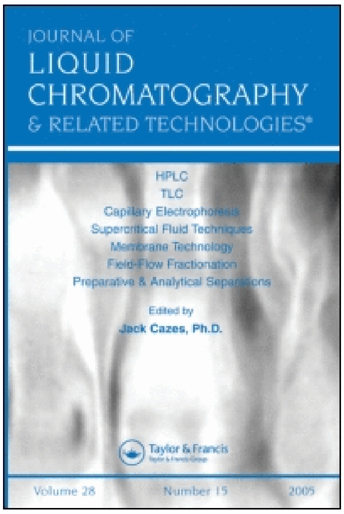

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Comment on Numerical Treatment of GPC Data

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COMMENT ON NUMERICAL TREATMENT OF GPC DATA

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ABSTRACT

The numerical treatment of a chromatogram to obtain the various molecular weight averages is discussed. The method used by Cooper and Matzinger to calculate the influence of the number of data points on M_n and M_w is criticized. Another model function is proposed. Calculations then show that the results obtained for M_n, M_w and M_z are approaching the theoretical values more and more by increasing the number of data points as it should be expected. This is in contradiction with the results of Cooper and Matzinger. The influence of the base-line correction is evaluated too.

INTRODUCTION

For a quantitative description of a molecular weight distribution of a polymer most people calculate a number of molecular weight averages like M_n, M_w, M_z. For that purpose the heights of the gel permeation chromatogram are measured at equal elution volume intervals. The molecular weights at each height are obtained from the corresponding calibration curve and the averages are calculated with

$$M_n = \sum H_i / \sum H_i/M_i$$
$$M_w = \sum H_i M_i / \sum H_i$$
$$M_z = \sum H_i M_i^2 / \sum H_i M_i$$

Recently Cooper and Matzinger (1) have studied the influence of the number of data points on the calculation of M_n and M_w. As a model they used a symmetrical, Gaussian-shaped chromatogram and a linear calibration curve. They found that the deviations in M_n and M_w from the theoretical values increased with an increasing number of data points, a result which the authors themselves call "surprisingly". The unsuspecting reader should perhaps come to the conclusion that it is advisable to use only a small number of data points, which, of course, cannot be true. The explanation of these strange results is that correct figures can only be obtained if the curve is integrated from zero to infinity. But Cooper and Matzinger discarded all heights lower than 1% of the maximum peak height, so that it is virtual impossible to obtain the correct M_n and M_w. Decreasing the number of data points increases the relative influence of the points at the extremes of the curve. This counteracts the neglection of the tails of the curve. Hence, it follows that theoretical distributions like the log normal, Schulz and Tung type are not suitable for such model calculations.

COMPUTATIONS

Real molecular weight distributions will never extend from $M = 1$ to $M = \infty$ for obvious reasons. A better function to represent a real chromatogram therefore is a function which becomes at finite values of the abscissa. Such a function is e.g.

$$H = V^k e^{-bV} - P \qquad (1)$$

where b and P are real constants and k is integer. This function has further the convenient property that it can be integrated for an arbitrary interval (2):

$$\int H\,dV = \frac{V^k e^{-bV}}{-b} + \frac{k}{b}\int V^{k-1} e^{-bV} dV - PV$$

When the calibration curve is linear the integrals for the calculations of M_n, M_w and M_z are of the same type. All averages have finite values for $P > 0$. I have evaluated this function with $k = 2$, $b = 1$ and $P = 0.01 \exp(-0.1)$. Combined with a linear calibration curve $M = \exp(V + 5)$ this gives a broad molecular weight distribution with which the desired effects can be clearly demonstrated. The heights are positive in the interval $0.1 < V < 9.128$ or $164 < M < 1,366,584$. The theoretical averages are $M_n = 1,171.7$, $M_w = 13,247$ and $M_z = 203974$. For a simulation of an ordinary measurement the chromatogram has been divided in 900 steps ($\Delta V = 0.01$), starting at $V = 0.1$ and each corresponding height has been rounded off to the next multiple of one thousandth of the maximum height. These heights have been used to calculate M_n, M_w and M_z in the usual way, with different step sizes in V. All calculations started at the same value of $V = 0.1$. The percent deviations of M_n, M_w and M_z as a function of the number of data points are shown in Figure 1. Two conclusions can be drawn from this figure. First that the errors tend to decrease when the number of data points increases. Secondly that the sign of the error varies irregularly in the case of M_w and M_z.

There is still another argument to use a small step size. When measuring heights, say at every whole count, the results will depend on the place where the measurements begin. This is illustrated in Figure 2, for the case that 10 points are taken with intervals of 90 small steps ($\Delta V = 1$). With this distribution measurement can start at height number one, two and so on until 90. Shifting the starting point causes changes in sign and magnitude of the deviations. The range over which the deviations vary decreases gradually when the number of points increases. For 100 points these ranges are 0.06%, 0.6% and 2.2% of M_n, M_w and M_z, respectively.

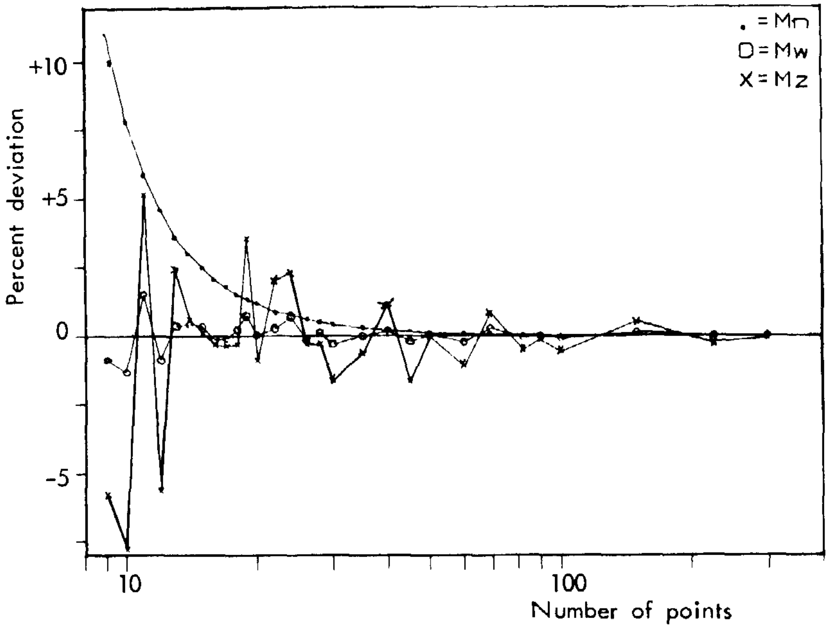

Figure 1 Percent deviation of M_n, M_w and M_z from their theoretical values as a function of the number of data points used.

DISCUSSION

The calculations show that a larger number of data points increases the accuracy of the molecular weight determinations. In general it is not possible to predict the sign and magnitude of the deviations in the molecular weight averages. The distribution which is used here as an example has a high molecular weight tail. Therefore, the largest variations are found for M_z. Distributions with a low molecular weight tail will show larger variations of M_n.

Another thing which is very important when dealing with broad distributions, is the drawing of the base-line. A change of P in

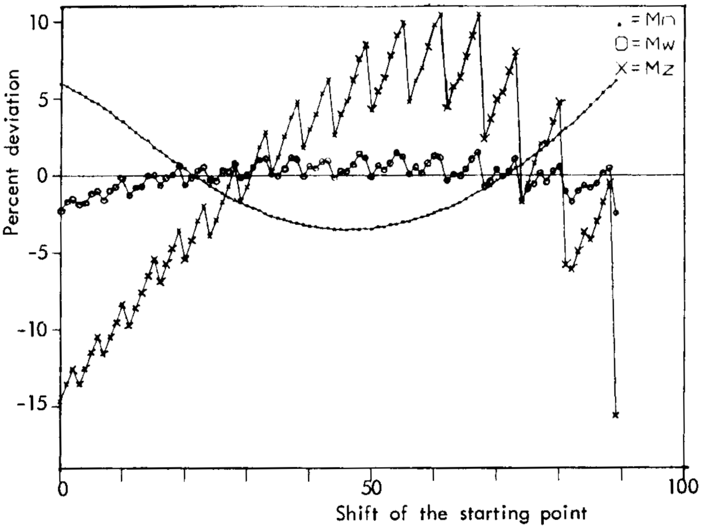

Figure 2 Percent deviation of M_n, M_w and M_z from their theoretical values as a function of the starting point.

equation (1) corresponds to a change of the level of the base-line. Lowering P with 10% (= 0.17% of the maximum height of the peak) gives increases of 0.1% of M_n, 5% of M_w and 13% of M_z. This clearly demonstrates the need of a constant, stable base-line and a very accurate registration of the detector signal.

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