## *The Use of Fast, Finite Fourier Transforms for the Solution of Tung's Equation*

Gel permeation chromatography (GPC)[1] is rapidly becoming a useful tool for the characterization of polymers. However, some difficulties arise in extracting the maximum amount of information from the GPC chromatogram. One of these problems is that axial diffusion occurs in the GPC column which results in peak broadening of the signal. Adjacent peaks have a tendency of running together and the apparent resolution of the instrument is reduced. Several investigators[2-8] have suggested mathematical methods of resolving this difficulty and the purpose of this comment is to suggest a possible improvement of one of them.[8]

The mathematical expression relating the experimental chromatogram $f(v)$, the true chromatogram $w(y)$, and the function $g(v)$ describing the instrument spreading can be represented by the integral equation[2]

$$f(v) = \int g(v - y)w(y)dy \tag{1}$$

where $v$ and $y$ represent the elution volume. Pierce and Armonas[7] and Tung[8] pointed out that a standard technique[9] for solving this type of integral equation is to make use of Fourier transforms. Subsequently, Pierce and Armonas[7] approximated $f(v)$ by a finite expansion in order to obtain a solution. Tung[8] advocated the use of numerical integration to obtain the desired Fourier transforms. In this comment we would like to suggest the use of fast Fourier transforms (FFT) as a possible alternative.

Recently an algorithm for obtaining fast finite Fourier transforms has been developed by Cooley and Tukey.[10] This procedure makes it possible to consider many more points from the experimental chromatogram than were previously used. It is not necessary to fit the data to an analytic expression since the transforms can be obtained directly from the experimental points. This also makes it possible to use experimental line shapes directly. Also mathematical filtration and smoothing operations can be performed on the transform of the experimental chromatogram. The use of experimental line shapes and smoothing of the data should eliminate the most important sources of artificially induced oscillations observed[6] in corrected chromatograms.

The disadvantage this method shares with the other transform methods[7,8] is that $g$ is explicitly assumed to be a function of $v - y$ only. That is, if a Gaussian line shape is assumed, the width $h$ cannot vary as a function of elution volume. Exactly how serious an error this produces in comparison with those produced by the assumed line shape and statistical fluctuations in the data is not entirely clear at this time. For a single-peak distribution, a single $g$ factor does not seem to cause much error.[4] In a more elaborate chromatogram, an "average $h$" could be used to approximately establish the number of components and their respective elution volumes. A nonliner least squares technique[11] could then be used in conjunction with a variable $h$ to obtain a more refined fit of the experimental chromatogram somewhat along the lines proposed by Smith.[3]

Practical applications of this method are currently being conducted in this laboratory. We will report our findings in more detail as soon as they become available.

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Received December 11, 1969