

SEC-Viscometer Detector Systems. II. Resolution Correction and Determination of Interdetector Volume

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SYNOPSIS

The closely related topics of resolution correction and the determination of interdetector volume were examined. In determining the interdetector volume (δ) by searching to superimpose two types of intrinsic viscosity calibration curve (one from narrow standards and one from a broad standard), the underlying equation based upon symmetrical axial dispersion theory was derived. This equation combined with experimental results showed that the local intrinsic viscosity value is very similarly affected by interdetector volume and by band spreading. The result supported the idea of using an effective δ to effect an axial dispersion correction to local intrinsic viscosity data. However, it also increased the difficulty of finding both δ and standard deviation (σ) simultaneously by numerical search. Furthermore, attempts to apply the method to the chromatograms of narrow standards showed inadequate superposition. Following calculation of skewing factors, the superposition problems were attributed to skewing of the chromatograms of the monodisperse polymer standards used. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In Part I, the coupled topics of calibration and determination of Mark-Houwink constants were examined. In this paper, resolution correction and its close association to the determination of interdetector volume are examined.

THEORY

Resolution Correction

A variety of molecular weights can exist at a specific value of retention volume for two main reasons: (i) fractionation by size has not been perfect (usually because of axial dispersion in the columns), so a variety of molecular sizes (and, hence, a variety of molecular weights) exist at a particular value of retention volume; (ii) the polymer is sufficiently com-

plex so that a unique relationship does not exist between molecular weight and molecular size. The latter reason is a fundamental limitation of size exclusion chromatography (SEC). For example, many different combinations of branch length, branch frequency, and molecular weight may combine to provide the same molecular size in solution. Then, even a perfect separation by size still results in a variety of molecular weights at any retention volume. It is a limitation that must be remembered when analyzing complex polymers.

This distinction is taken into account in the nomenclature used in subsequent sections as follows: The subscript *axd* means that the property is measured over a mixture of different molecular weights present at that retention volume because axial dispersion effects cause different molecular sizes to be present. The subscript *unc* means that the value is a fictitious computed value and needs correction because of a mismatch of perfect resolution and axial dispersion affected quantities in the equation used to obtain the value (a good example is \bar{M}_w calculated from a chromatogram uncorrected for axial dispersion using a conventionally obtained ["true"] mo-

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lecular weight calibration curve). In addition, to distinguish whole polymer properties from local properties, an overbar is placed above the former.

Axial Dispersion Correction of the Concentration Chromatogram

With regard to the former reason for molecular weight variety at any retention volume, "imperfect" resolution of molecular sizes, correction of the concentration chromatogram obtained from the differential refractive index detector (DRI) by calculating what the individual concentration values at each v_i would be without the presence of axial dispersion is referred to as deconvolution. It has been previously shown that for broad chromatograms the concentration values are practically unchanged by axial dispersion correction except at the extreme tails of the curves.¹⁻³ For narrow chromatograms, the concentration values are generally greatly affected across the whole chromatogram. According to theory,⁴ required corrections to the molecular weight averages calculated from the concentration chromatogram are independent of chromatogram breadth.

Deconvolution methods are now well developed for concentration chromatograms.⁵ However, it is necessary to provide the methods with a well-defined "shape function." This function describes the shape of the normalized chromatogram of a polymer with a single molecular weight. Typically, it is assumed to be Gaussian. Then, the required information is the standard deviation, σ . Obtaining σ as a function of retention volume is still an active area of research.⁶

One method of readily determining σ and, at the same time, discovering whether the "band spreading" is actually Gaussian was published by Balke and Hamielec.⁷ The following equations are used to obtain σ and another parameter, SK , which indicates the amount of skewing of the chromatogram of a truly monodisperse polymer:

$$\sigma = \frac{1}{D_2} \sqrt{2.303 \log \left\{ \frac{\bar{M}_n \bar{M}_{w,uc}}{\bar{M}_w \bar{M}_{n,uc}} \right\}} \quad (1)$$

$$SK = 2 \left\{ \frac{\bar{M}_w}{\bar{M}_{w,uc}} \exp \left(\frac{\sigma^2 D_2^2}{2} \right) - 1 \right\} \quad (2)$$

SK is zero for no skewing and D_2 is the slope of $\ln M$ versus v . The strength of these equations is that they are easily applied to readily available data. The weakness is that they rely on vendor values of molecular weight averages (\bar{M}_n and \bar{M}_w). Note that, as

mentioned above, the values of these averages calculated from the chromatogram involve the use of a true calibration curve and chromatogram heights are affected by axial dispersion, so they are denoted $\bar{M}_{n,uc}$ and $\bar{M}_{w,uc}$.

Axial Dispersion Correction of Local Intrinsic Viscosity Values

When an intrinsic viscosity detector is added to the SEC, correction of the local intrinsic viscosity values becomes important. Accuracy of these local values are of concern because they are used to estimate molecular weight distributions from universal calibration. Also, branching in a sample is estimated by ratioing these local values with corresponding values for a linear polymer. Axial dispersion effects can significantly affect accuracy of the local values of intrinsic viscosity without affecting whole polymer averages.

The most frequently used equation for correcting local values of intrinsic viscosity is that developed by Hamielec⁸:

$$\frac{[\eta]_i}{[\eta]_{i,axd}} = \left(\frac{F_i|_{v=v_i}}{F_i|_{v=v_i-D_{2\eta}\sigma^2}} \right) \exp \left\{ \frac{-(D_{2\eta}\sigma)^2}{2} \right\} \quad (3)$$

where the heights of the DRI chromatogram uncorrected for axial dispersion are symbolized by F_i and a subscript axd has been added to the measured intrinsic viscosity to indicate that axial dispersion effects are present. $D_{2\eta}$ is given by

$$D_{2\eta} = -2.303 \frac{\Delta \log[\eta]}{\Delta v} \quad (4)$$

According to eq. (3), the intrinsic viscosity correction for symmetrical axial dispersion is the product of two correction factors. The first of these is the ratio of two different heights of the DRI chromatogram and so depends upon the DRI chromatogram shape. The second depends only on the slope of the intrinsic viscosity calibration curve and the standard deviation of a truly monodisperse polymer. For a linear calibration curve and a Gaussian shape function of constant standard deviation, this second correction factor is a constant.

Determination of Interdetector Volume

A variety of methods have been proposed to obtain the interdetector volume, δ .⁹ The method, to be more fully examined in this paper, is based upon the idea of finding the value of δ that will superimpose the

intrinsic viscosity calibration curve obtained for a single broad molecular weight distribution linear homopolymer (Type IV calibration curve as defined in Ref. 10) on the corresponding intrinsic viscosity calibration curve obtained from a series of narrow standards (Type II calibration curve as defined in Ref. 10).^{9,11-15}

To illustrate the close relationship between this method of finding δ and the resolution correction, eq. (3) can be rearranged and written in terms of concentrations from the DRI instead of DRI chromatogram heights to provide

$$[\eta] |_{v=v_i} = \left(\frac{c_{i,axd} |_{v=v_i}}{c_{i,axd} |_{v=v_i - D_{2\eta}\sigma^2}} \right) \left(\frac{\eta_{spi,axd} |_{v=v_i - \delta}}{c_{i,axd} |_{v=v_i}} \right) \times \exp \left\{ \frac{-(D_{2\eta}\sigma)^2}{2} \right\} \quad (5)$$

where δ is defined as the volume from the column exit to the DRI less the volume from the columns to the differential viscometer (DV) (note that it therefore can be negative).

Therefore,

$$\log([\eta] |_{v=v_i}) = \log \left(\frac{\eta_{sp,axd} |_{v=v_i - \delta}}{c_{i,axd} |_{v=v_i - D_{2\eta}\sigma^2}} \right) - \left\{ \frac{1}{2.303} \frac{(D_{2\eta}\sigma)^2}{2} \right\} \quad (6)$$

Equation (6) shows that the Type IV intrinsic viscosity calibration curve corrected for axial dispersion is the result of two contributions: an intrinsic viscosity computed by shifting both the specific viscosity and concentration chromatograms and a constant term involving only the slope of the intrinsic viscosity calibration curve and the value of σ . It shows that when a simple interdetector volume search is used we are assuming σ to be zero. If the true value of σ is not zero, then the procedure causes additional shifting of the specific viscosity chromatogram and results in an "effective" δ to allow for not permitting the concentration chromatogram to shift in the calculation.

Previously, in the development of a "systematic approach" for establishing operating parameters for multidetector SEC systems, Mourey and Balke¹⁴ showed that "effective" values of σ could be obtained by specifying the value of δ and searching for σ , which, when substituted into eq. (3), would allow superposition of Type IV and Type II calibration curves for narrow standards. Equation (6) is simply

a combination of the two previously used equations and encourages the idea of conducting a simultaneous search for both σ and the "true" value of δ .

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 Lab narrow molecular weight distribution polystyrene standards were used.

A Waters 150C high-temperature size exclusion chromatography (SEC) 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 μ L 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. 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

Figure 1 shows the results of superimposing a Type IV calibration curve on a Type II curve (Part I¹⁰ defines the various calibration curve types) using Equation 6 for NBS 706 polystyrene with the assumption of perfect resolution ($\sigma = 0$). This is essentially a simple search for an "effective" interdetector volume. Some systematic deviation of the two lines were evident. However, the magnitude of this deviation is small and reproducibility was excellent. A value of -0.0766 mL (based on a flow rate of 0.5 mL per min through the DV) with an error standard deviation of 0.0024 mL was obtained from 10 replicate analyses of separate samples. The same method was also applied to nine samples of PSBR 300K. Again, superposition was excellent with the estimates of interdetector volume at -0.0789 mL and an error standard deviation of 0.0033 mL. (Vendor \bar{M}_n and \bar{M}_w for this sample were 125,000 and 300,000, respectively. \bar{M}_n and \bar{M}_w calculated using universal calibration and the determined interdetector volume were 101,200 and 298,700, respectively.)

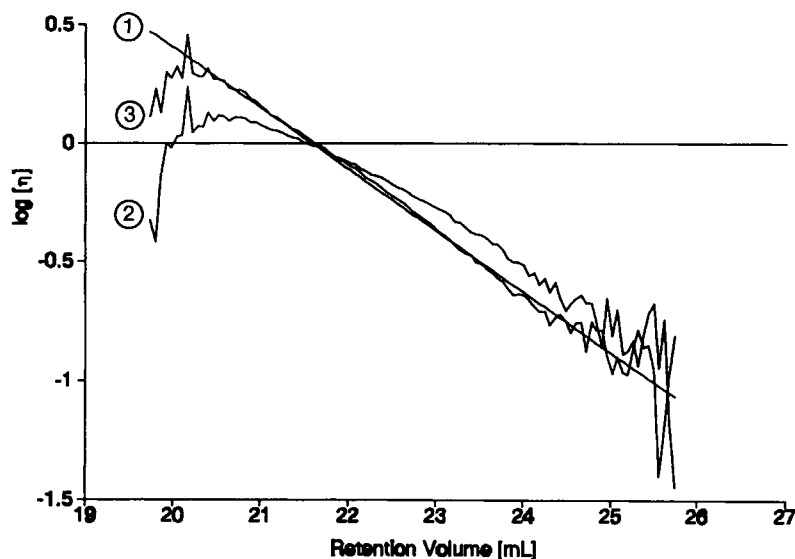


Figure 1 Result of a search for an "effective" interdetector volume for NBS 706 polystyrene: (1) narrow standard intrinsic viscosity calibration curve (Type II calibration); (2) measured intrinsic viscosity data with zero interdetector volume assumed; (3) measured intrinsic viscosity data using the value of interdetector volume obtained by the search.

Figure 2 shows the results of the same type of superposition, again using eq. (6) but this time assuming an interdetector volume of zero. In this case, a value of σ of 0.5 achieved a high degree of superposition of the two curves. Systematic deviation of the two lines is more evident than in Figure 1: the

fit is not as good. However, it is sufficient to demonstrate that both interdetector volume and resolution correction (via σ) can achieve very similar corrections to the intrinsic viscosity data of this broad sample. This was considered partly responsible for a lack of success in attempts to search for

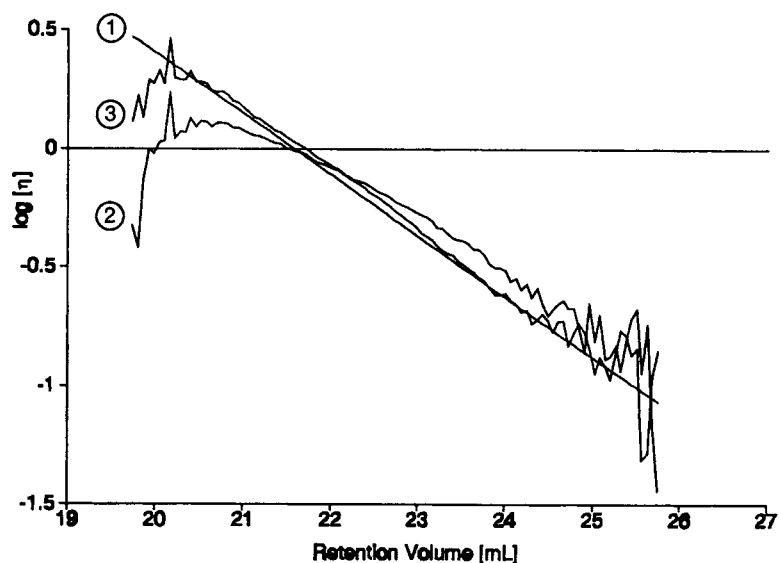


Figure 2 Result of a search for σ assuming $\delta = 0$ for NBS 706 polystyrene: (1) narrow standard intrinsic viscosity calibration curve (Type II calibration); (2) measured intrinsic viscosity data with zero interdetector volume assumed; (3) measured intrinsic viscosity data using the value of σ obtained by the search.

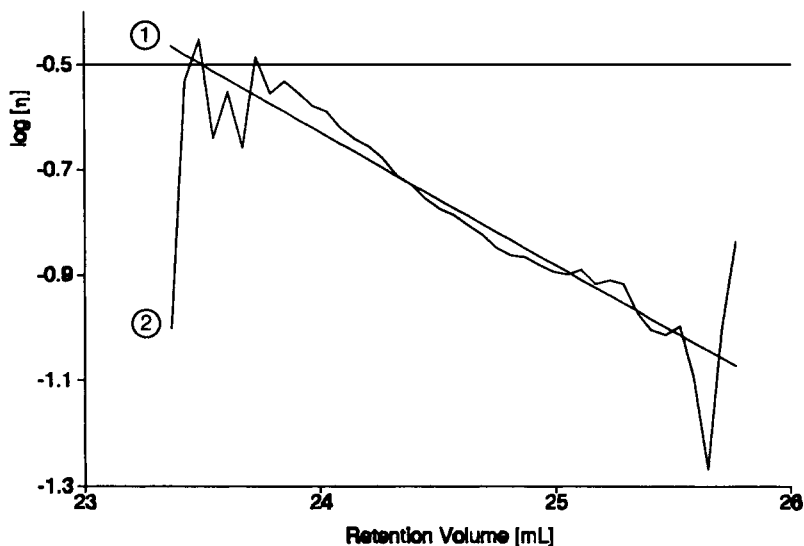


Figure 3 Results of a search for σ and δ simultaneously on a high molecular weight narrow distribution standard: (1) narrow standard intrinsic viscosity calibration curve (Type II calibration); (2) measured intrinsic viscosity data using the values of δ and σ obtained from the search.

interdetector volume and σ simultaneously. In all of these cases, the search invariably arrived at a σ of zero.

Figure 3 shows an attempt to search for the interdetector volume and σ using narrow standards. As this figure shows, a good superposition of the two curves was not possible. Results varied greatly depending on what type of "best fit" was obtained, with very high and very low molecular weights providing the worst situations.

Judging by the appearance of the narrow standard chromatograms, skewing of the shape function was considered a possible source of the inadequacy for the high molecular weights, and high noise, a source at the low molecular weights. Figure 4 shows a plot of the ratio of "true" to corrected molecular weight averages vs. peak molecular weight for duplicate injections of narrow standards. Calculated σ and SK values are shown in Figure 5 plotted vs. retention volume. Although, as mentioned above, these results

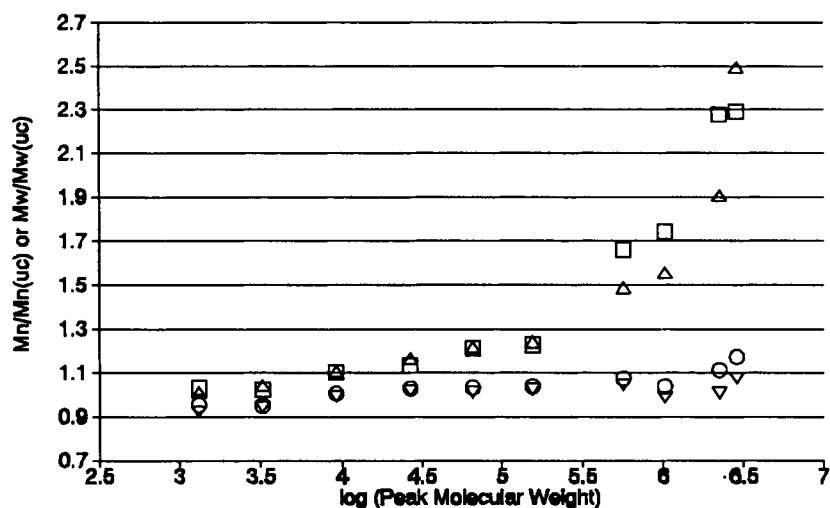


Figure 4 Ratio of corrected to uncorrected number-average molecular weight (Δ , \square) and weight-average molecular weight (∇ , \circ) for polystyrene standards vs. log (peak molecular weight).

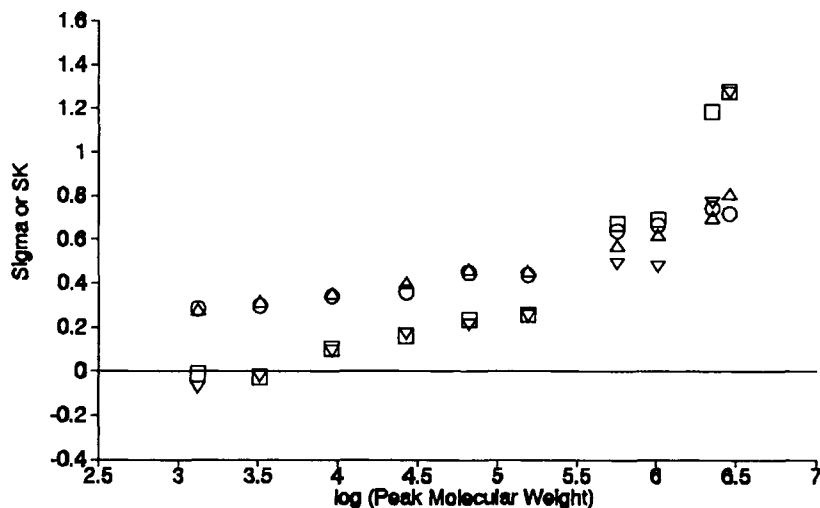


Figure 5 Values of σ (Δ , \circ) and SK (\square , ∇) obtained from eqs. (16) and (17) vs. \log (peak molecular weight).

are dependent upon vendor values of \bar{M}_n and \bar{M}_w , these results do provide additional evidence of skewing and may account for difficulties in applying eq. (6).

CONCLUSIONS

With regard to the interdetector volume (δ) search, an equation based upon symmetrical axial dispersion theory and experimental results combined to show that the local intrinsic viscosity value is very similarly affected by δ and σ . This supports the idea of using an effective δ to effect an axial dispersion correction to local intrinsic viscosity data. However, it also increases the difficulty of finding both δ and standard deviation (σ) simultaneously by numerical search. Furthermore, attempts to apply the method to the chromatograms of narrow standards showed inadequate superposition. Following calculation of skewing factors, the superposition problems were attributed to skewing of the chromatograms of the monodisperse polymer standards used.

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