

Tung L H. Method of calculating molecular weight distribution function from gel permeation chromatograms. *J. Appl. Polym. Sci.* **10**:375-85, 1966. [Physical Res. Lab., Dow Chemical Co., Midland, MI]

An integral equation taking account of peak overlapping in chromatograms is given to relate the experimental chromatogram and the true molecular weight distribution function. Three methods for solving the integral equation are described. The first method provides a special solution for samples obeying the log-normal distribution; the other two methods provide solutions for more general cases. The use of these solutions in the treatment of gel permeation chromatographic data is discussed. [The SCI® indicates that this paper has been cited over 185 times since 1966.]

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"When John Moore was developing gel permeation chromatography (GPC) at Dow Texas Research Center,¹ I was interested in polymer characterization at Dow Research in Michigan. At that time the best method to determine polymer molecular weight distribution was sedimentation velocity analysis on ultracentrifuges. Moore's method showed promise to be an order of magnitude better in speed and versatility. Among chromatographic methods GPC is unique in one respect that its unknowns contain thousands of components instead of a few. Baseline separation for these thousands of components is unattainable, nor is it desirable. To relate the chromatograms quantitatively to molecular weight distributions, the overlapping of the peaks in the experimental chromatograms should be corrected mathematically. This problem was more urgently felt at Midland when we tried to compare the results from GPC to those from sedimentation analysis. This paper was the outcome. In it I formulated an integral

equation describing the peak overlapping phenomenon and provided three numerical methods for solving it.

"The primary reason for this paper being frequently cited must be attributed to the success of Moore's method. As a consequence many workers started to worry about the same problem as I did. Another reason, I believe, was that none of the three numerical solutions provided in the paper was completely satisfactory. Later I published two more solutions² and so did many others. As of two years ago, a total of 36 solutions had appeared. Such activities caused a good deal of cross references. The nature of the problem of correcting peak overlapping, as I see it, is that in bringing better precision in chromatographic resolution by solving mathematically the integral equation, one trades away the precision in peak height detection. It is a compromise and no two workers are likely to agree where the line of compromise should be drawn. Thus more solutions might still be forthcoming but at this moment, I believe, the one provided by Ishige, Lee, and Hamielec³ and later advocated by Park and Craessley⁴ is the most practical. In fact it is being used routinely in our laboratory.

"It should be mentioned that the correction for peak overlapping (or more commonly known as spreading correction) is not as important in GPC as the corrections in some other physical methods. It would be hopeless to interpret data from sedimentation velocity analysis without the methods for correcting for the hydrostatic pressure effect, the diffusion effect, the concentration effect, etc. In GPC good quantitative results can be obtained if the distribution of the unknown is not too narrow and if efficient columns are used. Still there are too many cases where proper correction of peak overlapping would have provided better quantitative results and thus avoiding misinterpretations especially when results from different GPC units are used or when GPC results are compared with results from other methods."

1. **Moore J C.** Gel permeation chromatography. I. A new method for molecular weight distribution of high polymers. *J. Polym. Sci.* **A2**:835-43, 1964.
2. **Tung L H.** Correction of instrument spreading in gel-permeation chromatography. *J. Appl. Polym. Sci.* **13**:775-84, 1969.
3. **Ishige T S, Lee S I A Hamielec A E.** Solution of Tung's axial dispersion equation by numerical techniques. *J. Appl. Polym. Sci.* **15**:1607-22, 1971.
4. **Park W S & Gruessley W M.** On-line viscometry combined with gel permeation chromatography. I. Instrumental calibration and testing with linear polymers. *J. Polym. Sci. Polym. Phys. Ed.* **15**:71-83, 1977.