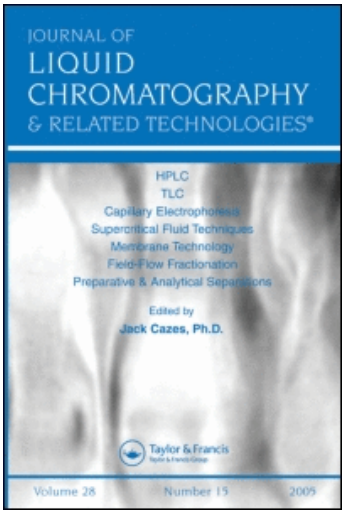

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Comments on the Numerical Treatment of CPC Data

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COMMENTS ON THE NUMERICAL TREATMENT OF GPC DATA

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ABSTRACT

The magnitude of the errors introduced in the calculated molecular mass averages is discussed in the case of gel permeation chromatography (GPC). It was shown, that neglecting the undetectable parts at both tails of a chromatogram, where the intensity of the curve is very small , results in serious errors. For chromatograms with Gaussian shapes it was found, that if the molecular mass limits of the calculations were set at ±3S (S is the standard deviation of the curve) the numerically calculated M_n and M_m values deviated by 1 to 10 % from the theoretical ones . The errors increased with increasing polydispersity and decreased as the number of data points increased. However, there was no significant difference in the results if the number of data points was greater than 20.

INTRODUCTION

Recently Cooper and Matzinger (1) published their admittedly surprising results on the effect of the number of data points for the calculated molecular

mass averages obtained from GPC chromatograms. They used curves of Gaussian shape generated by a computer. The molecular mass limits for the calculations were set at $\pm 3S$ (S is the standard deviation of the curve) and they used the generally accepted methods and assumptions to calculate the average molecular masses. They found that the differences in the numerically calculated and the theoretical values of the number- and mass-average molecular masses (M_n and M_m) was increasing as the number of the data points increased. For curves of high polydispersity, this deviation was always significant if the number of data points was large. Both of these fenomena can be explained by the effect of the neglected parts of the curves on the calculation of the M_n and M_m values.

COMPUTATIONS

The calculations were performed on a Hewlett Packard 9830 A desktop calculator, the program was written in BASIC language. For the sake of convenience, curves of Gaussian shape were used as 'theoretical' GPC chromatograms and a linear calibration curve (logaritmic molecular mass versus elution volume) was chosen. In this case the resulting molecular mass distribution (MMD) will be log normal:

$$MMD(\ln M) = \frac{\exp[-(\ln M - \ln M_0)^2/2S^2]}{S(2\pi)^{0.5}}$$

where M_0 is the molecular mass at the maximum of the log normal MMD, and

S is the standard deviation of the curve.

The theoretical molecular mass averages can be readily calculated (analytically) from the parameters of the log normal MMD (1). In the numerical calculation of the 'calculated' M_n and M_m the generally accepted methods and approximations were used (the same as in the paper of Cooper and Matzinger). In order to calculate the M_n and M_m values, the curves were divided into equal elution volume intervals (according to the number of data points). This implicitly involves two assumptions as follows. Each fraction of the chromatogram is represented by a single molecular mass (Mi) and its area is approximated by a rectangle. The height of a rectangle (Hi) is the height of the chromatogram at Mi and the center of it is located at Mi. This also means that, on both sides of a GPC curve, the real molecular mass limits of the calculations exceed the first and the last Mi values by the half of the interval between the data points. Neglecting this fact might cause serious errors in the determination of the molecular

mass limits, especially if the number of data points is small.

In this work the theoretical GPC curves were approximated by 5-50 points and the real molecular mass limits were set at ±2S, ±3S and ±4S respectively. The M_o values were chosen to be 10 and 100 thousand respectively.

RESULTS AND DISCUSSION

The effect of the molecular mass limits on the difference in the calculated and the theoretical molecular mass averages is shown in Figure 1. For a Gaussian chromatogram the height of the curve at ±2S is 13.5 % of the maximum, but at ±3S it is only 1.1 % and at ±4S 0.03 % of that. Since the 1.1 % value is approximately equal to the detection limits in the practice of GPC measurements, for real chromatograms there is no practical way to extend the calculations to the tails of the curves where this ratio is still smaller. This also means that the M_n and M_m values obtained from GPC measurements are subjects of errors, and these errors increase with increasing polydispersity and decreasing signal-to-noise ratio. Naturally, the shape of real GPC chromatograms is usually not Gaussian, and in rea-

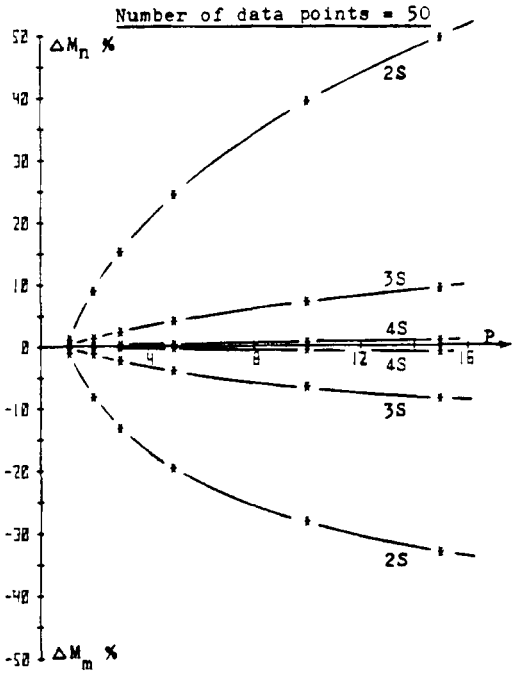

FIGURE 1 Comparison of the Theoretical and the Calculated Molecular Mass Averages. Differences (ΔM_n and ΔM_m) versus Polydispersity (P) for Different Molecular Mass Limits

lity, the MMD curves do not extend to plus and minus infinity; however, as the polymerization reactions are statistical ones, we can assume that in most synthetic polymer samples there is a significant amount of molecules which remains undetected at the tails of GPC chromatograms. The effect of these parts of the curves on the calculated molecular mass averages might be greater than the influence of the number of the data points. In their work, Cooper and Matzinger always set the first and the last Mi values to ±3S and by doing

so they implicitely extended the real molecular mass limits (by the half of the interval between the data points) as the number of points decreased.

The 'pure' effect of the number of data points on the calculated M_n and M_m values is shown in Figure 2. These results are in good agreement with the work of Lambert (2) who also found no further improvement in the accuracy of the molecular mass averages if the number of data points exceeded 20. Differences in the

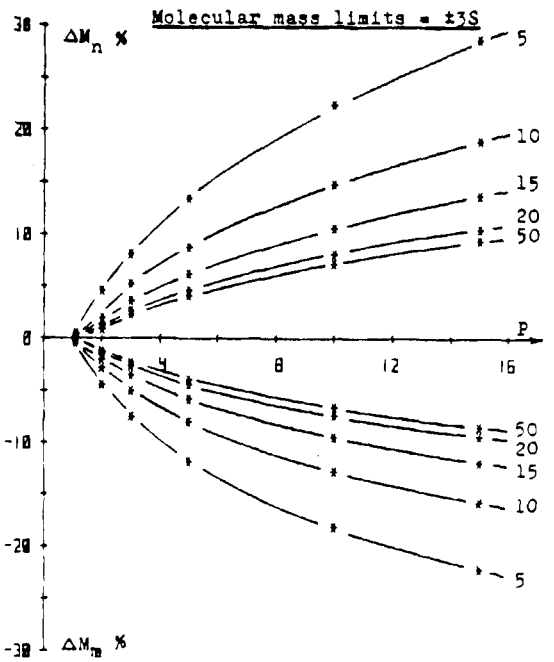

FIGURE 2 Comparison of the Theoretical and the Calculated Molecular Mass Averages. Differences (ΔM_n and ΔM_m) versus Polydispersity (P) for Different Numbers of Data Points

M_o values - as expected - had no influence on the relative errors in the calculated molecular mass averages.

CONCLUSIONS

Undetectable parts at the tails of GPC chromatograms, even where the height of the curve is smaller than 1 % of the maximum, might significantly affect the values of the calculated molecular mass averages. The magnitude of these errors sharply increases with decreasing signal-to-noise ratio. The M_n values obtained from model calculations were found to be higher and the M_m values lower than the theoretical ones. This effect increased with increasing polydispersity. Naturally, the magnitude of errors also depends on the shape of the molecular mass distribution.

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