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THE USE OF FAST, FINITE, FOURIER TRANSFORMS FOR THE SOLUTION OF TUNG'S EQUATION

II. THEORY AND APPLICATION

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SUMMARY

Recently it has been suggested that fast finite Fourier transforms be employed for the solution of TUNG's integral equation. The COOLEY AND TUKEY algorithm used in the present work is much faster than the usual Fourier method since the length of computation is proportional to $N \log_2(N)$ rather than N^2. This saves computer time and also enables a larger number of points to be used in order to facilitate computer plotting of the corrected chromatogram. First some of the basic properties of finite Fourier transform are presented in order to familiarize the reader with the approximations involved. Then several chromatograms, both analytical and simulated experimental are considered and some of the problems inherent in processing experimental chromatograms are discussed.

INTRODUCTION

Gel permeation chromatography (GPC)[1] is becoming popular for the characterization of molecular weight distributions of polymers. However, as a result of axial diffusion spreading occurs in the GPC instrument so that the molecular weight averages obtained from the chromatograms can be significantly different from the absolute molecular weight averages[2]. As a result some interest has been generated in developing methods by which the experimental chromatograms can be corrected for this effect[3-9]. Central to this endeavour is the solution of the integral equation:

$$z(t) = \int_{-\infty}^{\infty} x(t-\tau)y(\tau)\,d\tau \qquad (1)$$

which was first suggested by TUNG[3]. This equation relates z, the observed chromatogram to the true chromatogram y which is being spread by the function x. t and τ represent elution volumes. When x is a function of $t-\tau$ only, eqn. 1 can be solved using Fourier transforms[9,10]. The use of this type of solution in conjunction with numerical integration is not only slow but also seems to work better on analytical examples than on experimental data[2,11]. For this reason we have undertaken to investigate the use of fast finite Fourier transforms (FFFT)[12] as recently suggested by VLADIMI-

ROFF[13]. With this technique the length of computation becomes proportional to $N \log_2(N)$ rather than N^2. Even for a 32 point transform, this reduces the required computer time by a factor of 6. If large numbers of chromatograms must be processed the savings in money can be substantial. For the purposes of plotting, 32 points is really not enough as can be seen in Fig. 1. To obtain better plots, a larger number of points must be used resulting in greater savings when FFFT is employed. It was also suspected that this method might be used to investigate the nature of some numerical difficulties encountered by investigators attempting to process experimental chromatograms.

THEORY

Although a detailed theoretical analysis of the computational simplifications involved in the FFFT will not be presented here, some of the basic properties of the finite Fourier transforms (FFT) will be discussed in order to introduce the notation and to give the reader a feeling for the method. A more detailed discussion can be found elsewhere[14].

If $X(j)$, $j = 0, 1, \ldots, N-1$ is a sequence of N complex numbers, the finite Fourier transform of $X(j)$ is defined as:

$$A(n) = 1/N \sum_{j=0}^{N-1} X(j) e^{-2\pi i nj/N}$$

where $i = (-1)^{1/2}$. If $W_N = \exp(2\pi i/N)$ then:

$$A(n) = 1/N \sum_{j=0}^{N-1} X(j) W_N^{-uj}.$$

We also have the inverse finite transform:

$$X(j) = \sum_{n=0}^{N-1} A(n) W_N^{uj}.$$

This is a consequence of the orthogonality relationship of W_N^{uj}:

$$\sum_{j=0}^{N-1} W_N^{uj} W_N^{-mj} = \sum_{j=0}^{N-1} W_N^{(n-m)j} = N \text{ if } n = m \text{ Mode } N$$
$$= 0 \text{ otherwise}$$

A double arrow connecting two functions *i.e.* $X(j) \leftrightarrow A(n)$ is used to indicate a finite Fourier pair. The exponential function W_N is periodic in both n and j:

$$W_N^{nj} = W_N^{(n+N)j} = W_N^{n(j+N)}.$$

Therefore, $A(n)$ and $X(j)$, as defined by their finite transforms, are periodic in N. Also the convolution theorem holds:

$$1/N \sum_{k=0}^{N-1} X_1(k) X_2(j-k) = 1/N \sum_{k=0}^{N-1} X_1(j-k) X_2(k) \leftrightarrow A_1(n) A_2(n).$$

In this paper we are particularly interested in using the finite Fourier transform to approximate the Fourier integral:

$$a(f) = \int_{-\infty}^{\infty} x(t)e^{-2\pi ift}\,dt.$$

If $a(f)$ is sampled at intervals of length Δf and expressed at sampling points $n\Delta f$, $n = 0, \pm 1, \pm 2, \ldots$ then:

$$a(n\Delta f) = \int_{-\infty}^{\infty} x(t)e^{-2\pi int/T}\,dt,$$

where $T = 1/\Delta f$. $\mathrm{Exp}(-2\pi\, int/T)$ is a periodic function of t with period T. By changing the variables of integration it is possible to obtain:

$$a(n\Delta f) = \int_{0}^{T} x_p(t)e^{-2\pi int/T}\,dt,$$

where

$$x_p(t) = \sum_{k=-\infty}^{k=+\infty} x(t + kT).$$

The subscript p on a function will denote the periodic function formed by superposition of the non-periodic function shifted by all multiples of the fundamental period. This is the approximation introduced when the infinite transform is replaced by the finite transform. If $x(t)$ is zero outside certain limits so that $x_p(t) \approx x(t)$ this is a good approximation and the finite transform can be used to replace the infinite transform.

For the convolution integral of eqn. 1, the convolution theorem of Fourier theory states that if:

$$x(t) \leftrightarrow a(f)$$

$$y(t) \leftrightarrow b(f)$$

$$z(t) \leftrightarrow c(f),$$

then $c(f) = a(f)b(f)$. If $y(\tau)$ in eqn. 1 equals zero for $|\tau| > T_y$ then:

$$z(t) = \int_{-T_y}^{T_y} x(t-\tau)y(\tau)d\tau.$$

Approximating this integral by the trapezoidal rule gives:

$$z(j\Delta t) = \Delta t \sum_{k=-K}^{k=K} x((j-k)\Delta t)y(k\Delta t),$$

where $\Delta t = T/N$, $K = T_y/\Delta t$ and $j = 0, 1, 2, \ldots, N-1$. By the theorem on the convolution of FFT this will be approximated by $\Delta t NA(n)B(n)$. There is a wrap-around

error in this procedure. This is because values of X in the range $X(-K)$ to $X(N+K)$ must be used and the convolution is computed as though $X(j)$ repeated itself outside the $(0, N-1)$ interval. To avoid this type of difficulty it is necessary to include at least K zeroes on either side of x and y.

In other words the FFT can be introduced in two ways. One is through the observation that if $x_p(t) \approx x(t)$, then the FFT is a good approximation to the Fourier integral. The other is to approximate the integral in eqn. 1 using the trapezoidal rule and then employing the convolution property of FFT to obtain the desired result. Both these methods are related since they depend on the functions involved being small outside a certain region.

ANALYTICAL RESULTS

As we have seen, there are two justifications for employing FFFT. Actual application requires a judicious choice of F, T and N. In this respect it is important to take into account the relationships between these quantities:

$$N\Delta t = T \qquad 1/T = \Delta f$$

$$N\Delta f = F \qquad 1/F = \Delta t.$$

Usually T is determined by the experimental chromatogram, allowing a certain number of zeroes on both sides to keep from introducing wrap-around errors. N is then determined by having $F \approx 1$. Extending the calculation further into the frequency domain has no practical value since rounding errors will predominate. Once the transform of y is obtained using the formula $B(n) = C(n)/A(n)$, zeroes can be added at the end of B in order to increase N to N'. Δf and hence T is kept constant. The resulting inverse FFFT using N' points produces $Y(j)$ with a much smaller $\Delta t = T/N'$. This enables the computer to plot $Y(j)$. Otherwise a smooth curve must

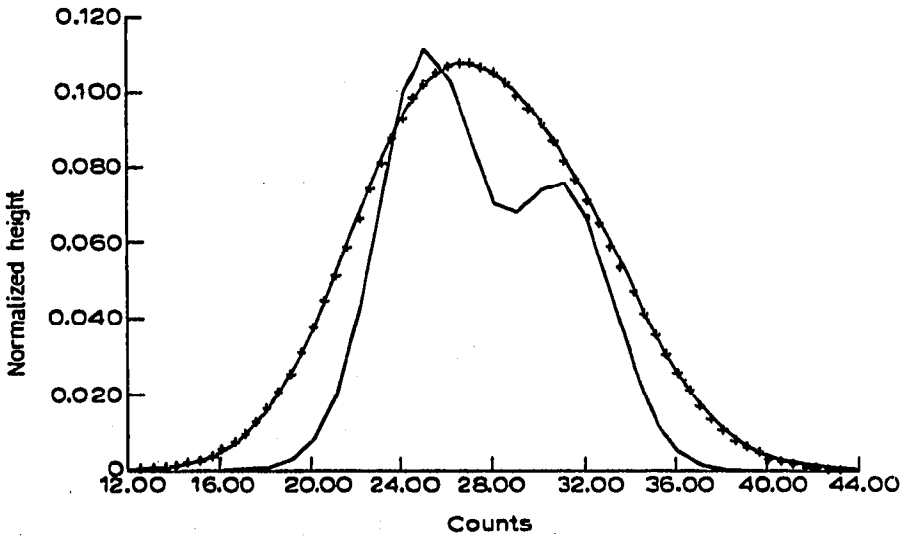

Fig. 1. A plot of TUNG's analytical test function $y(t)$ using only 32 points. ($\times\times\times$) $z(t)$; (———) $y(t)$.

be fitted through the processed points to avoid the type of plot illustrated in Fig. 1.

To explore the method analytically, the synthetic, two-peak distribution:

$$y(\tau) = (0.325/\sqrt{\pi})\,[0.6e^{-(0.325)^2(\tau-25)^2} + 0.4e^{-(0.325)^2(\tau-31)^2}]$$

suggested by TUNG[9] was utilized. A simple Gaussian of the form $x(\tau) = h(\pi)^{-1/2}$ $\exp(-h^2\tau^2)$ was used as the spreading function. This example is advantageous since

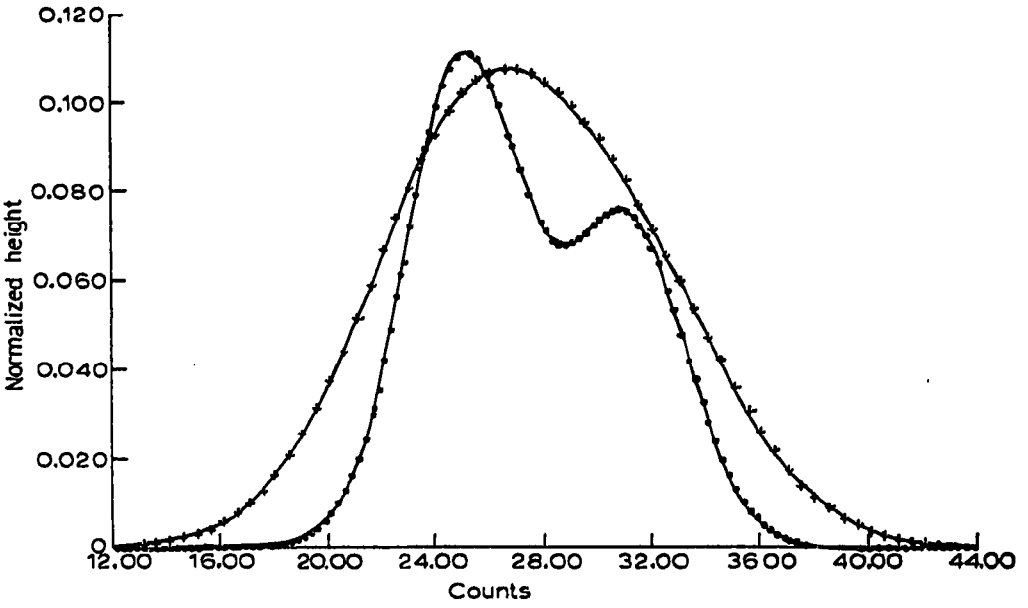

Fig. 2. A comparison of the exact $y(t)$ with $y_F(t)$ computed by FFFT with $h = 0.4$. (+++) $z(t)$; (·····) $y(t)$; (———) $y_F(t)$.

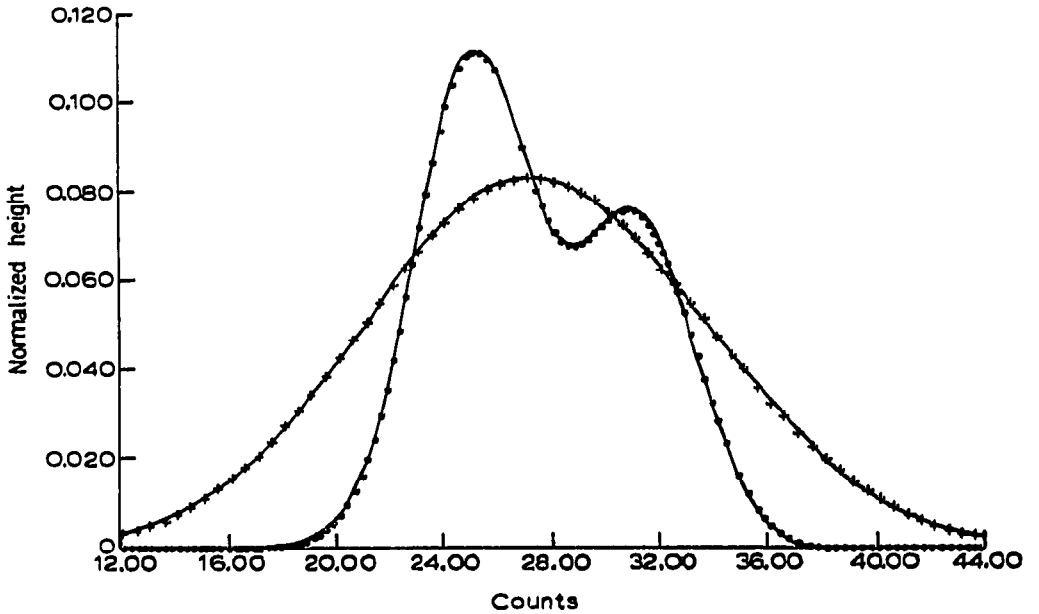

Fig. 3. A comparison of the exact $y(t)$ with $y_F(t)$ computed by FFFT with $h = 0.2$. (+++) $z(t)$; (·····) $y(t)$; (———) $y_F(t)$.

all the integrals of interest can be computed exactly and used for the purposes of comparison. Figs. 2 and 3 illustrate the plotted $y(\tau)$ obtained with $h = 0.4$ and $h = 0.2$, respectively, using a value of $N' = 1024$. For the case of $h = 0.2$ the results are worse since F had to be reduced to 1/2 and only 32 points were used from $z(t)$. However when the results are plotted, in Fig. 3 they can not be distinguished from the true values.

Once it had been established that the method and the relevant computer

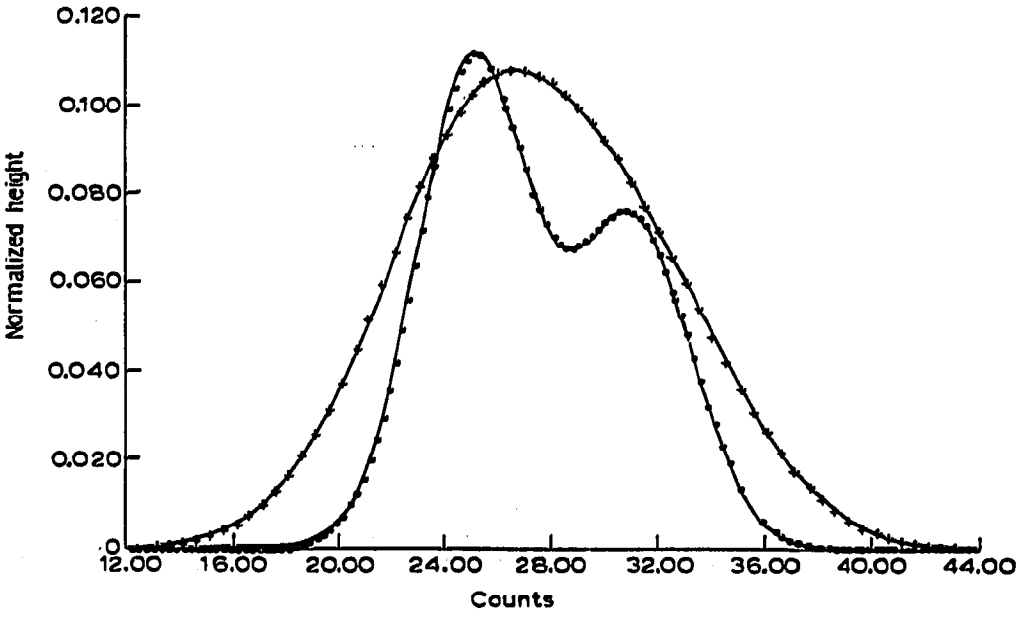

Fig. 4. A comparison of the exact $y(t)$ with $y_F(t)$ computed by neglecting values of $z(t) < 0.001\ (z(t))_{max}$ with $h = 0.4$. (+++) $z(t)$; (·····) $y(t)$; (———) $y_F(t)$.

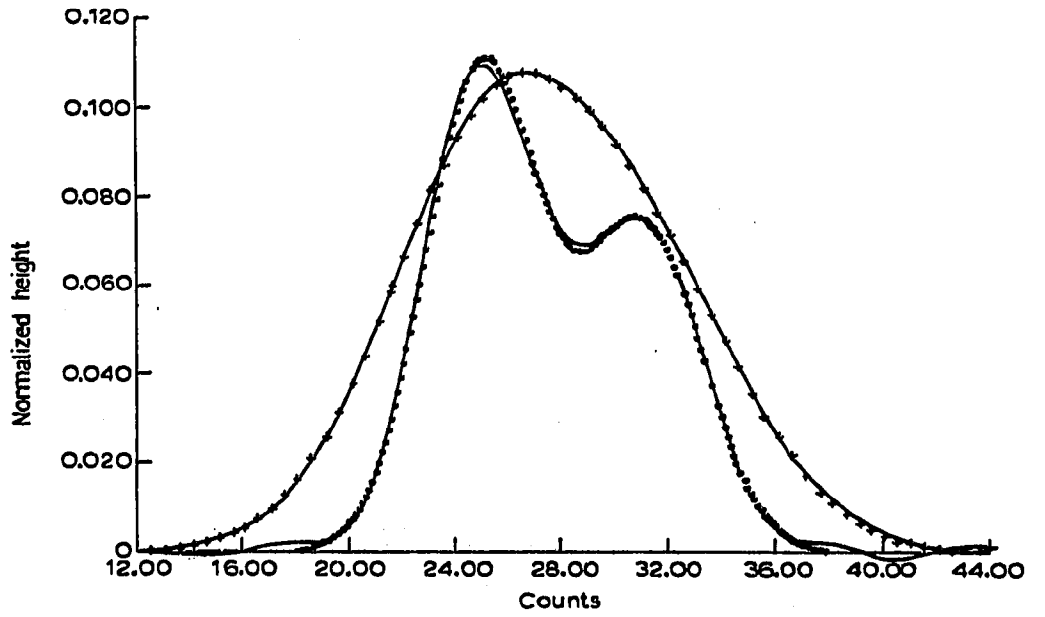

Fig. 5. A comparison of the exact $y(t)$ with $y_F(t)$ computed by neglecting values of $z(t) < 0.005\ (z(t))_{max}$ with $h = 0.4$. (+++) $z(t)$; (·····) $y(t)$; (———) $y_F(t)$.

programs worked well on this example, an attempt was made to process more realistic chromatograms. In particular it was desired to establish practical limits on F and to investigate the oscillations in y encountered by other workers[2,11].

The limit on the acquisition of data is the signal to noise ratio (S/N). In a typical GPC experiment one can not expect a value much in excess of 1000 to 1. With the FFFT method, the transform is computed to a certain number of decimal places. The exact number of places depends on the accuracy of the input data and

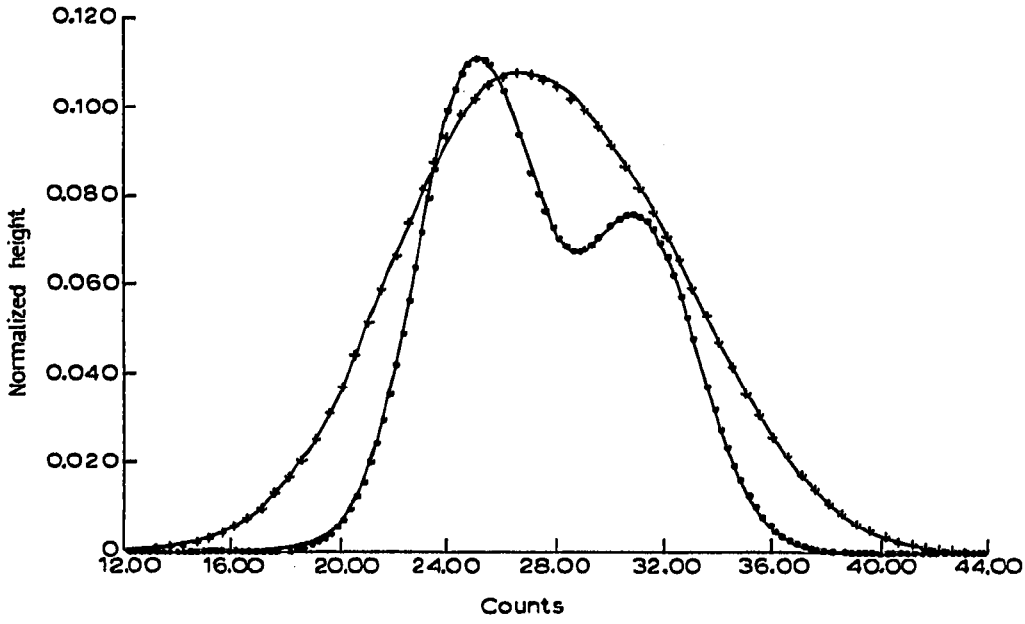

Fig. 6. A comparison of the exact $y(t)$ with $y_F(t)$ computed by rounding all values of $z(t)$ to 0.001 with $h = 0.4$. (+ + +) $z(t)$; (· · · · · ·) $y(t)$; (———) $y_F(t)$.

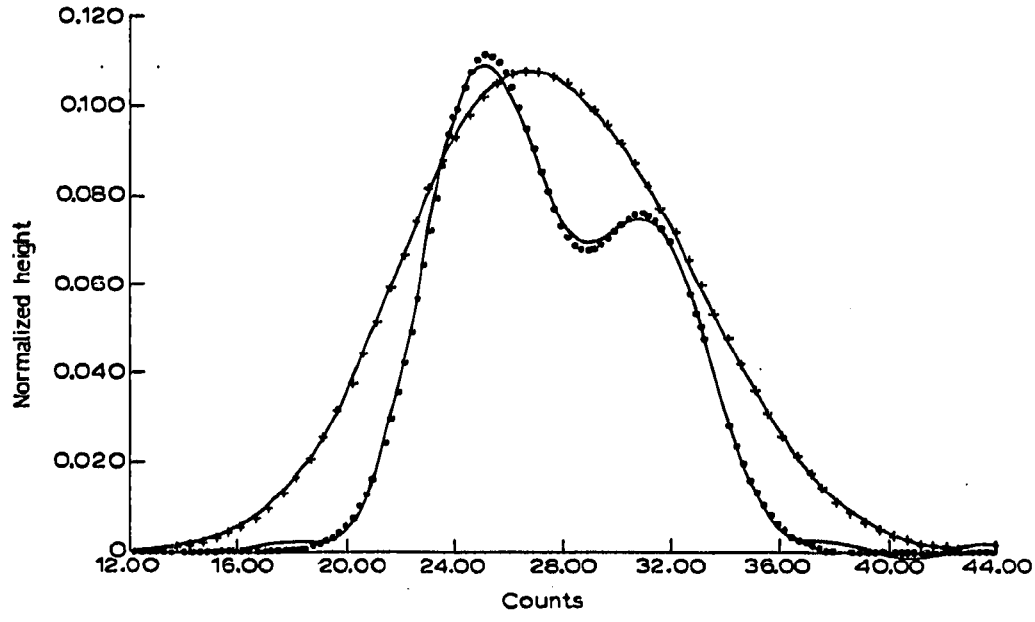

Fig. 7. A comparison of the exact $y(t)$ with $y_F(t)$ computed by rounding all values of $z(t)$ to 0.005 with $h = 0.4$. (+ + +) $z(t)$; (· · · · · ·) $y(t)$; (———) $y_F(t)$.

on the number of significant figures retained by the computer. In the case of GPC, the signal to noise ratio of the input data becomes the limiting factor so that the transform can not be calculated more accurately than one part in a thousand. Unfortunately this means that the smallest numbers in the transform never get much smaller (in absolute value) than 10^{-3} times the largest number. Thus $C(n)$ does not appear to approach zero asymptotically as it should. On the other hand the Gaussian is analytic and its transform can be calculated quite accurately. Since the transform of a Gaussian is itself a Gaussian it approaches zero rapidly. To obtain the transform of Y we divide by the transform of X. The division by small numbers produces large meaningless numbers which completely dominate the Fourier synthesis of Y. This can be easily illustrated by setting all the values of Z smaller than 0.1 % of the largest Z equal to zero.

To compensate this type of error, it was decided to set all elements of the transform of Z smaller than 0.1 % of the largest equal to zero since elements of this order of magnitude could not be computed accurately. This calculation for $h = 0.4$ is plotted in Fig. 4 and compared with the exact result. If the cut-off point is set at 0.5 %, the somewhat inferior fit of Fig. 5 is obtained.

Not only are the wings of real chromatograms affected by the noise but all the data are limited in accuracy. To simulate this all the values of Z were rounded to 0.1 %. The results were plotted in Fig. 6. With this S/N ratio no oscillations are seen to appear. When Z was rounded to 0.5 %, the plot of Fig. 7 was obtained. The results are similar to those of Fig. 5 and probably represent the limiting value of S/N which can be handled successfully by this method.

CONCLUSIONS

When the spreading function is not strongly dependent on elution volume the FFFT is an efficient method of solving TUNG's equation. It also becomes possible to employ enough points for the computer to plot the end product. It seems practical to allow the spreading function to determine F as has already been suggested[2], although this is not critical in the FFFT method. Providing a cut-off for the transform of Z which goes inversely as S/N seems to be reasonable on the basis of the few examples examined in this paper. However, this could probably be optimized further in individual cases. The possibility of processing chromatograms with a S/N greater than 200/1 without producing an unsatisfactory loss of accuracy is suggested. It should also be noted that since the FFFT method uses $\log_2(N)$ operations to compute a point rather than N operations, errors in the input data do not accumulate as rapidly[14] as in the usual method.

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