Application of the Fast Fourier Transform to Impedance Analysis of Nitrogen - Titanium-Dioxide and Lanthanum-Trifluoride Electrodes.

Kenneth Robert Carney

Louisiana State University and Agricultural & Mechanical College

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Application of the fast Fourier transform to impedance analysis of N-TiO₂ and LaF₃ electrodes

Carney, Kenneth Robert, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1988
APPLICATION OF THE FAST FOURIER TRANSFORM TO IMPEDANCE ANALYSIS OF N-TIO₂ AND LAF₃ ELECTRODES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Kenneth Robert Carney
B.S., Louisiana State University in Shreveport, 1981
December 1988
TO TAMMY AND CONNOR
ACKNOWLEDGEMENT

I would like to thank Dr. Robert J. Gale for his role as my research advisor. His challenge and guidance has been a major contribution to my education. He has also been a friend who has given freely of his experience and insight both scientific and otherwise. I would also like to thank Mr. Roberto L. Wong for his companionship during these years. It has been a true pleasure sharing a lab and office with him. It has been my good fortune to be able to spend time bouncing ideas off of him, often with some useful inspiration as the result. I also want to thank Betty Armstrong for her invaluable assistance in completing this work.

Finally and most importantly, I want to thank my wife Tammy for her great patience during the past several years and my son Connor Seamus for his contribution to my life over the past not so several years. Tammy is to be credited with a substantial contribution to this work through her encouragement and support, not to mention her typing and editing. Connor showed amazing patience and understanding for a three year old. He will undoubtedly be happy to know that his parents will again be sleeping rather than typing through the night.
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ABSTRACT

A study is presented of the utility of pulse derived waveforms for use in impedance analysis of electrochemical systems. Factors to be considered in optimization of pulse duration and also in the proper implementation of the FFT are discussed. Impedance results are presented for model circuits and for two nonfaradaic electrochemical systems - n-TiO₂ electrode in aqueous Na₂SO₄ and LaF₃ electrode in aqueous fluoride solution.

The techniques developed were applied to model circuits composed of aperiodic elements in order to quantify the decrease in precision with increasing frequency associated with pulse type waveforms. Using 8 bit digital sampling resolution and 512 point double precision Fourier transformation, model circuit results showed a relative standard deviation of approximately 0.5% for the first 20 harmonics and less than 2.5% for all harmonics up to the 50th. Modification of the waveform by analog high-pass filtering extended the useful range to almost 2 decades. Impedance measurements by pulse-Fourier transformation agreed with steady state a.c. results to within 1% at frequencies up to 100 kHz.
The technique was used to study the n-TiO$_2$/electrolyte interface via Mott-Schottky analysis. Reliable estimates were obtained for donor densities in n-TiO$_2$ crystals. Investigation of the shift in flatband potentials with pH showed nernstian behavior although the data showed a high degree of scatter.

Impedance studies were made of the fluoride selective LaF$_3$ membrane electrode in order to investigate reported concentration dependent conductance. Conductance was measured over frequencies between 500 Hz and 50 kHz. Studies were made using a standard addition method and an electrode immersion method. For the standard addition method, an apparent concentration dependence was seen in the frequency regime corresponding to a hydrated surface film on the membrane. Such concentration dependence was not seen for the immersion method. Relative standard deviations obtained for conductance values were on the order of 0.5% for frequencies up to 25 kHz.
INTRODUCTION

The use of mathematical transforms as a means of data analysis is far from new. For example, the use of logarithms dates back to Napier [1] (1614); LaPlace transform analysis (also called Operational Calculus) was applied to electrical engineering in 1892 by Oliver Heaviside [2]; and the closely related Fourier transform was first applied to a physical problem by Joseph Fourier in 1822 [3]. The long history of LaPlace transform in electrical engineering, coupled with the natural connection between electrical engineering and electrochemistry, makes the applications of transform analysis seem obvious; nevertheless, the first-mentioned application of the LaPlace transform to electrochemical data analysis was not until Winjen [4] in 1961.

Prior to 1965, the uses of transform analyses were restricted to formal analyses of mathematical functions; data were approximated by known functions which were solved analytically. Numerical solutions were too costly in terms of computer time. In 1965, however, the barrier of long computational time was largely overcome with the publication of "An Algorithm for the Machine Calculation of Complex Fourier Series" [5]. This was the Fast Fourier transform (FFT) algorithm, which
allowed the increased use of direct numerical Fourier techniques rather than indirect approximation techniques. Furthermore, advances in very large scale integration (VLSI) computer technology dramatically reduced the cost of computer time. By the early 1970's there was a flurry of numerical Fourier transform techniques in electrochemistry [6-17], as relatively inexpensive minicomputers became available in the laboratory.

Many of these early applications were to multiplexed a.c. polarography or measurement of "faradaic admittance" [8-15]. With this burst of electrochemical FFT applications, D. E. Smith and coworkers published a landmark comparison of periodic and nonperiodic waveforms that could be used for faradaic admittance (a.c. voltammetry) measurements [10]. The results of this comparison are summarized in Table I. Included in this comparison were pseudorandom white noise and, important to this work, rectangular pulse trains. Pseudorandom white noise (PRWN) is a computer generated waveform produced by using inverse Fourier transformation of a spectrum with constant magnitude vs. frequency and randomized phase vs. frequency. The randomized phase results in a waveform with a low crest factor (ratio of peak level to mean level). Of the
waveforms compared, this was shown to produce the highest quality data in terms of precision and accuracy of measured rate constants for an electrochemical reaction. A particular form of PRWN that was found applicable for faradaic measurements was "odd-harmonic" PRWN, which contains only odd harmonics of a fundamental frequency. Because nonlinear effects principally appear in second order terms of a Taylor series [18], nonlinearity is manifested most strongly in the even harmonics of the response. Thus if only odd harmonics are applied to the system, the absence of any significant even harmonic response indicates essentially linear behavior.

On the other hand, the rectangular pulse was stated to be the poorest choice of waveform for faradaic admittance measurement. Its noted disadvantages included poor precision, errors due to leakage, and induction of nonlinear responses in electrochemical cells [10]. Consequently, the use of pulse for FT impedance analysis virtually disappeared.

The pulse does have some advantages in comparison with more complex waveforms, primarily the ease of producing pulse type waveforms, compared to the relative expense and difficulty of producing arbitrary waveforms such as PRWN. In addition, the precise triggering of
waveform sampling devices is easier, and the time domain response is somewhat interpretable, while random and pseudo-random perturbations are not.

Finally, faradaic processes are a major contributor to nonlinear response, and, as Creason et al. warned, the comparison of the various perturbation waveforms specifically applies to faradaic impedance measurement. Therefore, caution should be used regarding the general applicability of the conclusions made by Smith and coworkers \[10\]. Furthermore, the comparison of Creason et al. undervalues the quality of the pulse response data versus "flat magnitude spectrum" waveforms, including PRWN. While the PRWN waveforms were generated using flat magnitude spectra of 2 mV per frequency component, the pulse used was only 2 mV for 2 milliseconds of a 100 millisecond observation period. Using the discrete Fourier transform result for a pulse train \[19\], the magnitude spectrum is

\[
\frac{AT}{T_0} \sin \left( \frac{\pi n T}{T_0} \right)
\]

where \( A \) is the pulse amplitude, \( T \) is the pulse duration, \( T_0 \) is the observation time and \( n \) is the harmonic number. Thus, the magnitude decreases from 0.04 mV at \( f=10 \) Hz (the fundamental harmonic of the measurement) to less than 0.01 mV at 400 Hz and so forth, according to the
(\sin X)/X function in equation (1). Thus the weighted power is far less than that of the other waveforms of similar amplitude.

Admittedly, for its application to faradaic admittance measurements, the large crest factor of the pulse required the use of small pulse heights and durations, but under conditions where faradaic processes are not significant (e.g. "slow" electron transfer kinetics), or where large bulk impedances are responsible for most of the potential drop across the cell, much larger pulse heights may be used [17]. In fact, pulses can actually give results superior to flat spectrum waveforms for the first several harmonics [20].

There is a recognized need for a low cost FT impedance method [21-23]. One example is in impedance measurements in moderately high to high frequency ranges. The Princeton Applied Research Model 273 potentiostat/galvanostat is a state of the art general purpose electrochemical instrument with arbitrary waveform capability, yet it is only capable of handling signals up to about 2 kHz, even with a high speed A/D option. We were in the surely not uncommon position of having no convenient means of doing multifrequency measurement above about 2 kHz. Thus, a simple FT technique was a third alternative to tedious single
frequency measurement or the purchase of expensive frequency sweep equipment. Furthermore, illustrating the value of pulse transform techniques for impedance measurements could lead to other potential uses where more complex arbitrary waveforms are not feasible; for example, light pulses in studying kinetics associated with photoelectrochemical or photoemission processes, and responses of chemical systems to changes in component concentrations (activity changes in ion-selective electrode systems).

In this work, methods have been developed using the FFT in conjunction with pulse trains and related waveforms (e.g. square wave and high pass filtered square wave) for impedance measurements on electrochemical systems. Three major concerns were:

(a) Could such measurements be reliably made with pulse heights substantially below 50 mV, thereby reducing nonlinear response? (b) What was the optimum ratio between pulse on and pulse off states? and (c) How seriously did the 1/f nature of pulse waveforms degrade impedance results in the higher harmonics?

The Pulse-FT impedance technique was used to study the n-TiO$_2$/electrolyte interface in comparison with steady state a.c. methods. Dummy cells were used to compare the Pulse-FT technique with the conventional
steady state a.c. technique, and to determine if systematic errors observed in the n-TiO₂ study were caused by the use of pulse type waveforms or were purely instrumental artifacts. Finally, an impedance study was made of the Orion 94-09 fluoride (LaF₃ membrane) ion-selective electrode in an attempt to evaluate its utility for ion-selective conductometric monitoring of fluoride ion.
<table>
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<th>Applied a.c. potential waveform type</th>
<th>Magnitude</th>
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<td>BLWN*</td>
<td>1 mV/f$^3$</td>
<td>3.00 (2.70)</td>
<td>0.82 (0.75)</td>
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<td>1.56 (1.49)</td>
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<td>Filtered rect. pulse (+pulse)</td>
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<td>23.4 (16.5)</td>
<td>11.5 (4.59)</td>
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<td></td>
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<td>24.9 (17.6)</td>
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<td>2 mV x 2 ms</td>
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*From reference 10. Results obtained from linear least squares fit of COT against $w^{1/2}$ data. Values in parentheses are after rejecting data values >2.5σ from original least squares line.

*BLWN = bandwidth-limited white noise

*Observation Period, $T_o$, = 100 msec, 100 harmonics used

*PRMN = pseudo-random white noise
THEORY

Two broad areas of theory apply to this work: Fourier transformation, and measurement of a.c. admittance/impedance of electrochemical systems.

In order to apply Fourier transformation to a variety of problems, including, but not limited to, admittance (impedance) calculations, a good, working understanding of Fourier transformation in general, and discrete Fourier transformation in particular, is necessary. This chapter addresses FT theory to the extent necessary for understanding its power for general data analyses and the most common problems with its use. More detail on all aspects of FT theory and applications are given in Brigham [1], Bracewell [2], Champeney [3] and, for a very pragmatic approach, Ramirez [4].

The admittance theory of electrochemical systems also is briefly presented below. The specifics of admittance of semiconductor-electrolyte interfaces with regard to surface states and space charge capacitances are covered, as these were phenomena that were used as a test comparison between the fast FT admittance technique and the more conventional a.c. technique. In connection with this, some discussion is necessary of potentiostat stability under the load imposed by electrochemical cells. Finally, in order to discuss the results of ion-selective electrode conductance measurements, some
background has been presented concerning the current transport mechanisms of ion-selective electrodes.

FOURIER TRANSFORM

The basis for the use of Fourier transformation in data analyses derives from Joseph Fourier's (1822) assertion that any periodic signal can be represented by a trigonometric series,

\[ y(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} \left[ a_n \cos(2\pi n f_0 t) + b_n \sin(2\pi n f_0 t) \right] \]

where

\[ a_n = \frac{2}{T_0} \int_{-T/2}^{T/2} y(t) \cos(2\pi n f_0 t) \, dt \]

\[ b_n = \frac{2}{T_0} \int_{-T/2}^{T/2} y(t) \sin(2\pi n f_0 t) \, dt \quad n = 1, 2, 3, \ldots \]

To = waveform period, and frequency \( f = 1/T_0 \).

Equations (2) - (4) can be rewritten in terms of complex coefficients, \( c_n \), to yield the complex Fourier series (5) and the Fourier integral (6) [1].

\[ y(t) = \sum_{n=-\infty}^{\infty} \left[ c_n \exp(j2\pi n f_0 t) \right] \]

\[ c_n = a_n - jb_n = (1/T_0) \cdot \int_{-T/2}^{T/2} y(t) \exp(-j2\pi n f_0 t) \, dt \]
Furthermore, it can be shown [1,5] that in the limit of $T_0 \rightarrow \infty$ (i.e. $f_0 \rightarrow 0$), equations (5) and (6) approach the integral definitions of the inverse Fourier transform (7) and forward Fourier transform (8), respectively.

(7) $y(t) = \int_{-\infty}^{\infty} y(f) \exp(+j2\pi ft) \, df$ \hspace{1cm} \text{Inverse FT}

(8) $Y(f) = \int_{-\infty}^{\infty} y(t) \exp(-j2\pi ft) \, dt$ \hspace{1cm} \text{Forward FT}

It may be noted that the designation of equation (7) as the inverse and equation (8) as the forward transform is purely conventional. Bracewell [2] uses the terms "minus-i" and "plus-i" rather than "forward" and "inverse" in order to emphasize this point. Because of the history in the electrical engineering literature, the Fourier transform equations (7) and (8) are often written in terms of angular frequency ($\omega = 2\pi f$) rather than in Hertz ($f$). These alternative definitions require the inclusion of the a factor, $1/2\pi$, in the inverse transform equation, or, for the sake of symmetry, $(1/2\pi)^{1/2}$ in both the forward and inverse transform equations. It is important to note that
expressions in terms of t and f, which are reciprocal variables, obviate the need for the $1/2\pi$ factor.

**General Properties of the Fourier Transform**

In order to use Fourier transformation as a general method for data analyses, it is helpful to have understanding of the various useful properties of the Fourier transform. Of prime importance is the property of existence, because theoretically there exist functions which do not have Fourier transforms. Causality is a sufficient condition for the existence of the Fourier transform and is also a necessary condition for physical realizability [3]. Thus, physical possibility is a sufficient condition for the existence of the Fourier transform of a signal. In other words, all real waveforms have a spectrum and all spectra will produce a waveform.

If the FT is to be used for more abstract uses, such as derived functions, the function must satisfy Dirichlet's conditions:

(a) $\int_{-\infty}^{\infty} |f(t)| \, dt < \infty$

(b) $f(t)$ must be piecewise continuous with a finite number of finite discontinuities.

where condition (a) is a sufficient condition and (b) is a necessary condition [6]. Thus, the function $t^{-1/2}$ does not have a Fourier transform because it has an
infinite discontinuity at $t_+ \to 0$. On the other hand, the response of an electrochemical system under diffusion control will have a Fourier transform because characteristic $t^{-1/2}$ dependence always fails at some time greater than zero, because of finite electron transfer kinetics and/or instrumental limitations.

The work presented here uses the properties of the Fourier transform for analyses of the responses by several electrochemical systems to external perturbations. Therefore, a brief introduction to the pertinent properties is given. More detail on these properties is given elsewhere [1,2,6]. The three most relevant properties are linearity, the convolution theorem, and scaling. Two other properties that are useful in interpreting Fourier transforms are the shifting theorems and symmetry. The properties of the Fourier transform are summarized in Table II.

Linearity of the transform means that the transform of a sum is the sum of transforms,

$$F\{g(t) + h(t)\} = F\{g(t)\} + F\{h(t)\}$$

Besides allowing a relatively simple intuitive connection between the time and frequency domain representations of linear systems, linearity means that for repetitive signals, ensemble averaging of time
domain arrays is equivalent to ensemble averaging of frequency domain arrays. This assumes that the system is invariant with time. As a result, signal/noise (S/N) improvement in the frequency spectrum can be achieved by Fourier transformation of the averaged time domain signal, and much processing time can be saved over the alternative method of averaging several frequency domain spectra. On the other hand, if the signal is not repetitive, e.g. random noise, averaging must be done in the frequency domain to similarly improve frequency domain precision.

As important as any property of the Fourier transform is the convolution theorem. According to this theorem, time domain convolution is equivalent to frequency domain multiplication, and, conversely, time domain multiplication is equivalent to frequency domain convolution. It is this property of converting integral and differential operations into algebraic operations that makes Fourier transformation such a widely applicable computational aid. Digital filtering in the time domain involves convolution with a smoothing function, such as those presented by Savitsky and Golay [7] and others [8,9,10]. Smith used the convolution theorem in digital filtering of electrochemical signals and implemented the filtering function by frequency domain multiplication [11]. Fourier transform smoothing
of data has been performed without the FFT, by incorporating FFT logic flow directly into a digital smoothing routine [12].

More important however, is the fact that deconvolution is equivalent to division in the Fourier domain. This is particularly important given the difficulty of "direct" digital deconvolution, which requires iterative approximation algorithms [13]. Fourier transform deconvolution has been used to remove instrumental distortion from chromatograms [14,15], to increase resolution in IR spectra [16,17], and to remove instrumental distortion from voltammetric data [18,19]. Whether or not they are presented as such, the admittance calculations presented in this and previous work are the Fourier domain deconvolution of the input signal, e(t), from the current response, i(t).

Closely related to convolution is the integration and differentiation of waveforms. Again, Fourier transformation allows these operations to be performed by algebraic operations in the Fourier domain. Integration is analogous to multiplication of the spectrum by \(-j/w\) where \(j^2 = -1\) and \(w\) = angular frequency, and differentiation is analogous to multiplication by \(jw\). These properties are important considerations in conditioning the input pulse waveform by analog filters. They also provide insight into the well known fact that
integration diminishes the effect of noise while differentiation enhances the effect of noise. Because differentiation corresponds to weighting the high frequency spectral components more heavily, random noise, which generally predominates at higher frequencies, is enhanced.

A third property of the Fourier transform is called the similarity property, or the scaling theorems. Time scaling and frequency scaling dictate that as a function becomes narrower in one domain, its Fourier domain representation becomes broader. Thus, the Fourier transform of the delta function is a constant, $F(\delta(t))=1$. The scaling theorems formalize the intuitive notion that signal changes on a short time scale imply the presence of higher frequencies, while changes on a longer time scale are indicative of lower frequencies. This is an important factor in choosing the excitation waveform since the narrower pulse implies, by the time scaling theorem, a broader frequency spectrum. The expansion or contraction of the signal (in time) or the spectrum (in frequency) is thought of as a change in scale, such that $f t$ is constant. This is called the uncertainty relation [2]. It provides the mathematical basis of Heisenberg's famous uncertainty principle.

The shift theorems are the time shift theorem and the frequency shift theorem, often called the modulation
theorem from its use in the electrical engineering literature. The symmetry of the two theorems can be seen in Table II. Shifting a signal in time causes a phase change in the spectrum that is proportional to both the size of the shift and the frequency. This means that the phase of the spectrum is dependent on the beginning point of waveform sampling. It is for this reason that, although the magnitude spectrum is unaffected, an accurate reference is necessary if accurate phase data are desired. Shifting a spectrum in frequency is well known in chemical instrumentation, as it corresponds to modulation of the signal. A common example is modulation of the d.c. output of a detector, i.e. shifting its frequency, which allows the use of frequency selective electronics to isolate the detector signal from background and flicker (1/f) noise. Both time and frequency shifting cause oscillations in the Fourier (reciprocal) domain. This similarity is obscured because it is more natural to think of modulating a signal than of "modulating" a spectrum (by delaying the signal). Nevertheless, it is important to avoid errors in trigger timing (commonly termed "trigger jitter") since a delay can "modulate" the frequency spectrum. If the spectrum of a waveform is $H(f) \exp(-j2\pi ft_1)$ and a reference waveform is given by $R(f) \exp(-j2\pi ft_2)$, where $f$ is frequency and $t_1$ and $t_2$ are
the delays of the trigger past some arbitrary fixed
point, then the normalized spectrum is:

\[
\begin{align*}
H(f) \exp[-j2\pi f T_1] &= \frac{H(f) \exp[-j2\pi f (T_1 - T_2)]}{R(f) \exp[-j2\pi f T_2]} R(f).
\end{align*}
\]

If there is not trigger error in the sampled waveforms
then \(T_1 = T_2\) and the exponential term is unity.
Conversely, if \(T_1 \neq T_2\), then the normalized spectrum will
contain oscillations due to the difference in triggering
points.

The above properties of the Fourier transform have
been discussed in terms of the continuous Fourier
transform. It should be noted that these properties are
entirely applicable to the discrete Fourier transform
(DFT) as well (Table II).

An interesting property of the DFT, related to the
multiplex advantage, might be called the "digitization
advantage". As pointed out by Horlick and Malmstadt
[20], the effective resolution of an analog to digital
converter (A/D) can be increased by digitizing a signal
containing more than ±1 bit of random noise and then
averaging in a processor with a longer word. For
example, the resolution of our 8 bit A/D can be
increased by ensemble averaging separate arrays in the
IBM System 9000 microcomputer using a 16 to 32 bit word.
Since the Fourier transform is essentially a complex weighted average it should, in like manner, increase the effective digital resolution of the measurement system beyond the expected 8 bits. In this context, it is not necessarily desirable to use ensemble averaging to reduce noise in the time domain signal to less than ± 1/2 bit.

The FFT is of course an implementation of the discrete Fourier transform. The DFT and its inverse are represented by equations (10) and (11):

\[
G(\frac{n}{N\Delta t}) = G(nf_o) = \sum_{k=0}^{N-1} g(k\Delta t) \exp(-j2\pi kn/N)
\]

\[
g(k\Delta t) = \frac{1}{N} \sum_{n=0}^{N-1} G(nf_o) \exp(j2\pi nk)
\]

Note that the discrete transform is a function only of array indices and size. The value of \(\Delta t\) does not enter into the calculation at all. The actual time scale is not part of the DFT and only has a role in the interpretation of the results.

Since the DFT is a digital approximation of the Fourier transform, certain restrictions on the nature of the input data are imposed. Obviously any array of
numbers can be put into an FFT program, but this does not mean valid results will be produced.

There are two errors of particular concern when applying the FFT to experimental data. They are "leakage" and aliasing. As will be shown later, both are general errors associated with digitally sampling an analog waveform for only a portion of its duration. According to the Nyquist sampling theorem, a waveform must be sampled twice per period of the highest frequency present in the signal. The Nyquist frequency $f_N$ is thus one half of the sampling frequency. A waveform is undersampled if the waveform contains frequencies above the Nyquist frequency, which will then be "aliased" as lower frequencies and will appear as if the actual spectrum were folded at $f_N$. (Figure 1A) If the aliased frequency is higher than $2f_N$, then it will be aliased as if the true spectrum were folded at $f=0$ and $f=f_N$, like Z-fold computer paper. It is important to note that the Nyquist limit is a theoretical one that holds only in the limit of infinite signal to noise ratio. In real (noisy) systems the waveform must be sampled more often, the practical lower limit being 4 to 8 times per period of the highest frequency [21].

Leakage arises from the use of a limited observation time to estimate the spectrum of a waveform that may have a much longer duration. Theoretically, it arises
when the waveform spectrum is convoluted with the Fourier transform of a sampling window.

Phenomenologically, it occurs when frequencies of the true spectrum are not sampled for an integral number of periods. In this case, the DFT estimated spectrum cannot give a value for these frequencies, because the only results calculated are for harmonics of $f_0=1/T_0$, where $T_0$ is the observation time. The power of these "off harmonic" frequencies then appears to have leaked into the adjacent harmonics (Figure 1b); hence the term "leakage".

To use the FFT for general data processing, an understanding of the above restrictions can be achieved by considering the DFT as a special case of the Fourier transform. Brigham [1] very effectively illustrates this graphically. The graphical derivation of the DFT pair, which corresponds to a continuous Fourier transform pair, is shown in Figure 2. Sampling of the time domain function $h(t)$ (Figure 2a) is represented by multiplication of $h(t)$ by an infinite series of impulse functions $\delta_0(t)$ (Figure 2b). The result is an exponentially decaying sequence of delta functions in the time domain, an infinitely long discrete array (Figure 2c). The corresponding frequency domain operation is the convolution of $H(f)$ with $\delta_0(f)$. It is significant here that the Fourier transform of a
sequence of impulses in time with a spacing of $\Delta t$ is a sequence of frequency domain impulses with a spacing of $1/2\Delta t$. Thus, convolution of $H(f)$ with $\Delta o(f)$ gives a function that is periodical in the frequency domain with a period of $1/2\Delta t$. The effect of aliasing can be seen in figure 2c, where the dotted lines show aliased frequencies. Because the sampling was less than the Nyquist limit, information is lost and frequency components above $f=1/2\Delta t$ are "folded" back into the interval $(-1/2\Delta t, +1/2\Delta t)$. In accordance with the time scaling theorem, if $\Delta t$ is reduced in the time domain, then the frequency domain impulse sequence is more widely spaced, and if it is made small enough, encompasses the entire bandwidth of $H(f)$, thereby broadening $h(t)$, until all components outside the interval $(-1/2\Delta t, +1/2\Delta t)$ are negligible. This is equivalent to saying that the discrete sequence in Figure 2c does not accurately represent $h(t)$. For this reason, the practice of inserting a low pass "anti-aliasing" filter into the sampling system is almost universally followed. The next step in the conceptual digitizing process is truncation of the discrete array in Figure 2c by multiplying it with a windowing function (Figure 2d). Normally this window is rectangular, as in the figure, but triangular or trapezoidal "apodization" functions are often used as well, all of whose time
domain forms taper more smoothly toward zero at the edge of the sampling window. The corresponding frequency domain process is convolution of the repetitive spectrum in Figure 2c with the spectrum of the windowing function in Figure 2d. At this point, the "leakage" or "windowing" error is introduced. Now the discrete array representing $h(t)$ is of finite length and can be placed in an array variable on a microcomputer, but the cost is the introduction of oscillation in the analogous representation of $H(f)$. Except for the special case of periodic waveforms, the effect of truncation cannot be eliminated, but only reduced, by increasing the observation period, $T_0$, thus increasing the rate at which the strength of the sidelobes decay to negligible values in the Fourier transform of the windowing function. This reduces the size of the oscillations in $H(f)$. Such a reduction can also be achieved by using a tapered windowing function, which has smaller sidelobes than the rectangular function. This alternative is actually a Fourier transform smoothing operation on $H(f)$ and, like most smoothing operations, distorts the original function.

The final step in the graphical derivation of the DFT pair is sampling $H(f)$ to produce the discrete frequency domain result. Now $H(f)$ is multiplied by a sequence of equidistant impulses with spacing $f_0=1/T_0$. 
The result is a discrete array corresponding to the DFT of \( h(t) \). This digitized process is, by the convolution theorem, equivalent to convolution of \( h(n\Delta t) \) with the Fourier transform of the frequency domain sampling function. The result, as when the time domain signal was sampled, is a periodic function of time with period \( T_0 \). Thus, it is sometimes said that the FFT "assumes" that the waveform is periodic. The elimination of leakage when \( T_0 \) is equal to the periodic waveform is due to the coincidence of the sampling point in the frequency domain with the points in \( \tilde{H}(f) \), where the oscillating deviations from \( H(f) \) are zero.

**Accuracy of the DFT as an Estimator of the Integral FT**

Periodic waveforms are most compatible with the DFT because, as illustrated in Figure 2g, the members of the DFT pair are themselves periodic. Thus, except for a scaling constant related to the observation time, \( T_0 \), the DFT values for a periodic waveform are exactly the same as those for the integral Fourier transform of that waveform, provided that the Nyquist sampling restriction has been obeyed and the waveform has been observed for an integral number of periods.

Another important class of waveforms is the finite duration waveform. Theoretically, time limitation and bandwidth limitation are mutually exclusive. In reality however, waveforms are always bandwidth limited and
appear to be time limited as the signal becomes undetectable (e.g. the commonly sampled exponential decay). An analogous situation is the digitized form of a signal with a very high S/N ratio; the digitized version may appear completely noise free even though there is, of course, noise in the signal. In the practical sense, then, time limited means "effectively time limited". For this signal, when sampled under Nyquist conditions over the exact duration of the waveform, the DFT again exactly represents the integral FT (except for the scaling factor).

These two cases represent two slightly different electrochemical experiments. The former is a steady state situation where the condition of the system is not necessarily the equilibrium condition. The latter is a true transient response experiment where a system, assumed to be at equilibrium, is perturbed by an impulse or by a single pulse cycle. In practice, there may be no difference between the two if the pulse repetition rate is sufficiently low. This advantageous situation allows for ensemble averaging of repetitive cycles to improve S/N and the use of a precessing trigger to increase effective sampling rate.

A third type of waveform is the arbitrary waveform, which is neither periodic nor of finite duration, but is, in all practicable systems, bandwidth limited.
These functions tend to suffer from error due to truncation of the time domain signal. Since the time domain signal is likely to have a considerably different value for the first and last points of the digital array, the time domain member of the DFT pair will have a discontinuity between successive periods. Consequently, the frequency domain function will have a ripple in it. This is very closely related to the leakage error discussed previously. The use of apodization functions is an effective and well developed way of reducing leakage errors.

One example of the arbitrary waveform is the step function, which has been used in this work in the form of step concentration changes to study the response of an ion selective electrode. Technically, it should be called a bandwidth limited step function if it is a response of a physical system. The step function, by definition, has a different value at the beginning and the end of the observation period. Thus, the biggest difficulty with analysis of step functions is leakage. Gabrielli has published a detailed discussion of DFT estimation of step response spectra and has shown that digital differentiation of the data before Fourier transformation provides a marked improvement in the quality of the results.
Another arbitrary waveform is random noise. This is mentioned because of a recent report on the fascinating concept that information can be gleaned by observing the random fluctuations in the system and analyzing them in the frequency domain [22]. As a result of these developments, Fourier analysis of these waveforms is likely to be of increasing importance.

ADMITTANCE MEASUREMENTS OF ELECTROCHEMICAL CELLS

General Theory

A large part of this work involves a novel method for measuring admittance spectra of electrochemical cells. Therefore, a brief discussion of admittance analysis as applied to such cells is in order. Detailed treatments have been given by Sluyters and Sluyters Rehbach [23,24], Smith [25] and MacDonald [26]. Admittance is the reciprocal of impedance and is one of a group of related properties termed "imittance" [30]. Imittance properties, other than admittance and impedance are the complex dielectric constant,

$$\epsilon = \epsilon^' + j\epsilon^'' = Y_x(jwC_0)$$

where $C_0$ is the geometric capacitance of the cell; and the complex modulus $\epsilon^{-1}$. Each of these properties has its own area of application; for example, dielectric spectroscopy is suitable for RF measurements where significant conduction by ionic transport is negligible.
Steady state admittance is given by

\[ Y(f) = Y'(f) + jY''(f) = I(f)/E(f) \]

where \( I(f) \) and \( E(f) \) are complex quantities. With the increasing availability of cost efficient computing power in the late 60's and early 70's, the use of transient or operational impedance based on Laplace transformation of system response to an external perturbation was expanded [27]. Defined in terms of the Laplace variable \( s = \sigma + j\omega \), the operational impedance is given as impedance

\[ (12) \quad Z(S) = E(S)/I(S) \]

or admittance

\[ (13) \quad Y(S) = I(S)/E(S). \]

Operational impedance makes use of the convolution property of the Laplace and Fourier transforms. Laplace transformation restricted to the imaginary axis (i.e. Fourier transformation) gives an operational admittance formally equivalent to steady state ac admittance. For causal (i.e. physically realizable) systems there is also a practical equivalence [28]. This is true not only for single frequency a.c. perturbations, but also for multifrequency inputs, such as step, pulse, impulse, and noise.

Electrochemical cells are inherently nonlinear and, if precautions are not taken, analyses of cell responses
using linear system analysis can be misleading. In order to apply a linear admittance model to an electrochemical cell, the system must be "sufficiently" linear. That is, potential excursions must be small enough that the second and higher order terms of the Taylor series describing the cell response can be neglected. Typically, this is about 5 to 10 mV (peak) across the interface [24]. Since the potential across the cell is divided between impedance due to the electrolyte medium, the interface and, in some cases, the bulk of the electrode, the actual applied signal can be considerably larger; as much as 100 mV (p-p) may be acceptable [29]. In all cases it is wise to verify the absence of nonlinearity effects, which are evident from unexpected current responses at harmonics of the perturbation frequency. The appearance of harmonics in nonlinear systems is the reason for the utility of odd harmonic perturbation waveforms; any resulting current at frequencies corresponding to even harmonics may be safely regarded as due to system nonlinearity.

Admittance analysis of a cell begins by modelling the cell as an equivalent circuit composed of aperiodic elements such as resistors and capacitors. An attempt is then made to relate these circuit elements and their potential dependencies to physical-chemical (molecular) properties of the system. A general equivalent circuit
for a cell with conducting electrodes is shown in Figure 3a, where the circuit elements are defined as follows:

- \( Y_i \): faradaic admittance of the counter electrode
- \( Y_w \): faradaic admittance of the working electrode
- \( C_d_i \): electrical double layer capacitance, counter electrode
- \( C_d_w \): electrical double layer capacitance, working electrode
- \( C_0 \): capacitance element due to geometry of the cell.
- \( G_e \): conductance of the electrolyte

For circuit elements in parallel, the admittances are additive and impedances add as reciprocals, \( Z^{-1} = Z_i^{-1} + Z_w^{-1} \). The reverse is true for series elements. Likewise, series resistances are additive and series capacitances add as reciprocals. If the cell is designed so that the counter electrode impedance is much less than that of the working electrode, then the effect of the counter electrode can be neglected and the cell is represented by Figure 3b. Faradaic admittance, \( Y_v \), can be broken down into a charge transfer component and a "Warburg" component which relates to diffusion limitation of mass transfer. In the cells examined in this work, however, \( Y_v \) approaches zero and is eliminated from the equivalent circuit, which consequently simplifies to that shown in Figure 3c. Finally, in most cases, \( C_0 \) is very small and can be eliminated from consideration except at relatively high frequencies.
This is the circuit shown in Figure 3d. Equivalent circuits can be derived on the basis of graphic displays of admittance or impedance data. The most common ways of analyzing data are through the use of complex plane (Cole-Cole) plots and Bode plots. In complex plane presentations, the data are plotted as $Y''(f)$ vs. $Y'(f)$ or $Z''(f)$ vs. $Z'(f)$. These graphs generally have one or more characteristic semicircles or linear regions corresponding to resistance-capacitance ensembles that represent electrochemical properties such as interfacial capacitance, bulk electrical resistance, and electron transfer kinetics. Often of interest are the constant phase elements, with a constant slope in the complex plane, the most well known being the previously mentioned Warburg impedance, describing a diffusion controlled system [24]. Examples of complex plane plots are shown in Figure 4. An alternate representation is the Bode plot, where $\log |Y(f)|$, $\log Y'(f)$ or $\log Y''(f)$ are plotted against $\log f$ (Figure 5). MacDonald [30] has combined these representations, using "three-dimensional perspective plotting" to simultaneously display $Y'(f)$ and $Y''(f)$ vs. $\log f$.

Two types of cells have been examined in this work: cells with semiconductor electrodes and cells with ion-selective electrodes. The object of study in these cells is the behavior of the electrode itself.
Admittance of Semiconducting Electrodes

With semiconducting electrodes, the equivalent circuit in figure 3d must be further modified to include the impedance of the electrode itself. Thus a series resistance is added to represent bulk resistance of the semiconductor and a series capacitance is added to represent the space charge capacitance of the semiconductor (Figure 6a). Using admittance analysis alone, the circuit in Figure 6a cannot be distinguished from the circuit in Figure 6b, where \( R_T = R_a + R_b \) and \( C_T^{-1} = C_a^{-1} + C_b^{-1} \). Additional information (e.g., dependence on chemical parameters) is required in order to separate contributions from each side of the interface. Often, however, \( R_a \ll R_b \) and \( C_{a1} \gg C_a \) so that \( R_T = R_b \) and \( C_T = C_a \). Normally this is the case; but, for verification, independent measurement of \( R_a \) and \( C_{a1} \) must be made. \( R_a \) can be determined by conductivity measurements. Estimation of \( C_{a1} \) is made by measuring \( C_T \) for electrodes with several different dopant levels \( (N_0) \) [30]; the variation with \( N_0 \) of the Y-intercept of \( 1/C_T^2 \) vs. \( E \) plots, is then proportional to \( 1/C_{a1}^2 \).

Thus, the most straightforward application of admittance analysis to semiconductors is the analysis of \( C_{ac} \). Measurement of \( C_{ac} \) and its linear Mott-Schottky relation, as \( (C_{ac})^{-2} \) versus applied bias potential, is a standard feature of semiconductor characterization.
Conventionally, \( C_{ac} \) is measured via the quadrature (\( 0=90^\circ \)) response to a single frequency sinusoid input of, typically, 1 kHz. The assumption is made that \( I_m = \omega C \). In other words, the admittance of the cell is assumed to be

\[
Y(\omega) = 0 + j\omega C_{ac}
\]

Actually, according to circuit 2b,

\[
Y(\omega) = \frac{(\omega C_{ac})^2 G_{eq}}{(\omega C_{ac})^2 + G_e} + j \frac{\omega C_{ac} G_{eq}}{(\omega C_{ac})^2 + G_e}
\]

which reduces to equation (14) as \( \omega \ll (RC)^{-1} \). Although often fulfilled, this condition may not apply in all cases. Furthermore, a frequency is often chosen arbitrarily, or on the basis of convention rather than on the basis of what frequency is optimum for the measurement of space charge capacitance.

The presence of surface states, energy levels due to surface phenomena, may also affect the nature of cell admittance as they may be represented by circuit elements with characteristic time constants in parallel with the primary space charge capacitance. The effect can be considerable if a single frequency measurement is used, as shown in Figure 7 [31].

Given these possibilities it is apparent that spectrum analysis is valuable for the investigation of
semiconductor/electrolyte systems both from the standpoint of obtaining precise space charge capacitance measurements and determining surface state behavior as a function of applied potential. The primary difficulty with making these measurements by Fourier transformation is the difficulty in obtaining a wide frequency range. Three separate 512 point measurements and transformations are necessary to obtain a 6 decade range, which is about the minimum required when using admittance analysis to study surface states.

The capacitance and conductance of the equivalent circuit can be determined from measured admittance data in two ways. First, and most directly, $C_{sc}$ can be read directly from a plot of $G_p/w$ (Figure 8) and $G_p$ can be read directly from a plot of $wC_{sc}$ (Figure 7). On the other hand, admittance data can be rearranged on the basis of the chosen equivalent circuit (Figure 6b) to give

$$C_{sc} = \frac{|Y(f)| G_p}{2\pi f \sqrt{G_p^2 - |Y(f)|^2}} \tag{16}$$

where $|Y(f)|$ = measured admittance magnitude and $G_p$ = high frequency limit of $|Y(f)|$. Given this, a precise determination of $C_{sc}$ can be made. Furthermore, as shown in Figure 9, deviations from the proposed model, apparent by a dependence on frequency of the calculated
value for $C_\infty$, are more apparent than in the original complex admittance data.

**Non-potentiometric Measurement Using Ion-Selective Electrodes**

The discovery in 1909 by Haber that certain glass membrane electrodes developed a potential difference across the membrane that was dependent on pH marked the beginning of potentiometry as a viable analytical technique. Today the glass pH electrode, a membrane electrode with a fixed site ion exchange membrane, is the most widely used ion-selective electrode. Other important fixed site electrodes are the LaF$_3$ fluoride electrode for measurement of fluoride and silver halide crystal electrodes for measurement of cyanide.

Membrane electrodes are used in chemical analysis via potentiometric measurement of the general cell:

```
Reference electrode 1 | filling solution | membrane test solution | Reference electrode 2
```

In such a cell, the ion-selective electrode is represented by reference electrode 1, the filling solution and the membrane. Solution 1 is essentially used to make electrical contact with one side of the membrane and is of known constant composition. In many cases, such as the silver halide electrodes, direct metallic contact is used. Since the ISE is internally
unchanging, changes in the cell potential can be ascribed to processes occurring at the interfaces with the test solution. Normally the potential difference across the reference electrode-test solution interface is constant, and potential changes arise predominantly from ion exchange at the membrane surface. If the ion exchange process involves only one (or a few) types of ion, then the cell potential responds selectively to the concentration of those ions in the test solution.

The theory of potentiometric response is well covered elsewhere [32-35]; of primary concern here is charge transport within the membrane itself, particularly the fluoride membrane. The fluoride electrode consists of single crystal LaF₃ doped with EuF₂ impurity. The conductance of the LaF₃ crystal is due to movement of F⁻ ions through crystal site vacancies called Frenkel defects. The incorporation of Eu(II) ions increases the number of defects and consequently increases membrane conductance [33]. The fluoride and glass electrodes both have hydrolyzed surface films but the fluoride electrode differs from the glass electrode in that the charge carriers in the fluoride membrane are the same species as the analyte. Both electrodes are represented by the same equivalent circuit [36,37]. The equivalent circuit for both electrodes, shown in Figure 10, is composed of two
complex impedance elements, each consisting of a parallel array of resistances, and a nonideal, frequency dependent RC series. One impedance element represents the bulk membrane and one represents a hydrolyzed surface film. The presence of frequency dependent circuit elements was attributed by Brand and Rechnitz to non-linear response [45]. In one study by Brand and Rechnitz [36], it was observed that values for the circuit elements varied from electrode to electrode; but the nernstian electrode response was unaffected by those differences.

In the early 1980's, Powley and Nieman [38-41] measured the conductance of ion-selective electrodes with a bipolar pulse conductance technique (BICON). BICON uses two pulses of opposite polarity, but of equal duration. Based on an equivalent circuit analysis, the assumption is that the capacitive current is exactly zero at the end of the second pulse, and the measured total current is proportional to the dc conductance. A point of importance regarding BICON is that the pulses used have large magnitudes (2-5V) [43].

Powley and Nieman have reported that the conductances of Ca\(^{2+}\) and F\(^{-}\) ion-selective electrodes vary systematically with concentration of the ion of interest [38-42]. The advantages claimed for this technique were faster response times than in
potentiometric methods (< 50 msec) and the ability to perform ion-selective measurements without a reference electrode. These advantages were not found in similar, earlier work by Brand and Rechnitz [36], using impedance measurement techniques. Subsequent work by Sandifer and Gross [44] using BICON raises doubts about the Powley and Nieman results as well. Later work by Powley and Nieman indicated that a reference electrode is, in fact, required. Further experiments therefore were necessary to attempt to resolve some of these unanswered questions and to improve our knowledge of those factors that effect and control ion-selective electrode measurements.
<table>
<thead>
<tr>
<th>Property</th>
<th>Fourier Transform</th>
<th>Discrete Fourier Transform</th>
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<tbody>
<tr>
<td>Linearity</td>
<td>$x(t) + y(t)$ = $X(f) + Y(f)$</td>
<td>$x(k) + y(k)$ = $X(n) + Y(n)$</td>
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<tr>
<td>Time Shifting</td>
<td>$h(t - t_0)$ = $H(f) \exp(-j2\pi ft_0)$</td>
<td>$h(k - i)$ = $H(n) \exp(-j2\pi ni/N)$</td>
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<tr>
<td>Frequency Shifting</td>
<td>$h(t) \exp(j2\pi f_0)$ = $H(f - f_0)$</td>
<td>$h(k) \exp(j2\pi k/N)$ = $H(n - i)$</td>
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<tr>
<td>Time Convolution Theorem</td>
<td>$y(t) * h(t)$ = $Y(f)H(f)$</td>
<td>$y(k) * h(k)$ = $Y(n)H(n)$</td>
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<tr>
<td>Frequency Convolution Theorem</td>
<td>$y(t)h(t)$ = $Y(f) * H(f)$</td>
<td>$y(k)h(k)$ = $\sum_{n=0}^{N-1} Y(n)*H(n)$</td>
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<td>Parseval's Theorem</td>
<td>$\int_{-\infty}^{\infty} h^2(t) dt = \int_{-\infty}^{\infty}</td>
<td>H(f)</td>
</tr>
<tr>
<td>Time Scaling</td>
<td>$h(kt)$ = $\frac{1}{k} H\left(\frac{f}{k}\right)$</td>
<td></td>
</tr>
<tr>
<td>Frequency Scaling</td>
<td>$\frac{1}{k} h(kt)$ = $H(kt)$</td>
<td></td>
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Figure 1a: Aliasing: frequencies above $f_N$ appear erroneously (open bars) in the FFT spectrum as if the true spectrum were folded about $f_N$.

Figure 1b: Leakage occurs when $T_0$ is not an integral multiple of waveform period.
Figure 2: Brigham's conceptual development of the FFT. (from reference 1)
Figure 3: Four possible equivalent circuits which may be used to represent an electrochemical cell. See text for significance of circuit elements.
(a) equivalent circuit for complete electrochemical cell.
(b) equivalent circuit if counter electrode admittance is neglected.
(c) simplification of (b) in the absence of faradaic processes.
(d) low frequency equivalent of (c) since $C_e$ is small.
Figure 4a: Complex plane projection (Cole-Cole plot) of simulated admittance for circuit 3C when $C_e \ll C_a$ and $R = 99.5 \, \Omega$. Frequency increases from left to right.
Figure 3: Bode diagram (log-log plot) for admittance of circuit 3C when $C_a \ll C_{a1}$. 

Admittance

$log(f)$

$(\alpha)_{eq}$
Figure 6: Three possible interpretations of simple equivalent circuit for a cell with a semiconducting electrode:

(a) equivalent circuit similar to Figure 3(d) but including the admittance of the electrode itself. The broken line represents the interface.

(b) a circuit which is indistinguishable from (a) on the basis of impedance/admittance spectra alone.

(c) interpretation of (b) when $R_b \gg R_a$ and $C_{bc} << C_{dl}$. 
Figure 7: Simulated log ($\omega C_p$) vs log ($f$) curve for model circuit with (solid line) and without (broken line) surface state analogues represented by $G_s$ and $C_s$. $G_b = 0.05 \Omega^{-1}$; $C_b = 0.53 \mu F$; $G_s = 0.001 \Omega^{-1}$; $C_s = 0.53 \mu F$. (based on reference 31)
Figure 8: Simulated log ($G_p/w$) vs log $f$ curve for model circuit with (solid line) and without (broken line) surface state analogues. Circuit elements are the same as for Figure 7.
Figure 9: log $C_m$ vs log ($f$) for n-TiO$_2$ calculated from admittance data on the basis of circuit 6C. Deviations from the model are apparent.
Figure 10: Equivalent circuit of Sandifer and Buck [37] for Fluoride and glass electrodes. $R_m$ and $Z_m$ represent bulk admittance; $R_L$ and $Z_L$ represent a hydrated surface film.
EXPERIMENTAL TECHNIQUES

INSTRUMENTAL APPROACHES

Three different instrumental approaches were used in this research. Although there was some overlap, essentially separate instrumental configurations were used in each of the three main sections of this work. The only common feature of all three sections is the use of the IBM System 9000 microcomputer for data collection/processing. The CS9000 was a 16 bit microcomputer based on an MC 68000 microprocessor with a clock speed of 8 MHz. All data were transferred by GPIB (IEEE-488) from the appropriate instrument. The programs, written in BASIC, are discussed subsequently.

Transient Current Response Experiments

Voltage pulses were applied at the external input of the potentiostat with a Princeton Applied Research (PAR) Model 175 Universal Waveform Programmer (Figure 11). The potentiostat used for virtually all TiO₂ related experiments was the PAR Model 173 potentiostat/galvanostat, operated exclusively in the potentiostatic mode, equipped with a model 179 current follower. The output of the current follower was filtered with an appropriate passive (RC) low pass filter to remove frequency components above the Nyquist sampling limit. The filtered signal was
digitized using a Tektronix Model 46B digital oscilloscope with 8 bit Y-axis and 9 bit X-axis resolution. The oscilloscope had built in ensemble averaging capability which allowed ensemble averaging up to 256 repetitive sweeps. Oscilloscope synchronization was by triggering the leading edge of the pulse from the waveform programmer.

**Steady State A.C. Experiments**

For comparison with the Fourier transform measurements, conventional single frequency Mott-Schottky experiments, essentially a.c. voltammetry at a semiconductor, were performed. For these experiments, the external source was a PAR Model 124 lock-in amplifier (Figure 12). The internal reference of the Model 124 was added to the PAR 173 input, and the current follower output was detected using phase selection detection at the reference signal frequency. There was, of course, no low pass filtering necessary. The analog output of the PAR 124, proportional to the strength of the detected signal, was measured with a Kiethley Model 179 TRMS digital multimeter, and transferred to the CS9000, via GPIB, for storage and processing.

**Ion-Selective Electrode Study**

The work with ion-selective electrodes represented a major change in instrumentation. The PAR 173/175
system was replaced with a PAR 273 potentiostat/galvanostat. The PAR 273 was a superior potentiostat to the older Model 173, and was controllable by the IBM CS9000. Waveform generation, experimental control, and data collection could all be performed via computer control for signals up to 2 kHz. Thus, instrumental configuration for the potentiometric and bipolar conductance studies consisted of attaching the cell to the leads of the potentiostat, and connecting the latter to the CS9000 by GPIB. For the admittance measurements, however, the technique introduced in the TiOz work was used. The configuration was as shown in Figure 12, except that the anti-alising filter was placed along with a first order high pass filter between the external pulse source and the potentiostat external adder input (Figure 13). This reduced the compliance requirements made on the potentiostat since unused frequency components were filtered out before the signal was input to the adder. This also reduced the chances of driving the cell into a nonlinear regime with excessive potential excursions. A major problem in the use of the PAR 273 was a design limitation in the grounding circuits that led to extremely high levels of high frequency noise (>1 MHz), apparently from digital switching in the microprocessors. This
necessitated the use of an additional low pass
(700 kHz) filter placed between the current follower
output and the oscilloscope.

SOFTWARE

Five major programs were written for acquisition
and analyses of data: FASTFOU4, for FFT computation;
LINPLOT, a versatile plotting routine; along with the
data acquisition programs, AVSCOPE6, DVMETERG and
PAR273. All programs were written in IBM CS-Basic
(version 1.2) running under the CSOS (version 1.13)
operating system. Using BASIC was inconvenient only
for the FFT programs, where a FORTRAN implementation
was naturally advantageous for reasons of time.
However, the flexibility of BASIC in I/O, especially
graphics, which was not available in our version of
CS-FORTRAN, compensated for the time disadvantage.

Fast Fourier Transform

The central piece of software in this research was
FASTFOU4, a listing of which is given in Appendix A.
This program used an implementation of the Cooley-
Tukey FFT algorithm, written in BASIC by Stanley and
The program was modified to run on the IBM System
9000. Further modifications enabled the generation of
the full N-1 harmonics rather than just the N/2 unique
harmonics of the Stanley and Peterson version; and also enabled the bit-reversal subroutine to use bitwise ANDing instead of arithmetic comparisons ("less than"). This resulted in a net reduction in computation time from 161 seconds to 90 seconds for a 1024 point transform. Computation time was further reduced by using multiple statements per line. The final version performed a full 1024 point FFT in 45 seconds, using double precision real (64 bit) calculations. This was too slow for anything approaching real-time calculations, so a FORTRAN version was written which performed the same calculations in 15 seconds, using single precision real (32 bit) math. This was still too slow for on-line use, and difficulties with the system I/O subroutines in the FORTRAN libraries made its use unsuitable.

The alternative for off-line use was batch processing of time domain data. FASTFOU6 was a modification of FASTFOU4 that read input file names from "DATA" statements in the BASIC code. This allowed the user to enter filenames into the program code and check for errors before the program was begun. The program would then perform FFT computations for up to 64 data files with an option for normalizing the results with respect to a
reference signal. FASTFOU6 included an error trap for likely errors such as incorrect filenames or nonexistent input files. Thus, the flexibility of the BASIC version effectively compensated for its speed deficiency.

**Graphics**

Since no graphics software was available for the System 9000, LINPLOT (Appendix B) was written to display data graphically. LINPLOT allowed data from several files to be plotted on one graph without necessarily using common abcissa values. This feature allowed comparison of data from several experiments, an important factor since the frequency range for one Fourier transform experiment covers only two or three decades. Thus, several FT experiments could be easily combined to see a much wider frequency range than was available from a single experiment. A choice of seven token symbols or continuous line plots was available for each data set, simplifying the comparison between several sets. The program fragments LOG2APP, XVSYAPP, logXAPP, and logYAPP were written for use with CS-BASIC's "APPEND" feature. Each of these fragments could be APPENDED to LINPLOT to produce log-log, X-Y, or semilog plots. These "appendix" routines are also listed in Appendix B.
Data Acquisition

A large part of the data was collected using the Tektronix 468 digital oscilloscope. The program to interface the CS9000 to the oscilloscope was AVSCOPE6, based on SCOPE2, written by R. J. Gale and R. E. Borjas [2]. AVSCOPE6, listed in Appendix C, took 512 point data arrays from the oscilloscope, averaged a user specified number of these arrays in double precision real variables, and scaled the results based on user specified oscilloscope range settings. The data were then saved on floppy disks for later analyses. The program would save up to four sequential 512 point arrays under a single filename. This allowed considerable averaging flexibility in conjunction with the oscilloscope's capability for ensemble averaging of up to 256 sweeps. The major limitation of the program was the long recycle time of the oscilloscope after data transfer (about 1.5 seconds) and the slow disk writes using CS-BASIC PRINT statements (3-5 second for 1024 points).

Some of the Mott-Schottky and other cyclic voltammetry data were digitized with the Keithley 179 TRMS digital multimeter and transferred to the computer by IEEE-488 communications, using DVMETERG (Appendix D). The Keithley meter stored data in binary coded decimal format and transmitted the data
as ASCII code in 6 bytes (5 digits + sign). DVMETERG read the data and, using CS-BASIC type conversion functions, converted the character string to real format. Data were then scaled according to a range setting specified by the user. Data could be acquired at a maximum rate of 4 points/second, with real-time graphic display of the results.

**Potentiostat Control**

The final major software written was "PAR" (Appendix E), a GPIB interface program for control of the PAR 273 potentiostat and subsequent data collection. The program, PAR, provides for an interactive dialogue with the potentiostat. All PAR 273 commands are accessible through this program. The fact that PAR is written in BASIC is actually an advantage. The relatively slow execution speed provides a control on the rate at which commands are transmitted to the potentiostat. Because separate microprocessors handle the communications and execution of the commands, the instrument easily succumbs to "command overrun" error as a new command arrives before the previous one is completed. The relatively ponderous command processing in PAR generally prevents command overrun.
The only significant problem with the program was that the System library IEEE driver timeout could not be enabled. This imposed two severe restrictions on the program: the potentiostat could not be polled with the system library polling routine and, more seriously, any command that required a response from the PAR 273 had to be followed by a "Listen" command (defined by Function key #1). The alternative of polling the instrument through software to see if a response was ready was not available. The problem with this was that if the F1 key was inadvertently hit when the PAR 273 had no output ready on the GPIB, the timeout was inoperative; the computer had to be rebooted from a cold start. Ordinarily this was only an inconvenience; the F1 key was far enough removed from the other working keys that the situation arose only rarely. The timeout problem seems to exist only in the version 1.13 system; when the routine was adapted to version 2.0, the timeout was operative. At the time, however, conversion of the entire program to CSOS 2.0 would have been too time consuming.

Features of PAR included user defined procedures that could be incorporated into the BASIC code. Comments in the program provided instructions for adding procedures. There was also facility for including a system function packet for invoking IEEE
driver functions. Finally, the user could create floppy disk "command files", containing series of commands to be sent to the PAR 273 when that file was called with a "DISK" option. This allowed easy and reliable recreation of experimental conditions. Data were transferred in 12 bit twos-complement format and were automatically converted to mA or mV, whichever was appropriate. If the automatic range selection option in the PAR 273 was active, the data were automatically scaled accordingly. Error traps were provided to account for a variety of errors, mostly associated with file handling or input format errors, and to close all files and the GPIB in the event of a fatal error.

CONSIDERATIONS IN SELECTION OF PERTURBATION WAVEFORMS

The original approach with the TiO₂ experiments was the same as the earlier approach of Creason et al. and others. By the time scaling property, if the pulse widths were small, the bandwidth of the signal would be large; for maximum spectral bandwidth duration of the pulse had to be a minimum. In the limit of zero pulse width, this is the traditional approach of observing the time domain impulse response. On the other hand, data quality in general, and particularly in lower harmonics, suffered if the pulse duration was
small; for maximum data quality the pulse duration had to be a maximum. In the limit of infinite pulse width, this is the traditional approach of observing the time domain step response. In the study of reverse biased semiconductor electrodes, there was considerable flexibility in waveform choice compared with the faradaic impedance measurements. The minimum pulse duration, \( t \), consistent with high quality low frequency data, corresponded to about three time constants of the exponentially decaying response. The observation time varied from 2.0\( t \) to 10\( t \). In practice, observation times greater than 4\( t \) were usually only interpolated results. Because, according to the above criteria, \( t \) was the time required for nearly complete relaxation of the "pulse on" transient, and because the following "pulse off" transient was roughly symmetrical, there was no data actually acquired after 2\( t \), and the additional time amounted essentially to zero-filling. According to Ernst [3], zero-filling, appending a string of zeros to extend a data record to twice the number of original data points, actually increases resolution, but any additional zero-filling amounts only to Fourier domain interpolation.

A difficulty with the use of the above pulses was that the spectrum was defined by a \((\sin X)/X\) function,
so not only did the magnitude generally decrease with increasing frequency, but it also passed through nodes at intervals of $1/T_0$. Thus there were regular frequency intervals at which the excitation magnitude approached zero. Obviously these were points where precision of impedance results was poor and where "catastrophic" errors were often found [4]. The occurrence of these nodes was difficult to account for in data processing software except at pulse durations of $T_0/k$, where $k$ is a positive integer. The behavior of the magnitude spectra for several pulse widths is shown in Figure 14.

Note especially that the behavior of the $T_0/2$ pulse, i.e. square wave, is particularly simple. For a square wave (Figure 14d), the frequency domain sampling points occur only at nodes and local maxima of the $(\sin X)/X$ function describing its Fourier transform. That leads to an odd harmonic waveform, in which even harmonics have a magnitude of zero and odd harmonics a magnitude inversely proportional to $f$. Furthermore, the spectrum of the waveform can be "flattened out" by appropriate filtering due to the Fourier relationship between differentiation with respect to time and multiplication by $jw$. In fact, advantage was taken of this property by using a "partially" differentiated square wave (high pass
filtered) as a perturbation signal. A truly differentiated square wave would produce a bipolar impulse pair, but with compromised quality of low frequency data. The use of "partial" differentiation allowed the maintenance of data quality while producing a distorted bipolar pulse. Coincidentally, Dobhoffer and Pilla [5] showed that a bipolar pulse was useful for reducing faradaic nonlinearities.

EXPERIMENTAL PROCEDURES

Unless specified otherwise, water used in all experiments was obtained from a glass Gilmont continuous still (Model V) and was stored in polyethylene carboys. All chemicals met ACS standards, and were used "as is" unless specified otherwise. Electrochemical cells were degassed for at least 20 minutes with solvent saturated argon that had been passed over copper catalyst to remove traces of oxygen. The exceptions to this were the ion-selective experiments, which were not degassed. Measurements were made in unstirred air jacketed glass cells, again with the exception of the ion-selective electrode studies. These were performed in 100 mL polypropylene beakers with slow magnetic stirring. In general, prepared solutions were stored in polyethylene bottles.
n-TiO₂ Admittance Measurements

Several pieces of single crystal n-TiO₂ which had previously been doped to $10^{19}$ cm$^{-3}$ by high temperature hydrogen reduction [6], were used as electrode material. In pretreatment, the crystals were soaked in a 1:1 mixture of concentrated sulphuric and nitric acids for two days, and then rinsed with distilled water. They had a semi-glossy blue-black appearance and were hydrophobic, resisting wetting with water.

Electrodes were prepared by scratching the back of the n-TiO₂ crystals with coarse emory cloth, a steel file or a utility blade. The roughened surfaces were coated with a 3:1 gallium-indium alloy which had a melting point of about 20-25°. Electrical contact was made with 20 ga. multi strand general purpose electrical wire. The electrode assembly was then coated with Devcon General Purpose (EK-1) white epoxy. Mott-Schottky measurements were made in 0.1 M Na₂SO₄ and with 5M NaOH used to adjust pH.

Measurements were made using conventional a.c. technique and the pulse-FT technique. Comparisons between the a.c. and FT techniques were made for both the n-TiO₂/0.1 M Na₂SO₄ interface and dummy cells constructed from aperiodic elements (resistors, capacitors).
The a.c. technique was performed with the experimental configuration shown in Figure 12. Quadrature (θ = +90°) currents were measured for the semiconductor cell, then space charge capacitance was calculated using the measured quadrature with the assumption that the low frequency limit (equation 14) applied. Dummy cells using RC series with varying capacitance were measured to make calibration curves of I vs. C. Amplitudes were kept to 10 mV and below. All a.c. Mott-Schottky experiments were repeated at several frequencies, usually in the range of 500 Hz to 3 kHz. The potential scan rate used was slow, 10 or 20 mV/sec.

Admittance measurements made with the pulse-FT technique were taken at discrete bias potentials, normally at +0.5, 0.7...+1.5V vs. SCE. The cell was left at open circuit between response measurements. The instrumental arrangement was that shown in Figure 11, using the PAR 173/175 potentiostat/waveform programmer. The philosophy behind pulse choices was that shorter pulses were better for high frequencies and longer pulses were better for low frequencies. Often the experiment was repeated with two different pulse lengths; for example, a short pulse of 0.1 To might be followed by a subsequent experiment using 0.4 To. A limitation on the upper frequency limit of the
measurements was that the PAR 175 would not produce pulses of less than 0.1 msec. Pulse amplitudes were limited to a maximum of 50 mV and were exclusively positive-going.

Data were collected with the Tektronix 468 digital storage oscilloscope with low pass filtering at the oscilloscope input. For these experiments, first order filters were used, with the corner frequency at the 100th harmonic of the spectrum being observed. This, combined with the 1/f decay of the perturbation spectrum, produced a second order rolloff in the measured spectrum, which reduced the effect of aliasing. Because the perturbation and response could not be measured simultaneously, the perturbation waveform was sampled using a high degree of averaging before cell response measurements began. Typically, on the order of 64 sweeps were averaged in the oscilloscope and 64 of the resulting arrays were averaged using AVSCOPE6. This measurement could be made with the cell at open circuit. Furthermore, because the perturbation signal, and hence its spectrum, remained unchanged throughout the experiment, except for a d.c. offset, only one or two highly averaged perturbation waveforms needed to be digitized. These would then serve as reference signals for all admittance calculations. Perturbation
waveforms were taken directly from the waveform programmer rather than through the potentiostat response to a known resistance. This had the major disadvantage of allowing gain-phase distortion by the potentiostat-current follower system to appear in the admittance spectra. Cell response was, of course, also measured with the Tektronix 460 oscilloscope, but with less averaging. Normally, 64 sweeps were averaged in the oscilloscope and no more than 8 arrays were averaged with AVSCOPE. To maintain a large bandwidth, the current range on the PAR 173 was kept as high as possible while maintaining an acceptable signal-to-noise ratio. The signal could be amplified to maximize digital resolution using the pre-amp of the oscilloscope, which in no case produced distortion at the frequencies studied. In order to increase the observed frequency range, it was necessary to perform the experiment twice (for a 4 decade frequency range) or three times (for a 6 decade range).

After the comparison of the performance of the pulse-FT technique to single frequency a.c. measurements, the effect of pH on the system response, particularly space charge capacitance and flat band potential, was studied. The pH of 0.1 M Na₂SO₄ was adjusted, using approximately 5M H₂SO₄ or NaOH, as required. The pH was monitored with a separate pH
electrode continuously immersed in the cell during these pH studies. The order of pH values used was varied, except that neutral and acidic solutions were always tested before those with pH > 8 because of the tendency of alkaline solutions to etch the TiO$_2$ surface. Solution pH ranged from 3.5 to 9.8.

Admittance spectra for dummy cells were obtained by both a.c. and pulse-FT measurements. The dummy cells, built from resistors and capacitors, were based on the simple RC model shown in Figure 3d. The resistors were accurately measured to three significant figures with the Keithley multimeter, and the capacitors used had a tolerance of ±5%. The values for dummy cells were chosen to be similar to $R_a$ and $C_{ac}$, as determined in the TiO$_2$ experiments. Thus 500 resistors were used, with capacitors having values from 0.001 µF to 1.0 µF. Unfortunately the PAR 173/175 system was no longer available, so comparisons between the a.c. and pulse techniques were made using a PINE RDE-3 and a newly introduced PAR 273 potentiostat. The procedure for making a.c. measurements of the dummy cells was the same as for semiconductor experiments except of course that measurements were made only at 0 V bias potential. Potentiostat frequency response measurements were made by adding single known frequency sinusoids at the external input, and
measuring the current response under a constant, purely resistive load. Phase selective measurements were made at frequencies up to 200 kHz with the PAR 124A lock-in amplifier. For frequencies from 200 kHz to 1 MHz, nonphase selective a.c. measurements were made using a Wavetek VCG114 oscillator as a source and the Tektronix oscilloscope for response amplitude measurements.

For Pulse measurement, the Global 4001 pulse generator was used to provide perturbation signals. Admittance measurements were made with the same procedure used previously. Additionally, input pulses were subjected to varying degrees of high pass filtering in order to reduce the disparity between amplitudes of high and low frequency Fourier components.

**Conductance Measurements on Fluoride Ion-Selective Electrode**

Ion-selective electrode (ISE) impedance was studied in the context of earlier BICON studies of the fluoride electrode by Powley and Nieman [7], in which electrode conductance was found to be dependent on analyte concentration. The purpose of the present work was to apply the pulse-Fourier transform admittance technique to investigate the reported link between electrode conductance and analyte
concentration, as well as to determine the influence of the large potential excursions of the BICON technique on electrode conductance. Electrode response was measured with three techniques: bipolar pulse conductance measurements, Fourier transform admittance measurements and potentiometric measurements.

The electrode studied was an Orion 94-09 fluoride electrode. The fluoride electrode was of the same type as used by Powley and Nieman and consisted of a LaF₃ membrane with an internal Ag/AgCl reference electrode.

A 10⁻¹ M fluoride solution was prepared from recrystallized sodium fluoride which had been dried at 110⁰C for 6 hours. This was diluted to provide 10⁻² M and 10⁻³ M fluoride solutions. These three solutions, which were stored in polyethylene bottles, were used to prepare solutions of 10⁻⁴ M to 10⁻⁵ M fluoride, by spiking 50.0 mL of total ionic strength adjusting buffer (TISAB) with 1 to 50 μL of the appropriate solution. All fluoride measurements were made using 1 M potassium acetate, adjusted to pH 5.5, as an ionic strength adjustor. The cell was a three electrode cell with a saturated calomel reference electrode (SCE) and a platinum mesh auxiliary electrode in a 100 mL polypropylene beaker. Solutions were stirred
magnetically during all experiments. Cork disks were placed under the cell to prevent solution heating by the stirrer.

**Bipolar pulse conductance measurements**

BICON experiments were performed using the modification by Powley and Nieman [7], in which a sequence of pulses with decreasing amplitudes was used to generate a linear current vs. pulse height curve, called an "i-V curve". The slope of this curve gives the electrode conductance and the y-intercept gives the so-called "zero pulse" current, said to be systematically related to analyte activity (although the relationship is neither linear nor even monotonic). In the present work, a sequence of six 100 μsec pulses, with amplitudes decreasing from 2V to 25 mV, was used. An example of the waveform used is shown in Figure 15. The pulses were applied by the 14-bit digital to analog converter of the PAR 273, from a computer generated array stored in memory. The current was digitally sampled, with 12-bit resolution, at the end of each pulse. The average of 16 sweeps was saved on disk by the CS 9000 for each of the several concentrations used. Changes of concentration were made by the standard addition method. The dc bias to which the pulse sequence was added was the open circuit potential of the cell containing ISA. A
relay in the PAR 273 insured that the cell was at open
circuit when data were not being recorded, thus
reducing the rate of electrode deterioration.

Fourier transform conductance measurements

After repeating the Powley and Nieman BICON
experiments, Fourier transform admittance measurements
were made on each of the electrodes, for several
analyte concentrations, using the procedure described
earlier for semiconductor electrodes. The Global 4001
output was high pass filtered by a first order 32 kHz
filter, and low pass filtered, at 50 kHz, by a third
order filter. This produced the bipolar waveform,
shown with its magnitude spectrum in Figures 16 and
17. Placement of the low pass filter before the PAR
273 external input reduced performance demand on the
control circuitry. This configuration was an
effective anti-aliasing procedure except for switching
noise from the current follower output. This was
eliminated by placing a 700 kHz low pass filter
between the current follower output and the
oscilloscope. Experimental conditions were otherwise
unchanged from those for the BICON experiments so that
the electrode would be subjected to the same
environment as in the Powley and Nieman work.
Admittance measurements were made over the frequency
range of 300 Hz to 50 kHz, corresponding to the time
scale on which the conductance response was said to occur.

**Potentiometric measurements**

Frequent potentiometric measurements were made to verify that the ion selective response of the electrode had not been damaged by the BICON on the Fourier transform admittance procedures. Response time measurements were made, rather than just steady state potential measurements, to provide an additional indicator of possible electrode degradation. Dynamic response to concentration changes was measured after immersion into a stirred solution of higher or lower concentration, or after injection of microliter quantities of the appropriate concentrated solution. Potential readings vs. SCE were taken by the PAR 273, at intervals of 25 milliseconds. The readings were averaged in blocks of twenty and saved in the data array, giving an effective time resolution of 0.5 second. The response was recorded for approximately four minutes, long enough for all but the lowest concentrations to come to a steady state.
Figure 11: Block diagram of instrumentation for data acquisition in n-TOA Pulse-FT admittance experiments.
Figure 12: Instrumental configuration for steady state a.c. admittance measurements
Figure 13: Instrumental configuration for Pulse-FT admittance study of Fluoride electrode.
Figure 14: Theoretical magnitude spectra for relative pulse widths of (a) 5\%, (b) 20\%, (c) 30\%, (d) 40\% and (e) 50\%.
relative pulse width: 20%

MAGNITUDE (arbitrary units)

DFT values
Integral FT values
Figure 15: BICON diminishing pulse sequence.
Figure 16: Filtered squarewave signal used for input in FT admittance measurements for Fluoride electrode.
Figure 17: Magnitude spectrum of filtered squarewave in Figure 16.
RESULTS

MOTT-SCHOTTKY ANALYSIS OF n-TiO₂

Mott-Schottky analysis is fundamental to the characterization of the semiconductor/electrolyte interface. It is usually used to obtain dopant densities and flat band potentials via the so-called Mott-Schottky equation, a linear relation between $C_{ac}^{-2}$ and applied potential, with dopant density and flat-band potential being key parameters. Ordinarily, space charge capacitance is obtained by steady state a.c. measurements during the application of a slow voltage ramp. The ability to rapidly obtain frequency dispersive information during a single Mott-Schottky experiment would facilitate the evaluation of experimental results in terms of the preceding admittance discussion. Furthermore, the potential speed advantage of a Fourier transform technique can reduce changes in the interface by parasitic electron transfer reactions during the voltage sweep.

Pulse-FT Measurement

As discussed in Chapter 3, the magnitude spectrum obtained by FFT depends upon the "relative pulse length", the fraction of the observation period, $T_0$, corresponding to the "pulse-on" state. In terms of the Fourier domain, the choice of relative pulse length determines the frequencies at which the $(\sin X)/X$
function, the Fourier transform of a pulse, will be \"sampled\". Experiments were performed on n-TiO_2 electrodes using relative pulse lengths of 10%, 20%, 30%, 40% and 60%. Analogously to Figure 14, the magnitude spectra of some experimental pulses are shown in Figure 18. Of particular interest is the occurrence of nodes and very small magnitudes at some frequencies in the magnitude spectra. Obviously at frequencies where the input magnitude is small, relative errors will be large. Consequently, admittance calculations (or any other normalization operation) will produce relatively low quality results. The \textit{a priori} exclusion of such frequencies is thus justified in interpreting experimental results. Though pulses with durations of \(T_0/k\), where \(k\) is a positive integer, theoretically have nodes at every \(k\)th harmonic, small deviations of pulse length from \(T_0/k\) can result in generally small non-zero magnitudes at the expected nodal points. For the higher harmonics, the expected nodal frequencies may even correspond to the larger magnitudes present. An extension of this concept leads to the result for a relative pulse length of 30% which deviates markedly from \(T_0/k\). The magnitude spectrum shown in Figure 18c contains apparently irregular variations in magnitude. While fewer nodes are expected in this spectrum, the occurrence of small magnitudes at irregular intervals
poses a similar problem that is more tedious to overcome.

It is important to note here that this phenomenon should not be considered leakage; leakage errors are actual deviations from expected Fourier transform coefficients. The values obtained are the correct values if the observation period is equal to the waveform period, but seemingly irregular behavior arises here from the nonintegral relationship between the pulse length and the waveform period. In terms of the conceptualization shown in Figure 2, the frequency domain "sampling" is not synchronized with the oscillations of the (sin X)/X function.

Typical admittance results: magnitude, quadrature and in-phase components, produced with FASTFOU6, are shown in Figures 19 and 20 for each of the two crystals. Each of these spectra covers roughly a 4 decade frequency range by combining the results of two separate measurements. The end of each measurement range is identified by a high density of data points in the graphs. It is apparent that the lower harmonics of each measurement produce relatively high quality results. The occurrence of obvious outliers resulting from small magnitudes in the input spectrum are also plainly visible. The most noticeable problem with these measurements is a general decrease in precision for the
higher harmonics in each frequency range. This problem, arising from the overall inverse proportionality between spectral magnitude and frequency, is seen at the highest frequencies on the graphs. It is significant that the higher harmonics suffer only from a decrease in precision and that, in general, there are no systematic errors associated with the data processing.

The data in Figures 19 and 20 are presented in a semilogarithmic format to provide a realistic picture of the type of scatter found in the admittance calculations deriving from this technique. The same spectra are presented in log-log format in Figures 21 and 22. The data in this case have been "combed", as was done by others in the past [10]. In Figures 21 and 22 however, only the data points that can be associated with small input magnitudes have been removed, rather than eliminating points on the basis of statistical deviation from an analytical model. One point emphasized by the logarithmic presentation, in which relative errors are converted to absolute errors, is that the increase in relative deviation at the higher harmonics is roughly as pronounced in the lower frequency range as in the higher range.

A major systematic error is shown in these spectra. Instrumental limitations, especially under such highly capacitive loads, contribute to a rolloff in the
Admittance spectrum. While, ideally, the in-phase component and magnitude should both approach a limiting value, they are seen to decrease at higher frequencies. The admittance quadrature was expected to decrease above a critical frequency, \( f_c = \frac{1}{2\pi RC} \), but the measured capacitance showed a much sharper decrease and, unexpectedly, became negative. Some of this error could have been eliminated by using the instrumental response with a known, purely resistive load as a reference waveform rather than the directly measured perturbation waveform. Interestingly though, part of this error would not be reduced by this procedure. The effect of instrumental response on the admittance results is discussed in a later section.

The above factors are significant in the extraction of space charge capacitance values, \( C_{sc} \), from admittance spectra. As mentioned, \( C_{sc} \) can be determined in two ways. First, measurements can be made in the low frequency limit, where the quadrature is determined predominantly by \( wC_{sc} \). Alternatively, the in-phase component can be used, by measuring the peak of a \( G_\phi/w \) vs. \( f \) curve. The value of this peak, occurring at \( f_c \), is equal to \( wC_{sc}/2 \) for the simplest model of the system. It is evident from Figures 21 and 22 that measurements at \( f_c \), the frequency at which \( G_\phi = wC_\phi \), can be more susceptible to instrumental distortion than
those in the low frequency regime, where $f \ll f_c$. In addition to instrumental considerations, the choice between using $w C_p$ and $G_p/w$ for determining $C_{ac}$ may be affected by the location of $f_c$ within the input spectrum. If $f_c$ corresponds to higher harmonics of the waveform, then, as seen above, the precision of the result will be somewhat poorer than if $f_c$ corresponds to a lower harmonic. If the low frequency limit corresponds to lower harmonics while $f_c$ corresponds to higher harmonics, then $C_{ac}$ may be more precisely derived from the admittance quadrature.

Because of the observed distortion in admittance data at frequencies near the $G_p/w$ peak, series capacitance values for the equivalent circuit were calculated using the low frequency Fourier transform data and the equation

$$y = 0 + jwC_s,$$

where $y$ is total admittance, $w$ is radial frequency and $C_s$ is the series, predominantly space charge capacitance.

The in-phase information was nevertheless useful for verifying an absence of major parallel capacitance such as might be associated with electrode surface states [1,2]. Linear regression of admittance quadrature on frequency (Hz) yielded a slope of $2\pi C_s$. The large magnitudes of the lower harmonics of the pulse were an
advantage here and allowed precise calculations of \( C_n \).
Based on the relative standard error associated with the
regression slope, the values obtained were generally
\( \pm 1\% \) at the 90\% confidence level.

\textbf{A.C. Measurements}

Concurrent a.c. measurements returned frequency
dependent capacitance values that decreased with
increasing frequency. This behavior can be explained in
part on the basis of Figure 21, which shows a lower than
expected \( f_c \) for these cells. Even at the lowest a.c.
frequency used, 500 Hz, the in-phase component is
significant. Thus the system is not in the "low
frequency" regime and the simplification of the equation

\begin{equation}
(18) \quad wC_p = \frac{wC_n G_p}{G_n^2 + (wC_n)^2}
\end{equation}

by neglecting \((wC_n)^2\) in the denominator did not apply
at these frequencies then, because the \((wC_n)^2\) term was
not negligible with respect to \( G_n^2 \). Calculations based
on the assumption \( wC_p \approx wC_n \) yielded low results because
\( wC_n \) was actually less than \( wC_p \). That this was the case
can be shown using the ratio of in-phase to quadrature
components or \( \cot \theta \), where \( \theta \) is the phase angle. This
can be seen from equation 18 to be:

\[ \cot \theta = \frac{\text{Re}(Y)}{\text{Im}(Y)} = \frac{wC_n}{G_n} \]

so that in the low frequency limit, where \( wC_n \ll G_n \),
\( \cot \theta \rightarrow 0 \). The value of \( \text{Re}(Y)/\text{Im}(Y) \) as a function of
frequency for this system is shown in Figure 23. A value of 0.6 for \( \cot \theta \) at 500 Hz, as obtained from Figure 23, corresponds to a phase angle of approximately 60°. This is roughly the same as the phase angle of 69° obtained when both components were measured by the a.c. method. Using phasor notation, the admittance quadrature is

\[
WC_p = |Y| \sin \theta
\]

Assuming a phase angle of 60° and correcting for the \( \sin \theta \) factor gives a calculated capacitance more in agreement with the FT determined values. An accurate value for the phase angle was not usually known, however, because only the quadrature was typically measured during the a.c. experiments. Thus the Fourier transform results were compared to the lowest frequency a.c. measurements, with the expectation that the a.c. results would yield systematically low capacitance values. Typical results for each technique are shown in Figure 24. Also shown are values calculated using FT admittance, assuming \( WC_p = WC_a \).

Correlation plots of FT results vs. a.c. results (Figure 25) showed a linear correlation, albeit with the expected systematic errors discussed above. A fuller validation of the pulse FT approach with respect to the steady state a.c. technique is discussed in a later section.
The obtained C₀ values were used to estimate dopant density (N₀) and the flat band potential (Vₐ₀) of the more highly doped electrode (Crystal I). Mott-Schottky plots, C₋² versus V₀, are described by the equation

\[ C₀₋² = \frac{2}{(\epsilon e N₀ A²)(V₀ - Vₐ₀ - kT/e)} \]

where \( \epsilon \) is the dielectric constant for TiO₂ (\( \epsilon = 172 \)), \( e \) is the electron charge, \( A \) is electrode area, \( k \) is Boltzmann's constant and \( V₀ \) is the applied bias potential. It is evident from equation 19 that the curve should be linear, with slope inversely proportional to ND and an intercept on the x-axis at \( Vₐ₀ + kT/e \). Mott-Schottky plots obtained for Crystal I are shown in Figure 26. The corresponding linear regression parameters are shown in Table III. The two FT experiments gave \( N₀ \) results differing by less than 0.5%. The donor density calculated from the a.c. experiment was 2.3% larger. This was not unexpected in light of the preceding discussion, and was not inconsistent with earlier reports of "frequency dependent" dopant densities [3,4]. The calculated \( N₀ \) is also consistent with the known value of \( \sim 10^{18} \) cm⁻³.

**Conclusions**

The Pulse - FT technique produced consistent results for the semiconductor involved. In fact, the results were superior from the standpoint of accurately
determining the equivalent circuit parameters. The ability to observe the admittance behavior rapidly, over a broader frequency range, pointed out that the system under study had an unusually low $f_c$ and allowed correction for it after the fact. The pulse-FT obtained a broader range of information less often (complex admittance at several frequencies but at fewer bias potentials). Only six potentials were used in the pulse-FT experiments; in the a.c. experiments the quadrature was measured at 50 potentials.

Thus, the pulse-FT technique produced Mott-Schottky results of equal or better precision than the a.c. technique and, in this case, more accurately.

The flat-band potential should show a nernstian dependence on pH due to the acid-base equilibrium at the hydrated TiO$_2$ surface [3,5,6]:

$$\text{TiO}_2 + H_2O \rightleftharpoons \text{TiO}^- + H_3O^+$$

This equilibrium is affected by the potential difference across the Hemholtz layer between the electrode surface and the electrolyte. Being analogous to series capacitances, the total capacitance would be:

$$C_T^{-1} = C_e^{-1} + C_H^{-1},$$

where $C_H$ is the capacitance representing the Hemholtz plane. The above chemical equilibrium thus introduces a shift in measured flat band potential of $-\frac{kT}{e}$ or $-59$ mV at 25°C, for each decade change in proton activity.
Tomkiewicz reported a pH dependent flat band potential for n-TiO$_2$ which varied by $-60$ mV/decade, although measurements were made at only 3 pH levels.

A series of experiments in 0.1M sodium sulphate solutions of varying pH produced widely varying flat-band potentials. A linear regression line did yield a slope of $-62$ mV/decade, compared to the theoretical value of $-59$ mV/decade, although the correlation coefficient was only 0.311 (Table IV). The V$_{fb}$ vs. pH data are shown in Figure 27. The error bars show a large uncertainty for V$_{fb}$ estimates. The variability in these data is probably due to variations in electrode surface with time. It is well known that the admittance of n-TiO$_2$ behavior can exhibit a considerable dependence on the history of the electrode [3,4,12].

The Mott-Schottky slope on the other hand should ideally be constant, being affected only by area, dielectric constant and dopant level. The data shown in Figure 28 exhibit a marked increase in slope at higher pH. This clearly coincides with etching of the crystal surface; electrodes subjected to high pH were easily wetted, whereas fresh electrodes were quite hydrophobic.

The high sensitivity of the interfacial dielectric constant interaction with the solution makes for a potentially excellent chemical sensor [13]. This same
property may also be the source of the large variability in $V_p$, as the above mentioned Helmholtz layer capacitance responds to changes other than pH, such as changes in surface area. In connection with this, it is significant that the electrodes were used repeatedly between polishing procedures. Although the experimental conditions for most experiments did not cause the visibly obvious change in electrode surface, it is entirely possible that surface changes on a more subtle scale were responsible for the poor reproducibility in flat band potentials.

MODEL CIRCUITS

The presence of obvious systematic artifacts in the results with TiO$_2$ required further tests of the FT pulse technique with dummy circuits composed of known circuit elements. Mock three electrode cells were prepared using resistors and capacitors, according to Figure 29, where $Z_e$ was composed of either a pure resistance or a resistance-capacitance series. The use of $R_*$ on the order of 50 $\Omega$ produced a closer approximation to actual experimental conditions. $R_*$ represented the solution resistance between the auxiliary and reference electrodes. This is important because potentiostat performance is known to deteriorate, in terms of stability, when $R_*$ is nonzero [1]. The system in
Figure 29 was still somewhat idealized because the impedance of the reference electrode was neglected and such resistance also decreases instrumental stability. 

Response for Purely Resistive Dummy Cells

Pure resistances were used to test the ability of the pulse-FT technique to reproduce known values under the most stable load: pure resistive impedance with no reactive component due to cell capacitance (e.g. electrical double layer). Typical conductance results are shown in Figure 30. It is apparent that the response is significantly attenuated by the PAR 173 at frequencies above 20 kHz. The distortion in this case was maximized by the use of the waveform generator output as the reference signal. If the reference waveform used was the system response under a known resistive load, then much of this distortion would have been eliminated by the admittance calculation. This assumes the instrumental rolloff has the same profile for the reference and cell responses as is often, but not always, the case. The main artifact of the above "gain-phase" error would then be a decrease in precision due to the reduced magnitudes of higher frequency components in the measured signals. This could present a major problem in using simple pulse waveforms which have magnitude spectra that generally decrease as 1/f in the first place. A log-log plot of the system magnitude
response is shown in Figure 31. The reduced precision due to the 1/f nature of the pulse is again noticeable in the higher harmonics. Furthermore, comparison of curves a and b in Figures 30 and 31 illustrates how the cell impedance can have a significant effect on system response. Even though the two curves are for the same 1 mA/V current range, the magnitude response for the 20 Ω load is down by a factor of 1/√2 at roughly 5 kHz while the corresponding frequency for the 200 Ω load is approximately 50 kHz. The results of resistance measurements made using \( T_0 = 0.1 \) sec. and \( T = 0.02 \) sec (frequency range from 10 to 1000 Hz) are given in Table V. The corresponding semilog plot is shown in Figure 32. The estimated value of \( R \) using the average of all 100 harmonics was remarkably accurate considering that values at some higher harmonics were incorrect by ±1000%! Nevertheless if only the first 20 harmonics were used, uncertainty in the measured value was reduced by a factor of ten (Table VI). The resistances were supplied by a General Radio decade resistance box and were accurate to ±2% of their nominal value. The close agreement between the median and mean of the data suggest that the errors were normally distributed. The relative standard error (r.s.e.) over the first 10 harmonics averaged 0.2%. This high precision was typical for the first several harmonics and the relative
error varied from less than 0.1% up to 0.4%. The relative precision did not vary with signal size. Roughly constant relative precision over a range of signal sizes should be expected if the limiting factor in the result is the A/D precision. This is because the preamp in the digital oscilloscope could be varied so that the same fraction of the A/D range was used even for signals with different amplitudes. Not at all surprisingly, the precision of the results decreased as more harmonics were used in the average, but the standard error over the first fifty harmonics was still only on the order of 1%.

The effect on precision of the $1/f$ decrease in the pulse spectrum can also be seen in the admittance data for a 100 ohm resistor (Table VII).

Again, the general increase in standard error with frequency was seen to be still only in the 1-2% range. Table VII also contains the results from a comparison of three different pulse durations. The number of data points lying more than 4 standard errors from the median for each pulse is given in Table VIII. The poor precision at frequencies above the 50th harmonic is quite apparent. Significantly, the difference between pulses is not particularly large; all three pulse durations gave reasonably good results below the 50th harmonic. The only advantage of the 20% pulse was that
the discarded frequencies came regularly at every fifth harmonic.

The ability to make resistance measurements is not, of course, a great claim for an admittance technique, but the above measurements do provide an idea of the type of precision one can expect in the measurement of more complex systems without such an obvious admittance spectrum. Relevant to measurement of phenomena such as space charge capacitance in semiconductor electrodes is the accuracy with which capacitance values can be measured. Thus, RC circuits with known resistance and capacitance were also measured.

Response for Dummy Cells Having Reactive Elements

Admittance spectra for these dummy cells, as shown in Figure 33, have the same type of systematic distortion as the n-TiO$_2$ systems in the previous section. The admittance is larger than expected at frequencies near $f_c$, followed by a strong decrease at higher frequencies. The rolloff due to amplifier bandwidth limitation was expected from the results with pure resistances, but the unexpectedly high currents arose from the presence of a reactive element (capacitance). As can be seen in Figure 34, the smaller capacitance (and higher $f_c$) circuits produce the expected quadrature, but the in-phase component was larger than expected, in this case by a factor of 4. At
higher frequencies, closer to \( f_c \), distortion of the in-phase component was smaller, but still quite significant (Figure 35).

The result was that accurate capacitance values could be obtained from the \( \omega C_p \) in the low frequency regime for the test circuits, but resistance values based on the in-phase component were grossly in error. Furthermore, the signal attenuation at higher frequencies (Figure 30) prevented use of the high frequency limit estimation of \( R \). Numerical results are presented in Table IX. The capacitance values were calculated from the slope of \( \omega C_p \) vs. \( \omega \) (using linear regression), assuming \( C_p = C_e \). The series resistance was estimated from the slope, \( m \), of the \( G_p \) vs. \( \omega \) curve, which is linear at low frequencies. In the low frequency limit of \((\omega C_e)^2 < G_e^2\), \( m = C_e^2/G_e \) and \( R_e = C_e^2/m \). The precision of this estimate is limited primarily by the small magnitude of the in-phase component at low frequencies.

Apparently, the presence of a reactive component interacts with the feedback system and causes gain-phase errors, in addition to those caused by the more simple signal attenuation in purely resistive loads. The behavior of these systems is consistent with the discussion of Fitch [9] concerning the reference signal used for PRWN-FT a.c. polarographic measurements.
According to Fitch, the equivalent circuit of the reference circuit should match as closely as possible the equivalent circuit of the system under study or "excessive currents will be found at higher frequencies." These higher currents he attributes to aliasing, but the PRWN work was done with more sophisticated filters than were used here, and on the basis of the preceding resistance measurements, aliasing does not seem a likely cause for the "excessive currents." Certainly here at least, the source of the error arises in the potentiostat control circuitry. The effect of capacitance potentiostat stability, as discussed by Roe [8], is shown in Figure 36 in terms of the ratio of input potential to actual applied potential. Analogously, the ratio of measured admittance to predicted admittance, shown in Figure 37, shows the same behavior.

Comparison between Pulse-FT and a.c. Techniques

A final concern was whether distortion of the response by the potentiostat/current follower was accentuated by the use of an input pulse. A series of experiments, using dummy cells as above, was performed using the PAR 273 potentiostat with both steady state a.c. and pulse-FT admittance measurements. The steady state a.c. admittance magnitude, shown for several dummy cells in Figure 38, exhibits the same type of behavior.
as the pulse-FT result with the PAR 173 (Figure 39). The results of the comparison are summarized in the correlation plots presented in Figure 40 and in Table X. The strong correlation between the methods shows that the distortion was not aggravated by higher demands placed on the potentiostat by an input pulse.

NONPOTENCIOMETRIC USE OF FLUORIDE ELECTRODE

Bipolar Conductance Measurements

The original bipolar conductance (BICON) experiments of Powley et al. [7] consisted of current measurements at a single, precisely timed point in the cycle of a bipolar pulse waveform; point 'A' in Figure 41a. A subsequent modification of the technique used a pulse sequence with decreasing pulse heights (Figure 41b). A plot of I vs. $V_{\text{pulse}}$ gave a slope supposedly equivalent to the electrode conductance. The latter technique was used with test solutions of fluoride in an acetate buffer. The conductance obtained from the I vs. $V_{\text{pulse}}$ (I-V) slope was shown to vary in a systematic but complex manner.

In the current work, an Orion 94-09 fluoride electrode was measured using the two techniques above, as well as a further modification in which the current was measured at the end of the first, positive going, pulse (point B in Figure 41b).
Fluoride Measurement using BICON with pulse train

Before using Pulse-FT impedance measurements to examine the relationship between conductance and fluoride concentration, an attempt was made to repeat the earlier BICON experiments using the PAR 273 potentiostat under computer control. The cell response to the pulse sequence was measured to verify that there was in fact a concentration dependence and to note how changes in the application of the technique influenced the results.

"I-V" curves were obtained at each fluoride ion concentration using the current at the end of the negative-going or reverse pulse, as per Powley and Nieman. These curves were in fact linear, with slopes having relative standard errors (r.s.e.) of approximately 0.2% (Table XI). Linear regression of I-V slope (i.e. "conductance") on log [F] showed a significant linear correlation (95% confidence level) if the measurement was made less than 2 seconds after injection of the fluoride standard. If the measurement was made after 60 seconds however, the correlation coefficient was below the critical value of 0.95. There was no significant difference between the estimated I-V curves at t < 2 seconds and t = 60 seconds, but errors in the slope estimate increased from r.s.e. = 17% at t = 2 sec to r.s.e. = 32% at t = 60 sec. Thus, there
was a significant positive correlation between "conductance" and fluoride concentration if the measurement was made quickly, but the correlation was less certain at longer immersion times because of the increased error on slope estimates. The 2 sec. and 60 sec. results are plotted against log $[F^-]$ in Figure 42.

Slope estimates for I-V curves obtained from the forward, positive-going pulses had smaller associated uncertainties, with r.s.e. of only 0.1% (Table XII). Slope estimates were also consistently lower than those obtained from the negative-going pulses. Linear regression of thus obtained conductance against log $[F^-]$ showed a very strong correlation with a correlation coefficient greater than 0.999. An increase in uncertainty of the parameter estimates with increased immersion time was observed in this case, as with the reverse pulses, but even at 60 seconds the correlation was significant at the 99% confidence level. The resulting curves are shown in Figure 43. A comparison of the linear regression results in Table XIII shows a much more definitive correlation associated with the "conductance" or "I-V" slope derived from the positive-going pulses than with that obtained from the negative-going pulses.
Measurements with single pulse

The original BICON technique of measuring current at the end of the reverse pulse of a single bipolar pulse waveform was used to examine the correlation between \( I \) and \( \log [F^-] \). The measured current as a function of concentration can be seen in Figure 44 for pulse heights of \(-2000 \, \text{mV}\) and \(-200 \, \text{mV}\). The corresponding linear regression data in Table XIV show a significant relationship between current for the \(-2000 \, \text{mV}\) pulse at 2 sec and 60 sec following the standard addition. The slope for the measurement at 60 sec however, is not significantly different from zero based on a \( t \) test at the 95% confidence level. As with the above \( I-V \) experiments, the uncertainty increases for longer immersion times.

The cell current was also measured at the end of the positive-going pulse, and again, looking at the above \( I-V \) results, it is not surprising that the forward currents provided similar results with lower uncertainties. These results are illustrated both graphically (Figure 45) and numerically (Table XIV). The regression results indicated a correlation between current and concentration. Once again the 60 second measurements are of lower precision, but even so, a significant correlation and a non-zero slope were
obtained at pulse heights of +2000 mV and +200 mV for measurements at 2 seconds and 60 seconds.

**Analysis of Variance**

Using a one-way analysis of variance (Table XV), the standard deviation for the method was estimated to be 5.9 μA using the ±2000 mV pulse and 0.6 μA with the +200 mV pulse. These two values correspond to 3% of the full scale A/D range that was used. The estimated standard deviation for the -200 mV pulse current was significantly larger at 2.4 μA or 12% of the A/D range. The comparison of the variance between columns (concentrations) and the variance within columns (replicates) showed that there was a significant difference between concentrations. Comparison of the column averages showed a consistently increasing magnitude with concentration for all except the -200 mV measurements, in agreement with the linear regression results. Similar examination of the I-V slopes also demonstrated a significant, positive variation with fluoride concentration. The standard deviation for slopes obtained using the positive pulses was 84 microsiemens (r.s.d. = 0.05%). The standard deviation for slopes obtained using the negative pulses was 160 microsiemens, corresponding to a relative standard deviation of 0.9%. Again, there was a significant, consistently positive trend with fluoride
concentration, as expected from the linear regression results.

**Pulse-FT Admittance**

**Immersion Procedure**

Admittance measurements were made by pulse-Fourier transformation immediately following the transfer of the equilibrated electrode from fluoride free TISAB to solutions containing between $10^{-7}$ and $10^{-6}$ M fluoride. Several additional measurements were made between immersions, and also after potentiometric equilibrium had been reached. The observed frequency range was limited to two decades, 500 Hz to 50 kHz. Because the goal in these experiments was to observe the admittance behavior in the time between immersion and the establishment of a potentiometric steady state, it was necessary to make rapid measurements. Consequently, the use of multiple observation periods to increase the frequency range was not feasible.

The results were similar to those obtained by the frequency sweep method of Brand and Rechnitz [11]. The electrode exhibited characteristics of a parallel RC network at all observed concentrations and times. A plot of impedance in the complex plane was semicircular except at lower frequencies, where it was typical of a constant phase element such as a Warburg impedance (Figures 46 and 47). The data at higher frequencies,
above about 13 kHz, also showed deviations from ideal RC behavior; but, based on the results in earlier sections, this was attributed to instrumental artifacts. Values of parallel resistance ($R_p$), capacitance ($C_p$) and series resistance ($R_s$) were calculated for the equivalent circuit in Figure 48a, using an iterative least squares procedure. These are given in Table XVI. Only frequencies between 3500 Hz and 11500 Hz were used to fit the model because of the above mentioned deviations at frequencies outside this range. The comparable values of Brand and Rechnitz were based on the equivalent circuit in Figure 48b, using a high frequency limiting value of $Z'$ to obtain $C_p$.

**Standard Addition Procedure**

The behavior of conductance, $G = \text{Re}(Y)$, as a function of frequency for the Standard Addition (SA) method is shown in Figure 49. These curves, averages of four spectra at each concentration, show somewhat greater electrode conductance in higher fluoride concentrations at lower frequencies. At frequencies above about 10 kHz however, such a systematic variation in conductance is not apparent. Results for the linear regression of $G$ on $\log [F']$ are given in Table XVII for frequencies of 500 Hz, 3500 Hz, 7500 Hz and 10500 Hz. These frequencies correspond to three distinct regions of the complex impedance plane: the low frequency
"constant phase" region (500 Hz), the "transition" region (3500 Hz) and the higher frequency "RC" region (7500 Hz, 10500 Hz). At 500 Hz and 3500 Hz, linear regression analysis showed a high correlation between G and log [F'], significant at the 95% confidence level. On the other hand, at 7500 Hz and 10500 Hz, no such correlation could be identified.

When the results of the "immersion" experiment were similarly treated, the results showed no significant linear correlation at any frequency. This is shown in Table XVIII. Although the linear regression results did not show a significant correlation, it seemed apparent from the graphs of the data that there was an upward trend in conductance with fluoride concentration (Figure 50).

Analysis of Variance

One-way analysis of variance (ANOVA) was applied to the results of the two methods in order to determine if significant differences in electrode conductance were present in different solutions. A difference between the results at various experimental levels (e.g. different fluoride concentrations) is suggested if the variance between levels is significantly greater than the variance within levels. As can be seen in Table XIX, the differences between concentrations for the BA method do in fact seem to be significant, even at
the 99% confidence level. Only the results at the highest frequency tested, 10.5 kHz, yield an F ratio below the critical value of 5.95. As mentioned earlier, the data above about 10 kHz may be distorted by instrumental response characteristics. Given these results in conjunction with the preceding linear regression results, it seems reasonable that some positive correlation exists between conductance and concentration in this experiment, although the relationship may not be strictly linear. The mean sum of squares within columns (SSE) provides an estimate for the variance due to the method. Thus, the standard deviation for this method was about 0.1 to 0.2 microsiemens. This corresponds to r.s.d. = 0.2%. It must be stressed that these ANOVA results apply only to the SA experiments performed here, in which there is no movement of the electrode between solutions, and serial concentration increases are made instead by addition of known quantities of a standard solution. The replicate measurements are separate admittance measurements made in the same stirred solution at 2, 10, 15, and 20 seconds after injection of the standard. This is analogous to the method used by Powley and Nieman with the BICON technique. Because no movement of the electrode occurs between successive spectra, the r.s.d. 
obtained in the BA experiments is probably a lower limit for the pulse-FT technique implemented here. The 0.2% r.s.d. found here is the same as was found in the preceding dummy cell measurements. It is interesting that 0.2% is smaller than the A/D resolution of the original measurements, which was no better than 1 part in 256 or 0.4%. Also, as would be expected on the basis of preceding semiconductor and dummy cell experiments, the r.s.d. does not increase significantly over the first twenty harmonics of the spectrum.

ANOVA results for the immersion method reinforced the linear regression results, clearly showing no significant difference in electrode conductance when immersed in $10^{-5}$ M and $10^{-7}$ M fluoride solutions. Electrode conductance in fluoride free solutions was found to vary over a range of about 5% among replicates. An attempt to compensate for this was made by subtracting blank values from the conductance obtained in the succeeding fluoride solutions. The differences between concentrations were found to be insignificant, both in a direct comparison of conductance values and in a comparison of conductances with blank values subtracted. Because the immersion method, unlike the SA method, required a physical transfer of the electrodes between a fluoride free solution and a fluoride containing solution, poorer precision for measured
values was expected. This was in fact the case. The
standard deviation for the immersion experiments was in
the 2 - 4 microsiemens range (r.s.d. = 2.5 - 5%),
roughly an order of magnitude larger than the standard
deviation for the BA method.

When electrode admittance was measured under more
conventional conditions, i.e. at potentiometric
equilibrium, the electrode conductance was again found
to be insignificantly affected by fluoride
concentration. Standard deviations were essentially the
same for the previous immersion method and again did not
vary with frequency up to 10.5 kHz. The precision of
the three different measurement procedures - standard
addition, immersion and potentiometric equilibrium - are
summarized in Table XX.

Conclusions

It is quite interesting that current measurements
on the reverse pulse of the ±200 mV bipolar pulse pair
showed a similar result to Powley and Niemani initially
increasing with fluoride concentration and then
decreasing with further additions in fluoride. In
contrast, larger pulses and the current on the forward
(positive) pulse of the ±200 mV pair showed a monotonic
increase with fluoride concentration. One striking fact
was that consistently higher uncertainties were
associated with results from the negative-going pulses.
This was true for both the direct current measurements and the "conductance" calculated from the I-V curves. The results from BICON measurements seem to show a definite tendency to increase with fluoride concentration, especially for large pulses. Previous studies have not shown however, whether this increase is caused by increasing fluoride concentration or by mere coincidence. The result could be due to temperature change, since neither this nor previous work used thermostatted cells; or to drift, which is characteristic of the fluoride electrodes, both in potentiometric and conductometric use [14].

One point that must be stressed is that the BICON measured conductance is surely not conductance in the ordinary sense, as used to discuss electrochemical cells. Electrochemical cells are not electrical circuits composed of linear elements; equivalent circuits are only models. The application of pulses as large as \pm 200 \text{ mV}, and certainly those on the order of volts, cannot be discussed in terms of equivalent circuit models for equilibrium conditions. The fact that the BICON conductance varies with concentration rather than activity, as was pointed out earlier [15], indicates a current controlled by mass transport.

Corresponding FT impedance data show a similar increase in conductance with fluoride concentration when
the standard addition method is used. The observed change occurs only in the 500 to 3500 Hz region, which is associated with the "constant phase" portion of the spectrum. This region corresponds to slower processes in a hydrolyzed surface film [11,16,17]. According to Brand and Rechnitz, the semicircle representing these processes extends down into sub-Hertz frequencies. Hence, only the higher frequency portion is visible in the present data and the semicircular behavior is not seen.

The fact that a solution-dependent change in electrode conductance occurs in a surface film is not surprising; apparent surface resistance coinciding with long time constants (i.e. low frequencies) have been attributed to mass transport limitations in the film [18].

The disappearance of any apparent concentration dependence when immersion or equilibrium measurements were made suggests that the above conductance changes were in some way connected with the standard addition procedure. On the other hand, the increased uncertainty may simply mask very small changes; the standard deviation for the latter two methods was more than an order of magnitude greater than that for the standard addition procedure.
Although not so for equilibrium measurements, admittance quadrature data were very erratic for the immersion and standard addition methods. In fact, in no case was there any discernable relationship between quadrature and concentration. It is interesting that very unusual negative inductance-like behavior of the quadrature was observed in situations where one would expect mass transport to be occurring; that is, during the early moments after a change in fluoride concentration. Variability in the quadrature may reflect the reaction of an extremely sensitive indicator to the difficulties of reproducing surface conditions at the electrode surface [19].

In conclusion, it does not seem very likely that conductometric use of the fluoride electrode will soon, if ever, be a useful quantitative technique; nevertheless, it might well prove worthwhile to pursue further the nature of the capacitive current response in this regard.
### TABLE III

**Mott-Schottky Results via A.C. and Pulse-FT Techniques**

<table>
<thead>
<tr>
<th></th>
<th>a.c. $9500$ Hz</th>
<th>FT #1</th>
<th>FT #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>slope ($\times 10^{-2}$ ($\mu$F $^{-1}$)-$^{-1}$V)</td>
<td>0.81</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>Std. error</td>
<td>0.050</td>
<td>0.042</td>
<td>0.055</td>
</tr>
<tr>
<td>$V_{mb}$ (V vs. SCE)</td>
<td>-3.5</td>
<td>-2.1</td>
<td>-1.9</td>
</tr>
<tr>
<td>Std. error</td>
<td>0.21</td>
<td>0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>$N_D$ ($\times 10^{16}$ cm$^{-3}$)</td>
<td>7.1</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>Std. error</td>
<td>0.44</td>
<td>0.22</td>
<td>0.28</td>
</tr>
</tbody>
</table>
TABLE IV

Linear Regression of $V_{fb}$ on Solution pH

<table>
<thead>
<tr>
<th>Slope</th>
<th>y-intercept</th>
<th>std. err.</th>
<th>std. error</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.059 V/pH unit</td>
<td>-1.2 V vs. SCE</td>
<td>0.080</td>
<td>0.56</td>
</tr>
<tr>
<td>r</td>
<td>0.311</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE V

**Pulse-FT Results for Known Resistances Using 100 Harmonics**

<table>
<thead>
<tr>
<th>R (ohms)</th>
<th>20</th>
<th>200</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>20.3</td>
<td>197</td>
<td>1986</td>
</tr>
<tr>
<td>Mean</td>
<td>20.1</td>
<td>196</td>
<td>1960</td>
</tr>
<tr>
<td>Std. Error</td>
<td>0.8</td>
<td>7</td>
<td>50</td>
</tr>
<tr>
<td>Rel. Std. Err.</td>
<td>4%</td>
<td>4%</td>
<td>2%</td>
</tr>
</tbody>
</table>

### TABLE VI

**Pulse-FT Results for Known Resistances Using 20 Harmonics**

<table>
<thead>
<tr>
<th>R (ohms)</th>
<th>20</th>
<th>200</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>20.0</td>
<td>196.8</td>
<td>1985</td>
</tr>
<tr>
<td>Std. Error</td>
<td>0.1</td>
<td>0.7</td>
<td>4</td>
</tr>
<tr>
<td>Rel. Std. Err.</td>
<td>0.5%</td>
<td>0.4%</td>
<td>0.2%</td>
</tr>
</tbody>
</table>
### TABLE VII

**Effect of Harmonic Number on Measured Resistance for Different Relative Pulse Lengths**

<table>
<thead>
<tr>
<th>Harmonics</th>
<th>20% pulse</th>
<th>30% pulse</th>
<th>40% pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-10</td>
<td>100.5 (0.2)</td>
<td>100.8 (0.3)</td>
<td>99.8 (0.4)</td>
</tr>
<tr>
<td>11-20</td>
<td>100.1 (0.4)</td>
<td>99.5 (0.6)</td>
<td>101.1 (0.5)</td>
</tr>
<tr>
<td>21-30</td>
<td>101.4 (0.6)</td>
<td>100.0 (0.8)</td>
<td>100.4 (1.8)</td>
</tr>
<tr>
<td>31-40</td>
<td>101.8 (1.2)</td>
<td>100.4 (4.1)</td>
<td>98.3 (1.0)</td>
</tr>
<tr>
<td>41-50</td>
<td>100.6 (0.9)</td>
<td>101.7 (1.4)</td>
<td>97.6 (1.3)</td>
</tr>
</tbody>
</table>

Fundamental=10 Hz
* data in ohms, std. error in parentheses
### TABLE VIII

**Number of Data Points More Than 4r From the Median of First 100 Harmonics**

<table>
<thead>
<tr>
<th>Harmonics</th>
<th>20% pulse</th>
<th>30% pulse</th>
<th>40% pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-10</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11-20</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>21-30</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>31-40</td>
<td>2</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>41-50</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>51-60</td>
<td>3</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>61-70</td>
<td>5</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>71-80</td>
<td>8</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>81-90</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>91-100</td>
<td>6</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>35</strong></td>
<td><strong>38</strong></td>
<td><strong>22</strong></td>
</tr>
</tbody>
</table>

*Fundamental=10 Hz*
### TABLE IX

**Experimentally Determined Values for Known Capacitance**

<table>
<thead>
<tr>
<th>Capacitance</th>
<th>Experimental Value (± r.e.e.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.022 μF</td>
</tr>
<tr>
<td>B</td>
<td>0.05</td>
</tr>
<tr>
<td>C</td>
<td>0.10</td>
</tr>
<tr>
<td>D</td>
<td>0.47</td>
</tr>
<tr>
<td>E</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*RC series, R=99.5 for all*
TABLE X

**Linear Regression Estimates for Correlation Between F.T. and a.c. Techniques**

<table>
<thead>
<tr>
<th></th>
<th>Magnitude</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Slope</strong></td>
<td>1.007</td>
<td>1.012</td>
</tr>
<tr>
<td><strong>std. error</strong></td>
<td>0.0049</td>
<td>0.0081</td>
</tr>
<tr>
<td><strong>Y-intercept</strong></td>
<td>2.0 x 10^-4</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>std. error</strong></td>
<td>2.9 x 10^-4</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>r</strong></td>
<td>0.9992996</td>
<td>0.9985855</td>
</tr>
</tbody>
</table>
### TABLE XI

**Linear Regression Estimates of I-V Slopes for Negative-Going Pulses**

<table>
<thead>
<tr>
<th>mol/L F⁻</th>
<th>blank</th>
<th>10⁻²</th>
<th>10⁻³</th>
<th>10⁻⁴</th>
<th>10⁻⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t&lt;2 sec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>slope (µS)</td>
<td>184.3</td>
<td>185.6</td>
<td>186.0</td>
<td>186.1</td>
<td>186.5</td>
</tr>
<tr>
<td>std. error</td>
<td>0.36</td>
<td>0.30</td>
<td>0.29</td>
<td>0.27</td>
<td>0.30</td>
</tr>
<tr>
<td>t=60 sec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>slope (µS)</td>
<td>184.6</td>
<td>185.7</td>
<td>185.7</td>
<td>186.4</td>
<td>186.4</td>
</tr>
<tr>
<td>std. error</td>
<td>0.29</td>
<td>0.31</td>
<td>0.27</td>
<td>0.28</td>
<td>0.31</td>
</tr>
</tbody>
</table>

### TABLE XII

**Linear Regression Estimates of I-V Slopes for Positive-Going Pulses**

<table>
<thead>
<tr>
<th>mol/L F⁻</th>
<th>blank</th>
<th>10⁻²</th>
<th>10⁻³</th>
<th>10⁻⁴</th>
<th>10⁻⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t&lt;2 sec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>slope (µS)</td>
<td>172.9</td>
<td>173.8</td>
<td>174.1</td>
<td>174.4</td>
<td>174.7</td>
</tr>
<tr>
<td>std. error</td>
<td>0.16</td>
<td>0.10</td>
<td>0.15</td>
<td>0.19</td>
<td>0.14</td>
</tr>
<tr>
<td>t=60 sec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>slope (µS)</td>
<td>172.9</td>
<td>173.9</td>
<td>174.3</td>
<td>174.5</td>
<td>174.8</td>
</tr>
<tr>
<td>std. error</td>
<td>0.13</td>
<td>0.16</td>
<td>0.15</td>
<td>0.15</td>
<td>0.11</td>
</tr>
</tbody>
</table>
TABLE XIII

Least Squares Lines for Variation
of I-V Slope with log(F-)

<table>
<thead>
<tr>
<th></th>
<th>positive pulses</th>
<th>negative pulses</th>
</tr>
</thead>
<tbody>
<tr>
<td>t&lt;2 sec.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>slope</td>
<td>2.79 μS/decade</td>
<td>3.0 μS/decade</td>
</tr>
<tr>
<td>std. error</td>
<td>0.021</td>
<td>0.53</td>
</tr>
<tr>
<td>Y-intercept</td>
<td>1.75788 μS</td>
<td>1.877 μS</td>
</tr>
<tr>
<td>std. error</td>
<td>0.00004</td>
<td>0.0012</td>
</tr>
<tr>
<td>r</td>
<td>0.999945</td>
<td>0.969858</td>
</tr>
<tr>
<td>t=60 sec.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>slope (μS)</td>
<td>2.8 μS/decade</td>
<td>3.1 μS/decade</td>
</tr>
<tr>
<td>std. error</td>
<td>0.16</td>
<td>0.88</td>
</tr>
<tr>
<td>Y-intercept</td>
<td>1.7905 μS</td>
<td>1.878 μS</td>
</tr>
<tr>
<td>std. error</td>
<td>0.00036</td>
<td>0.0020</td>
</tr>
<tr>
<td>r</td>
<td>0.996532</td>
<td>0.928272</td>
</tr>
<tr>
<td></td>
<td>-200 mV</td>
<td>-2000 mV</td>
</tr>
<tr>
<td>------------------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>( t&lt;2 \text{ sec.} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>slope (( \mu \text{A}/\text{decade} ))</td>
<td>-0.08</td>
<td>-0.4</td>
</tr>
<tr>
<td>std. error</td>
<td>0.029</td>
<td>0.15</td>
</tr>
<tr>
<td>Y-intercept (( \mu \text{A} ))</td>
<td>38.4</td>
<td>390</td>
</tr>
<tr>
<td>std. error</td>
<td>0.07</td>
<td>83</td>
</tr>
<tr>
<td>( r )</td>
<td>0.888313</td>
<td>0.879403</td>
</tr>
<tr>
<td>( t=60 \text{ sec.} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>slope (( \mu \text{A}/\text{decade} ))</td>
<td>-0.08</td>
<td>-0.6</td>
</tr>
<tr>
<td>std. error</td>
<td>0.038</td>
<td>0.15</td>
</tr>
<tr>
<td>Y-intercept (( \mu \text{A} ))</td>
<td>38.4</td>
<td>390</td>
</tr>
<tr>
<td>std. error</td>
<td>0.08</td>
<td>87</td>
</tr>
<tr>
<td>( r )</td>
<td>0.822141</td>
<td>0.947670</td>
</tr>
</tbody>
</table>
**TABLE XV**

*Sample One Way ANOVA Table for Comparing Measured Current at Different Fluoride Levels*

<table>
<thead>
<tr>
<th>Replicates</th>
<th>Levels:  $10^{-7}$M</th>
<th>$10^{-6}$M</th>
<th>$10^{-5}$M</th>
<th>$10^{-4}$M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1a</td>
<td>34.53</td>
<td>34.66</td>
<td>34.82</td>
<td>35.14</td>
</tr>
<tr>
<td>Day 1b</td>
<td>34.59</td>
<td>34.66</td>
<td>34.88</td>
<td>35.17</td>
</tr>
<tr>
<td>Day 2a</td>
<td>35.54</td>
<td>35.72</td>
<td>35.88</td>
<td>36.22</td>
</tr>
<tr>
<td>Day 2b</td>
<td>35.60</td>
<td>35.72</td>
<td>35.86</td>
<td>36.26</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>N:</th>
<th>16</th>
<th>d.f.</th>
<th>MSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS: 8687</td>
<td>15</td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>SSc: 8682</td>
<td>3 2894</td>
<td>B011</td>
<td></td>
</tr>
<tr>
<td>SSw1: 4</td>
<td>12 0.33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Estimated std. dev. for method = 0.6 µA

*Data are in µAmps; Pulse = +200 mV*
## TABLE XVI

**Equivalent Circuit Elements for Fluoride Electrode**

<table>
<thead>
<tr>
<th></th>
<th>$R_0$ (kΩ)</th>
<th>$C_0$ (μF)</th>
<th>$R_1$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 M $F^-$</td>
<td>2.70</td>
<td>9.05 x 10^{-3}</td>
<td>5.8</td>
</tr>
<tr>
<td>1 x 10^{-7} M</td>
<td>2.90</td>
<td>8.23 x 10^{-3}</td>
<td>5.9</td>
</tr>
<tr>
<td>1 x 10^{-4} M</td>
<td>3.35</td>
<td>7.36 x 10^{-3}</td>
<td>6.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$R_0$ (kΩ)</th>
<th>$C_0$ (μF)</th>
<th>$R_1$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>t=60 seconds</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 M $F^-$</td>
<td>2.84</td>
<td>9.0 x 10^{-3}</td>
<td>5.8</td>
</tr>
<tr>
<td>1 x 10^{-7} M</td>
<td>3.06</td>
<td>8.1 x 10^{-3}</td>
<td>5.9</td>
</tr>
<tr>
<td>1 x 10^{-4} M</td>
<td>2.98</td>
<td>7.1 x 10^{-3}</td>
<td>6.0</td>
</tr>
</tbody>
</table>

**Brand & Rechnitz (1970)**

all conc’ns      5   6 x 10^{-3}   6
TABLE XVII

Regression Results for Std. Addition Method

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Slope (µS/decade)</th>
<th>y-intercept (µS)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 Hz</td>
<td>0.33 ± 0.040</td>
<td>76.5 ± 0.11</td>
<td>0.97754</td>
</tr>
<tr>
<td>3500 Hz</td>
<td>0.42 ± 0.080</td>
<td>84.8 ± 0.18</td>
<td>0.96543</td>
</tr>
<tr>
<td>7500 Hz</td>
<td>0.25 ± 0.052</td>
<td>81.7 ± 0.23</td>
<td>0.78615</td>
</tr>
<tr>
<td>10500 Hz</td>
<td>0.1 ± 0.14</td>
<td>79.2 ± 0.32</td>
<td>0.29678</td>
</tr>
</tbody>
</table>

Ranges are ±1 std. error
D.f. = 2  r_c = .950 at 95% confidence level

TABLE XVIII

Regression Results for Immersion Method

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Slope (µS/decade)</th>
<th>y-intercept (µS)</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 Hz</td>
<td>0.3 ± 0.24</td>
<td>104.3 ± 0.52</td>
<td>0.6622</td>
</tr>
<tr>
<td>3500 Hz</td>
<td>0.6 ± 0.44</td>
<td>115.0 ± 0.92</td>
<td>0.6935</td>
</tr>
<tr>
<td>7500 Hz</td>
<td>0.5 ± 0.39</td>
<td>125.6 ± 0.87</td>
<td>0.6443</td>
</tr>
<tr>
<td>10500 Hz</td>
<td>0.6 ± 0.20</td>
<td>166. ± 1.9</td>
<td>0.8865</td>
</tr>
</tbody>
</table>

Ranges are ±1 std. error
D.f. = 2  r_c = .950 at 95% confidence level
### TABLE XIX

**Analysis of Variance Results for the Standard Addition Procedure**

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$\eta^2$ between cols. (df=12)</th>
<th>$\eta^2$ within cols. (df=3)</th>
<th>$F$</th>
<th>est. $\sigma$ for method</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 Hz</td>
<td>0.7695</td>
<td>0.03072</td>
<td>25.1</td>
<td>0.18 $\mu$S</td>
</tr>
<tr>
<td>3500 Hz</td>
<td>1.5720</td>
<td>0.01184</td>
<td>124.4</td>
<td>0.11 $\mu$S</td>
</tr>
<tr>
<td>7500 Hz</td>
<td>0.5304</td>
<td>0.03791</td>
<td>14.0</td>
<td>0.19 $\mu$S</td>
</tr>
<tr>
<td>10.5 kHz</td>
<td>0.3001</td>
<td>0.06630</td>
<td>4.5</td>
<td>0.26 $\mu$S</td>
</tr>
</tbody>
</table>

* corresponds to data in $\mu$S

**critical value is 5.95 @ 95% confidence level
<table>
<thead>
<tr>
<th></th>
<th>Std. Addn.</th>
<th>Immersion</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 Hz</td>
<td>0.2 μS</td>
<td>2.5 μS</td>
<td>2.5 μS</td>
</tr>
<tr>
<td>3500</td>
<td>0.1</td>
<td>4.0</td>
<td>2.6</td>
</tr>
<tr>
<td>7500</td>
<td>0.1</td>
<td>4.3</td>
<td>---</td>
</tr>
<tr>
<td>10500</td>
<td>0.3</td>
<td>4.2</td>
<td>1.9</td>
</tr>
</tbody>
</table>

**TABLE XX**

Standard Deviation for Three Methods
Figure 18: Magnitude spectra of experimental pulse widths of 20\%, 30\% and 40\%.
Figure 19: Total admittance of n-TiO$_2$ crystal No. 1, $N_0 \approx 10^{-14}$ cm$^{-3}$. Total frequency range covered by two measurements having $T_0 = 0.1$ sec and 0.001 sec respectively.

Crystal 1

Admittance

- $\square$ magnitude
- $+$ quadrature
- $\circ$ in-phase
Figure 20: Total admittance of n-TiO$_2$ crystal No. 2 having a much lower donor density than crystal No. 1.
Figures 21, 22: Log-Log plots of n-TiO admittance
Figure 23: Cot θ vs frequency for n-TiO₂ crystal No. 1 showing significant in-phase component at frequencies below 1 kHz.
Capacitance determinations
comparison of a.c. and FT techniques

Figure 24: Capacitance for crystal No. 1 obtained by Pulse-FT admittance and by steady state a.c. quadrature at 500 Hz.
Figure 25: Correlation plots of two FT measurements vs a.c. quadrature measurement at 500 Hz for several potentials. Solid line is least squares fit showing approximately 10% proportional error.
Figure 26: Mott-Schottky plots for crystal No. 1.
Figure 27: Variation of $V_{fb}$ with pH. Solid line is least squares fit with $-62$ mV/decade slope. Error bars are for 90% confidence level.
Figure 28: Mott-Schottky slope vs pH in 0.5M Na₂SO₄ for crystal No. 1. Error bars are for 90% confidence level.
Figure 29: Schematic diagram for dummy cells used to compare FT and a.c. techniques. Analogies with real cell are: AE = auxiliary electrode, Ref = reference electrode, WE = working electrode.
PAR 173 response under resistive loads

Figure 30: In-phase response for PAR 173 potentiostat under purely resistive loads. Current range: 1mA/V for a) 20Ω; b) 200Ω; 0.1mA/V for c) 2000Ω.
PAR 173 response under resistive loads

1 mA and 0.1 mA current ranges

Figure 31: Magnitude response for PAR 173. Current ranges and resistances are the same as for Figure 30.
Figure 32: 100 ohm resistance measured using pulse width of 0.2 $T_0$ for $T_0 = 50$ msec and 0.5 msec. Note the occurrence of outliers at every fifth harmonic and poor precision in the higher harmonics.
Figure 33a: Admittance measured by Pulse-FT for RC series circuit $R = 99.5$, $C = 0.022 \mu F$. 
Figure 33b: Admittance measured by Pulse-FT for RC series with $R = 99.5$, $C = 0.10 \mu F$. 

Admittance vs. log($f$)

$R = 99.5$ ; $C = 0.10 \mu F$
Figure 33c: Admittance measured by Pulse-FT for RC series $R = 99.5$, $C = 0.50 \, \mu F$. 

$R = 9.3 ; C = 0.50 \, \mu F$ 

Admittance vs. log(f)
Figure 34: Admittance quadrature and expected values for three RC circuits. $R = 99.5$. 

Im(Y) vs. log(f)

To=.01 sec; RPW=20%
Figure 35: In-phase admittance corresponding to Figure 34.
Figure 36: Effect of potentiostatic instability on $V_r/V_e$, where $V_e$ is the externally applied voltage and $V_r$ is the potential vs. reference actually applied to the working electrode. (From reference 8)
Figure 37: Ratio of measured to calculated admittance magnitude for three RC circuits. The cresting nature becomes problematic at lower frequencies as $C$ is increased.
Ratio of $J_{YIm}$ to $J_{YIc}$

$T_0 = 1$ msec, $T = 0.2$ msec, 10 mA/V

Ratio

$1.5$ $1.4$ $1.3$ $1.2$ $1.1$ $1.0$ $0.9$ $0.8$ $0.7$ $0.6$ $0.5$

$\log(f/\text{Hz})$

$0.022 \mu\text{F}$
Ratio of $I_Ylm$ to $I_Ylc$

$T_0 = 1$ msec; $t = 2$ msec; $10$ mA/V

![Graph showing the ratio of $I_Ylm$ to $I_Ylc$ against log($f$/Hz). The graph includes data points for $0.10$ μF and a line representing $1$.](image-url)
Ratio of $|Y|_{im}$ to $|Y|_{lc}$

To = 1 msec; t = 2 msec; 10 mA/V

$\log(f/Hz)$

$\triangle$ 0.5 uF

1
Figure 38: Admittance magnitudes for several RC circuits with the PAR 273 potentiostat measured by Pulse-FT. $R = 99.5$ for all.
a.c. steady state results

Figure 39: Admittance magnitudes for several RC circuits with the PAR 273 steady state a.c. measured with a digital oscilloscope. Circuits are the same as for Figure 38.
Correlation of F.T. vs. o.c.

Figure 40: Correlation plots for Pulse-FT measured magnitude and phase versus steady state a.c. results.

Correlation F.T. vs. a.c. Technique
Figure 41: (a) Single-pulse BICON waveform.
(b) Diminishing amplitude pulse sequence.
PAR273 waveform for single pulse BICON

<table>
<thead>
<tr>
<th>Time (milliseconds)</th>
<th>Relative pulse height</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>-1</td>
</tr>
</tbody>
</table>
PAR273 waveform for multi-pulse BICON

- Relative pulse height vs. time (milliseconds)

- Points A and B are marked for reference.
Conductance vs. $\log([F^-])$ calculated from negative I/V curves

Figure 42: BICOND conductance calculated from I-V slopes for negative-going pulses at $t = 2$ and $t = 60$ seconds. Solid line is linear regression estimate for both times.
Figure 43: BICON conductance calculated from I-V slopes for positive-going pulses $t = 2$ and $t = 60$ seconds.
Figure 44: Current on reverse (negative-going) pulse for bipolar pulse pairs of ±200 mV and ±2000 mV.
Figure 45: Current vs. log([F^-]/M)

Current on the forward (positive-going) pulse of ±200 mV and ±2000 mV waveforms.
Figure 46: Complex impedance plane projection of Orion 94-09 Fluoride electrode impedance. Solid line is least squares fit to data points between 3500 and 10500 Hz.
Figure 47: Real and Imaginary components of electrode impedance for the Orion Fluoride electrode. Solid lines are least squares fits to data between 3500 and 10500 Hz.
Figure 48: (a) Equivalent circuit used in the current work.
(b) Equivalent circuit used by Brand and Rechnitz [11].
Figure 49: Change in electrode conductance with fluoride concentration for the SA method at (a) 500 Hz, (b) 3500 Hz, (c) 7500 Hz and (d) 10500 Hz. Ordinate range is approximately 2% for all.
G vs \log([F^-]/M)

conductance (mS)

data

regression line

500 Hz
Conduelone* (mS)

$G$ vs. $\log[F^-]$

$3500$ Hz

Conductance (mS)

$\log([F^-]/M)$

Data points and regression line.
G vs. log\([F^-]\)

7500 Hz

Conductance (mS)

\[0.0795 \quad 0.0796 \quad 0.0797 \quad 0.0798 \quad 0.0799 \quad 0.0800 \quad 0.0801 \quad 0.0802 \quad 0.0803 \quad 0.0804 \quad 0.0805 \quad 0.0806 \quad 0.0807 \quad 0.0808 \quad 0.0809 \quad 0.0811\]

\[\log([F^-]/M)\]

\[\Delta \quad \text{data} \quad \text{--- regression line}\]
Conductance \( G \) vs. \( \log[F^-] \)

<table>
<thead>
<tr>
<th>( \log[F^-] )</th>
<th>Conductance (mS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-7.5</td>
<td>0.0785</td>
</tr>
<tr>
<td>-6.5</td>
<td>0.0791</td>
</tr>
<tr>
<td>-5.5</td>
<td>0.0793</td>
</tr>
<tr>
<td>-4.5</td>
<td>0.0794</td>
</tr>
<tr>
<td>-3.5</td>
<td>0.0796</td>
</tr>
</tbody>
</table>

Data points and regression line.
Figure 50: Change in electrode conductance with fluoride concentration for the immersion method at (a) 500 Hz, (b) 3500 Hz, (c) 7500 Hz and (d) 10500 Hz. Ordinate range is approximately 4% for all.
$G$ vs. $\log[\text{m}^{-1}]$ (immersion)

Conductance (mS)

0.105
0.1045
0.104
0.1035
0.103
0.1015
0.101

-7.5 -6.5 -5.5 -4.5 -3.5

$\log[(\text{F}^{-1}\text{M}^{-1})]$

Data
Regression line
Conductance (mS) vs. log[F⁻] (immersion)

-7.5 -5.5 -3.5 -6.5 -4.5

-7.5 -5.5 -3.5

G vs. log[F⁻] (immersion)
The Fourier transform is a powerful mathematical tool for solving differential-integral problems. The coincident development of fast algorithms and more economical computing power has made the Fourier transform a commonly available tool for microcomputer equipped laboratories. Thus, the solution of a range of problems using numerical FT applications are routinely available.

One application of Fourier transformation is the frequency domain deconvolution of an applied potential waveform from the inherent response function of an electrochemical cell, i.e. admittance spectrum calculations. Though the technique was first developed in the early 1970's, the use of FT for obtaining multiplexed admittance data has not gained widespread popularity. This is, in part, because of the need for relatively sophisticated hardware for waveform generation. The use of simple waveforms such as pulse trains was rejected on the basis of poor precision and excessive distortion of data by nonlinear responses, exacerbated by the relatively high peak value (in the time domain) required to obtain sufficient spectral magnitudes for higher harmonics.
In this work, a more detailed study was undertaken of the problems associated with use of pulse type waveforms for impedance analysis of electrochemical systems. Pulse-FT analysis of n-TiO$_2$ electrodes and model RC circuits showed that relatively good results (precision $\approx 1\%$ r.s.e. or less) for data up to the 50th harmonic and excellent results ($\approx 0.1\%$ r.s.e.) up to the 20th harmonic could be easily obtained using simple pulses. Comparisons with steady state a.c. results showed excellent agreement.

The admittance spectra obtained for the n-TiO$_2$/0.1M Na$_2$SO$_4$ interface, were used to perform Mott-Schottky analysis. The slope of the Mott-Schottky lines gave reasonable estimates for donor densities; and replicate analyses yielded $N_d$ values that agreed to within 0.5%. Flat-band potentials were also estimated from the Mott-Schottky data. A slope of $-62$ mV/pH unit was obtained, although the precision of the flat-band estimates was poor. This reinforces the results of earlier researchers, who reported a slope close to the theoretical $-59$ mV/pH (at 25°C).

Results from the n-TiO$_2$ studies showed a consistent systematic error resulting in artificially high in-phase and/or quadrature currents followed with a rapid rolloff at higher frequencies. Comparison with a.c. experiments showed that this was not due to the use of a pulse
sequence as an input waveform, but rather to the highly capacitive nature of the semiconductor/electrolyte interphase. The semiconducting nature of the electrode, which is advantageous in that larger applied potentials may be used, also causes difficulty when used with a potentiostat optimized for low resistance, low capacitance cells. The time constant associated with the cell interacts with that of the potentiostat to cause distortions at frequencies as low as hundreds of Hertz. The use of the critical frequency, \( f = (2\pi RC)^{-1} \), for obtaining capacitance and resistance values was problematic because of these interactions. Factors that were detrimental to system stability were:

(a) high cell capacitance
(b) high cell resistivity, either in the solution or the electrode
(c) low ratio of uncompensated resistance (between the reference and working electrodes) to total cell resistance (between the auxiliary and working electrodes)
(d) high reference electrode impedance, and  
(e) absence of faradaic conductance.

Nevertheless, the pulse-FT technique was able to accurately determine capacitance values in model RC circuits when the low frequency forms of cell admittance equations were used.

Studies of the Orion 94-09 fluoride electrode, using bipolar conductance measurements (BICON), gave strong evidence of a concentration-dependent response for fluoride when a standard addition procedure was
used. The same procedure using pulse-FT admittance data showed a similar correlation between fluoride concentration and conductance, measured as the in-phase component of total admittance, at frequencies corresponding to a hydrated LaF₃ surface film. This correlation was not observed when admittance was measured on transfer of the electrode from a fluoride free solution, or after equilibrium with the fluoride solution. Whether the correlation does not exist, or is simply masked by increased uncertainty in the conductance, is unclear. The highly variable quadrature response suggested that it may be a more sensitive indicator than conductance for use in fluoride determination, although no correlation with fluoride concentration was found here.

A key modification of the pulse waveform was made for use in the fluoride electrode study. A 50% relative pulse length (i.e. square wave) provided an odd harmonic waveform, and analog filtering was used to reduce the rate of decay, with frequency, in the magnitude spectrum. This had the added advantage of reducing the root-mean-square potential applied to the cell. This, along with the bipolar nature of the resulting waveform should be of considerable advantage if the waveform is applied to the study of more nonlinear systems, e.g. those involving faradaic processes.
Finally, the potential of pulse type waveforms for electrochemical impedance analysis is much higher than is generally considered. With appropriate considerations, precise results can be obtained up to possibly 100 harmonics, using only an 8-bit A/D. Use of the bipolar, high-pass filtered square wave may also allow its application to faradaic systems without undue nonlinear current response.
REFERENCES

CHAPTER I


CHAPTER II


CHAPTER III


CHAPTER IV


2. K. Rajeshwar in Molten Salt Techniques, v2.


Appendix A

FASTFD4.MAC

1 REM----FASTFD4 .Computes FFT of time function stored on disk.
2 ! Displays magnitude spectrum as bar graph or table of values
3 ! accepts up to 1024 data points Real and imaginary arrays are
4 ! unscrambled 4/25/84
5 ! Calculates Admittance K. Carney
6 !
7 !###########################################################################
8 !########################################################################### Input data###########################################################################
9 !###########################################################################
10 INPUT "ENTER RECORD DURATION(in seconds) " ;PW
11 INPUT "2-L NO.DATA POINTS, ENTER L " ;LX
12 NX=2*LX ; N=NX ; T=PW/N
13 NINX=N ! IF N<512 THEN NINX=512 ELSE NINX=N ! for zero filling
14 DIM IX(2048), IZ(2048), IX3(2048), BI(2048), R1(2048), R2(2048)
15 MAT IX1=IER MAT IX2=IER MAT IX3=IER MAT S=IER
16 INPUT "NAME OF DATA FILE FOR INPUT " ;DFIL0
17 OPEN DFIL0 FOR INPUT AS FILE 01
18 MAT IX1=IER MAT IX2=IER
19 INPUT 01 11(I2) FOR IX=0 TO NINX-1
20 CLOSE 01
21 INPUT "DO YOU WANT A LISTING OF THE GENERATED TIME FUNCTION? (Y/N) " ;AY
22 IF AY="N" THEN 610
23 IF AY="Y" THEN 90
24 B=0
25 FOR IX=0 TO N-1
26 IF ABS(I1(IX))>B THEN B=ABS(I1(IX))
27 NEXT IX
28 CLS + LINE(75,50,587,50) + LINE(75,50,75,460)
29 PSET(100,100) FOR X10=75 TO 587 STEP 3
30 DIV=512/N ; YDIV=400/(2NB)
31 FOR IX=75 TO 587 STEP 32DIV
32 LINE(IX,50,IX,45) ; TEXT(IX-312/N,400/(2IBI)
33 FOR IX1=75+32*DIV TO 587 STEP 32DIV
34 TEXT(IX,30,(IX-75)),DIV))
35 NEXT IX
36 FOR IX=0 TO N-1 TO N-1 ; I1(IX) = I1(IX)/N ; MAT IX2=IER
37 NEXT 21489 TO Et-THE
38 PRINT "CALCULATION IN PROGRESS"*
39 PRINT "SAMPLE POINT NO.") ; TEXT(30,100,"INTENSITY(Z-max=1)",1,1)
40 FOR IX=0 TO N-2
41 LINE(75+2IBDIV,IX1(IX)+YDIV+2602,75+(IX+1)+YDIV+2602)
42 NEXT I1(IX) FOR IX=0 TO N-1 ; I1(IX) = I1(IX)/N ; MAT IX4=IER
43 TD26=TIME
440 PRINT "FFT CALCULATION IN PROGRESS"*
450 FOR IX1=212Z=1;V=28PI/N
460 FOR IX=1 TO LX
470 LOCATE 2,2IX1;PRINT IX
480 IX=INT(131/IX)

195
810 GOSUB 2630
820 21-COD(V8Y0) ; z2-BIN(V8Y2)
830 FOR UX=1 TO 14-1X
840 A1=X1(UX)*X2(UX)*B1=X2X1(UX)+Z2X1(UX)+Z2X2(UX)+X1(UX)
850 B2=Z2X2(UX)+Z2X2(UX)+Z2X2(UX)
860 NEXT UX
870 X1(UX)=A1+B1; X2(UX)=A2+B2 ; XI(XUX)+XI(XUX)+A1*B1; X2(XUX)+A2-B21010 NEXT UX
890 NEXT UX
900 NEXT UX
910 IF YX<UX THEN 1205
913 TR=X1(UX)*X1(UX)*11(UX)*X2(UX)+Z2(UX)*Z2(UX)+X1(UX)=TR+I2(VY)=11
920 NEXT UX
922 IF DFIL<0 THEN 1205
925 MAT 11=UX ; MAT K2=UX
927 GOT0 1370
928 IF DFIL<>0 THEN OPEN DFIL AS FILE 3 ELSE 1350
930 PRINT 3,11(0) ; MAT PRINT 3,12(11/2)
931 PRINT 3,12(0) ; MAT PRINT 3,12(11/2)
932 CLOSE 35
935 PRINT " MAGNITUDE CALCULATIONS IN PROGRESS"
937 FOR UX=0 TO UX/2 ; X1(UX)=B2R(X1(UX)*X2(UUX)+Z2(UUX)+Z2(UUX)) ; NEXT UX
940 IF ERR THEN 1430
942 REM Screen output ?????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????????
1870 FOR IX=100 TO 450 STEP 30
1890 LINE(70,IX,60,IX) : TEXT(45,IX-20,NUM((IX-50)/400),1,1)
1910 NEIT IX
1930 FOR IX=70+320DIV2 TO 710 STEP 320DIV2 : X-axis label
1950 LINE(IX,50,IX,40) : TEXT(IX-8,22,NUM((IX-70)/DIV2))
1970 NEIT IX
1990 TEXT(325,5,"HARMONIC") : TEXT(30,100,"MAGNITUDE",1,1)
2010 GOTO 2230
2020 "REM------------------------------------------------------------
2030 REM Table of values 
2050 U=0
2070 Z=0
2090 PRINT"HARMONIC";TAB(14);"REAL";TAB(30);"IMAGINARY";TAB(30);"MAGNITUDE"
2110 INPUT U;TAB(10);I1(U);TAB(30);I2(U);TAB(50);I3(U)
2130 UM=U+I2=Z=1
2170 IF IX=22 THEN 2190
2171 CALL GETKEY(P1,P2,P3,P4,P5)
2173 IF PS<>0 THEN 2171
2174 IF P1=80 THEN 2210 ELSE GOTO 2070
2190 IF U=W/2 THEN 2130
2200 "REM-----------------------------------------------------------------
2210 REM TERMINATE ? 
2230 INPUT Q* : PRINT"DO YOU WANT ANOTHER OUTPUT \( Y/N \)? * : INPUT A8
2250 IF A8="Y" THEN 1450
2270 IF A8="N" THEN 2230
2290 INPUT " \( Y/N \)? *;A8
2310 IF A8="Y" THEN 50 ELSE 2370
2320 "REM-----------------------------------------------------------------
2330 PRINT "NAME of Output files for \( ;DFIL0; \) as \( <.ADM> \), \( <.GOW> \), \( <.MCP> \)"
2340 PRINT "or \( <cr> \) to suppress output of a record "
2341 INPUT "ADM? \( ;DFIL0; \) INPUT "GOW? \( ;DFIL10; \) INPUT "MCP? \( ;DFIL20; \)
2350 PRINT "NAME of E(u) FILE as \( <xxxx.FFT> \) " : INPUT DFIL30
2351 IF DFIL30<>"" THEN GOTO 2430
2352 OPEN DFIL30 FOR INPUT AS FILE 02
2354 FOR O1=0 TO W/2 : INPUT 02,R1(O1) : NEIT O1
2360 FOR O2=0 TO W/2 : INPUT 02,R2(O2) : NEIT O2
2430 GOTO 2450
2450 M=R1(U1)R1(U1)+R2(U1)R2(U1)
2470 IF M=0 THEN 2530
2490 IF DFIL0<>"" THEN 2430
2490 IF DFIL10<>"" THEN 2530
2492 IF DFIL20<>"" THEN 2530
2500 PRINT S3,13(I1) FOR IX=1STPTX TO W/2 STEP INSTPX
2510 NEXT U1
2520 "REM-----------------------------------------------------------------
2530 FOR IX=1 TO 511 : XI(U1)=I1(U1)/(U1/100) : NEIT U1
2540 IF IX<>1 THEN 2492
2548 IF DFIL0<>"" THEN 2530
2550 PRINT O3,X3(IX) FOR IX=1STPTX TO W/2 STEP INSTPX
2551 CLOSE 03
2559 IF DFIL1**" THEN 2564 ELSE OPEN DFIL10 AS FILE 04
2560 PRINT 04,II(IX) FOR IX=FBTP1 TO LSTPT1 STEP INSTP1
2561 CLOSE 04
2564 IF DFIL2**" THEN 2570 ELSE OPEN DFIL20 AS FILE 05
2565 PRINT 05,12(IX) FOR IX=FBTP2 TO LSTPT2 STEP INSTP2
2566 CLOSE 05
2570 CLOSE 02
2580 INPUT "NAME OF NEW INPUT FILE ":DFIL0
2581 IF DFIL0='') THEN GOTO 150
2590 END !---------------------------END OF MAIN
2600 !-------------------------------------------------------------------Bit reversal routine !
2610 !-------------------------------------------------------------------
2630 Y=0
2631 FOR W=1 TO L1 :NTY=2^(W-1) &
          IF (IX AND NTY)>NTY THEN Y=Y OR 2^(L1-W))
2660 NEXT W
2770 RETURN
APPENDIX B

LINPLOT.BAS

0 DO ERROR GOTO 29010
2 ! Program: LINPLOT.BAS plot on a rectangular coordinate system
4 ! several sets of XY data files. X is independent variable and is
6 ! defined in subroutine 2900. Y values may be transformed in sub-
8 ! routine 2800. Automatic scaling according to values in the first
10 ! data set is accomplished by setting B1=1(for x),2(for y),3(for x,y)
12 ! Other values for B1 result in scaling according to XMAX,YMIN,YMAX,
14 ! YMIN. X0,Y0 are the coordinates for the origin of the plot.
16 !
18 ! SUBROUTINE LIST:
20 ! AXES =1000 SCALE =1500
22 ! NEWCURVE=2500 VTRANS=2800
24 ! DEFX =2900 PLOTXY=3000
26 ! This version, LINPLOT2, has been improved to make it easier to transform
28 ! data. Data input has been moved inside Sub2800(y-transformation). This
29 ! allows which contain more than one array of data with a common x-axis to
30 ! be easily plotted (see FMAGAPP.BAS). Also, the x-increment value can be
32 ! input from the keyboard as '1/xx', where xx is numeric.
34 ! end of comments
36 ! constants
38 ! 60 B1=2X
40 YMAX=1.000000;YMIN=0.000000
42 XMAX=0;YMIN=0
44 X0=70;Y0=50;XREF=0
46 DIM X(2048),Y(2048)
48 ! main program
50 !
52 ! SUB 1000
54 ! SUB 2500
56 IF (B1 AND 31)<0 THEN SUB 1500
58 SUB 3000
60 FILL(72,449,760,470,0);LOCATE 0,7;INPUT **;B0
62 IF B0<>** THEN GOTO 250
64 SUB 2500220;SUB 3000
66 FILL(72,449,760,470,0);LOCATE 0,7;INPUT **;B0
68 IF B0==** THEN GOTO 210
70 SUB 3000
72 END
74 !*******************************************************************************
76 ! End of main program*******************************************************************************
78 !*******************************************************************************
80 !*******************************************************************************
82 !*******************************************************************************
84 !*******************************************************************************
86 !*******************************************************************************
88 !*******************************************************************************
90 !*******************************************************************************
92 !*******************************************************************************
94 !*******************************************************************************
96 !*******************************************************************************
98 !*******************************************************************************
100 CLS
102 IF (B1 AND 13)=1 THEN GOTO 1250
104 PRINT "Axes: X=640 pixels Y=400 pixels "
106
1030 INPUT "1/PN= fundamental x increment; ENTER PN ";NOVAR$  
1040 PRINT "MIN= ";INMIN  
1050 INPUT "ENTER number of harmonics of 1/PN ";N  
1052 IF LEFT(NOVAR$,2)="1/" THEN PN=1/VAL(RIGHT(NOVAR$,3)) ELSE PN=VAL(NOVAR$)  
1054 ILSP=INMIN1033 GOSUB 2900  
1060:  
1070: draw axis  
1080 CLS  
1090 LINE(XO-10,YO,IO+640,YO) :LINE(XO,YO-10,XO,YO+400)  
1100:  
1110: scale x axis  
1120 DELX=IN/PN  
1130 IF XMIN<=XMIN THEN XMIN=XMIN+DELX  
1140 INCX=640/(XMAX-XMIN) :INCR=64 :SUBINC=INCR/5  
1150 YCO=YO :ICO=IO  
1160 TEXT(ICO-30,YO-30,NUM$(XMIN))  
1170: label x axis  
1180 FOR II=0 TO 9  
1190 FOR KI=1 TO 5  
1200 ICO=ICO+SUBINC :LINE(ICO,YO,ICO,YO-5)  
1210 NEXT KI  
1220 LINE(ICO,YO-5,ICO,YO-10) :YF=((ICO-IO)/INCR)+YMIN  
1230 NEXT IX  
1250 IF (IX AND 2i)=2 THEN GOTO 1400  
1260:  
1270: scale y axis  
1280 YINC=400/(YMAX-YMIN) :INCR=40 :SUBINC=INCR/5  
1290:  
1300: label y axis  
1310 YCO=YO :ICO=IO  
1315 TEXT(XO-30,YCO-20,NUM$(YMIN)),1,1)  
1320 FOR IX=0 TO 9  
1330 FOR KI=1 TO 5  
1340 YCO=YCO+SUBINC :LINE(XO,YCO,XO-5,YCO)  
1350 NEXT KI  
1360 LINE(XO-5,YCO,XO-10,YCO) :YF=((YCO-YO)/INCR)+YMIN  
1370 TEXT(10-30,YCO-20,NUM$(YF),1,1)  
1380 NEXT IX  
1390:  
1400 RETURN  
1490: >>>>END of subroutine 'AXES' >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>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201

1550 IF X(i) < XMIN THEN XMIN = X(i)
1560 IF X(i) > XMAX THEN XMAX = X(i)
1570 NEXT IX
1580 !
1590 ! get scaling factors for x axis
1600 SX = SGN(XMAX) * IMAX = ABS(XMAX) * Ti = LOG10(XMAX)
1610 IF Ti < 0 THEN Ti = INT(Ti) ELSE Ti = INT(Ti)
1620 Ti = 10^ Ti
1630 JX = 0
1640 WHILE TiJX > XMAX : JX = JX + 1 : NEXT
1660 !
1670 IF SX < 0 THEN JX = JX + 1
1680 XMAX = TiSJSX
1690 !
1700 SX = SGN(XMIN) * IMIN = ABS(XMIN)
1710 Ti = LOG10(XMIN)
1720 IF Ti < 0 THEN Ti = INT(Ti) ELSE Ti = INT(Ti)
1730 Ti = 10^ Ti
1740 !
1750 JX = 0
1760 WHILE TiJX < XMIN : JX = JX + 1 : NEXT
1770 !
1780 IF SX > 0 THEN JX = JX + 1
1790 XMIN = TiSJSX
1800 !
1810 SI = SX AND -2
1820 ! Turn off autoscale x flag
1821 !
1822 TINCR = 641SUBINC = TINCR / 5
1824 YCD = YO YCD = IO
1826 TEXT(XCD-30, Y0-30, NUM(XMIN))
1828 ! label x axis
1830 FOR IX = 0 TO 9
1832 FOR YK = 1 TO 5
1834 XCO = XCD + SUBINC : LINE(XCO, Y0, XCD, Y0-5)
1836 NEXT KX
1838 LINE(XCD, Y0-5, XCD, Y0-10) : IP = (XCD-10) / TINCR * XMIN
1840 TEXT(XCD-35, Y0-30, NUM(IP))
1842 NEXT IX
1844 !
1850 IF (BX AND 21) < 0 THEN GOTO 2200: do the following iff y flag is on
1860 YMAX = -1E99 YMIN = 1E99
1870 !
1880 ! find YMAX, YMIN
1890 FOR IX = 0 TO N-1
1900 IF Y(i) < YMIN THEN YMIN = Y(i)
1910 IF Y(i) > YMAX THEN YMAX = Y(i)
1920 NEXT IX
1930 !
2040 0
2050 0
2060 0
2070 0
2080 0
2090 0
2100 0
2110 0
2120 0
2130 0
2140 0
2150 0
2160 0
2170 0
2180 0
2190 0
2200 0
2210 0
2220 0
2230 0
2240 0
2250 0
2260 0
2270 0
2280 0
2290 0
2300 0
2310 0
2320 0
2330 0
2340 0
2350 0
2360 0
2370 0
2380 0
2390 0
2400 0
2410 0
2420 0
2430 0
2440 0
2450 0
2460 0
2470 0
2480 0
2490 0
2500 0
2540 FILL(72,449,760,470,0) LOCATE 0,7
   PRINT "Number of points ": INPUT "":NNEW
2550 IF NNEW<0 THEN N=NNEW
2560 '
2570 FILL(72,449,760,470,0) LOCATE 0,7
   PRINT "X value for first point (<cr>=":ILEF;"": INPUT "":NOVAR
2580 IF NOVAR<>"" THEN ILEF=VAL(NOVAR)
2585 IF N=NNEW OR PM=PN OR NOVAR<>"" THEN GOSUB 2900 ! define x values
2590 !
2600 FILL(72,449,760,470,0) LOCATE 0,7
   PRINT "Name of input data file ":NDFIL
2602 ACHDI=0
2605 IF HDFIL="NEW" THEN ACHDI=1
2606 IF HDFIL="LINE" THEN ACHDI=2
2608 IF ACHDI=0 OR ACHDI=2 THEN 2610
2609 DM ACHDI GOTO 10000,10050
2610 IF HDFIL="" THEN GOTO 2680 ELSE DFIL=HDFIL
2660 GOSUB 2800 ! transform y values
2680 FILL(72,449,760,470,0) LOCATE 0,7
   PRINT "Choose tokens (1) 2) 3) 4) 5) 6) 7) 0) ":YCD=457
2682 XCD=223 : FILL(XCD-1,YCD-1,YCD+1,YCD)
2684 XCD=268 : LINE(XCD-2,YCD,YCD+2,YCD) : LINE(XCD,YCD+2,YCD,YCD-2)
2686 XCD=314 : FILL(XCD-2,YCD-2,YCD,YCD+2) : FILL(XCD-1,YCD-1,YCD+1,YCD+1)
2688 XCD=359 : LINE(XCD-2,YCD-2,YCD,YCD+2) : LINE(XCD+2,YCD-2,YCD,YCD+2)
2690 XCD=404 : FILL(XCD-2,YCD-1,YCD+2,YCD+1) : FILL(XCD-1,YCD-2,YCD+1,YCD+2)
2692 XCD=449 : LINE(XCD-3,YCD,YCD+3) : LINE(XCD-3,YCD,YCD,YCD+3)
2694 XCD=495 : ELLIPSE(XCD,YCD,YCD+1,YCD+4) : ELLIPSE(XCD,YCD+4,YCD+1,YCD)
   FILL(XCD+1,YCD-1,YCD+1,YCD+1) : YCD=0 : XCD=0
2696 LOCATE 0,63 : INPUT ":": TOKM1
2698 IF TOKM1=1 THEN GOTO 2680
2700 IF TOKM1<>0 THEN TOKM1=TOKM1
2701 !
2710 RETURN
2790 !$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
2791 !$$$$END of subroutine 'NEWCURVE'$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
2792 !$$$$Begin NEWCURVE:YTRANS $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
2793 !$$$$
2800 REM a subroutine to transform y values before plotting
2805 MAT Y=ER
2806 OPEN DFIL FOR INPUT AS FILE 01
2807 INPUT 01 Y(N) FOR N=0 TO N-1
2811 CLOSE 01
2850 ! insert the desired transformation algorithm here
2890 REM
2891 return
2893 !$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
2894 !$$$$Begin NEWCURVE:DEFX $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
2895 !$$$$
2896 ! Default is to define X(I) as II/PN
2900!
2950 $\text{X}(\text{II})=\text{LEF}+1.0/\text{PNI} \text{ FOR II}=0 \text{ TO N}-1$
2995!
2990 \text{RETURN}
2991! 
2992! 
2993! 
2994! 
2995! 
3000 \text{FILL}(72,449,760,470,0)
3005 \text{IF TONX}=0 \text{ THEN 3600}
3006 \text{IF TONX}<0 \text{ THEN PMODI}=2 \text{ ELSE PMODI}=1
3007 \text{TONX}=\text{ABS}(\text{TONX})
3010 \text{ON TONX GOTO 3040,3110,3260,3330,3460,3500,3580,3600}
3020!
3030! squares
3040 \text{FOR II}=0 \text{ TO N}-1
3041 \text{IF Y(II)}<\text{YMIN OR X(II)}<\text{XMIN THEN GOTO 3070}
3050 \text{ICO}=\text{ICO}+1\text{ IF X(II)}<\text{XMIN THEN XINC}=\text{YO}+(\text{Y(II)}-\text{YMIN})\times \text{INCR}
3060 \text{FILL(ICO-1,YCO-1,ICO+1,YCO+1,PMODI)}
3070 \text{NEXT II}
3080 \text{GOTO 3600}
3090!
3100! crosses +
3110 \text{FOR II}=0 \text{ TO N}-1
3111 \text{IF Y(II)}\times \text{YMIN OR X(II)}<\text{XMIN THEN GOTO 3140}
3120 \text{ICO}=\text{ICO}+1\text{ IF X(II)}<\text{XMIN THEN XINC}=\text{YCO}+(\text{Y(II)}-\text{YMIN})\times \text{INCR}
3130 \text{LINE(ICO-2,YCD-2,YCO-2,YCD-2,PMODI)}\text{ LINE(ICO,YCO-2,YCO+2,PMODI)}
3140 \text{NEXT II}
3150 \text{GOTO 3600}
3160!
3170! stars
3180 \text{FOR II}=0 \text{ TO N}-1
3181 \text{IF Y(II)}<\text{YMIN OR X(II)}<\text{XMIN THEN GOTO 3220}
3190 \text{ICO}=\text{ICO}+1\text{ IF X(II)}<\text{XMIN THEN XINC}=\text{YCO}+(\text{Y(II)}-\text{YMIN})\times \text{INCR}
3200 \text{ELLIPSE(ICO,YCD-2,YCO-2,YCD-2,PMODI)}\text{ ELLIPSE(ICO,YCD-2,YCO-2,PMODI)}
3210 \text{FILL(ICO-1,YCO-1,ICO+1,YCO+1,PMODI)}
3220 \text{NEXT II}
3230 \text{GOTO 3600}
3240!
3250! open squares
3260 \text{FOR II}=0 \text{ TO N}-1
3261 \text{IF Y(II)}\times \text{YMIN OR X(II)}<\text{XMIN THEN GOTO 3290}
3270 \text{ICO}=\text{ICO}+1\text{ IF X(II)}<\text{XMIN THEN XINC}=\text{YCO}+(\text{Y(II)}-\text{YMIN})\times \text{INCR}
3280 \text{FILL(ICO-2,YCD-2,YCO+2,YCD-2,PMODI)}\text{ FILL(ICO-1,YCO-1,ICO+1,YCO+1,0,PMODI)}
3290 \text{NEXT II}
3300 \text{GOTO 3600}
3310!
3320: crosses x
3330: FOR IX=0 TO N-1
3331: IF Y(I)<YM IN OR X(I)<XMIN THEN GOTO 3360
3340: ICO=IO+(I(I)-XMIN)*INC R ; YCO=YO+(Y(I)-YMIN)*INC R
3350: LINE(ICO-2,YCO-2,ICO+2,YCO+2,PMODI):LINE(ICO+2,YCO-2,ICO-2,YCO+2,PMODI)
3360: NEXT IX
3370: GOTO 3600
3380: !
3390: line
3400: ICO=IO+(I(I)-XMIN)*INC R ; YCO=YO+(Y(I)-YMIN)*INC R
3410: FOR IX=1 TO N-2
3411: ICO1=IO+(I(I)-XMIN)*INC R ; YCO1=YO+(Y(I)-YMIN)*INC R
3420: LINE(ICO1,YCO1,ICO1,YCO1,PMODI):ICO=ICO1 :YCO=YCO1
3430: NEXT IX
3440: GOTO 3600
3445: NEXT IX
3449: !
3450: diamond
3460: FOR IX=0 TO N-1
3470: IF Y(I)<YM IN OR X(I)<XMIN THEN GOTO 3490
3475: ICO=IO+(I(I)-XMIN)*INC R ; YCO=YO+(Y(I)-YMIN)*INC R
3480: FILL(ICO-2,YCO-1,ICO+2,YCO+1,PMODI):FILL(ICO-1,YCO-2,ICO+1,YCO+2,PMODI)
3490: NEXT IX
3491: GOTO 3600
3495: !
3499: 'open diamond
3500: FOR IX=0 TO N-13510 IF Y(I)<YM IN OR X(I)<XMIN THEN GOTO 3540
3520: ICO=IO+(I(I)-XMIN)*INC R ; YCO=YO+(Y(I)-YMIN)*INC R
3530: LINE(ICO-3,YCO,ICO+3,YCO,PMODI):LINE(ICO-3,YCO,ICO+3,YCO,PMODI)
3540: NEXT IX
3560: RETURN
9900: !$$$$$$$$$$$$$END of subroutine PLOTXY $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
9901: !$$$$$$$$$$$$$$
9902: !$$$$$$$$$$
9903: !$$$$$$END OF SUBROUTINE LIST $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
9904: !
9905: !$$$$Alternate command routines $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
9909: !$$$$$$Clear plotting area $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
10000: FILL(IO=1,YO=1,IO+640,YO+400,0)
10010: GOTO 2500
10049: !$$$$$$Draw a line using graph coordinates $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
10050: FILL(72,449,769,470,0):LOCATE 0,76
10051: !INPUT "IX,Y1,X2,Y2,mode for line ":IXI,Y1,XI2,Y2,NN
10052: IYOFFX=IO-IMININCR :IYOFFX=YO-YMININCR
10053: IXI=IXI+INCR:IYOFFX=IX1+INCR
10054: IXI=IXI+INCR:IYOFFX=IXI+INCR
10055: IXI=IXI+INCR:IYOFFX=IXI+INCR
10056: LINE(IX1,Y1,IX2,Y2,NN)
10060: GOTO 2500
11000: !$$$$$$END OF PROGRAM $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
11001: !
29000 \# \\
29001 \# \$ERROR TRAP routine\\n29009 \# \$ERROR Can't open file error\\n29010 IF ERL<>2906 OR ERR<>5 THEN 29020\\n29012 FILL(72,449,760,470,0) \:LOCATE 0,7\%\\n:PRINT DFILs;: not found; enter new filename \";INPUT \"DFILs;\n29014 RESUME 2906\\n29015 \# 8\n29019 \# End of file on read \$ERROR\\n29020 IF ERL<>2907 OR ERR<>11 THEN 29050\\n29022 FILL(72,449,760,470,0) \:LOCATE 0,7\%\\n:PRINT \"File contains only \";I\"; points\"\\n29024 \(Y\(\text{ERR}\)=0 FOR \text{ERR}=1\% TO N-1\\n29026 RESUME 2908\\n29027 \# 8\n29049 \# Error condition not listed\$ERROR\\n29050 PRINT \"\$ERROR \";ERRs; in Line \";ERL\\n29052 CLOSE 81,82,83\\n30000 END

"Append" files for LIMPLOT.BAS

\textbf{IVBYAPP.BAS}\\n60 BI=3\\n2910 FILL(72,449,760,470,0)\\n2912 \textbf{LOCATE 0,7} ;INPUT "Input file for I \";XFILs;\\n2914 IF XFILs;=" THEN 2919\\n2915 OPEN XFILs; FOR INPUT AS FILE \$2\\n2916 INPUT \$2 X IX(II) FOR IX=0 TO N-1\\n2917 \textbf{CLOSE \$2} ;IX\(=\)Y\\n2919 IF IX\(\triangleright\)Y THEN 2912\\n2930 \textbf{REN}

\textbf{LOG2APP.BAS}\\n100 \textbf{INPUT "log(IMIN), log(IMAI) \";IMIN,IMAI}\\n101 \textbf{REN}\\n1020 \textbf{REN}\\n1030 \textbf{REN}\\n1040 \textbf{REN}\\n1050 \textbf{REN}\\n1590 \textbf{GOTO 1810} \# skip X-scaling based on powers of 10\\n1940 \textbf{GOTO 2160} \# skip Y-scaling based on powers of 10\\n2930 \textbf{FOR IX=0 TO N-1}\\n2951 IF Y(IX)\(\triangleright\)0 THEN \textbf{GOTO 2953}\\n2952 Y(IX)\(=\)YMIN-1 \# GOTO 2990\\n2953 Y(IX)\(=\)LOG10(ABS(Y(IX)))\\n2954 \textbf{NEXT IX}\\n2959 IPW=1.0/PM\\n2970 X(IX)\(=\)LOG10(XLEF+IPW-XI\(\times\)I) \textbf{FOR IX=0 TO N-1}
**LOGIAPP.RAB**

100 INPUT "log(IMIN), log(IMAX) ";IMIN,IMAX
1010 REM
1020 REM
1030 REM
1040 REM
1050 REM
1590 GOTO 1810  ! skip X-scaling based on powers of 10
2949 XPM=1.0/PM
2950 X(II)=LOG10(XLEF+XPM*II) FOR II=0 TO N-1

**LOGYAPP.RAB**

1940 GOTO 2160  ! skip Y-scaling based on powers of 10
2850 FOR II=0 TO N-1
2851 IF Y(II)<0 THEN GOTO 2853
2852 Y(II)=YMIN-1 GOTO 2890
2853 Y(II)=LOG10(ABS(Y(II)))
2854 NEXT II
10 ON ERROR GOTO 1000
20 DEFINT I-N
30 DIM IN(250),LFP(4),TDT(516),YDFTA(516),DIGTOT(2048),IREC(10)
31 DATA ONE,TWO,THREE,FOUR,FIVE,SIX,SEVEN,EIGHT
32 READ IREC(10) FOR I=1 TO 8
40 LFP(1)=231;LFP(2)=21;LFP(3)=0;LFP(4)=0
50 DCODE$="";ITHE$="";LENG$=RN=NL=E=CHR$(101)+CHR$(131)+CLS
70 AIF AVBCODES.DAS collects data from TEXAS oscilloscope, averages a
90 BIF "selected number of arrays, displays results graphically & saves"  
90 CIF "it in a 2048 point array sequential with previous results to" 
91 DIF "give a specified number of records per file." 
100 PRINT A0 ;PRINT B0 ;PRINT C0 ;PRINT D0 ;L0
105 PRINT IPRINT &
110 PRINT "Date code is ";DCODE$;" if you wish to change, edit line 50"  
110 PRINT IINPUT "Number of arrays to be averaged ";NINO RN=N &  
110 PRINT IAINCR=1.5625/N
115 INPUT "Number of records per file ";NRECC
120 CALL SYSOPEN(6,"#USB?",2,0,0,0)
125 CLS PRINT IPRINT "Set scope and hit any key to get baseline "  
160 CALL GETKEY(AABC,ASCN,AKB1,AKB2,AER)
161 IF AER<>0 THEN GOTO 160
169 : 
200 CALL BREAD(6,IN(1),692,15,13,10)
201 CALL SYSFUNC(6,LFP(1))
202 GOSUB 9000
205 : 
210 PRINT "Name of ";NRECS;" record file";IINPUT DFIL$  
220 DFIL$=DCODE$+DFIL$+ITHE$;OPEN DFIL$ FOR OUTPUT AS FILE 93  
224 INPUT "Y scaling factor or 0 for no scaling ";YSDEL
226 IF YSCALE=0 THEN YSCALE=25
228 YSCALE=YSCALE/(25+RN)
250 PRINT L0;"strike any key to begin data acquisition"
252 CALL GETKEY(AABC,ASCN,AKB1,AKB2,AER)
253 IF AER<>0 THEN GOTO 252
254 CLS IN$1=RECS$12 : KB$1=0
255 FOR IREC=1 TO NRECC
260 NAT TOT=IER
280 FOR I=1 TO N
300 CALL BREAD(6,IN(1),692,15,13,10)
320 CALL SYSFUNC(6,LFP(1))
340 K=0:PRINT I1 IF LB$=2 THEN GOTO 390
346 K=K+1 : TOT(K)=TOT(K)+(IN(LEN)+255)
380 HL=LEN : HM=LEN+256
400 FOR J=0 TO NA : K=K+1 : TOT(K)=TOT(K)+(IN(J)+255) AND 255)
420 K=K+1 : TOT(K)=TOT(K)+(IN(J) AND 255) : NEXT J
440 NEXT I
450 LOCATE 0,0:PRINT "Record number ";IREC(IREC);" complete"
460 LINE(50+iX,AINCH+TOT(iX)+15+iX,AINCH+TOT(iX+i)); FOR iX=1 TO 511
465 NAT TOT=TOT-YOFFA
466 NAT TOT=(YSCALE)*TOT
470 FOR iX=1 TO 512:KBIGX=KBIGX+iX;BIGTOT(KBIGX)=TOT(iX);NEXT iX
495 NEXT IREC
499 PRINT 03 BIGTOT(iX) FOR iX=1 TO KBIGX
500 CLOSE 03
500 CLOSE 03:PRINT "End; C=collect data"
520 CALL GETKEY(AABC,ASCN,AKBL,AKB2,AE)R
540 IF AER<>0 THEN GOTO 820
560 IF AABC<>7 THEN GOTO 210
580 CALL SYSCLOSE(6)
900 END
1000 PRINT "Error ";ERR;" in line ";ERL
1010 CLOSE 01,02,03,06
1020 CALL SYSCLOSE(6)
1030 GOTO 900
8994 !
8995 !
8996 !
8997 !
8998 !
8999 ! Subroutine IOFF get Offset Y offset, length and value of header
9000 DATA=""
9010 FOR iX=1 TO 100
9020 AS=CVT$((IN(iX)+1)&
9030 ; IF (LEFT(A0,1)="Z") OR (RIGHT(A0,2)="Z") THEN GOTO 9100
9040 DATA$=DATA$+AS
9050 NEXT iX
9100 IF LEFT(A0,1)="Z" GOTO 9140
9120 LENG=iX+2;LBYTE=1;DATA$=DATA$+AS ;GOTO 9160
9140 LENG=iX+2;LBYTE=1;DATA$=DATA$+AS
9160 OFFST=0
9180 FOR iX=LENG+1 TO LENG+100
9200 AFFST=AFFST+(IN(iX)/256) AND 255)+(IN(iX) AND 255):NEXT iX
9220 AFFST=RND(AFFST/200):NAT YOFFA=CDN:MAT YOFFA=(AFFST)\YOFFA
9240 RETURN
APPENDIX D

DV MET ER . BAS

0 ON ERROR GOTO 1000
1 ! DV MET ER. BAS -- A program similar to DV MET ER to collect data points ##
2 ! from the KEITHLEY 179 TRMS DIGITAL MULTIMETER. The output is in the##
3 ! format F5.2. Sampling intervals greater than 0.25 seconds are available.
4 ! Graphic display is given at acquisition time.
5 !
6 !
7 !
8 !
9 !
10 ILEFT=50 : IRIGH T=450 : YTOPX=450 : YBOTX=50
15 CLS
20 DIM B(1024), T(1024), SIX(10), FP(KI(6))
25 ON ERROR GOTO 1000
30 CALL SYSOPEN(6, 50, 2, 0, 0, 0)
31 OPEN "BKP.D" AS FILE 07
40 LOCATE 0,10: INPUT "Sampling interval (seconds): " ; INCR
50 LOCATE 0,45: INPUT "Number of data points: " ; INI
60 LOCATE 1,15: INPUT "ENTER DVM range setting in V or mA": RANG
62 FILL (145, 435, 750, 445, 0)
64 GOSUB 510
70 YMAX=20000 : YMAX in aV, aMA or ohms
80 DI=600/YMAX : DXX=600/(2*YMAX) : Doffs=YMAX
82 FP(KI(1))=4 : FP(KI(2))=20 : FP(KI(3))=0 : FP(KI(4))=4 : FP(KI(5))=4 : FP(KI(6))=0
90 LINE (ILEFTX, YBOTX, IRIGHTX, YBOTX) : LINE (ILEFTX, YBOTX, ILEFTX, YTOPX)
100 YCOX=YBOTX : XCOX=ILEFTX : YADDX=(YTOPX-YBOTX)/4 : XADDX=(IRIGHTX-ILEFTX)/10
110 FOR IX=1 TO 5 : LINE (ILEFTX, YCOX, ILEFTX-10, YCOX) : YCOX=YCOX+YADDX: NEXT IX
120 FOR IX=1 TO 3 : LINE (ICOX, YBOTX, ICOX, YBOTX-10) : ICOX=ICOX+XADDX: NEXT IX
130!
140 LOCATE 1,15: PRINT "Hit SPACEBAR to collect data any other key to abort."
150 CALL GETKEY(ABC, ISCN, KBI, KB2, IEC)
160 IF IEC<>0 THEN 150
170 IF IABC<>32 THEN 420
175 FILL (145, 435, 750, 445, 0)
177 CALL SYSFUNC(17, FP(KI(1)))
178 WAIT(10)
179 CALL SYSFUNC(17, FP(KI(4)))
180 NOW=TIME(): T(0)=NOW
190 FOR IX=1 TO N
200 DATA="
210 UNTIL TIME>N
220 NEXT
230 T(JJ)=TIME(): NOW=NOW+INCR
240 CALL BREAD(6, SIX(1), 6, 400, 900, 0)
250 FOR IX=1 TO 3 : DATA=DATA+CVTSY(SIX(IX)) : NEXT IX
255 S(JJ)=VAL(DATA)
260 ICOX=0.3+D1*J1*LEFTZ ;YCOX=DY1(S(J1)+OFFS)+YBOTW
270 LINE(YCOX,YCOX,YCOX<5,YCOX)
280 NEXT J1 290 T(J1)=S(J1)-T(J1) FOR J1=1 TO NZ
295 MAT B=(RAM)<.9
300 LOCATE 1,15;INPUT "Name of output file ",DFILE
305 FILL(145,435,750,445,0)
310 IF DFILE="NONE" OR DFILE="" THEN 420
320 OPEN DFILE FOR OUTPUT AS FILE 03
330 MAT PRINT 03 B(NX);PRINT 03 "Time ordinates (seconds)";MAT PRINT 03 T(NX)
340 COMMENT="LOCATE 1,15;PRINT "Type comments for end of file (\EBC) to end"
350 CALL GETKEY(1ABC,1BCN,1BD1,1BD2,1EC)
360 IF IEC<>0 THEN 350 370 IF IABC<>27 THEN 410
380 NCHAR=CHR$(1ABC);PRINT NCHAR; \COMM=\COMM+NCHAR
390 IF LEN(\COMM)<80 THEN 350
400 PRINT 03 \COMM; \COMM="" 1GOTO 350
410 PRINT 03 \COMM 1CLOSE 03
415 FILL(145,435,750,445,0)
420 LOCATE 1,15;INPUT "COLLECT more data? ",A8
425 FILL(145,435,750,445,0)
430 IF A8="Y" OR A8="YES" THEN 140
440 IF A8<">M" AND A8<">NO" THEN 420
450 CALL SYSCL0SE(b)
451 CLOSE 07
460 END
500 : SUBROUTINE to adjust scaling factor for data values according to Range
510 IF RANG<>0.2 THEN 520
515 RANG=0.01 1GOTO 550
520 IF RANG<2 THEN 530
525 RANG=0.10 1GOTO 550
530 IF RANG<>20 THEN 540
535 RANG=1.00 1GOTO 550
540 IF RANG<>200 THEN 560
545 RANG=10
550 RETURN
560 LOCATE 1,15;INPUT "Choose 0.2; 2.0; 20 or 200 setting ",RANG
565 FILL(145,435,750,445,0)
570 GOTO 510
999 : ERROR TRAP ROUTINE
1000 IF ERL=235 THEN
1100 : PROBABLE ERROR: Data out of range for meter
1110 IF ERL=320 THEN RESUME 300 ! PROBABLE ERROR: Invalid output file name
1190 PRINT "Error ",ERR1, in line ";ERL : RESUME 450
1110 B(J1)=0 ;RESUME 260
APPENDIX E

PAR273.PAS

1 ! $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
500 !
501 ! *************************************************************
502 ! *************************************************************
503 ! ** Subroutine: SPOLL **
504 ! ** Conducts poll of PAR 273 and waits if PAR is not ready to per- **
505 ! ** form a task. The contents of the Status Byte are displayed **
506 ! *************************************************************
507 ! *************************************************************
508 REIN ------ Call Serial Poll and sort bits ------
510 CMD="ST"
511 GOSUB 2010
512 GOSUB 1510
513 FILL(0,400,760,420,0)
514 FX(27,2)=VAL(DATA)
515 MAT BI=ER
530 FOR ISP1=1 TO 0 STEP -1
550 MX=2-ISP1
570 IF FX(27,2)(MX) THEN GOTO 630
590 IF (ISP1)=1 IF FX(27,2)=FX(27,2)-MX
610 IF FX(27,2)=0 THEN ISP1=0
630 NEXT ISP1
650 LOCATE 20,10 ;PRINT USING B06, BI(01); ;PRINT USING B46, BI(41)
670 LOCATE 21,10 ;PRINT USING B18, BI(11); ;PRINT USING B58, BI(51)
690 LOCATE 22,10 ;PRINT USING B26, BI(21); ;PRINT USING B66, BI(61)
710 LOCATE 23,10 ;PRINT USING B34, BI(31); ;PRINT USING B74, BI(71)
750 IF BI(11)=0 THEN 750
731 CMD="ERR"
732 GOSUB 2010
733 GOSUB 1510
734 WAIT(5);FILL(0,400,760,460,0)
750 BFZ=BFX OR 1%
770 RETURN
1000 !
1001 ! *************************************************************
1002 ! *************************************************************
1003 ! ** Subroutine: DECISIONS **
1004 ! ** This routine routes program flow to (a) PAR 273 commands, **
1005 ! ** (b) available program commands or (c) specific defined PROCEDURES **
1006 ! ** PROCEDURES are denoted by preceding the Procedure name by 'D' **
1007 ! ** and are added to the program as follows: **
1008 ! ** 1. Include an FI CMD="$procname" THEN CTI=n statement as done **
1009 ! ** below. **
1010 ! ** 2. Write the PROCEDURE as a subroutine at the end of this pro- **
1011 ! ** gram. **
1012 ! ** 3. Place the line number of the beginning of the subroutine in **
1013 ! ** the GOSUB list in line 380 such that it corresponds to CTI=n **
1014 ! ** 4. Include the procedure name in the menu list of the command **
1015 ! ** information subroutine **
1016 ! *************************************************************
214

1019: ** Addition of PROCEDURES is best done through the text editor **

1020 IF LEFT(CMD9,1)="*" THEN GOTO 1150

1030 CTX=1 ; JX=0 ; X=0 ; 50 THEN CMD9="LISTEN" THEN CTX=2

1070 IF CMD9="SYSPUNC" THEN CTX=4

1090 IF CMD9="SAVE" THEN CTX=3

1095 IF CMD9="DISK" THEN CTX=5

1110 GOTO 1190

1130 REM ---- ---- ---- ---- ---- ---- ---- ---- ---- ---- ---- ---- ---- Procedure control list ----

1150 CTX=1 ; X=1

1155 FILL(0,145,760,450,0) ; SFI=SFI AND 65532

1160 IF CMD9="BCV" THEN CTX=2

1170 LOCATE 16,1 ; PRINT SPACE$(80)

1190 RETURN

1191 !

1500 ! $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$

1501 ! $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$

1502 ! $ Subroutine: READSUB  $#

1503 # # Reads PAR 273 responses in dialog. This routine does not read $#

1504 # $ data points from PAR memory except for those accessed by DCIdump $#

1505 # $ curve) and DP (dump point). The transfer of curves by BD (binary $#

1506 # $ dump) is accomplished in a separate subroutine. Data is sent as $#

1507 $ # ASCII code which is converted to string values and displayed.  $#

1508 ! $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$

1509 ! $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$

1510 ! $BSUB 510

1530 NAT AI=IER ; DATA=""

1550 CALL SREADAI(AI,IA(IX),120,10,13,0)

1590 FOR IX=1 TO 60

1610 T8=CVATX(AI(IX))

1615 LI=ASCII(LEFT(T8,IX)) ; RI=ASCII(RIGHT(T8,23))

1616 IF LI=101 OR LI=13 THEN T8="+T8"

1617 IF RI=101 OR RI=13 THEN T8=T8++

1620 DATA=DATA+T8

1630 NEXT IX

1650 DATA=CVATY(DATA,201) ! Eliminate extra spaces,<CR>,<LF>..

1670 LOCATE 3,18 ; PRINT DATA

1690 RETURN

2000 !

2001 ! $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$

2002 ! $ Subroutine: WRITESUB  $#

2003 ! $ Write routine for dialog with PAR. Uses AX(n) as message array. $#

2004 ! $ WRITESUB is not used for curve transfers to PAR $#

2005 ! $ Subroutine 3010 (BSUB) reads contents of BD response. Subroutine $#

2006 ! $ # 2510 (BSUB) is used for Binary Load both to send the BL command $#

2007 ! $ and to send the curve. $#

2008 ! $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$

2009 ! $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$

2010 ! $ NAT AI=IER ; CG="*" ; IZ=1Z

2015 IF LEFT(CMD9,2)="BL" THEN GOTO 2030

2020 GO SUB 2510

2025 GOTO 2162
2030 UNTIL C$=""
2050 C$=MID(CMD$,11,2); Ai((1+1)/2Z)=CVT$(C$);II=II+2
2070 NEXT
2090 Ai((1+1)/2Z)=13
2110 CALL WRITE(1,Ai(1),120,041,13,0)
2130 IF LEFT(CMD$,2Z)="BD" THEN GOSUB 3010
2142 RETURN
2900 !
2901 !******************************************************************************
2902 !******************************************************************************
2903 ! ** Subroutine: BLSUB **
2904 ! ** This routine is specifically for sending the BL command to PAR **
2905 ! ** with the curve points following. It is accessed only through sub- **
2906 ! ** routine WRITESUB **
2907 !******************************************************************************
2908 !******************************************************************************
2910 LS=LEN(CMD$); C$="" ; i1=1
2930 UNTIL LEFT(C$,1)=**
2950 C$=RIGHT(CMD$,11-11)
2970 i1=i1+1
2990 NEXT
3010 MPTS$=VAL(C$)
3050 LOCATE 4,10:INPUT *Name of disk file containing curve points?";DFILE
3070 IF DFILE="" THEN GOTO 2790
3072 C$="" ; J1=1
3074 UNTIL C$=""
3076 C$=MID(CMD$,11,2) ; CI(J1)=CVT$(C$)
3078 J1=J1+1
3080 NEXT
3082 CI(J1-1)=13
3086 OPEN DFILE AS FILE 4
3088 FOR J=6 TO MPTS$+5
3090 INPUT 4,CI(J)
3092 NEXT J
3094 CLOSE 4
3096 CALL WRITE(1,CI(1),2100,804,80D,0)
3099 RETURN
3000 !
3001 !******************************************************************************
3002 !******************************************************************************
3003 ! ** Subroutine: BSUB **
3004 ! ** Reads curve from PAR after BD is sent by WRITESUB and converts **
3005 ! ** the data to millimeters. I/E setting is automatically retrieved or**
3006 ! ** if auto-ranging is on the data is unpacked for I measurements only**
3007 ! ** since all other measurements read true in mV. SIE from PAR is used**
3008 ! ** to determine if samples contain I values or not. **
3009 !******************************************************************************
3010 MAT CI=JER;MAT Y=JER; L$=LEN(CMD$); C$="" ; i1=1
3012 CALL BREAD(1,CI(1),4094,4X,13,0)
3015 Ai(i1)=CVT$("AR") ; A121=13281
3016 CALL SBWRITE(1,AX(1),3,4X,13X,0)
3017 CALL SBREAD(1,AX(1),2,4X,13X,0)
3018 AX=VAL(CVTIX(AX(1)))
3019 AX(1)=CVTIX("SI") ; AX(2)=CVTIX("E") ; AX(3)=CVTIX("N")+13
3020 CALL SBWRITE(1,AX(1),6,4X,13X,0)
3021 CALL SBREAD(1,AX(1),4,4X,13X,0)
3022 IGAIN=VAL(CVTIX(AX(1)))
3032 UNTIL LEFT(AX,1)=" "
3031 CP=RIGHT(AX(6),11-IX)
3033 IX=IX+1
3034 NEXT
3040 NPTS=VAL(CS)
3070 IF (AX AND IX)=0 THEN GOTO 3270
3080 Rem ------------- Unpack data from I/E range information ---------------
3130 COLD=0
3135 FOR IX=1% TO NPTS
3140 IF EOLD=(CX(IX) AND -4096%) THEN 3180
3145 EOLD=CX(IX) AND -4096% : ESCSCALE=CI(IX)/4096X-1% : ESCSCALE=(10"ESCALE")/IGAIN
3180 CI(IX)=CSEXICX(IX) AND 4095X ; IF CI(IX)>2048 THEN CX(IX)=CX(IX)-4096X
3181 Y(IX)=ESCALEICX(IX)
3183 NEXT IX
3250 GOTO 3610
3260 REM ------------- Autoranging off, data not packed ---------------
3270 NAT AX=IER
3290 AX(1)=CVTIX("SI") ; AX(2)=CVTIX("E") ; AX(3)=13
3310 CALL SBWRITE(1,AX(1),6,04X,13X,0)
3330 CALL SBREAD(1,AX(1),3,04X,13X,0)
3350 SIEX=VAL(CVTIX(AX(1)))3370 IF (SIEX AND 1X)=1 THEN GOTO 3490
3450 NAT Y=C3470 GOTO 3610
3480 Rem ------------- Data is current; convert to milliamps ---------------
3490 NAT AX=IER
3510 AX(1)=CVTIX("1/"") ; AX(2)=CVTIX("E") ; AX(3)=13
3530 CALL SBWRITE(1,AX(1),6,04X,13X,0)
3550 CALL SBREAD(1,AX(1),3,04X,13X,0)
3570 E=VAL(CVTIX(AX(1)))3370 IF (EAND 1X)=1 THEN 3610 RETURN
3610 RETURN
4000 !
4001 !********************************************************************************
4002 !********************************************************************************
4003 ! $ Subroutine: SAVE  
4004 ! $ This routine will writes either to the monitor or to disk and 
4005 ! $ will save (a) the latest BD curve, (b) the latest DATA variable  
4006 ! $ or (c) a message from the keyboard.  
4007 ! $********************************************************************************
4008 !********************************************************************************
4010 FILL(0,145,760,450,0)
4030 BFI=BF1 AND 32764% ! Input prompt and command info off
4050 LOCATE 0,10
4051 INPUT "Name of output file('SCR', 'SERO0') or 'I' to ret to main ";DFIL
4070 IF DFIL="I" THEN GOTO 3610
4730 \texttt{NEXT IX}
4735 \texttt{RETURN}
4800 \texttt{REM ----- Write DATA# to Screen -----}
4810 \texttt{PRINT DATA#}
4820 \texttt{RETURN}
4900 \texttt{REM ----- Write keyboard message to screen (redundant) -----}
4910 \texttt{LOCATE 6,10:PRINT SPACE$(40)}
4920 \texttt{LOCATE 6,10:PRINT "Enter message (up to 132 characters)"}
4930 \texttt{INPUT "", H56#}
4940 \texttt{RETURN}
4950 \texttt{REM ----- Write curve to COM1(PC)
4952 \texttt{REM The data is written to "SEROO" configured as modem with the ff}
4954 \texttt{REM parameters; 1200 (baud rate),7 (data bits),0 (odd parity) and}
4955 \texttt{REM one stop bit. Using any PC com program data can be saved to PC}
4956 \texttt{REM using 'COM1'
4958 \texttt{REM setting}
4960 \texttt{B1H FPK(6)}
4964 \texttt{OPEN "SEROO" AS FILE 03}
4966 \texttt{FPK(1)=20:FPK(2)=0:FPK(3)=22:FPK(4)=0:64+16:FPK(5)=0}
4968 \texttt{CALL SYSFUNC(3,FPK(1))}
4972 \texttt{RETURN}
5000 ;
5001 ; \texttt{~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~}
5002 ; \texttt{~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~}
5003 ; \texttt{### SUBROUTINE: FUNSUB \#}
5004 ; \texttt{IEEE-488 driver functions includes menu of functions. Function \#}
5005 ; \texttt{### packets (FX(n)) are defined in subroutine DATASUB \#}
5006 ; \texttt{~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~}
5010 \texttt{LOCATE 18,1:PRINT SPACE$(70)}
5011 \texttt{LOCATE 18,1:PRINT "SYSFUNCS not currently available":WAIT(50)}
5020 \texttt{RETURN}
5300 ;
5301 ; \texttt{~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~}
5302 ; \texttt{~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~}
5303 ; \texttt{### SUBROUTINE: DISK \#}
5304 ; \texttt{Reads PAR commands from a text file or if the +option is used \#}
5305 ; \texttt{creates a text file from this subroutine \#}
5306 ; \texttt{~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~}
5310 \texttt{SFX=SFX AND 32764
5312 \texttt{FILL(0,69,760,450,0)
5320 \texttt{LOCATE 2,0:PRINT SPACE$(80):PRINT "Clear old CMD"}
5325 \texttt{LOCATE 2,0:PRINT "}
5330 \texttt{"Enter name of file to be read, <c> to create a new file or <cr> to quit"}
5335 \texttt{LOCATE 3,0:PRINT SPACE$(80):LOCATE 3,0:INPUT "Command file ":\texttt{COMFILE}}
5340 \texttt{IF COMFILE<>"":DR LEFT(COMFILE,1)="":THEN 5400
5345 \texttt{IF COMFILE="":THEN GOTO 5600
5350 \texttt{OPEN COMFILE\#PAR FOR INPUT AS FILE \#4}
5355 \texttt{CMD=\"}
5360 \texttt{UNTIL CMD="END"
5365 \texttt{INPUT \#4 CMD#}
5370 \texttt{GOSUB 2010 UNLESS CMD="END"
5375 \texttt{NEXT}
CLOSE 04
GOTO 5800
LOCATE 3,0:PRINT SPACE$(00):LOCATE 3,06:
   "Enter PAR273 action commands only. Enter 'END' to quit"
LOCATE 4,3:PRINT &
   "Create file named "CONFIL"
   IF CONFIL="" THEN 5800
   OPEN CONFIL=*.PAR* FOR OUTPUT AS FILE 04
   "Enter PAR273 action commands only. Enter 'END' to quit"
   CHD0=""
   UNTIL CHD=""END"
   INPUT "Create file a a a e d"
   CHD0 : PRINT #0 CMD0
   NEXT
   CLOSE 04
RETURN

LOCATE 5,1:PRINT A109:"The following commands are available:"
PRINT
   (a) PAR 273 commands, using space as delimiter between
   values (see PAR 273 operation manual)"
   (b) LISTEN (Function 1) reads dialog response of PAR
   DISK loads series of PAR 273 commands from a*
   user created diskfile."
   SYSFUNC accesses functions available from the
   IEEE-488 driver program (MENU provided)"
   SAVE writes data and messages to disk. Prompts"*)
   provided"
   exit to exit from the program"
   (c) PROCEDURES"
   "CV cyclic voltammetry or Mott-Schottky"
PRINT A109;"6F3=6F1 OR 2%"
RETURN

1 : "DEFKEYS"
   ** Subroutine: DEFKEYS **
   ** Defines convenient commands on F keys and writes a menu **
   ** in the console box at the bottom of the monitor screen **
   ** Keys are defined for LISTEN, ERA, READI READE, READAUX **
   OPEN *MKBD* AS FILE 03
   IX(1)=14% IX(2)=3% IX(3)=0 ; FPRT to clear old F-key table
   CALL SYSFUNC(3,IX(1))
LOCATE 17,1: PRINT "ERROR ";ERR1" in line ";ERL
RLI=1
IF ERR<>5 THEN GOTO 7430
IF ERL=2686 THEN RLI=2
IF ERL=4190 THEN RLI=3
IF ERL=5550 THEN RLI=8
IF ERL=5405 THEN RLI=9
GOTO 7690
IF ERR<>4 THEN GOTO 7490
IF ERL=4190 THEN RLI=4
GOTO 7690
IF ERR<>5 AND ERR<11 THEN GOTO 7550
IF ERL=2670 THEN RLI=5
GOTO 7690
IF ERR<>50 OR ERL>4210 GOTO 7610
CLOSE #3: RLI=3
GOTO 7690
IF ERR<>55 THEN GOTO 7670
IF ERL=4330 THEN RLI=6
IF ERL=4650 THEN RLI=7
IF RLI=1 THEN GOTO 7870
INPUT ":<CR>" to continue any character to end ";A#"
IF A<>"" THEN GOTO 7870
ON RLI 60 TO 7870,7750,7770,7790,7810,7830,7850,7852,7856
RESUME 2630
RESUME 4050
RESUME 4740
RESUME 2610
RESUME 4320
RESUME 4420
LOCATE 10,10:PRINT "Error in opening ":";CONFILE;"" for input. 
RESUME 3535
LOCATE 10,10:PRINT "Error in opening ":";CONFILE;"" for output. 
RESUME 5600
CALL SYSCLOSE(1)
FILL(0,0,760,450,2)
CLOSE 82,83,84
END
010 LOCATE 18,1 ;PRINT CMD0; 'has not been defined'
020 RETURN
0510 : ;SUBROUTINE PROC.CV
0520 : ;Cyclic voltammetry subroutine. Performs CV experiment with only
0530 : ;the entry of potential limits and potential sweep rate. This allows
0540 : ;more convenient parameters choice than the ramping program of the
0550 : ;PAR 273 and a more flexible waveform than the CV command.
0560 : ;Nernst-Schottky experiments are performed by using
0570 : ;with an external lock-in amplifier
0580 : ;..............................................................................
0590 : ;LOCATE 2,3 ;PRINT "Procedure:;" "CMD0"
0600 : ;LOCATE 5,5 ;INPUT "Nernst-Schottky measurements?(y/cr)" ;"1A0
0610 : ;IF A0="Y" THEN A0="SIE 4" ELSE A0="SIE 1"
0620 : ;CMD0="MN 1|1|A0|1|PAN 0|INTRP 1|BCV 0|FP 0"
0630 : ;GOSUB 2010
0640 : ;"CMD0 sent
0650 : ;LOCATE 5,5 ;PRINT "Enter potentials as eV vs ref."
0660 : ;LOCATE 6,10 ;PRINT "Initial potential"
0670 : ;LOCATE 7,10 ;PRINT "First reversal potential"
0680 : ;LOCATE 8,10 ;PRINT "Second reversal potential"
0690 : ;LOCATE 10,10 ;PRINT "Sweep rate (eV/sec)"
0700 : ;LOCATE 11,10 ;PRINT "Number of data points"
0710 : ;FILL(335,240,760,380,0)
0720 : ;LOCATE 6,35 ;INPUT "|1|INITI"
0730 : ;LOCATE 7,35 ;INPUT "|1|ER1Z"
0740 : ;LOCATE 8,35 ;INPUT "|1|ER2Z"
0750 : ;LOCATE 10,35 ;INPUT "|1|Y"
0760 : ;LOCATE 11,35 ;INPUT "|1|N"
0770 : ;CMD0="LP|""NUM10(INITI(N-1))"
0780 : ;GOSUB 2010
0790 : ;A0="|1|DIAS|""NUM10(INITI) ;CMD0=CMD0+A0
0800 : ;ER1Z=ER1Z-INITI ;ER2Z=ER2Z-INITI
0810 : ;DE=ABS(ER2Z-ER1Z)
0820 : ;IF DE>2000 THEN GOTO 0570

"
A0="\n R 2"
B650 IF DE<200 THEN A0="\n R 1"
B660 IF DE<20 THEN A0="\n R 0"
B662 NR=VAL(RIGHT(A0,4))
B670 CMD0=CMD0+A0
B690 EINC=2(EINC/N)/TS=(EINC/V)*660;SPP=10:TN=TS/SPP
B700 IF TN<500 THEN B710
B702 IF TN>1000 THEN B730
B704 UNTIL TN>1000
B706 TN=2TN+1:SPP=SPP+2
B708 NEIT
B710 IF SPP<1 THEN GOTO B567
B711 GOTO B730
B715 UNTIL TN>5000
B717 TN=TN/2:SPP=SPP/2
B719 NEIT
B720 GOTO B700
B730 TN=INT(TN+.5)
B740 A0="\n TN"+NUM18(TN)+";S/P"+NUM18(SPP)
B750 CMD0=CMD0+A0
B760 GOSUB 2010
B762 GOSUB 9110
B764 GOSUB 2010
B770 IF CMD0 END "CMD0 sent"
B780 LOCATE 14,10:PRINT "Data acquired for last cycle only"
B790 LOCATE 13,10:INPUT "Number of sweeps ((cr)=1)";MSWP
B800 IF MSWP=0 THEN MSWP=1
B810 LOCATE 13,10:PRINT "Cell is on; hit any key to start or 'I' to escape"
B820 CMD0="\n 1"
B830 GOSUB 2010
B840 CALL GETKEY(P1,P2,P3,P4,P5)
B850 IF P3<>0 THEN GOTO B850
B855 IF P1<>0 THEN GOTO B850
B870 LOCATE 13,10:PRINT "Sweep in progress; hit any key to stop"
B880 CMD0="\n SWP"+NUM18(MSWP)
B890 GOSUB 2010
B896 CMD0="\n TC"+GOSUB 2010
B900 CMD0="\n 1"+GOSUB 2010
B905 GOSUB 1510
B910 CALL GETKEY(P1,P2,P3,P4,P5)
B912 IF P3=0 THEN GOTO B930
B914 IF (INT(VAR(DATA0)) AND 321)<32 THEN GOTO B900
B930 CMD0="\n 0"
B940 GOSUB 2010
B945 FILL(0,80,760,160,0)
B950 LOCATE 14,10:PRINT "Sweep finished";SPACE(25)
B951 IF P3<>0 THEN GOTO B960
B952 LOCATE 14,10:PRINT "Sweep stopped"
B960 LOCATE 13,10:PRINT & "Save data(S); Repeat(R); Change settings(C); (cr)to return to PAR273"
B970 LOCATE 13,78:INPUT "";A0
8972 IF A$="I" THEN GOTO 8960
8975 FILL(0,225,760,265,0)
8980 IF A$="" THEN GOTO 9060
8990 IF A$="C" THEN GOTO 8556
9000 IF A$="R" THEN GOTO 8780
9010 IF A$="S" THEN GOTO 8960
9020 CMD$="BD 0 *<NUM10(N)"
9030 GOSUB 2010
9040 GOSUB 4010
9050 GOTO 8960
9060 RETURN
9101 Subroutine to generate ramp
9110 CMD$="INITIAL 0 0"
9120 MR=20:10:MR
9130 CPT=NABS(ERI1/(2*DE)); CVAL=B3*ERI1/MR
9131 CPT=INT(CPT+.5); CVAL=INT(CVAL+.5*SGN(CVAL))
9140 A$="1"; VERTEX "+NUM10(CPT)+""+NUM10(CVAL)
9150 CPT=CPT+2*: CVAL=B3*ERI2/MR
9151 CPT=INT(CPT+.5); CVAL=INT(CVAL+.5*SGN(CVAL))
9160 A$="A"; VERTEX "+NUM10(CPT)+""+NUM10(CVAL)
9165 A$="A"; VERTEX "+NUM10(N-1)+"0"
9170 CMD$=CMD$+A$
9180 LOCATE 19,1 : PRINT CMD$
9190 RETURN
Kenneth Robert Carney was born in Defuniak Springs, Florida on May 31, 1958. He received his High School diploma from Bossier High School in Bossier City, Louisiana in May of 1976. He was awarded the Bachelor of Science Degree in Chemistry from Louisiana State University in Shreveport in May of 1981.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Kenneth R. Carney

Major Field: (Analytical) Chemistry

Title of Dissertation: Application of the Fast Fourier Transform to Impedance Analysis of n-TiO$_2$ and LaF$_3$ Electrodes

Approved:

[Signatures and names of the major professor and chairman, dean of the graduate school, and examining committee members]

EXAMINING COMMITTEE:

[Signatures of committee members]

Date of Examination: December 2, 1988