Applications of the Fourier Transform In Chemical Instrumentation: A Computer Simulation With Mathcad

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ABSTRACT: *Chemical instrumentation based on FT is well known by experimental scientists and technicians; however, their mathematical principles are poorly understood. Unfortunately, the black-box design of many commercial instruments makes this double aim difficult to implement. Well designed computer simulations are one way of providing the background of this experience. Mathcad is one of the four most popular computational packages used in academic and industrial environments. Mathcad combines some of the best features from spreadsheets (like MS Excel) and symbolic math programs.. Mathcad contains functions for performing the discrete Fourier transform and its inverse. The function FFT returns the Fourier transform of a 2N element vector of real data representing measurements at regular intervals in the time domain. The function IFFT returns the inverse Fourier transform of a vector of real data representing values in the frequency domain.*

This paper describes two applications of the Fourier transform for data manipulation in chemical instrumentation by means of the Mathcad symbolic computational package, (version 2000 Professional for Windows on a PC-compatible). Both applications have similar aims, to improve the quality of spectroscopic or chromatographic signals It explores the advantages of the Fourier transform and digital filtering to smooth a noisy signal with a improvement of the signal-to-noise ratio of 45. The simulation of the convolution is carried out; the effect of the bandwidth of the filter function (slit of grating in spectrometry and dead volume in chromatography) and the effect of phase shift among the analytical signal and the filter signal are described. Deconvolution allows to recover the starting signal corresponding to a laser-excited fluorescence decay.

1   INTRODUCTION

The Fourier Transform (FT) is basically a mathematical tool which recognizes that there are two ways of describing many physical processes: One way treats the process as serial, either in time or in space; the alternative way of describing a physical process is to represent it in function of the frequency (time-inverse) or spatial frequency (space-inverse). Therefore, the FT is a mathematical technique that separates a time-domain signal into its corresponding frequency components.

In the past, the FT process was tedious, it involved transforming a continuous distribution of data and it was only used when no substitute could be found. Nowadays, the most instrumental data are discrete (digital), i.e, sampled at regular time intervals. Thus the availability of computers and of the so-called Discrete Fourier Transform (DFT) and Fast Fourier Transform (FFT) (descriptive name of computational algorithms for rapidly evaluating the DTF), have allowed the FT to be easily accessible and result in a great development of the instrumentation. Theory of Fourier transform can be found in specialized monographs (1-4).

The applications of FT in chemical instrumentation are manifold and it seems, upon examining the literature, that there are few techniques to which FT has not been introduced at one stage or another, either in data collection process or in data handling. General applications in different topics of chemistry have been reported (5-7). Specific examples can be found in X ray crystallography (8), infrared and Raman spectroscopy (9-13), infrared imaging microscopy (14), mass spectrometry (15-16), nuclear magnetic resonance, NMR (17), and electrochemical techniques (18).

Chemical instrumentation based on FT is well known by experimental scientists and technicians; however, their mathematical principles are poorly understood. Ideally, an instrument should be known both in theory and operation. Unfortunately, the black-box design of many commercial instruments makes this double aim difficult to implement.

Well designed computer simulations are one way of providing the background of this experience. Mathcad is one of the four most popular computational packages used in academic and industrial environments (19). The other three programs are Matlab, Maple and Mathematica. However, Mathcad combines some of the best features from spreadsheets (like MS Excel) and symbolic math programs. The ease with which Mathcad lets type formulae, data and text and its capability for drawing graphs, it makes Mathcad a powerful tool to develop a variety of instructional programs.

The use of Mathcad in chemistry curriculum has been discussed elsewhere (20-24) and in the last years have been published several monographs about the application of Mathcad in several chemistry and physics topics (25-26). In a previous paper we described the use of Mathcad for the simulation of a lock-in amplifier (20). In this article, we report two applications of Fourier transform by means of the program Mathcad (version 2000 Professional) for Windows on a PC-compatible: 1) smooth a noisy signal by Fourier transform and filtering, and 2) the Fourier self convolution and deconvolution of signals. Both applications have similar aims, to improve the quality of spectroscopic or chromatographic signals.

2 FUNDAMENTALS

The *Direct* Fourier transform of a function *f(t)* is given by:

$$F(\omega) = \int_{-\infty}^{\infty} f(t) e^{-i.\omega.t} dt \tag{1}$$

Analogously, the *inverse* Fourier transform of a function *F(ω)* is given by:

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) e^{i.\omega.t} d\omega \tag{2}$$

where ω is the angular frequency, $\omega = 2\pi f$, and i is the imaginary unit.

Computation of Fourier transforms in interval [-∞, ∞] is difficult and hence the discrete Fourier transform is used to convert a digitised waveform from the time domain to the frequency domain. The DFT is given as

$$F(k\Delta f) = \frac{1}{N} \Delta t \sum_{n=0}^{N-1} f(n\Delta t) \exp(-i2\pi k n \Delta t \Delta f) \tag{3}$$

where N is the total number of points in the digitised waveform, (N is a power of 2, e.g. 2^9), n is the index of the waveform sampled in the time domain ($n = 0, 1, \ldots, N-1$), k is the index of the calculated frequency components ($k = 0, 1, \ldots, N/2$), Δf is the frequency interval, Δt is the sampling interval in the time domain, $f(n\Delta t)$ is the time-domain representation of the waveform to be Fourier transform, and $F(k\Delta f)$ is the frequency-domain representation of the sampled waveform.

Mathcad contains functions for performing the discrete Fourier transform and its inverse. The function FFT returns the Fourier transform of a 2^N element vector of real data representing measurements at regular intervals in the time domain. The function IFFT returns the inverse Fourier transform of a vector of real data representing values in the frequency domain.

3   RESULTS AND DISCUSSION

Consider a Gaussian signal represented by the following parameters and equation

$N := 2^9 \qquad n := 0\,..\,N-1$ Data span and range variable   (4)

$t := 200$ Total range of time   (5)

      (6)

$t_n := n \cdot \dfrac{t}{N}$ Time of each sample

$$Signal_n := 3 \cdot exp\left[-\frac{(t_n - 30)^2}{100} \right] + 2 \cdot exp\left[-\frac{(t_n - 50)^2}{50} \right] + 1.5 \cdot exp\left[-\frac{(t_n - 125)^2}{75} \right] \quad (7)$$
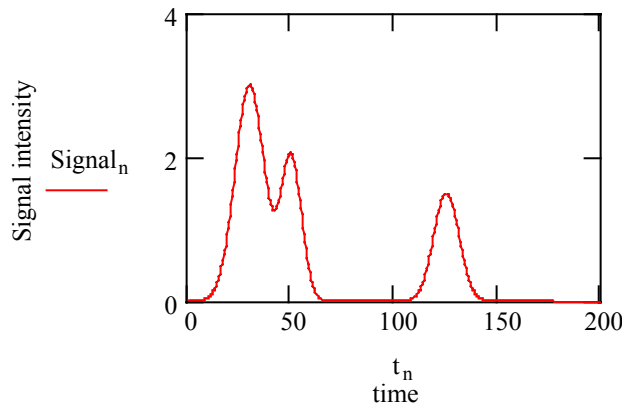
Input Gaussian Signal

Figure 1:Signal of three Gaussians

Figure 1 shows a Gaussian signal with three peaks centered at times of 30, 50 and 12 and intensities of 3, 2 and 1.5 respectively. This signal can be representative of chromatografic or spectroscopic data.

A similar treatment can be used to obtain the parameters and the equations for a noisy signal.

$p := 1$ Noise level   (8)

$Noise_n := \left(1 + \dfrac{1}{2} \cdot rnd(1) - 0.5 \right) \cdot p$ Random noise   (9)

$SNoise_n := Signal_n \cdot Noise_n$ Input noisy signal   (10)

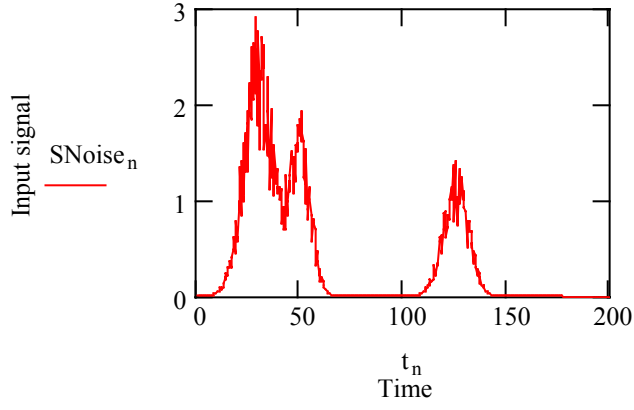Figure 2: Noisy signal

Figure 2 shows the input noisy signal. The random noise effect can be displayed by modifying the value of the variable p. The signal-to-noise ratio (SNR), can be estimat as the ratio between the maximum value of the signal and the standard deviatic noise. Thus, we obtain

$$signal := \max(SNoise) \qquad\qquad signal = 2.91 \qquad\qquad (11)$$

$$noise := stdev(Noise) \qquad\qquad noise = 0.144 \qquad\qquad (12)$$

$$\frac{signal}{noise} = 20.18 \qquad\qquad SNR \qquad\qquad (13)$$

To obtain the Fourier transform and the inverse Fourier transform we use the followir parameters and equations:

$$k := 0 .. \frac{N}{2} \qquad\qquad \text{Range variable of the transform} \qquad\qquad (14)$$

$$f_k := \frac{k}{t_{N-1}} \qquad\qquad \text{Frequency} \qquad\qquad (15)$$

$$Y := FFT(Signal) \qquad\qquad \text{Fourier transform of the signal} \qquad\qquad (16)$$

$$Z := IFFT(Y) \qquad\qquad \text{Inverse Fourier transform of signal} \qquad\qquad (17)$$
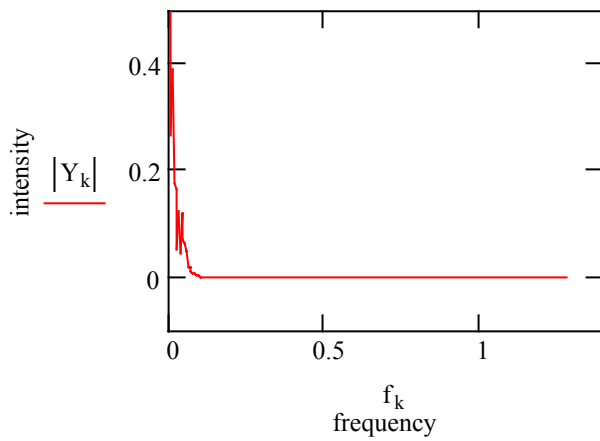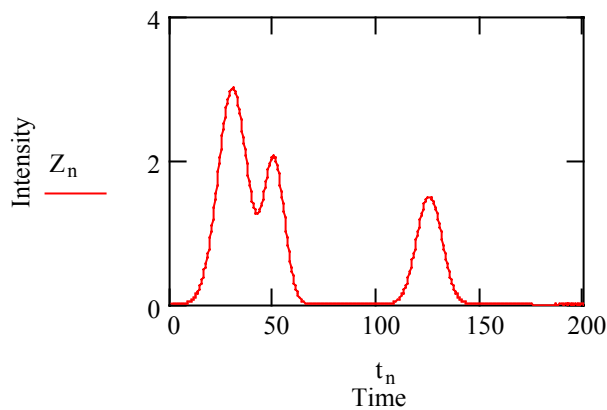
Figure 3: Fourier transform of signal

Figure 4: Inverse Fourier Transform

Figure 3 shows that the Fourier transform of signal displays frequencies of up to abo
= 0.1. We can see that by means of   the inverse Fourier transform, Figure 4, the init
signal is recovered.

Since the most of the spectrometric and chromatographic detectors measure the inten
and, integrating over time, it uses the power spectrum, square of the Fourier transfo
which is proportional to   signal intensity.   In order to achieve a better inspection it
more convenient to use the semilogarithm plot of the power spectrum. Thus, Figure
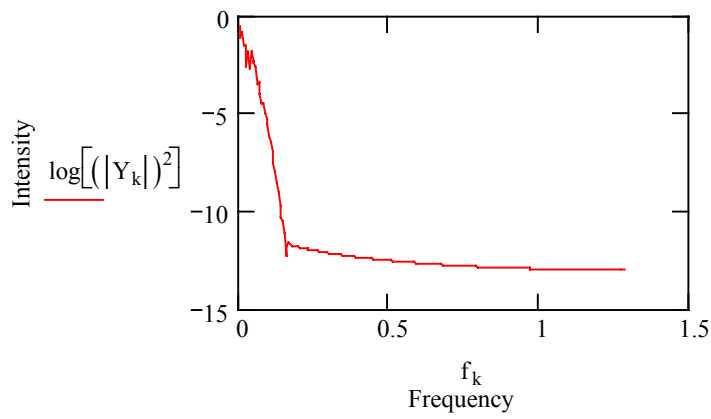shows a sharp variation of $\log(Y^2)$ up to frecuencies about 0.1.

Figure 5: Logarithm of power spectrum

A similar treatment can be used to obtain the Fourier transform and the inverse Fourier transform for the noisy signal. Results are shown in Figures 6 and 7 respectively.

$$F := FFT(SNoise) \qquad \text{Fourier transform of the noisy signal} \qquad (18)$$

$$W := IFFT(F) \qquad \text{Inverse transform Fourier of noisy signal} \qquad (19)$$
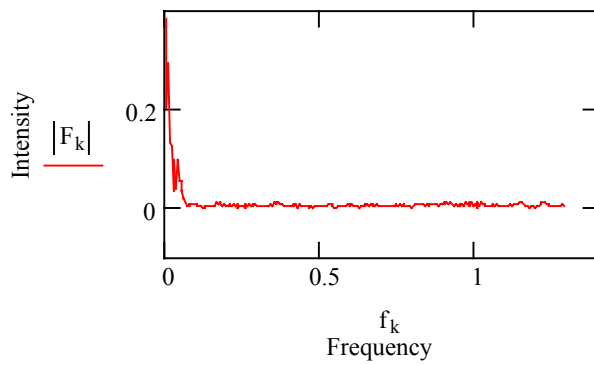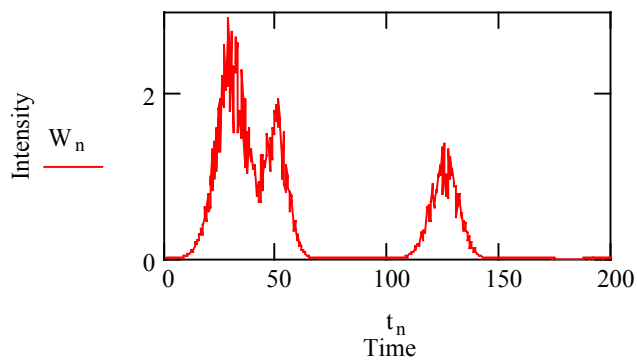

Figure 6: FT of the noisy signal

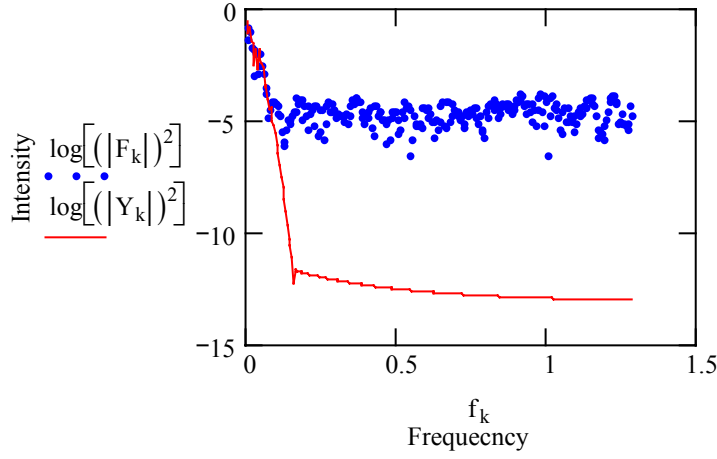Figure 7: Inverse FT of the noisy signal

Figure 8:Power spectrum of signals

Figure 8 shows the power spectrum of both for the initial signal and the same signal v
noise. Figure 9 illustrates that upon applying a cut-off filter of low-pass that allo
passing only the low frequencies contained in the transform Fourier signal, e.g
approximately $f < 0.1$, followed by the inverse Fourier transform, will remove the
noise from the signal. The filter function, the filtered Fourier transform and its inve
are defined as follows:

$$\text{Filter}(k) := \left[\left(f_k > 0 \right) \cdot f_k < 0.1 \right] \quad \text{Low-pass filter} \tag{20}$$

$$T_k := F_k \cdot \text{Filter}(k) \qquad \text{Filtered Fourier transform} \tag{21}$$

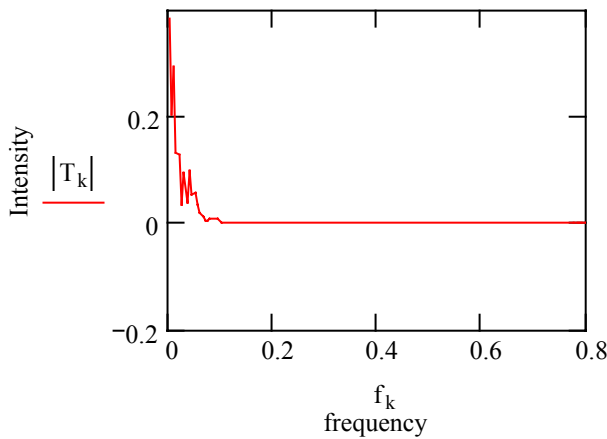$$U := \text{IFFT}(T) \qquad \text{Inverse Fourier transform of filtered signal} \tag{22}$$
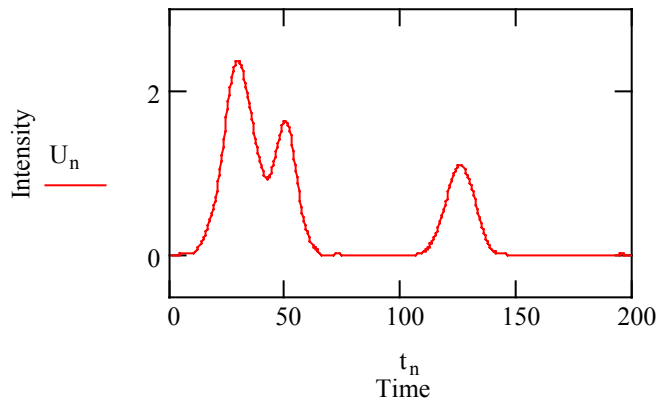

Figure 9:Filtered Fourier transform

Figure 10: Filtered signal

Figure 10 shows that the inverse Fourier transform of the filtered signal , Un, is very similar to the starting signal, Figure 1. However, there is also noise at the lower frecu components which is not eliminated and cause a litle distortion of the signal. If used a low-pass filter of cut-off frequecy lower and near to zero, then that would remove the frequencies of the signal and the distorsion increases, being the result negative. So the filter function should be choosen so that removes most of the noise not distorting the shapes of the analitical signal of interest.

The Fourier transform can be much more specific, picking out or reject a single frequency or specific set of frequencies. So, it is possible to tune a particular frequency, via lock-in amplifier (20), or selectively remove specific noise (60,120,180 Hz) leaving the frequencies of signal unaffected.

The performance of the Fourier transform and filtering in reducing baseline noise can be estimated from the standard deviation over a range where the baseline only is involved, Table 1, (e.g, times in the range 170-180 , Figure 10). So we take the following range and variable :

$x := 440 .. 460$ $V_x := U_n$ Range and new variable   (23)
                                            for the time

$signalfilt = max(U)$ $signalfilt = 2.368$ Maximum value of U   (24)

$noisefilt = stdev(V)$ $noisefilt = 2.548 \times 10^{-3}$ Standard deviation of noise   (25)

$\dfrac{signalfilt}{noisefilt} = 929.173$ SNR in filtered signal   (26)

Table 1.- Filtered signal and time in baseline

$U_x =$	$t_x =$
$-7.946 \cdot 10^{-4}$	171.875
$1.378 \cdot 10^{-3}$	172.266
$3.481 \cdot 10^{-3}$	172.656
$5.394 \cdot 10^{-3}$	173.047
$7.007 \cdot 10^{-3}$	173.438
$8.226 \cdot 10^{-3}$	173.828
$8.978 \cdot 10^{-3}$	174.219
$9.219 \cdot 10^{-3}$	174.609
$8.932 \cdot 10^{-3}$	175
$8.13 \cdot 10^{-3}$	175.391
$6.857 \cdot 10^{-3}$	175.781
$5.182 \cdot 10^{-3}$	176.172
$3.2 \cdot 10^{-3}$	176.563
$1.022 \cdot 10^{-3}$	176.953
$-1.229 \cdot 10^{-3}$	177.344
$-3.423 \cdot 10^{-3}$	177.734
$-5.434 \cdot 10^{-3}$	178.125
$-7.147 \cdot 10^{-3}$	178.516
$-8.46 \cdot 10^{-3}$	178.906
$-9.296 \cdot 10^{-3}$	179.297
$-9.602 \cdot 10^{-3}$	179.688

We can observe that the Fourier transform and filtering increases the SNR by a fact of about 45, from 20 (eq.13) to 930 (eq.26). Commercial instruments are equipped with Fourier transform and filtering functions that reject a specific set of frecuencies, selecttively remove noise, while leaving the other frequencies unaffec

4   CONCLUSIONS

This document presents two applications of the Fourier transform in chemical instrumentation by means of the solver MATHCAD. It describes the smoothing of a noisy signal and the simulation of the convolution of signals. The effect of the bandwidth of the filter function and the effect of the phase shift are investigated. Deconvolution of a laser-excited fluorescence signal is also described.

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