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# Data Treatment in GPC

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# Data Treatment in GPC

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**Summary**

For high polymer samples, the peaks of individual components are not separable in GPC chromatograms. The interpretation of such chromatograms is different from that for other types of chromatograms. The outline of a computation procedure for treating such GPC chromatograms is given.

## INTRODUCTION

In GPC chromatograms for monomeric compounds and oligomers, the individual components appear as separate peaks. These GPC chromatograms are interpreted in the same manner as that used in other types of chromatography. After the peaks are identified, the area under each of the peaks is measured to give the relative concentration of that component. For high polymer samples, the peaks of the individual components are no longer separable. The conversion of such chromatograms to the molecular weight distributions of the samples requires special considerations.

In the GPC manual by Waters Associates, an account for such a conversion has been given. In an instrument manual, however, the scope of discussion has to be limited. For many simple applications Waters' procedure is adequate, but to achieve the maximum accuracy for GPC, a more refined data treatment is required. For this reason many laboratories have adopted their own procedures for treating GPC chromatograms. The outline of a procedure used in our laboratory is given below. Hopefully, it will serve to illustrate the steps involved in the interpretation of the chromatograms for high polymer samples.

## GENERAL CONSIDERATIONS

As mentioned above, complex computation is not always required in GPC. For instance, visual inspection of the GPC recorder traces is adequate to compare the relative breadth of distribution for some samples determined by the same GPC equipment using the same set of columns. Sometimes such information is all that one needs and no interpretation of any kind is necessary.

More often, however, it is desired to represent the distribution on a molecular weight scale. A knowledge for the relation between the elution volume and the molecular weight is needed for such a conversion. The distribution curves are usually normalized and the average molecular weights for the sample are usually calculated. Simple numerical integration steps are therefore involved in the computation.

For the most precise treatment of high polymer chromatograms, correction for instrumental spreading becomes necessary. This spreading is caused by many band spreading mechanisms in the instrument, and because of it, a high polymer chromatogram is a composite of the overlapping curves of all its components. The height of such a chromatogram no longer reflects the relative abundance of the component at the corresponding elution volume; it also depends on the abundance of the neighboring components. At the ends of the chromatograms there are curve portions representing components which do not even exist in the sample.

In order to correct for such spreading, the spreading characteristics for the instrument must be determined. This makes computations more complex and requires the use of a high-speed digital computer. Such a correction improves the accuracy of all chromatograms but is especially important when the distribution of the sample is narrow.

## CONVERSION TO MOLECULAR WEIGHT DISTRIBUTION

In Waters' manual the integral molecular weight distribution is calculated from the chromatograms. To obtain the more demonstrative differential distribution curve from the integral distribution, numerical differentiation must be carried out. The chromatograms are thus integrated first and then differentiated. Such a process automatically takes into consideration the weighing factor involved in changing the scale from elution volume to molecular weight but at the same time sacrifices the accuracy which is potentially attainable by GPC.

The direct conversion of a chromatogram to differential distribution

is more accurate. Let $v$ represent the elution volume or count; $M$ the molecular weight; $f_M(M)$ the differential molecular weight distribution function; and $f(v)$ the chromatogram

$$f_M(M) = f(v)(-dv/dM) \tag{1}$$

The weighing factor, $-dv/dM$, is obtainable from the molecular weight calibration. In GPC such a calibration is usually plotted on a semilogarithmic graph with molecular weight on the logarithmic scale. The slope of the calibration on such a plot is $d \log M/dv$ and

$$dv/dM = \left(\frac{1}{M \times (d \log M/dv) \times 2.303}\right) \tag{2}$$

In the special case where the relation between $\log M$ and $v$ is linear, $d \log M/dv$ is a constant. When this relation is not linear, numerical differentiation of the calibration curve is needed.

It is often more convenient to represent the molecular weight distribution on a semilogarithmic plot. Let this distribution of log molecular weight be represented by $f_L(\log M)$, then

$$f_L(\log M) = -f(v)(1/[d \log M/dv]) \tag{3}$$

or

$$f_L(\log M) = f_M(M)(1/2.303M) \tag{4}$$

If $f(v)$ has already been normalized, the $f_M(M)$ and $f_L(\log M)$ computed from the above equations are also normalized. The average molecular weights can be calculated by using any one of the three $f$ functions. For example, the weight-average molecular weight, $M_w$, is

$$M_w = \frac{\int M f_M(M)\, dM}{\int f_M(M)\, dM} = \frac{\int M f(v)\, dv}{\int f(v)\, dv} = \frac{\int M f_L(\log M)\, d \log M}{\int f_L(\log M)\, d \log M} \tag{5}$$

## MOLECULAR WEIGHT CALIBRATION

Coll (*1*) has discussed the calibration of molecular weight for GPC. Moore (*2*) and other early workers have assumed that the relation between the logarithm of molecular weight and elution volume is linear. In practice, however, only when a very small range of elution volume is used can the relation be assumed linear. The calibration curve is usually of the shape shown in Fig. 1. The deviation from linearity is the largest at the high and the low molecular weight regions. Many in-

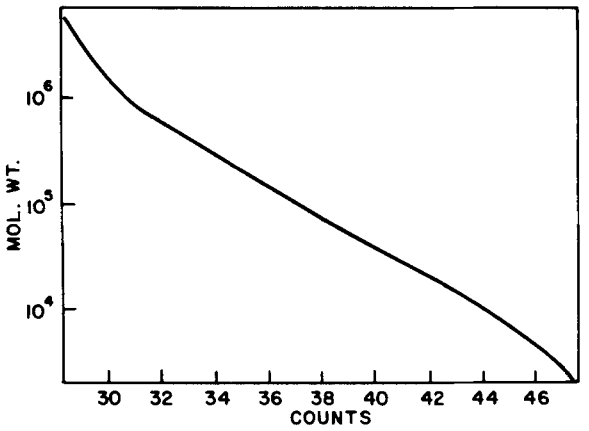


FIG. 1. Typical molecular weight calibration of GPC.



consistencies in GPC results can be traced to the improper use of the molecular weight calibration relation.

In our computation procedure the molecular weight calibration is represented by a polynomial. The calibration points obtained experimentally using standard samples are plotted first on a semilogarithmic graph paper. A smooth curve is drawn through the experimental points and extended to near interstitial volume on one end and the elution volume for monomers on the other end. The extrapolation of the calibration curve to the interstitial volume often is done in an arbitrary manner. Until very high molecular weight standard samples are available, such an uncertainty seems unavoidable. The polynomial is made to fit the smooth curve by the method of moments using the orthogonal Legendre polynomials. The best fit is selected from a set of polynomials with degrees ranging from 3 to 32. As the calibration curve does not contain abrupt slope changes, the selected polynomial usually is found to be indistinguishable from the plotted curve.

## CORRECTION FOR INSTRUMENTAL SPREADING

The relationship between the experimental chromatogram, $f(v)$, and the chromatogram after the correction of instrumental spreading, $w(v)$, can be expressed by the convolution integral equation

$$f(v) = \int w(y)g(v - y)\, dy \tag{6}$$

where $y$ is the elution volume under the integral sign and $g(v - y)$ is a function that describes the shape of the band spreading curve. Ex-

perimentally, low molecular weight compounds have been observed to give the Gaussian spreading in GPC, that is

$$g(v - y) = (h/\sqrt{\pi}) \exp\{-h^2(v - y)^2\} \quad (7)$$

where $h$ is a parameter describing the width of the spreading and $h$ is related to the standard deviation, $\sigma$, of the Gaussian distribution by

$$h = 1/\sigma\sqrt{2} \quad (8)$$

For high molecular weight species the shape of the spreading function cannot be determined directly because thus far there are no truly monodisperse high molecular weight polymer samples. It is indisputable that skewing does occur in the spreading for very high molecular weight polymer species (*3*), particularly at fast flow rates. The shapes of the chromatograms of the currently available high molecular weight narrow distribution polystyrene samples, however, cannot be used to estimate the extent of skewing nor can they even be used to judge whether skewing does occur at all. These samples are themselves skewed in the distribution. In our computation procedure the Gaussian spreading is assumed because using an incorrect degree of skewing may very likely introduce larger errors than using the simpler Gaussian spreading. Moreover, it has been demonstrated (*4*) that Gaussian spreading is a good approximation for polyethylene to a molecular weight at least as high as 460,000.

A number of methods (*5*) for solving the integral Eq. (5) have been published. The earlier methods have been evaluated by Duerksen and Hamielec (*6*). Our current computation procedure uses a method (*7*) that employs a fourth degree polynomial to fit the experimental chromatogram a section at a time. This method is fast and only in rare occasions does it give solutions with artificial oscillations.

## CALIBRATION OF INSTRUMENTAL SPREADING

The proper use of the method for correcting instrumental spreading requires a precise calibration of the spreading characteristics of the instrument. Having made the Gaussian spreading assumption, we reduced this calibration to the determination of the parameter $h$ in Eq. (7) as a function of the elution volume. This can be accomplished by a reverse-flow technique (*4*) using standard samples which are not truly monodispersed.

When a polydisperse sample is sent through a GPC column, its chromatogram is broadened by two processes, a desirable spreading

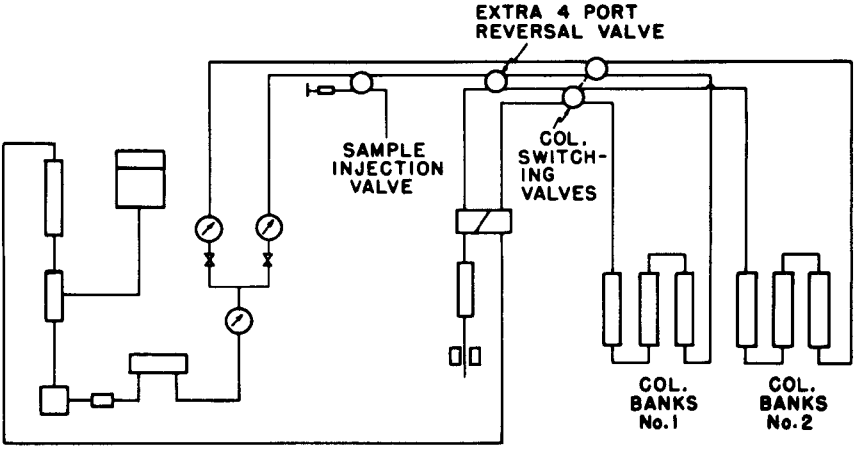


FIG. 2. Schematic GPC flow diagram with reverse-flow valve.



which separates the molecules according to their sizes and the undesirable instrumental spreading. If the elution of the sample is allowed to proceed to some part of the column and then the direction of flow is reversed, the size separation process is also reversed but the instrumental spreading continues to broaden the peak. The resulting chromatogram therefore reflects only the instrumental spreading.

To use the reverse-flow technique, a special four-port valve shown in Fig. 2 needs to be installed. In the experiments the peak position for the standard samples are predetermined. Then each sample is in-

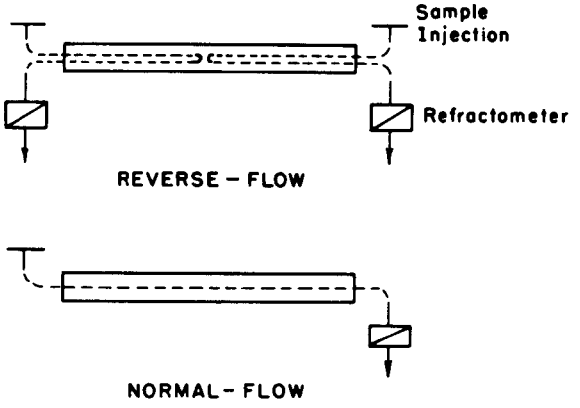


FIG. 3. Reverse-flow scheme.

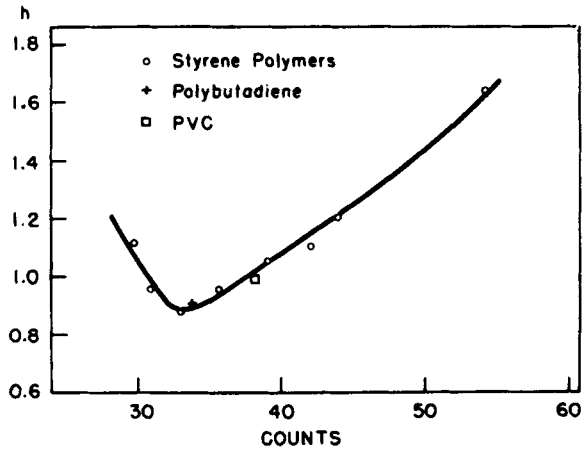


FIG. 4. Variation of the parameter $h$ with elution counts.



jected twice. The first injection is made when the flow of the eluting solvent is in the normal direction. As the elution volume reaches one-half of that of the peak position of the sample, the flow is instantly reversed. The resulting chromatogram is used to compute the $h$ parameter for the front half of the column. The process is repeated with a second injection of the sample when the flow is in the reverse direction. The chromatogram produced is then used to determine the $h$ parameter for the second half of the columns. Figure 3 shows the reverse flow process schematically. The overall $h$ for the sample is calculated from the equation

$$h = \sqrt{2}/\sqrt{(1/h^2_{\text{front}}) + (1/h^2_{\text{back}})} \tag{9}$$

The $h$ values determined for our present GPC instrument are shown in Fig. 4. Two of the points in the figure represent values determined for a polybutadiene sample and a PVC sample. The rest of the points are values for standard polystyrene samples. All of the points are shown to follow a single curve. The spreading characteristics appears then to depend only on the elution volume regardless of the chemical composition of the polymer.

The reverse-flow method is tedious experimentally. Each sample requires two injections and the automatic sample injection device cannot be used for the injection. Hendrickson (*8*), Hamielec and Ray (*9*), and recently we (*10*) have proposed methods of computing $h$ from

the regular chromatograms normally required for the calibration of molecular weight to calibrate the instrumental spreading as well.

In the computation procedure we again represent the curve in Fig. 4 by a polynomial. The coefficients of the polynomial are determined in the same manner as that used for the molecular weight calibration.

## DESCRIPTION OF THE COMPUTER PROGRAM

In our computer program the coefficients defining the polynomials for the two types of calibrations are fed to the computer just before the input for the actual chromatogram data sets. The computation for the correction of instrumental spreading is carried out first. The molecular weight distribution is then converted from the corrected chromatogram and also from the uncorrected chromatogram. Both the distribution of log molecular weight, $f_L(\log M)$, and the conventional differential distribution, $f_M(M)$, are calculated. The number-average, weight-average, and $z$-average molecular weights are calculated for both the corrected and uncorrected distributions.

If the instrumental spreading calibration is not fed to the computer before the data sets, only the results for the uncorrected chromatogram are calculated. If the molecular weight calibration is not fed in then, the correction for instrumental spreading is still carried out but the conversion to molecular weight is left out. If both calibrations are not

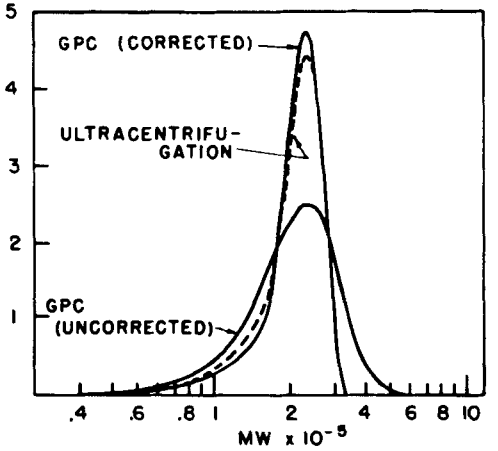


FIG. 5. Molecular weight distribution of a narrow distribution polystyrene sample.

fed to the computer, an error message will be printed. Various plotting options are also incorporated in the computation program.

Figure 5 shows the molecular weight distribution of a polystyrene sample calculated from the experimental chromatogram using our computer program and calibration procedures. Also shown in the figure is the distribution determined by sedimentation velocity measurement on a Spinco Model E ultracentrifuge. The agreement between the distribution calculated from the corrected chromatogram and the one determined by ultracentrifugation is within the uncertainty of the ultracentrifugation experiments. The uncorrected distribution from GPC is shown to be quite unsatisfactory for this sample. The sample has a $M_w/M_n$ ratio of about 1.1. For broader samples the correction for instrumental spreading is less important. Our GPC unit consists of six columns with porosity ranging from $10^6$ to $8 \times 10^2$ A. These columns are the high plate count type purchased from Waters Associates.



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