GPC Data Interpretation

W. W. YAU and S. W. FLEMING, *Engineering Physics Laboratory,*
E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware 19898

Synopsis

A rigorous procedure for reducing gel permeation chromatography elution data to differential molecular weight distribution curves is discussed and demonstrated by two sample calculations. The errors introduced by failure to correct the ordinates of the elution curve by means of a differential calibration curve are identified, and a simple graphical conversion procedure is illustrated.

Introduction

A rigorous procedure for converting gel permeation chromatographic (GPC) data to molecular weight distribution (MWD) curves has been discussed by Rodriguez and Clark[1] and Pickett et al.[2] Pickett's computer program for reducing GPC data incorporates this procedure, but a number of recent publications show that the advantages of this conversion procedure may not be properly recognized. In many publications the means of converting elution curves to molecular weight distribution curves is not clearly described or documented, leading to uncertainty as to whether correct procedure was recognized and followed. The purpose of this paper is to recommend a rigorous, yet simple, conversion procedure that we have found useful for reducing GPC data and to illustrate the misleading results that can be obtained when this basic procedure is not followed.

In a GPC analysis the elution volume V can be related to the molecular weight M of the sample by calibrating the system with polymer samples of known molecular weights. The curve which shows $\log M$ versus V is often referred to as the calibration curve. As Moore[3] has pointed out, however, the curve obtained by replacing the elution volume scale under the GPC elution curve with $\log M$ does not, in general, represent the true MWD curve. This is true even when the abscissa is corrected for nonlinearities in the calibration curve; the ordinate values must also be corrected, as will be shown.

A differential MWD curve may be represented by a plot of $dw/d(\log M)$ versus $\log M$. In a GPC analysis the concentration c of the effluent polymer solution is recorded as a function of the elution volume V. If the curve is normalized for the area under the curve, the ordinate becomes dw/dV, where w is the weight fraction of polymer eluted up to elution volume V. In order to convert a GPC elution curve to the corresponding MWD, we write:

$$\frac{dw}{d(\log M)} = (dw/dV)\,[dV/d(\log M)]$$ (1)

The quantity dw/dV is the ordinate of the normalized elution curve, and $dV/d(\log M)$ is simply the reciprocal of the slope of the usual calibration curve. These two quantities can be determined at any elution volume directly from the elution curve and calibration curve, respectively. Their product, when plotted against the corresponding values of $\log M$ at appropriate intervals, delineates the desired MWD curve. Since the calibration curve is rarely linear over the entire range of interest, the use of this procedure is, in general, necessary to obtain an accurate MWD curve.

Two examples are given that illustrate the errors introduced by failure to correct the ordinate values. Then follows a graphical procedure that not only demonstrates the described method but also provides a simple means of carrying out the calculation manually. In these examples columns of
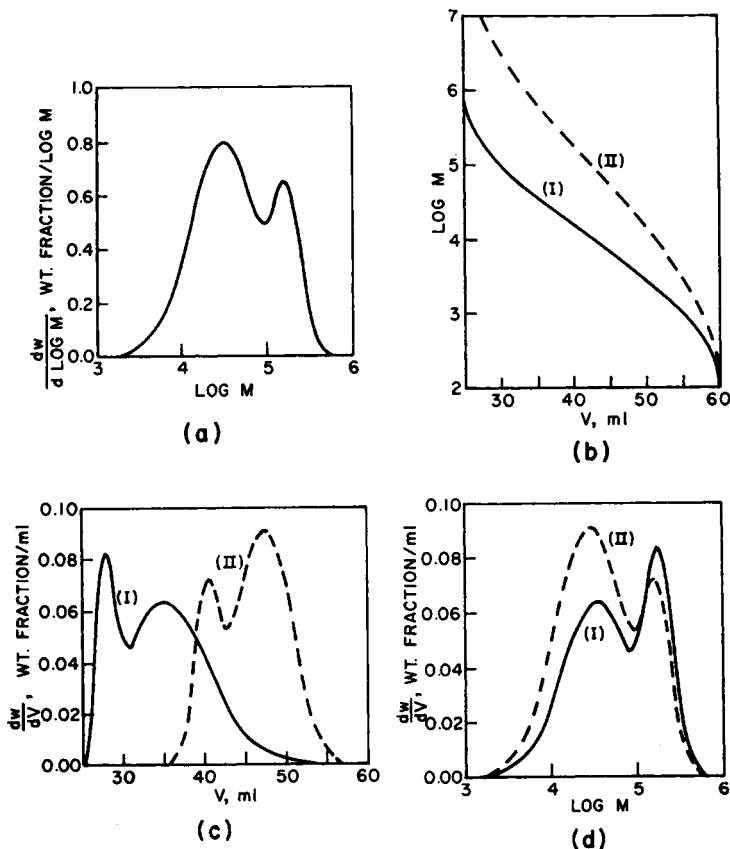

Fig. 1. GPC curves for identical samples through two different columns: (a) MWD curve; (b) calibration curves; (c) elution curves; (d) plot of dw/dV vs. $\log M$.

negligible axial dispersion are assumed, to allow clearer illustration of the conversion procedure itself.

Comparison of GPC Data Obtained from Different Columns

In this example a polymer sample having a bimodal MWD (Fig. 1a) and two GPC columns having nonlinear calibration curves (Fig. 1b) are assumed. The GPC elution curves that would be obtained by fractionating this polymer on each of the two columns are shown in Figure 1c. These elution curves were generated for this illustration from the assumed MWD by using the reverse of the procedure outlined above. The curves shown in Figure 1d are obtained from the elution curves by use of the calibration curves to correct only the abscissa scale, by replacing V with log M.

* Large differences can be seen between the two curves in Figure 1d. It is not possible to identify these curves as being the data obtained from identical samples. This shows that GPC elution curves taken from different columns are not directly comparable even when calibration curves are used
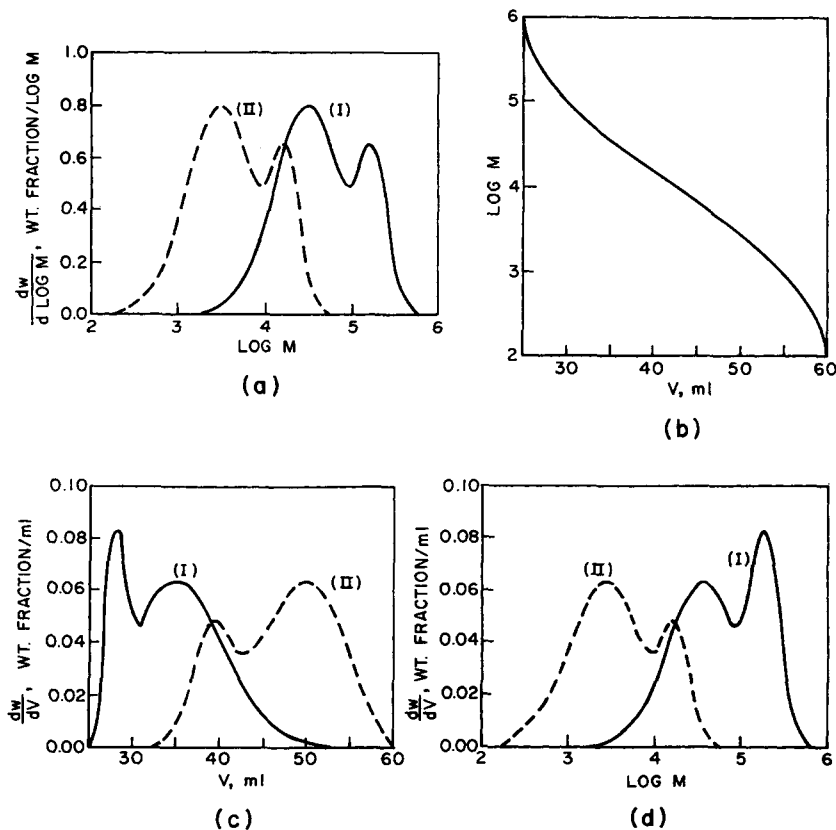

Fig. 2. GPC curves for samples of two molecular weights through one column: (a) MWD curves; (b) calibration curve; (c) elution curves; (d) plot of dw/dV vs. log M.

to correct the log M scale; the ordinates must also be corrected through use of the differential calibration curves.

Comparison of GPC Data Obtained from One Column

In this example two polymer samples having bimodal MWD (Fig. 2a) are assumed. These two MWD's are identical, except that distributions are shifted one decade. Therefore, the polydispersity of these two samples, as well as the relative amounts of the low and high molecular weight peaks, must be equal.

Figure 2b shows the calibration curve of an assumed GPC column. The GPC elution curves of these two samples that would be obtained by using this assumed column are shown in Figure 2c. Figure 2d shows the plot of dw/dV versus log M for each sample. The procedure for obtaining the curves of Figures 2c and 2d is the same as that described in the previous example.

It is seen that the identity of the two MWD curves is lost in Figure 2d. The relative amount of the high molecular weight peak (smaller elution volume) appears to be different for the two samples. This indicates that the curves shown in these figures are unevenly distorted at the high and the low molecular weight ends of the curves. It follows that accurate comparison of GPC data, obtained even from the same column, is not necessarily possible without use of the differential calibration curves. As MWD curves are intrinsic characteristics of the samples and are independent of column characteristics, they are the only valid common basis for comparison of GPC data.

Conversion Procedure

The proper GPC–MWD conversion can be facilitated by first preparing a plot of $dV/d(\log M)$ versus log M; this plot is readily obtained by measuring the slope of the usual calibration curve. This differential curve, like the calibration curve itself, is a characteristic of the column and need not be redetermined for repeat samples.

Figure 3 shows a graphic representation of the computation steps involved in this conversion. For performing the operation manually a layout of the curves, as shown in the figure, is helpful. Assuming we have the elution curve A, the calibration curve B, and the differential calibration curve C, all expressed in consistent units as shown, one may proceed as follows. Read a, the value of the elution curve A at some point; read across to curve B, then down to curve C; read the value c at this point; multiply a and c to get the value of d. The curve D generated on the log M axis by values of d so obtained is the true MWD curve. This curve corresponds to those shown in Figures 1a and 2a in the preceding examples.

Zone-broadening caused by axial dispersion in the GPC column is not considered in the conversion procedure discussed above. In the cases in which zone-broadening is appreciable the GPC elution curve must first
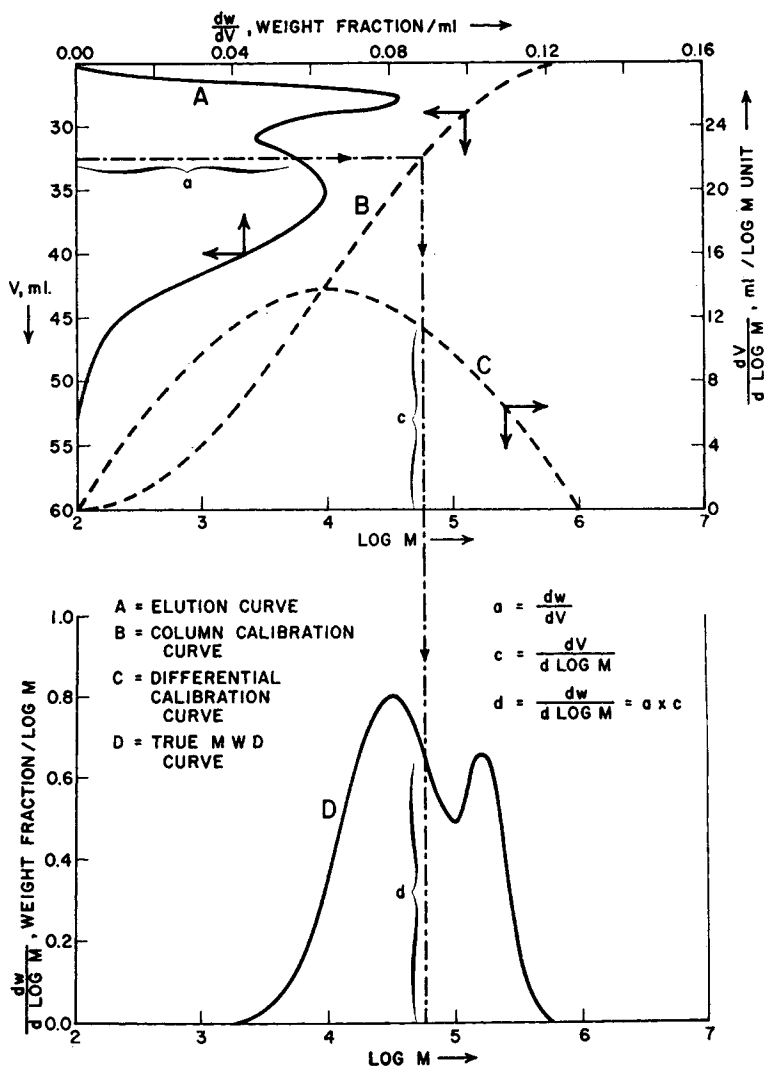
Fig. 3. Conversion of GPC elution curves to MWD curves.

be corrected for this dispersion effect, before conversion to the MWD curve. Correction programs for this have been discussed by Hess and Kratz[4] and Tung.[5]

Conclusion

As demonstrated in these examples, the assumption of a linear calibration curve, often used in MWD calculations, may lead to significant errors in the final result. Since the exact GPC–MWD conversion illustrated above can be readily performed without any assumption of linearity, we believe that such an assumption is not justified and should be avoided. This point of

view is entirely compatible with, and in fact reinforces, the view recently expressed by Coll and Prusinowski,[6] that calibration curves should appear with all published GPC results.

References

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