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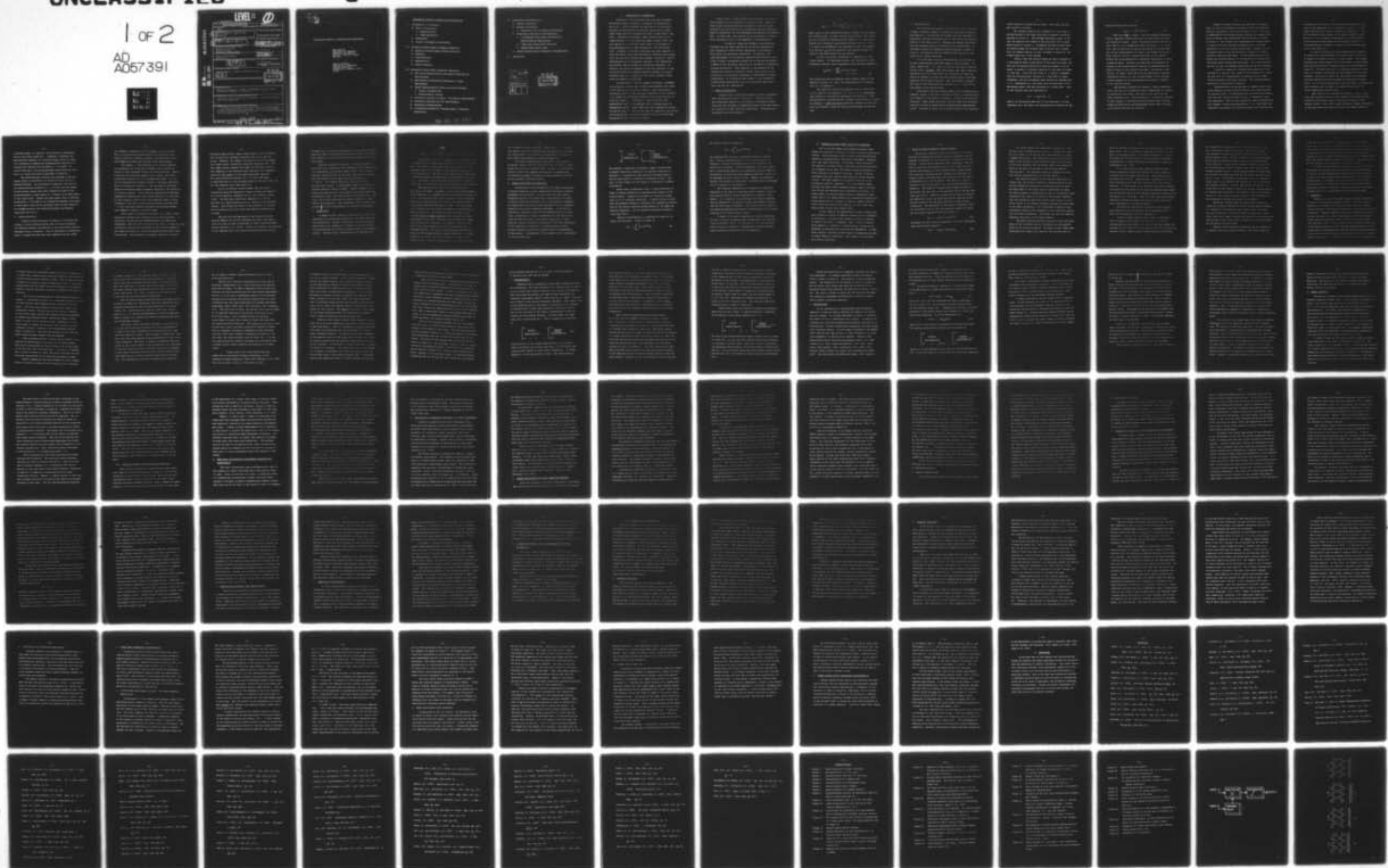
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**Correlation Methods in Chemical Data Measurement**

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## I. INTRODUCTION TO CORRELATION

Correlation techniques have long been used to measure and process signals in physics, chemistry and engineering. Lee et al., (1950) discussed the application of correlation analysis to the detection of periodic communication signals rather early and later reviewed the topic in some detail (Lee, 1960). Correlation techniques, again applied primarily to communications, have also been discussed by Lange (1967) and were applied at a relatively early stage to the analysis of electroencephelographic data (Rosenblith, 1959 and Barlow, 1959). Although correlation techniques have been employed in these and other fields with considerable advantage and success, their use has unfortunately been somewhat limited by a lack of understanding of the principles involved in the computation, utilization, and measurement of correlation functions. In addition, for practical purposes it has been difficult to use correlation techniques because effective methods and instrumentation were not available for the rapid, automatic evaluation of correlation functions.

In this chapter, we will attempt to present a treatment of correlation analysis that is both understandable and useful to the practicing scientist or chemist. Many treatments of correlation analysis lose the basic simplicity of the technique in an excess of mathematical equations and in applications to arbitrary waveforms. Throughout, a qualitative or semi-quantitative view will be adopted, with a minimum amount of mathematical detail. While some rigor will necessarily be sacrificed by this approach, we feel that the importance and utility of the ubiquitous correlation operation will be rendered most meaningful to the majority of readers.

Today, there is rapid growth in the utilization of correlation methods for the measurement of chemical data. Many computer signal processing methods are based on correlation and scientists are increasingly using techniques that are inherently based on correlation for the measurement and generation of chemical data. In large part, this upswing in the utilization of correlation techniques is due to developments in instrumentation.

A number of commercial hardware correlators are available and the ready availability of digital computers in most laboratories makes software approaches to correlation both simple and relatively inexpensive. In addition, the rapid development of increasingly sophisticated electronic circuitry in small inexpensive packages can be expected to produce a number of new and unique approaches to the design of laboratory-oriented correlators. These advances in instrumentation and software are certain to generate further rapid growth in the utilization of correlation techniques in experimental science; consequently, it is essential that workers in all branches of science become increasingly aware of correlation operations, their use and their application.

A. WHAT IS CORRELATION?

Simply stated, correlation analysis provides information about the coherence within a signal or between two signals. The correlation function of two signals is obtained by evaluating the time averaged or integrated product of the two signals as a function of their relative displacement. Mathematically, correlation can be expressed as:

$$c_{ab}(\tau) = \lim_{t \rightarrow \infty} \frac{1}{2t} \int_{-t}^{+t} a(t) b(t + \tau) dx \quad (1)$$

where  $c_{ab}(\tau)$  is the correlation function between the two signals  $a(t)$  and  $b(t)$ , and  $\tau$  is their relative displacement. The signals can be a function of essentially any variable, e.g. wavelength, retardation, frequency, accelerating voltage, time etc. Thus, if  $a$  and  $b$  are considered to be functions of time, the correlation function  $c_{ab}$  will be related to and plotted against the relative time delay between the two signals.

In most situations, correlation is implemented on digitized signals. For digitized signals, the calculation of the correlation function can be expressed by the following summation:

$$c_{ab}(n\Delta t) = \sum_t a(t) b(t \pm n\Delta t) \quad n = 0, 1, 2, \dots \quad (2)$$

The signals can only be displaced some integral number of the sampling interval,  $\Delta x$ . Thus, the displacement  $n\Delta x$  is equivalent to  $\tau$  in Equation 1.

Two different correlation operations can be identified. If  $a(t)$  and  $b(t)$  are identical (i.e. if  $a = b$ ), an autocorrelation function is obtained by application of Equation 1. Thus, autocorrelation indicates whether coherence exists within a signal. In contrast, a cross-correlation function, produced if  $a(t)$  and  $b(t)$  are different, shows the similarities between the two signals.

## 1. Autocorrelation

To illustrate the process of correlation, let us consider a simple instrument capable of producing a correlation function. From Equation 1, correlating two signals that are functions of time merely involves multiplying one of them ( $a(t)$ ) by a delayed version of the other ( $b(t-\tau)$ ), averaging the product and expressing the averaged value as a function of the chosen delay. An instrument capable of performing these procedures is shown in Figure 1; its operation can be understood most simply by autocorrelating a simple sine wave.

If a sine wave is to be autocorrelated, it will have to be sent simultaneously into both inputs of the correlator. To begin, assume that  $\tau = 0$ ; that is, that the sine wave is multiplied by itself in phase. When this occurs, the output from the multiplier will be a  $\text{sine}^2$  wave, as illustrated in Figure 2a; this will produce an output from the averager equal to the mean square of the original sine wave. Thus as plotted in Figure 3, the value of the autocorrelation function at  $\tau = 0$  will be the mean square of the original wave.

Now imagine that the variable delay in the autocorrelation computer (Figure 1) has been increased (manually or automatically) by an amount of time equal to one-quarter period of the original sine wave. Under these conditions, the sine wave will be multiplied by a version of itself which is effectively phase-shifted by  $90^\circ$ . As shown in Figure 2b, this multiplication will generate

a wave having an average value of zero. This value has also been plotted in Figure 3.

The variable delay is now increased to a time equal to one-half period of the input sine wave to produce a situation depicted in Figure 2c. The averaged multiplier output is now just the negative mean square of the sine wave, and is again shown plotted in Figure 3. Increasing the delay another quarter period causes the original wave to be  $270^\circ$  out of phase with its delayed replica, so that, as shown in Figure 2d, the product again has a zero average.

Finally, when the variable delay has been increased to a time exactly equal to one period of the input sine wave, the wave and its delayed replica will once more appear to be in phase, to produce a situation identical to that when the delay ( $\tau$ ) was zero. From this and Figure 3, it should be apparent that the autocorrelation function of a sine wave is itself sinusoidal, but has its maximum value shifted to coincide with  $\tau = 0$ . Mathematically, this means that the sine wave, of indeterminate phase, has been converted to a cosine wave. Thus, if the original wave were expressed as

$$a(t) = A \cos(2\pi ft + \theta) \quad (3)$$

where  $A$  is the maximum amplitude of the sine wave,  $f$  is its frequency and  $\theta$  its phase, the autocorrelation function of the

wave would follow the relation:

$$c_{aa}(\tau) = \frac{A^2}{2} \cos(2\pi f\tau) \quad (4)$$

From this result, Figure 3, and the preceding discussion, several important characteristics of the autocorrelation function should be evident. First, the autocorrelation function is even; that is, it is symmetrical about the point  $\tau = 0$ . In effect, this is identical to saying that either of the two channels of the autocorrelator of Figure 1 can contain the variable delay network, and that changing the delay to the opposite channel has the mathematically interpreted consequence of using a negative delay. Secondly, the amplitude and frequency (or period) of the autocorrelation function are unambiguously related to those of the original sine wave. The period of the two are, of course, identical while the amplitude of the autocorrelation function is just the mean square of the original. A third property of the autocorrelation function of Figure 3 is its infinite length.

Any periodic function will display a similar characteristic since any such waveform is just a combination of a number of constituent sine waves, each with its own amplitude and phase characteristics. This periodicity or coherence, observed in most signals, is the feature which enables them to be separated so effectively from superimposed noise, which is ordinarily neither periodic nor coherent.

Finally, although frequency and amplitude information about the original waveform is carried in the autocorrelation function, the phase of the original signal is lost. This fact is emphasized by the autocorrelation function of a square wave, shown in Figure 4 and constructed just as for the sine wave of Figure 2. The triangle wave autocorrelation function shown in Figure 4 contains the same frequencies (i.e. sine wave components) as did the original square wave. However, in the triangular wave all the sine waves are in phase, to produce a different summation wave shape. In the understanding of the square wave autocorrelation, it is instructive to imagine the two square waves sliding past each other. The autocorrelation function is just the changing mutual area of the two functions.

A familiar example of a related autocorrelation is the scanning of a spectral line (image of the entrance slit) across the exit slit of a monochromator to produce the slit width limited triangular resolution function. This autocorrelation operation is illustrated in Figure 5.

Autocorrelation on non-periodic or random (noise) waveforms produces markedly different results from those obtained for periodic waves. To understand this, we need only recognize that any wave, whether periodic or not, is composed of sine wave components. Each of these components, when autocorrelated, will produce a cosine wave beginning at  $\tau = 0$ . When many such components are present in a parent waveform, the resulting auto-

correlation will just be the sum of the autocorrelation functions of the components, as illustrated in Figure 6. A true random waveform (white noise) contains all frequencies. The cosine autocorrelation images of all these frequencies reinforce at  $\tau = 0$  to produce a value equal to the mean square of the original random signal and at any point beyond  $\tau = 0$  they destructively interfere to produce a time averaged value of zero (see Figure 7).

In order to obtain this ideal autocorrelation function of random noise, the bandwidth of the noise must be infinite. Of course, no process in nature is truly random. Real random waveforms are "band-limited" and do not produce a single spike upon autocorrelation but instead a shape such as portrayed in Figure 8a. The functional form is a decaying exponential whose width is inversely proportional to the bandwidth of the noise waveform. Note that in Figure 8a, both sides of the autocorrelation function have been included to demonstrate its symmetry. In all other presentations, only one side of the autocorrelation function will be given; the reader should recall the actual symmetrical characteristic.

When Figure 8a is compared with Figures 3 and 4, it is clear why autocorrelation is such a powerful technique for the extraction of periodic signals from noise (Hieftje, 1972a; Hieftje, 1972b). Most noise, being inherently random, contributes to the autocorrelation function only at very small values of  $\tau$ .

A periodic signal, in contrast, will continue to contribute even at very large values of  $\tau$ . Therefore, to measure the amplitude and frequency of a periodic signal buried in noise, it is necessary to examine the autocorrelation function at a location well removed from the central ( $\tau = 0$ ) peak. To clarify this point, the autocorrelogram (autocorrelation function) of a noisy sine wave is portrayed in Figure 8b.

The autocorrelation function also provides a very convenient means of determining the signal-to-noise ratio of a measured waveform. As illustrated in Figure 8b, the value of the autocorrelation function at  $\tau = 0$  is just the mean square of the original signal plus noise, whereas the peak of the autocorrelogram at large values of  $\tau$  is equal to the mean square of the signal alone. Because the mean square value is directly proportional to the power of an alternating waveform, the signal-to-noise power ratio can be calculated from the mean square of the signal divided by the difference between the measured quantities ( $S+N$  and  $S$ ).

## 2. Cross-correlation

Cross-correlation analysis is similar in structure and concept to autocorrelation except that in cross-correlation the coherence between two waveforms is examined rather than the coherence within a waveform. From our discussion of autocorrelation, it should be clear that this coherence can only exist

for frequency components which are common to the two waves. This is true because multiplication of two sinusoidal waveforms of different frequency produces a waveform which is itself symmetrical about zero and has a zero time average.

For example, if two waveforms to be cross-correlated are sinusoidal and of the same frequency, the situation is similar to that discussed earlier for autocorrelation. However, unless the two sine waves happen to be in phase, the cross-correlation function will not be symmetrical about  $\tau = 0$ , but will be displaced by an amount related to the phase difference. This is illustrated in Figure 9. For two waves of different shape but containing common frequency components, the situation is even more complex. A sine wave and square wave of the same fundamental frequency will thus cross-correlate to a sine wave of that frequency, which is the only component common to both. Furthermore, the shift of the cross-correlation function from  $\tau = 0$  will once more indicate the phase relationship between that frequency component in the two waves.

With random or stochastic waveforms (i.e. noise), cross-correlation behaves quite differently from autocorrelation. In particular, because any two random waveforms are inherently independent, they will not correlate at any point, so that the cross-correlation function will everywhere be zero as the product of two random functions will itself be random and thus have a zero time average. This property is extremely important in signal

processing applications, where a noisy signal is to be detected with the aid of an available reference wave at the same frequency. Consider, for example, the detection of a noisy square wave signal using a noise-free sinusoidal reference wave. The only common feature between the signal and reference waves is that component at the reference wave frequency; this component alone will thus appear in the cross-correlation function. The cross-correlation function (at  $\tau = 0$ ) will then have an amplitude equal to the averaged product of the noise free signal and reference waves (See Figure 10).

It will be obvious to most readers that the cross-correlation operation depicted in Figure 10 forms the basis of the lock-in amplifier (Malmstadt et al, 1974; Hieftje, 1972a, 1972b). The only major additional component in a lock-in amplifier is a phase shifting circuit, usually on the reference channel. This allows the output of the correlator to be maximized by ensuring that the signal and reference waveforms are in phase.

The fact that the amplitude of the cross-correlation function depends both on the reference and signal wave amplitudes can often be used to advantage in signal processing applications (Hieftje et al, 1973b). Merely by increasing the magnitude of the reference wave, the cross-correlogram amplitude can be

enlarged; this is clearly advantageous over the autocorrelation operation, where no reference wave exists and the final correlation function is only as large as the mean square of the original signal.

From the foregoing discussion, it should be apparent that correlation operations, while outwardly and mathematically a bit forbidding, are actually quite simple. Also, several important characteristics of both auto- and cross-correlation have been shown to be of importance to the detection of signals. The examples shown have primarily utilized periodic type signals. A considerable number of signals of chemical interest consist of peaks. Several examples illustrating the application of correlation to the measurement and processing of peak like signals will be discussed later. But first, two related areas must be covered, convolution and Fourier transformation. Some knowledge of these areas is important for a full understanding of correlation operations.

#### B. CONVOLUTION

A number of the aspects of correlation that have been introduced are perhaps more familiar to the reader under the term convolution. However, convolution, an operation which occurs during the generation or measurement of all signals, can be considered to be merely a special kind of correlation process. Mathematically, convolution can be expressed as

$$\text{con}_{ab}(t) = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-t}^{+t} a(t) b(-t + \tau) dt \quad (5)$$

If equations 5 and 1 are compared, their only difference is observed to be a minus sign in front of the  $t$  of the  $b$  function. The effect of this minus sign is to reverse the  $b(t)$  function (from left to right) on the time axis before it is multiplied by  $a(t)$ . The rest of the shifting, multiplying and averaging procedures are identical to those employed in correlation. Therefore, correlation and convolution are identical, except that in convolution, one of the signals is first reversed.

The reason for this can be best understood with the aid of an example. Consider a rapid signal change (step) being displayed on a recorder having a relatively long time constant. The recorded signal will, of course, not be identical with the original step but will reflect the response time of the recorder (McWilliam and Bolton, 1969). For simplicity, let us assume that the recorder's response is exponential, as shown in Figure 11. By convention both the input to the recorder and its response function are expressed with time increasing to the right. Therefore, if we imagine the input signal entering the recorder, it is apparent that the left side of the signal would enter first and encounter the response function. For this to occur properly, either the signal or the response function must be reversed. It is conventional to reverse the response function. Thus the recorded signal is then the convolution of the input step and

the recorder's response function. Notice that, if a correlation between those two functions were produced by the recorder, the leading edge of the recorder's output would be curved upward rather than downward, as shown in Figure 11.

From these considerations, convolution can be seen to be merely a special kind of correlation and can often be implemented and utilized in similar ways. In fact, in those many instances in which the response function  $b(t)$  is symmetrical, its inversion produces no change, so that correlation and convolution provide identical results.

### C. FOURIER TRANSFORMS IN CORRELATION

As mentioned in the introduction, the ready availability of digital computers in most laboratories facilitates software approaches to correlation. In particular, the Fast Fourier Transform algorithm has essentially revolutionized the extent to which correlation techniques can be implemented on computers and indeed many correlation based techniques are more commonly referred to as Fourier transform techniques. In addition to providing a convenient route for the implementation of correlation, a knowledge of Fourier transforms also aids the utilization and understanding of correlation operations. A very important theorem concerning correlation states that correlation of two waveforms is equivalent to multiplication of their Fourier transforms followed by inverse Fourier transformation of the product. Schematically, this sequence can be represented in the following way:

$$\begin{array}{ccc}
 a(t) & * & b(t) = c(\tau)_{ab} & (6) \\
 \downarrow & \text{FOURIER} & \downarrow & \uparrow \\
 & \text{TRANSFORMATION} & & \text{INVERSE} \\
 & & & \text{FOURIER} \\
 & & & \text{TRANSFORMATION} \\
 A(f) & \times & B(f) = C(f)_{AB} & (7)
 \end{array}$$

The asterisk in Equation 6 is merely a common shorthand way to denote correlation; Equation 6 is therefore identical to Equation 1. It should be noted that this shorthand form is used by many authors to designate convolution as well. However, in this chapter we will employ it exclusively to denote correlation.

Notice that in Equations 6 and 7, cross-correlation is shown to involve nothing but a multiplication process in the Fourier domain. Simple as this aspect of correlation might seem, it is of paramount importance. A large fraction of software and hardware methods for obtaining the correlation function rely on the Fourier transform method because of its speed and relative simplicity. Let us consider the Fourier process in a bit more detail.

Fourier transformation is a mathematical means of relating two functions. It may be stated as:

$$a(t) = \int_{-\infty}^{+\infty} A(f) e^{2\pi i t f} df \quad (8)$$

The inverse Fourier transform is:

$$A(f) = \int_{-\infty}^{+\infty} a(t)e^{-2\pi itf} dt \quad (9)$$

The functions  $a(t)$  and  $A(f)$  constitute a Fourier transform pair. Fourier transformation, as it is usually applied in chemistry, involves the determination of the frequency composition of a waveform. Often the waveform ( $a(t)$ ) will represent a time-varying property of a substance or device under investigation, in which case the frequency composition ( $A(f)$ ) will be expressed in units of  $\text{sec}^{-1}$  or Hz. However, as discussed earlier with regard to correlation, a waveform being transformed can be a function of any variable.

The frequency composition of a waveform is ordinarily expressed in the form of a spectrum, which is merely a plot of the relative density of each component as a function of frequency. It is important to distinguish this kind of spectrum from one produced by an optical or other spectrometric instrument so often used in chemistry. For clarity, we will refer to the spectrum produced upon Fourier transformation as the Fourier spectrum or the Fourier domain signal.

A number of the basic properties of Fourier transforms and their relation to spectroscopic measurements have been discussed by Horlick (1971). In the next section, the important role of Fourier transforms in implementing correlation based signal processing operations will be emphasized.

## II. CORRELATION BASED SIGNAL PROCESSING OPERATIONS

One of the most common areas where correlation techniques are utilized in chemistry is in the software processing of signals. Here processing refers to such varied operations as smoothing, differentiation, resolution enhancement, deconvolution, and signal detection. In the main, these operations are applied to a signal after it has been digitized and stored in a computer and as such, this type of signal processing is often referred to as digital filtering. Digital filtering techniques have been used for many years to process chemical signals. The basic equation for digital filtering is the correlation equation, Equation 1. In a now classic paper, Savitzky and Golay (1964) presented several types of correlation filters for smoothing and differentiation of data. In recent years, the Fourier domain route of correlation (Equations 6 and 7) has become popular for implementing digital filtering operations on a variety of chemical signals (Horlick 1972a; Betty and Horlick 1976; Hayes et al 1973; Bush 1974, Caprini 1970; Inouye 1969; Kirmse 1971).

In this chapter, the application of Fourier domain digital filters to signals of chemical interest will be presented. In particular, a digital filter based on a simple trapezoid is shown to be uniquely versatile. When applied to signals using Equation 7; smoothing, differentiation, resolution enhancement or deconvolution can easily be implemented. In addition, digital filtering is often used as a preprocessing step in signal detection operations. This aspect of correlation will also be discussed.

A. BASICS OF FOURIER DOMAIN DIGITAL FILTERING

The Fourier transform route of correlation is an effective way of implementing digital filtering operations and all examples illustrated in this section were carried out in this fashion. A Fast Fourier Transform (FFT) (Singleton, 1969) was used to carry out the transformation of the signals and the inverse transformation of the filtered Fourier domain signal. This algorithm, of which several versions are available, is simply a rapid, efficient means for calculation of the Fourier transformation of a set of points. The input to a typical program is a set of real data (i.e. a digitized waveform in a computer). The output of a typical FFT program consists of two series, the real part of the transform  $[X(J)]$  and the imaginary part  $[Y(J)]$ . These two outputs can be used to generate two additional series, the amplitude Fourier spectrum of the original waveform and the phase spectrum of these Fourier frequencies. The amplitudes of the Fourier frequencies  $[A(J)]$  are calculated from the real and imaginary outputs by taking the root sum of squares of the two series i.e.:

$$A(J) = [X(J)^2 + Y(J)^2]^{1/2} \quad (10)$$

The phases of these Fourier frequencies  $[P(J)]$  are calculated using the following equation:

$$P(J) = \arctan [Y(J)/X(J)] \quad (11)$$

All these outputs are illustrated in Figure 12. The original input waveform (Figure 12a) is a typical peak signal. The real output of the FFT for this input waveform is simply a damped cosine wave. The frequency of this cosine wave depends on the position of the peak with respect to the origin of the input waveform, the functional form of the damping depends on the shape of the peak in the original waveform (Horlick, 1971). The imaginary output is a damped sine wave with similar characteristics to the real output.

The amplitude spectrum of the Fourier frequencies indicates that the original waveform is composed mainly of low Fourier frequencies along with a relatively large dc level. The amplitudes of the higher Fourier frequencies are small but their presence is significant in that it is primarily these frequencies that make up the noise in the original waveform. Thus the information about the original peak occurs in a different region of the Fourier frequency spectrum than does some of the noise information. This difference in spectral characteristics enables noise information to be attenuated without loss of signal information. This forms the basis for spectral smoothing operations in the Fourier domain.

The phase spectrum provides information about the phase angle of the individual Fourier frequencies at one specific point on the original waveform. The phase is most useful when calculated with respect to a point on the original wave at

which the Fourier frequencies all have approximately the same phase angle. For the waveform illustrated in Figure 12a, this point is the peak maximum. This phase coherence is, in fact, the reason for the existence of the peak when the waveform is interpreted as a Fourier Summation of individual frequencies (Malmstadt et al., 1974).

It is clear from the phase spectrum that the lower Fourier frequencies which characterize the signal shape are in phase while the higher ones are not. The fluctuation of the phase angle of the higher Fourier frequencies is a definite indication that they arise from noise in the original waveform. In other words, it is unlikely that Fourier frequencies resulting from noise in the original waveform would happen to have the same phase as the Fourier frequencies resulting from the signal (i.e. the peak). Thus, the phase spectrum provides additional information about the distribution of signal and noise frequencies in the Fourier domain.

All filtering operations illustrated in this section were carried out on the real part of the transform ( $X(J)$ ). Thus,  $X(J)$  corresponds to  $A(f)$  in Equation 7.

A Fourier domain digital filter ( $B(f)$  in Equation 7) that is versatile and simple is a trapezoid. It can be characterized by four indices ( $N_1, N_2, N_3, N_4$ ) that define the vertices of the trapezoid (Betty and Horlick, 1976; Coddington and Horlick, 1973a). Typical Fourier domain digital filters that

can be obtained by manipulation of the integer values of the four indices are shown in Figure 13. The vertical dotted line indicates the position of the first point (0Hz) of the Fourier domain signal. Digital filtering is implemented simply by multiplying the Fourier domain signal by the appropriate filter function. Signal points between  $N_1$  and  $N_2$ , and  $N_3$  and  $N_4$  are multiplied by the "y" value of the slope, which varies linearly between 0 and 1. Signal points between  $N_2$  and  $N_3$  are not altered, and those less than  $N_1$  and greater than  $N_4$  are set equal to zero. To implement a particular filter the operator simply types in the desired four indices,  $N_1$ ,  $N_2$ ,  $N_3$  and  $N_4$  at the computer terminal. If  $N_1$  is zero and  $N_2$  is equal to 1, a filter such as that shown in Figure 13a results; whereas setting  $N_1$  negative and  $N_2$  positive ( $>1$ ) results in the filter shown in Figure 13e. The remaining figures indicate other possible filters obtained by varying the values of the indices.

Additional Fourier domain digital filters can be obtained by successive application of the filters shown in Figure 13. Successive application of the filters shown in Figures 13b and 13c results in the filter shown in Figure 14a. Similarly, the filter shown in Figure 14b results from two successive applications of the filter shown in Figure 13e, once with  $N_2=N_3$  and the second time with  $N_3=N_4$ .

Several signal processing operations can be carried out on spectra using these digital filters. The filter shown in

Figure 13a is used for general purpose smoothing and high frequency noise elimination. Diagnosis of noise information is often useful and can be carried out using the filter shown in Figure 13f. Differentiation can be accomplished using the filters shown in Figures 13b, 13c, 13d and 14a and deconvolution can be approximated using the filters shown in Figures 13e and 14b. These operations are all discussed and illustrated in the next section.

It should be mentioned here that Fourier domain correlation operations are analogous to the apodization data handling step of Fourier transform spectroscopy (Coddling and Horlick, (1973a). In Fourier transform spectroscopy the measured signal (called an interferogram) is analogous to the real output of the Fourier transformation of a conventional spectral signal (Figure 12b). Apodization (digital filtering) is applied directly to the interferogram before it is transformed to the desired spectrum.

#### B. SMOOTHING

Smoothing is one of the most frequent software processing operations implemented on chemical signals. The basic aim of smoothing is to improve the signal-to-noise ratio of a signal thereby enabling a more precise measurement of the desired chemical information. Numerous approaches exist for implementing smoothing but most are based on a direct application of the correlation integral (Savitzky and Golay, 1964) or its Fourier domain equivalent (Horlick, 1972a). It was noted in the last section that some of the noise information in the original waveform appears at different Fourier frequencies than does the signal or peak information, with the noise Fourier frequencies dominating the upper or higher Fourier frequencies. On the basis of this different distribution

of signal and noise information among the Fourier frequencies, it is clear that a simple boxcar truncation function can be used as a Fourier domain noise reduction filter. This is shown in Figure 15 which is a pictorial analog of Equations 6 and 7. Note that multiplication by the abrupt truncation function in the Fourier domain is exactly equivalent to direct correlation with the sinc function.

The filtering and diagnosis of high frequency noise on a signal is illustrated in Figure 16. A spectrum is shown in Figure 16a that contains high frequency noise, particularly on the peaks. This noise was caused by a faulty power supply in a measurement system. The real part of the Fourier transform of this noisy signal (Figure 16b) clearly reveals the presence of excess high frequency noise. The Fourier domain signal shown in Figure 16b is 256 points long. Application of the filter shown in Figure 13a with  $N1=0$ ,  $N2=1$ ,  $N3=99$  and  $N4=100$  (trapezoid indices) results in the retransformed spectrum shown in Figure 16c. Note that the majority of the high frequency noise has been removed from the spectrum.

From a diagnostic point of view it may be useful to determine the distribution of the noise in the signal domain. This can be accomplished by using a filter with indices equal to 99, 100, 255, 256 (see Figure 13f). The result of applying such a filter is shown in Figure 16d, which indicates that the noise was concentrated in the region of the spectral peaks.

Further examples of the effectiveness of Fourier domain digital filtering in removing high frequency noise components

are shown in Figure 17. The spectrum shown in Figure 17a contains an intense fixed frequency noise component. Its transform (Figure 17b) indicates that the noise is concentrated at about the 125th word. A filter with indices equal to 0, 1, 99, 100 easily removes this narrow-band high-frequency noise component (see Figure 17c). Also, if desired, a software notch filter could be set up for noise of this type.

With low level signals quantizing noise can become serious as shown in Figure 17d. Quantizing noise has considerable high frequency components as shown by the transform of this signal (Figure 17e). Application of a digital filter with indices equal to 0, 1, 2, 100 and retransformation yields the spectrum shown in Figure 17f, in which the effects of quantization noise are considerably reduced.

The abrupt filter utilized in Figures 15, 16 and 17 (a, b, c) may not be the most desirable for certain measurements. If some of the signal information is truncated abruptly, spurious side lobes will result. This is shown in Figure 18a. However, with very noisy spectra it may be desirable to have a low cutoff frequency. This will, in general, necessitate the truncation of some of the higher Fourier frequencies that contribute to the peak information and as such the peak will be broadened. In this case a smoothing function can be used to minimize the side lobes such as a linear truncation (see Figures 18b and 13a). The broadening of the peak is often quite acceptable

and is simply a standard trade-off between signal-to-noise ratio and resolution.

Several other smoothing functions can be used such as Gaussians, exponentials, etc., and at this point the question might well be asked, "Is there a smoothing function that will optimize the signal-to-noise ratio for peak height measurement?" Suffice it to say that a considerable amount of work has been reported in this general area and the characteristics of such a matched filter have been established for optimal peak height measurement (Turin, 1960; Root, 1970; Helstrom, 1968; Champeney, 1974). When the noise is white, the matched filter has the shape of the amplitude spectrum of the Fourier frequencies of the noise free signal. Such a matched filter for the peak signal shown in Figure 15a is shown in Figure 18c along with the resulting smoothed spectrum. This operation amounts to cross-correlating a noisy line with a noise-free version of itself. This is a powerful correlation technique for peak detection (Horlick, 1973) and is further illustrated in Figure 19. In this case, the signal-to-noise ratio is quite low ( $\sim 2.21$ ) but the cross-correlation function resulting from correlation with a matched filter clearly indicates the presence of the peak signal.

A major point that often bothers many who would like to use digital filtering techniques, is the question of signal distortion (Yule, 1972; Tominaga et al, 1972). What must be kept in mind, is that often the goal

of digital filtering is optimization of the measurement of a *particular* signal parameter. If the desired parameter is peak height, as indicated above, then a so-called matched filter can be used which, although it distorts peak shape by broadening, optimizes the signal-to-noise ratio (peak height/rms base line noise) for peak height measurement. If it is also desirable to preserve as well as possible the observed line shape, attempt to recover the "real" line shape (deconvolution) or optimally measure other peak parameters such as position, area or width then specific digital filters must be designed for this purpose. The optimal processing of the signal for all these parameters cannot be simultaneously achieved using a single correlation (filtering) operation.

Clearly a wide range of Fourier domain smoothing functions can be utilized depending on the signal processing goals of the experimenter. Thus it is difficult to present hard and fast rules for determining the form and extent of a Fourier domain smoothing function. The choice can be highly dependent on the specific nature of the signal and the noise, the amount of filtering desired and the degree of signal distortion that can be tolerated. In particular, it may be difficult to choose the extent of truncation. One simple approach to this problem is to measure, if possible, the signal of interest under conditions that yield a high signal-to-noise ratio. Transformation of the signal will result in a well defined Fourier spec-

trum and the point beyond which little or no signal information is present can easily be established.

Bush (1974) has presented a quantitative approach to the choice of the truncation point. As noted early the upper or higher Fourier frequency components are essentially due to noise in the original signal. In fact the components are noise like themselves in appearance and have a characteristic standard deviation. Bush's method of setting a truncation point is to calculate the standard deviation for these upper Fourier frequency components and then successively repeat the calculation each time including an additional point from the low frequency end. When a significant change in the standard deviation is noted, it can be assumed that signal information has been included and hence, the truncation point can be set.

Some of the truncation problems and side lobe generation that occur in Fourier domain smoothing operations do so because of the nature of the signal. This has been discussed in the literature (Hayes et al, 1973) with respect to filtering electroanalytical data and a clever but simple solution presented. The nature of the problem and the solution are presented in Figure 20. The "original" signal is shown in Figure 20a and is an exponential decay. If filtered in the Fourier domain directly (Figures 20b, c and d) signal distortion results. However, if the original signal is translated and/or rotated so that the initial and final values are zero before

being filtered (Figures 20e, f, g, h and i) the introduction of spurious side lobes can be avoided.

C. DIFFERENTIATION

Differentiation of spectra is often used to modify the spectral information. The first derivative of a spectral peak is used as an aid in exact peak location (Morrey, 1968; Walters and Malmstadt, 1966) and higher derivatives are used for peak sharpening i.e. resolution enhancement (Martin, 1959; Allen et al, 1964). The derivative theorem of the Fourier transforms (Bracewell, 1965) states that if the imaginary part of the Fourier transformation of a function is multiplied by a linear ramp starting at the origin the result is the real part of the Fourier transformation of the derivative of the original function. In other words, the imaginary part is multiplied by  $f$ . This is summarized by Equation 12.

$$\begin{array}{ccc} a(t) & & a'(t) \\ \downarrow & \text{FOURIER} & \uparrow \\ & \text{TRANSFORMATION} & \text{INVERSE} \\ & & \text{FOURIER} \\ & & \text{TRANSFORMATION} \\ A(f) & \times & f \\ & & = f'A(f) \end{array} \quad (12)$$

Multiplication by this linear ramp function in the Fourier domain eliminates the dc level and attenuates low Fourier frequencies with respect to high Fourier frequencies. It simply amounts to a high pass digital filter. The accentuation of

high Fourier frequencies is a well known characteristic of a differentiation step (Stauffer and Sakai, 1968). The accentuation should not be carried out beyond the point at which the signal Fourier frequencies disappear or else the resulting derivative will be very noisy. Thus, some low pass digital filtering of the Fourier frequencies should always be used in conjunction with differentiation. This is directly analogous to techniques used in the design of analog differentiating circuits using active filters. In addition, as with analog differentiation, the quality of the differential is dependent upon the high and low frequency cutoffs relative to the signal frequencies.

Such a Fourier domain digital filter can easily be set up using the trapezoid function as shown in Figure 13b. The effect of such a digital differentiating filter on a spectrum is illustrated in Figure 21. The original spectrum is a doublet and is shown in Figure 21a. The Fourier domain differentiating filter is shown in Figure 21b and it was applied in a manner analogous to that depicted in Figure 15. Note that both high and low pass filtering are readily carried out in one simple multiplication step. The resulting first derivative spectrum is shown in Figure 21c. The first derivative is perhaps of minimal used in processing peak type signals although it has found application in detecting peak locations using its zero crossing. However, if the filter shown in Figures 13b and

and 21b is applied instead to the *real* part of the Fourier transform of the signal and the resulting function (which now is the imaginary part of the Fourier transform of the first derivative of the signal) is retransformed, a resolution enhanced signal is obtained. This is illustrated in Figure 22, in which the real part of the Fourier transform (Figure 22b) of the spectral signal shown in Figure 22a is multiplied by the digital filter shown in Figure 13b with indices equal to 1, 125, 125, 250. Note that the signals and transform in Figure 22 are all 512 points long. The resulting resolution enhanced signal is shown in Figure 22c.

Higher derivatives can easily be obtained by successive application of this filter. A second derivative is obtained by multiplying in the Fourier domain by  $f^2$ , i.e.:

$$\begin{array}{ccc} a(t) & & a''(t) \\ \downarrow & \text{FOURIER} & \uparrow \\ & \text{TRANSFORMATION} & \text{INVERSE} \\ & & \text{FOURIER} \\ & & \text{TRANSFORMATION} \quad (13) \\ A(f) & \times f^2 = & f^2 \cdot A(f) \end{array}$$

The form of the second derivative Fourier domain filter is shown in Figure 14a. As with the first derivative, low pass filtering is necessary to control noise. This filter may be achieved by two successive applications of the filters shown in Figures 13b and 13c. It has also been found that very similar results can be obtained with the filter shown in Figure 13d (Betty and Horlick, 1976).

Second differentiation is a powerful technique for resolution enhancement. An example presented by Kelly and Horlick (1974) is shown in Figure 23. The signal is a noisy Lorentzian doublet. The composition of the doublet is shown in Figure 23a and the actual noisy signal upon which the second derivative resolution enhancement operation was performed is shown in Figure 23b. The result is shown in Figure 23c and indicates the excellent resolution enhancement possible with a relatively simple Fourier domain correlation operation.

#### D. DECONVOLUTION

In the introduction it was mentioned that convolution (Equation 5) could be used to describe the effect of an instrument on a signal. It is often desirable to remove, if possible, the effects of such a convolution from a signal. Procedures for reversing the convolution operation are generally referred to as deconvolution. Various deconvolution procedures have been widely used to process signals. An early paper by Bracewell and Roberts (1954) dealing with applications to radio astronomy is an excellent introduction to deconvolution methods. Numerous other authors have studied deconvolution methods (Jones et al, 1967; Jansson et al, 1968; Dromey and Morrison, 1970; Izatt, 1969; Moore, 1968; Saksena, 1968; Vladimeroff, 1971; Szoke, 1972; Horlick, 1972b; Brouwer and Jansen, 1973; Stockham and Cannon, 1975). The last authors (Stockham and Cannon, 1975) present a

so-called blind deconvolution, useful in situations where it is either difficult or impossible to know or measure the instrument response function. They have applied their technique to the deconvolution of early Caruso recordings and blurred photographs.

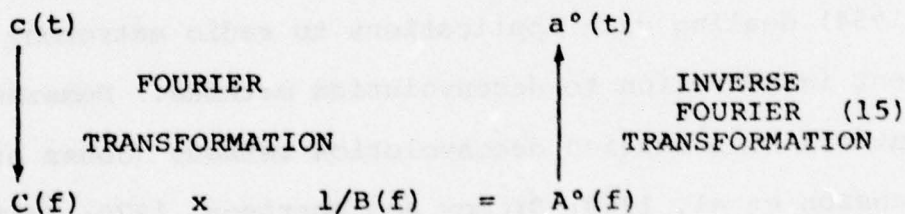
As with correlation, convolution, in the Fourier domain can be described as a simple multiplication analogous to Equation 7:

$$A(f) \times B(f) = C(f)_{AB} \quad (7)$$

where  $A(f)$ ,  $B(f)$  and  $C(f)$  represent the Fourier transforms of the real signal  $a(t)$ , the instrument response function  $b(t)$  and the observed signal  $c(t)$ . Deconvolution is simply a division operation in the Fourier domain which attempts to reverse the convolution operation. It can be represented as:

$$A^\circ(f) = C(f)_{AB}/B(f) \quad (14)$$

where  $A^\circ(f)$  is the Fourier transform of the deconvolved signal. The complete deconvolution process can be outlined as:



where  $c(t)$  is the observed signal and  $a^\circ(t)$  the deconvolved signal. It is very important to note that the convolution operation

is not, in general reversible i.e.  $a^\circ(t) \neq a(t)$ . This point has been discussed in the literature (Bracewell and Roberts, 1954; Rautian, 1958; Horlick, 1972b).

It is clear from Equation 15 that deconvolution is simply a standard cross-correlation operation. It can be thought of as a Fourier domain digital filtering operation with a rather specialized filter function which is the reciprocal of the Fourier Transform of the instrument response function.

A common application area for deconvolution is spectroscopy. In spectroscopy, the signal is the spectrum which is to be measured and the instrument response function is the resolution function which is frequently determined by the slit width (Figure 5). In many cases the response function can be determined by measuring the profile of a narrow line (Horlick, 1972b). Such a measured line profile and its Fourier transform are shown in Figure 24. Thus the deconvolution Fourier domain

digital filter is simply the reciprocal of the function shown in Figure 24b.

However, the reciprocal of this function becomes very large at higher Fourier frequencies and deconvolution, as with the case of differentiation, can accentuate the high Fourier frequencies to such an extent that noise will obscure the deconvolved signal. The solution to this problem is to combine some low pass filtering with deconvolution. Thus, a Fourier domain deconvolution filter has a form such as that shown in Figure 25. Note that it is not unlike the second derivative digital filter. An example of the resolution enhancement that can be achieved with such a controlled deconvolution is shown in Figure 26 (Kelly and Horlick, 1974). The original spectrum was that shown in Figure 23b.

Finally it is possible, using filters such as those shown in Figures 13e and 14b to approximate deconvolution resolution enhancement techniques. The main value of these filters for resolution enhancement (as compared to differentiation methods) is that with less attenuation of the low Fourier frequencies, there is less generation of negative sidelobes.

These examples illustrate the power and ease of Fourier

domain digital filtering. With the simple functions shown in this section a large number of sophisticated signal processing operations can readily be carried out. In addition, an important aspect of Fourier domain correlation operations is that it is, in most cases, considerably easier to design a digital filter in the Fourier domain than it is in the signal domain. For example, the form of a Fourier domain notch filter is intuitively clear from Figure 17b while the form of a notch filter that could be directly applied to the signal (Figure 17a) via the convolution equation (Equation 1) is not readily apparent. Thus, the Fourier domain approach to digital filtering considerably enhances an experimenters capability in developing unique digital filters for specific signal processing needs.

In conclusion, the comment made about signal distortion towards the end of the smoothing section can be reiterated here. In contrast to smoothing operations, the goal of resolution enhancement is optimization of the measurement of peak position. This is often achieved by derivative and deconvolution techniques such as those illustrated here that generate narrower spectral peak shapes, at times with significant distortion of the peak shape, in order to optimize the precision of peak position measurement. In addition, resolution enhancement is usually achieved at the expense of amplitude signal-to-noise ratio. However, as mentioned before *optimal* processing of the

spectral information for both peak height and peak position cannot be simultaneously achieved using a single filtering operation. Realization of this important concept facilitates intelligent and effective utilization of correlation based digital filtering techniques.

#### E. SIGNAL DETECTION

Correlation is often a useful preprocessing step in a signal detection operation (Black, 1969). If two signals are composed of peaks, a relatively large value of the correlation function at  $\tau = 0$  is a strong indication that the two signals are similar (See Figure 19). In a sense, the correlation operation is a way of concentrating the information about the similarity of two signals into the magnitude of a single point. Even the smoothing aspect of correlation discussed earlier can be looked at from the point of view of signal detection, i.e. finding or detecting a peak in a noisy base line. For example, correlation techniques have been developed to a high degree of sophistication for the detection of radar signals (Root, 1970).

A simple example of the signal detection aspect of correlation (Malmstadt et al, 1974) is presented in Figure 27. The signal (Figure 27a) is a sequence of binary pulses and the reference is a triplet sequence (Figure 27b). The cross-correlation function between the two waveforms is shown in Figure 27c. The maxima in the cross-correlation function indicates positions on the signal where signal information most like the reference waveform is to be found.

The application of cross-correlation techniques to the identification of spectra patterns is shown in Figures 28 and 29 (Horlick, 1973). Emission spectra of Co, Ni and Fe in the region of 3430 to 3500 Å are shown in Figure 28. Consider the Co spectrum as the sought-for spectral information. The Co, Ni and Fe spectra were cross-correlated with the Co spectrum. The resulting cross-correlation functions are shown in Figure 29. Figure 29a is the cross-correlation function of the Co spectrum with itself and in this case it can more accurately be called an autocorrelation function. The pattern has a relatively large maximum at  $\tau = 0$  indicating that the two spectra as expected have common spectral features. The rest of the function contains information about relative peak separations but unless the original spectra are quite simple, this information is not readily interpretable. Also, since this pattern represents an autocorrelation, it is symmetrical about  $\tau = 0$ .

The Co spectrum was then cross-correlated with the Ni spectrum and Fe spectrum. The resulting cross-correlation functions are shown in Figures 29b and 29c. These functions show no distinct maximum at  $\tau = 0$  indicating that the two spectra in each case share little similar spectral information. In addition, no symmetry is associated with the cross-correlation function. However, a complex pattern is still present as peaks overlap and coincide as the spectra are shifted relative to each other. All the cross-correlation functions

shown in Figure 29 have the same vertical axis of sensitivity thus, in this example, the behavior of the cross-correlation pattern at  $\tau = 0$  allows the identification of the Co spectrum in the measured set of spectra.

It should be noted that many learning machine approaches to pattern recognition use a similar preprocessing step. The unknown pattern is multiplied point by point by a specific vector and then the products are summed to obtain a number upon which a decision can be made about the identification of the pattern (Jurs et al, 1969). This is, of course, identical to the operation involved in evaluating the magnitude of the  $\tau = 0$  point in the cross-correlation function. In addition, an AND-sum operation has been found useful in identifying binary patterns derived from spectra (Grotch, 1970; Coddington and Horlick, 1973b). This operation involves evaluating the logical AND-operation between two binary patterns and then summing the resulting logical "ones" and hence is a binary analog of correlation.

### III. CORRELATION BASED SIGNAL GENERATION OPERATIONS

The correlation operation is ubiquitously present whenever chemical signals are generated or measured. The intimate connection of correlation and convolution makes this clear as any measured signal is the convolution of the "real" signal with the instrument response function. Also, a number of common hardware based signal processing techniques that are applicable

to the measurement of a rather large number of chemical parameters can be considered as correlation based techniques. These include the lock-in amplifier and boxcar integrator whose correlation nature has been discussed in some detail in the literature (Hieftje, 1972a; Hieftje, 1972b; Malmstadt et al, 1974).

However, in recent years, a number of measurement techniques have been developed where the correlation operation is more explicitly involved in the signal generation and measurement steps. A number of these measurements will be described in this section to provide the reader with a feel for the nature and utility of correlation based measurement techniques. Correlation techniques have, of course, been applied to a number of areas other than those high-lighted here. The coverage here is not meant to be exhaustive but simply representative. Several additional examples are also presented in Section IV where work of a more instrumental nature and emphasis is discussed.

A. SHOT NOISE AUTOCORRELATION MEASUREMENT TECHNIQUE FOR PHOTOCURRENTS.

The output photocurrent from a photomultiplier tube is not constant but rather fluctuates due to the quantum nature of light. These fluctuations are generally termed shot noise. In a conventional dc measurement system, the output photocurrent is low pass filtered to minimize the intensity of the shot noise and the dc level of the current is taken as a measure

of the light intensity. Pao et al., (1966) and Pao and Griffiths (1967) have indicated that at low light levels and/or wide measurement bandwidths, there may be more signal power in the shot noise component of the photocurrent than in the dc component. Furthermore, since the amplitude of the shot noise varies as the square root of the signal level, the average value of the square of the shot noise component (shot noise power) should be linearly related to light intensity. The measurement of this value can be achieved by autocorrelation of the output shot noise from the PM tube with the value at  $\tau = 0$  equal to the desired shot noise power. A number of workers have successfully used this technique for the measurement of photocurrents (Griffiths, 1967; Cleary, 1967; Griffiths and Pao, 1967; Alfano and Ockman, 1968; Anderson and Cleary, 1970).

The instrumentation for this autocorrelation measurement is quite simple. All that is needed is an analog multiplier with a low pass filtered output. A measurement system that has been successfully utilized for this autocorrelation is shown in Figure 30. The analog multiplier unit used to square the signal was a PAR Model 230 and it has a low pass filtered output. Other analog multipliers such as Analog Devices 426A could also be used.

The linearity of the shot noise autocorrelation measurement system is shown in Figure 31. The output of the multiplier

unit is plotted on a log-log plot vs the dc photocurrent as measured with a conventional system. The slope of this plot is  $45^\circ$  indicating that the multiplier output varies linearly with photocurrent and hence is linearly dependent on the incident light level.

B. APPLICATION OF CORRELATION TECHNIQUES IN FLAME SPECTROMETRY.

A number of signal-to-noise ratio enhancement techniques have been applied to flame spectrometric measurements including tuned amplification, lock-in amplification, signal averaging, dc integration, boxcar integration and photon counting, some of which as mentioned above, can be considered as correlation techniques. However, more recently, an explicit cross-correlation technique has been applied to flame spectrometry for the purpose of signal-to-noise ratio enhancement (Hieftje et al, 1973b).

The cross-correlation technique was applied to atomic fluorescence spectrometry. The intensity of the primary light source (a rhodium hollow cathode lamp) was sinusoidally modulated utilizing a programmable power supply. The photocurrent resulting from the atomic fluorescence of rhodium was cross-correlated (Model 3721A Hewlett-Packard Correlator) with the sine wave reference used to modulate the lamp intensity. Cross-correlation was compared to lock-in amplification and the limit of detection for rhodium was 0.16 ppm using the correlator and 0.91 ppm using lock-in amplification. Also, it was shown that

the cross-correlation technique was particularly superior in the presence of significant amounts of impulse noise. This is illustrated in Figures 32 and 33.

In this study, impulse noise was simulated by striking a brief spark from a Tesla coil to the grounded photomultiplier housing. In Figure 32 it is seen that large excursions are produced in the output of the lock-in amplifier whenever an impulse (marked by arrows) occurs. The correlator output shown in Figure 33 is considerably less susceptible to impulse noise. The impulse, which still caused deviation in the output signal, can now be simply discarded as being obviously deviant from the otherwise smooth sinusoidally varying cross-correlation function. Both the lock-in amplifier and correlation measurements were made using a 100 ppm rhodium solution.

Cross-correlation techniques have also been used by Hieftje et al, (1973a) in a study of source modulation waveforms for improved signal-to-noise ratio in atomic absorption spectrometry. In this case sine wave, square wave, ripple, pulse, and pseudo-random pulse modulations of the source intensity were studied. The demodulation step in order to generate the output signal can, in all cases, be interpreted as a single point cross-correlation with zero delay (Garforth, 1970; Malmstadt et al, 1974).

#### C. SYSTEM CHARACTERIZATION USING CORRELATION METHODS.

There are a number of scientific measurements and studies that necessitate the characterization of the frequency response

of a system. Correlation techniques utilizing random input waveforms are beginning to revolutionize these measurements. In order to understand how correlation techniques enable the characterization of a system, we must digress a bit. Let us imagine the system that we wish to investigate is a "black box" which has an input which enables us to perturb it, and an output which enables us to observe the effect of the perturbation. Our purpose will now be to determine a relationship between the input and output of the "black box" which will enable us to characterize its frequency response. The nature of the frequency response can often then be used to study important physical, biological or chemical parameters of the system contained in the black box.

One method of characterization that has long been studied and employed by workers in various fields is to determine the transfer function of the "black box". While the details of the transfer function need not concern us here, one kind of transfer function is particularly useful -- the impulse response function. The impulse response function is merely the output that our system would produce if perturbed with an input consisting of an impulse, that is, a very sharp spike.

From Fourier transform considerations (Bracewell, 1965) it is known that an ideal "infinitely fast" impulse has a flat frequency spectrum, i.e. contains all frequencies. Therefore, perturbing our black box with the impulse is equivalent to

simultaneously sending all frequencies into the input at once. Under these conditions, the output of the black box will contain all frequencies, but some will have been attenuated, distorted, phase shifted, or altered in some other way by the system. In short, the impulse response function is effectively a time domain representation of the frequency response of the system. As such, Fourier analysis of the impulse response function is frequently utilized to further aid characterization of the system.

In addition to the impulse response function, the step response function can also be used in a somewhat similar fashion and this was illustrated in Figure 11 as an example of convolution. Thus the impulse response function is simply the convolution of the input impulse with the system response function. However, the correlation operation can be advantageously employed in a more explicit way for the determination of the impulse response function of a system.

Recall Figure 7, in which the autocorrelation of a random function was shown to produce a sharply peaked function centered at  $\tau = 0$ . The impulse is therefore merely a phase related representation of the random waveform. Because of this relationship, perturbing the black box with a random wave should generate an output equivalent in frequency content to that produced by an impulse perturbation. The random waveform, like the impulse, contains all frequencies, although all are not being sent simul-

taneously into the system. The output of the system also contains all these frequencies altered as described before for the impulse input. It is much more difficult to characterize these alterations, i.e. visually discern the impulse response of the system, in the apparently random output waveform. The key, however, is simply to cross-correlate the output waveform from the system with the random input which will produce the desired impulse response function (Hewlett-Packard, 1969). This process is illustrated in Figure 34.

From the foregoing, it is evident that an impulse response function, useful in characterizing a device, can be generated using either an impulse or a random function as an input signal. The important consequence of this observation is that, with a random waveform, the frequency components being used to perturb the device can be spread out over a long period of time, thereby avoiding the sudden, intense perturbation created by an impulse. Because the "black box" need only accept a small fraction of the total combined amplitude of all frequency components at any given time, the amplitude of each component can be increased manyfold, and a clearer, more noise-free record of the impulse response function be obtained. Thus the random input, cross-correlation approach to system characterization is very powerful. Its wide spread usage has been somewhat hampered by lack

of convenient correlation instrumentation but the appearance of commercial correlators is beginning to make it the method of choice. A wide range of mechanical, electrical, biological, acoustical and chemical systems have been studied by this technique. As a simple example, consider the black box to be a large motor. In this case the input to the motor would merely be the current to the motor's windings, the output would be an observed rotation of a motor. Information about the relationship between these two quantities would, of course, be of interest to an engineer wishing to employ the motor in a specific application. However, it would be highly undesirable to excite the motor with an impulse, because at the very least, it is likely that the motor's windings would be damaged by this sudden application of a large current. Instead, the engineer can apply a randomly varying current to the motor and observe and correlate the slight variation in output rotation rates which are produced. In this application, an additional advantage derived is that the motor can be observed under normal operating conditions, that is, while it is rotating.

Among the more prominent chemical applications of this technique are Fourier transform NMR methods and characterization of electrode processes.

#### 1. Fourier Transform NMR

It is clear that Fourier transform methods (Farrar, 1970)

have revolutionized nuclear magnetic resonance spectrometry. It is not our intention here to in any way review this very large field, but simply to indicate how the technique relates to correlation methods. As first implemented (Ernst and Anderson, 1966), a pulse of radio-frequency energy was used to excite the free induction decay characteristic of nuclear spin relaxation. In effect, the free induction decay signal is merely a special form of impulse response function which, upon Fourier transformation, yields the desired spectrum. More recently, it has been shown by Ernst (1970) and others (Kaiser, 1970) that application of the radio frequency energy in a random fashion (stochastic excitation) and subsequent cross-correlation can produce even better signal characteristics. In particular, because the instantaneous power of the randomly-applied radio frequency signal can be much lower, the average power can be much higher without producing nuclear saturation. This higher average power in turn provides higher signal-to-noise ratios in the final detected signal or allows reduction in the amount of time necessary to obtain an NMR spectrum at any desired signal-to-noise ratio. A related technique, although not strictly a correlation method, is Fourier synthesized excitation (Tomlinson and Hill, 1973) in which the input excitation pulse contains only a selected number of frequencies.

## 2. Electrochemical Systems

A number of workers, using techniques similar to those discussed above for Fourier transform NMR, have studied and characterized electrochemical systems. This has included impulse methods (Birke, 1971), Fourier syntheses techniques (Kojima and Fujiwara, 1971; Creason and Smith, 1972a; Creason and Smith, 1973; Glover and Smith, 1973) and the application of random and pseudo-random noise as applied potential signals (Creason and Smith, 1972b).

### D. CORRELATION ANALYSIS OF NOISE-"FLUCTUATION SPECTROSCOPY"

In recent years, a number of new and unique scientific measurements have been carried out that are based on the correlation analysis of noise. The first measurements, and the majority to date, have involved the analysis of scattered laser light by autocorrelating intensity fluctuations. More recently noise correlation methods have also been applied to the measurement of chemical kinetic information using fluorescence and conductivity fluctuation measurements. This is an exciting and rapidly developing field and we will briefly review it in this section.

An early review on the subject of utilizing the measurement of light fluctuations as a spectroscopic tool was presented by Wolf in 1964 (Wolf, 1965). In particular, it is possible to measure spectral information about the line width of a laser line

and/or a Doppler broadened Rayleigh scattered laser line by autocorrelating intensity fluctuations. As the technique has evolved, a host of names have become associated with it, among them: light beating spectroscopy, photon correlation spectroscopy, heterodyne laser beat frequency spectroscopy, optical mixing spectroscopy, intensity correlation spectroscopy, intensity fluctuation spectroscopy, and laser Doppler spectroscopy. Reviews of the field have been presented by Cummins and Swinney (1970) and Berne and Pecora (1974) and Cummins and Pike (1974) have edited a recent volume devoted to Photon Correlation and Light Beating Spectroscopy.

At present, the largest application of this technique is in the measurement of flow and flow related parameters such as diffusion coefficients with most effort centered on biochemical systems. A typical experiment involves the measurement of the time-varying scattered radiation (intensity fluctuation) from a flowing system being illuminated by a powerful argon ion laser. Autocorrelation of these intensity fluctuations in the scattered signal can provide information about the flowing system. In a recent experiment, (Ware and Flygare, 1971) simultaneous measurement of electrophoretic mobility and the diffusion coefficient of bovine serum albumin was carried out utilizing such light scattering techniques. Since that time, there have been many applications of this technique to flow related measurements. Among them, a further study by Ware and Flygare (1972) applied to

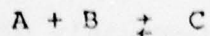
fibrinogen, a study of electrokinetic phenomena (Uzgiris, 1972; Uzgiris, 1974), blood flow (Tanaka and Benedek, 1975), plasmas (Ogata and Matsuura, 1974), air flow (Durrani and Greated, 1975) and macromolecular diffusion coefficients (Pusey et al, 1974). A full review of this rapidly expanding field is beyond the scope of this chapter. However, the interested reader is encouraged to review the original publications as many applications are certainly of chemical interest.

Very recently, noise correlation methods have been extended to the measurement of chemical kinetic parameters utilizing fluorescence and conductivity fluctuations. Fluorescence correlation spectroscopy has been discussed in some detail by Magde et al, (1972), Elson and Magde (1974) and Magde et al. (1974). Feher and Weissman (1973) have determined the kinetic parameters of the dissociation reaction of beryllium sulfate by correlation of conductivity fluctuations. Chen (1973) has also discussed the measurement of kinetic parameters utilizing fluctuations. The basis of this method of determining kinetic parameters can be understood in terms of the random perturbations discussed in the previous section on system characterization.

As chemists, we should recognize that, on a molecular or atomic basis, all species are being continuously perturbed stochastically. Collisions among chemical species, random dissociation reactions, and other occurrences all act as perturbations. The reaction of the chemical system to these perturbations can

however, not be random but must follow the physical and chemical kinetic laws governing those particular species. Thus the measurement of a particular response function of the chemical system should be able to be achieved without the explicit random input depicted for the black box in the last section. The input would be the naturally occurring random perturbations within and around the chemical system under study. Observation of some property of one or more of the species in the system should then provide information about the temporal behavior of that species. Thus in the laser scattering experiments, the intensity fluctuations in the scattered laser light reflect concentration fluctuations due to diffusion of macromolecules.

In the more recent work of Feher and Weissman (1973) and Elson and Magde (1974) concentration fluctuations are reflected in conductivity and fluorescence intensity fluctuations from which, by autocorrelation, chemical kinetic information can be obtained. To understand these experiments, consider the simple reaction shown below:



We would ordinarily think of this chemical reaction as being at equilibrium. Of course, any true chemical "equilibrium" is really a dynamic system, involving both forward ( $k_1$ ) and ( $k_{-1}$ ) reverse reactions. Therefore, the concentrations of all reactants and products in the reaction are continuously changing

because of natural, stochastic perturbation around and within them. However, as in the preceding examples, the chemical species cannot react instantaneously to these perturbations but must change in concentration in accordance with their own kinetic characteristics. Thus, if the concentration of species C was observed over a period of time, its kinetic behavior could be deduced by autocorrelation analysis of its concentration fluctuations.

Although this method of measuring chemical kinetics has not been broadly explored and is not yet widely recognized, it is certain to be of great significance in the future. It enables reaction kinetics to be observed under essentially equilibrium conditions, thereby simplifying mechanistic interpretation of the kinetic information. In addition, it is unnecessary to externally perturb the system. Extremely rapid kinetics can be observed, in fact, the speed with which kinetics can be observed is limited only by the response time of the devices being used to monitor the chosen species. These and other potential advantages are discussed further in the references cited in this section. Certainly one "advantage", mentioned by Feher and Weissman is "the personal satisfaction of using rather than fighting noise". Clearly noise correlation represents a new, powerful and elegant technique. It provides both unique measurement capabilities for chemical parameters and fresh insight into chemical systems.

Finally a related area, that of calculating molecular motion information by Fourier transforming infrared and Raman spectral band shapes should be mentioned. The result is a so-called time correlation function that can provide information about molecular rotation (Gordon, 1965; Shimizu, 1965). In a sense, the laser scattering experiments are just line broadening measurements. However, the spectral resolution necessary for its observation is beyond the capability of essentially all conventional techniques except perhaps the Fabry-Perot interferometer and thus new approaches such as the intensity correlation method were developed. In the infrared, however, the broadening of the spectral lines by molecular rotation can be measured directly by conventional spectroscopic techniques and the peak shape transformed by software to give the autocorrelation function. However, more recently, Rayleigh light scattering techniques have been used to measure orientational correlation functions in liquids as very short time behavior can be observed (Dill et al, 1975).

E. CORRELATION SPECTROSCOPY AND INTERFEROMETRY.

Correlation spectroscopy is basically a hardware method of cross-correlating a measured spectrum with a stored replica of the sought for spectrum (Williams and Politz, 1968; Davies, 1970). Typically a mask replica of the sought for spectrum is positioned in the exit focal plane of a spectrometer and either the mask or the spectrum is oscillated to generate a chopped

signal whose amplitude is a maximum when the spectrum most closely matches the exit mask. Note that this is essentially identical to the software cross-correlation operation depicted in Section II, E for the Co, Ni and Fe spectra except that only the value of the cross-correlation function at  $\tau = 0$  is being evaluated with this mask technique. One of the main application areas for this technique has been the detection of gaseous air pollutants and recent studies utilizing this technique have been presented by Strojek et al, (1975) and by Walter and Flanigan (1975).

Similar correlation techniques have also been used to process interferograms obtained from a Michelson interferometer as used in Fourier transform spectroscopy (Davies, 1970; Dick and Levy, 1970). With this technique quantitative information can be obtained from an interferogram without the necessity of Fourier transformation. This method has excellent potential for providing simple systems to process interferograms.

#### F. CORRELATION CHROMATOGRAPHY

In normal chromatographic operations, there can be an appreciable delay between the injection of a sample and readout of the peak information. Correlation techniques have been investigated with the idea of achieving continuous chromatographic analysis (Annino and Bullock, 1973). As mentioned in Section III, C a system can be characterized by measuring its impulse response function. The injection of a sample into a chromato-

graph can be considered as an impulsive input, thus a normal chromatogram is the impulse response function of the chromatograph. It was seen in Section III, C that the same information could be measured utilizing a random input function and cross-correlating the system output with the random input. This is the basis of correlation chromatography.

To produce a correlation chromatograph, a random or pseudo random command signal is used to control the sample valve to switch it back and forth between the sample stream and carrier gas or standard sample. When the output signal of the chromatograph is cross-correlated with the pseudo random input control signal, the result is a correlation function that has the appearance of a normal single injection chromatogram.

Although quite similar to a normal single impulse chromatogram, the correlogram differs in the following respects. Since it contains the average information obtained from a number of injections, it provides a more reliable estimate of the signal. Also, as new information appears in the output, the oldest is rejected and a new updated correlogram is calculated and displayed. This implies the possibility of creating a chromatographic system in which the sample valve rapidly and repeatedly injects samples and which displays a chromatogram following sample concentration variations more or less continuously. Finally, the correlogram has an increased signal-to-noise ratio compared to a single impulse chromatogram due to the fact that random

noise does not correlate and therefore is automatically cancelled in the operation. Although some of these ideas have been verified experimentally, correlation chromatography suffers certain limitations because of nonlinearities in the chromatographic system. The practical aspects and limitations of correlation chromatography are discussed in detail by Annino and Bullock (1973).

G. A CORRELATION METHOD FOR THE MEASUREMENT OF DECAYING EXPONENTIALS.

In a recent paper by Miller et al, (1975) a cross-correlation method for the measurement of decaying exponentials is presented. The measurement system was actually applied to semiconductor transient signals but it should be applicable to any situation where similar signals are measured. This is an excellent paper to read in order to get a feel for the correlation approach to measurement.

The basic idea of this correlation measurement system is shown in Figure 35. Clearly, this is just a hardware implementation of matched filtering (Section II, B) where the noisy exponential is cross-correlated with a noise free exponential. The performance of the correlator is discussed and compared with boxcar integration and lock-in amplification for the same measurement. In addition, the utility of alternative weighing functions to the exponential is assessed.

#### IV. CORRELATION INSTRUMENTATION

From the foregoing sections, it is clear that correlation techniques can be effectively applied to a wide range of chemical measurement and signal processing situations. However, one of the most serious drawbacks to the wide spread utilization of correlation techniques has been the unavailability of suitable computational methods or instrumentation for carrying out the correlation operation. In the last few years, significant progress has been made in both software and hardware approaches for the implementation of correlation. In addition, present developments in certain large scale integrated circuits such as diode arrays and CCD's should provide, in the near future, very inexpensive devices capable of sophisticated correlation operations. The areas to which correlation techniques are now being applied have been greatly expanded by these instrumental developments.

##### A. SOFTWARE APPROACHES

With the wide spread use of small computers in the chemical laboratory correlation techniques can easily be implemented on a variety of signals using software. Data can be read into the computer in a variety of ways, but for most flexibility in a laboratory environment, the basic computer system should include an analog-to-digital converter for acquisition of signals and standard analog outputs such as a plotter and a

scope or graphics unit so that the correlation function and signals can be conveniently displayed.

A minicomputer system that has been used for a variety of correlation applications in one of the authors laboratories is shown in Figure 36. The analog input consists of a sample and hold amplifier with a 50 nsec aperture time (Analogic MP-250) coupled to a 10 bit ADC with a conversion time of 10  $\mu$ sec (Analogic M 2810). Data acquisition is initiated by a start pulse indicative of the beginning of the signal and is clocked in at a rate appropriate to accurate sampling of the specific signal (Kelly and Horlick, 1973). Data can be displayed on an oscilloscope or a strip chart recorder via a DAC, listed on the DEC writer terminal or permanently stored on magnetic tape (DEC tape) for further processing. The computer is a DEC PDP8/e with 16K of core and a DEC tape-based OS/8 operating system. The software was written primarily in FORTRAN. Machine language (SABR) was used to input data from the ADC and output data to the DAC via a DEC DR8-EA 12-channel buffered digital I/O. The machine language commands could be inserted directly in the FORTRAN program, a feature that has proven to be exceptionally convenient and powerful in our laboratories. Obviously, a number of other systems could be used, but that shown in Figure 36 is typical of the capability required in a flexible system for laboratory oriented correlation applications utilizing a minicomputer.

The basic equation of a discrete correlation operation (Equation 2) is easy to program and simple programs for the direct implementation of correlation filtering operations were presented by Savitzky and Golay (1964). However, for moderately large arrays correlation can be quite time consuming on computers. The Fourier transform route of correlation is often a much quicker computational route. In particular, the Fast Fourier Transform algorithm has essentially revolutionized the extent to which correlation techniques are utilized for processing scientific signals. The Fourier transform route of correlation was discussed in Section I and emphasized throughout Section II.

Finally, it should be mentioned that many manufacturers are now providing complete software based systems that are applicable to correlation analysis. Among these are the DECLAB-11/10 systems and the TEKTRONIX digital processing oscilloscope (Ramirez, 1975). These systems can be obtained with the ADC, DAC and graphics hardware necessary for a very powerful correlation signal processing system. In addition, complete software packages are available such as DEC's Lab Applications-11 (Dulaney, 1975) that contains FFT capability. These and similar systems can provide the experimenter with very flexible and powerful correlation signal processing capability.

## B. HARDWARE CORRELATORS

At the present time, it is really in the hardware area that some of the most exciting advances are occurring in the development of systems that are capable of evaluating correlation functions. Despite the relatively high cost of most commercial hardware correlators a number of electronic components and subsystems are now available which allow the design and construction of sophisticated but inexpensive correlation instrumentation.

There are, of course, many approaches that can be taken in the design of a hardware correlator. One of the simplest basic designs is that shown in Figure 37a. This correlator consists of a four quadrant multiplier and a low pass filter. A four quadrant multiplier is simply an analog multiplier capable of multiplying two analog signals of any polarity. Units such as Analog Devices Model 426A has better than 1% accuracy and sells for less than \$50. Units with better than 4% accuracy can be purchased for about \$10. Thus the correlator illustrated in Figure 37a is indeed inexpensive.

A remarkably large number of correlation measurements can be carried out with this simple instrument. As illustrated in Figure 10, this correlator forms the basis of the lock-in amplifier. With relatively simple additional circuitry (Horlick and Betty, 1975; Malmstadt et al, 1974) inexpensive lock-in

amplifiers can easily be constructed from this basic unit. In addition, the correlation discussed in Section III, A and the demodulation correlation measurement (Hieftje et al, 1973a) mentioned in Section III, B can both be carried out with this simple correlator.

The versatility and applicability of this correlator can be greatly extended by the addition of a function generator as shown in Figure 37b. This correlator is primarily applicable to repetitive signals. A simple function generator is shown in Figure 38a along with the appropriate waveforms. It consists of a variable delay monostable and a gate monostable, where the gate function is the waveform sent to the multiplier. With this function generator, our correlator becomes the familiar boxcar integrator (Malmstadt et al, 1974; Hieftje, 1972a; Hieftje, 1972b) and in this application the four quadrant multiplier can even be replaced by an analog FET gate.

A simple modification of this function generator is shown in Figure 38b in which an OA differentiator (high pass filter) and a clipping circuit are connected to the output of the gate monostable. Now the function generator is capable of generating a variety of decaying exponentials and matched filter correlation measurements can be carried out such as that discussed in Section III, G (See Figure 35). Obviously, this approach is applicable to a wide variety of measurements, limited only the experimenters ability and

ingenuity in designing appropriate function generators.

The correlators illustrated in Figure 37 are limited in that essentially only the value of the correlation at  $\tau = 0$  is evaluated, although some variation in  $\tau$  is possible with the function generators shown in Figure 38 by adjusting the delay monostable. However, for more general purpose correlation operations, an instrument such as that shown in Figure 39a is necessary (Malmstadt et al, 1974).

This correlator is capable of correlating a reference waveform stored in a digital memory with a repetitive analog waveform with the resulting correlation function being plotted on a recorder. The correlator consists of two basic sections, a digital storage and shifting section for the reference waveform and the analog correlation unit previously described. The desired reference waveform is first read into the N-word circulating shift register memory via the analog-to-digital convertor. One point of the correlation function between this reference waveform and a repetitive analog signal can then be evaluated by triggering the circulation of the memory with a pulse indicative of the start of the signal repetition. After sufficient products have been integrated to reach a steady state value at the output of the low pass filter, the sequencer sends a single extra clock pulse to the shift register which shifts the position of the reference waveform, relative to the start pulse, one clock period. The value of the correlation function

at this new relative position is then evaluated by repetitive multiplication and integration and then the shift pulse is again applied. In this manner, the complete correlation function can slowly be evaluated and plotted on a recorder.

Even though this correlator is considerably more sophisticated than those shown in Figure 37, it is not particularly difficult or expensive to build. For example, typical medium speed 10 bit DAC's and ADC's can be obtained for \$50 and \$100. In the past, a major stumbling block in building such a correlator would have been the memory. However, a wide variety of inexpensive shift register memories are now available and the construction of an N-word circulating shift register memory is relatively simple using these IC's. For example, 1024 by one bit shift registers can be obtained in a single 8 pin IC package (Signetics 2533) for less than \$15. Ten of these, appropriately interconnected, provides a 1024 word 10 bit shift register memory. Other memories of shorter lengths are available that combine more than one register on each IC such as dual - 256 bit (Signetics 2527) and hex - 32 bit (Signetics 2518) shift register memories. Also the combination of the ADC, shift register memory, and DAC constitute what is known as a transient recorder (Malmstadt et al, 1974). These instruments are available commercially (Biomation, 10411 Bubb Road, Cupertino, California 95014) or can be built following designs such as that of Korte and Denton (1973) and Daum and Zamie (1974).

Many variations and extensions of the basic design shown in Figure 39a are possible. If it is only necessary to cross-correlate the signal with a binary pattern this correlator can be simplified to that shown in Figure 39b where the N-word memory is replaced with an N-bit circulating shift register memory. Now a single 8 pin IC can store up to a 1024 bit binary pattern. Such a unit can be useful for pattern detection (Coddling and Horlick, 1973b) or can be used as a versatile scanning boxcar integrator (Malmstadt et al, 1974). If the signal is not repetitive or if autocorrelations are to be evaluated, then a second memory section must be added as shown in Figure 40. Also if desired, the correlation function evaluation could be carried out digitally rather than using the analog approach presented in these examples. At this point, one reaches the rather complex and expensive (but powerful) completely digital hardware correlators available from such sources as Hewlett-Packard (Hewlett-Packard, 1969), Saicor (Honeywell Signal Analysis Operation, Test Instruments Division, 595 Old Willets Path, Hauppauge, New York 11787), Spectral Dynamics Corporation, P.O. Box 671, San Diego, CA 92112, and Elsytic, 212 Michael Drive, Syosset, New York 11791. However, it should be clear from this discussion, that correlation instrumentation need not be looked upon as complex and expensive. The simple correlators depicted here are quite capable of carrying out a wide variety of sophisticated and useful correlation operations.

## 1. Correlators for Fluctuation Spectroscopy

Although convention autocorrelation instrumentation is applicable to fluctuation spectroscopy measurements, many workers have constructed their own correlators, particularly autocorrelators capable of processing a PM tube signal measured in a photon counting mode. The correlators are often referred to as digital correlators or photon correlators. Some are solely hardware based and others combine external hardware and conventional minicomputers.

The general nature of the photon autocorrelation measurement has been discussed by Pusey et al. (1974). A 1024-channel digital correlator was presented by Ables et al. (1975), and fast digital correlator for weak optical signals by Corti (1974). Digital correlators using minicomputers have been developed by Wijnaendts van Resandt (1974) and by Gray et al, (1975). Also, a number of simple schemes for measuring autocorrelation functions of fluctuating signals are presented by Kam et al, (1975).

### C. DIODE ARRAY CORRELATION INSTRUMENTATION

Integrated circuits based on diode arrays and charge coupled devices (CCD's) show promise of providing remarkably sophisticated correlation instrumentation and operations in very compact packages. These devices have initially been developed for electronic imaging applications (Talmi, 1975). In this form a photodiode array has facilitated the development of an analog cross-correlation readout system for spectrochemical applications. More recently, diode arrays have also been fabricated as analog shift registers and tapped analog delay lines. The unique applicability of these devices to correlation measurements will be discussed in this section.

#### 1. A Photodiode Array Based Correlator for Spectrochemical Applications.

A photograph of a 512 element self-scanning linear silicon photodiode array is shown in Figure 41. The thin line across the center is the actual array of diodes. They are 0.001" high and the elements are on 0.001" spacing; thus this array is 0.512" long. The array, complete with scanning circuitry is packaged in an 18 pin dual-in-line IC package. A simplified schematic of the complete integrated circuit is shown in Figure 42. Each photodiode is connected to the output line by a FET switch. The FET switches are controlled by a single bit that is shifted through the shift register. Readout is accomplished using two

TTL level signals, a start pulse and a clock. Although the actual circuitry is somewhat more complex than that shown in Figure 42, the start pulse can be thought of as setting the first bit of the shift register and the clock then cycles the bit through the shift register reading out the array.

The photodiodes operate in the charge storage mode and hence are inherently integrating type detectors. When a particular FET switch is closed by the bit in the shift register, the diode is charged up to its full reverse bias potential. This reverse bias charge, stored on the equivalent capacitance of the PN junction, can then be discharged between scans by photon generated charge carriers (light falling on the diode) and by thermally generated charge carriers (dark current). Thus the signal level necessary on the subsequent scan to re-establish reverse bias on the diode is a measure of the total light intensity and dark current integrated over the time between scans of the array. Thus this device can be considered as a 512 element analog shift register with parallel optical inputs and a serial electrical output.

A unique cross-correlation readout system for spectrochemical measurements has been developed utilizing this sensor as the detector (Horlick and Coddling, 1973). A block diagram of the cross-correlation readout system is shown in Figure 43a. The photodiode array was mounted in the focal plane of the monochromator. A 256 element array was used for this application

and about  $110 \text{ \AA}$  of spectral information could be simultaneously observed. A typical output signal for a triplet spectrum is shown schematically in Figure 43b as it would appear on an oscilloscope at point X in Figure 43a. The array was clocked at a rate of 30 kHz so a complete spectrum ( $110 \text{ \AA}$  region) was read-out in 3.5 msec. The repetition time (time between start pulses) was 60 msec (17 spectra/sec).

The nature of the correlator is the same as that shown in Figure 37b. The function generator for this application is shown in Figure 44. It consists of three delay monostable (DM)-gate monostable (GM) combinations and a system of operational amplifiers. Using this function generator, any of the output waveforms can be generated in synchronism with the spectral trace from the photodiode array. The simple pulse waveform is shown in Figure 43b as it would appear on an oscilloscope at point Y in Figure 43a.

In order to vary  $\tau$  and hence cross-correlate a spectral region with a particular pulse waveform, the monochromator was scanned slowly ( $0.2 \text{ \AA sec}$ ). This results in the spectrum being slowly scanned past the electronic gate. This is exactly analogous to scanning a dispersed spectrum past a mechanical exit slit (see Figure 5). Thus the pulse gate amounts to an "electronic exit slit". In contrast to the mechanical slit, the electronic slit can take on several unique forms (Figure 44a). Useful modifications of the spectral information can be carried

out by cross-correlation with certain types of bipolar pulses. Two examples are shown in Figure 45. The sequence shown in Figure 45a illustrates a cross-correlation that results in resolution enhancement and that in Figure 45b in an approximate first derivative. The bipolar pulse shown in Figure 45a is a square approximation to a second derivative response function and that in Figure 45b to a first derivative response function. Thus these direct cross-correlations are analogous to the Fourier domain filtering discussed in Section II, C.

Thus this analog cross-correlation system provides a unique and versatile approach to spectrometric readout. A wide range of powerful spectral signal processing operations in addition to those illustrated here, can also be effectively implemented with this system. For example, mask correlation spectroscopy discussed in Section III, E could be flexibly implemented with this system as the mask could be replaced by a characteristic electronic gating waveform.

## 2. Diode Array Analog Shift Registers.

As mentioned in the last section, the photodiode array is really an analog shift register with parallel optical inputs and a serial electrical output. Diode array devices are now available that are complete analog shift registers (delay lines) with serial electrical input and output. A simplified schematic of a SAM-128V Serial Analog Memory (128 diodes) available from

Reticon Corp., 910 Benicia Ave., Sunnyvale, California 94086 is shown in Figure 46. The diodes are shown only as their equivalent capacitors. The read-in shift register controls the sequential sampling of the analog input signal and the read-out shift register controls the sequential interrogation of the diode (capacitor) memory elements. The read-in and read-out rates are independent, thus the analog signal can be reconstructed with a different time base. Also, each memory capacitor has a FET buffer stage, thus read-out (unlike that with the photodiode array) is non-destructive. However, with present devices the retention time without significant degradation (because of "dark" current) is 40 msec at room temperature.

Clearly this type of device is potentially an extremely powerful circuit element for incorporation into correlation instrumentation. This single IC, with appropriate clocking circuitry can function as a complete transient recorder. Thus, some of the correlation instrumentation shown in Section IV, B could be considerably simplified utilizing this device. In addition, this particular serial analog memory possesses some features which make it uniquely applicable to binary sequence correlation. Readout, as mentioned above, is controlled by the readout shift register. If a bit exists in the  $n$ th stage, the  $n$ th cell will be read out. Thus if a specific binary sequence is clocked into the readout shift register, the output will be the summation of the products of the binary sequence and the stored

analog information. This application amounts to the rapid cross-correlation of a stored analog signal with a moving binary sequence. Thus a number of powerful signal detection correlations can be carried out with what amounts to a single 18 pin integrated circuit as the correlator.

### 3. Tapped Analog Delay Line

A variation of the analog shift register known as a tapped analog delay line is capable of implementing a number of unique correlation operations on analog signals, particularly matched filtering. A schematic of a tapped analog delay line is shown in Figure 47. Basically the device consists of an analog shift register (delay line) with output taps on each storage element. Many applications can be implemented with a small number of delay elements and the unit shown in Figure 47 has only 9 delay elements and taps. The output of the tapped analog delay line is simply the weighed sum (as set by the resistor values) of 9 sequential signal values. Thus an analog signal can be cross-correlated (filtered) by an desired 9 point correlation filter simply by choosing appropriate resistor values. In addition, not all taps need be connected to a single output amplifier, thus an incredibly wide range of filtering operations are possible with such a device.

As a simple example, a conventional low pass filter can be simulated by giving tap 1 the most weight and the following

taps exponentially decreasing weight. It is well known that such a filter can distort a peak signal because only the present and past values contribute to the output value (Savitzky and Golay, 1964). In the past this was essentially impossible to avoid by real time analog techniques and could only be avoided by using digital data processing. However, with the tapped analog delay line filter a trivial modification achieves the desired result. It is simply necessary to give tap 5 the most weight and then give the taps on either side exponentially decreasing weight. In this manner, symmetrical doubled sided exponential filtering can be implemented. Clearly, such devices are destined to be widely employed in scientific instrumentation as real time analog correlators. A serial analog delay line, based on diode arrays, with 24 storage cells and 12 equally spaced taps is presently available from Reticon (TAD-12).

An analog data processor for chart records, whose capability is analogous to that of a tapped analog delay line, has been constructed by Minami et al, (1969). This processor was based on an array of ten independent diodes, a detector which is used in conventional punched tape readers. It was capable of evaluating the cross-correlation between a number of 10 point correlation functions (exponential, boxcar (moving average), and Savitzky-Golay type filtering functions) and any type of data in the form of recorder traces.

D. CHARGE COUPLED DEVICE CORRELATION INSTRUMENTATION

Charge coupled devices (CCD's) are relatively new electronic devices that are applicable to both electronic imaging and analog shift register applications. A schematic of CCD operation is shown in Figure 48. Basically, the CCD concept involves manipulation of charge on the surface of a semiconductor by moving a potential minimum (Boyle and Smith, 1970). In the structure shown in Figure 48, every third electrode is connected to a common conductor. Initially (Figure 48a) voltage

$V_2$  is greater than  $V_1$ . This generates a depletion region under electrodes 1, 4, 7.... and any positive charge present or generated near one of these electrodes (such as 1 and 7) will collect near it. If a voltage  $V_3$  ( $V_3 > V_2$ ) is applied to electrodes 2, 5, 8....(Figure 48b) the charge will be transferred from one electrode to the next. In the final sequence (Figure 48c) the voltage  $V_2$  is now applied to electrodes 2, 5 and 8. Thus the CCD is really an elegantly simple analog shift register.

As with diode arrays, most of the initial applications of CCD's have been in electronic imaging (Talmi, 1975), although they are now being applied to both analog and digital shift register applications. A 100 element linear CCD device is available (GEC Semiconductors, East Lane Wembley, Middlesex, England HA9 7PP) that is an imaging device and hence has 100 parallel optical inputs and also has a serial analog input so it can be used as an analog shift register and a line imager either separately or simultaneously. In addition, tapped CCD's are being developed for various analog signal processing applications (Tiemann et al, 1974; Beny and Husson 1975).

The basic implementation of CCD based correlation operations is analogous to that with diode arrays. CCD's are somewhat simpler to fabricate and perhaps will become the device of choice in the future. Also, interest remains high in the development of addition solid state devices with correlation signal processing capability. Recently, considerable research has been carried out

on the development of correlators based on acoustic wave interactions (Menager and Desonmiere, 1975; Reeder and Gilden, 1973; Jones et al, 1972).

#### V. CONCLUSIONS

It has been seen in this chapter that correlation techniques are powerful and widely applicable methods for the generation and processing of chemical information. Very often correlation techniques provided unique measurement capability as well as fresh insight into the applicability and limitations of a particular method. Also it was seen that correlation provides a remarkably unifying point of view from which to consider and assess the wide range of measurement and processing techniques available to scientists. Present and future instrumental and conceptual developments are sure to extend even further the power and utility of correlation methods.

REFERENCES

- Ables, J.G., Cooper, B.F.C., Hunt, A.J., Morrey, G.G., and  
Brook, J.W. (1975). Rev. Sci. Instrum. 46, 269.
- Alfano, R.R., and Ockman, N. (1968). J. Opt. Soc. Amer. 58, 90.
- Allen, L.C., Gladney, H.M., and Glarum, S.H. (1964). J. Chem.  
Phys. 40, 3135.
- Anderson, R., and Cleary, J. (1970). J. Opt. Soc. Amer. 60, 531.
- Annino, R., and Bullock, L.E. (1973). Anal. Chem. 45, 1221.
- Barlow, J.S. (1959). IRE Trans. Medical Electronics ME-6, 179.
- Beny, H.F., and Husson, C. (1975). Proc. IEEE 63, 822.
- Berne, B.J., and Pecora, R. (1974). Ann. Rev. Phys. Chem. 25, 233.
- Betty, K.R., and Horlick, G. (1976). Appl. Spectrosc. (In Press).
- Birke, R.L. (1971). Anal. Chem. 43, 1253.
- Black, W.W. (1969). Nucl. Instrum. Meth. 71, 317.
- Boyle, W.S., and Smith, G.E. (1970). Bell Syst. Tech. J. 49, 587.
- Bracewell, R. (1965). "The Fourier Transform and Its Application"  
McGraw Hill, New York, N.Y.

Bracewell, R., and Roberts, J.A. (1954). Australian J. Phys.

7, 616.

Brouwer, G., and Jansen, J.A.J. (1973). Anal. Chem. 45, 2239.

Bush, C.A. (1974). Anal. Chem. 46, 890.

Caprini, M., Cohn-Sfetcu, S., and Manof, A.M. (1970). IEEE

Trans. Audio Electroacoustics AU-18, 389.

Champeney, D.C. (1974). "Fourier Transforms and Their Physical

Applications", Academic Press, London.

Chen, Y., (1973). J. Chem. Phys. 59, 5810.

Cleary, J. (1967). J. Opt. Soc. Amer. 57, 841.

Codding, E.G., and Horlick, G. (1973a). Appl. Spectrosc. 27, 85.

Codding, E.G., and Horlick, G. (1973b). Appl. Spectrosc. 27, 366.

Corti, M., DeAgostini, A., and Degiorgio, V. (1974). Rev. Sci.

Instrum. 45, 888.

Creason, S.C., and Smith, D.E. (1972a). J. Electroanal. Chem.

40, 1.

Creason, S.C., and Smith, D.E. (1972b). *Electroanal. Chem.* 36,

App 1.

Creason, S.C., and Smith, D.E. (1973). *Anal. Chem.* 45, 2401.

Cummins, H.Z., and Swinney, H.L. (1970). "Light Beating Spectro-

scopy" in "Progress in Optics", Vol. 8, E. Wolf, Ed.,

North-Holland Publishing Company, Amsterdam. p. 135.

Cummins, H.Z., and Pike, E.R. (1974). Eds. "Photon Correlation

and Light Beating Spectroscopy", Plenum Press, New

York, N.Y.

Daum, P.H., and Zamie, P. (1974). *Anal. Chem.* 46, 1347.

Davies, J.H. (1970). *Anal. Chem.* 42(6), 101A.

Dick, R., and Levy, G. (1971) in "Aspen International Conference

on Fourier Spectroscopy, 1970", Vanasse, G.A., Stair,

A.T. Jr., and Baker, D.J. Eds. Air Force Cambridge

Research Laboratories, Special Report, No. 114 (Avail-

able from the National Technical Information Service).

Dill, J.F., Litovitz, T.A., and Bucaro, J.A. (1975). J. Chem.

Phys. 62, 3839.

Dromey, R.G., and Morrison, J.D. (1970). Int. J. Mass. Spectrom.

Ion Phys. 4, 475.

Dulaney, G. (1975). Anal. Chem. 47, 24A.

Durrani, T.S., and Greated, C.A. (1975). Appl. Opt. 14, 778.

Elson, E.L., and Magde, D. (1974). Biopolymers 13, 1.

Ernst, R.R. (1970). J. Mag. Res. 3, 10.

Ernst, R.R., and Anderson, W.A. (1966). Rev. Sci. Instrum. 37, 93.

Farrar, T.C. (1970). Anal. Chem. 42(4), 109A.

Feher, G., and Weissman, M. (1973). Proc. Nat. Acad. Sci. USA

70, 870.

Garforth, P.J. (1970). Electron. Inst. Digest 6(8), 7.

Glover, D.E., and Smith, D.E. (1973). Anal. Chem. 45, 1869.

Gordon, R.G. (1965). J. Chem. Phys. 43, 1307.

Gray, A.L., Hallett, F.R., and Rae, A. (1975). J. Phys. E.:

Sci. Instrum. 8, 501.

Griffiths, J.E. (1967). Appl. Spectrosc. 5, 762.

Griffiths, J. E., and Pao, Y.-H. (1967). J. Chem. Phys. 46, 1679.

Grotch, S.L. (1970). Anal. Chem. 42, 1214.

Hayes, J.W., Glover, D.E., Smith, D.E., and Overton, M.W. (1973).

Anal. Chem. 45, 277.

Helstrom, C.W. (1968). "Statistical Theory of Signal Detection",

Pergamon Press, Oxford.

Hewlett-Packard Journal (1969). Vol. 21 (Nov.).

Hieftje, G.M. (1972a). Anal. Chem. 44(6), 81A.

Hieftje, G.M. (1972b). Anal. Chem. 44(7), 69A.

Hieftje, G.M., Holder, B.E., Maddux, A.S. Jr., and Lim, R. (1973a).

Anal. Chem. 45, 238.

Hieftje, G.M., Bystroff, R.I., and Lim, R. (1973b). Anal. Chem.

45, 253.

Horlick, G. (1971). Anal. Chem. 43(8), 61A.

Horlick, G. (1972a). Anal. Chem. 44, 943.

Horlick, G. (1972b). Appl. Spectrosc. 26, 395.

Horlick, G. (1973). Anal. Chem. 45, 319.

Horlick, G., and Coddling, E.G. (1973). Anal. Chem. 45, 1749.

Horlick, G., and Betty, K.R. (1975). Anal. Chem. 47, 363.

Inouye, T., Harper, T., and Rasmussen, N.C. (1969). Nucl.

Instrum. Meth. 67, 125.

Izatt, J.R., Sakai, H., and Benedict, W.S. (1969). J. Opt. Soc.

Amer. 59, 19.

Jansson, P.A., Hunt, R.H., and Plyler, E.K. (1968). J. Opt. Soc.

Amer. 58, 1665.

Jones, R.N., Venkataragharan, R., and Hopkens, J.W. (1967).

Spectrochim. Acta. 23A, 925.

Jones, W.S., Kempf, R.A., and Hartmann, C.S. (1972). Microwave

J. 15(5), 43.

Jurs, P.J., Kowalski, B.R., Isenhour, T.L., and Reilly, C.N.

(1969). Anal. Chem. 41, 691.

Kaiser, R. (1970). J. Mag. Res. 3, 28.

Kam, Z., Shore, H.B., and Feher, G. (1975). Rev. Sci. Instrum.

46, 269.

- Kelly, P.C., and Horlick, G. (1973). Anal. Chem. 45, 518.
- Kelly, P.C., and Horlick, G. (1974). Anal. Chem. 45, 2130.
- Kirmse, D.W., and Westerberg, A.W. (1971). Anal. Chem. 43, 1035.
- Kojima, H., and Fujiwara, S. (1971). Bull. Chem. Soc. Japan  
44, 2158.
- Korte, N.E., and Denton, M.B. (1973). Chemical Instrumentation  
5(1), 33.
- Lange, F.H. (1967). "Correlation Techniques", D. Van Nostrand,  
Princeton, N.J.
- Lee, Y.W. (1960). "Statistical Theory of Communication". John  
Wiley & Sons, New York, N.Y.
- Lee, Y.W., Cheatham, T.P. Jr., and Wiesmer, J.B. (1950). Proc.  
IRE 38, 1165.
- Magde, D., Elson, E., and Webb, W.W. (1972). Phys. Rev. Lett.  
29, 705.
- Magde, D., Elson, E., and Webb, W.W. (1974). Biopolymers 13, 29.

- Malmstadt, H.V., Enke, C.G., Crouch, S.R., and Horlick, G.  
(1974). "Optimization of Electronic Measurements",  
W.A. Benjamin, Menlo Park, CA.
- Martin, A.E. (1959). Spectrochim. Acta. 14, 97.
- McWilliam, I.G., and Bolton, H.C. (1969). Anal. Chem. 41, 1755.
- Menager, O., and Desormiere, B. (1975). Appl. Phys. Lett. 27, 1.
- Miller, G.L., Ramirey, J.V., Robinson, D.A.H. (1975). J. Appl.  
Phys. 46, 2638.
- Minami, S., Tsutsui, S., and Onoda, H. (1969). Appl. Opt. 8, 1217.
- Moore, L. (1968). Brit. J. Appl. Phys. 1(2), 237.
- Morrey, J.R. (1968). Anal. Chem. 40, 905.
- Ogata, A., and Matsura, K. (1974). Rev. Sci. Instrum. 45, 1077.
- Pao, Y.H., and Griffiths, J.E. (1967). J. Chem. Phys. 46, 1671.
- Pao, Y.H., Zitter, R.N., and Griffiths, J.E. (1966). J. Opt.  
Soc. Amer. 56, 1133.
- Pusey, P.N., Koppel, D.E., Schaefer, P.W., Camerini-Otero, R.D.,  
and Koenig, S.H. (1974). Biochemistry 13, 952.

Ramirez, R. (1975). *Electronics* 48(13), 98.

Rautian, S.G. (1958). *Soviet Physics Uspekki* 66(1), 245.

Reeder, T.M., and Gilden, M. (1973). *Appl. Phys. Lett.* 22, 8.

Root, W.L. (1970). *Proc. IEEE.* 58, 610.

Rosenbleth, W.A. (1959). "Processing Neuroelectric Data", The  
MIT Press, Cambridge, Mass.

Saksena, B.D., Agarwal, K.C., Pahwa, D.R., and Pradhan, M.M.  
(1968). *Spectrochim. Acta.* 24A, 1981.

Savitzky, A., and Golay, M.J.E. (1964). *Anal. Chem.* 36, 1627.

Shimizu, H. (1965). *J. Chem. Phys.* 43, 2453.

Singleton, R.S. (1969). *IEEE Trans. Audio Electroacoustics*  
AU-17, 166.

Stauffer, F.R., and Sakai, H. (1968). *Appl. Opt.* 7, 61.

Stockham, T.G. Jr., Cannon, T.M., and Ingebretsen, R.B. (1975).  
*Proc. IEEE* 63, 678.

Strojek, J.W., Yates, D., and Kuwana, T. (1975). *Anal. Chem.*  
47, 1050.

- Szoke, J. (1972). Chem. Phys. Lett. 15, 404.
- Talmi, Y. (1975). Anal. Chem. 47, 697A.
- Tanaka, T., and Benedek, G.B. (1975). Appl. Opt. 14, 189.
- Tiemann, J.J., Engeler, W.E., Baertsch, R.D., and Brown, D.M.  
(1974). Electronics 47(23), 113.
- Tominaga, H., Dojyo, M., and Tanaka, M. (1972). Nucl. Instrum.  
Meth. 98, 69.
- Tomlinson, B.L., and Hill, H.D.W. (1973). J. Chem. Phys. 59, 1775.
- Turin, G.L. (1960). IRE Trans. Information Theory, IT-6, 311
- Uzgiris, E.E. (1972). Opt. Commun. 6, 55.
- Uzgiris, E.E. (1974). Rev. Sci. Instrum. 45, 74.
- Vladimeroff, T. (1971). J. Chromatogr. 55, 175.
- Walter, H. Jr., and Flanigan, D. (1975). Appl. Opt. 14, 1423.
- Walters, J.P., and Malmstadt, H.V. (1966). Appl. Spectrosc.  
20, 193.
- Ware, B.R., and Flygare, W.H. (1971). Chem. Phys. Lett. 12, 81.

Ware, B.R., and Flygare, W.H. (1972). J. Coll. Interf. Sci.

39, 670.

Wijnaendts van Resandt, R.W. (1974). Rev. Sci. Instrum. 45, 1507.

Williams, D.T., and Kolitz, B.L. (1968). Appl. Opt. 7, 607.

Wolf, E. (1965). Japan J. of Appl. Phys. 4 (Sup 1), 1.

Yule, H.P. (1972). Anal. Chem. 44, 1245.

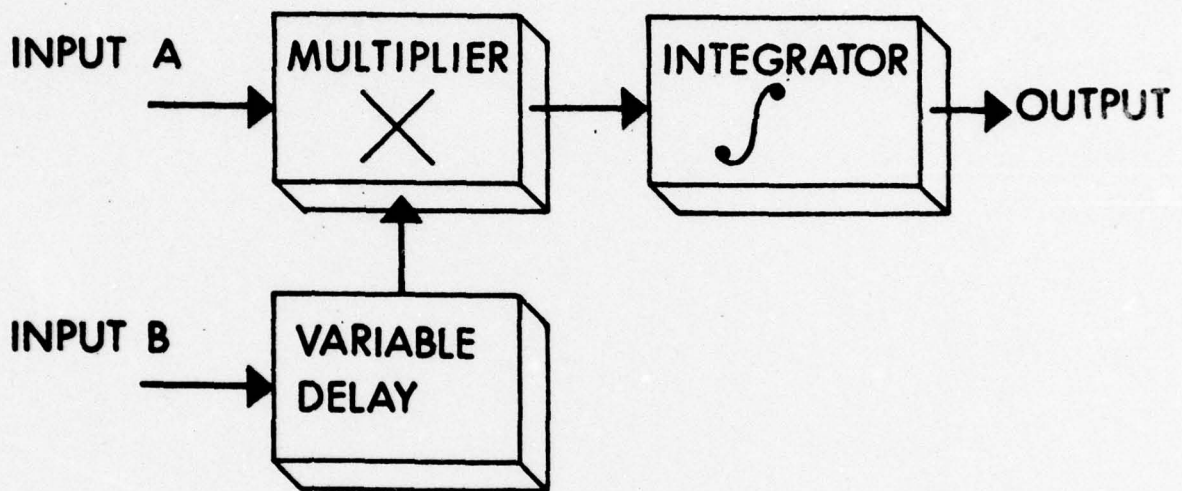
FIGURE CAPTIONS

- Figure 1      Block diagram of a simple correlator.
- Figure 2      Autocorrelation of a sine wave.
- Figure 3      Autocorrelation function of a sine wave.
- Figure 4      Autocorrelation of a square wave.
- Figure 5      Autocorrelation of a rectangular pulse.
- Figure 6      Cosine autocorrelation images.
- Figure 7      Autocorrelation of a random waveform.
- Figure 8      Autocorrelation function of bandlimited noise (a)  
and of a noisy sine wave (b).
- Figure 9      Cross-correlation function of two sine waves.
- Figure 10     Cross-correlation of a sine and square wave  
(lock-in amplifier) at  $\tau = 0$ .
- Figure 11     Convolution and correlation of a step waveform  
with an exponential instrument response function.
- Figure 12     FFT outputs resulting from Fourier transformation  
of a simple peak signal. The phase spectrum (12e)  
is modulo  $2\pi$ .
- Figure 13     Fourier domain digital filters.
- Figure 14     Second derivative (a) and "deconvolution" (b)  
Fourier domain digital filters.
- Figure 15     Smoothing of a signal by direct cross-correlation  
(a,b,c) and by Fourier domain digital filtering  
(a,d,e,f,c).
- Figure 16     Removal and analysis of high frequency noise on  
a signal.

- Figure 17 Removal of fixed frequency noise (a,b,c) and minimization of quantizing noise (d,e,f) by Fourier domain digital filtering.
- Figure 18 Fourier domain smoothing functions and the resulting smoothed peak. The original peak is shown in Figure 15a.
- Figure 19 Low signal-to-noise ratio peak signals and the smoothed peaks as determined by cross-correlation with a noise free peak (matched filter).
- Figure 20 Effects of conventional and modified Fourier transform smoothing algorithms on an exponential decay function. (Hayes et al., 1973).
- Figure 21 First derivative of a spectrum. The Fourier domain differentiating filter (b) is applied in a manner analogous to that depicted in Figure 15.
- Figure 22 Resolution enhancement using a "first derivative" type Fourier domain digital filter.
- Figure 23 Resolution enhancement using a Fourier domain second derivative digital filter.
- Figure 24 Spectral response function (a) and its Fourier transform (b).
- Figure 25 A Fourier domain deconvolution digital filter.
- Figure 26 Deconvolution of the noisy Lorentzian doublet shown in Figure 23b.

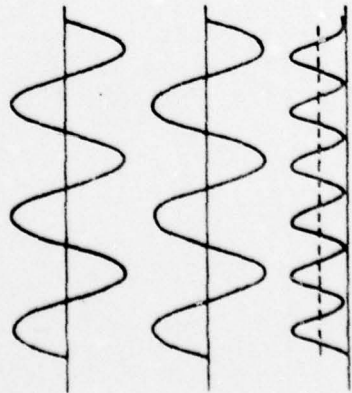
- Figure 27      Pattern detection by cross-correlation. (a) Signal waveform, (b) sought-for pattern, (c) cross-correlation function.
- Figure 28      Cobalt, nickel and iron spectra.
- Figure 29      Cross-correlation functions for Co and Co (a), Co and Ni (b), and Co and Fe (c) spectra.
- Figure 30      Block diagram of noise autocorrelation measurement system for photocurrents.
- Figure 31      Linearity of the shot noise autocorrelation measurement system.
- Figure 32      Chart records illustrating the effect of impulse noise on a lock-in amplifier output. Arrows indicate introduction of impulses. (a) 10 sec time constant, (b) 1 sec time constant.
- Figure 33      Illustration of the effect of impulse noise on the correlator output. Effective time constant was 13 sec.
- Figure 34      Determination of system impulse response and frequency characteristics using random noise.
- Figure 35      Block diagram of a correlation measurement system for the measurement of decaying exponentials (Miller et al., 1975).
- Figure 36      Block diagram of a minicomputer data acquisition system applicable to laboratory correlation measurements.

- Figure 37 Basic analog correlators.
- Figure 38 Typical function generators for (a) a gate waveform and (b) a decaying exponential.
- Figure 39 (a) Correlator for repetitive signals.  
(b) Binary pattern correlator (digital scanning boxcar integrator).
- Figure 40 General purpose hybrid correlator.
- Figure 41 Photograph of a 512 element photodiode array.
- Figure 42 Schematic of photodiode array.
- Figure 43 Block diagram of the cross-correlation readout system (a) and schematic waveforms at points X and Y (b).
- Figure 44 Function generator (a) and schematic representation of output waveforms from the gate monostables (b). (resistor values are in  $k\Omega$ )
- Figure 45 Resolution enhancement (a) and differentiation (b) using the cross-correlation readout system.
- Figure 46 Schematic of a diode array serial analog memory.
- Figure 47 Tapped analog delay line.
- Figure 48 Schematic of CCD operation.



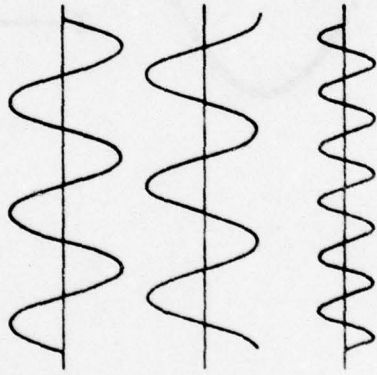
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$\tau = 0^\circ$



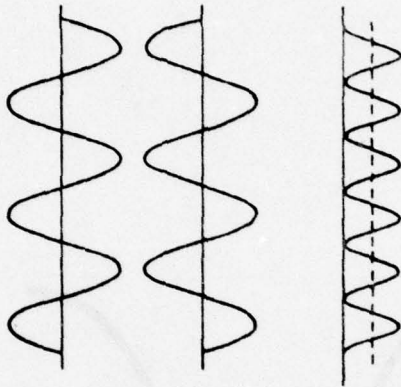
(a)

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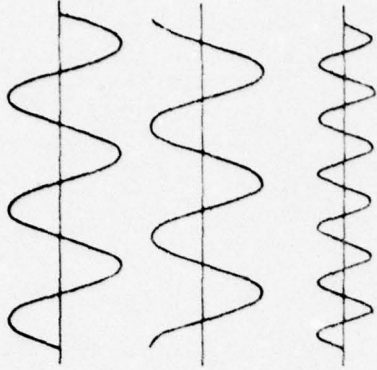
(b)

$\tau = 180^\circ$



(c)

$\tau = 270^\circ$



(d)

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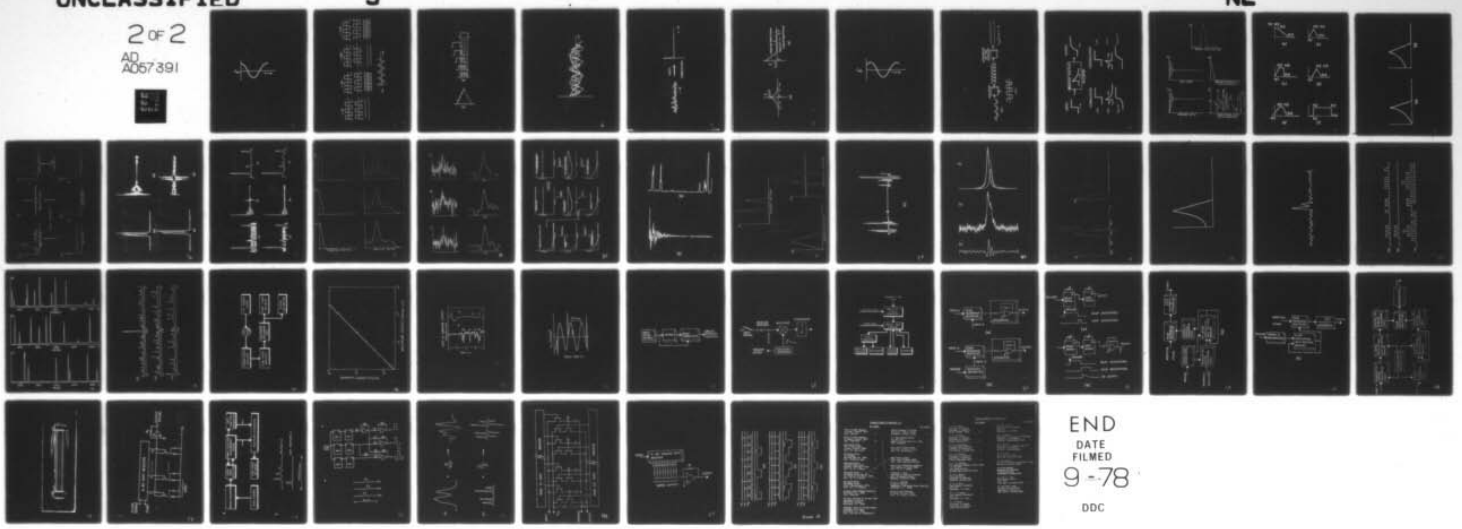
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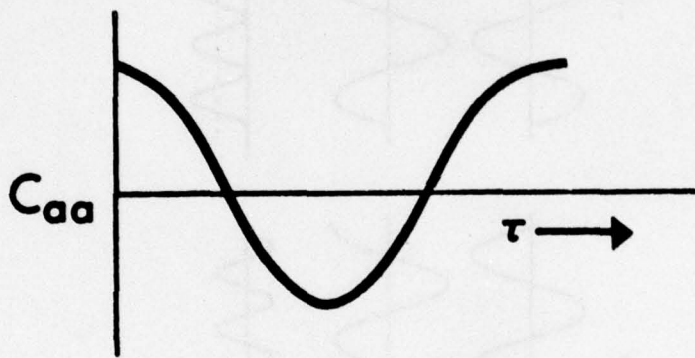
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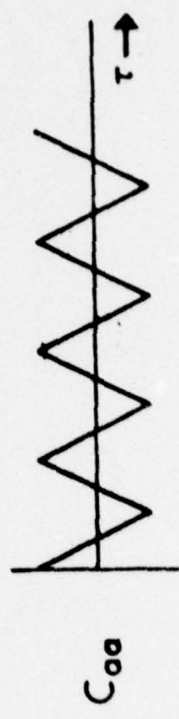
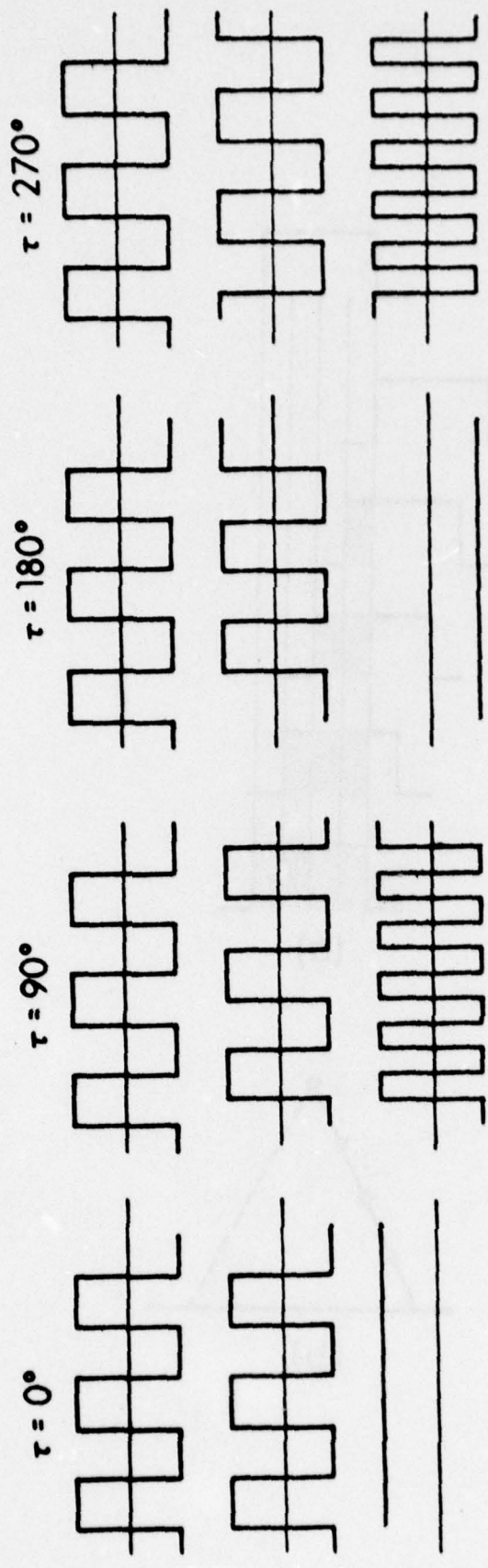


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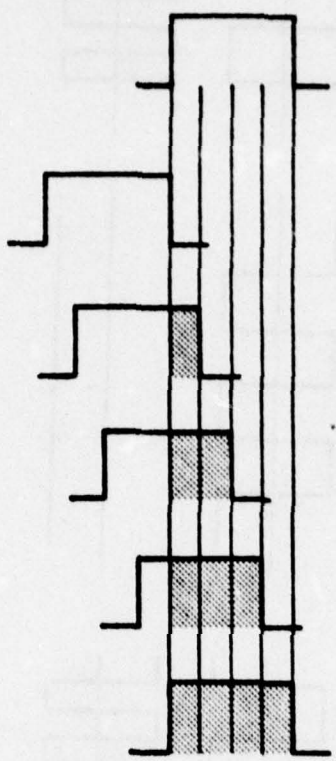
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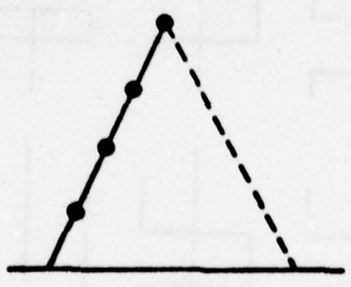


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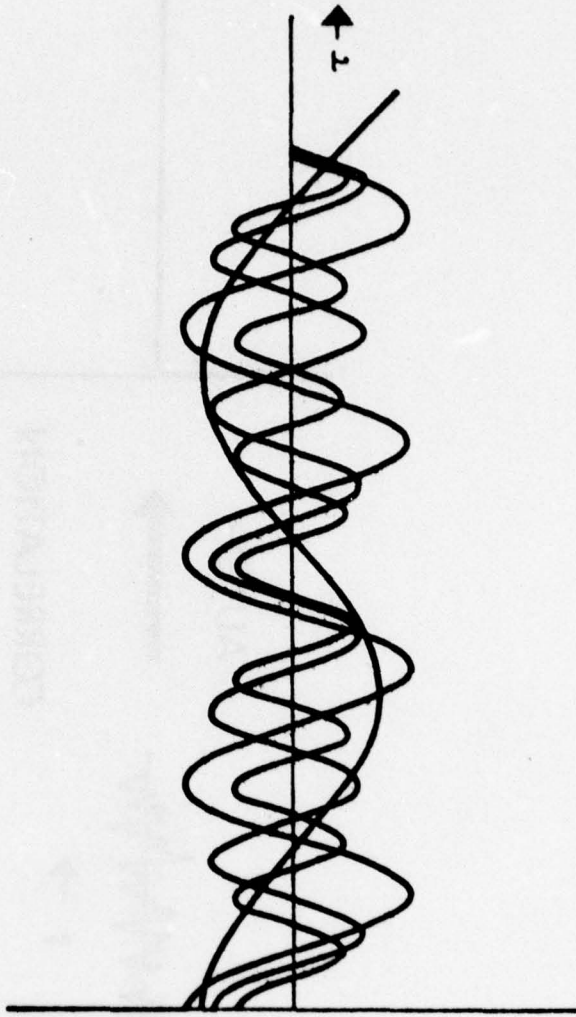


(a)



(b)

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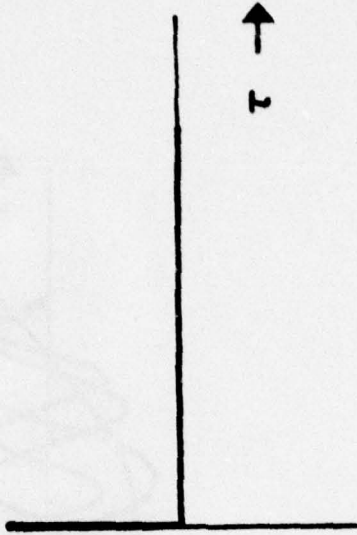


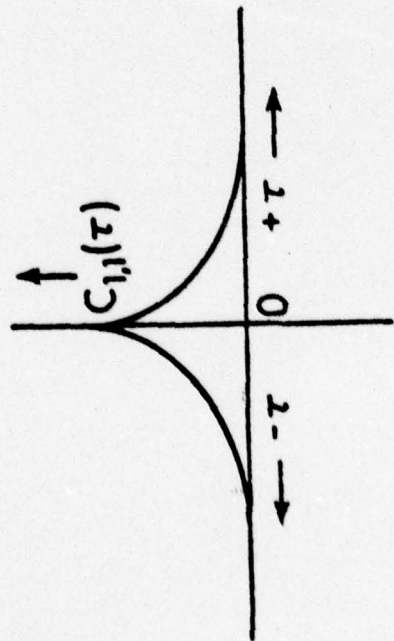
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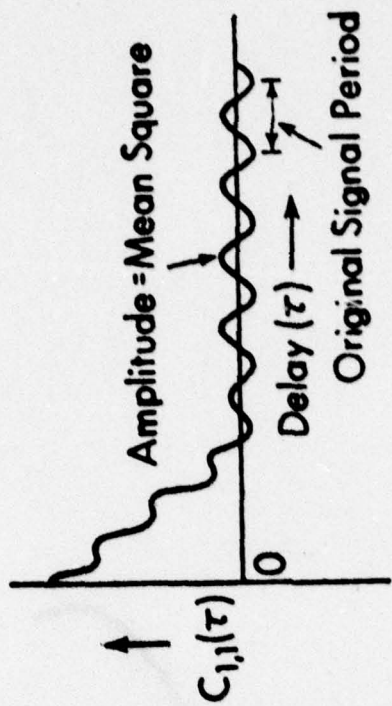


CORRELATION





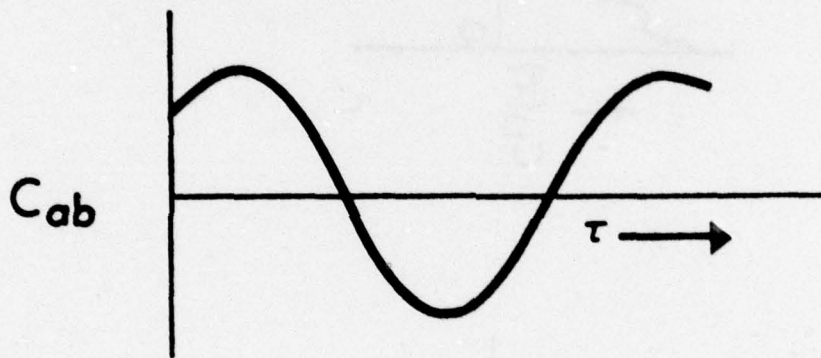
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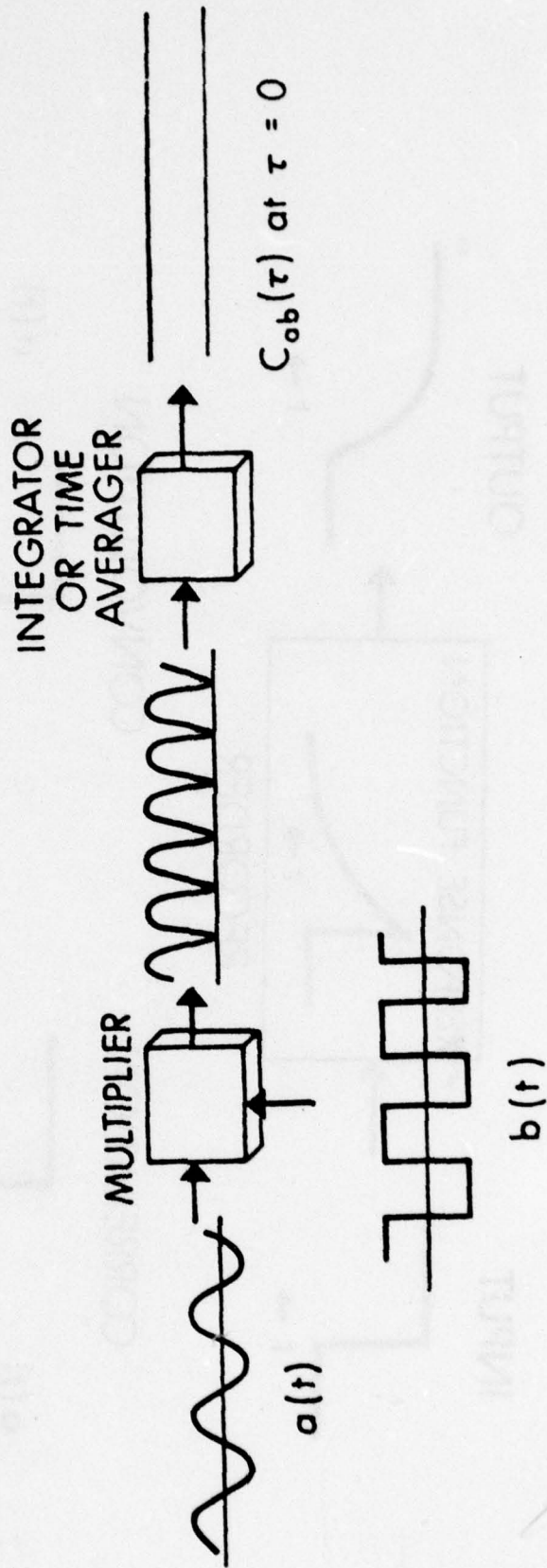
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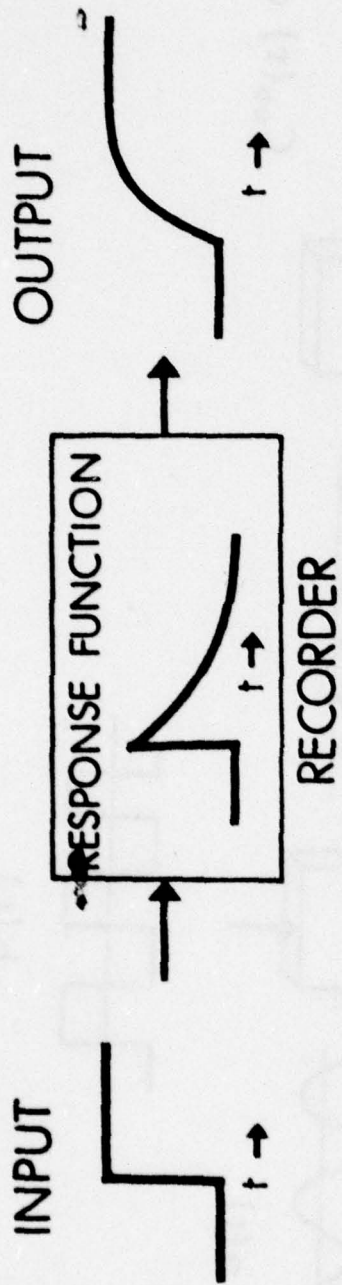
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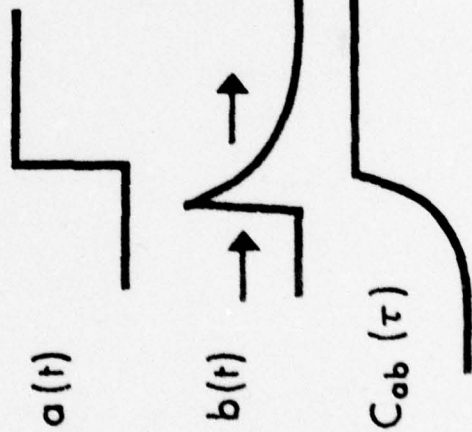


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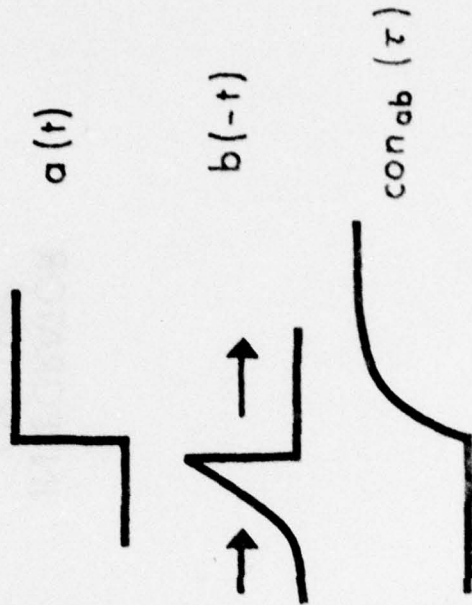


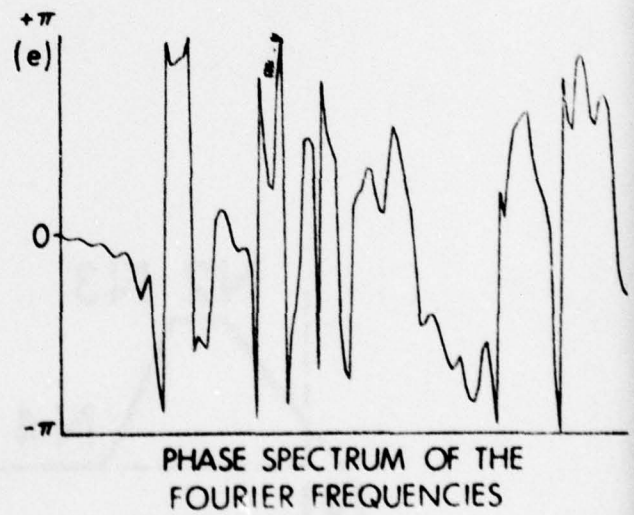
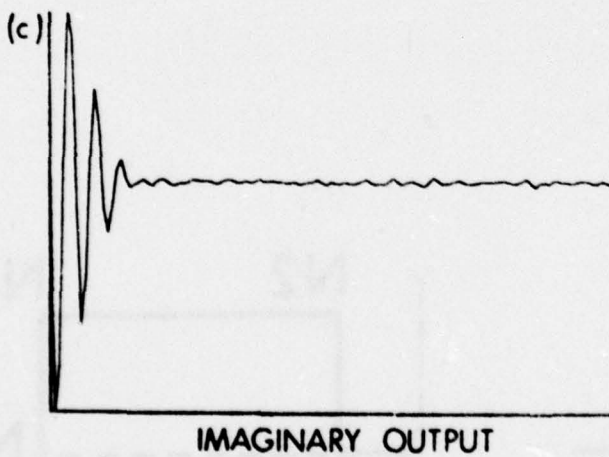
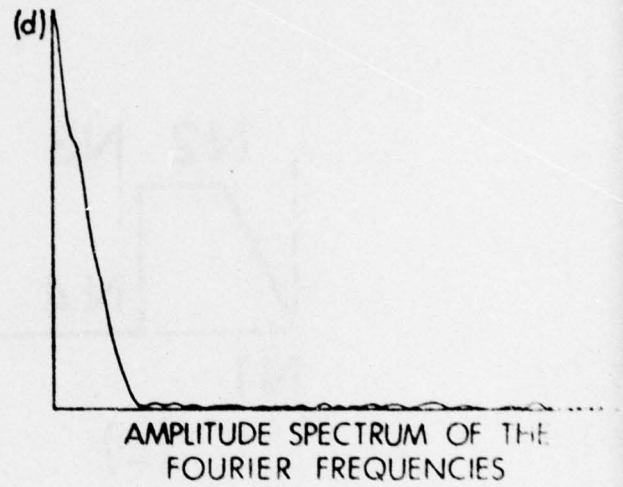
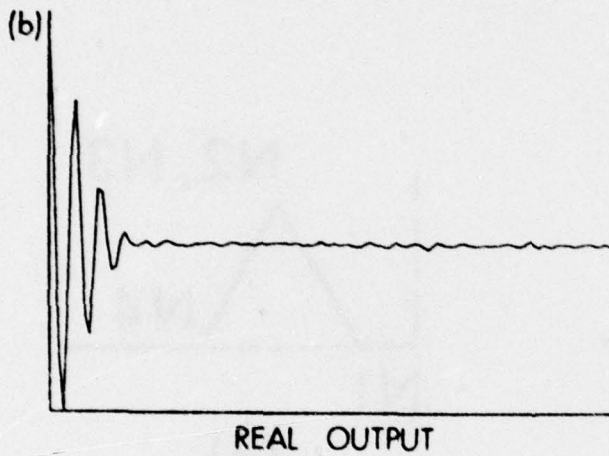
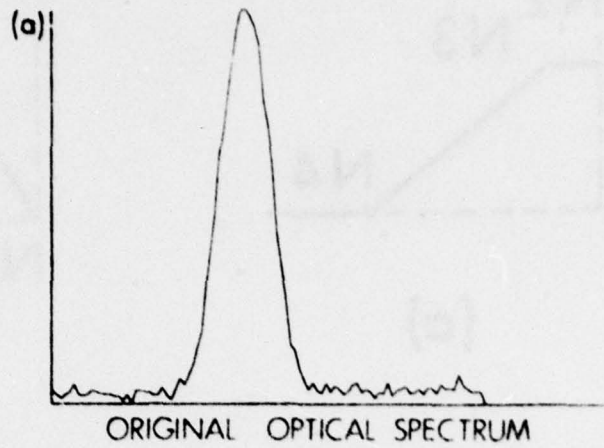


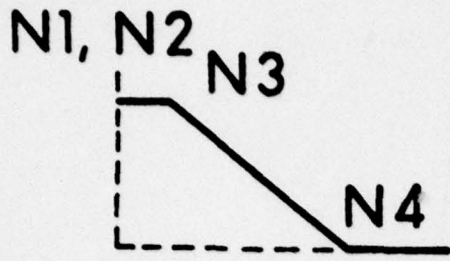
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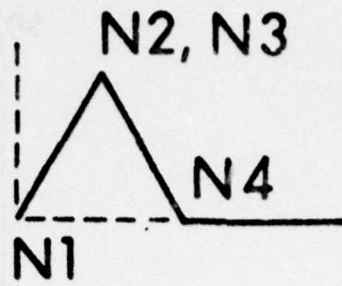
CONVOLUTION



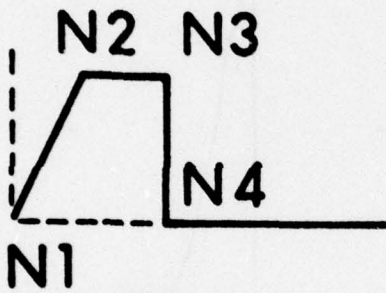




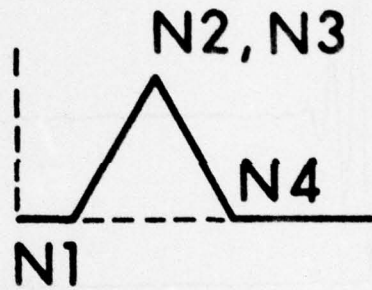
(a)



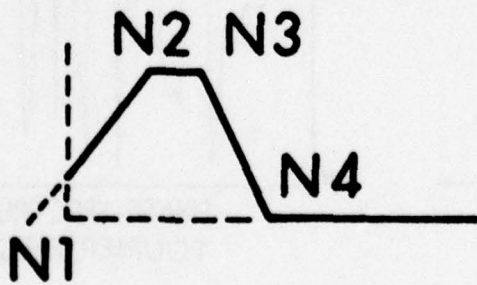
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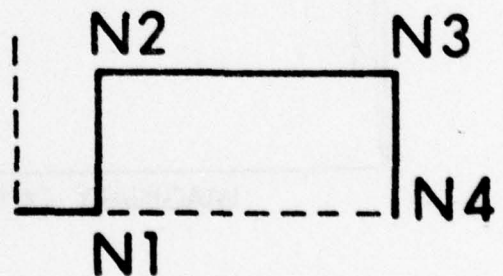
(c)



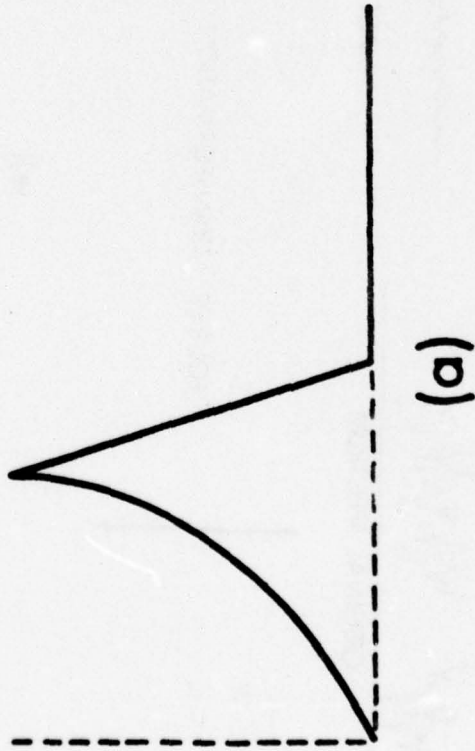
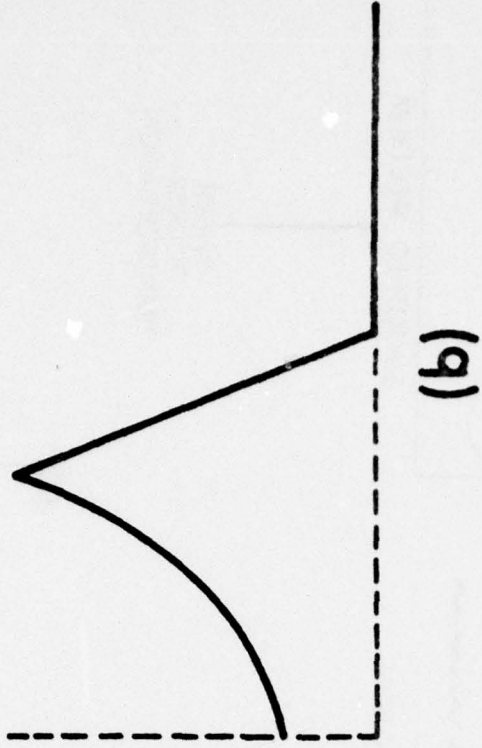
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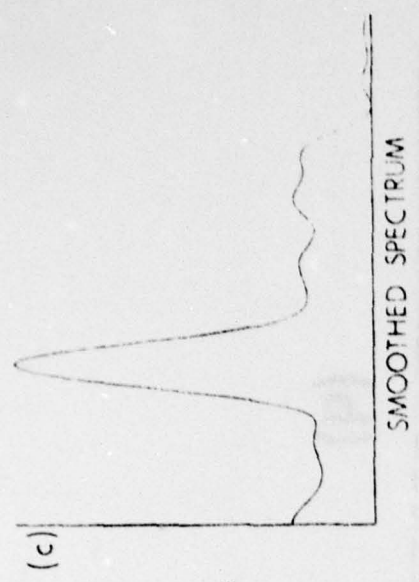
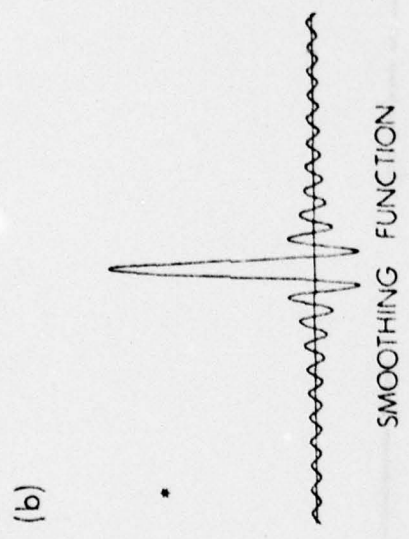
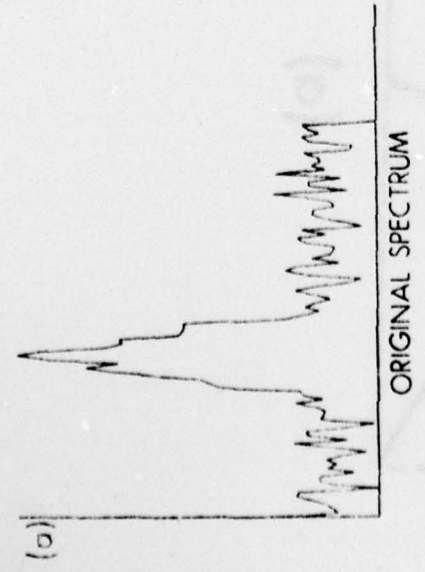


(e)



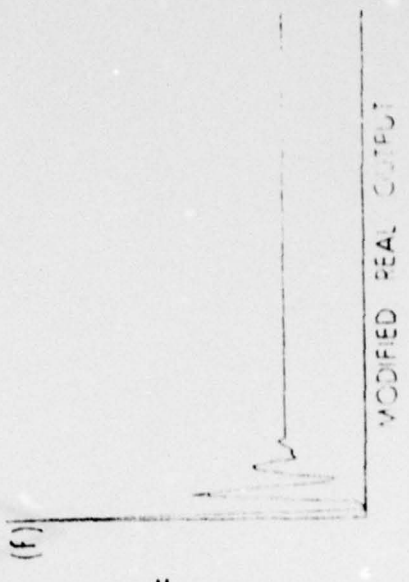
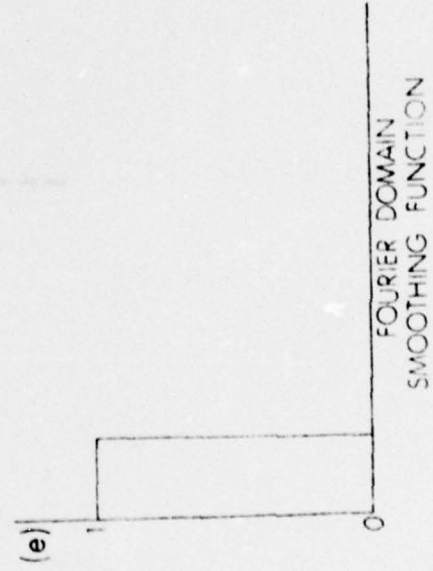
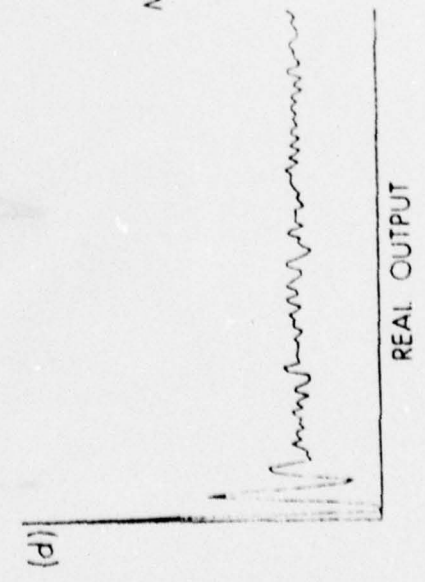
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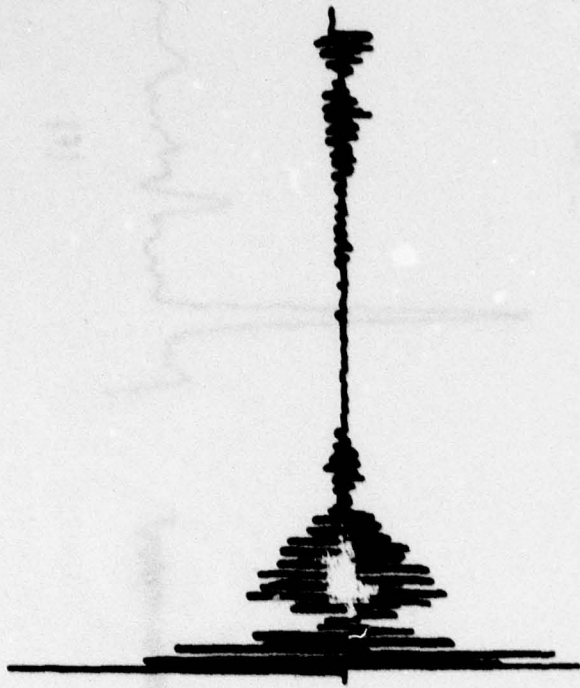


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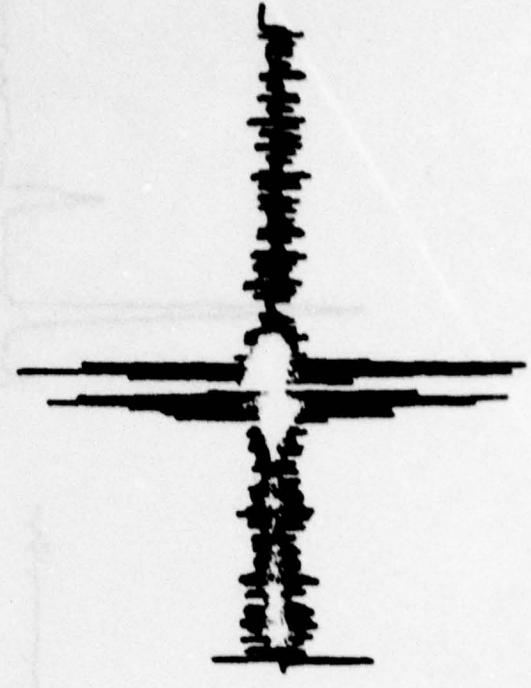
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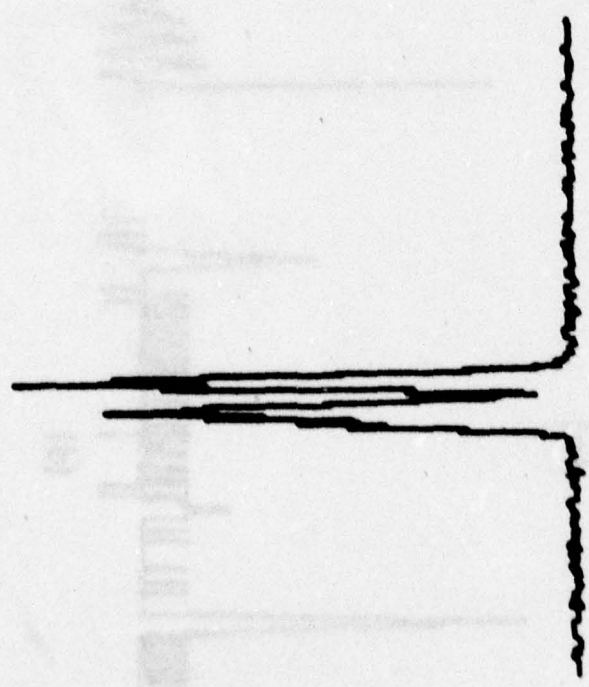
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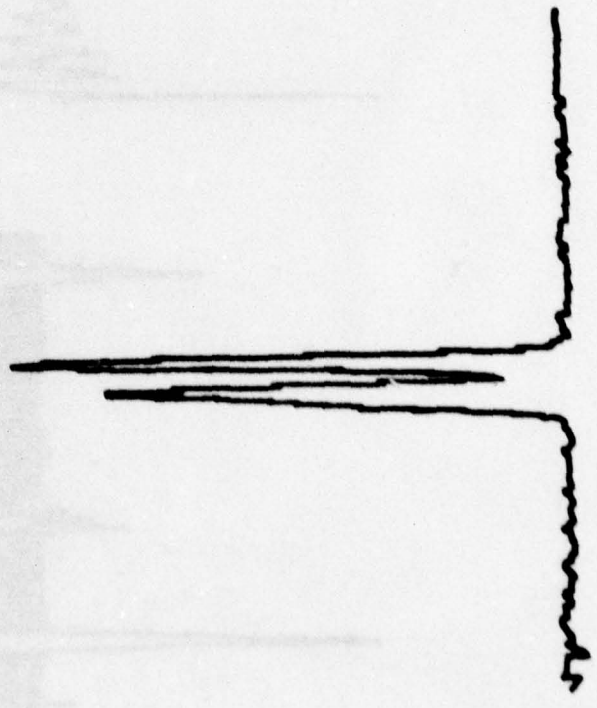
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(d)

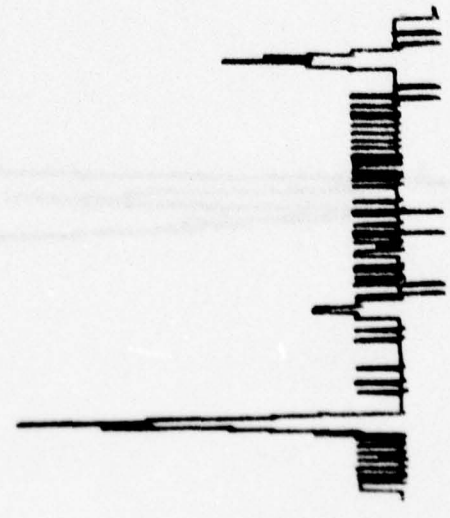
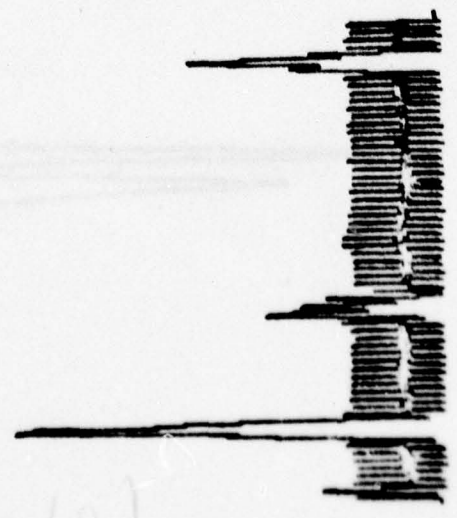
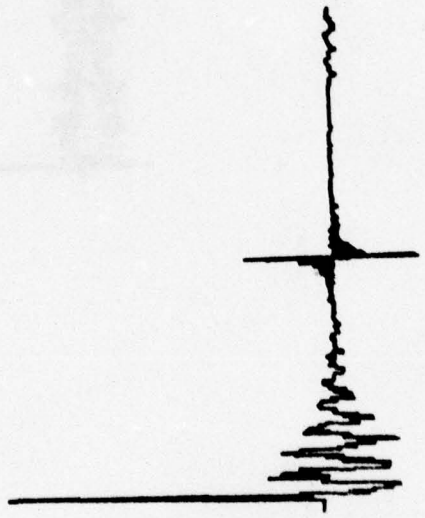
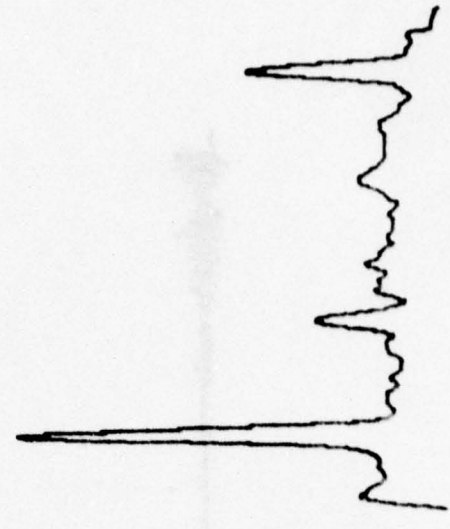
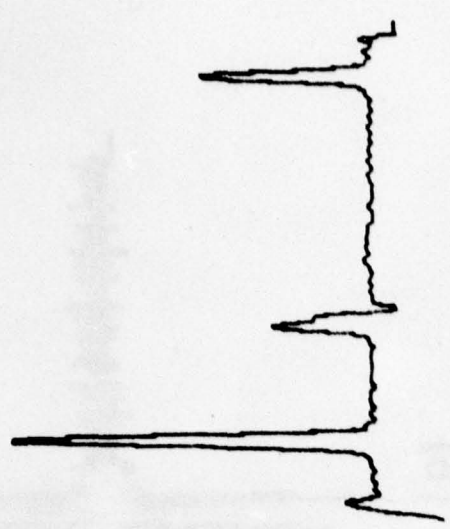


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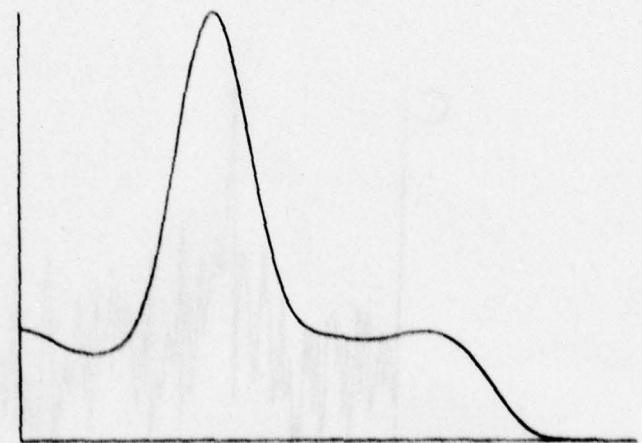
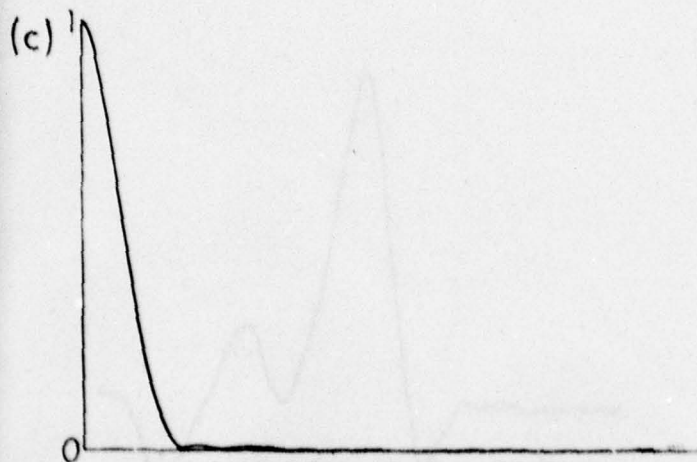
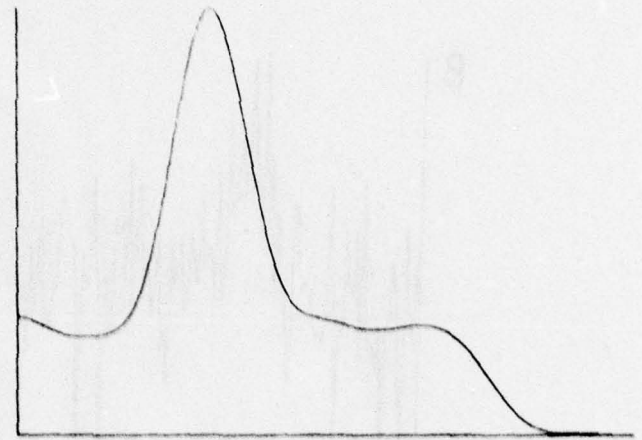
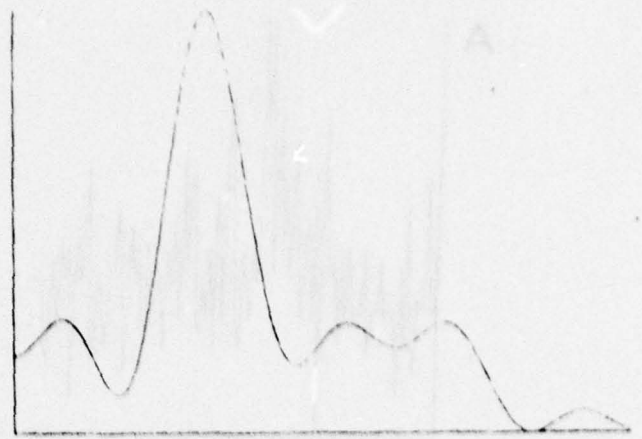
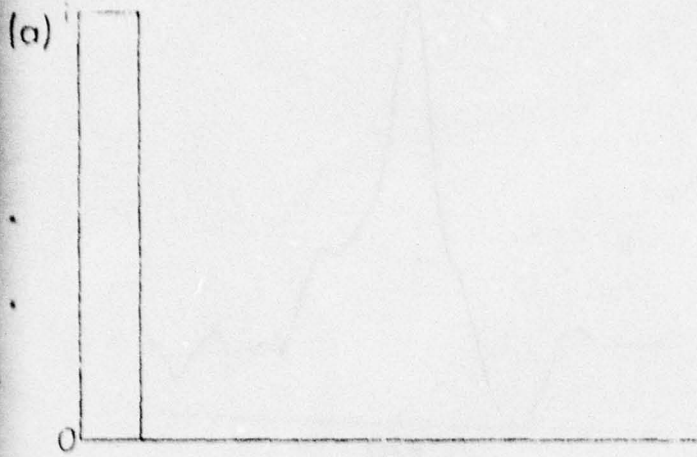


(c)

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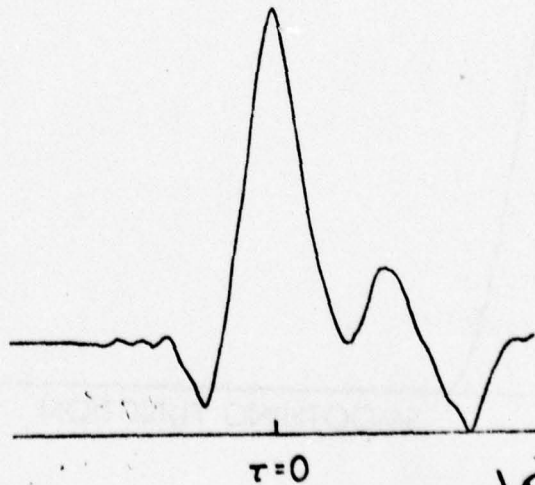
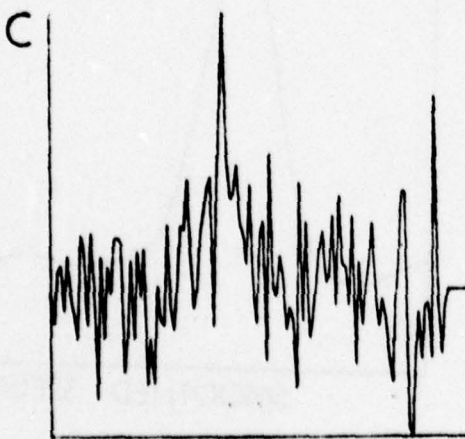
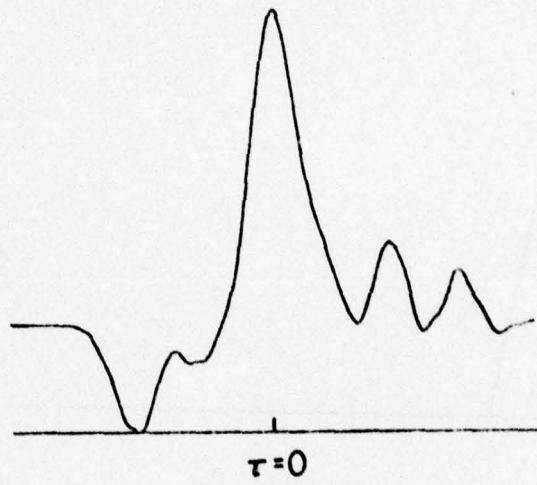
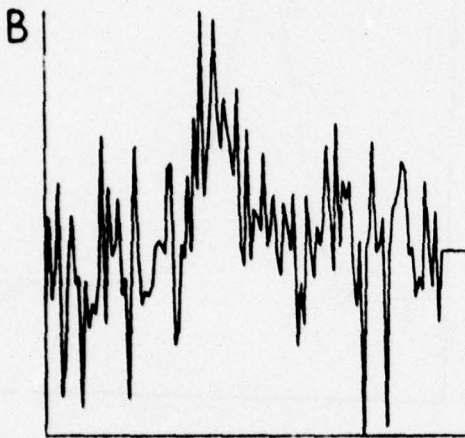
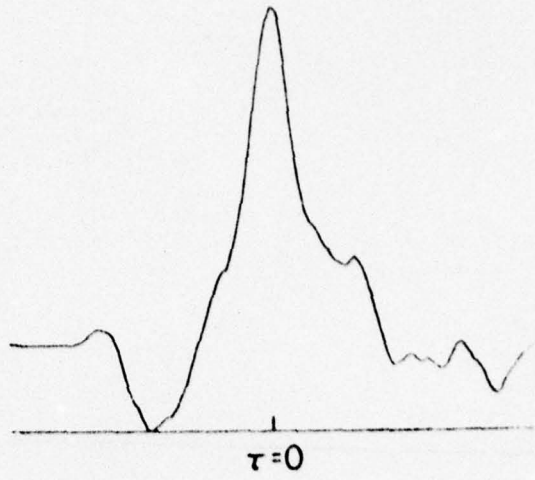
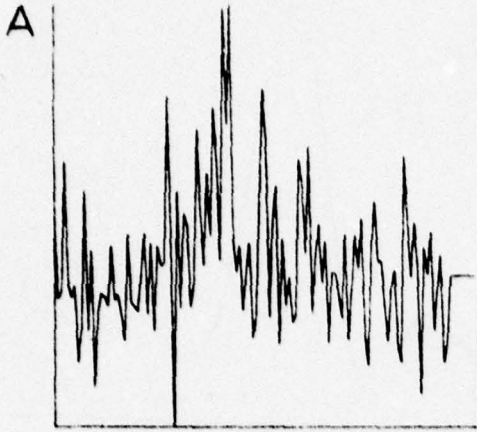


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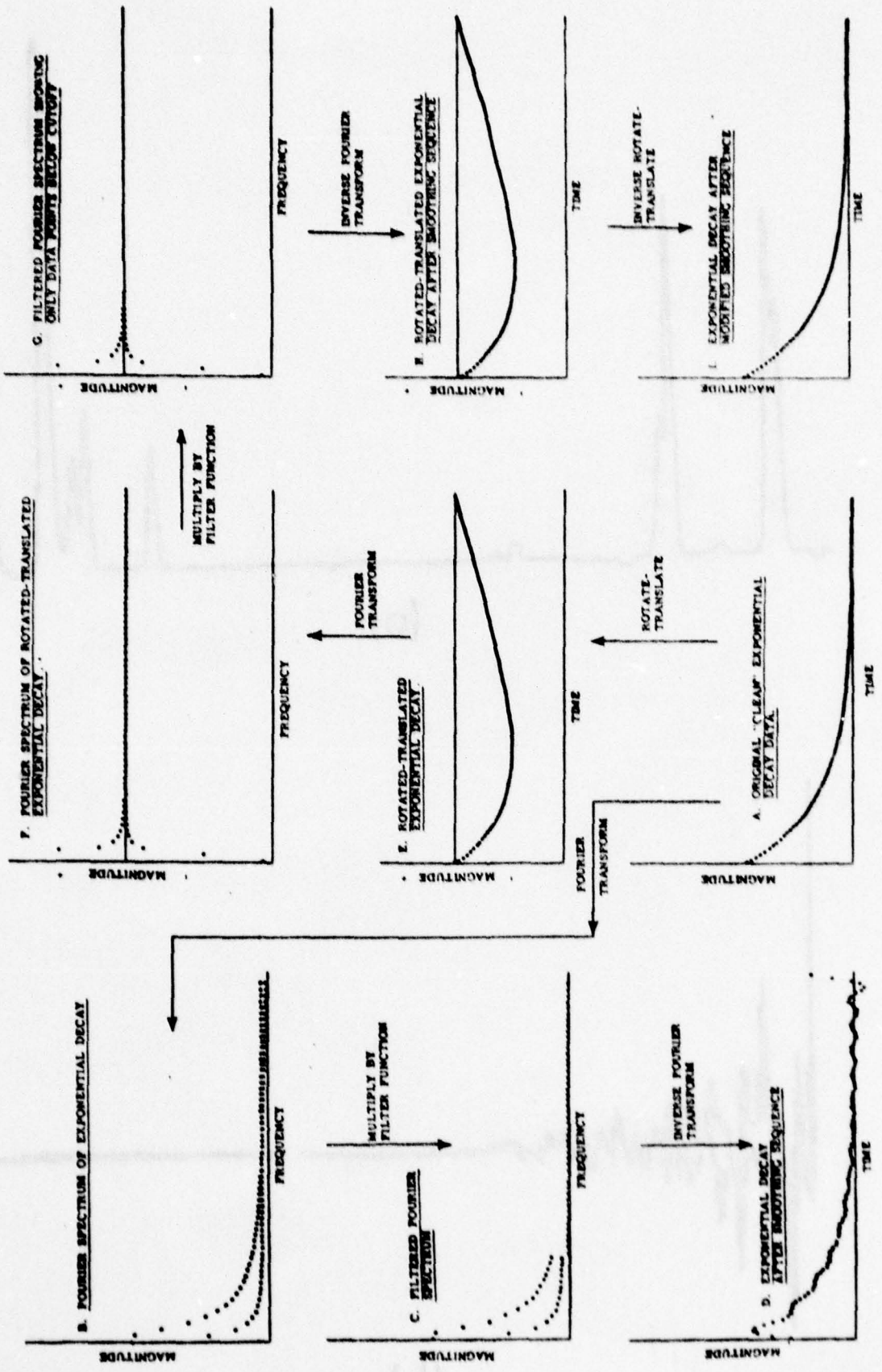
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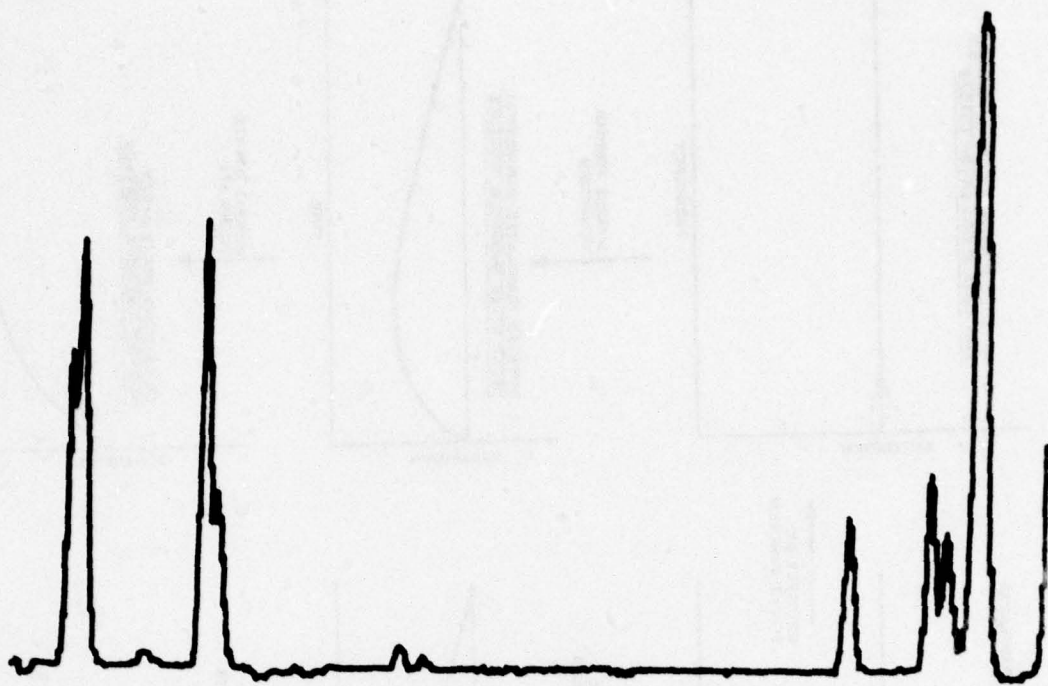
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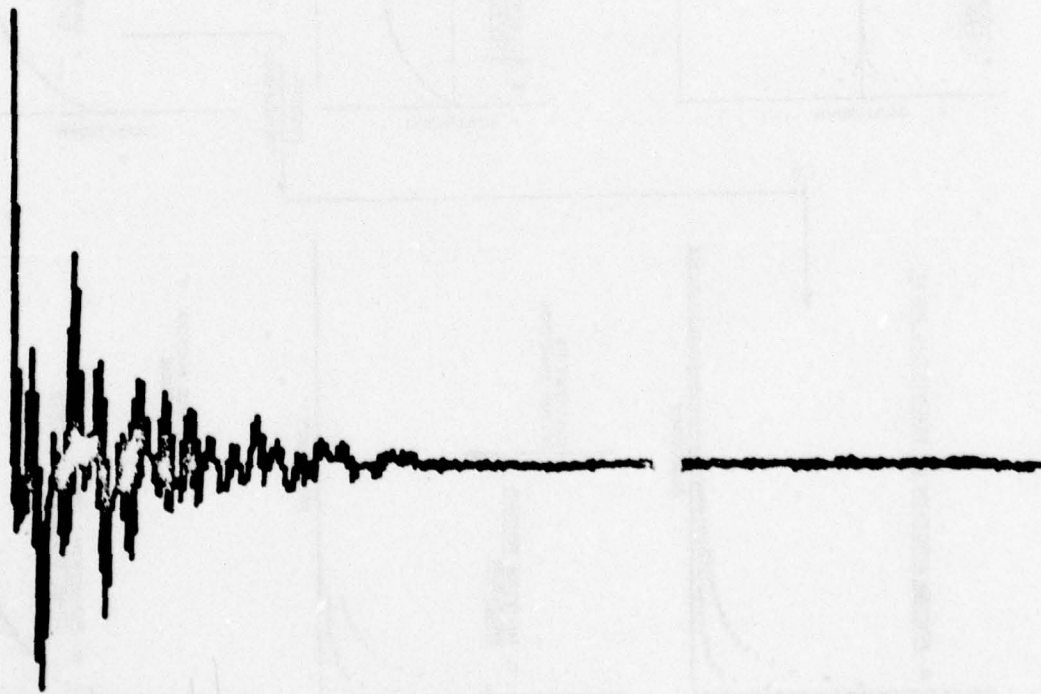
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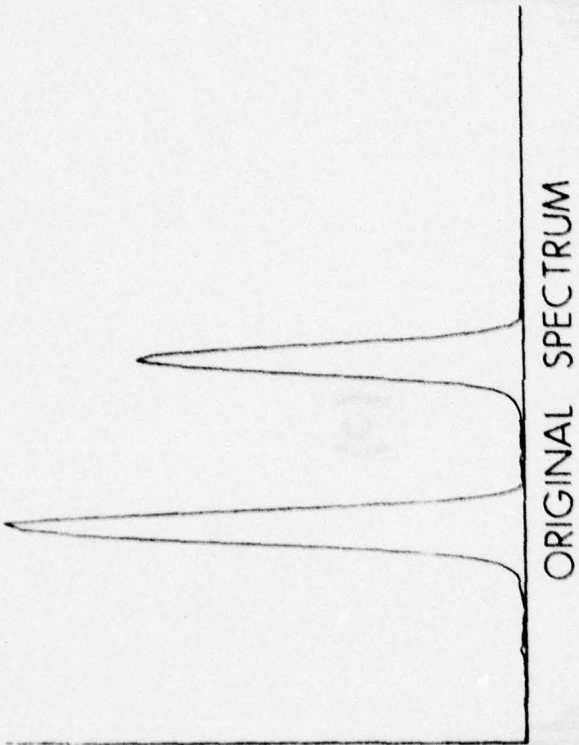


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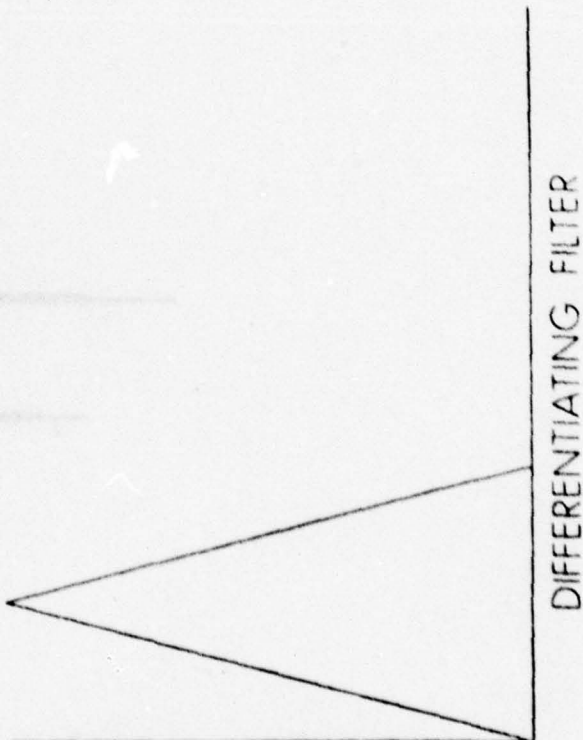
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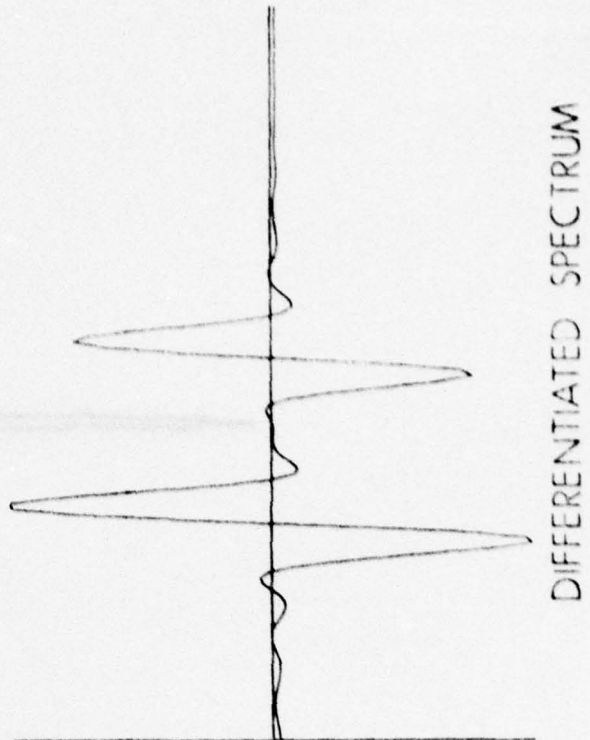
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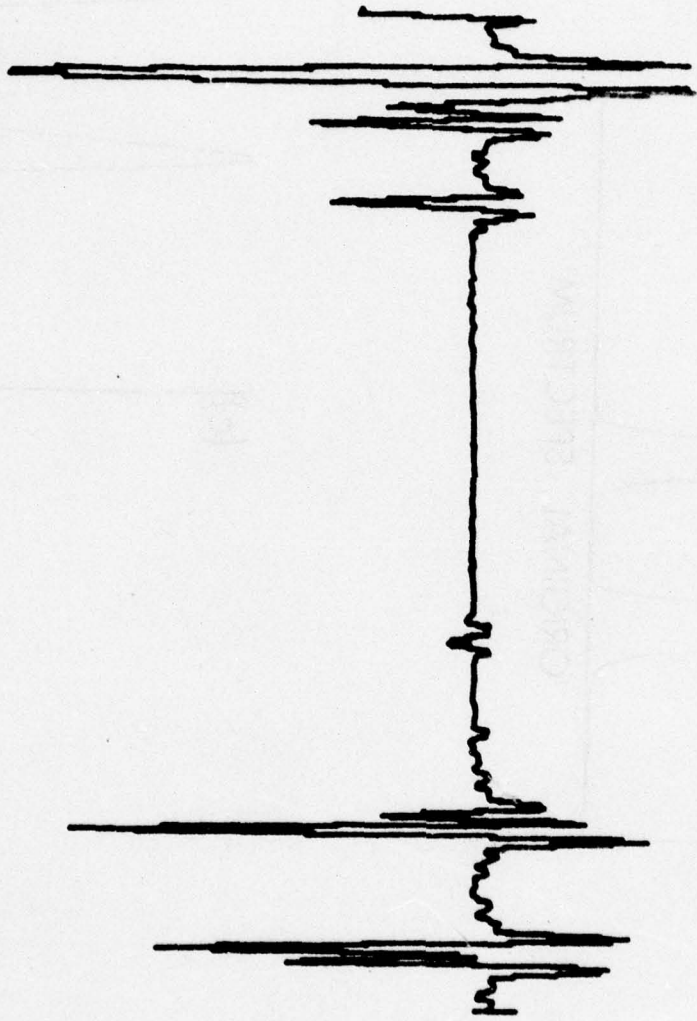
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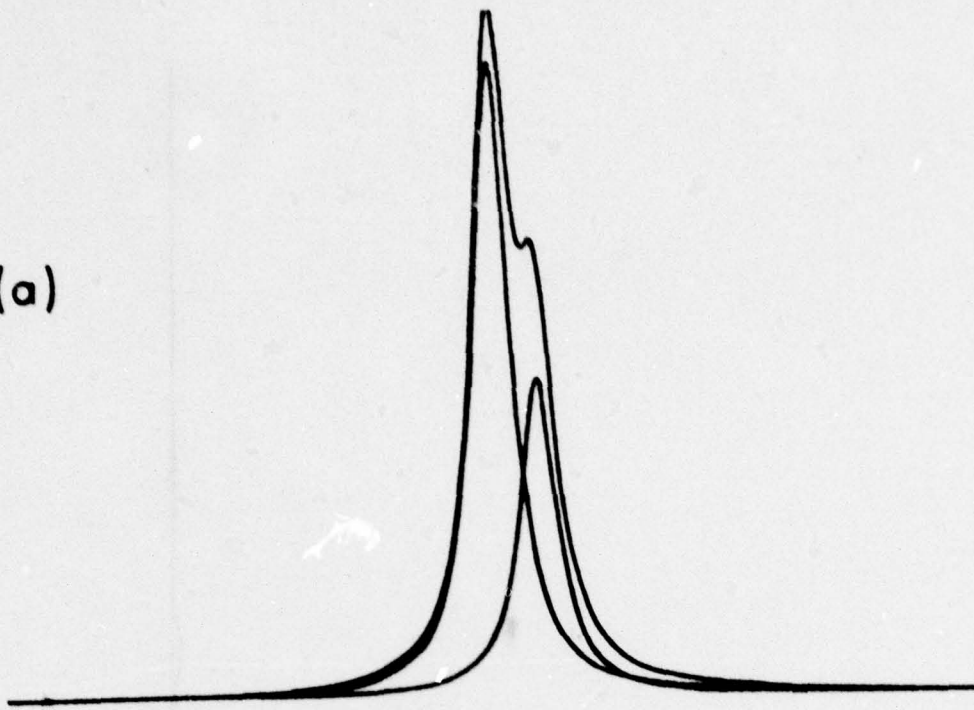


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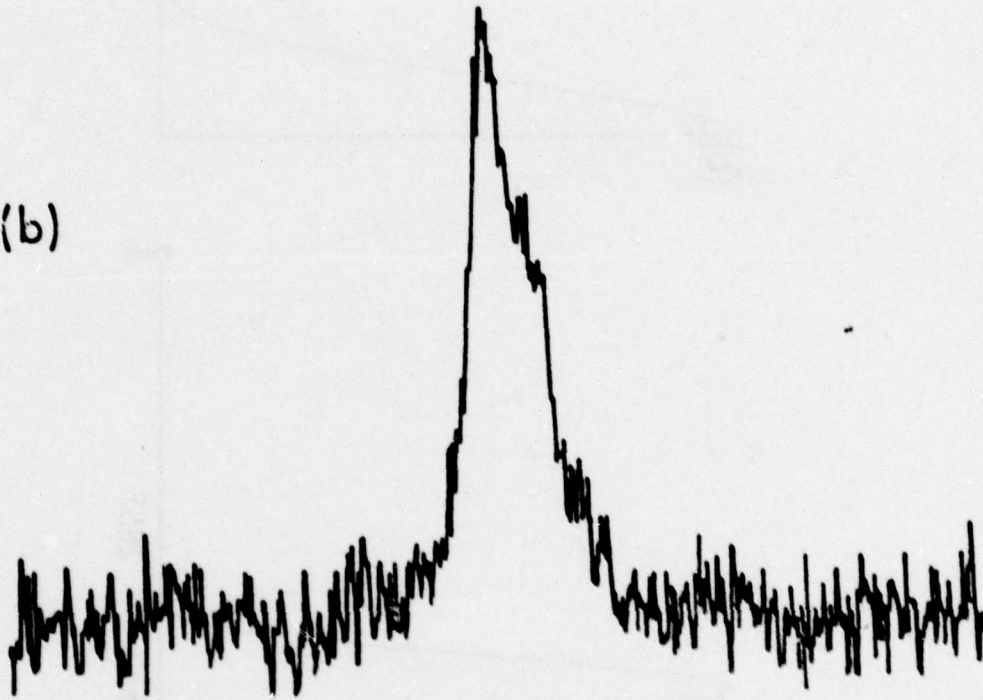


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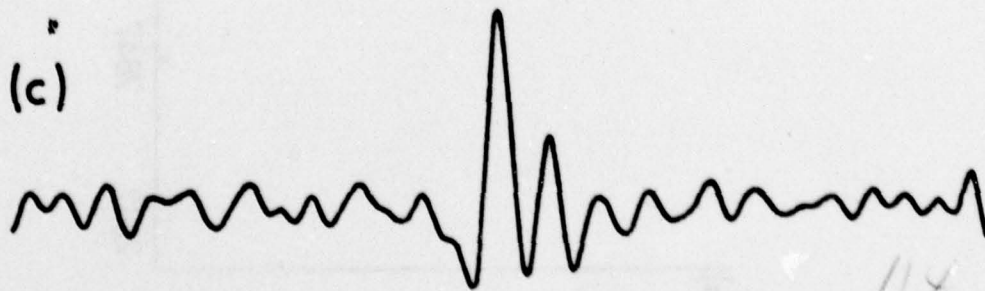
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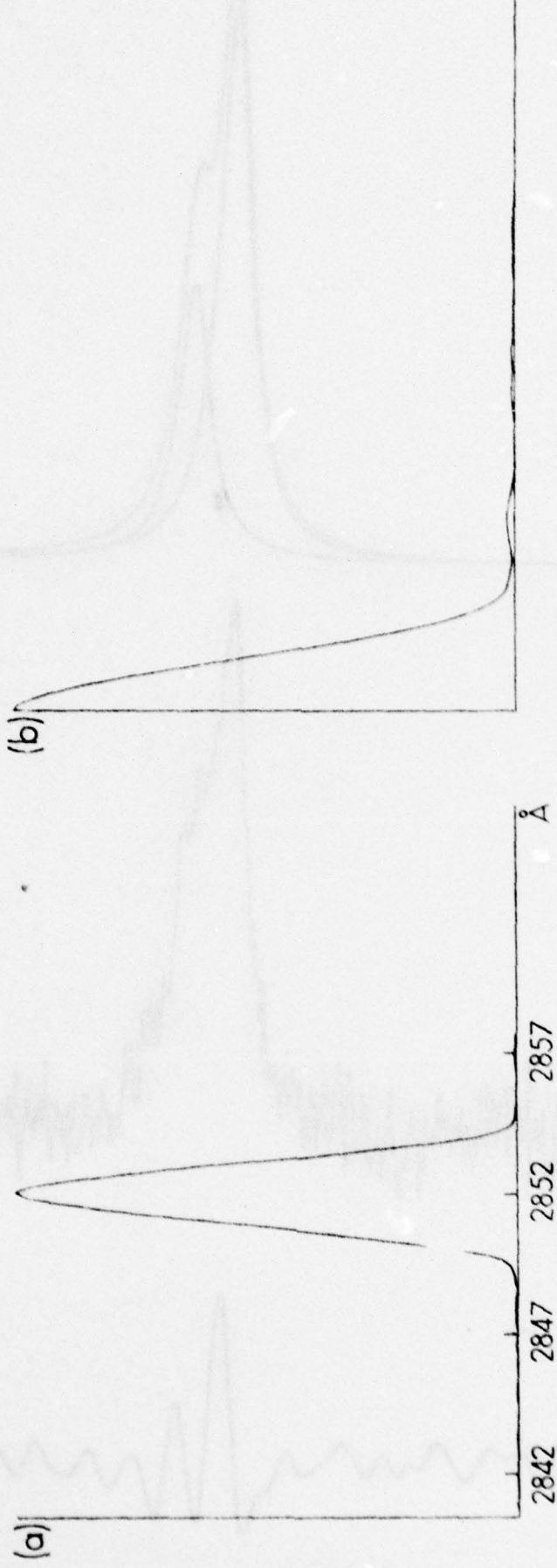


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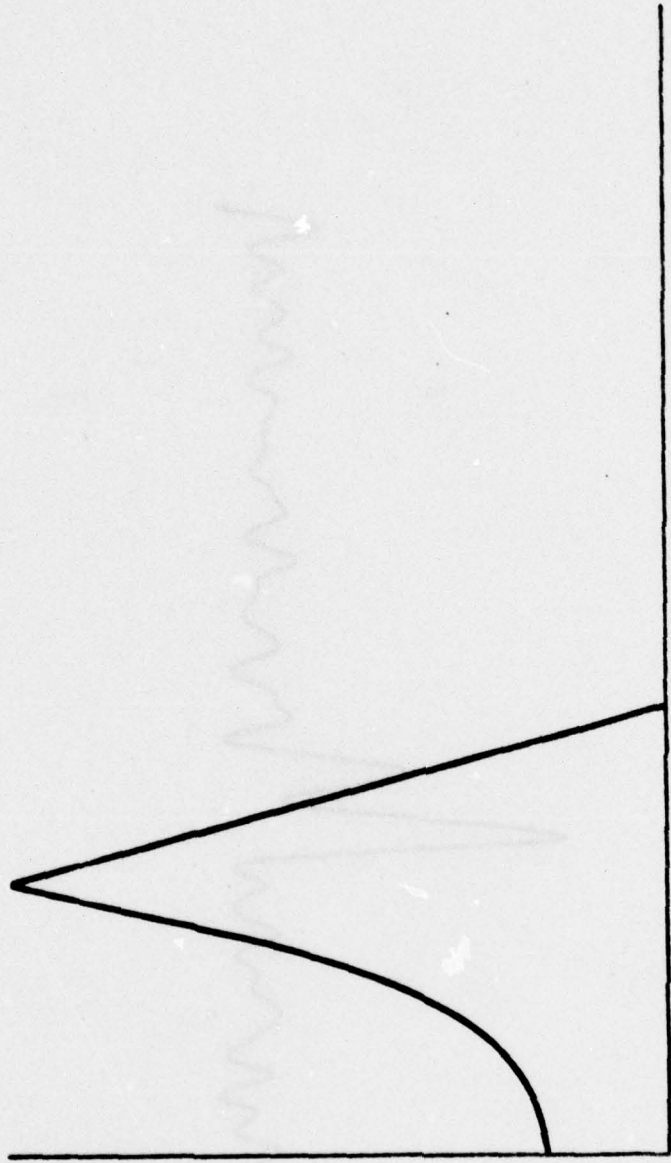


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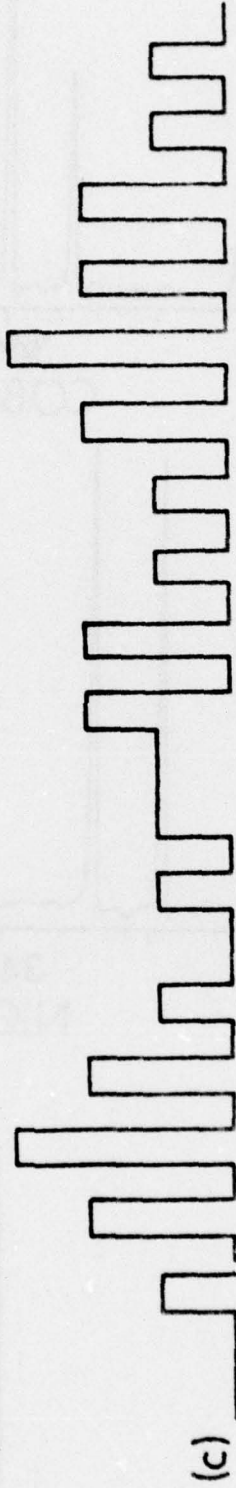
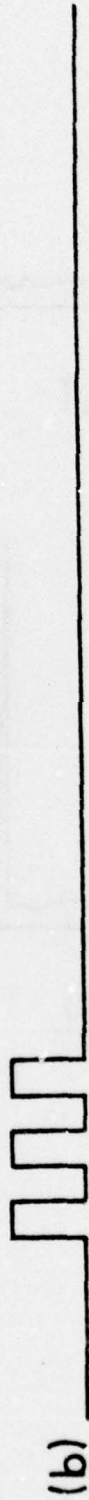


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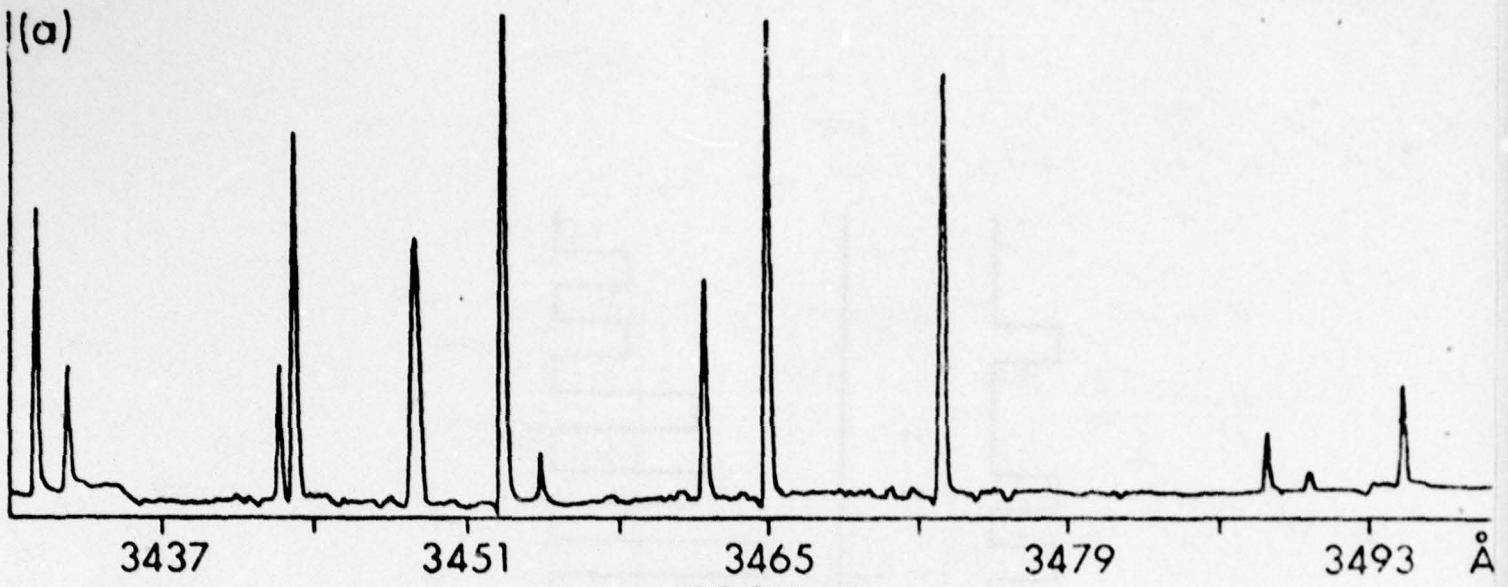
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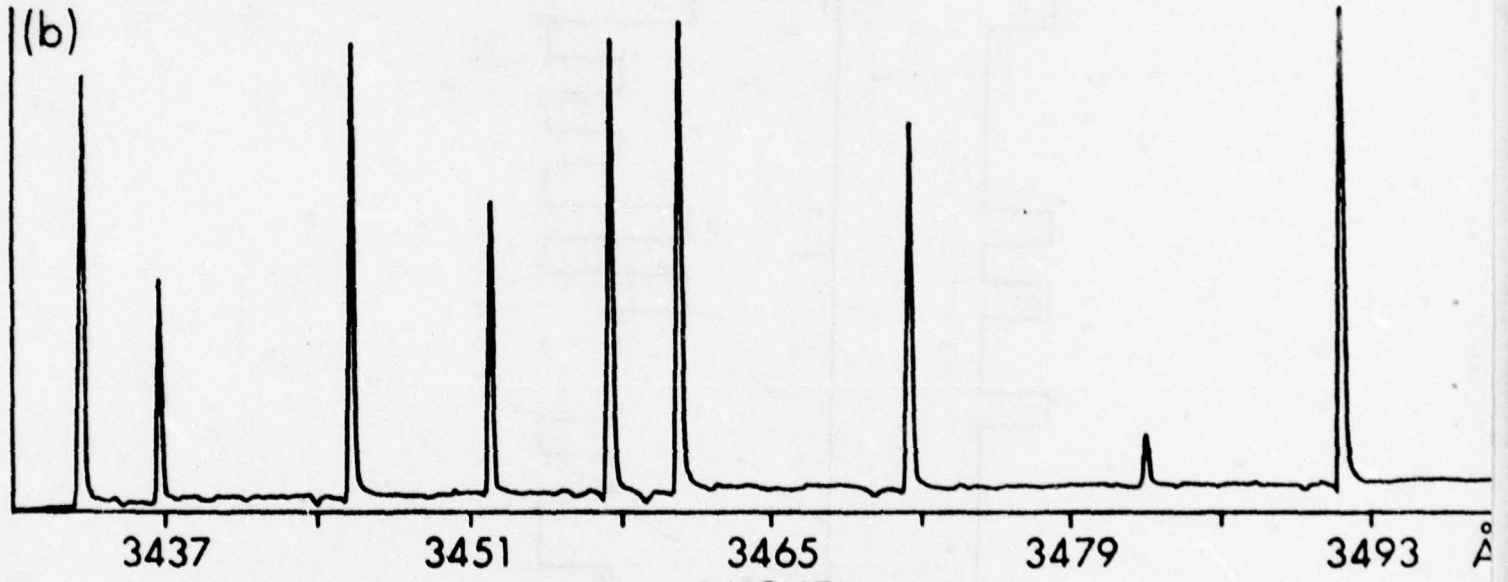


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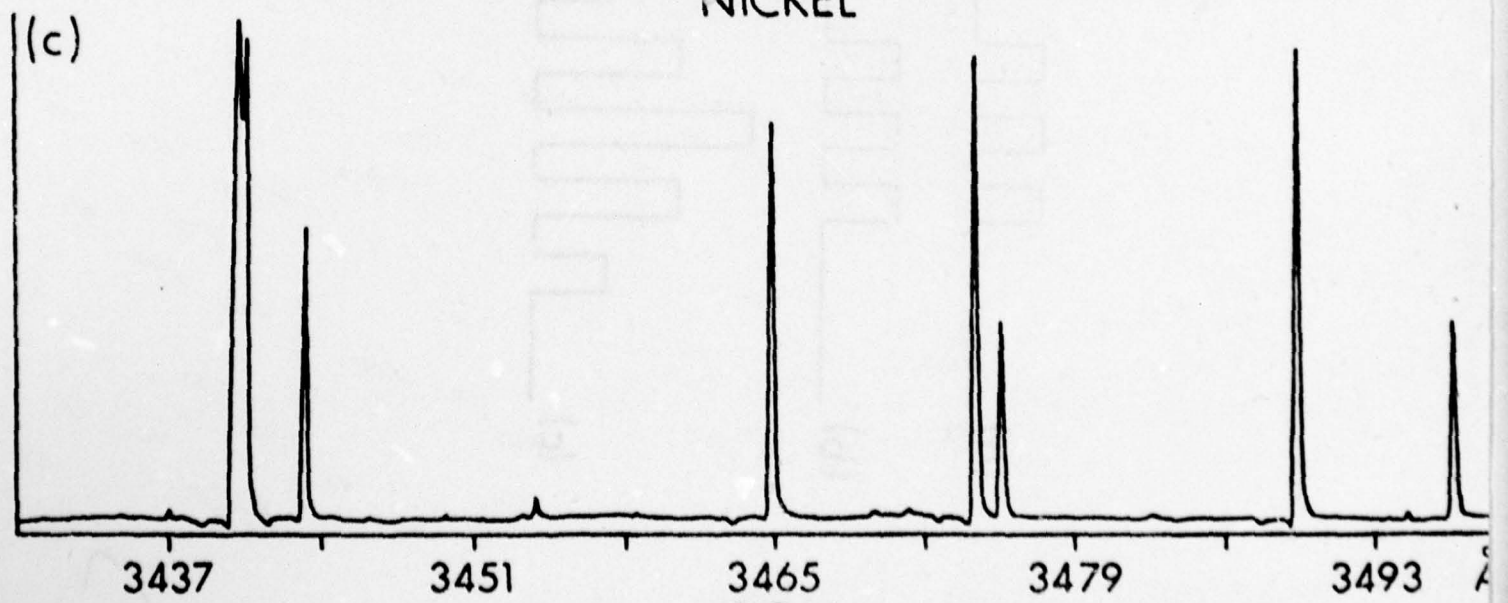
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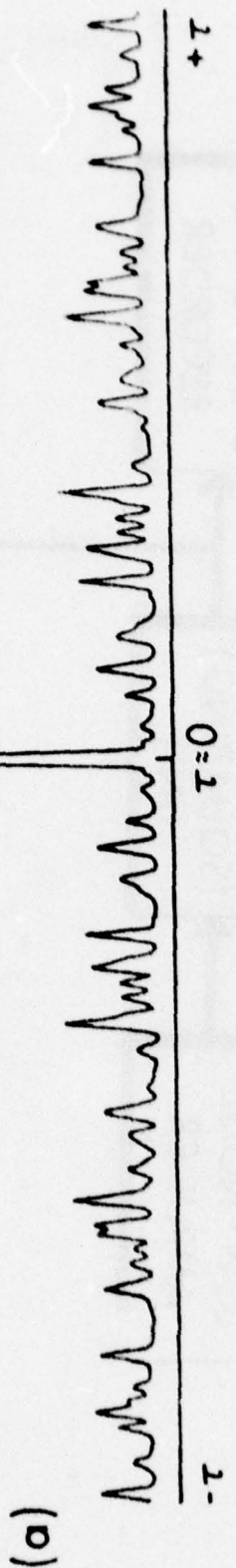
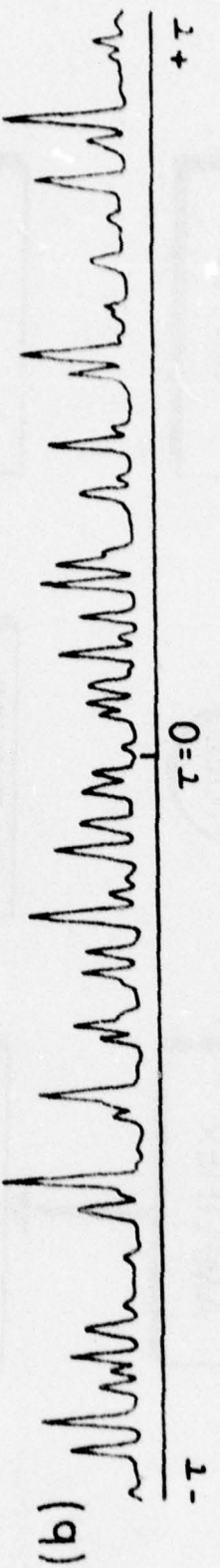
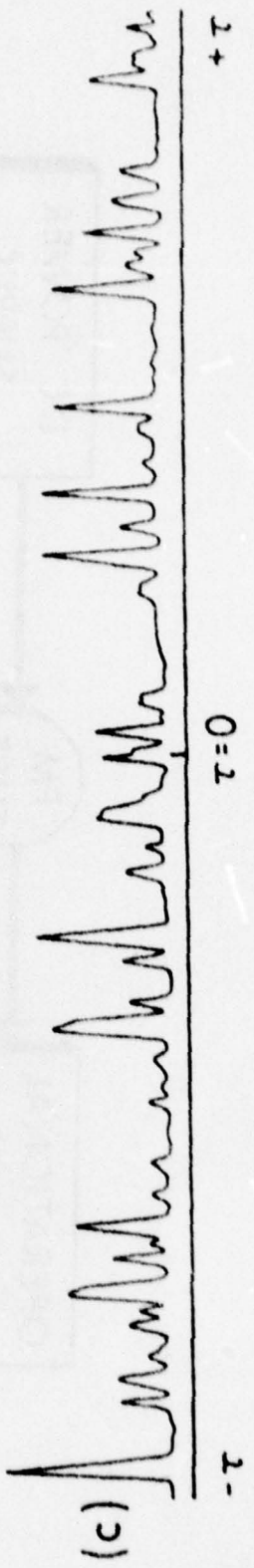
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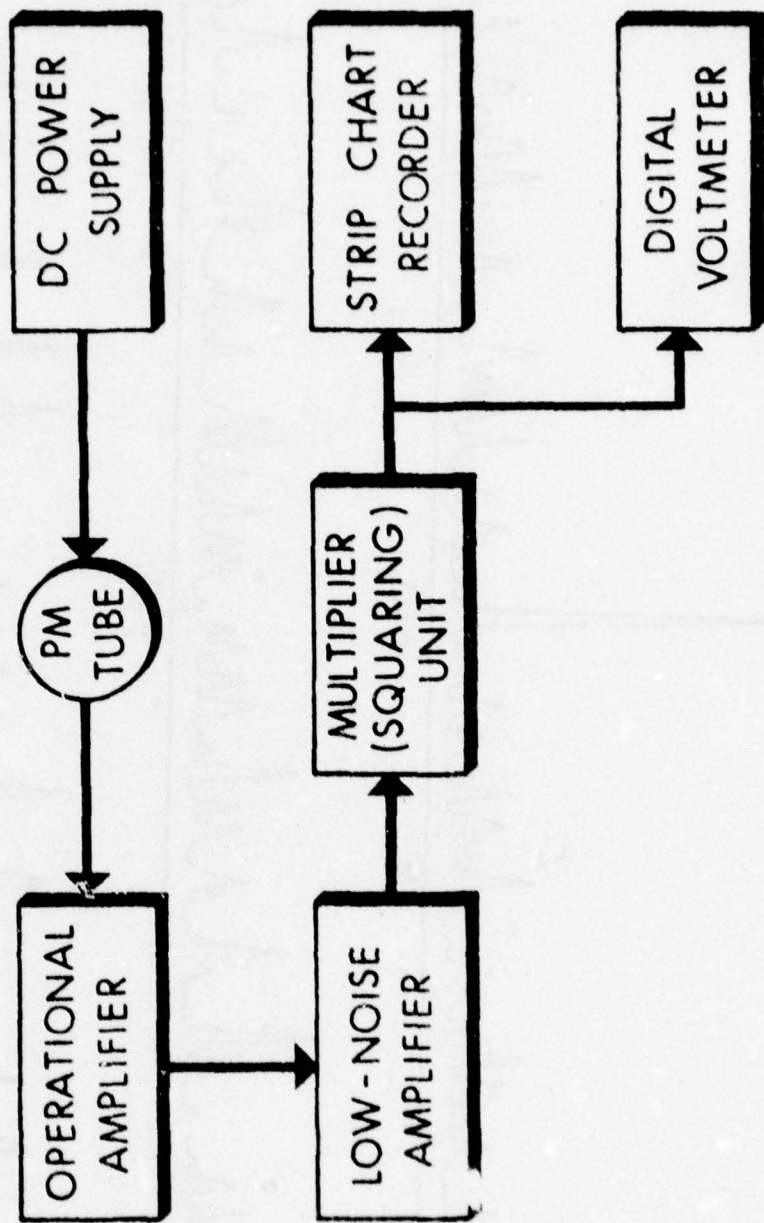


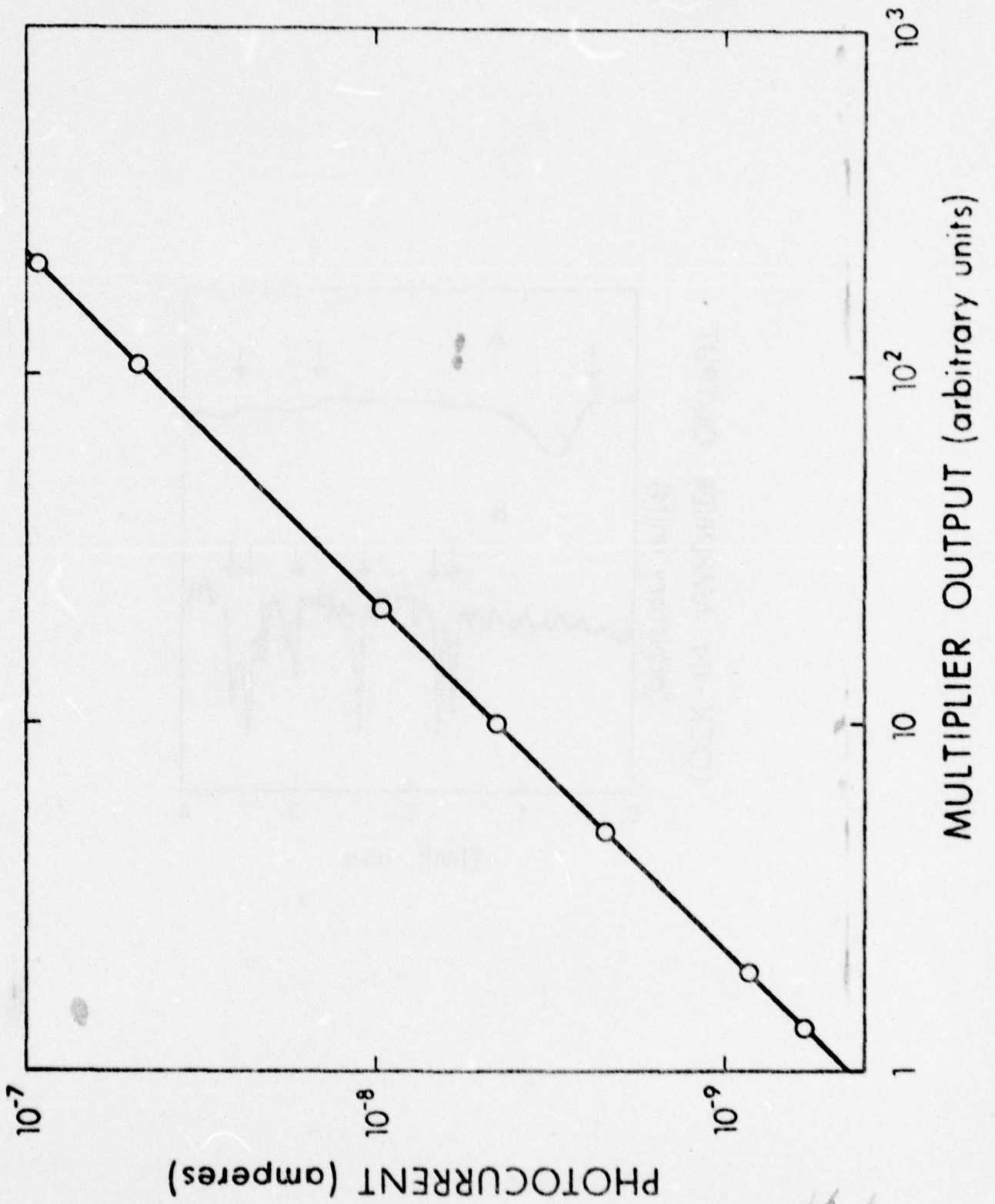
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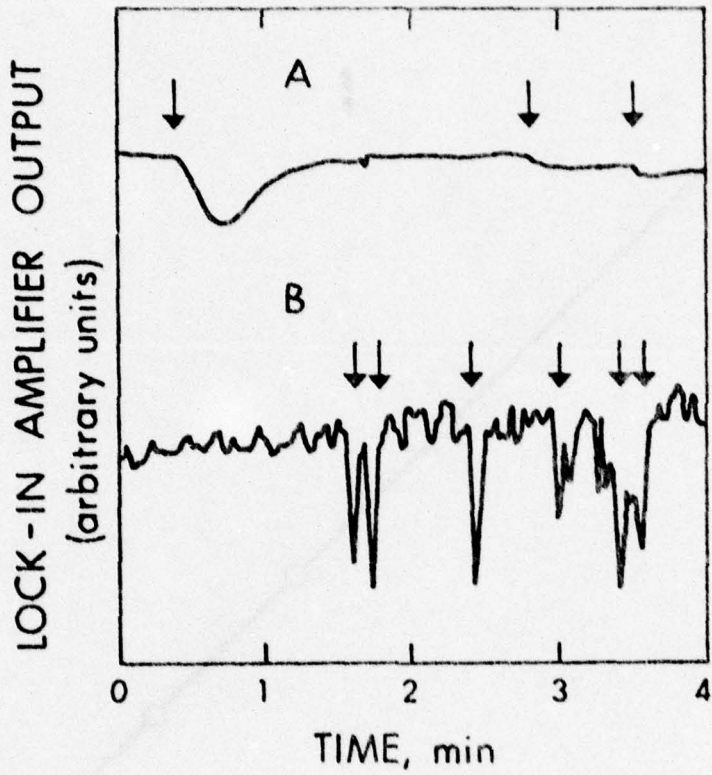


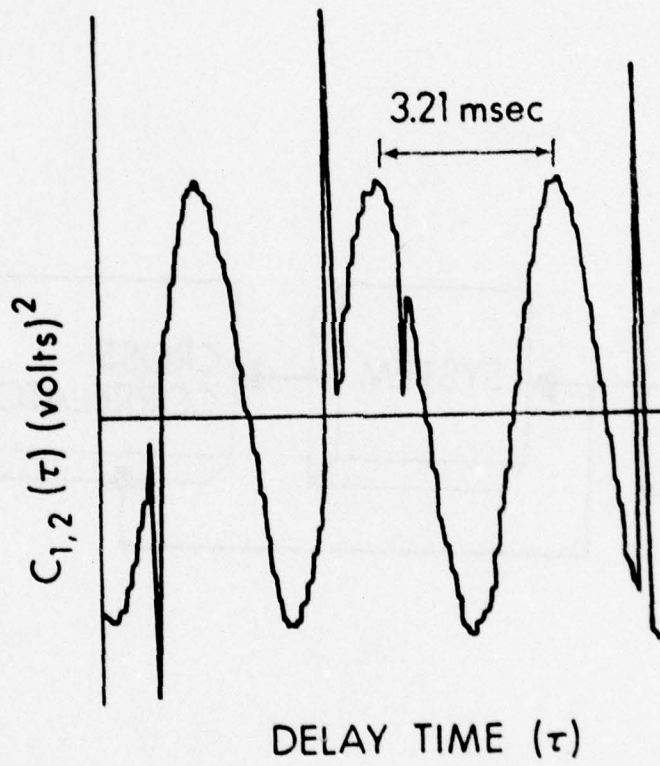




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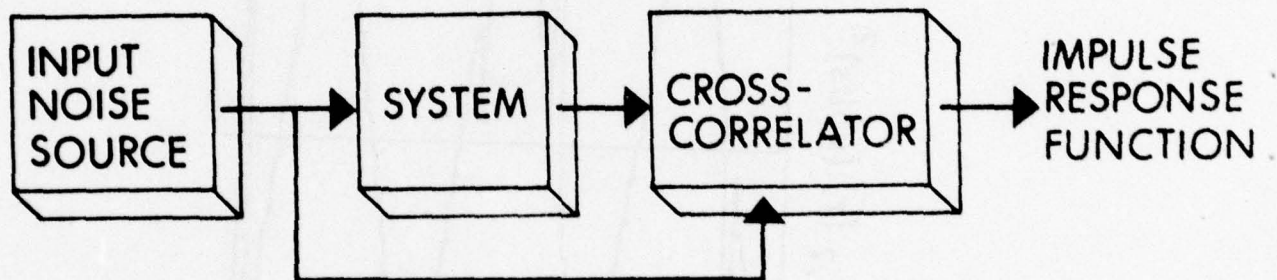
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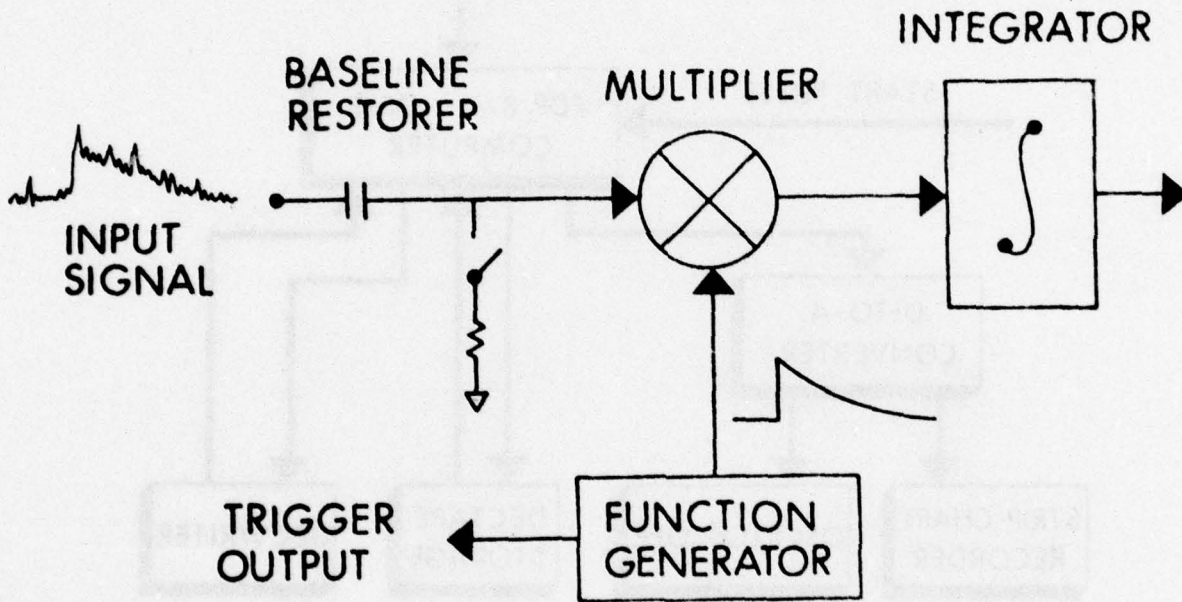




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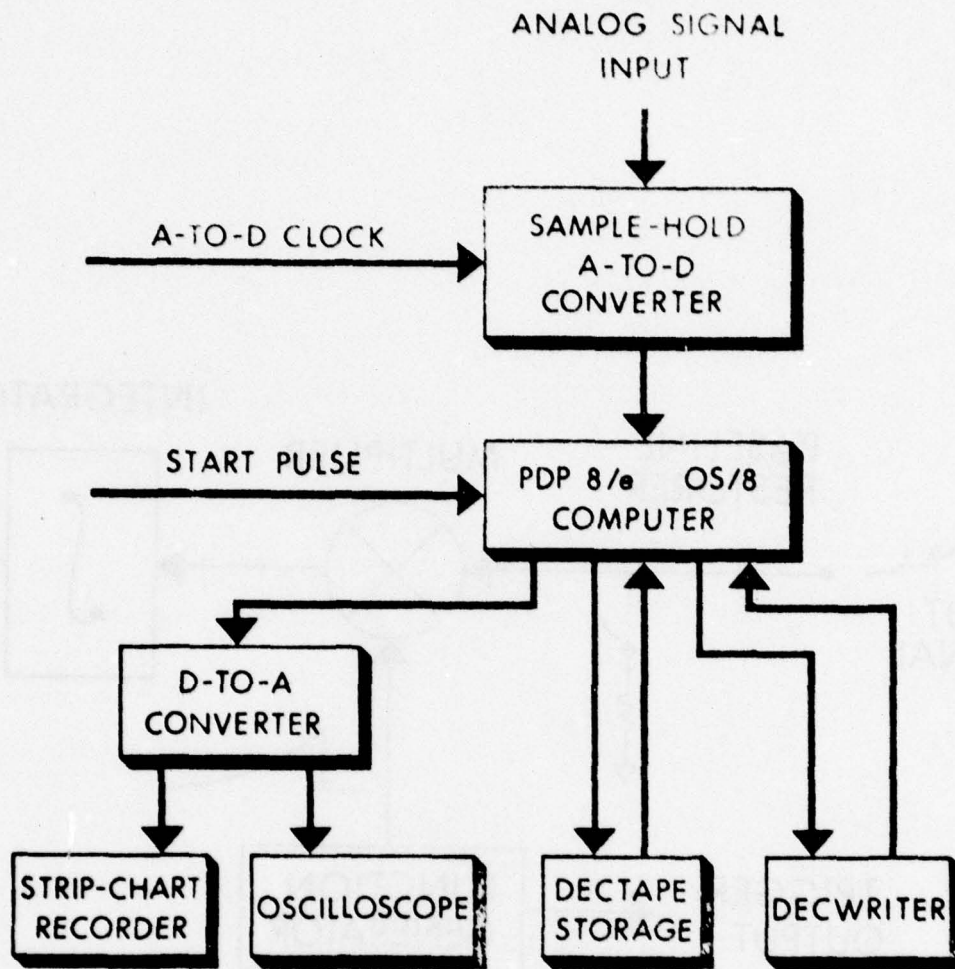
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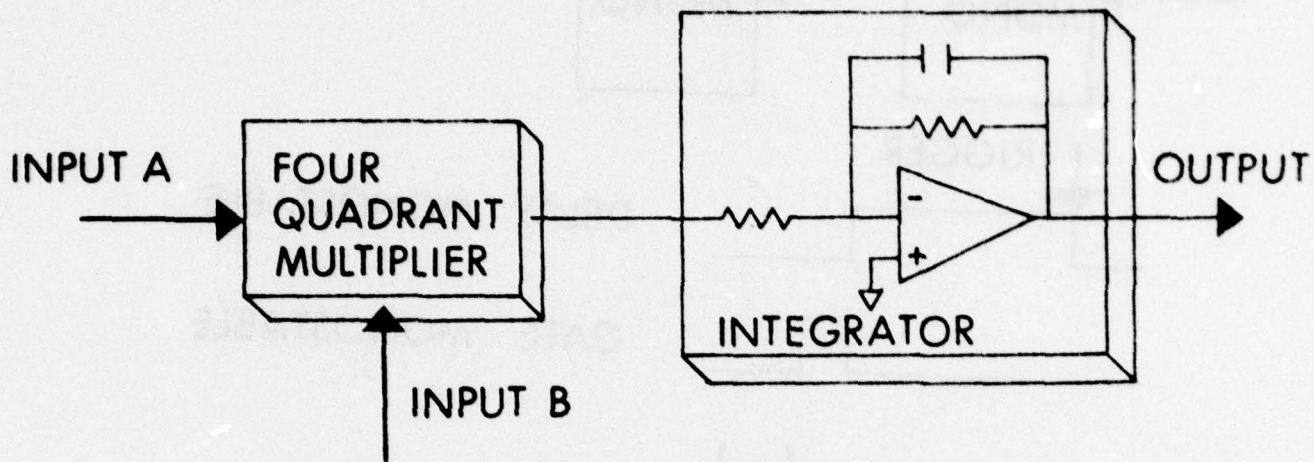




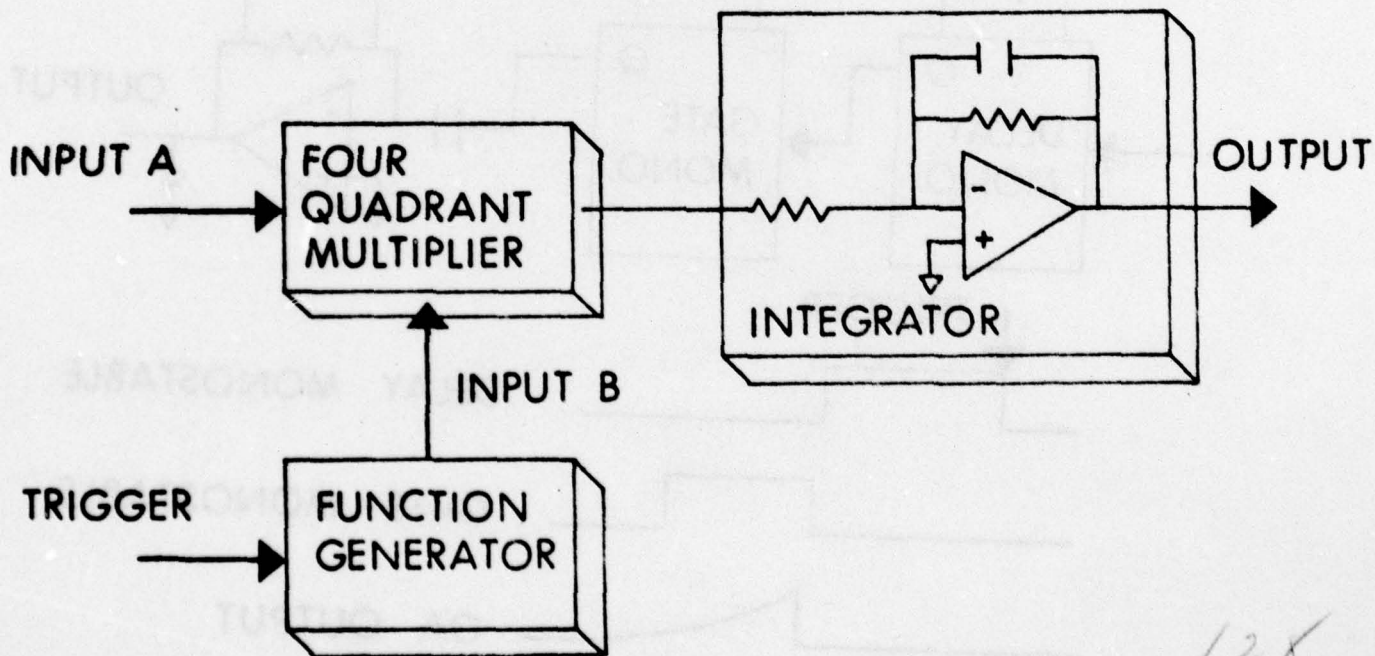
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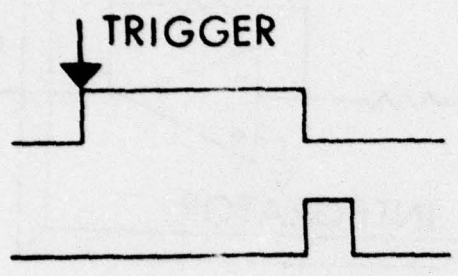
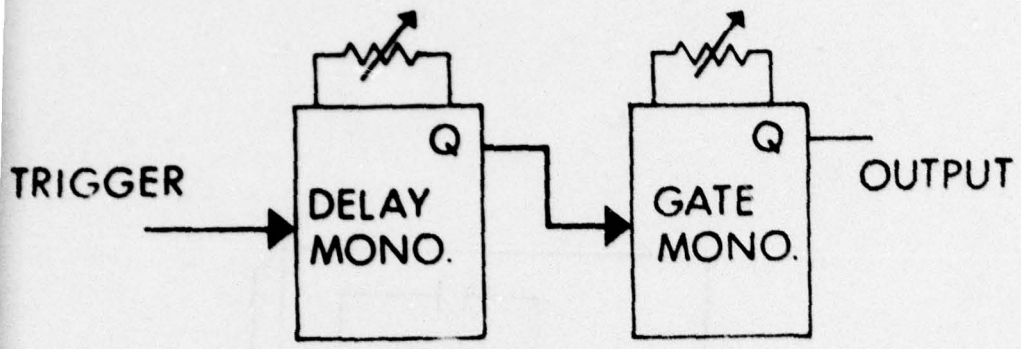
(a)



(b)

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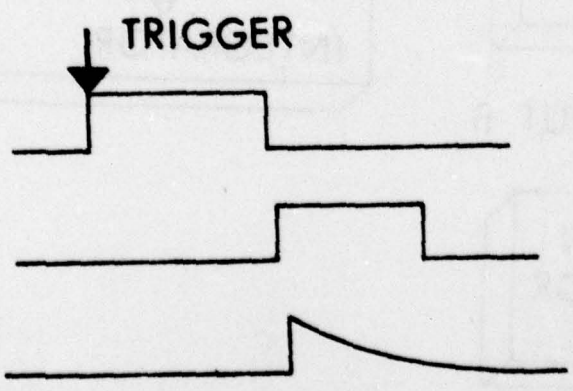
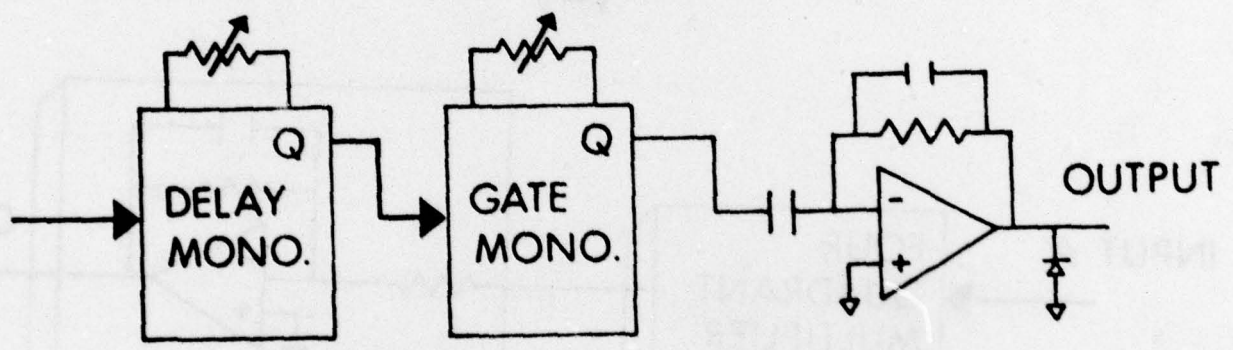
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DELAY MONOSTABLE

GATE MONOSTABLE

(a)



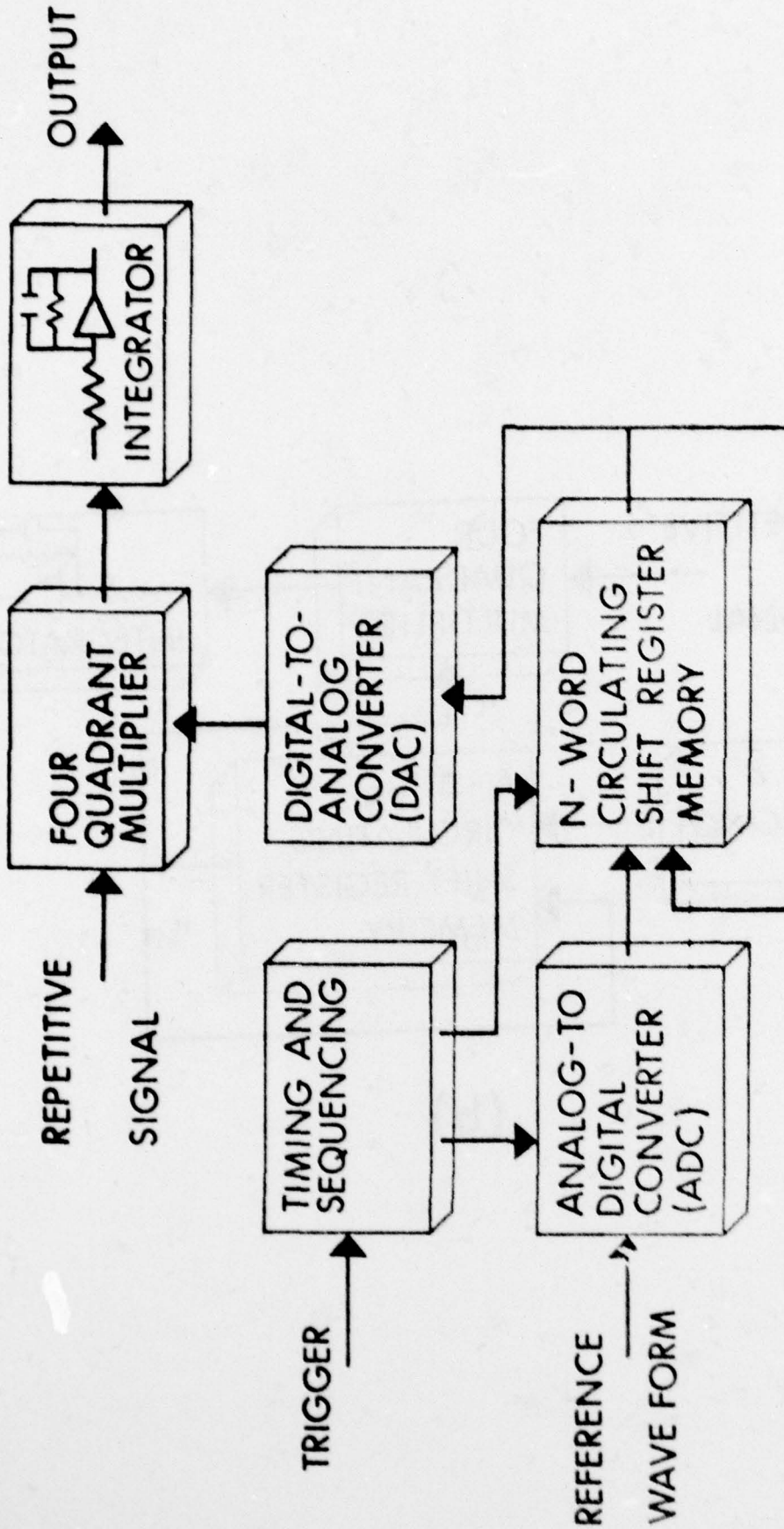
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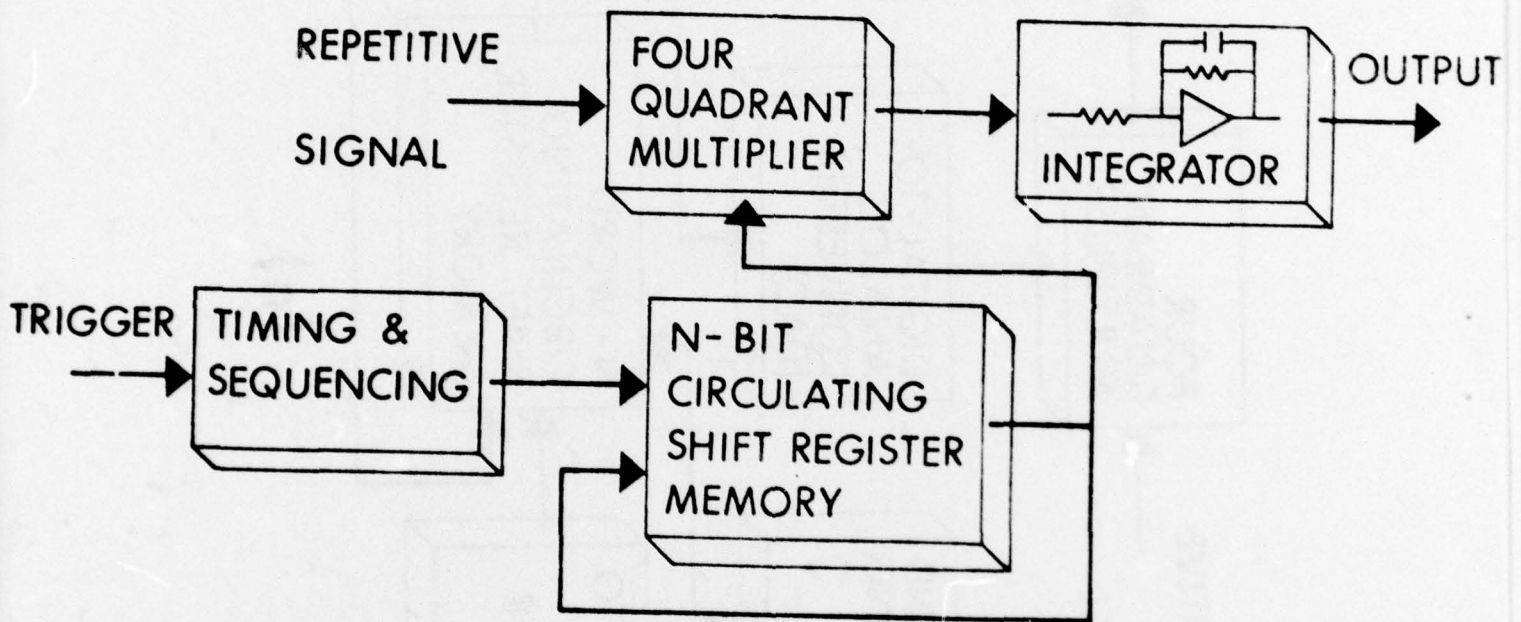
OA OUTPUT

(b)

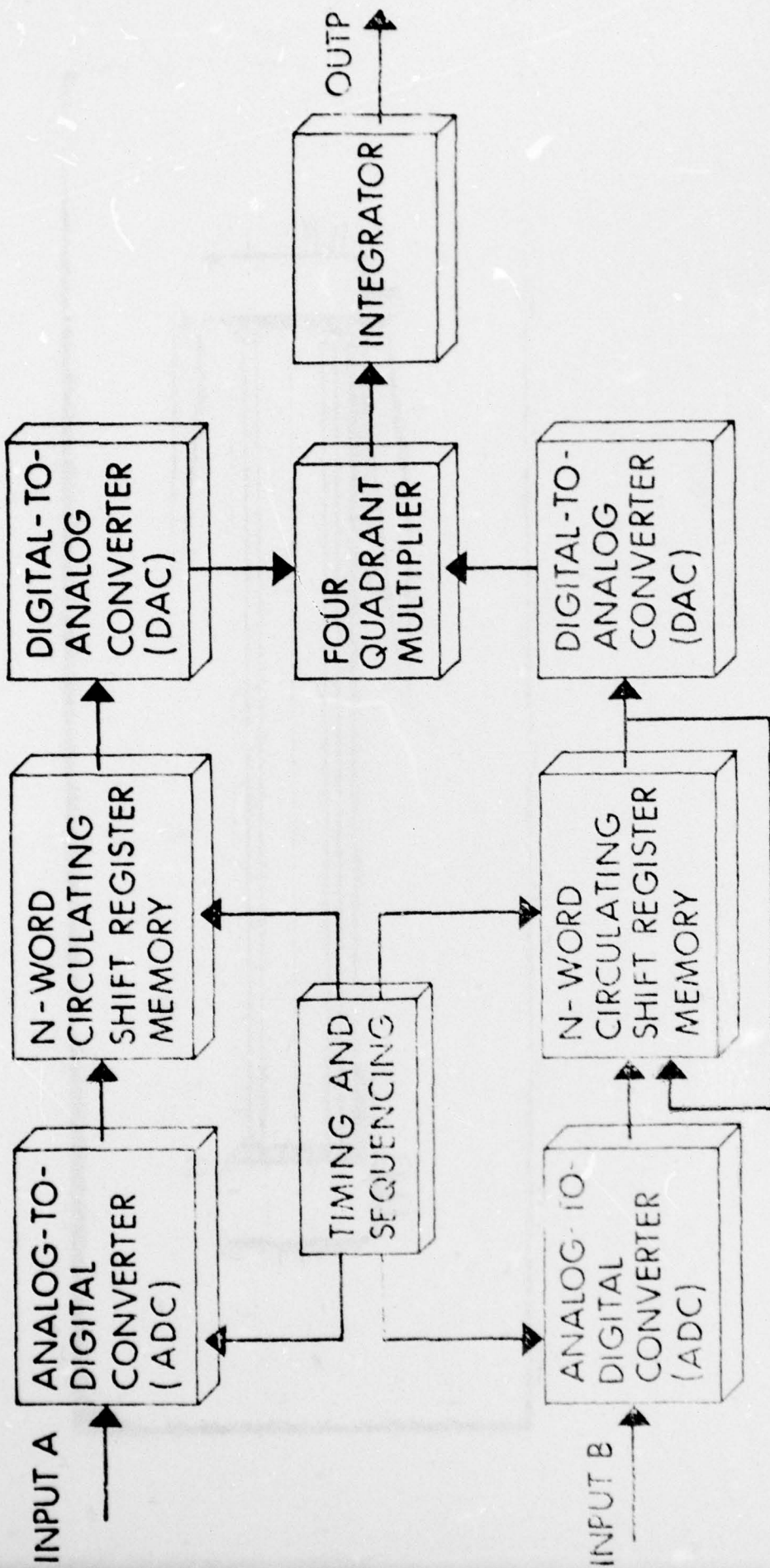
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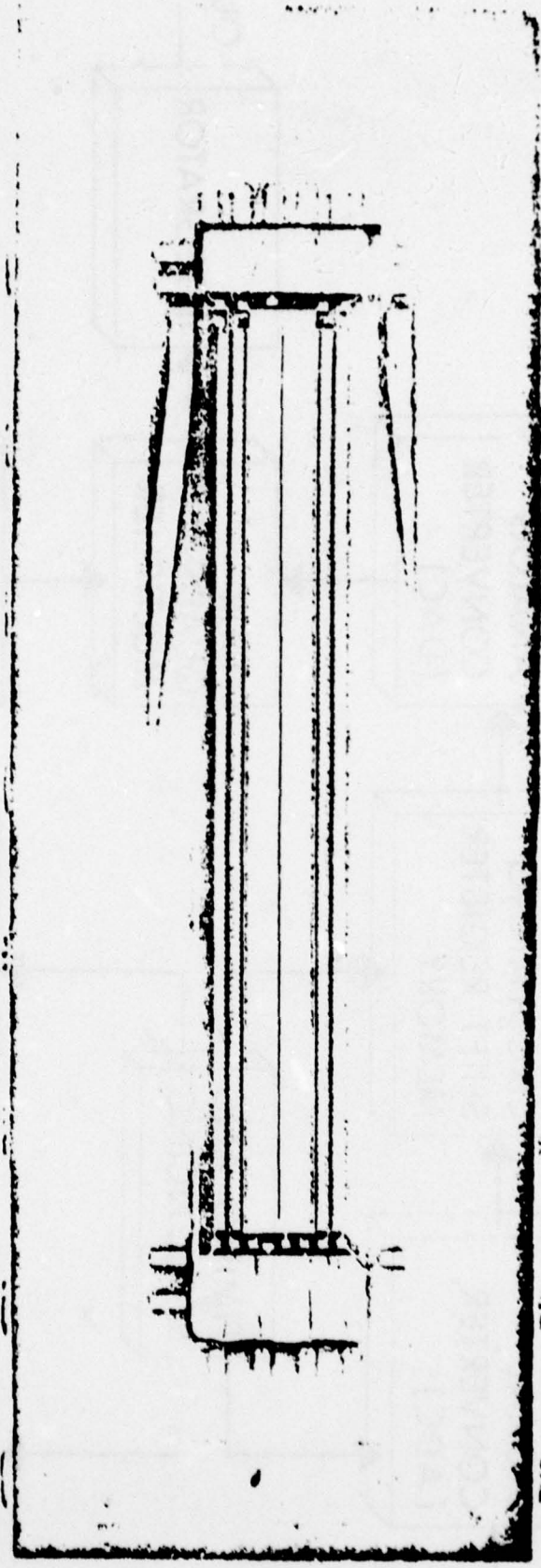
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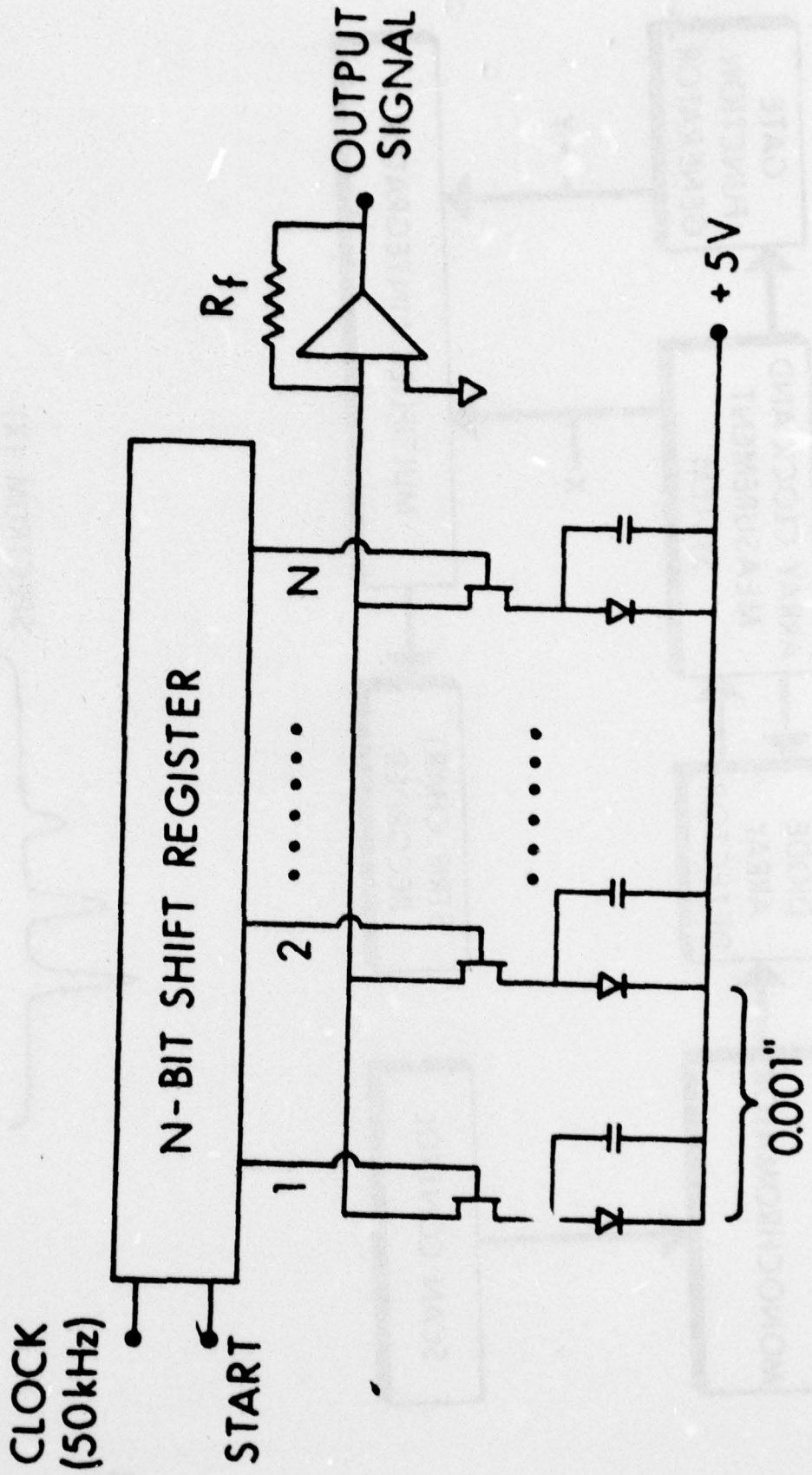


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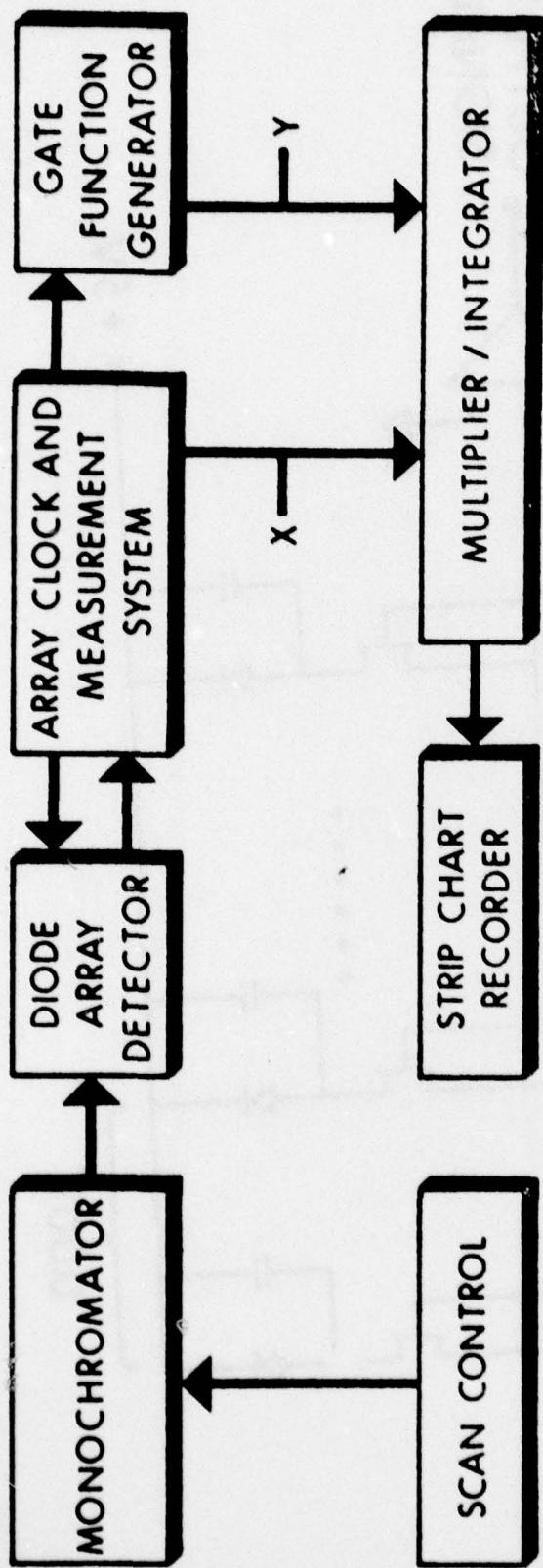


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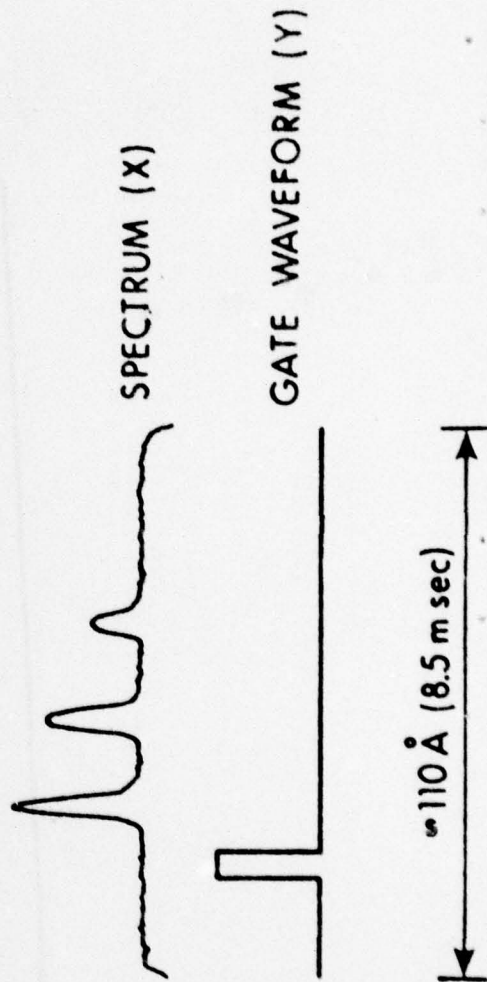




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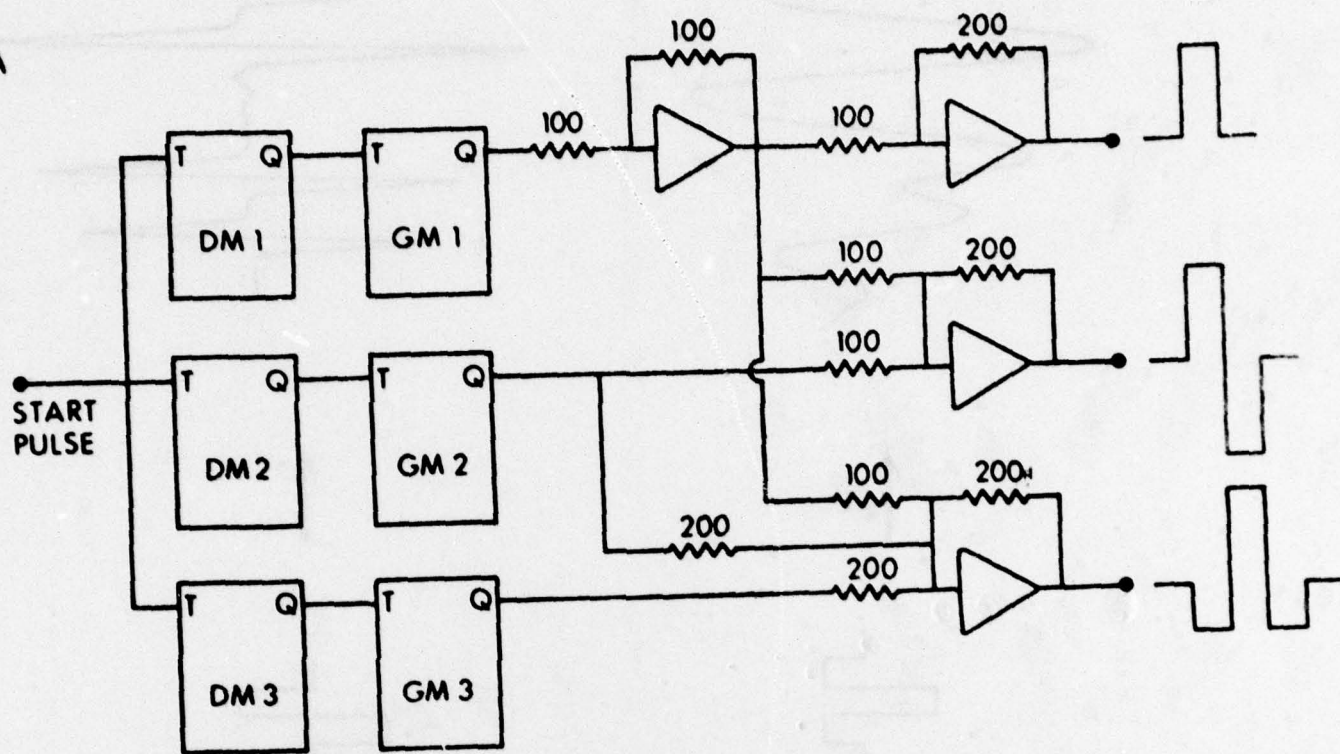


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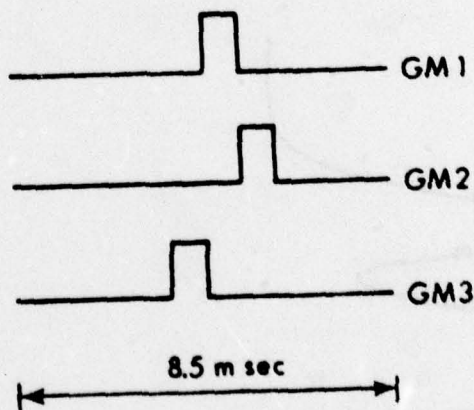


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A

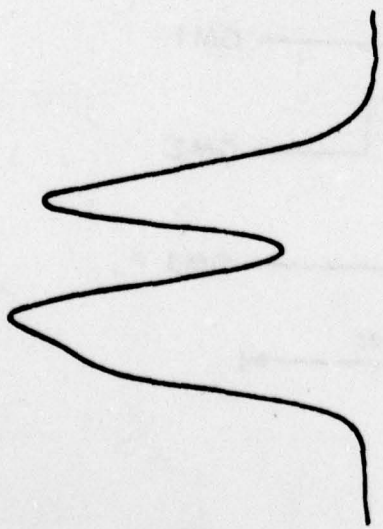


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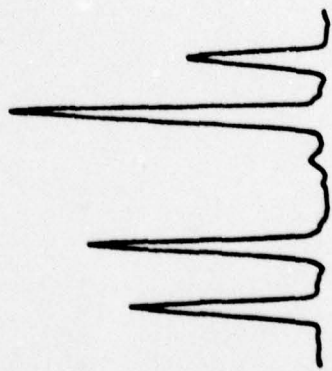
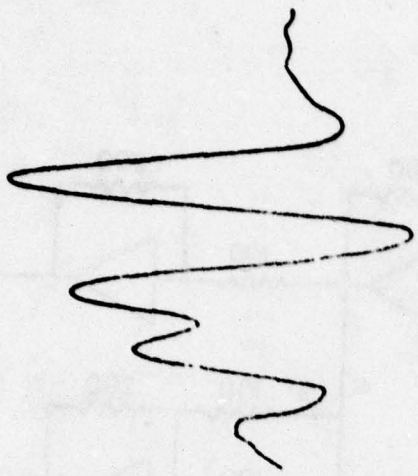
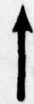
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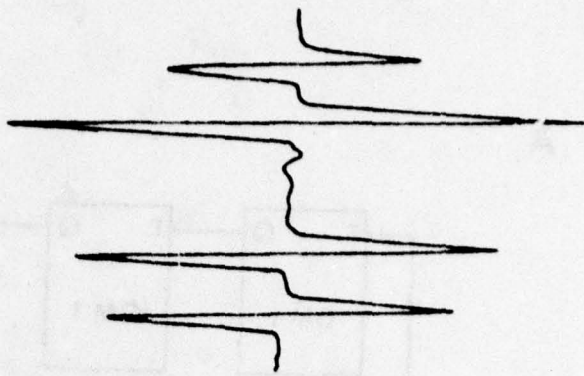
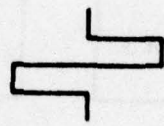
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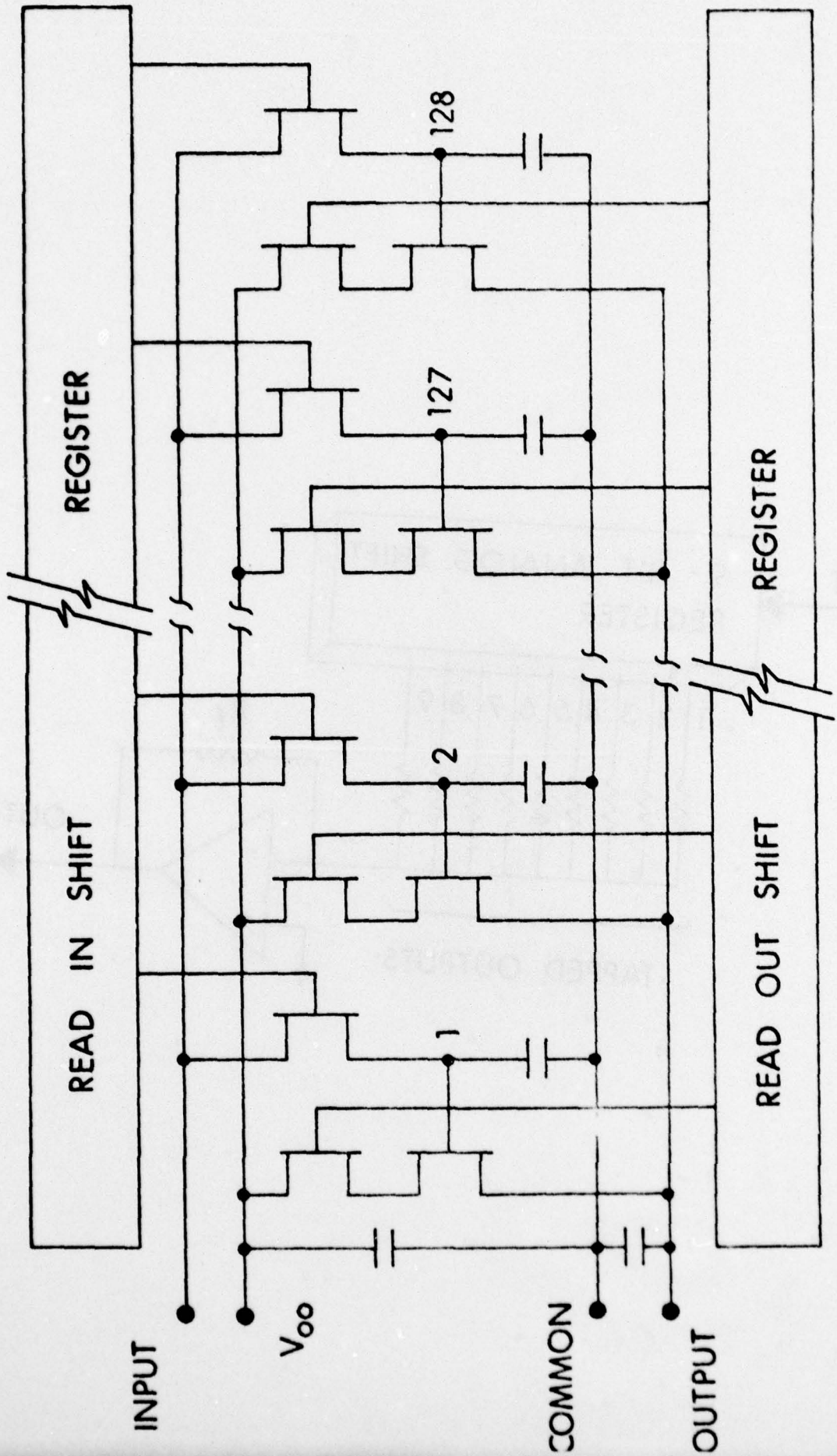
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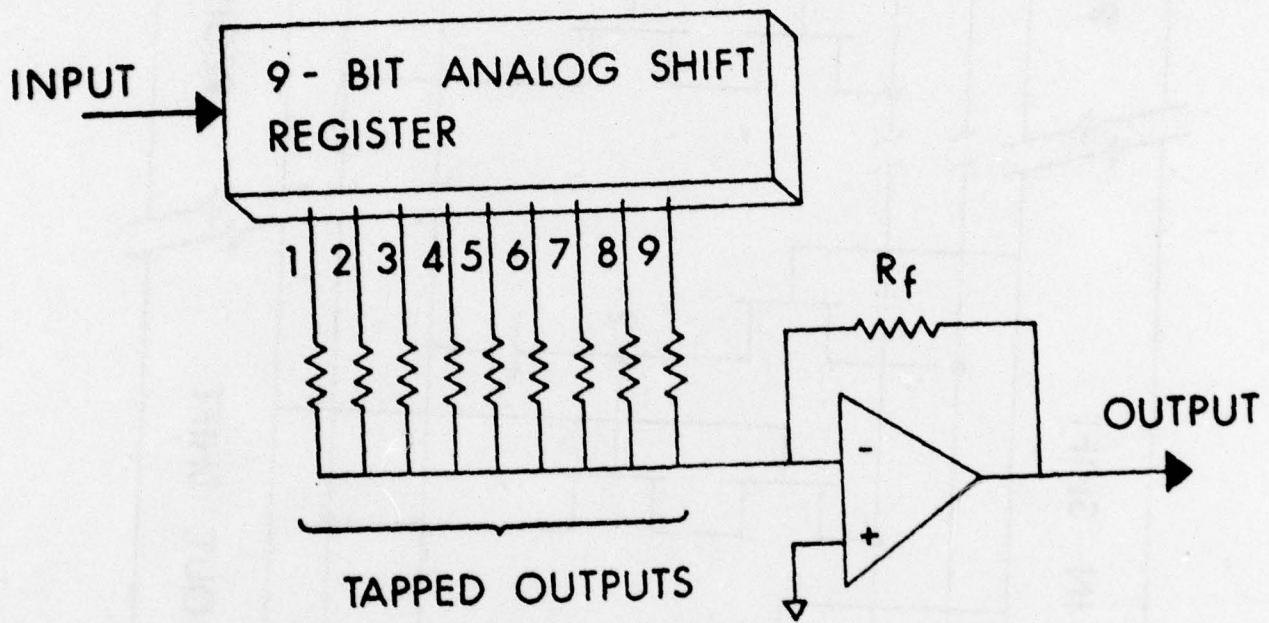
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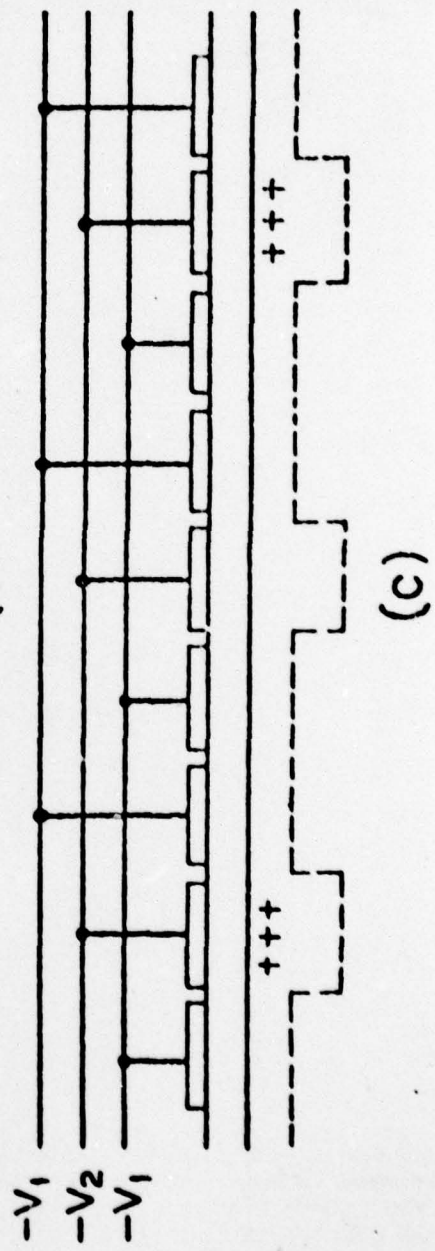
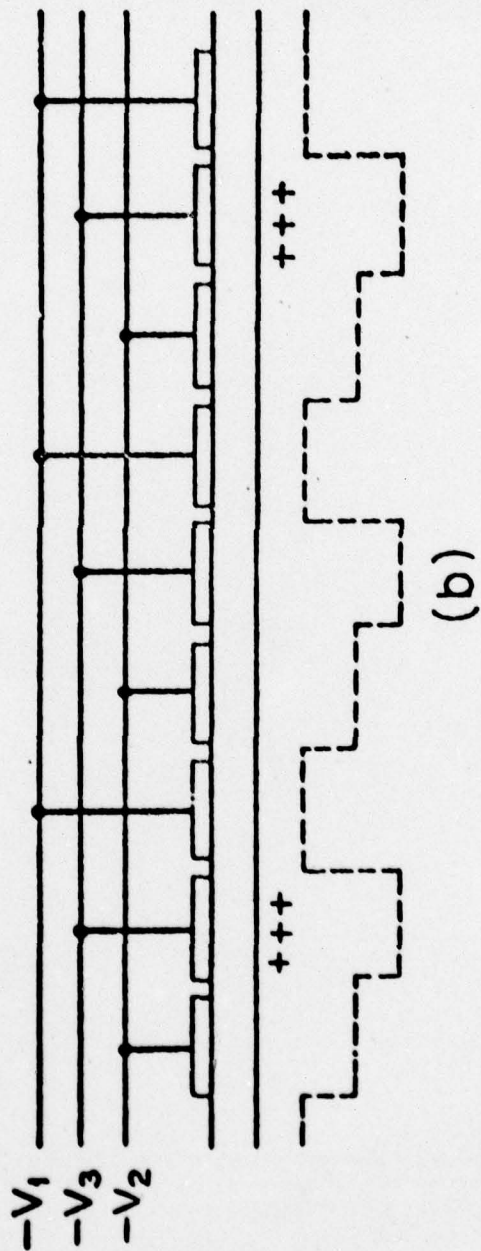
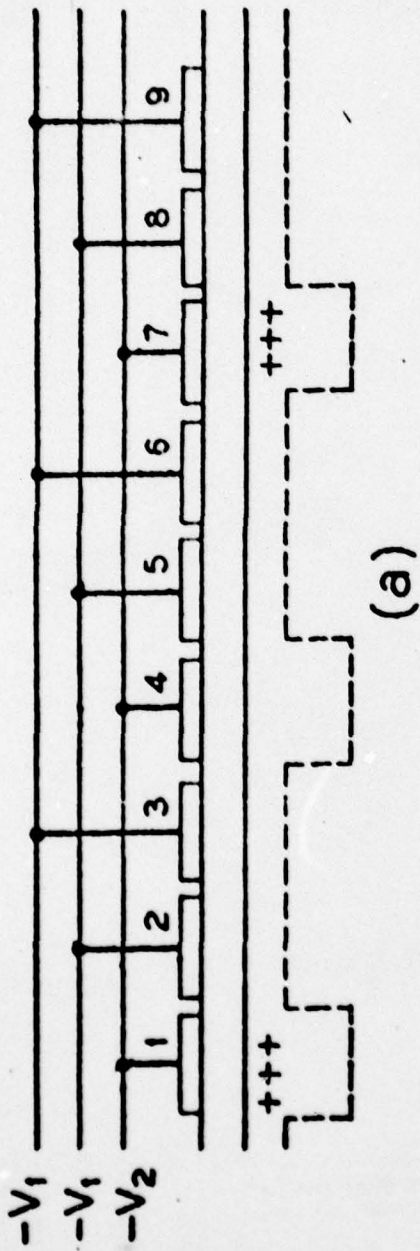


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FIGURE 48

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