrinsic viscosity.

Determination of interdetector volume is discussed below. Using an interdetector volume of −0.0766 mL, the universal calibration curve, and the measured intrinsic viscosity for each of 10 NBS 706 samples, the molecular weight averages were again calculated and are shown in Table I. Results are significantly improved for all averages. The result for M_z remains much too high probably because the calibration curve extrapolation is inaccurate at the high molecular weight end.

Further analysis of axial dispersion effects is provided below. However, at this point, it can be seen that although the system is operating with high reproducibility, axial dispersion effects and definition of the calibration curve at very high molecular weights are a source of difficulty with these columns.

Fitting of Narrow Standard Calibration Curves

Figures 1 and 2 show the molecular weight calibration curve (Type I) and the intrinsic viscosity calibration curve (Type II), respectively, fit by both a fourth-order polynomial and by a least-squares spline fit. Table I compares molecular weight averages obtained from each of the two fits of Figure 1. Close inspection of the fits using plots of residuals showed a significant improvement in fitting of the calibration curves when splines were used. However, judging from the molecular weight averages, the ex-

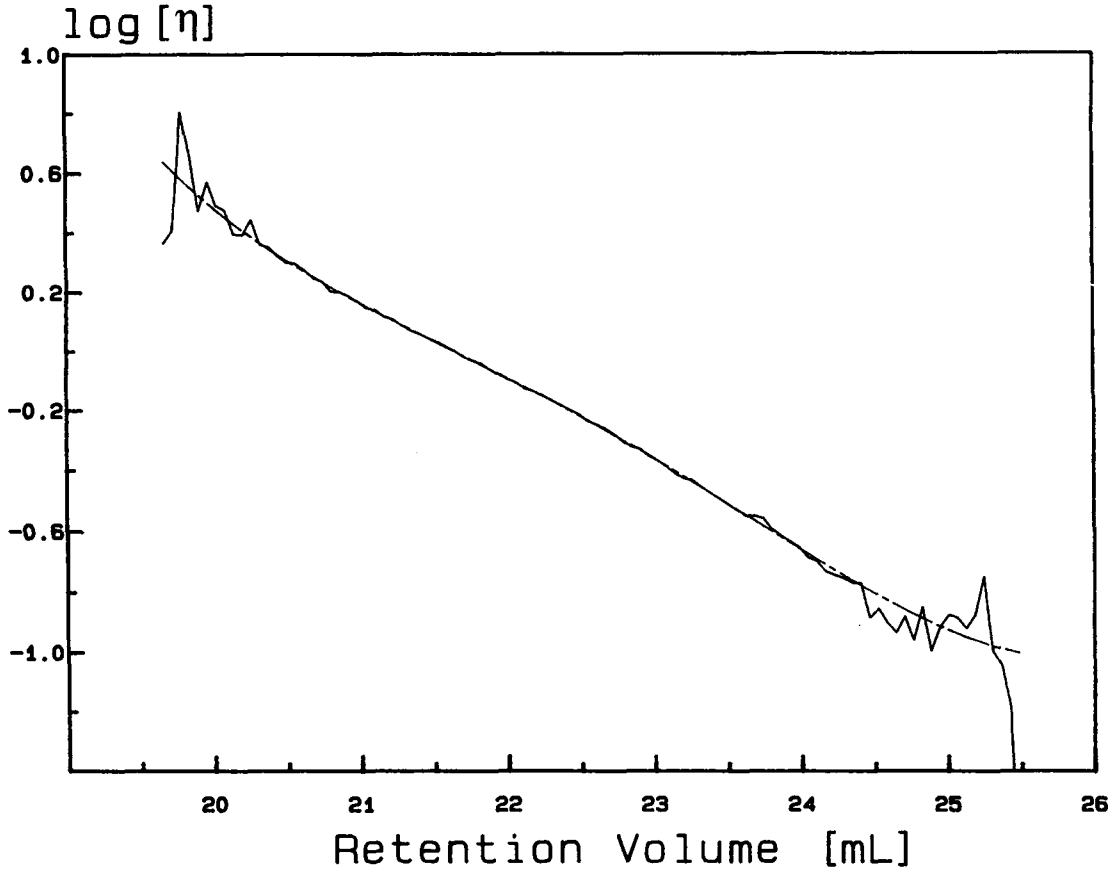

Figure 7 Local intrinsic viscosities of an NBS 706 polystyrene sample measured by the DV (——) vs. retention volume and an weighted fit of a fourth-order polynomial (- - -) (a Type IV calibration curve).

isting extrapolation of the spline fit beyond the highest molecular weight was inferior to that of the polynomial. Various means to improve the extrapolation were considered. When all aspects were examined, it was decided that for these data the improvement was not worth the extra computational effort. A fourth-order polynomial was used throughout the work instead.

Fitting of Measured Local Intrinsic Viscosities

Figure 3 shows the local intrinsic viscosity values of the NBS 706 polystyrene standard measured by DV and plotted vs. retention volume (a Type IV calibration curve) along with a fit of the data using simple (unweighted) linear regression employing a fourth-order polynomial. The inadequacy of this fit becomes startlingly evident by using a plot of the percent deviation of the fitted line to the experimental $\log[\eta]$ data as a function of retention volume. This "plot of residuals" is shown in Figure 4. There we see that there is a systematic variation of the data about the fitted line. The reason for this result is that the fit is being strongly affected by points of poor reproducibility.

Figure 5 shows the fractional error of concentration and specific viscosity chromatograms, respectively, as calculated from five replicate injections of different samples of PSBR 300K polystyrene. We can clearly see excellent reproducibility of the central portion of the chromatograms in contrast to the curve tails. Figure 6 shows the reproducibility of the local intrinsic viscosity values calculated from chromatograms. Also shown are two estimates of the reproducibility obtained from eq. (11). One of these estimates was obtained by using each individual value on the curves of Figure 5. This estimate was higher than expected.

The reason for this was found to be due to a significant covariance between local specific viscosity and local concentration values, i.e., the values are not statistically independent. When the effect was taken into account through a modification of eq. (11) to include a covariance term, the values predicted

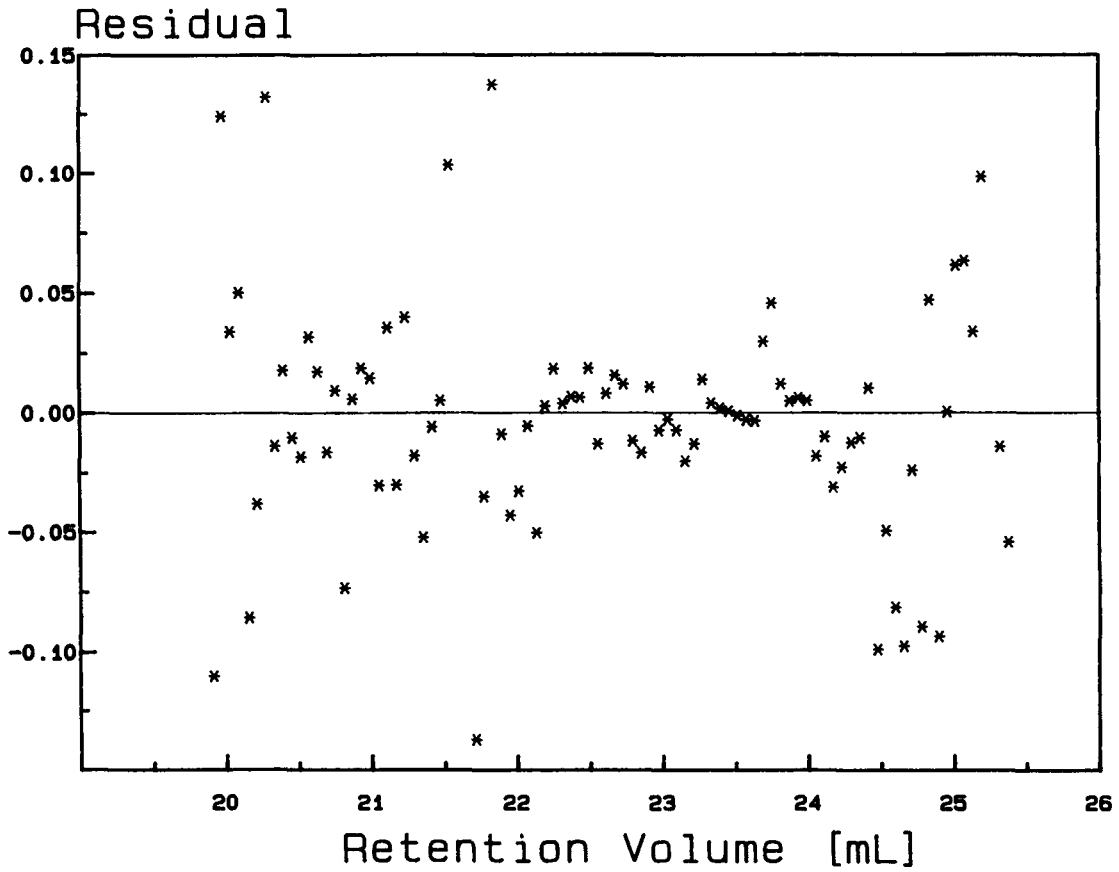

Figure 8 Plot of residuals for intrinsic viscosity vs. retention volume for Figure 7. Residuals are calculated as $(1/s_{\log[\eta]_i})^{0.5}(\log[\eta]_i - \log[\eta]_{i,\text{polynomial}})$.

by the modified equation superimposed on those obtained from eq. (15).

If the consequence of this is a significant covariance between different values of $\log[\eta]_i$, then the simple expression for the weighting factors given by eq. (13) may be inadequate and new weighting factors that utilize the covariance information would then be considered. Recent calculation of these covariances (i.e., the covariances between $\log[\eta]_i$ values) for one set of samples has shown them to be negligible. From a pragmatic viewpoint, the adequacy of any weighting factors used can readily be examined by plotting $\omega^{0.5}(\log[\eta]_i - \log[\eta]_{i,\text{polynomial}})$ on the ordinate vs. v_i on the abscissa). Such figures are termed simply "plots of residuals" in this paper. A random band of scatter about the ordinate zero value with width unchanged at different points along the abscissa value shows satisfactory weighting.[16]

Also, for practical chromatography, an easy way of estimating the weighting factors is required. The method examined was to set the variance of local specific viscosity ($s^2_{\eta_{sp,i}}$) and the variance of local concentration ($s^2_{c,i}$) in eq. (11) equal to reasonable constant values instead of allowing them to vary with retention volume. In Figure 5, curve 3 was obtained by characterizing the concentration noise by a value for the variance of the concentration as constant at 2.9189×10^{-13} $(g/mL)^2$ and the specific viscosity noise by a constant error variance value of 1.1283×10^{-9}. With regard to Figure 5, the notable aspect is that all the fractional error curves are very similar in shape. This is important because the reciprocal of the error variance at each retention volume is to be used as the weighting factor for each respective data point. The degree to which one point is weighted *relative to another* determines the resulting fit. In fact, it can be shown that if the individual heights of all of these curves are proportional to each other, then they will all provide the same weighting.

Figure 7 shows the result of a weighted least-squares fit of a fourth-order polynomial to the same NBS 706 DV data as was fit in Figure 3. However, in this case, the weighting factor used was $1/s_{\log[\eta]i}$

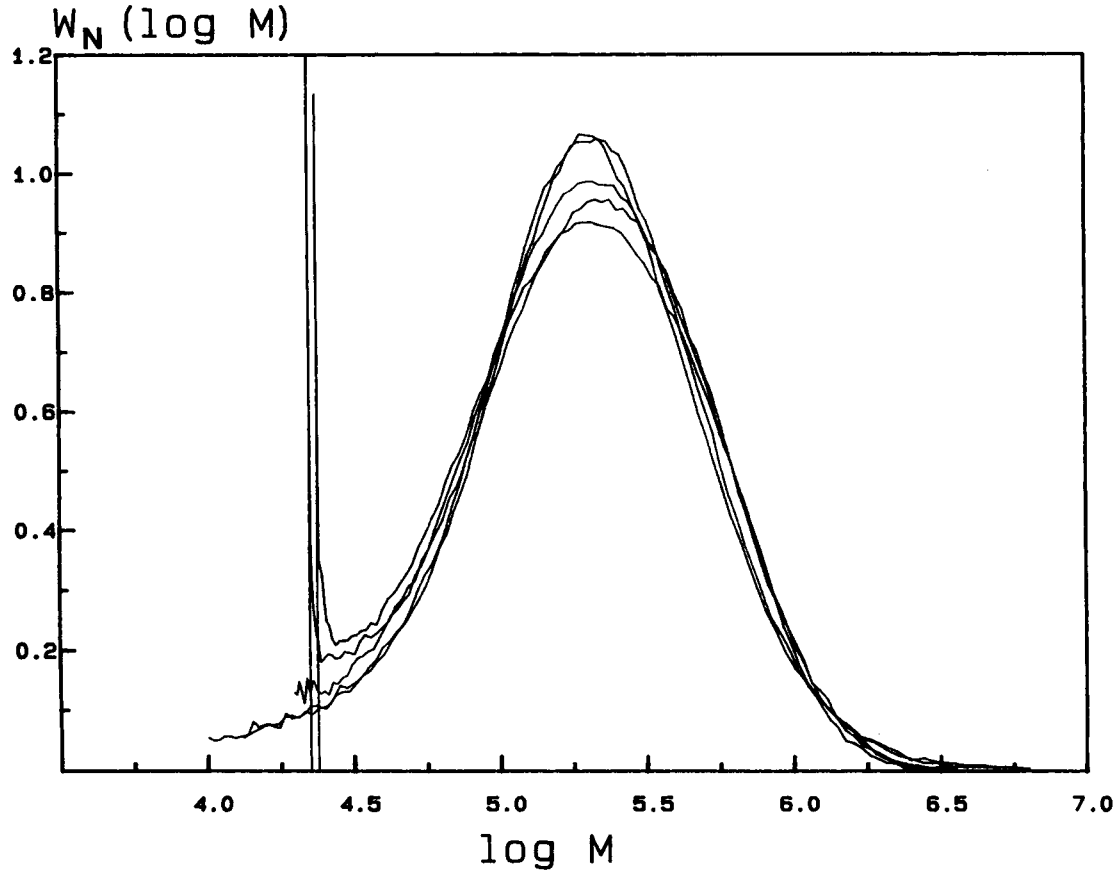

Figure 9 Molecular weight distributions of NBS 706 calculated using an unweighted fit to the Type IV calibration curve.

rather than $1/s^2_{\log[\eta]i}$. It was empirically determined that the lighter weighting provided by the latter ignored so much of the data for this sample that an obvious trend was evident in the plot of residuals. Figure 8 is the plot of residuals when the former weighting factor was used. No trend is evident and the band of scatter is of uniform width. In this case, the weighting used was based upon curve 3 of Figure 6 (i.e., using average error variance values to generate the curve in Fig. 6). Other average values were also tried and, as anticipated, there was very little sensitivity of the weighting to the selection of reasonable average values. In comparison to Figure 4, the plot of residuals (Fig. 8) shows a much more random distribution of data points about the fitted line.

Figure 9 shows the five molecular weight distributions obtained for NBS 706 when the fit obtained from the unweighted least squares was used to obtain the molecular weight calibration curve from the universal calibration curve. Figure 10 shows the same results calculated using the weighted least-squares lines. The marked improvement in results by allowing the data to contribute to the fit relative to their reproducibility is clearly evident. The molecular weight averages shown in Table I were calculated using the weighted fits.

Linear polyethylene sample NBS 1475 was analyzed by using the same weighted least-squares method and weighting factor definition to fit its DV data. The molecular weight calibration curve was then obtained by combining this fit with the universal calibration curve using eq. (5). The molecular weight averages obtained as an average of three analyses each are shown in Table II.

Agreement with vendor values was excellent and scatter among the analyses was less than 5%. This result may be partly due to the fact that the NBS 1475 sample eluted over the central range of our narrow standard calibration curves (Types I and II calibration curves) and so was unaffected by extrapolation of these curves beyond the last high molecular weight point.

It can happen that a portion of the data is judged too important not to be fit despite its poor reproducibility. Figure 11 shows an example where this

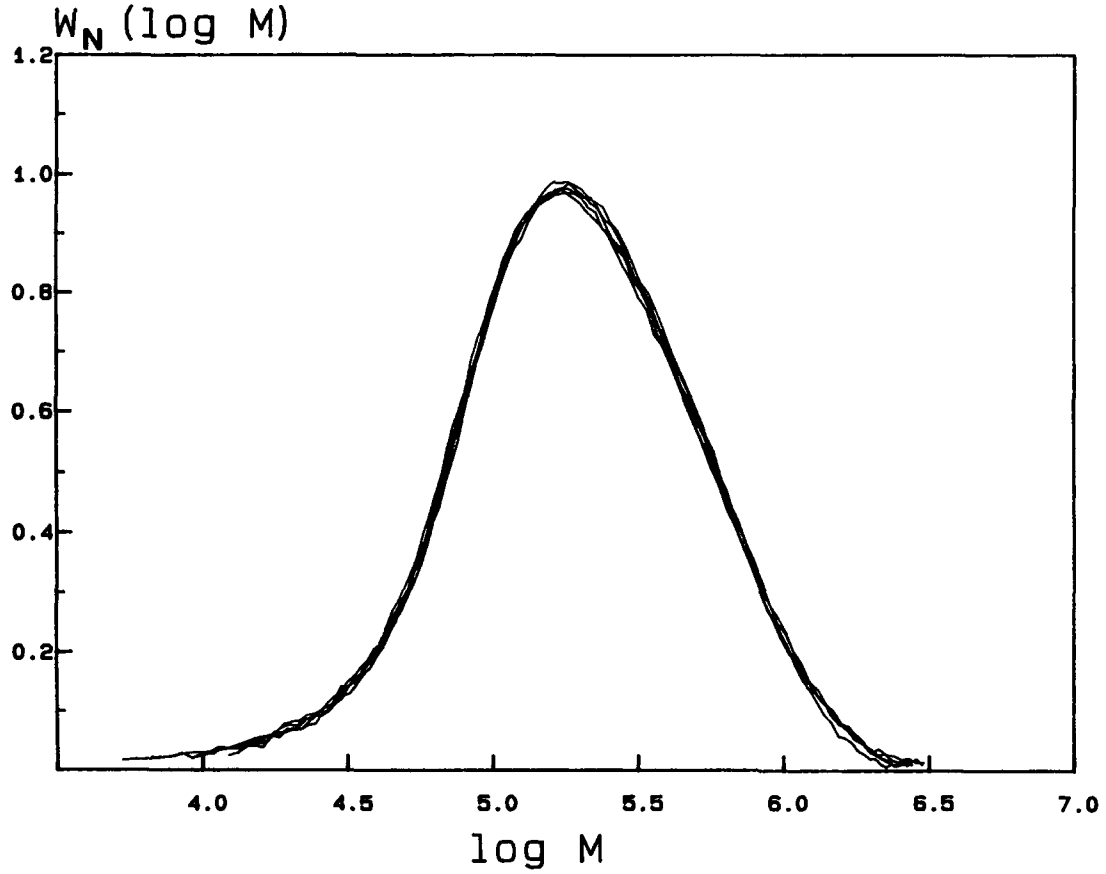

Figure 10 Molecular weight distributions of NBS 706 calculated using a weighted fit to the Type IV calibration curve.

Table II Molecular Weight Averages of Linear Polyethylene (NBS 1475)

Molecular Weight Average	Vendor Value	Calculated Value	% Deviation
$\bar{M}_n$	18,310	19,524	0.97
$\bar{M}_w$	53,070	56,292	6.17
$\bar{M}_z$	138,000	146,357	6.07

could be the case. It shows intrinsic viscosity data from the DV for branched polyethylene NBS 1476. The fit to this Type IV calibration using weighted and unweighted least squares is also shown. The weighted fit was based upon the concentration and specific viscosity chromatograms of the polyethylene sample using the same average errors for concentration and specific viscosity as were used for Figure 6. These average values were substituted into eqs. (11) and (14) to obtain $s^2_{\log[\eta]_i}$ and the weighting factors were then calculated as $1/s_{\log[\eta]_i}$. The unweighted fit passes through the noisy high molecular weight portion of the data but provides a poor fit of the more reproducible central portion. The weighted fit almost ignores the very high molecular weight portion. As before, the weighted fit obtained was found to be insensitive to average values used to characterize noise in the DRI and DV chromatograms. If the high molecular weight tail is judged to be important, then the statistically based weighting factors for the points at the tail can be multiplied by some factors based upon this importance. An al-

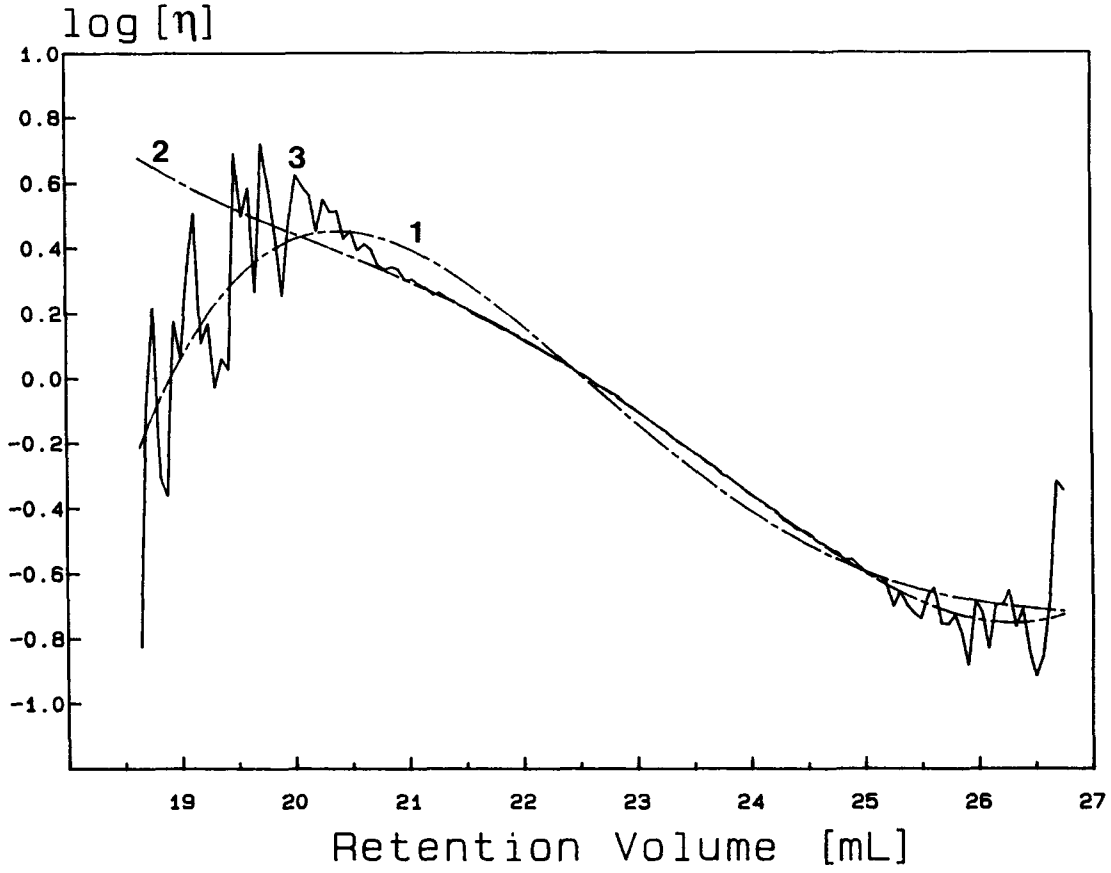

Figure 11 (1) Unweighted and (2) weighted fits of the Type IV calibration curve data of (3) branched polyethylene NBS 1476.

ternative, and likely better solution, is to increase the concentration of the injected sample with a view to obtaining more reproducibility of the tail alone. The problem with this latter solution, of course, is concentration effects on resolution and calibration.

Determination of Mark–Houwink Constants

For a sample of linear polyethylene NBS 1475, Figure 12 shows the traditional method of obtaining these constants [from eq. 8], and Figure 13, the new method based upon eq. 9 assuming negligible error in the $\log J_i$ values compared to the $\log [\eta]_i$ values. Also shown are the data for branched NBS 1476 polyethylene. A similar comparative analysis of the 10 replicate NBS 706 samples was also carried out. As is evident from the values of K and a shown in Table III, no significant difference was observed in the K and a values obtained, although there was some slight improvement in precision evident from the new method. It should be noted that the traditional plot seems to provide a more sensitive indicator of branching than does the new one. This was attributed to the presence of the intrinsic viscosity of the branched sample being in both the abscissa and the ordinate.

CONCLUSIONS

Weighting in least-squares fitting of measured local intrinsic viscosity calibration curves for samples proved extremely important to the interpretation of results. Random error in the detector signals was quantitatively measured. A simple method of deriving weighting factors based upon average concentration and specific viscosity errors was shown to greatly improve the precision of calculated molecular weight distributions.

The problem of reliably extrapolating the fitted curves to allow for differences in sensitivity among

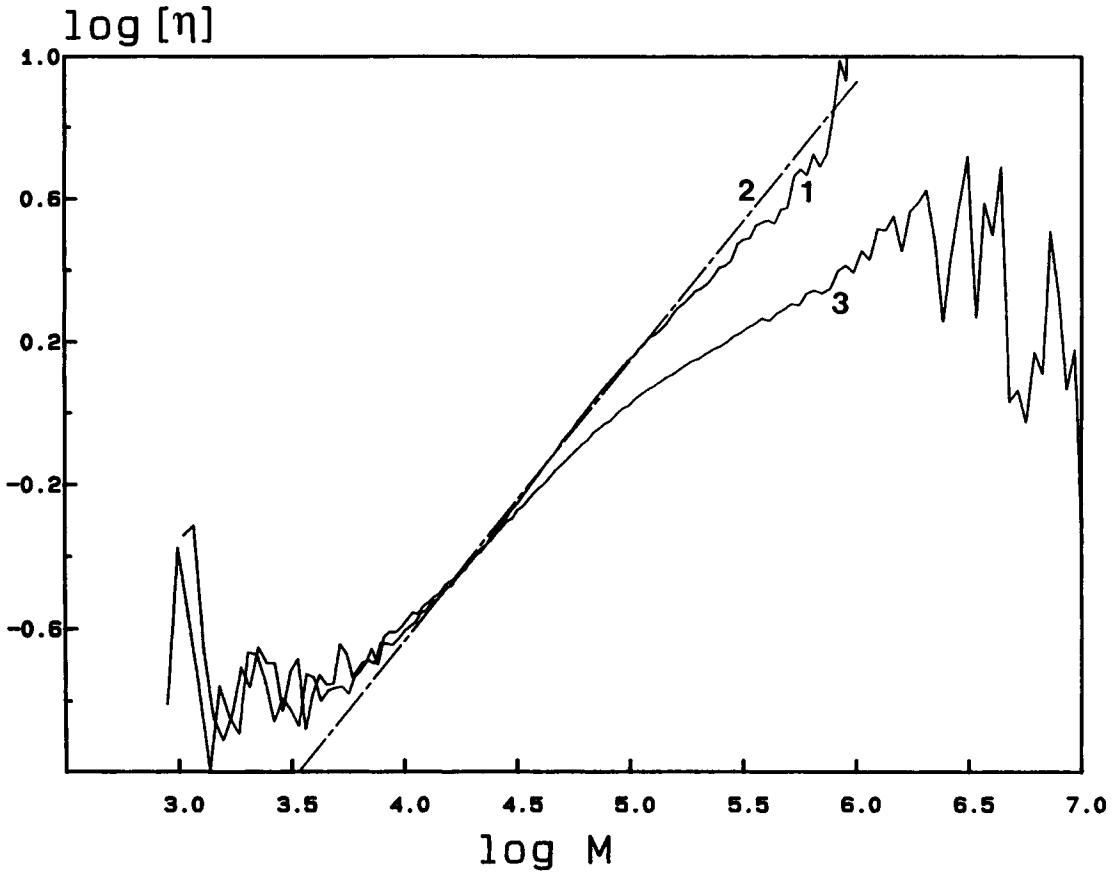

Figure 12 Traditional method of obtaining the Mark–Houwink constants: (1) data for linear polyethylene NBS 1475; (2) weighted fit to the NBS 1475 data; (3) data for branched polyethylene NBS 1476.

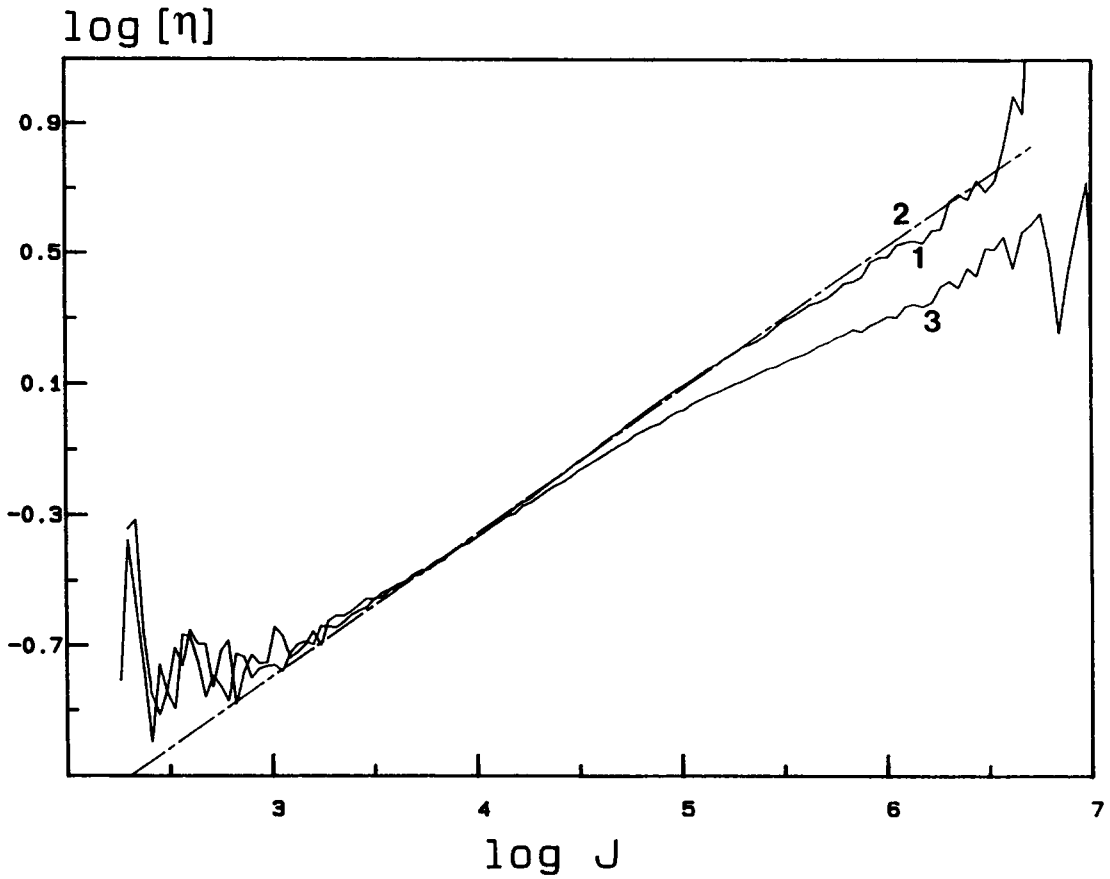

Figure 13 New method of obtaining the Mark–Houwink constants: (1) data for linear polyethylene NBS 1475; (2) weighted fit to the NBS 1475 data; (3) data for branched polyethylene NBS 1476.

detectors has yet to be examined. Extrapolation of the fitted curves beyond the range of the data is inadvisable because any such empirically based curve can behave in unpredictable ways beyond the last data point.

A method of fitting data from the SEC–DV system to obtain more statistically sound Mark–Houwink constants was derived. The traditional method plots the logarithm of intrinsic viscosity of the sample on both axes. For the data used here, the new method involves fitting a plot of logarithm of the intrinsic viscosity of the sample vs. logarithm of the universal calibration curve parameter, J_i. For these data, both methods provided essentially equivalent values of K and a. The traditional method does provide a plot that is likely more sensitive to the effect of branching than does the new method. However, the advantage of the new method is that the assumptions providing a basis for linear regression are more likely to be valid.

Table III Comparison of Methods of Determining Mark–Houwink Constants

	Mark-Houwink Constants Traditional Method [Eq. (8)]		Mark–Houwink Constants New Method [Eq. (9)]	
Sample	$K \times 10^4$	a	$K \times 10^4$	a
PSBR 300K (5 analyses)	4.24 ± 0.12	0.609 ± 0.003	4.14 ± 0.11	0.610 ± 0.002
NBS 706 (10 analyses)	3.58 ± 0.33	0.615 ± 0.007	3.53 ± 0.31	0.617 ± 0.007
NBS 1475 (3 analyses)	1.77 ± 0.00	0.782 ± 0.004	1.73 ± 0.00	0.784 ± 0.004

Least-squares cubic spline fitting of calibration curves is sometimes necessary for accurate results. In this paper, fitting of the narrow standard calibration curves using splines did not provide sufficient advantage to offset the extra computational work. A fourth-order polynomial was used throughout the work.

The previously published "systematic approach" for multidetector SEC again proved to be very useful in establishing system parameters in this SEC–DV system.

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REFERENCES

1. S. T. Balke, *Quantitative Column Liquid Chromatography, A Survey of Chemometric Methods,* Elsevier, Amsterdam, 1984.
2. S. T. Balke, P. Cheung, R. Lew, and T. H. Mourey, *J. Liq. Chromatogr.,* **13,** 2929 (1990).
3. T. H. Mourey and S. M. Miller, *J. Liq. Chromatogr.,* **13,** 693 (1990).
4. P. Cheung, S. T. Balke, and T. H. Mourey, *J. Liq. Chromatogr.,* **15,** 39 (1992).
5. S. T. Balke, P. Cheung, L. Jeng, and R. Lew, *J. Appl. Polym. Sci. Appl. Polym. Symp.,* **48,** 259 (1991).
6. T. H. Mourey and S. T. Balke, in *First International GPC–Viscometry Symposium,* Houston, TX, April 24–26, 1991, ACS Symp. Series, to appear.
7. S. T. Balke, R. Thitiratsakul, R. Lew, P. Cheung, and T. H. Mourey, in *First International GPC–Viscometry Symposium,* Houston, TX, April 24–26, 1991, ACS Symp. Series, to appear.
8. A. E. Hamielec and A. C. Ouano, *J. Liq. Chromatogr.,* **1,** 111 (1978).
9. R. Lew, S. T. Balke, and T. H. Mourey, *J. Appl. Polym. Sci. Appl. Polym. Symp.,* 139 (1990).
10. S. T. Balke, *J. Appl. Polym. Sci. Appl. Polym. Symp.,* **43,** 5 (1989).
11. A. E. Hamielec and H. Meyer, in *Developments in Polymer Characterisation—5,* J. V. Dawkins, Ed., Elsevier, London, 1986, pp. 95–130.
12. S. T. Balke, in *Detection and Data Analysis in SEC,* T. Provder, Ed., American Chemical Society, Washington, DC, 1987, pp. 202–219.
13. T. H. Mourey, S. M. Miller, and S. T. Balke, *J. Liq. Chromatogr.,* **13,** 435 (1990).
14. L. H. Garcia Rubio, in *Detection and Data Analysis in SEC,* T. Provder, Ed., American Chemical Society, Washington, DC, 1987, pp. 220–239.
15. R. Amin Sanayei and K. F. O'Driscoll, in *Proceedings of the Division of Polymeric Materials Science and Engineering,* American Chemical Society, Washington, DC, Vol. 65, Fall Meeting, 1991, New York, pp. 196–197.
16. N. R. Draper and H. Smith, *Applied Regression Analysis,* 2nd ed., Wiley, New York, 1981, pp. 108–121.

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