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TRACE VOLTAMMETRY USING MICROELECTRODES AND MODULATION TECHNIQUES

The Ohio State University

Ph.D. 1987

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TRACE VOLTAMMETRY USING MICROELECTRODES
AND MODULATION TECHNIQUES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

By

Sheila Ann Schuette

* * * * *

The Ohio State University

1987

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FIELD OF STUDY

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CHAPTER I

INTRODUCTION

The analysis of trace components in samples has become progressively more difficult due to the ever increasing demands for sensitivity placed by governmental agencies, medical facilities and industrial laboratories. No single technique possesses all of the necessary qualities required for the detection of all types of sample constituents, and selection of a suitable technique must be based on the specific needs of each analysis. Although the most important requirement for trace analysis is a low limit of detection, other factors must be considered if the technique is to be used on a day-to-day basis in a routine testing laboratory. Selectivity and reproducibility are as important as sensitivity, while ease of operation and cost can not be overlooked.

Electrochemical techniques offer many advantages for trace analysis. The foremost of these advantages is the sensitivity of an electrochemical measurement. The signal usually measured in an electroanalytical technique is current; with the advent of sophisticated electronics a very
small current signal can be greatly amplified and easily measured. This advantage is very important when one realizes that the currents measured at trace levels are in the nanoamp to picoamp range, corresponding to extremely small amounts of material. Other features of electroanalytical techniques that offer advantages for routine trace analysis are wide dynamic range (10^6), reproducible quantitation, low cost, and their applicability to microscale analyses. Finally, because only certain functional groups can undergo oxidation or reduction reactions, the techniques are selective. In addition to the selectivity arising from this electroactivity requirement, the potential applied to the electrode can also be adjusted to discriminate between various electroactive species.

Polarography is one electrochemical technique that has found widespread acceptance in the analytical laboratory, primarily for the determination of metal ions. Heyrovsky first demonstrated that a dropping mercury electrode could provide the basis for this powerful analytical tool in 1922 [1]. Improvements such as the static mercury drop electrode and stripping polarography have provided even greater detection capabilities. Extremely sensitive determinations can be performed on these types of mercury electrodes; detection limits of 10^-9 M are common, and are often even lower [58].
Polarography is an example of a class of techniques called voltammetry. The term polarography is used when the electrode is mercury, while the term voltammetry usually indicates that a solid electrode is used. Voltammetry has not met with the same success as polarography in analytical applications, although linear scan voltammetry and cyclic voltammetry have been extensively employed for mechanistic studies. The lower popularity of voltammetry for analytical applications is due mainly to the large background currents exhibited at solid electrodes.

In conventional dc voltammetry a potential ramp is applied to an electrochemical cell and the resultant current is measured. The electrochemical cell consists of three electrodes immersed in a solution containing a supporting electrolyte and the analyte of interest. The redox reaction occurs at the interface of the working electrode (WE) and the solution. The potential applied at the WE is measured by the reference electrode (RE), while the auxiliary electrode (AE) provides a path through which the majority of the current can flow without affecting the potential of the RE. The plot of current vs. applied potential is called a voltammogram.

The current signal measured in a voltammetric experiment is the total current produced at the working electrode and arises from several sources, equation 1.1 [2].

\[ i_{total} = i_{far} + i_{ch} + i_{surf} + i_{elec} \] (1.1)
Here, \( i_{far} \) is the analytical signal of interest; \( i_{Ch} \) is the charging current produced from the rearrangement of ions in the double layer arising from the variation of the applied potential; \( i_{surf} \) is the current produced by the redox reactions of species adsorbed on the electrode surface and, in the case of carbon electrodes, of functional groups present on the electrode surface itself; and \( i_{elec} \) is the current produced by any redox reactions of the electrolyte. By proper choice of electrolyte, the latter source of background current can be neglected. With solutions of normal concentration, the other background currents are negligibly small and do not interfere in the measurement. However, when performing trace analyses, the analytical current signal is very small and can be easily obscured by the much larger background currents.

These background currents occur on all electrodes, but they are particularly severe on solid electrodes. Although mercury electrodes, and in particular the dropping mercury electrode (DME), have found widespread use due to their constantly renewed and hence reproducible surfaces, particularly for the detection of metal ions, they possess certain limitations that can only be addressed by solid electrodes. The primary limitation of mercury is its usable potential range; the low oxidation potential of mercury precludes its use for the study of species that oxidize above about 0.2 V. In addition, because mercury is a liquid
it is unsuitable for many applications, including in vivo analysis. The features of solid electrodes that make them preferable to mercury for many applications are a wider potential range and the sturdiness and machinability that come from a solid electrode. The solid electrodes in common use are made from either the noble metals (platinum or gold) or from various types of carbon, including glassy (vitreous) carbon and carbon paste. As was just mentioned, the disadvantage of solid electrodes is their susceptibility to background surface reactions. For example, the formation of oxide layers on platinum or gold electrode surfaces in aqueous media is a common interference.

Recently, reports involving voltammetry with solid electrodes of small dimension have appeared in the literature [3-16]. These microelectrodes offer certain advantages when used for voltammetry, including enhanced diffusion characteristics and very low cell time constants due to their low capacitance. In addition, their small tip diameters make them useful for in vivo monitoring of electroactive materials, and their relative freedom from convective currents is of value in HPLC applications. The unique characteristics of microelectrodes can also be exploited to discriminate against the various types of background current that afflict trace voltammetry.

Various methods have been devised to reduce the contribution of the large background currents inherent to
solid electrodes to the total measured current. Although the size of these currents can be diminished considerably by various techniques, they can not be eliminated altogether. The aim of this work was, therefore, to first differentiate between the analytical current and the interfering background currents and then discriminate against the latter in such a way that they are effectively eliminated from the signal. Modulation techniques can provide the means for differentiating the various types of currents, while the unique characteristics of microelectrodes allow one to discriminate against the background currents encountered in solid electrode voltammetry. When the modulated current is detected by a lock-in amplifier (LIA), extremely sensitive analyses are possible. The synergistic combination of microelectrodes with modulation techniques thus offers a means to perform trace voltammetry on solid electrodes. Following a review of existing modulation methods, several new modulation techniques that take advantage of the unique characteristics of microelectrodes will be presented and discussed.
A vast array of modulation schemes have been used in electrochemistry to differentiate the faradaic current signal from the various types of background currents that plague trace voltammetry. These techniques can be broadly classified into two groups: those that discriminate against charging current and those that discriminate against the current arising from surface reactions. The techniques that allow the rejection of charging current from the faradaic signal by using small-amplitude potential modulation can be grouped together under the title of alternating current voltammetry, whereas those techniques that eliminate surface current by modulating mass transport are termed hydrodynamic modulation voltammetry. In addition to the above, there are several techniques that take advantage of the non-linear behavior of the faradaic process to discriminate against the background currents encountered in trace voltammetry.

**Alternating Current Voltammetry**

Charging current arises from variations in electrode potential and surface concentrations, according to equation 1.2 [17]:

\[ i_{ch} = C \frac{dE}{dt} + E \frac{dC}{dt} \]  

(1.2)

C = concentration at electrode surface
E = electrode potential

The first term is generally dominant, and is caused by the rearrangement of ions in the double layer after the imposition of a potential change. The double layer, the interface of the electrode surface and the electrolyte solution, behaves in a manner analogous to a capacitor. When the potential across the cell is changed, an excess charge develops on the electrode surface. The ions in solution then rearrange to produce an equal but opposite charge in the thin layer adjacent to the electrode to compensate for this excess charge. The current that flows during this process is the charging current, and its magnitude depends on the capacitance of the double layer. Unlike an ideal capacitor, the double-layer capacitance is usually a function of applied potential [18]. For stationary electrodes, the second term in equation 1.2 generally becomes significant only near the point of zero charge [17]. This term is, however, quite significant for the DME due to the fact that the increasing area of the growing drop results in an increase in capacitance.

By exploiting the fact that the charging current responds differently than the faradaic current upon application of potential, one can discriminate against the former. In alternating current (ac) voltammetry, a small-amplitude potential waveform is superimposed on the dc potential ramp applied to the cell. This time-varying
signal can be a square wave, a sawtooth wave, a sine wave or a triangular wave, although square and sinusoidal waves have been used predominantly. Because the charging current has decay characteristics that differ from those of the faradaic signal, the two types of current can be distinguished. For example, upon application of a potential pulse or step, the charging current decays exponentially according to equation 1.3 [19],

\[
ich = \frac{\Delta E}{R_s} e^{-\frac{t}{R_s C_d l}} \tag{1.3}
\]

\(\Delta E\) = amplitude of potential step

\(R_s\) = resistance of electrochemical cell

\(C_d l\) = double-layer capacitance

while the faradaic current decays in proportion to \(t^{-1/2}\), equation 1.4. [20], when the applied potential is stepped to a value where the redox reaction occurs at a diffusion-limited rate.

\[
ifar = \frac{nFAD^{1/2}C^*}{\pi t^{1/2}} \tag{1.4}
\]

\(n\) = number of electrons

\(F\) = Faraday constant

\(A\) = electrode area

\(D\) = diffusion coefficient of electrocative species

\(C^*\) = bulk concentration of electroactive species

If a waveform comprised of potential pulses is superimposed on the potential ramp applied to the cell, the charging
current will decay away much more rapidly than the faradaic current after each pulse, and the current sampled near the end of each pulse will be high in the ratio of faradaic to charging current, Figure 1, p. 11.

If a sine wave is chosen as the potential perturbation waveform, the two types of current can again be distinguished. When the sinusoidal potential perturbation is superimposed on the potential ramp, equation 1.5, the current arising from double-layer effects is also sinusoidal in shape, but leads the applied potential by 90°, equation 1.6. [21].

\[
E = E_{dc} - \Delta E \sin(\omega t) \quad (1.5) \\
i_{ch} = ACd_{1}\Delta E \cos(\omega t) \quad (1.6)
\]

\( E_{dc} = \) dc component of potential
\( \Delta E = \) amplitude of applied alternating potential
\( \omega = \) angular frequency

For a reversible system, the faradaic component of the current leads the applied potential by 45°, equation 1.7. [22].

\[
i_{far} = \frac{n^2F^2A^*}{R} (\omega D)^{1/2}_{1/2} \frac{\sin \omega t + \frac{n}{4}}{\cosh^2\left(\frac{j}{2}\right)} \quad (1.7)
\]

where \( j = \frac{nF}{RT} (E_{dc} - E_{1/2}) \quad (1.8) \)

\( E_{1/2} = \) reversible half-wave potential
\( R = \) Molar gas constant

This phase difference of 45° between the charging and
Figure 1. Current vs. time waveform for charging current decay (trace a) and faradaic current decay (trace b) upon application of a potential step, $E_{app}$. 
faradaic components of the current, Figure 2, p. 13, allows one to distinguish between the two. Using phase-sensitive detection, the charging current can, in principle, be eliminated since it is exactly 90° out of phase with the applied potential. If only that current that is in phase with the applied potential is monitored, the contribution from charging current should be zero and an output representing 70% of the maximum faradaic current will be obtained [23]. This decrease in signal is more that offset by the increase in signal to background (S/B). For quasi- and irreversible systems the faradaic current will be less than 45° out of phase with the applied potential, and some trial and error must be used to determine the optimum phase relationship.

If should be pointed out that the basic principles of square wave voltammetry and phase-selective sinusoidal ac voltammetry are the same. Both techniques discriminate against charging current by taking advantage of the fact that the RC time constant associated with the double-layer charging process is smaller than that of the faradaic process [24]. The techniques differ in that square wave voltammetry is a time-domain technique while sinusoidal ac voltammetry operates in the frequency domain [25]. The voltammograms obtained from either of these techniques are also similar. An alternating current voltammogram resembles the derivative of a conventional dc voltammogram, a
Figure 2. Waveforms illustrating the phase shifts between charging current (trace a), faradaic current (trace b), and the applied sinusoidal potential (trace c).
symmetrical peak centered about $E^0$. This peak-shaped wave results in greater sensitivity than a conventionally-shaped voltammogram, and the resolution between successive peaks is also much improved.

A detailed review of alternating current voltammetry would be unwieldy and therefore only the major developments will be outlined. The interested reader is referred to more detailed discussions, as well as reviews of the many analytical applications of ac voltammetry [22,24,26-28]. As mentioned previously, the two major types of alternating current voltammetry employ either a sine wave or a square wave as the perturbing waveform superimposed on the slowly-varying potential ramp. The techniques are known as sinusoidal alternating current voltammetry and square wave voltammetry, respectively. Although these two techniques were developed simultaneously, they will be considered separately for simplicity. It is important to note that the majority of this work was carried out on some type of mercury electrode.

Sinusoidal ac polarography was first reported in 1938 by Müller et al. [29]. Early experiments were aimed at developing more rapid methods of analysis and better ways of determining half-wave potentials, and often employed large-amplitude alternating voltages [30]. Insight into the actual processes occurring at a DME in the presence of an alternating field was first shown by Grahame [31]. In 1946
Breyer and co-workers developed an instrument suitable for ac polarographic analysis [32], and began a systematic study of ac polarography using a small-amplitude sinusoidal voltage superimposed on the dc applied potential [33,34]. By observing the variation in amplitude of the ac component of the current, they obtained well-defined polarographic waves for reversible systems, but found that the sensitivity of their technique was limited by the presence of a large charging current in the ac signal.

In a 1950 patent [35], Jessop suggested that phase-sensitive measurement could be used to eliminate this background charging current. In Jessop's polarograph, the phase discrimination was accomplished by means of a phase-selective rectifier. An instrument based on this design was made commercially available and several applications of the technique appeared in the literature [27]. Although some improvement in sensitivity was shown, it was still limited by the capillary noise of the DME and the high inherent noise of the electromechanical switching arrangement.

In 1960 Smith and Reinmuth [36] reported on an electronic phase-selective detector that was used in conjunction with a hanging mercury drop electrode (HMDE); thus, both of the aforementioned sources of noise were eliminated. Detection limits below $10^{-8}$ M were obtained, using a potential modulation frequency of 38 Hz. They also reported that very high frequencies were attainable for
studying the kinetics of fast electrode processes. Smith presented a detailed derivation of the theory of ac polarography in a 1966 monograph [22], and later demonstrated the analytical and mechanistic utility of the technique in a study of 24 pharmaceutically-important compounds [37].

In 1974 Blutstein and Bond [38] reported a technique they called ac cyclic voltammetry, in which a sinusoidal alternating potential was superimposed onto the triangular dc voltage ramp used in cyclic voltammetry. Bond and Smith and co-workers subsequently teamed up to produce several studies on the theoretical and experimental aspects of ac cyclic voltammetry. They considered the case of electrode reactions involving solution-soluble redox couples at both stationary planar and spherical electrodes [39], and also the case of electrode reactions involving amalgam formation [40].

Square wave polarography was first reported by Barker and Jenkins in 1952 [41]. They found that a 225 Hz square wave voltage was more efficient than the usual sinusoidal voltage used in ac voltammetry for eliminating the charging current at a DME. The ac component of the current was measured shortly before each sudden change in the applied potential, when the charging current from the previous pulse was negligible, and detection limits of $2 \times 10^{-7}$ M were obtained for reversible species. Barker subsequently
developed the theory for this technique and also reported on improved instrumentation that resulted in detection limits of $4 \times 10^{-8}$ M for reversibly reduced metal ions at a DME [42]. The limit to sensitivity was attributed to the noise originating in the capillary of the DME. Barker's technique was also limited by the necessity of very slow scan rates. For scan rates faster than a few mV/s, the slope of the linear dc ramp would be high enough to reintroduce background charging current into the signal. The early analytical applications of Barker's technique were mainly carried out by Milner and co-workers [43].

Ramaley and Krause developed the theory for a variation of Barker's technique that used a square wave potential superimposed on a staircase rather than a linear voltage ramp [44]. The use of the staircase ramp allowed faster scan rates (20 mV/s) than were possible with the linear ramp because the current measurement occurred at a point in the waveform where the ramp was flat and did not contribute any charging current to the signal. This technique employed a HMDE to eliminate any capillary noise, and detection limits of $2.5 \times 10^{-8}$ M were reported for a reversible system undergoing a three-electron transfer [45].

In 1977 Osteryoung and co-workers reported a technique that combined the staircase potential ramp developed by Ramaley and Krause with a dropping mercury electrode [46]. They wanted to retain the advantages of the
DME's constantly renewed surface by carrying out an entire experiment during the lifetime of a single drop, which would require that the potential range of interest be scanned at a rate of approximately 100 mV/s. By shifting the phase of the square wave 180° relative to the staircase, they were able to employ much larger step heights, and hence faster scan rates, than Ramaley and Krause without any loss in sensitivity. The theory was derived for the case of a stationary planar electrode [46], and a companion paper [47] provided experimental verification of the theory. A detection limit of $7 \times 10^{-8}$ M was obtained for a reversible species undergoing a two-electron transfer. The theory for systems complicated by electrode kinetics or homogeneous reactions has also been presented and validated [48,49].

The techniques described above are all limited to fairly low modulation frequencies when used for trace analysis. In sinusoidal ac voltammetry, for example, charging current increases directly with frequency, whereas the faradaic current only increases with the square root of frequency (see eqns. 1.6 and 1.7). In phase-selective sinusoidal ac voltammetry, the theoretical situation where the charging current should be zero when measured at 0° relative to the perturbing waveform is not realized experimentally due to resistive effects [24]. The use of three-electrode potentiostats and positive feedback helps to reduce the iR drop to where considerable discrimination
against charging current is obtained, but, because charging current cannot be completely eliminated, the use of low frequencies is favored [24]. In addition, low scan rates must be employed due to the "slow scan limit", equation 1.9 [39].

$$\Delta E \omega \gg \nu$$  \hspace{1cm} (1.9)

$\nu =$ scan rate of dc potential

Finally, even under the most favorable circumstances, the sensitivity of sinusoidal ac voltammetry is limited by the fact that only 70% of the maximum faradaic current can be retained.

Low modulation frequencies must also be employed in square wave voltammetry (SWV) because of the time required to allow the charging current to decay. In aqueous media it takes approximately $5RC$ after the application of a potential pulse for the charging current to approach zero [24]; this length of time, in addition to the time needed for measuring the faradaic component of the current, ultimately limits the modulation frequency that can be used. The recovery of faradaic current is even lower here than with phase-selective ac voltammetry. The faradaic component of the current is largest just after the potential step and it, too, has decayed by the time a measurement free of charging current can be taken. A final limitation of SWV is the fact that since the current measurement is discontinuous, precise timing is needed to control the signal acquisition, as well
as the input waveform and signal averaging sequences. The recent introduction of commercial instrumentation [50] has minimized this disadvantage, but the technique is still limited by the fact that it must reject a large portion of the faradaic signal early in each half cycle.

**Hydrodynamic Modulation Voltammetry**

The amount of current obtained in an electrochemical experiment is governed by the amount of material that can reach the electrode to undergo reaction. Mass transport of a species from the bulk of solution to the electrode surface occurs by a combination of several processes, equation 1.10 [51].

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F D_i C_i}{RT} \frac{\partial \phi(x)}{\partial x} + C_i v(x) \quad (1.10)
\]

\( J_i(x) \) = flux of species i at distance x from the electrode surface

\( \frac{\partial C_i(x)}{\partial x} \) = concentration gradient at distance x

\( \frac{\partial \phi(x)}{\partial x} \) = potential gradient

\( z_i \) = charge on species i

\( v(x) \) = velocity with which a volume element in solution moves along the axis

The three terms on the right side of the Nernst-Planck equation represent the three modes of mass transport: diffusion, migration, and convection, respectively. Diffusion, the movement of a species under the influence of a concentration gradient, is described by Fick's laws [52]. In most electrochemical experiments it is the
dominant form of mass transfer. Migration is an undesirable process that occurs when a charged species moves under the influence of a potential gradient; its effect can be minimized by the addition of excess supporting electrolyte. The final mode of mass transport, and that which is most relevant to the present discussion, is convection. Convection may be caused by such natural forces as a density gradient, or it may be forced by agitation of either the electrode or solution.

Techniques employing forced convection have been used to increase the mass transport of electroactive species from the bulk of solution to the electrode surface. The Nernst diffusion layer model has been used to provide a picture of what occurs in solution under conditions of forced convection, Figure 3, p. 22 [53]. This model assumed that although convection was the dominant form of mass transfer in the bulk of solution, the thin layer of solution in contact with the electrode was motionless and that therefore diffusion alone controlled mass transfer in this region. The concentration gradient within this layer, called the Nernst diffusion layer, \( \delta_N \), was further assumed to be linear, equation 1.11 [54].

\[
J = \frac{D(C^* - C_e)}{\delta_N}
\]

(1.11)

\( C^* \) = bulk concentration
\( C_e \) = concentration at electrode surface

The limiting current, \( i_L \), could then be defined by equation
Figure 3. Representation of the Nernst diffusion layer.
Although neither of the assumptions made by Nernst is strictly correct, the above equations are still useful qualitatively. The limiting current is proportional to concentration, provided that the experimental conditions are kept constant, and every effect that reduces $\delta_N$ increases the mass flow and hence the limiting current. The qualitative nature of Nernst's treatment does not, however, allow the thickness of $\delta_N$ to be calculated, nor the variation of $\delta_N$ with solution parameters to be predicted.

A more accurate description was presented by Levich, who explained the differences between his boundary layer concept and that of Nernst's in the following way [56]:

1. Our analysis accounts for the motion of the liquid and the convective mass transfer induced by it, while in the Nernst layer, the liquid is considered static.
2. In our treatment, convective and molecular diffusion both across and along the boundary layer are taken into account. However, in the Nernst theory, it is assumed that the thickness of the layer does not change along the entire surface of the body, and diffusion in the tangential direction is entirely disregarded. Actually, the thickness of the diffusion layer varies substantially along the surface, owing to the tangential transport of particles.
3. The thickness of the Nernst layer was assumed to be constant for a given regime of motion. But in fact, the diffusion boundary layer has no clearly defined boundary. It is simply that region where the concentration gradient is at a maximum.

Levich also recognized that mass transfer is analogous to
heat transfer, and used similar dimensionless parameters to solve the convective diffusion equations. Dimensionless parameters are characteristic parameters whose dimensions cancel when they are grouped together [57]. The dimensionless parameters used in mass transfer are given in Table 1, p. 25. The Sherwood Number reflects the contribution of diffusion to mass transport that exists in the mixed convective diffusion process. The Schmidt Number is a ratio that reflects those properties of the liquid that characterize velocity transport with pure diffusional transport. It is independent of both the flow velocity and the electrode dimensions. A high Sc indicates that convective mass transfer dominates. The Reynolds number most directly reflects the experimental parameters as it is the only dimensionless group that contains the solution flow velocity. It is a measure of how smooth the flow is around an electrode surface; at low values of Re, the flow is laminar, while high Re values indicate turbulent flow. Laminar flow is necessary if the mass transfer is to be described theoretically.

Methods employing forced convection take advantage of the fact that as the flux of electroactive species to the electrode is increased, there is a concomitant increase in the amount of current obtained. As the velocity of the electrode or solution is increased, the boundary layer between the electrode surface and the bulk solution becomes
### TABLE 1

Dimensionless Parameters Used in Mass Transport

<table>
<thead>
<tr>
<th>Dimensionless Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sherwood Number</td>
<td>$Sh = \frac{JL}{D(C^b - C_e)}$ (1.13)</td>
</tr>
<tr>
<td>Schmidt Number</td>
<td>$Sc = \frac{v}{D}$ (1.14)</td>
</tr>
<tr>
<td>Reynolds Number</td>
<td>$Re = \frac{UL}{v}$ (1.15)</td>
</tr>
</tbody>
</table>

$L =$ length of electrode along which solution flow occurs  
$v =$ kinematic viscosity  
$U =$ solution velocity
thinner. The concentration gradient within this layer becomes steeper, resulting in increased current. This increase in current is depicted in Figure 4a, p. 27, for an electrode moving at two velocities, where $U_2 > U_1$. Because the current signal is larger, the signal to background ratio is also better, allowing discrimination against any background processes occurring on the electrode surface. As mentioned previously, these surface processes may arise from a change in the oxidation state of functional groups present on the surface of carbon electrodes, or from the formation of oxides or adsorbed hydrogen films on platinum or gold electrodes.

A better way to discriminate against these background currents is to modulate the velocity of the hydrodynamic motion, Figure 4b, p. 27. The increase in current is retained, but because the mass transport rate is modulated by the electrode motion, an alternating current is produced that depends only on the concentration of the freely diffusing analyte dissolved in solution. The current arising from the surface processes is not mass transport controlled, and will therefore be constant, or dc, in nature. By demodulating only the faradaic ac signal, discrimination against background surface processes is achieved.

Hydrodynamic modulation voltammetry and its applications have been reviewed recently by Wang [2]. The
Figure 4. Comparison between (a) constant forced convection and (b) hydrodynamically-modulated forced convection.
rotating disk electrode (RDE) has been used extensively for HMV studies, in part because it is one of the few systems for which the hydrodynamic equations and the convective diffusion equation have been solved [58]. Bruckenstein and Miller and co-workers [59-63] have employed the RDE for hydrodynamic modulation voltammetry (HMRDE), whereby the electrode's rotation speed is varied sinusoidally about some center speed at a rate of 3-15 Hz. Although this modulated current is only a fraction of the total current produced, it is free from any contributions from factors that do not depend on the mass transfer rate. Detection limits as low as $5 \times 10^{-9}$ M have been obtained with this technique [60].

In pulsed-rotation voltammetry (PRV) the rotation rate of a RDE is switched between two speeds at a rate $< 0.1$ Hz [64]. The difference current is then measured at discrete applied potentials and the voltammogram is plotted pointwise. Blaedel and Engstrom [64] reported a detection limit of $1 \times 10^{-8}$ M for the ferri-/ferrocyanide system.

Blaedel and co-workers have also developed a number of techniques based on flow-through solid electrodes, including stopped- and pulsed-flow and stopped- and pulsed-rotation voltammetry [65-70]. In the later technique, the rotation rate of a RDE, immersed in a flowing stream, is switched between rotation speeds and the difference current is measured. These techniques employ modulation frequencies of $0.1-1$ Hz and, except in the case of pulsed-flow voltammetry
[68], plot the voltammogram in a pointwise fashion after
discrete potential changes. Wang and co-workers have
developed further variations of stopped-flow and stopped-
rotation voltammetry which incorporate potential scanning
[71,72]. Detection limits in the nM range have been
reported [67,70].

Vibrating wire electrodes have also been employed for
HMV. Pratt and Johnson studied the hydrodynamics of a wire
electrode that was vibrated in a reciprocating fashion
perpendicular to its axis [73,74]. Both frequency and
amplitude modulation were examined and produced equivalent
voltammograms, but the instrumental requirements of
frequency modulation were more complex. Using 10 Hz
amplitude modulation, detection limits of ca. 10⁻⁸ M were
observed. The detection limit was improved (3 x 10⁻⁹ M)
when the modulation technique was combined with flow
injection analysis.

All of the techniques described above also employ low
modulation frequencies. In the case of the HMRDE, it was
found that the concentration profile adjusted slowly to a
sudden change in the rotation speed compared to the rapid
readjustment of the fluid velocity [61]. Although the
theory has been improved to cover a wider range of
modulation frequencies [62,75,76], the modulation frequency
must be small compared to the center rotation speed to
ensure that the modulated component of the current at the
fundamental frequency is a significant fraction of the total modulated current. HMV techniques employing stopped or pulsed streams suffer from low modulation frequencies due to the inability to rapidly change the flow rate of the solution through the electrode. Similarly, the modulation frequency of stopped-rotation voltammetry is limited by the inertia and response time of the motor-electrode assembly [2]. Pratt [73] examined the current produced at twice the fundamental vibration frequency of the wire electrode, but its small amplitude precluded its application to analytical determinations, and he modulated the amplitude of the vibration for detection limit studies. Higher modulation frequencies would be desirable for trace voltammetry due to the discrimination against flicker noise at higher frequencies, the easier processing of higher frequency signals, and the ability to employ faster potential scan rates.

**Mixed Modulation Techniques**

In this section several miscellaneous groups of modulation techniques will be described. The first group is comprised of those techniques that combine alternating current voltammetry with some type of forced convection. These methods thus have the advantage of increased flux of the electroactive species to the electrode surface, resulting in a larger ac signal than would be obtained if one relied on diffusion alone. This increase in current,
combined with the fact that the measurements are made under steady state conditions, should provide better detection limits than either single method. It is important to note that the hydrodynamic motion is not modulated in these examples.

In 1977, Bruckenstein and co-workers [77] compared the detection limits obtained at a RDE with conventional dc voltammetry and with phase-selective ac voltammetry. They found that the combination of the ac technique with the RDE was only about five times more sensitive than the dc method, and attributed this lack of a more marked improvement to the fact that the RDE is not greatly affected by the presence of background charging current. However, they concluded that the combined technique would exhibit more of an advantage for differentiating between several species having similar half-wave potentials, or for discriminating against an interfering, kinetically slow process in the presence of a kinetically fast reaction.

That same year, Tokuda and Matsuda [78] developed the theory of ac voltammetry at a RDE for a reversible electrode process, and, in a subsequent paper [79], presented the theory for quasi- and irreversible electrode processes. They considered three types of potential perturbation waveforms - sinusoidal, rectangular, and triangular - superimposed on the dc potential. Using the concept of boundary layers, they described three regimes to explain the
relative importance of convection and ac potential modulation. If the thickness of the diffusion layer due to ac polarization is small in comparison with the convective diffusion boundary layer thickness, the ac perturbation will dominate and the ac currents obtained will be relatively insensitive to convective mass transport. This situation can be realized experimentally by the use of high potential modulation frequencies. The other extreme is the case where the convective diffusion layer is thinner than that due to ac polarization, and the magnitude of the alternating current response is determined by the rotation rate of the RDE. This situation would occur for high rotation speeds or low frequency potential modulation. In the intermediate region, the diffusion layer thicknesses determined by the potential modulation and rotation speed are similar, and this coupling produces a complex effect on the ac response. In their derivations, Tokuda and Matsuda used the case where the ac potential perturbation dominated.

The theory for ac voltammetry at both tubular and channel electrodes was presented for reversible electrode processes by Compton and Sealy [80]. Their theory also assumes that the thickness of the ac diffusion layer is small compared to the hydrodynamic boundary layer. At low potential modulation frequencies, the effect of convection is apparent and the amplitude of the ac response reaches a steady value. A plot of ac current amplitude vs. frequency
is shown in Figure 5, p. 34. No experimental data was presented for sensitivity comparisons.

The second group of mixed modulation techniques takes advantage of the fact that the concentration of an electroactive species is a nonlinear function of applied potential. By analogy with a nonlinear circuit element, the alternating current produced by the imposition of an alternating potential will contain higher harmonics in addition to the fundamental frequency. The amplitudes of successively higher harmonics decrease roughly with the inverse power of the harmonic [81]. Although the amount of current produced at these higher harmonics is smaller than that at the fundamental frequency, the charging current, which behaves linearly, is extremely small [24]. This discrimination against the double layer charging process allows extremely sensitive determinations of reversible species using second harmonic ac voltammetry. Although there have been reports of detecting third and even higher harmonics [81], the decrease in signal makes trace level analysis almost impossible. The voltammogram obtained in a second harmonic experiment has the shape of a derivative of the normal peak-shaped ac voltammogram, or the second derivative of a dc voltammogram. The wave shows two peaks with either a zero crossing or minimum at $E_0'$, depending on whether or not phase-sensitive detection is used.
Figure 5. Amplitude of alternating current vs. modulation frequency. (Taken from reference 80.)
If the applied potential contains signals of two or more frequencies, the nonlinear behavior of the cell will result in the production of sum and difference frequencies [82], just as sidebands are produced by the mixing of two frequencies in other nonlinear devices, equation 1.16:

\[
\left( \sin \omega_1 t \right) \left( \sin \omega_2 t \right) = \frac{\cos(\omega_1 t - \omega_2 t) - \cos(\omega_1 t + \omega_2 t)}{2} \quad (1.16)
\]

Here again the charging process is discriminated against, due to its more linear behavior. The intermodulation voltammogram is similar in shape to that obtained with the second harmonic technique. Note that if the two applied signals in an intermodulation experiment were of the same frequency, and the sum frequency were monitored, the result would be the same as the second harmonic process.

In addition to the enhanced discrimination against charging current, both of these techniques offer the advantage of detection at a higher frequency. In the case of second harmonic ac voltammetry, the frequency of the applied potential perturbation can be higher than those used in simple ac voltammetry due to the lower amount of charging current present in the signal. In addition, detection at the second harmonic is less susceptible to flicker noise. The intermodulation method also allows one to shift the frequency of the detection process. In this case the detection frequency can be either higher, lower, or somewhere in between the input frequencies, depending on the frequencies used and whether the sum or difference frequency
is monitored. This type of frequency shifting has been more commonly used with spectroscopic techniques such as Raman and NMR [83,84], but the basic principles are the same.

The exploitation of nonlinear electrochemical effects for analytical purposes was first reported in 1958 by Bauer and Elving [85]. By blocking the larger fundamental frequency component with tuned filters, they were able to obtain second harmonic ac polarograms, and noted the almost complete absence of charging current in the signal. Smith [86] demonstrated that phase-selective detection could also be used with this method to further reduce the effect of charging current. For further details on either the theory or applications of phase-selective second harmonic ac voltammetry, several monographs by Smith are recommended [22,28]. Neeb reported on a technique he called intermodulation polarography in 1962 [87], and suggested its usefulness for analytical determinations. He later presented the optimal conditions for phase-selective intermodulation ac voltammetry [88].

Because of the similarity of these two techniques, they have been compared in the literature. Early studies [81] demonstrated that although second harmonic and intermodulation voltammograms were identical for a reversible process and yielded comparable detection limits, the instrumentation required for second harmonic voltammetry was less complex. A later study by Bond and co-workers [89]
compared the two phase-selective techniques, and found significantly more charging current associated with the intermodulated signal than the second harmonic. They also pointed out that the instrumentation was more complicated for the intermodulation technique, and recommended the use of second harmonic ac voltammetry.
SCOPE OF RESEARCH

In the previous section we discussed how different modulation techniques could be used to discriminate against the various background currents that interfere in trace voltammetry. Although these methods have met with some success, they are still limited by the presence of residual charging current and the need to employ fairly low modulation frequencies. In this section we will see how the use of microelectrodes with potential and hydrodynamic modulation techniques should address these limitations. In addition, a new technique that combines both potential and hydrodynamic modulation in a single experiment will be discussed.

As the name suggests, microelectrodes are electrodes of extremely small dimension, typically less than 50 μm in diameter. Disk- and cylinder-shaped microelectrodes are used predominately, although other geometries have been employed [90,91]. Aside from the obvious fact that the minuscule size of a microelectrode allows measurements to be made in confining places, the small area of these electrodes results in several unusual features. These unique characteristics of microelectrodes have been discussed by Wightman [7], and therefore only the major points will be mentioned here.
Unlike conventionally-sized electrodes where edge effects are minimal, nonlinear diffusion is the predominant mode of mass transport to a stationary microelectrode [92], due to the fact that the electrode radius is less than $(Dt)^{1/2}$. This enhanced flux of electroactive species due to radial diffusion results in higher current densities and steady-state currents. Time-independent currents allow precise measurements that are unaffected by any variations in the applied potential. A steady-state voltammogram is sigmoidal in shape, with the reverse scan essentially following the initial scan. Of course, the time scale of measurement also determines the type of voltammogram obtained. If the scan rate were increased to a point where diffusion again becomes planar, then the voltammogram obtained at a microelectrode would be the same as that obtained at a larger electrode using normal scan rates.

Another feature of microelectrodes is the fact that the double-layer capacitance is directly proportional to the electrode area. This low capacitance has several important effects on charging current. First, the magnitude of the charging current is smaller for smaller electrodes. The faradaic current also decreases with electrode size, but, because of the enhanced diffusion mentioned above, the ratio of faradaic to charging current is larger at a microelectrode than at a conventionally-sized one. A more important ramification of the low capacitance can be seen
from equation 1.3. The decay time of the charging current is seen to be exponentially dependent on the capacitance. Thus the charging current will decay very rapidly after the application of a potential pulse to a microelectrode. The cell time constant using a microdisk electrode can be calculated from equation 1.17 [15].

\[ R_{cell}C_{dl} = \frac{\pi \rho_s C^0 r_o}{4} + \rho_e L C^0 \]  

(1.17)

\[ \rho_s = \text{solution resistivity} \]
\[ C^0 = \text{double layer capacitance} \]
\[ r_o = \text{radius of microdisk electrode} \]
\[ \rho_e = \text{electrode resistivity} \]
\[ L = \text{total microelectrode length} \]

For typical values (\( r_o = 12.5 \mu m \), \( C^0 = 40 \mu f/cm^2 \), \( \rho_s = 2.8 \) ohm-cm, \( L = 1 \text{ cm} \), \( \rho_e = 10^{-5} \) ohm-cm), the time constant of a cell using a platinum microdisk electrode 25 \( \mu m \) in diameter is 0.11 \( \mu s \). The value of the second term in equation 1.17 is less than 1 \( ns \), indicating that the internal resistance of the microelectrode does not contribute significantly to the time constant of the cell.

One of the disadvantages of microelectrodes is the much smaller currents to be measured. When microelectrodes are used for trace voltammetry this current becomes extremely minute. Although modern electronics has advanced to the point where the measurement of nanoamp or even picoamp currents is possible with care, the detection of small dc
currents is not yet trivial. Extremely small alternating current signals are much more easily detected using a lock-in amplifier (LIA). Therefore, the LIA was chosen to monitor the small alternating currents produced by microelectrodes when they are employed for modulation voltammetry. The specific advantages of using solid microelectrodes with various modulation techniques are discussed below.

When microdisk electrodes are used in conjunction with square wave alternating current voltammetry several advantages will arise. As mentioned above, the small diameter of the electrode results in a cell time constant of a few µs, leading to a rapid decay of the charging current after a potential pulse. It will be shown that these sharp charging current spikes can be effectively eliminated from the current signal by a simple electronic switch, with minimal effect on the faradaic response. The fast charging current decay will also permit the use of high modulation frequencies and fast voltammetric scan rates. The current generated by a simple square wave potential like that originally used by Barker will then be demodulated by a lock-in amplifier to provide high sensitivity voltammetric analysis. The LIA is an excellent device for extracting the small current signals inherent to trace analysis with microelectrodes, and its exceptional signal to noise characteristics allow effective discrimination of the
analytical signal from the significant background currents associated with solid electrodes. Finally, it will be shown that the solid microelectrodes permit access to a wider potential range than the mercury electrodes generally used in pulse voltammetry.

It will also be demonstrated that the unique features of microelectrodes also offer advantages when they are used with hydrodynamic modulation voltammetry. In this case, consider a microcylinder electrode vibrating perpendicular to its axis. The small diameter of the microelectrode will result in a low Reynolds number even when the electrode is vibrated at relatively high velocities. The result is a more laminar flow pattern of the solution around the electrode and an instantaneous current that tracks the electrode velocity. Efficient modulation can thus be carried out at much higher frequencies than those previously employed in HMV, allowing better discrimination against flicker noise, faster voltammetric scan rates, and easier signal processing. Another advantage is that the modulation apparatus used here is simple due to the low mass of the electrode. A final advantage, and one that is true of microelectrodes in general, is that the amount of sample consumed will be small, permitting the analysis of samples of small volume or low concentration.

It should also be pointed out that although the cross-sectional area, and hence the current, is increased at a
microcylinder electrode compared to a microdisk electrode, the cell time constant is still quite small since it depends on electrode radius rather than area. Using equation 1.18 [9], the time constant of a 25 μm diameter platinum wire that is 3 mm in length is calculated to be about 1 μs.

\[
R_{cellCdl} = \frac{2 \rho_e L c_0 h}{r_o} + c_0 \rho_s r_o \ln \left( \frac{r_1}{r_o} \right) \quad (1.18)
\]

\( h \) = length of electrode exposed to solution

\( r_1 \) = radius of auxiliary electrode

Although this time constant is approximately ten times longer than that for a microdisk electrode of the same diameter, it is still faster than the risetime of the electronics used to measure the current, and the electrode area has been increased by a factor of almost 500.

We have just seen how the unique characteristics of microelectrodes should offer many new advantages when they are combined with either a potential modulation technique to discriminate against charging current or a hydrodynamic modulation technique to discriminate against background surface currents. An obvious next step would be to discriminate against both types of background current simultaneously by performing a double modulation experiment. When both the applied potential and the electrode motion are modulated, it will be shown that the resultant current contains contributions from both. For example, consider a microwire electrode that is vibrating sinusoidally at some
frequency. If the applied potential is also modulated in a sinusoidal manner at some lower frequency, the current obtained will be an amplitude-modulated sine wave. This is the same phenomenon that is exploited in AM radio. That is, the higher frequency current arising from the hydrodynamic modulation is the "carrier", whose amplitude is modulated by the applied potential.

It will be shown in the theory section by Fourier analysis that, in addition to the individual fundamental frequencies and their harmonics, several new frequency components are present in this wave, which differ from the carrier by plus and minus the modulating frequency. In AM radio, these new frequencies are called sidebands, but we will refer to them as sum (beat) and difference (heterodyne) frequencies. It is important to understand that these new components have only appeared because the electrochemical cell is a nonlinear device. Simply adding two waves of a different frequencies does not of itself produce these new sum and difference frequencies [93].

At first glance, this double modulation experiment may not seem to differ much from the intermodulation experiment discussed earlier. However, there are several key differences. In the case of intermodulation, the two modulating signals both perturb the applied potential. Because a small amount of charging current is present in each of the resultant fundamental current signals, charging
current is also present in the sum and difference frequency signals, although its effect has been diminished by the fact that it is more linear than the faradaic process. In addition, there is no discrimination against the current arising from background surface processes. Experimentally, the double modulation process more closely resembles the other mixed modulation techniques discussed earlier, those where ac voltammetry was performed on an electrode undergoing forced convection. In this later case, however, the hydrodynamic motion is not modulated and therefore sum and difference frequencies will not be present. In the double modulation experiment the applied potential is modulated for discrimination against charging current and the hydrodynamic motion is modulated for discrimination against background surface processes. The sum and difference frequencies that result from this double modulation are therefore free from both types of background current. By demodulating only these frequency components of the current, very sensitive voltammetric analyses are obtained.

In conclusion, the aim of this work was to improve the detection limits at solid electrodes by exploiting the advantages of microelectrodes when used in conjunction with modulation techniques. This work is divided into three major parts. The first portion will demonstrate how the fast RC time constant of a microdisk electrode can be used
to essentially eliminate charging current in square wave alternating current voltammetry. The second portion will show how the small diameter of a vibrating microwire electrode allows the use of high modulation frequencies in hydrodynamic modulation voltammetry. Finally, these two techniques will be combined in a double modulation experiment. This is the first time that two independent parameters have been modulated in voltammetry and their sum and/or difference frequency monitored.
CHAPTER II

THEORY

Square Wave Voltammetry

Waveforms illustrating the square wave voltammetric approach taken here are shown in Figure 6, p. 48, for the oxidation of ferrocene. Trace a is the applied potential, which consists of a symmetric square wave, as originally used by Barker. The average potential is constant. Trace b is the current/time response for a background electrolyte solution, showing only the rapid charging current transient for a small electrode. Curve c is the background response after the initial 70 \(\mu\)s of the current transient of each half cycle is removed by an electronic switch. Curve d is the current/time waveform with ferrocene present and a potential modulation centered at \(E_{1/2}\), and curve e is the same waveform with the switch present. When the waveform shown in e is monitored by a lock-in amplifier, the LIA averages the current waveform after inverting every other half cycle. Since the RC constant for the cell is a few \(\mu\)s and the square wave modulation period is typically a few ms, very little of the current/time waveform need be rejected to
Figure 6. Waveforms for the oxidation of 1 mM ferrocene at a 125 μm diameter electrode in 0.1 M TBAP in acetonitrile. Curve a is the applied potential with ordinate being \( E_{\text{app}} - E_{1/2} \). Curves b and c are current vs. time waveforms for a blank solution, with c including the electronic switch described in the text. The nonuniform heights of the charging current transients in trace b are artifacts of the digital oscilloscope used for data acquisition. The spikes are of equal height at constant dc potential. Curves d and e are current vs. time waveforms for ferrocene, with e including the switch. Square wave amplitude was 60 mV, frequency was 300 Hz.
Figure 6
eliminate the charging current completely.

The theoretical current/time response for a symmetric square wave potential modulation with fixed dc potential may be calculated from a modified form the general equation of Rifkin and Evans [94]. For the case of sudden imposition of a symmetric square wave potential on a solution containing only a reduced form, the \( t \) and \( \tau \) variables in the Rifkin and Evans expression may be stated in terms of the square wave frequency \( f_e \):

\[
t = \frac{(m + \delta - 1)}{2f_e}
\]

\[
\tau = \frac{(j - 1)}{2f_e}
\]

where \( m \) and \( j \) are integers and \( \delta \) is the time into the \((m-1)\)th half cycle, in units of \(1/2f_e\), where the current is measured. Given these definitions, the current is given by equations 2.3 - 2.6,

\[
i_{m-1} = n\text{FACR} \left( \frac{2D_Rf_e}{\pi} \right)^{1/2} \sum_{j=1}^{m} \frac{\Delta \Psi_j}{(m - j + \delta)^{1/2}}
\]

\[
\Delta \Psi_j = \frac{\Theta_j - 1}{\Theta_j - 1 + \gamma} - \frac{\Theta_j}{\Theta_j + \gamma}
\]

\[
\Theta_j = \begin{cases} 
\exp \left[ \frac{nF}{RT} \left( E_{dc} + \frac{\Delta E}{2} \right) \right] & \text{for odd } j \\
\exp \left[ \frac{nF}{RT} \left( E_{dc} - \frac{\Delta E}{2} \right) \right] & \text{for even } j
\end{cases}
\]

normalized current \( i_N = \frac{i}{n\text{FACR} \left( \frac{\pi}{2D_Rf_e} \right)^{1/2}} \)

where \( \Delta E \) is the square wave amplitude, \( \Theta_0 = 0 \), and \( \gamma = \)
\((D_R/D_O)^{1/2}\). The waveform calculated from equation 2.1 is shown in Figure 7, p. 52, and the calculated currents at the end of each half cycle are given in Table 2, p. 53. The computer programs used to calculate the theoretical current waveform and the values in Table 2 can be found in Appendix A. Although the current for the forward half cycle approaches a constant value slowly, the difference between the current at the end of the forward and reverse half cycles reaches a steady state very quickly. This difference current changes by 0.6% from the 5th to the 50th cycle, indicating that a steady state is reached to within less than 1% in five cycles after a change in dc potential. The LIA may be modeled mathematically by inverting every other half cycle and integrating the resulting waveform. The ac input coupling on the LIA removes any dc nonmodulated components in the waveform, so the LIA output is proportional to the average current after the reducing half cycle has been inverted. This average ac current is also given in Table 2, p. 53, demonstrating that the modulated current also reaches the steady state in a few cycles after a dc potential change. This derivation assumes planar diffusion, a condition not generally met for small electrodes [7,8]. However, on the ms time scale of the modulated potential, diffusion will be essentially planar and the difference current will be affected very slightly by nonplanar diffusion.
Figure 7. Theoretical current vs. time profile for a square wave potential imposed at $t = 0$, with $\Delta E = 60$ mV and $E_{dc} = E_{1/2}$. Normalized current is defined in the text.
<table>
<thead>
<tr>
<th>Cycle Number</th>
<th>Normalized Currenta</th>
<th>Normalized Difference Currentb</th>
<th>Normalized Average AC Currentc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7626</td>
<td>0.9166</td>
<td>1.8339</td>
</tr>
<tr>
<td>2</td>
<td>0.4572</td>
<td>0.6518</td>
<td>1.3755</td>
</tr>
<tr>
<td>3</td>
<td>0.4295</td>
<td>0.6445</td>
<td>1.3661</td>
</tr>
<tr>
<td>4</td>
<td>0.4136</td>
<td>0.6414</td>
<td>1.3624</td>
</tr>
<tr>
<td>5</td>
<td>0.4030</td>
<td>0.6398</td>
<td>1.3606</td>
</tr>
<tr>
<td>10</td>
<td>0.3773</td>
<td>0.6371</td>
<td>1.3577</td>
</tr>
<tr>
<td>15</td>
<td>0.3662</td>
<td>0.6365</td>
<td>1.3570</td>
</tr>
<tr>
<td>50</td>
<td>0.3442</td>
<td>0.6358</td>
<td>1.3563</td>
</tr>
</tbody>
</table>

a Defined by equation 2.6 at the end of each forward cycle.

b Current at end of forward half cycle less the current at the end of reverse half cycle.

c Determined by numerical integration of current waveforms, with every other half cycle inverted to mimic a LIA.
If an electronic switch is placed between the current amplifier and the LIA, the rapid charging current decay associated with each potential change is eliminated before demodulation. The effect of such a switch may be predicted theoretically by zeroing the appropriate current values from Figure 6, waveform e before integrating. The effect of the current switch on the average ac current is shown in Table 3, p. 55. The computer programs used to calculate the effect of the switch can again be found in Appendix A. Due to the rapid decay of charging current, a switch lasting the length of many cell time constants will have a minor effect on the faradaic current. For example, a 50 μm diameter electrode in 1 M KCl has a time constant of less than 1 μs [15]. For a 200 Hz square wave, a 10 μs switch would remove less than 2% of the faradaic ac current while eliminating 99.99% of the charging current. Once the switch duration becomes longer than approximately 10 cell time constants, further increases will yield negligible improvement in charging current rejection, but will significantly decrease the faradaic response.

The theoretical peak height and width depend on ΔE and frequency in a manner similar to that of sinusoidal ac polarography [22] and staircase square-wave voltammetry [46]. The peak height is linear with \( f^{1/2} \) and ΔE for short switch duration and small ΔE. For large ΔE (> 50 mV), the peak height is nonlinear and the peak width broadens, as
TABLE 3
Theoretical Effect of Current Switch on LIA Output

<table>
<thead>
<tr>
<th>Switch Length(^a)</th>
<th>Average AC Current(^b)</th>
<th>(i_s/i_o)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.357</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>1.256</td>
<td>0.926</td>
</tr>
<tr>
<td>4</td>
<td>1.166</td>
<td>0.859</td>
</tr>
<tr>
<td>10</td>
<td>0.9803</td>
<td>0.722</td>
</tr>
<tr>
<td>14</td>
<td>0.8899</td>
<td>0.656</td>
</tr>
<tr>
<td>20</td>
<td>0.7790</td>
<td>0.574</td>
</tr>
<tr>
<td>30</td>
<td>0.6319</td>
<td>0.466</td>
</tr>
<tr>
<td>50</td>
<td>0.4077</td>
<td>0.300</td>
</tr>
</tbody>
</table>

\(^a\) Expressed as % of half cycle.

\(^b\) 15th cycle, for \(\Delta E = 60\ mV, E_{dc} = E_1/2\).

\(^c\) Ratio of average ac current with the switch present to that without.
shown in Table 4, p. 57. The effect of switch duration on frequency dependence is discussed in a later chapter.
## TABLE 4

Theoretical Effect of $\Delta E$ on Peak Height and Width

<table>
<thead>
<tr>
<th>$\Delta E$ (mV)</th>
<th>Normalized Average AC Current</th>
<th>Peak Width at Half Height (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0.0251$</td>
<td>90.58</td>
</tr>
<tr>
<td>10</td>
<td>$0.2505$</td>
<td>90.92</td>
</tr>
<tr>
<td>20</td>
<td>$0.4963$</td>
<td>91.96</td>
</tr>
<tr>
<td>40</td>
<td>$0.9573$</td>
<td>96.06</td>
</tr>
<tr>
<td>50</td>
<td>$1.166$</td>
<td>99.10</td>
</tr>
<tr>
<td>60</td>
<td>$1.357$</td>
<td>102.78</td>
</tr>
<tr>
<td>80</td>
<td>$1.683$</td>
<td>112.00</td>
</tr>
<tr>
<td>100</td>
<td>$1.937$</td>
<td>123.46</td>
</tr>
</tbody>
</table>
Hydrodynamic Modulation Voltammetry

As mentioned in the previous chapter, a vibrating microcylinder electrode permits the use of higher modulation frequencies and lower sample volumes than are possible with rotating disk, tubular, or conventional wire electrodes, but has the consequence of less well-defined hydrodynamics. The fact that the hydrodynamics are complex, and therefore not amenable to accurate theories, necessitates an empirical formulation of the hydrodynamic current, as will be discussed below. This formulation assumes that the mass transfer is at a steady state even though the velocity of the electrode is being modulated and that the microcylinder electrode can be treated as a stationary body with a constant flow of solution around it.

Consider the general equation for faradaic current for a reduction, equation 2.7, based on the generalized mass transport parameter, \( m_o \) [58].

\[
\frac{1}{nFA} = m_o \left( C_o^* - C_{ox}^* \right)
\]  

(2.7)

For the steady-state condition existing in a convective system, \( m_o \) is a constant dependent on the particular convective arrangement, and has been determined analytically for certain well-behaved systems like the RDE [58]. For the case of a microcylinder electrode vibrating perpendicular to its axis, it will be demonstrated empirically that the current, and therefore \( m_o \), are monotonic functions of the
electrode velocity through the solution. Although the hydrodynamics of a cylinder moving through a fluid are complex, and analytical solutions are not available, an approximate relationship for the dependence of \( m_0 \) on time can be deduced by assuming that \( m_0 \) is proportional to the electrode velocity raised to some power \( x \). For an electrode oscillating at some frequency \( f_h \), the position can be given by equation 2.8, where \( A_m \) is a constant (which will include a function of the diffusion coefficient) and \( t \) is time.

\[
\text{Position} = A_m \sin(2\pi f_h t) \tag{2.8}
\]

The scalar velocity, which is the absolute value of the waveform driving the vibrator, after a 90° phase shift, is then given by equation 2.9.

\[
\text{Velocity} = 2\pi f_h \left| \cos(2\pi f_h t) \right| x \tag{2.9}
\]

The phase terms in these expressions have been ignored for the sake of simplicity.

If one assumes the simplest model of a solution moving past the electrode at some fixed velocity, then the instantaneous current will track the scalar velocity. This relationship between electrode position, velocity, and current is depicted schematically in Figure 8, p. 60. The current waveform appears to be a full-wave-rectified function of the electrode velocity due to its indifference to the "sign" of the velocity. Note that this results in the fundamental frequency of the current waveform being twice that of the waveform driving the vibrator. The
Figure 8. Theoretical position, velocity, and current vs. time waveforms for a microcylinder electrode vibrating at 80 Hz. The absolute magnitude of the current depends upon the size and diameter of the microcylinder electrode used.
magnitude of the current is smallest at the extremes of the electrode excursion, where the instantaneous velocity is lowest, and greatest near the mean position.

In real systems, the current does not decrease to zero when the electrode velocity equals zero, and the modulation efficiency is not generally 100%. The mass transport parameter, \( m_0 \), is thus more accurately represented by equation 2.10.

\[
m_0 = m_{ss} + M m_{ss} \left| \cos(2\pi f_h t) \right|^x
\]  

(2.10)

\( m_{ss} \) = steady state, dc mass transport coefficient
\( M \) is the modulation efficiency and may range from 0 to 1 or more, but for the vibrating microcylinder electrode used here, \( M \) has a value between 0.25 and 0.95 (electrode diameter 100 - 25 \( \mu \)m).

At a mass transport-limited potential, the current waveform will have the shape predicted by equations 2.7 and 2.10, with \( C_{ox} = 0 \). By fitting the experimental data to equation 2.9, the power \( x \) was found to be 0.7, and equation 2.11 was found to be a reasonable approximation of the hydrodynamic current, despite the complexity of the hydrodynamic situation.

\[
i_h = n F A m_{ss} + n F A M m_{ss} \left| \cos(2\pi f_h t) \right|^{0.7}
\]  

(2.11)

The alternating current waveform calculated from equation 2.11 is shown in Figure 9, p. 62, for a diffusion-limited potential.
Figure 9. Theoretical current vs. time waveform for a microcylinder electrode vibrating at 80 Hz. $M = 0.95$ and $m_{ss} = 1$. 
Double Modulation Voltammetry

The double modulation experiment may be pictured qualitatively as shown in Figure 10, p. 64, which depicts concentration vs. distance profiles based on the Nernst diffusion layer model. The curves in Figure 10a correspond to different electrode velocities, resulting in different boundary layer thicknesses. The higher velocity corresponds to a steeper concentration gradient, and hence a larger current. As the velocity is modulated, the depth of the concentration gradient is also modulated and an alternating current results. In Figure 10b, the electrode velocity is held constant but the surface concentration is altered by varying the potential. At low potential modulation frequencies the Nernst model remains valid and the concentration gradient will vary with applied potential. An alternating current at the frequency of the potential modulation is produced. When both the electrode velocity and the applied potential are varied in a double-modulation experiment, the complex effects on the concentration gradients and resulting current may be demodulated to provide useful analytical information.

Consider first, however, the case of steady-state mass transport without hydrodynamic modulation (i.e. constant forced convection). The potential dependence of the current for a reversible system is easily calculated by assuming that the surface concentration of the oxidized
Figure 10. Concentration vs. distance profiles based on the Nernst diffusion layer model. A: Profile obtained at two different electrode velocities, $U_1 > U_2$. B: Profile obtained at constant electrode velocity but different applied potentials, $E_1 > E_2$ for reduction.
species is driven by the applied potential via the Nernst equation. If the potential is then modulated sinusoidally, the resulting current waveform would be similar to that obtained for ac voltammetry, except that the mass transport is at a convective steady state rather than solely diffusion-controlled. This current is given by equation 2.12, and plotted in Figure 11, p. 66.

\[ i_e = nFAM_0C^* \left( \frac{1}{1+6} \right) \]  

(2.12)

where \( \theta = \exp \left[ \frac{nF}{RT} (E_{dc} - E^0 + \frac{E}{2PP} \sin(2\pi f_e t)) \right] \)  

(2.13)

Now consider a vibrating microcylinder electrode whose current is governed by equations 2.7 and 2.10. If the potential is varied slowly relative to \( f_h \), the current will vary predictably as \( C_{ox}^* \) is altered by the applied potential. In the limit of low \( f_e \), one is merely scanning the potential sinusoidally and the result is a hydrodynamically-modulated current whose magnitude is determined by the applied potential. The situation can be described mathematically by substituting equation 2.10 into equation 2.12, to produce equation 2.14.

\[ i_{total} = nFAC_{ox}^* \left( \frac{1}{1+\theta} \right) \left[ m_{SS} + Mm_{SS} \cos(2\pi f_h t) \right] \]  

(2.14)

The theoretical raw current waveform calculated from equation 2.14 is shown in Figure 12, p. 67, for \( f_e = 13 \) Hz and \( f_h = 160 \) Hz. As will be shown experimentally, equation 2.14 is valid on a quantitative basis provided \( f_e \) is
Figure 11. Theoretical current vs. time waveform for an electrode undergoing constant forced convection and sinusoidal potential modulation. $f_e = 13$ Hz, $\Delta E = 60$ mV, $E_{dc} = E_{1/2}$, and $m_0 = 1$. 
Figure 12. Theoretical current vs. time waveform for an electrode undergoing both potential modulation and hydrodynamic modulation. \( f_h = 160 \, \text{Hz}, \, f_e = 13 \, \text{Hz}, \) \( \Delta E = 60 \, \text{mV}, \, E_{dc} = E_{1/2}, \, M = 0.95, \) and \( m_{bb} = 1. \)
significantly lower than $f_h$. As was discussed earlier, the behavior of the ac current depends on the relative thicknesses of the diffusion layer due to the applied potential and the hydrodynamic boundary layer. When the hydrodynamic boundary layer is thin relative to that which would be produced by the ac potential perturbation, the current is independent of $f_e$. At the other extreme of high $f_e$, the ac diffusion layer is thin relative to the hydrodynamic layer, and the hydrodynamic motion has little effect on the waveform. In this limit of high $f_e$, $i_e$ varies with the square root of $f_e$. In all cases examined here, the low $f_e$ limit is assumed, and it will later be demonstrated that equation 2.14 is valid.

For the case where $f_e \ll f_h$, equation 2.14 describes an amplitude-modulated waveform of fundamental frequency $2f_h$, with the amplitude modulated at frequency $f_e$. It is possible to demodulate the raw current by successive synchronous detection first at $2f_h$, and then at $f_e$. Alternatively, it may be noted that equation 2.14 is the product of two sinusoidal functions, and both the hydrodynamic and potential modulation factors may be expressed as Fourier summations of the fundamental and harmonic terms. Equations 2.15 and 2.16 contain the first three terms of the Fourier series for potential and hydrodynamic modulation, respectively. The fundamental for the hydrodynamic term equals $2f_h$, as noted earlier.
\[
\left(1 + \theta \right) = A_0 + A_1 \cos 2\pi f_e + A_2 \cos 2\pi (2f_e) + \ldots
\]  
(2.15)

\[
\frac{m_o}{m_{ss}} = B_0 + B_1 \cos 2\pi (2f_h) + B_2 \cos 2\pi (4f_h) + \ldots
\]  
(2.16)

Equation 2.17 then results from substitution of the first two terms of each Fourier series into equation 2.14, and subsequent rearrangement and trigonometric substitution. Note that the resulting product contains terms for the fundamental frequencies of each modulation mode, and the sum and difference frequencies, \(2f_h \pm f_e\).

\[
\frac{i}{nFAC_{ox}m_{ss}} = A_0 B_0 + A_1 B_0 \cos (2\pi f_e) + A_0 B_1 \cos 2\pi (2f_h) + \frac{A_1 B_1 \sin [2\pi (2f_h + f_e)]}{2} + \frac{A_1 B_1 \sin [2\pi (2f_h - f_e)]}{2} + \ldots
\]  
(2.17)

If more terms were included in equations 2.15 and 2.16, then higher order terms such as \(2f_e + 2f_h\), \(f_e + 4f_h\), etc. would be predicted in the raw current waveform of equation 2.17.

From an analytical standpoint, it is important to note that the capacitive and surface background processes will not have hydrodynamically-modulated components, i.e. \(B_1\), \(B_2\), etc. in the above equations would be zero for a blank solution that contains no freely-diffusing analyte. Thus the terms at \(2f_h + f_e\) and \(2f_h - f_e\) will not contain contributions from either charging current or current arising from surface redox processes such as oxide formation. This fact is the basis for background rejection using the double modulation approach.
Figure 13, pp. 71-74 are plots of magnitude vs. frequency determined from the Fourier transforms of the waveforms shown in Figures 9, 11, 12. Figure 13A, p. 72, is for the pure hydrodynamic current, and shows the fundamental and second harmonic of the hydrodynamic fundamental. (Recall that the fundamental hydrodynamic frequency is $2f_h$, twice the vibrator frequency.) Figure 13B, p. 73, shows the fundamental and harmonics of the potential modulation, with the harmonics resulting from the distortion of the pure sinusoidal potential waveform embodied in equation 2.12. The Fourier transform of the double-modulated current shown in Figure 12 is given in Figure 13C, p. 74, and includes the fundamental frequencies of each individual modulation, plus the sum and difference frequencies predicted by equation 2.17. While a variety of combinations of the two frequencies are evident in the theoretical frequency spectrum, only the two fundamentals and the sum and difference frequencies are useful analytically, since the other components are small and provide no new information.

The raw waveform may be determined as a function of potential by varying $E_{dc}$. After carrying out the Fourier transforms on these raw waveforms, the dependence of each frequency component on $E_{dc}$ may be predicted, with the results shown in Figure 14, p. 75. Trace a is the magnitude of the $f_h$ component, and has the shape of a classical hydrodynamic voltammogram since it contains no ac potential.
Figure 13. Fourier transforms of theoretical current waveforms. A). Fourier transform of potential modulation waveform, $f_e = 13$ Hz. B). Fourier transform of hydrodynamic modulation waveform, $f_h = 160$ Hz. C). Fourier transform of double modulation waveform, $f_e = 13$ Hz, $f_h = 160$ Hz.
Figure 13A.
Figure 13B
Figure 13C.
Figure 14. Dependence of each frequency component on $E_{dc}$: a) $f_h$ component, b) $f_e$ component, and c) $f_h + f_e$ component. Calculated from equation 2.14 with $f_e = 13$ Hz, $f_h = 160$ Hz, $\Delta E = 60$ mV, and $E_{dc} = E_{1/2}$. Scale = 0.4 arbitrary units for trace a and 0.2 arbitrary units for traces b and c.
perturbation. This component results from the hydrodynamic modulation of the dc potential, embodied in the third term on the right side of equation 2.17. Trace b is at the potential modulation fundamental, and has the shape of a classical ac voltammogram. It results from the potential modulation of the dc term of the hydrodynamic waveform, given by the second term of equation 2.17. It is qualitatively equivalent to modulating the potential of a steady-state hydrodynamic system such as the RDE at a constant rotation speed.

Trace c in Figure 14 results from either the $2f_h + f_e$ or $2f_h - f_e$ frequency component, and should combine several features of both modulation techniques. First, the double-modulated voltammogram (DMV) has the appearance of a peak-shaped ac voltammogram rather than the sigmoidal shape of a conventional hydrodynamic voltammogram, improving resolution and background correction. Second, since the hydrodynamically-modulated current results only from freely-diffusing material, the DMV peak should have a greatly reduced background from capacitance and background surface processes. For background currents that are not mass transport-controlled, the second term on the right side of equation 2.14, and therefore $B_1, B_2, \ldots$, will be zero and the $2f_h + f_e$ components will be negligible. Thus one is able to observe ac voltammograms with a great reduction of background signal, a feature of clear importance when using
solid electrodes.

Figure 15, p. 78, shows several DMV voltammograms calculated for different values of $\Delta E$, demonstrating the predictable increase in peak width as the potential modulation amplitude is increased. As with other potential modulation techniques [22,46], the peak width is a weak function of $\Delta E$ when $\Delta E$ is less than about 50 mV. Figure 16, p. 80, shows several theoretical plots of the demodulated currents as functions of $\Delta E$. As expected, the purely hydrodynamic current is independent of $\Delta E$, since it is a function of only $E_{dc}$. The magnitude of the ac currents at $f_e$ and $2f_h + f_e$ increase linearly at small $\Delta E$, and then exhibit negative curvature when $\Delta E$ is greater than approximately 50 mV.

The assumptions which were used to derive equation 2.17 are significant, but may be met with proper experimental design. The semi-empirical expression for the hydrodynamic current (equation 2.11) is validated by a close fit to experimentally-observed current waveforms. It was also assumed that the potential is varied slowly relative to $f_h$, i.e. that the hydrodynamic boundary layer is thin relative to that for the potential perturbation. For a microcylinder electrode vibrated at 80 Hz, the average hydrodynamic boundary layer is about 3 $\mu$m thick, whereas that for one period of a 3 Hz potential modulation is 20 $\mu$m. For the parameters used here, it is valid to assume that the limit
Figure 15. Theoretical voltammograms for various values of $\Delta E$. $f_e = 13$ Hz, $f_h = 160$ Hz, and $E_{dc} = E_1/2$. Curves a-h are for $\Delta E = 10, 20, 30, 40, 50, 60, 80,$ and $100$ mV, respectively. Scale = 0.1 arbitrary units.
Figure 15.
Figure 16. Dependence of each frequency component on $\Delta E$. a) $f_e$, b) $f_h$, and c) $f_h \pm f_e$. 
of low \( f_e \) applies. Support for this conclusion is provided by the experimentally-observed independence of the current at \( 2f_h + f_e \) with variations in \( f_e \) at low \( f_e \). In physical terms, this means that the hydrodynamic concentration profile is adjusting rapidly to changes in potential.

The alternative approach to monitoring sum and difference frequencies is to note (as pointed out earlier) that equation 2.17 represents an amplitude-modulated waveform with a carrier frequency of \( 2f_h \). If the raw double-modulated waveform is demodulated at \( 2f_h \) with a lock-in amplifier, the output will be a slightly distorted sine wave with frequency \( f_e \). If this signal is again demodulated with a LIA, a dc signal proportional to the double-modulated current will result. The term from the Fourier expansion relevant to this approach is \( A_1B_1(\cos 2\pi f_e)(\cos 2\pi 2f_h) \), so the expected double-demodulated signal will be proportional to \( A_1B_1 \). This response will have the same qualitative appearance as the double-modulated voltammogram of Figure 14. It may be viewed as a potential perturbation imposed on a hydrodynamically-modulated voltammogram. Detection of this component by either by sequential demodulation or by single demodulation at \( 2f_h + f_e \) provides similar information, but it will be shown that the sequential approach performs better experimentally.
CHAPTER III

EXPERIMENTAL

Electronic Apparatus

1. Square Wave Voltammetry

A schematic diagram of the apparatus is shown in Figure 17, p. 83. A three-electrode potentiostat based on a summing amplifier was constructed and used to control the potential, and the current from the platinum microdisk electrode was amplified by a Keithley model 427 current amplifier with a gain of $10^4$ to $10^7$ V/A. A square wave from a function generator was summed with a ramp to produce the required waveform, with the square-wave amplitude and slope rate adjusted as desired. The current amplifier output was passed to a PARC 186A lock-in amplifier via an electronic switch driven by the square wave. The switch was constructed to operate in the following manner: The exclusive OR gate caused the monostable multivibrator to pulse on both the rising and falling transitions of the square wave. The monostable output drove a bipolar CMOS switch which open circuited the current signal during the active phase of the monostable. Thus the capacitive current
Figure 17. Schematic diagram for square wave voltammetry apparatus.
signal occurring on square wave transitions was prevented from reaching the LIA and did not contribute to the demodulated signal. The period of the monostable was adjustable over a 1-100 μs range. For most experiments, the LIA output was recorded on a strip-chart or X-Y recorder. Experiments carried out on a fast time scale were recorded with a Textronix 7854 digital scope interfaced to an Apple II+ microcomputer. The current sensitivity of the measurement circuit was calibrated with precision resistors and voltage source. Conventional differential pulse voltammograms were carried out with a PARC 174 pulse polarograph.

The risetime of the cell and electronics was determined by a square wave potential perturbation applied to a cell containing background electrolyte (TBAP in acetonitrile). The current response showed a 20 μs risetime followed by an RC decay with a 4 μs time constant. Similar experiments on fast dummy cells demonstrated that the response characteristics were those of the current amplifier rather than the cell. Measurements of the cell RC with faster, less sensitive current amplifiers indicated a cell time constant of less than 3 μs with a 25 μm diameter electrode.

2. Hydrodynamic Modulation Voltammetry

The experimental apparatus used is shown in Figure 18, p. 85. The vibration apparatus consisted of a PM mini-shaker type 4810 vibration exciter (Bruel & Kjaer
Figure 18. Experimental arrangement for hydrodynamic modulation voltammetry.
Instruments, Marlborough, MA) driven by a 4 V p-p sine wave produced after amplification from a function generator. The vibrator was subject to a mechanical resonance at about 50 Hz which disturbed the observed current, and this frequency was avoided. The platinum microcylinder electrode was held vertically and vibrated perpendicular to its axis. A conventional three-electrode potentiostat based on a summing amplifier was used to control the potential, and the current from the microcylinder electrode was amplified by a Keithley Model 427 current amplifier with a gain of $10^4$-$10^7$ V/A. The current amplifier was operated with a rise time of 0.01 ms. The output from the current amplifier was demodulated by a PARC 186A lock-in amplifier, operated in the 2f mode, at a phase angle of 90° relative to the function generator driving the vibrator. The LIA output (output time constant = 0.1 s) was recorded on an X-Y recorder. Raw current waveforms were recorded with a Textronix 7854 digital scope interfaced to an Apple II+ microcomputer.

The amplitude of the vibrating microcylinder electrode was determined with a model FC-14 optical comparator (Jones and Lamson, Springfield, VT). The average velocity was then obtained by multiplying the vibration frequency by twice the peak-to-peak amplitude. Table 5, p. 87, gives the measured amplitudes and calculated velocities of a 25 μm diameter platinum microcylinder electrode vibrating at several frequencies.
Table 5
Amplitude and Velocity of a Vibrating Microcylinder Electrode

<table>
<thead>
<tr>
<th>Vibration Frequency (Hz)</th>
<th>Peak-to-Peak Amplitude (mm)</th>
<th>Average Electrode Velocity (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.8128</td>
<td>4.877</td>
</tr>
<tr>
<td>40</td>
<td>0.8128</td>
<td>6.502</td>
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<tr>
<td>60</td>
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<td>110</td>
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<td>130</td>
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</tr>
<tr>
<td>150</td>
<td>0.5207</td>
<td>15.621</td>
</tr>
</tbody>
</table>
3. Double Modulation Voltammetry

As mentioned in the previous chapter, there are two ways to detect the double modulated current signal. The first way is to monitor the sum frequency directly, as shown schematically in Figure 19, p. 89. This method requires the use of a triple function generator to produce the two sinusoidal input modulation waveforms used for the potential modulation and hydrodynamic modulation, as well as the reference frequency for the LIA. The triple function generator used here was designed and constructed by the OSU electronic shop, and a schematic diagram of the apparatus is given in Appendix B. Basically, the function generator works in the following manner: A master clock is used to produce the four signals needed - \( f_e \), \( f_v \), \( 2f_v = h \), and \( f_e + f_h \). Remember that the frequency of the hydrodynamic current, \( f_h \), is twice that used to drive the vibration apparatus, \( f_v \). At this point the frequencies of the waveforms are 100 times higher than they will be at the output of the function generator, due to the fact that it is easier to mix two frequencies and obtain their sum at higher frequencies. The waveforms are all square waves at this point and their phases are locked. After the waveforms have been divided by 100, the appropriate waveforms are then shaped into sine waves. The frequency of the waveform used to drive the potential was variable from 1 to 999 Hz, while that used to drive the vibrator could be varied from 1 to
Figure 19. Schematic diagram of the double modulation apparatus used to detect the sum frequency.
500 Hz.

The other apparatus used in this first detection scheme was identical to that used in the individual modulation experiments. The working electrode was a platinum microcylinder electrode. The LIA was operated at a phase of 105° relative to the reference sum frequency produced by the triple function generator. The output time constant of the LIA was varied from 0.01 s to 0.1 s, depending on the amount of suppression desired to remove the oscillation present in the output signal.

The second method used to detect the double-modulated signal employed two LIAs and is depicted schematically in Figure 20, p. 91. In this technique, the signals used to perform the potential and hydrodynamic modulation were provided by two individual function generators, which also provided the respective reference signals to the LIAs. The current was first demodulated by a PARC model 186A LIA, operated in the 2f mode, at a phase angle of 210° relative to the function generator driving the vibrator. This LIA output (output time constant = 0.03 s) was then demodulated a second time by a PARC model 1501 LIA at a phase angle of -150° relative to the function generator providing the potential modulation. The output time constant of this LIA was 3 s, with a 1 s post filter.

The response of this double lock-in amplifier approach was verified with a synthetic signal. This signal was
Figure 20. Schematic diagram of the double modulation apparatus using the two LIA approach.
generated from the theoretical equations presented earlier and input to the LIA system via an A/D converter. The program used is given in Appendix A. When a signal of typical amplitude was input to the LIAs, the dc output was 96% of the expected value.

**Fabrication of Microelectrodes**

The platinum microdisk electrodes were constructed by sealing various diameters (25, 50, and 125 \( \mu \text{m} \)) of platinum wire (Goodfellow Metals, Cambridge, England) into glass capillaries under vacuum. The capillaries were drawn from 2.92 mm o.d. type 0120 potash soda lead glass (Corning). The platinum microcylinder electrodes were fabricated in a similar fashion using platinum wires (10, 25, 50, 125, 356, and 810 \( \mu \text{m} \) diameter) of various length, but were sealed without vacuum. The length of the exposed microcylinder electrodes was approximately 3 mm. All electrodes were backfilled with conductive silver epoxy, and a copper wire provided an electrical connection.

The completed microdisk electrodes were sanded with 600 grit sandpaper to expose the Pt disk, and then polished with 15 and 6 \( \mu \text{m} \) diamond compounds, followed by a series of alumina slurries down to 0.05 \( \mu \text{m} \). After the initial polishing, cleaning with 0.05 \( \mu \text{m} \) alumina was employed between experiments. The completed microcylinder electrodes were cleaned by soaking in concentrated H\(_2\)SO\(_4\), followed by rinsing with copious amounts of Nanopure water (Sybron
Barnstead, Boston, MA). This procedure was also followed between experiments.

The reference and auxiliary electrodes were conventional, consisting of either an aqueous saturated calomel electrode (SCE) or a saturated sodium calomel electrode (SSCE), and a Pt wire.

**Chemical Reagents**

Ferrocene was obtained from Strem Chemicals (Danvers, MA) and was purified by sublimation according to a published procedure [95]. 1,1'-Bis(hydroxymethyl)ferrocene (BHMF) was a gift from T. Kuwana. Tetrabutylammonium perchlorate (Southwestern Analytical) and high purity UV-grade acetonitrile (Burdick and Jackson) were used as received. For the square wave voltammetric experiments, all solutions were deaerated with argon prior to use.
CHAPTER IV

RESULTS AND DISCUSSION

Square Wave Voltammetry

Current vs. time waveforms for background and ferrocene solutions are shown in Figure 6, p. 48 for a square wave potential modulation centered at the half wave potential. The transients with the switch in the circuit show virtual elimination of the charging current for switch times of a few tens of μs. The 70 μs switch time chosen for this work corresponds to the 20 μs amplifier risetime, followed by about 12 effective cell time constants. At 200 Hz, a 70 μs switch removes only 10% of the faradaic response while eliminating all but 6 parts in 10^6 of the charging current for a constant dc potential. The small remaining peaks discernible in Figure 6c are caused by background faradaic processes rather than by charging current.

The time required to reach a steady state ac response was measured by suddenly imposing a square wave centered at E°' and monitoring the LIA output. The 95% risetime of the demodulated signal was 35 ms for a 300 Hz square wave and a LIA time constant of 10 ms. The LIA output leveled off at 94
about 50 ms, indicating that an electrochemical steady state had been reached during the 150 cycles occurring in the first 50 ms. Although the theory predicts a steady state in 5-10 cycles, the response of the LIA output is determined by the LIA time constant rather than the time required to reach the electrochemical steady state. After a dc potential change the demodulated signal will level off to within 5% after three LIA time constants have elapsed. The observed LIA output was compared to that predicted from equation 2.3 and Table 2 after substitution of the various constants. The observed current was consistently 70% of the expected value at 200 Hz. When a simple RC dummy cell replaced the electrochemical cell, the LIA output was 62% of the expected value. The negative error appears to result from the shape of the waveform; the LIA is not designed to monitor sharp transients and therefore does not effectively process the early portion of the faradaic response. The input bandwidth of the LIA is insufficient to amplify all of the high frequency components contained in the raw current vs. time waveform.

Voltammograms were recorded by sweeping the potential at a rate which was slow relative to both the square wave frequency and the LIA time constant. Figure 21, p. 96 shows a series of voltammograms recorded at several square wave amplitudes. The peak height and shape are similar to those observed with ac polarography, with the peak height being
Figure 21. Experimental square wave voltammograms. $f = 200$ Hz, bulk ferrocene concentration = 1.02 mM, electrode diameter 125 µm, 70 µs switch time, $\phi = 180^\circ$. Curves a-h are for $\Delta E = 10, 20, 30, 40, 50, 60, 80,$ and 100 mV, respectively. LIA time constant = 30 ms.
linearly dependent on $\Delta E$ up to about 40 MV, Figure 22, p. 98. The effect of the switch was to decrease the magnitude of the peak height vs. $\Delta E$ curve, but did not affect its shape. From equation 2.1, one would predict that the demodulated signal would be proportional to the square root of the square wave modulation frequency when the switch is not included in the circuit. A plot of peak amplitude vs. $f^{1/2}$ is linear ($r = 0.99996$) over the frequency range from 200 Hz to 3 kHz for ferrocene oxidation, Figure 23, p. 99. With the switch present, the signal vs. $f^{1/2}$ plot is not linear and shows a maximum when the switch time is about 20% of the square wave half cycle. As the frequency is increased with constant switch time, a smaller, non-linear fraction of the half cycle reaches the LIA, and a smaller demodulated output results.

The dependence of the demodulated current on phase angle differs significantly from that for a simple sine wave due to the sharp transient response of the current. Figure 24, p. 100, shows the signal vs. $\phi$ for several switch lengths. As would be predicted from the current waveforms, the maximum signal occurred at 0 or 180°, depending on the sign of the current. Voltammograms on blank solutions showed that the background response was minimized at 150°, where it was 14% as large as its maximum value at 180°. At 150° the solution faradaic response was 36% of its maximum value, so a better signal/background ratio was obtained by
Figure 22. Peak current vs. \( \Delta E \) for various switch lengths. Switch times are those indicated; other conditions as in Figure 21, except the electrode diameter was 25 \( \mu \text{m} \).
Figure 23. Peak current vs. square root of potential modulation frequency for various switch lengths. Switch times are those indicated; other conditions as in Figure 22. $\Delta E = 60$ mv.
Figure 24. Average ac current vs. LIA phase angle, $\phi$. Switch times are those indicated; other conditions as in Figure 23.
detection at a phase shift of 150°.

Calibration curves of ac signal vs. concentration for a 200 Hz, 60 mV modulation were linear from 2.0 × 10⁻⁷ to 9.78 × 10⁻⁴ M ferrocene (slope of log-log plot = 1.023, correlation coefficient = 0.9996), Figure 25, p. 102. At 2 × 10⁻⁷ M, the signal to background noise level was 2/1, and the analytical peak was superimposed on a sloping background. Studies in aqueous solution using 1,1'-bis(hydroxymethyl)ferrocene gave detections limits of 8 × 10⁻⁶ M. These detection limits are not as low as the 10⁻⁹-10⁻⁸ M levels reported for square wave voltammetry at a mercury electrode, mainly because mercury has a lower faradaic background response than solid electrodes. Only a few detection limits for pulse voltammetric techniques have been reported for solid electrodes, but are generally 10⁻⁶-10⁻⁷ M for differential pulse voltammetry (DPV) [8,96,97]. A comparison of square wave vs. conventional differential pulse voltammetry on microdisk electrodes is shown in Figure 26, p. 103, with conditions being comparable for both methods. The two techniques had similar S/N for "large" (0.1-2 mm) electrodes, but the square wave technique exhibited better S/N than DPV for microelectrodes having diameters less than 50 µm. Ewing et al. have reported a modified pulse voltammetric method for use with very small electrodes for in vivo analysis [8]. Their approach differs substantially from either conventional DPV or a square wave
Figure 25. Calibration curve for square wave voltammetry. 
$f = 200$ Hz, $\Delta E = 60$ mV, 70 $\mu$s switch time, $\phi = 150^\circ$, 25 $\mu$m diameter Pt electrode.
Figure 26. Comparison of square wave technique to conventional DPV. Curves a and c are for DPV at 125 and 25 μm diameter electrodes, respectively, on 6.5 μM ferrocene at 2 mV/s. Curves b and d are for the square wave technique on the same electrodes and solutions, except the scan rate was 10 mV/s. S: 100 pA (a), 1 nA (b), 20 pA (c), and 50 pA (d). $\phi = 150^\circ$. 
approach, but they observe micromolar detection limits with microdisk electrodes by using an integrative current sampling technique with analog filtering. It should be noted that the scan rate for the square wave technique in Figure 26 is five times faster than that for DPV.

The results presented so far were obtained at relatively slow scan rates of 5-10 mV/s. At millimolar concentration levels, the scan rate may be increased to 100 mV/s for a 200 Hz square wave modulation frequency, or 950 Mv/s at 3000 Hz, with minimal effects on the appearance of the voltammogram. For a 1 ms LIA time constant, the peaks shifted positively by 20 mV at the faster scan rates, with no observable broadening. This shift appears to be caused by instrumental effects, since longer time constants caused larger shifts and peak broadening. These scan rates allow analysis times of a few seconds, much shorter than the several minutes generally required with DPV. At lower concentrations, the increase in background current at high scan rates or modulation frequencies is more apparent, so there is a tradeoff between sensitivity and analysis time. Figure 27, p. 105, demonstrates submicromolar detection limits with a 12 s analysis time for a 200 Hz modulation frequency.

Several points about the square wave technique presented here deserve special note. First, the electronic switch which removes charging current from the raw current
Figure 27. Square wave voltammograms for ferrocene/TBAP at 48 mV/s. $\Delta E = 60$ mV, $\phi = 150^\circ$, 70 $\mu$s switch time, 125 $\mu$m diameter Pt electrode. (a) $6.3 \times 10^{-7}$ M; (b) $2.5 \times 10^{-6}$ M.
vs. time waveform is essential to the technique. Without it, the charging current would be demodulated by the LIA and no advantage of a fast cell time constant would be realized. The use of both hardware [98] and software [99] LIA's for monitoring square-wave voltammograms have been reported, but the charging current was input to the LIA as with sinusoidal ac techniques. Second, the dE/dt term of the charging current resulting from the voltammetric scan is cancelled out by the demodulation process. The increase in background current observed at high scan rates is probably a second order effect resulting from the change in capacitance of background process with potential. Third, the duration of the switch will remove as much of the charging current transient as desired, with loss of the faradaic signal occurring at longer switch times. As long as the cell time constant is much shorter than the half period of the potential modulation, the charging current may be effectively eliminated. Fourth, a LIA is essentially an integrative detector with outstanding performance when applied to small, noisy signals. Except for the short switch period that removes charging current, the LIA processes the entire ac current waveform, with a large improvement in signal to noise ratio. When applied to the small currents from microelectrodes, synchronous demodulation will yield better S/N than techniques like DPV which measure only a fraction of the current transient. For
example, the magnitude of the ac current in Figure 26d is ca. 100 pA, and lower currents would occur for smaller microelectrodes. Fifth, high modulation frequencies are possible due to the short RC of microelectrodes. High frequencies do not improve detection limits because the surface faradaic current increases linearly with f, while the diffusion current is linear with $f^{1/2}$.

Nevertheless, high frequencies may be useful for examining fast charge transfer kinetics or fast chemical reactions associated with charge transfer. The high frequencies also permit the use of higher scan rates. Sixth, the 25 μm electrodes used here have sufficiently short time constants in TBAP/acetonitrile to eliminate charging current with minimal effect on the faradaic response, and smaller electrodes would provide no additional benefit. However, if smaller electrodes are required by the application (e.g. in vivo electrochemistry), the LIA would be a significant aid in monitoring the very weak signals.

The detection limit for the square wave method was limited by the presence of background currents from sources other than the charging current. Surface faradaic reactions and slow changes in the solid electrode surface yield currents that do not decay as rapidly as charging current and are therefore integrated by the LIA. These currents have different decay characteristics than the diffusion current, and therefore possess a different phase shift relative to
the applied square wave potential. Thus the interference from these background processes may be minimized, but not completely eliminated, by proper choice of phase angle.

As mentioned earlier, the present technique differs significantly from the square wave technique that uses a square potential modulation superimposed on a staircase dc potential [44,46-48,100]. In the technique reported here, a linear dc ramp simplifies the electronics but does not contribute to the charging current, since the current signal is ac coupled to the LIA. The electronics associated with synchronous detection are generally simpler than those required for the staircase approach, but this advantage is diminishing as computer-controlled instrumentation continues to be developed [50]. For the common case of metal ion analysis with a mercury drop electrode, the well-developed staircase method is superior to the present technique in terms of scan rate and detection limit. However, when the potential range of mercury is insufficient and a solid electrode is employed, or when a very small electrode is required, the technique described here may be advantageous. Since solid electrodes generally have high background responses due to surface faradaic reactions, the improved S/N of the LIA allows improved background correction. The excellent signal to noise ratio of the synchronous demodulation process permits good discrimination of an analytical peak superimposed on a background signal. The
improved S/N is particularly important for very small microelectrodes, where the current is in the pA range and the measured signal is noisy. A potential disadvantage of the square wave method for in vivo analysis is the rapid electrolysis occurring in response to the square wave potential perturbation. As has been pointed out [8], electrodes lose activity in vivo due to adsorbed products, etc., and a low-duty cycle method is preferable. The rapid scans allowed by this square-wave technique may alleviate this pitfall.
Hydrodynamic Modulation Voltammetry

Figure 28, p. 111, shows the current waveforms obtained when two cylinder electrodes of different diameter are vibrated sinusoidally. Figure 28A is the raw current waveform obtained from a 25 μm diameter electrode, and Figure 28B is that from a 356 μm diameter electrode, both of which are vibrated at 80 Hz. The peak-to-peak amplitude of the vibration is 0.8 mm, resulting in an average velocity of 13 cm/s. The lower trace in each diagram is the current waveform obtained when the electrode is vibrated at a potential where the redox reaction does not occur. The upper trace is the current waveform obtained that results when the applied potential is held at a value where the oxidation of ferrocene to ferrocinium ion occurs at a diffusion-limited rate.

Although the theoretical model presented earlier is oversimplified for the complex case of a cylinder moving at varying velocity, the waveform of Figure 28A does have the approximate shape predicted by the model. Except for a slight asymmetry, apparently due to irregularities in the mechanical vibrator, the observed and theoretical waveforms agree, indicating that equation 2.11 is a reasonably accurate expression for the hydrodynamic current. Fourier transforms of both the experimental and theoretical waveforms show a dominant component at $2f_h$, with harmonics at $4f_h$ and $6f_h$, as well as a small contribution at $f_h$ due to
Figure 28. Current waveforms from 0.91 mM ferrocene/0.1 M TBAP in acetonitrile. Modulation frequency, 160 Hz; applied potential, 0.0 V vs. SCE (A1,B1) or 0.6 V vs. SCE (A2,B2). (A) 25 μm diameter Pt microcylinder electrode. Electrode length, 3.0 mm. (B) 356 μm diameter Pt wire electrode. Electrode length, 3.1 mm.
Figure 28.
the vibration asymmetry. As the electrode diameter is increased (Figure 28B), the modulation amplitude decreases significantly relative to the average current, and the waveform resembles a distorted sine wave. In both cases, the observed current is modulated at 160 Hz, which is twice the frequency of the vibration. It should be noted that the 160 Hz modulation frequency of the current obtained with the microelectrode is much higher than the 1-15 Hz frequencies used in previous approaches and will improve the rejection of flicker noise by the detection electronics.

It is obvious from Figure 28 that the modulated current comprises a much larger fraction of the total current for the smaller diameter electrode. Figure 29, p. 114, shows the effect of electrode diameter on the modulation efficiency, defined here as the ratio of the p-p amplitude of the ac current to the average current. There is a dramatic increase in the modulation efficiency as the diameter of the wire electrode is decreased below 200 μm. The diameters of the electrodes used by Pratt [73] in his vibrating wire experiments were all greater than 300 μm, leading to much smaller modulation efficiencies.

The effect of electrode diameter on modulation efficiency can be understood qualitatively by considering the Reynolds number, Re, equation 1.15. The use of a Reynolds number assumes that the vibrating electrode can be considered a cylinder moving through a fluid rather than
Figure 29. Experimental modulation efficiency vs. diameter of vibrating microcylinder electrode. Modulation frequency, 160 Hz; 0.91 mM ferrocene/0.1 M TBAP in acetonitrile.
reciprocating, a reasonable assumption since the vibration amplitude is large relative to the wire diameter. At low values of Re (<1), Plate I, p. 116, the flow of solution around the electrode is laminar and symmetric, and the convective mass transport rate is directly related to the velocity of the electrode through the solution. In this case, the observed instantaneous current is directly dependent on the electrode velocity, and the current will be modulated by a modulation of the electrode velocity. At Re greater than about 5, Plate II, p. 117, separation of the boundary layer occurs behind the electrode, and recirculating eddies are formed. These elongate with increasing Re and eventually break into very irregular flow patterns when Re exceeds about 40 \([10]\). For these higher Reynolds numbers, Plate III, p. 118, there will not be a direct relationship between current and electrode velocity, and it will be difficult to modulate the current. At a given Re, a smaller electrode will have a higher velocity, and therefore a higher vibration frequency. For example, at 80 Hz, a 25 \(\mu\)m diameter electrode has an average Re of 7.4. For the same Re, a 2 mm diameter electrode could only be modulated at 1 Hz. These conclusions should be considered qualitative, but it is clear that a smaller electrode can be modulated at a higher frequency for a given Re.
Plate I

Circular cylinder at Re = 1.54. The flow has not yet separated at the rear. Direction of flow given by arrow.
(Taken from reference 101, p. 20.)
Plate II

Circular cylinder at $Re = 9.6$. The flow has separated to form a pair of recirculating eddies. Direction of flow given by arrow. (Taken from reference 101, p. 28.)
Circular cylinder at \( \text{Re} = 2000 \). At this Reynolds number one may properly speak of a boundary layer. It is laminar over the front, separates, and breaks up into a turbulent wake. Direction of flow given by arrow. (Taken from reference 101, p. 31.)
The current waveforms of Figure 28 may be demodulated by a lock-in amplifier to generate a dc output proportional to the ac current. A plot of LIA output is shown in Figure 30, p. 120, where the applied potential was scanned at 10 mV/s. The voltammogram has the sigmoidal shape expected for hydrodynamic voltammetry, with excellent signal-to-noise ratio for micromolar concentrations. While the magnitude of the current is in the nA to pA range for the smaller electrodes, such low values are easily measured due to the excellent noise characteristics of synchronous detection. Voltammograms at concentrations near the detection limit are shown in Figure 31, p. 121. The reference signal for the LIA was provided by the function generator that drives the mini-shaker and was doubled internally by the LIA. The potential was scanned at 10 mV/s, a rate that was slow relative to both the vibration frequency and the LIA time constant.

Calibration curves of ac signal vs. ferrocene concentration for a 25 m diameter microcylinder electrode vibrated at 80 Hz were linear from \(3.0 \times 10^{-8}\) to \(1.2 \times 10^{-3}\) M (slope of log-log plot = \(0.969\), correlation coefficient = \(0.995\)), Figure 32, p. 122. At \(3.0 \times 10^{-8}\) M, the ratio of signal to the root mean square signal from a blank was 2.0. Similar experiments carried out with BHMF in pH 7 buffer gave a detection limit of \(9 \times 10^{-7}\) M. These detection limits are comparable to those obtained with the HMV.
Figure 30. Experimental voltammogram obtained from $5 \times 10^{-6}$ M ferrocene/$0.1$ M TBAP in acetonitrile. Scan rate, $10$ mV/s; electrode diameter, $25$ μm; modulation frequency, $160$ Hz.
Figure 31. Voltammograms obtained at low concentration. Conditions are as in Figure 30. (A) $1.1 \times 10^{-7}$ M ferrocene and (B) $2.1 \times 10^{-7}$ M ferrocene.
Figure 32. Calibration curve for hydrodynamic modulation voltammetry.
techniques cited earlier [60,71-73].

Figure 33, p. 124, demonstrates the extent of background rejection with HMV at a microcylinder electrode. All voltammograms were obtained with platinum electrodes in aqueous buffer in the presence and absence of 0.17 M bis(hydroxymethy)ferrocene (BHMF). For a conventional voltammogram (A) from a 1.5 mm diameter Pt disk, the BHMF signal is barely discernible above the blank. For a microcylinder electrode with hydrodynamic modulation (B), the background is minimal and the BHMF signal is dominant. The background voltammogram remained flat for potentials up to 1.3 V vs. SCE, at which point the increase in dc current caused the current amplifier to overload. The ratio of BHMF signal to background current increases from 2.7 for the Pt disk (measured for the oxidation peak at 0.25 V vs. SCE) to 210 for the microcylinder electrode operated in the HMV mode (measured for the oxidation peak at 0.35 V vs. SCE). This increase in signal-to-background current may be due in part to the enhanced diffusion at the microelectrode, although this effect would not be large for a 25 μm diameter electrode. A conventional voltammogram using the same microcylinder electrode in the same solution but without vibration yielded large background currents and a low signal-to-background ratio (S/B), indicating that the major enhancement in S/B resulted from hydrodynamic modulation rather than enhanced diffusion.
Figure 33. Comparison of cyclic voltammograms using a conventionally-sized Pt disk electrode with hydrodynamic modulation voltammograms using a Pt microcylinder electrode. Solid lines were obtained from 0.17 mM BHMF in pH 7 citric acid/phosphate buffer, while the dashed lines are of the blank buffer solution. Scan rate, 50 mV/s. (A) Conventional voltammogram from a 1.5 mm diameter Pt disk electrode, scale = 1 A. (B) HMV from a 25 μm diameter Pt electrode vibrating at 80 Hz, scale = 50 nA.
Figure 33
Little was gained by using electrodes with diameters smaller than 25 \( \mu m \). While the modulation efficiency increases with smaller diameter, the area decreases, and the absolute current becomes small enough to introduce noise during amplification. A diameter of 25 \( \mu m \) is a good compromise between hydrodynamic characteristics and absolute signal size. In addition, smaller electrodes are insufficiently stiff to tolerate vibration at the frequencies employed. It should also be noted that microdisk electrodes were unsuitable for these experiments due to very small modulation efficiencies. The hydrodynamics of a flat disk moving through a fluid are quite different from those of a cylinder sweeping through a fluid, and this accounts for the observed difference in modulation efficiencies.

The combination of HMV and microelectrodes results in four analytically useful features. First, the small electrode size yields a low Reynolds number at relatively high electrode velocities. The result is good modulation efficiency at relatively high frequencies, and the reduction of flicker noise in the detection process. In addition, the higher modulation frequency permits the use of higher voltammetric scan rates than could be used with lower modulation frequencies. Second, the modulation apparatus is simple due to the low mass of the electrode. High frequencies and electrode velocities may be achieved with
low vibration amplitude, light-duty drivers, and small solution volume. Third, the small absolute currents minimize absolute sample consumption, so very low concentrations or small sample volumes are permissible. Fourth, the background signal at a Pt electrode in water is greatly reduced, and the useful positive potential scale is extended.
Double Modulation Voltammetry

The raw current waveform shown in Figure 34, p. 129, results when both the applied potential and the velocity of the microcylinder electrode are modulated sinusoidally. The 60 mV p-p potential modulation was centered at $E_0'$ and the vibration frequency was 80 Hz. Several qualitative features of this complex waveform deserve note, all of which were predicted from equation 2.17, which is reproduced here as equation 4.1.

\[
\frac{i}{nFAC_{ox}^{*}} = A_0B_0 + A_1B_0\cos(2\pi f_e) + A_0B_1\cos2\pi(2f_h) +
\]

\[
\frac{A_1B_1\sin[2\pi(2f_h + f_e)] + A_1B_1\sin[2\pi(2f_h - f_e)]}{2} + \ldots
\]

First, the dominant low frequency component at frequency $f_e$ results from potential modulation of the hydrodynamic steady state current, i.e. the second term of equation 4.1.

Second, the "fundamental" hydrodynamic component at $2f_h$ is also prominent, as predicted from the third term of equation 4.1. Third, the envelope of the hydrodynamic modulation is itself modulated at $f_e$; the magnitude is large at the peaks of the $f_e$ waveform and smaller at the valleys. The amplitude modulation of the $2f_h$ hydrodynamic "carrier" results in the fourth and fifth terms of equation 4.1. It may also be expressed as the term from which the fourth and fifth terms of equation 4.1 were derived, i.e. $A_1B_1(\cos 2\pi f_e)\cos 2\pi(2f_h)$. This expression describes an amplitude-
Figure 34. Experimental double-modulated current waveform. 1.4 mM ferrocene/0.1 M TBAP in acetonitrile. $f_e = 7 \text{ Hz}$, $f_h = 160 \text{ Hz}$, $\Delta E = 60 \text{ mV}$, $E_{app} = 0.44 \text{ V vs. SCE}$, 25 $\mu$m diameter Pt microcylinder electrode.
modulated waveform with carrier frequency $2f_h$, and modulation frequency $f_e$, and can be restated as the sum and difference frequencies in equation 4.1.

The fundamental and sideband frequencies are apparent in the Fourier transform of the raw current waveform, Figure 35, p. 131. When the individual frequency components at $f_e$, $f_h$, and $f_e + f_h$ were each monitored with a LIA while the dc potential was scanned, the voltammograms shown in Figure 36, p. 132, resulted. The demodulated currents are proportional to the amplitudes of the Fourier components at the various frequencies, and correspond to the theoretical voltammograms of Figure 14, p. 75. The sigmoidal response at $2f_h$, trace a, is the same as would be obtained from a simple hydrodynamic modulation experiment, with no effect from the potential modulation. Trace b, obtained by monitoring $f_e$, is analogous to the classical ac voltammetric response, with mass transport at steady state. The voltammogram obtained at $2f_h + f_e$ arises from the double-modulated signal, trace c. While smaller in absolute magnitude, it has the same shape as the simple ac voltammogram, with comparable peak width, Table 6, p. 133.

The $f_e$ and $2f_h$ voltammograms in Figure 36 were easily recorded using a single LIA with either the potential modulation waveform serving as a reference (for $f_e$) or by monitoring the second harmonic of the waveform driving the vibrator. The $2f_h + f_e$ component was significantly more
Figure 35. Fourier transform of experimental double-modulated current waveform. Conditions as in Figure 34, except $f_e = 13$ Hz.
Figure 36. Experimental voltammograms of each frequency component. 7 × 10⁻⁵ M ferrocene/0.1 M TBAP in acetonitrile. $f_e = 13$ Hz, $f_h = 160$ Hz, $\Delta E = 50$ mV, 10 mV/s scan rate, 25 μm diameter Pt microcylinder electrode. a) $f_h$ detected at 90°, b) $f_e$ detected at 45°, and c) $f_h + f_e$ detected at 105°. 0.3 s LIA rise time.
Table 6
Comparison of Peak Widths^a

<table>
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<th>ΔE (mV)</th>
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<th>Peak Width for DMV^b (mV)</th>
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<td>122.5</td>
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^a Experimentally-determined peak widths at half the maximum peak height.

^b The peak width is determined by the response characteristics of the LIA, rather than ΔE at low values of ΔE.
difficult to record, since the reference waveform for the LIA had to be synthesized from $f_e$ and $f_h$ with suitable and constant phase. An experimental consequence of using the $2f_h + f_e$ frequency is very important to the practical utility of double modulation voltammetry. Figure 37, p. 135, shows voltammograms obtained at $2f_h + f_e$ for several different LIA output time constants. At slow time constants, Figure 37a, the DMV response has the predicted peak shape already demonstrated in Figure 36. At slightly faster time constants, Figure 37b, a slight, low frequency (~1 Hz) oscillation is apparent at and near the peak potential. At faster time constants, Figure 37b, the oscillation is more pronounced and seriously interferes with analytical measurements. At low concentrations, this oscillation was apparent even at slow time constants. Its frequency and magnitude depended strongly on the choice of $f_e$ and $f_h$, on the proximity of $E_{dc}$ to $E^\circ$, and its frequency was higher on the negative side of $E^\circ$ than on the positive side. The most likely source of the oscillation is a beat frequency between the $2f_h + f_e$ component and other frequencies present in the raw waveform, particularly $2f_h$. The response at the sum frequency is relatively small compared to those at $2f_h$ and $f_e$, and these larger components may interfere. Whatever its origin, the oscillatory interference adversely affected detection limits to the point where analytical utility was compromised.
Figure 37. Voltammograms obtained by detecting the sum frequency component. 0.83 MM ferrocene/0.1 M TBAP in acetonitrile. $f_e = 13$ Hz, $f_v = 80$ Hz, $\Delta E = 60$ mV, $\phi = 90^\circ$, 10 mV/s scan rate. LIA output time constant: a) 0.3 s, b) 0.1 s, and c) 0.03 s.
One of the principal interferences to the \(2f_h + f_e\) response is the amplitude-modulated hydrodynamic fundamental at \(2f_h\). Fortunately, this component may be monitored directly using two lock-in amplifiers, as alluded to earlier. Voltammograms using the apparatus of Figure 20, p. 91, are shown in Figure 38, p. 137. While similar in appearance to the voltammograms shown in Figure 37, the amplitude-modulated hydrodynamic modulation voltammograms (AMHMV) obtained with two LIAs are less prone to the interfering oscillations. The peak response was linear from \(4.3 \times 10^{-7}\) to \(6.5 \times 10^{-4}\) M bis(hydroxymethyl)ferrocene, with a slope of \(7.32 \times 10^{-5}\) A/molar (correlation coefficient = 0.9989). The slope of the log response vs. log concentration plot was 1.07, with a correlation coefficient of 0.9973, over three decades, Figure 39, p. 138.

The dependence of the AMHMV response on \(\Delta E\), Figure 40, p. 139, is qualitatively similar to that predicted theoretically, and also to analogous plots for conventional ac voltammetry and the square wave technique discussed here previously. The major advantage of DMV over these methods is the rejection of background current, as shown in Figure 41, p. 140. Trace A is a conventional cyclic voltammogram of \(6.5 \times 10^{-4}\) M BHMF in water, with the BHMF response barely discernible over the background faradaic processes. Trace B is the AMHMV response for a ten times less concentrated BHMF solution, having both excellent background suppression and
Figure 38. Voltammograms obtained by the two LIA approach. 0.65 mM BHMF in pH 7 phosphate buffer. $f_h = 160$ Hz, $f_e = 3$ Hz, 25 μm diameter Pt microcylinder electrode, 1 mV/s scan rate. Curves a-e are for $\Delta E = 20, 40, 60, 80, 100$ mV, respectively.
Figure 39. Calibration curve for double modulation voltammetry. Conditions as in Figure 38.
Figure 40. $\Delta E$ dependence of AMHMV frequency component. Conditions as in Figure 38.
Figure 41. Comparison of cyclic voltammograms using a conventionally-sized Pt disk electrode with double modulation voltammograms using a Pt microcylinder electrode. Solid lines were obtained from BHMF in pH 7 citric acid/phosphate buffer, while the dashed lines are of the blank buffer solution. A) Conventional voltammogram from a 1.5 mm diameter Pt disk electrode; [BHMF] = 6.5 \times 10^{-4} \text{ M}. Scale: \( X = 50 \text{ mV}, Y = 4 \text{ \mu A} \). B) AMHMV from a 25 \mu m diameter Pt microcylinder electrode; [BHMF] = 6.5 \times 10^{-5} \text{ M}. Scale: \( X = 100 \text{ mV}, Y = 1.25 \text{ nA} \).
extended anodic range. The upper limit on potential was determined by overload of the electronics from the large nonmodulated components present in the raw current waveform.

Figure 42, p. 143, shows voltammograms obtained at micromolar levels for BHMF in water. The Fourier transforms shown in Figure 43, p. 144, compare the frequency components present in a blank solution with those present at low concentration. The detection limit for the AMHMV method, defined as the concentration of BHMF in pH 7 phosphate buffer where the signal is twice the rms noise of the blank, was 3 \times 10^{-7} \text{ M}. For the same conditions, microcylinder hydrodynamic modulation voltammetry, without potential modulation, had a detection limit of 9 \times 10^{-7} \text{ M}. Double modulation experiments using the sum frequency component, 2f_h + f_e, gave detection limits of only 1.2 \times 10^{-6} \text{ M}. Comparisons of the detection limits obtained by double modulation voltammetry and the individual modulation techniques are in Table 7, p. 146.

For the range of f_e from 3 to 130 Hz, the AMHMV response varied by less than 33\%, indicating essentially no dependence on f_e. This observation validates the assumption that the hydrodynamic boundary layer is thin relative to that produced by the potential perturbation. The peak phase for the AMHMV signal occurred at 210° for the first LIA (at 2f_h) and -150° for the second LIA (at f_e). The magnitudes of the voltammograms obtained by monitoring either the sum
Figure 42. Double modulation voltammograms obtained at low concentration. Conditions as in Figure 38. Concentration of BHMF in pH 7 phosphate buffer: a) 1.7 µM, b) 2.6 µM, and c) 3.9 µM.
Figure 43. Fourier transforms of current waveforms obtained for a blank solution and at low concentration. $f_v = 160 \text{ Hz}$, $f_e = 13 \text{ Hz}$, $\Delta E = 50 \text{ mV}$, 0.45 V vs. SSCE. a) blank 0.1 M TBAP in acetonitrile and b) $7 \times 10^{-5}$ M ferrocene/0.1 M TBAP in acetonitrile.
Frequency (Hz/100)

Figure 43.
Table 7
Comparison of Detection Limits

<table>
<thead>
<tr>
<th>Technique</th>
<th>Detection Limit for ferrocene (M)</th>
<th>Detection Limit for BHMF (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWV</td>
<td>$2 \times 10^{-7}$</td>
<td>$8 \times 10^{-6}$</td>
</tr>
<tr>
<td>HMV</td>
<td>$3 \times 10^{-8}$</td>
<td>$9 \times 10^{-7}$</td>
</tr>
<tr>
<td>DMV (SUM)</td>
<td>---</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>DMV (AMHMV)</td>
<td>---</td>
<td>$4 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
frequency or the AMHMV component increased linearly with ΔE up to about 50 mV, then exhibited a negative deviation from linearity, as predicted theoretically.

There are two major factors which affect the analytical utility of the potential/hydrodynamic double modulation approach: the nature of the raw modulated current and the method by which it is demodulated to produce a useful response. The key feature of the raw current is the fact that only mass-transport-controlled reversible and quasi-reversible redox systems will be modulated at both $f_e$ and $2f_h$. Stated mathematically, $B_1$ in equation 4.1 will be zero for any process which is unaffected by mass transport, e.g. capacitance and surface background reactions. Thus the third and fourth terms in equation 4.1, corresponding to monitoring the $2f_h$ or $2f_h + f_e$ components, are zero for surface or capacitive processes. If only the hydrodynamic modulation is considered, this feature is basically the same as that exploited in other hydrodynamic modulation methods, with one significant exception. The microcylinder electrode permits the use of higher modulation frequencies, reducing flicker noise and shifting the frequency up into a range more suitable for detection by a LIA. Before considering the potential modulation, the net result of using a microcylinder electrode is higher performance than other HMV techniques with respect to modulation frequency, at the cost of more complex solution hydrodynamics, which can only be
described in less rigorous terms than a RDE or flow electrode.

The imposition of potential modulation on an already hydrodynamically-modulated current is given mathematically by setting $A_1$ to a nonzero value. The second term of equation 4.1 will produce the large fundamental oscillation at $f_e$, but this term will not discriminate against background current because both $A_1$ and $B_g$ may be nonzero for surface or capacitive processes. For example, formation of a platinum oxide species will be potential dependent ($A_1 \neq 0$) and will have a nonzero value even at fixed potential ($B_g \neq 0$). Thus the current at $f_e$ will include current from the major background processes common to solid electrodes and the detection limits of conventional ac voltammetry will be dictated by the presence of these currents. The fourth and fifth terms of equation 4.1 incorporate double modulation, and retain the background rejection capabilities of single hydrodynamic modulation. Since $B_1$ is zero for non-mass-transport-controlled currents, these terms will be comparable to the third term with respect to background rejection. In addition, the nonzero character of $A_1$ indicates that only potential-modulated processes will contribute to the fourth and fifth terms. The result is the requirement that a process be both mass-transport-controlled and potential-modulated to contribute to the current at $2f_h + f_e$. The Fourier transform of the raw current in Figure
35, p. 131, verifies that such frequency components exist.

Once the existence of the double-modulated response in the raw waveform has been established, there remains the technical issue of monitoring a particular frequency component, whose magnitude may be small, in the presence of substantially larger components. The conceptually simple approach of monitoring single frequencies with a LIA produced the voltammograms shown in Figure 36, but it is not the optimum approach for detecting the $2f_h + f_e$ component, due to interferences from nearby components. The result of this interference was distorted voltammograms and relatively poor detection limits. The mathematically equivalent AMHMV approach is free from this interference, and leads to better detection limits. Both methods have comparably good linearity with concentration, and share the background rejection resulting from hydrodynamic modulation.

While double modulation techniques do permit sensitive voltammetric experiments on solid electrodes in aqueous solution, there is a trade-off in speed and electrode life. The potential modulation frequency, $f_e$, must be much less than the hydrodynamic modulation frequency, $2f_h$, both to validate the assumptions of the theory and to permit successive demodulation by two lock-in amplifiers. A low $f_e$ requires a fairly long LIA time constant (~1-3 s), forcing the use of slow scan rates. The net result is a scan time comparable to differential pulse polarography. In addition,
the double modulation scheme drives the faradaic process fairly hard, with the potential for electrode fouling. The current densities will typically be comparable to microdisk electrodes rather than the usual millimeter-scale solid electrodes.

The advantages of double modulation voltammetry are several, and will be particularly important when background current is severe. First, Figure 41 demonstrates the outstanding rejection of background current compared to conventional voltammetry. When compared the HMV, the AMHMV technique has the advantage of a peak, rather than wave, response, leading to improved detection limits and resolution. As has been amply demonstrated with differential pulse polarography compared to dc polarography [58], a peak response is more analytically useful. Finally, the rejection of background current extends the potential range of the electrode/electrolyte combination farther into the solvent breakdown region, permitting significant (0.2 - 0.3 V) extension of the useable potential range accessible to solid electrodes.
CHAPTER V

SUMMARY

This work has demonstrated that several new features of microelectrodes can be exploited to discriminate against both types of background currents encountered in trace voltammetry at solid electrodes. The fast RC time constant of a microdisk electrode was utilized in square wave voltammetry to effectively eliminate the charging current present in the signal. The switch that was constructed to prevent the charging current from reaching the detector is essential to this technique; without it, the charging current would be demodulated by the detector and the advantage of a fast cell time constant would be lost. This fast cell time constant also allowed the use of high modulation frequencies and fast voltammetric scan rates. The lock-in amplifier used to demodulate the signal is also necessary for this technique. The excellent signal-to-noise characteristics of the LIA and the integrative nature of the detection process permitted the detection of the small, noisy currents obtained at microdisk electrodes, resulting in better S/N than techniques that measure only a fraction
of the current waveform.

Another unusual feature of microelectrodes that was reported in this work is the low Reynolds numbers obtained when microelectrodes are used for hydrodynamic voltammetry. A lower Reynolds number permits the use of much higher velocities, resulting in the use of higher modulation frequencies than have been used in previous HMV techniques, as well as faster voltammetric scan rates. The extremely high modulation efficiencies obtained when a vibrating microcylinder electrode is used for HMV were also a consequence of the low Reynolds number. Discrimination against the background surface reactions occurring on a platinum electrode in aqueous media was also demonstrated.

This work is also the first time that a potential modulation technique and a hydrodynamic modulation technique have been merged in a double modulation experiment to remove both types of background currents simultaneously. In addition to the fact that both charging current and the current arising from background surface processes are eliminated, it was shown that the voltammograms obtained from this new technique incorporate characteristics from each of the individual modulation techniques. For example, the shape of the voltammogram resembles that obtained from a potential modulation technique, that of a peak rather than a sigmoidally-shaped wave, and the useable positive potential range is extended, as with hydrodynamic modulation.
voltammetry.

In addition to employing these techniques for trace analysis, they may also be useful in other applications. For example, the high frequencies attainable with the square wave modulation technique should be useful for studying fast charge transfer kinetics and the fast chemical reactions associated with charge transfer. The high sensitivity could also be exploited to probe the reactions of functional groups present on the surface of carbon electrodes, and observe how these functional groups might change after various electrode pretreatment procedures have been performed.

Another promising area of application is the use of either the HMV or DMV technique in conjunction with high performance liquid chromatography (HPLC). Electrochemical detectors are among the most sensitive available for HPLC, but they are not commonly used due to their inherent sensitivity to small changes in the mobile phase flow rate. Another factor that limits the usefulness of LC/EC is the need to add supporting electrolyte to the mobile phase when using electrodes of conventional size. This requirement can generally be met with reversed-phase and ion-exchange chromatographic techniques, but is difficult to achieve with other methods. Both of these limitations can be easily overcome by using a vibrating microcylinder electrode as the detector. Small variations in the pump output would be
negligible compared to the high electrode velocities employed, and the small size of the microelectrode would eliminate the need for conducting mobile phases. Wightman [7,11] has shown that voltammetric experiments can be carried out in highly resistive solvents with microelectrodes. Because less current is passed at these minute electrodes, iR problems are much less severe.
REFERENCES

1. J. Heyrovsky, Chem. Listy, 16 (1922) 256.


19. ibid., p. 11.

20. ibid., p. 143.


51. A.J. Bard and L.R. Faulkner, Electrochemical Methods,
52. ibid., pp. 130-132.


54. ibid., p. 70

55. ibid.


APPENDIX A

Computer Programs
PROGRAM SQUARE WAVE

BASIC program used to calculate up to 30 cycles of the theoretical current waveform obtained from square wave potential modulation.
SQUARE WAVE

2 B = 2
5 REM 7/24/84
10 REM CALCULATES CURRENT RESPONSE
20 REM FOR SQUARE WAVE OF AMPLITUDE
40 REM DE AND AVERAGE DC LEVEL OF ED
50 REM ED=EDC-EONEHALF
60 REM REF: ANAL. CHM. 48 1616 (1976)
70 REM ASSUMES A REDUCTION, OX ONLY
80 REM IN BULK SOLUTION AT T=0
90 REM TAKES 50 DATA POINTS PER HALF CYCLE
95 REM UP TO 30 CYCLES
100 DIM I(1500),TH(3)
110 INPUT "ENTER EDC AND DELE, MV "; ED, DE
120 GA = 1
130 REM GA IS SQRT (DOX/DRED)
140 F * 0.03892s REM F/RT, MV
150 TH(0) = 1E10
160 TH(1) = EXP (F * (ED - (DE / 2)))
170 TH(2) = EXP (F * (ED + (DE / 2)))
180 INPUT "ENTER TOTAL TIME, CYCLE TIME ";TT,CT
190 REM CYCLE TIME IS ONE SQUARE WAVE PERIOD
200 NS = 2 * TT / CT; REM NS=NUMBER OF STEPS
210 DT = TT / NS; REM TIME OF ONE STEP
220 REM CALCULATE FIRST STEP
220 FOR X = 1 TO 50
224 TS = (DT * (X / 50))
230 D1 = (TH(0) * (TH(0) + GA)) / (TH(0) * (TH(0) + GA))
240 D2 = (TH(1) * (TH(0) + GA)) / (TH(0) * (TH(1) + GA))
250 DS = D1 - D2
260 I(X) = DS / SQR (TS)
266 NEXT X
270 REM BIG LOOP FOR STEPS 2 TO NS
280 FOR S = 2 TO NS
281 FOR X = 1 TO 50
282 TS = (S - 1) + (DT * X / 50))
290 I((S - 1) * 50 + X) = 0
300 FL = -1
310 FOR A = 1 TO S
320 IF FL = 1 THEN HJ = TH(2);H1 = TH(1)
330 IF FL = -1 THEN HJ = TH(1);H1 = TH(2)
340 H0 = TH(0)
350 D1 = (H1 * (H0 + GA)) / (H0 * (H1 + GA))
360 D2 = (HJ * (H0 + GA)) / (H0 * (HJ + GA))
370 I((S - 1) * 50 + X) = I((S - 1) * 50 + X) + (D1 - D2) / SQR (TS - TA)
380 FL = - FL
390 NEXT A
398 NEXT X
400 NEXT S
410 INPUT "FILENAME?"; F$
420 D$ = CHR$ (4)
430 PRINT D$; "OPEN"; F$
440 PRINT D$; "WRITE"; F$
450 PRINT (50 * NS); PRINT (DT / 50); PRINT B; PRINT B;
    PRINT B; PRINT B; PRINT B; PRINT B
460 FOR Q = 1 TO (50 * NS); PRINT I(Q); NEXT Q
470 PRINT D$; "CLOSE"; F$
480 END
PROGRAM LAST CYCLE CURRENT

BASIC program used to calculate the last cycle of the theoretical current waveform obtained from square wave potential modulation when the number of cycles is greater than 30.
LAST CYCLE CURRENT

2 B = 2
5 REM REVISED 9/29/84
10 REM CALCULATES CURRENT RESPONSE
15 REM OF FINAL CYCLE OF WAVEFORM
20 REM FOR SQUARE WAVE OF AMPLITUDE
40 REM DE AND AVERAGE DC LEVEL OF ED
50 REM ED=EDE-1/2
60 REM REF: ANAL. CHEM. 48 1616 (1976)
70 REM ASSUMES A REDUCTION, OX ONLY
80 REM IN BULK SOLUTION AT T=0
90 REM TAKES 50 DATA POINTS PER HALF CYCLE
100 DIM I(1500), TH(3)
110 INPUT "ENTER EDC AND DELE, MV";ED,DE
120 GA = 1
130 REM GA IS SQRT(DOX/DRED)
140 F = 0.03892: REM F/RT, MV
150 TH(0) = 1E16
160 TH(1) = EXP (F * (ED - (DE / 2)))
170 TH(2) = EXP (F * (ED + (DE / 2)))
180 INPUT "ENTER TOTAL TIME, CYCLE TIME";TT,CT
190 REM CYCLE TIME IS ONE SQUARE WAVE PERIOD
200 NS = 2* TT / CT: REM NS=NUMBER OF STEPS
210 DT = TT / NS: REM TIME OF ONE STEP
220 REM CALCULATE FIRST STEP
220 FOR X = 1 TO 50
224 TS = DT * (X / 50)
230 D1 = (TH(0) * (TH(0) + GA)) / (TH(0) * (TH(0) + GA))
240 D2 = (TH(1) * (TH(0) + GA)) / (TH(0) * (TH(1) + GA))
250 DS = D1 - D2
260 I(X) = DS / SQR(TS)
264 NEXT X
270 REM BIG LOOP FOR STEPS 2 TO NS
280 FOR S = NS - 1 TO NS
284 FOR X = 1 TO 50
288 TS = (S - 1) + (DT * (X / 50))
290 I((S - 1) * 50 + X) = 0
300 FL = -1
310 FOR A = 1 TO S
320 IF FL = 1 THEN HJ = TH(2); H1 = TH(1)
330 IF FL = -1 THEN HJ = TH(1); H1 = TH(2)
340 H0 = TH(0)
350 D1 = (H1 * (H0 + GA)) / (H0 * (H1 + GA))
360 D2 = (HJ * (H0 + GA)) / (H0 * (HJ + GA))
365 TA = (A - 1) * DT
370 I((S - 1) * 50 + X) = I((S - 1) * 50 + X) + (D1 - D2) / SQR(TS - TA)
380 FL = -FL
390 NEXT A
398 NEXT X
400 NEXT S
410 INPUT "FILENAME?";F$
420 D$ = CHR$ (4)
430 PRINT D$;"OPEN";F$
440 PRINT D$;"WRITE";F$
450 PRINT 100: PRINT (DT / 50): PRINT B: PRINT B: PRINT B:
   PRINT B: PRINT B: PRINT B: PRINT B
460 FOR Q = (50 * NS) - 99 TO 50 * NS: PRINT I(Q): NEXT Q
470 PRINT D$;"CLOSE";F$
480 END
PROGRAM 2% SWITCH

BASIC program used to calculate the theoretical current waveform obtained from square wave potential modulation when the switch is present. Example here is for a switch lasting 2% of each half cycle.
2% SWITCH

2 B = 2
5 REM 9/30/84
10 REM CALCULATES CURRENT RESPONSE
20 REM FOR SQUARE WAVE OF AMPLITUDE
40 REM DE AND AVERAGE DC LEVEL OF ED
50 REM ED=EDC=EONEHALF
60 REM REF: ANAL. CHEM. 48 1616 (1976)
70 REM ASSUMES A REDUCTION, OX ONLY
80 REM IN BULK SOLUTION AT T=0
90 REM TAKES 50 DATA POINTS PER HALF CYCLE
95 REM UP TO 50 CYCLES
96 REM TWO PERCENT SWITCH PRESENT
100 DIM I(1500), TH(3)
110 INPUT "ENTER EDC AND DELE, MV ";ED,DE
120 GA = 1
130 REM GA IS SQRT(DOX / DRED)
140 F = 0.3892: REM F/RT, MV
150 TH(0) = 1E10
160 TH(1) = EXP (F * (ED - (DE / 2)))
170 TH(2) = EXP (F * (ED + (DE / 2)))
180 INPUT "ENTER TOTAL TIME, CYCLE TIME ";TT,CT
190 REM CYCLE TIME IS ONE SQUARE WAVE PERIOD
200 NS = 2 * TT / CT: REM NS = NUMBER OF STEPS
210 DT = TT / NS: REM TIME OF ONE STEP
220 REM CALCULATE FIRST STEP
222 FOR X = 1 TO 50
224 TS = (DT * (X / 50))
230 D1 = (TH(0) * (TH(0) + GA)) / (TH(0) * (TH(0) + GA))
240 D2 = (TH(1) * (TH(0) + GA)) / (TH(0) * (TH(1) + GA))
250 DS = D1 - D2
260 I(X) = DS / SQR (TS)
266 NEXT X
270 REM BIG LOOP FOR STEPS 2 TO NS
280 FOR S = 2 TO NS
281 FOR X = 1 TO 50
282 TS = (S - 1) + (DT * (X / 50))
290 I((S - 1) * 50 + X) = 0
300 FL = -1
310 FOR A = 1 TO S
320 IF FL = 1 THEN HJ = TH(2);H1 = TH(1)
330 IF FL = -1 THEN HJ = TH(1);H1 = TH(2)
340 H0 = TH(0)
350 D1 = (H1 * (HO + GA)) / (H0 * (H1 + GA))
360 D2 = (HJ * (HO + GA)) / (H0 * (HJ + GA))
365 TA = (A - 1) * DT
370 I((S - 1) * 50 + X) = I((S - 1) * 50 + X) + (D1 - D2) / SQR (TS -TA)
380 FL = -FL
390 NEXT A
398 NEXT X
400 NEXT S
401 FOR Q = (50 * NS) STEP 50 : I(Q) = 0 : NEXT Q
410 INPUT "FILENAME?"; F$
420 D$ = CHR$(4)
430 PRINT D$; "OPEN"; F$
440 PRINT D$; "WRITE"; F$
450 PRINT (50 * NS); PRINT (DT / 50); PRINT B; PRINT B;
    PRINT B; PRINT B; PRINT B; PRINT B; PRINT B
460 FOR Q = 1 TO (50 * NS); PRINT I(Q); NEXT Q
470 PRINT D$; "CLOSE"; F$
480 END
PROGRAM INTEGRATE LAST CYCLE

BASIC program used to mimic the lock-in amplifier. It first ac couples, and then integrates, the theoretical square wave current waveform.
INTEGRATE LAST CYCLE

2 B = 2
5 REM 7/30/84 SAS
10 REM READS LAST 100 DATA POINTS
20 REM (IE LAST FULL CYCLE)
30 REM OF SQUARE WAVE CURRENT RESPONSE
40 REM IT THEN AC COUPLE
50 REM THE CURRENT RESPONSE
60 REM FINALLY, IT INTEGRATES BY
70 REM TAKING THE AVERAGE BETWEEN
80 REM SUCCESSIVE DATA POINTS
90 INPUT "FILENAME?";F$
100 PRINT CHR$ (4);"OPEN";F$
110 PRINT CHR$ (4);"READ";F$
120 INPUT A
130 FOR I = 1 TO 8: INPUT B: NEXT I
140 DIM A(A)
150 FOR I = 1 TO A: INPUT A(I): NEXT I
160 PRINT CHR$ (4);"CLOSE";F$
170 REM AC COUPLES:
180 REM Z = LOCK-IN AMPLIFIER "ZERO"
190 Q = 0
200 FOR I = A - 99 TO A: Q = Q + A(I): NEXT U
210 Z = Q / 100
220 REM INTEGRATES:
230 INPUT "FILENAME?";F$
240 D$ = CHR (4)
250 PRINT D$;"OPEN";F$
260 PRINT D$;"WRITE";F$
270 PRINT 99: PRINT 0.02: PRINT B: PRINT B: PRINT B: PRINT B: PRINT B: PRINT B
280 Q = 0
290 FOR I = A - 99 TO A - 51
300 Q = Q + ((A(I) - Z) + (A(I + 1) - Z)) * 0.01
301 PRINT Q
302 NEXT I
305 FOR I = A - 50 TO A - 1
306 Q = Q + (ABS (A(I) - Z) + ABS (A(I + 1) - Z)) * 0.01
310 PRINT Q
320 NEXT I
330 PRINT D$;"CLOSE";F$
340 END
PROGRAM WFGEN1

Programs used to generate the synthetic double-modulated current waveform, written by Scott Barnicki.
10 REM N = NUMBER OF PTS. IN WAVEFORM
20 REM FE = MOD FREQ OF POT
30 REM FH = MO FREQ OF VIBR
40 REM DTA = POT MOD AMP (MV)
50 REM EDC = APPL. POT IN MV
60 REM
70 HMOE: PRINT: INPUT "APPLIED DC POTENTIAL (MV):"; EDC
80 PRINT: PRINT: INPUT "POTENTIAL MODULATION AMPLITUDE:"; DTA
90 PRINT: PRINT: PRINT "MAKING WAVEFORM TABLE......"
100 H = 26.5: FE = 1: PI = 3.14159
110 N = 4028
120 FOR J = 0 TO 4027
130 X = (1 / N) * J
140 VEL = (ABS(SIN(2 * PI * FH * X)))
150 SUM = SIN(2 * PI * FE * X)
160 Y = VEL / (1 + EXP(F * (EDC + (DTA * 0.5 * SUM))))
170 A = Y * 409.6 + 2048
180 HB = INT(A / 256)
190 POKE 12288 + J, HB
200 LB = INT(A - (HB * 256))
210 POKE 8192 + J, LB
220 IF J > 0 AND J / 76 = INT(J / 76) THEN HB = HB + 64:
230 POKE 12288 + J, HB
240 IF J > 0 AND J / 38 = INT(J / 38) THEN HB = HB + 32:
250 POKE 12288 + J, HB: IF J = 2014 THEN POKE 12288 + J, HB - 16
260 NEXT J
270 X = PEEK(16315): X = X + 128: POKE 16315, X
280 PRINT: PRINT "DONE"
290 CALL 65338: CALL 65338
300 PRINT: PRINT: PRINT "PRESS ANY KEY TO BEGIN"
310 GET A$
1 DALB EQU $C510
2 DAHB EQU $C511
3 STROBE EQU $C50F    ; D/A STROBE
4 * SET INITIAL CONDITIONS
5   LDY #$00
6   STY $FE
7   STY $FC
8   STA $C058    ; TURN OFF ANN0
9   STA $C05A    ; TURN OFF ANN1
10 * PUT OUT WAVE FORM
11 START   LDA #$20
12      STA $FD
13      LDA #$30
14      STA $FF
15      LDA ($FC),Y
16      STA DALB
17      LDA ($FE),Y
18      STA DAHB
19      STA STROBE
20      INY
21 *PUT OUT PULSES
22      STA $C059
23      STA $C05B
24 *WAIT TIL NEXT POINT
25      LDX #9
26 IWAIT   DEX
27      BNE IWAIT
28 NORMAML   LDA ($FC),Y
29      STA DALB
30      LDA ($FE),Y
31      CMP #$10
32      BLT NORFIN
33      CMP #$20
34      BLT P0OFF
35      CMP #$ 40
36      BGE PUL1
37 *TURN OFF PULSES
38      AND #$0F
39      STA DAHB
40      STA STROBE
41      STA $C05A
42 CHANGE   INY
43      BEQ DEL1
44      LDX #7
45 WAIT1   DEX
46      BNE WAIT1
47      JMP NORMAL
48 DEL1      INC $FD
49      INC $FF
50      LDX #4
51 WAIT2   DEX
NOP
BNE WAIT2
JMP NORMAL
SEND PULSE1
PUL1 CMP #$80
BGE PUL0
STA $C05B
AND #$0F
STA DAHB
STA STROBE
INY
BNE DEL2
INC $FD
INC $FF
LDX #5
WAIT4 DEX
BNE WAIT4
JMP NORMAL
DEL2 LDX #4
WAIT3 DEX
BNE WAIT3
NOP
JMP NORMAL
P0OFF AND #$0F
STA DAHB
STA STROBE
STA $C05B
JMP CHANGE
*END OF WFORM
PUL0 AND #$0F
STA DAHB
STA STROBE
LDY #$00
NOP
NOP
JMP START
NORFIN STA DAHB
STA STROBE
INY
BNE DNORM
INC $FD
INC $FF
LDX #6
WAIT5 DEX
NOP
BNE WAIT5
JMP NORMAL
DNORM LDX #9
WAIT DEX
BNE WAIT
JMP NORMAL
APPENDIX B

Schematic Diagrams of Triple Function Generator
Figure 44. Block diagram of triple function generator used for double modulation voltammetry.

BCD = Binary coded decimal
PLL = Phase locked loop
Prog. down cntr = Programmable down counter
clk = Clock
ref = Reference
vco = Voltage-controlled oscillator
cmp = Comparator
LPF = Low pass filter
clr = Clear
Figure 44
Figure 45. Block diagram of sine wave generator.

A. Symmetry adjustment, +0.04 V.

B. Cusp removal adjustment. Peaked sine wave, +0.12 - +1.3 V.

C. Cusp removal adjustment. Clean sine wave, +0.6 - +3.5 V.