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Robinson, Robert Steven

THE DEVELOPMENT AND USE OF A HIGH SPEED SPECTROELECTROCHEMICAL TECHNIQUE FOR TRANSIENT STUDIES OF THE SOLUTION KINETICS OF CHLORPROMAZINE RADICAL CATION

The Ohio State University

Ph.D. 1984

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THE DEVELOPMENT AND USE OF A HIGH SPEED SPECTROELECTROCHEMICAL TECHNIQUE FOR TRANSIENT STUDIES OF THE SOLUTION KINETICS OF CHLORPROMAZINE RADICAL CATION

DISSERTATION

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

By

Robert Steven Robinson, B.S.

The Ohio State University

1984

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Chapter 1
INTRODUCTION

Existing techniques for the examination of solution charge transfer reactions have been complemented by the development of various electrochemical methods for examining such reactions (1-4). Short-lived reactive species may be generated in a precise manner with a controlled-potential technique, often with better selectivity than competitive methods such as pulse radiolysis. The decay of such species may be monitored by observation of electrochemical cell current (chronoamperometry).

It is necessary and desirable to monitor transient species immediately after their formation. In the realm of chronoamperometry, many techniques have attempted to decrease the time required to charge the electrode-solution double layer and monitor cell electrolysis current. The majority of chronoamperometric techniques are concerned with potentiostatic charging of the double layer, after which the electrolysis current follows more or less predictable diffusion controlled behavior. Methods used to minimize the time required to charge the electrode-solution double layer have included the application of various potential compensation schemes (5-9), elaborate theoretical modeling and construction of potential control
circuitry (6-21), and a galvanostatic charge injection technique (9, 22).

The net conclusion of these workers is that electrochemical studies in the sub-millisecond region are difficult, and those faster than a few hundreds of microseconds are impossible without a time-consuming and elaborate fine-tuning procedure involving the electrochemical cell and potentiostat. Despite the extreme amount of effort devoted to improving electrochemical cell transient response, the best attainable transient response for truly potentiostatic electrolysis has been limited to a few microseconds.

Other attempts at microsecond and submicrosecond electrochemistry have used various pulsed methods for perturbation of the cell and generation of data. Galvanostatic techniques (23-40) inject a small charge into the electrochemical cell, and deduce the behavior of electrogenerated species by monitoring the relaxation of the charge; such techniques have been used for the micro- to submicrosecond time scale. Payne (41, 42) used time domain reflectometry to study double layer characteristics and hydrogen adsorption on the nanosecond time scale. While the temporal resolution of these techniques may appear impressive at first glance, it should be pointed out that because of their pulsed nature, they are not generally suitable for measurements occurring on a longer time scale. Furthermore, neither galvanostatic nor reflectometric methods are designed to attain complete charging of the double layer; they are therefore useless as far as research requiring controlled-potential electrolysis is concerned.
If a product of the electrochemical charge transfer is a chromophore, an optical probe can be used to follow the progress of electrolysis, as was done by Kuwana et al. (43) with an optically transparent tin oxide electrode. While much excellent research has been performed using current measurements, the optical method possesses several advantages. The charging of the electrode-solution double layer, which occurs during a potential step, introduces an error in the current measurement which can obscure information collected at short times (13,44). The optical signal is not affected by the double layer charging current, except for the delay encountered in reaching the desired electrode potential during double layer charging. Because the current measured in chronoamperometry can be comprised of currents produced by several species, optical methods possess greater selectivity; a particular species of interest may be monitored by selecting the appropriate wavelength. This can simplify the deduction of multi-step mechanisms. Spectroscopic monitoring is often the method of choice for the identification of reactive intermediates. Additionally, because the resolution of purely electrochemical techniques limit their usefulness in providing structural information, the addition of a spectroscopic probe is especially valuable in light of the structural information that can be obtained about electrogenerated species.

Generally, the combination of spectroscopy and electrochemistry, or spectroelectrochemistry, involves the use of an optical spectrometry system (light source, detector, and data acquisition system), and an electrochemical cell consisting of working and
counter/reference electrodes and a source of potential or current. The configurations of cell and optics used for the observation of the generation of chromophore, of which four are shown in Figure 1, may be grouped into two categories (namely, those using optically transparent and those using optically opaque electrodes). With optically transparent electrodes (OTEs)(45), the optical beam is transmitted through the electrode, sampling the layer of chromophore generated after stepping the electrode potential. Such electrodes are normally fabricated by the deposition of thin metal films on a transparent substrate such as glass or quartz. Platinum, gold, or tin oxide are commonly used for this purpose.

OTEs may be used for internal reflection spectroelectrochemistry, where the beam is passed at a glancing angle with respect to the electrode surface from the electrode side of the electrode-solution interface. The optical beam passes a short distance (a few hundred nanometers) into the solution, sampling the chromophore being generated near the electrode surface. Unfortunately, in internal reflection spectroelectrochemistry the optical response is strongly dependent upon the incident angle, and the optical properties of the electrode are potential dependent. Knowledge of the refractive indices of the substrate, electrode film, and solution are essential for proper theoretical modeling of this technique. Prediction of the optical response also requires the use of an empirically adjustable penetration parameter(46), which will lead to uncertainty in the interpretation of the results. Additionally, because only the portion of the diffusion layer closest to the electrode (thickness of a few
Figure 1. Four electrode / probe beam configurations used in spectroelectrochemistry: transmission, internal reflection, parallel, and external reflection.
hundred nanometers) is observed, internal reflection experiments are necessarily limited to experiments of only a few milliseconds duration, e.g., experiments where the diffusion layer thickness is less than a few hundred nanometers.

Another OTE configuration consists of a fine mesh screen, or minigrid, normally made of gold because of its high ductility, although gold minigrids with electrodeposited mercury (47) or sputtered platinum coatings have been used. Such electrodes are suitable for steady-state measurements, particularly inside the sample compartment of a conventional spectrophotometer. Minigrid electrodes are often sandwiched between the optical windows of the electrochemical cell, reducing the effective volume of the cell (thin-layer spectroelectrochemistry). Bulk electrolysis of the solution may thus be accomplished in a few tens of seconds, allowing the recording of the spectrum of electrogenerated chromophore.

Other spectroelectrochemical techniques sample the diffusion layer by external reflection; the optical beam enters the diffusion layer from the "outside" of the layer, and is reflected from (48,49), diffracted from (50), or passed parallel (51) to the surface of the electrode. The latter configuration is used in an effort to increase the sensitivity of this technique. Since the absorbance is dependent upon the diffusion layer thickness, the absorbance observed in a single reflection spectroelectrochemical experiment will be small, because the diffusion layer thickness in a typical spectroelectrochemical experiment lasting less than one second will be a few tens of microns or less. Therefore, a strong chromophore and
signal averaging is normally required to obtain useful signals. The path length may be increased by passing the optical beam parallel to or at low angles (52,53) with respect to the electrode surface. Electrodes used for external reflection spectroelectrochemistry include wires or discs fabricated of the desired material.

External reflection was the configuration chosen for this work for several reasons. The sensitivity of this method is at least a factor of two greater than methods using single-pass OTE cells. Since the beam passes through the diffusion layer twice, the optical signal is twice as large as for a transmission experiment. Although the reflectivity of the electrode will be dependent upon the electrode potential (54-60), resulting in a background signal, the experimental conditions may be chosen to minimize its contribution to the total signal. The sensitivity of both transmission and reflection spectroelectrochemistry can be improved with an optical arrangement permitting the optical beam to impinge upon the electrode surface several times, increasing the effective path length of the beam through the diffusion layer. Techniques using multiple reflections for increased sensitivity are particularly sensitive to electrode reflectivity changes during modulation of the electrode potential, because the electrode reflectivity background will be enhanced by the same factor as the absorbance from electrogenerated chromophore.

Operation of an external reflection experiment at glancing incidence will increase the sensitivity of the experiment (52) without also increasing the background absorbance, thereby minimizing the contribution of the background absorbance to the total signal. Because
the electrode reflectivity change during potential modulation is also strongly angle dependent, the beam incidence angle may also be adjusted for the optimum signal-to-background ratio. This method of background reduction is not easily adaptable to multiple reflection experiments because the incidence angle is determined by the cell design.

A wide variety of electrode materials are available for external reflection spectroelectrochemistry. The only requirement is that the electrode material be sufficiently rigid to allow polishing to obtain a reflective surface. The most popular materials are glassy carbon, platinum, and gold. Electrodes constructed of these materials are considerably more rugged than thin film electrodes. Thin film electrodes are very sensitive to both mechanical and electrical damage. Scratches in a thin film electrode’s surface cannot be repaired as easily as a solid metal electrode (polishing). A thin film electrode can be damaged by the passage of high cell currents. This would occur if the reference electrode is accidentally disconnected, or, more often, due to instability in and oscillation of the potentiostat system. Repair of a thin film electrode means construction of a new electrode.

The transient response of an electrochemical cell is primarily dependent upon the product of the values of the cell resistance and capacitance. Thin film electrodes exhibit poor transient response because of the product of their large capacitance and high resistance. While minigrid electrodes possess low resistance, their surface area and therefore capacitance is relatively large. Multiple reflection
techniques (both internal and external) also require a relatively large working electrode, a factor which will contribute to poor transient response. The large cell currents produced during electrolysis with minigrid or thin film electrodes can cause substantial iR drops over the surface of the electrode, resulting in poor homogeneity of potential over the electrode surface. This effect is particularly severe if the electrode is used in a thin layer cell, because of the high resistance of the thin layer of solution. The transient response of minigrid electrodes is further constrained by the fact that a significant optical response is not observed until electrogenerated chromophore has had time to diffuse into the space between the grid wires(61).

Obviously, attempts at minimization of response delay due to double layer charging will benefit the usefulness of an electrochemical technique for kinetic studies, particularly when fast reactions are involved. The previous limit of 4 microseconds for obtaining useful optical signals at a planar electrode(22) represents the state of the art for a potential step technique.

The purpose of the research described here is to extend the usable time scale for the observation of electrochemical processes. Furthermore, the improved transient response of such a technique will be used to advantage in demonstrating its application to the examination of fast solution charge transfer reactions. A particular class of charge transfer reactions involves drugs based on the phenothiazine nucleus. Such drugs, particularly chlorpromazine (CPZ), have proven very useful in the treatment of mental disorders such as
schizophrenia, and have therefore prompted much research into their pharmacology and reactions. The radical cation formed by the one-electron oxidation of chlorpromazine, the structure of which is shown in Figure 2, is a chromophore and is thus amenable to the optical monitoring technique (53).

![Figure 2. Chlorpromazine Radical Cation Molecular Structure.](image-url)
Chapter 2

THEORETICAL CALCULATIONS AND DISCUSSION

1. Introduction

One of the principal goals of this work is the improvement of electrochemical cell transient response for the observation of fast electrochemical processes. The transient response of an electrochemical cell is primarily dependent upon the product of the values of the cell resistance and capacitance. Electrodes with both low surface area and low resistance may be fabricated from gold and platinum wires with diameters of tens of microns. Such electrodes have been used for voltammetric studies (62-70). Electrodes with surface areas of less than $10^{-3}$ square centimeters, hereafter referred to as microelectrodes, possess many advantages over conventional electrodes of greater surface area. The improvement in transient response with microelectrodes is apparent when their low surface area is considered. For a solution resistance of 500 ohms, the rise time of the potential for an electrode with a surface area of 1 cm$^2$ would be $3RC$ or 30 milliseconds, assuming a typical double-layer capacitance of 20 microfarads/cm$^2$. Based upon this argument, the rise time for microelectrodes with surface areas between $10^{-5}$ and $10^{-3}$ cm$^2$ would be
between $3 \times 10^{-7}$ and $3 \times 10^{-5}$ seconds.

The low surface area also results in a proportionately smaller electrical current being passed during an experiment. The current passed during a potential step experiment decays from its initial peak value after the initiation of the potential step, and is equal to the sum of the Faradaic and double layer charging currents.

The Faradaic electrochemical cell current for a diffusion-controlled reduction at a planar electrode is given by (71)

$$i_f = nFAD_{ox}^{1/2}C_{box}^{(1/2)}$$

where $i_f$ = Faradaic cell current (amperes), $n$ = electrons transferred during charge transfer, $F$ = Faraday's constant (96485 C/equiv), $A$ = electrode area (cm$^2$), $D_{ox}$ = diffusion coefficient of the oxidized form of the electroactive species (cm$^2$/sec), $C_{box}$ = concentration of electroactive species (mol/cm$^3$), and $t$ = time (seconds). The capacitive charging current can be calculated from the relation (72)

$$i_c = E_{step}^{(t/RC_{dl})R_s^{-1}}$$

where $E_{step}$ = magnitude of potential step, $R_s$ = solution resistance (ohms), and $C_{dl}$ the working electrode double-layer capacitance (microfarads/cm$^2$). With values encountered in a typical spectroelectrochemical experiment ($n = 1, D = 5 \times 10^{-6}, C_b = 3 \times 10^{-3}, R_s$
500 ohms, $E_{\text{step}} = 0.5V$, $C_{d1} = 20$ microfarads/cm$^2$), the cell current after a time of 1 millisecond has elapsed can be calculated to be 13 milliamperes (assuming an electrode area of 1 cm$^2$). This current imposed upon a cell resistance of 500 ohms will result in a cell potential error of $i \times R$, or over 6 volts.

Differentiation of Equation (2) shows that the value of $i_c$ is maximized for particular values of $R_g$, $C_{d1}$, and $t$; namely, when $t = R_g C_{d1}$. Increasing the value of $R$ will diminish the peak charging current, but will always result in an increase in $iR$ potential error. A plot of $\log(i_c)$ from Equation (2) vs. $R_g$ and $t$ ($C_{d1} = 1F$, $E_{\text{step}} = 1V$) is shown in Figure 3. Note the "hump" in the plot, which occurs at $t = R_g$; $i_c$ is maximized for the $R_g$ and $t$ corresponding to these values. The ripples in the current surface can also be seen as false minima in the solution of $di_c/dR_g = 0$. It is important to note that for a particular value of $R_g$ the peak charging current for microelectrodes and large surface area electrodes will be the same, but the decay of the charging current will occur at a more rapid rate with microelectrodes, because of the latter's lower capacitance. (Direct comparisons of currents based on $R_g$ for different electrodes cannot be made by simply substituting small electrodes for large ones. $R_g$ for microelectrodes will be larger because of their lower surface area, as will be shown.)

The $iR$ error of 6 volts calculated above for large surface area electrodes is an error of serious magnitude in an electrochemical experiment, and is the reason such experiments are conducted with a three-electrode cell configuration. The reference electrode is placed
Figure 3.

Plot of electrode charging current (vertical axis) vs. cell resistance and time (Equation 2). Cell capacitance is normalized to 1.0F. R_s is varied from 1 to 21; t from 0 to 15.
in the feedback loop of an amplifier which controls the cell potential. The amplifier applies a correction potential equal to the error potential. This method is designed to ensure that the working electrode is held at the desired potential. A problem with this approach is that it is not possible to compensate for 100 percent of the iR error, because of the uncompensated potential error which arises over the finite distance between the reference and working electrodes. This uncompensated error is particularly severe immediately after the potential is stepped. The addition of a positive feedback circuit to the basic potentiostat is normally used to minimize the effect of uncompensated potential error. The positive feedback circuit employs a current sensing resistor whose value is analogous to the cell's uncompensated resistance. The value of this resistor is critical for application of the proper amount of positive feedback; the correct value can only be estimated(73), therefore the magnitude of the applied correction may be in error. Furthermore, such control systems have a tendency to become unstable and often oscillate for a short period of time before settling to the desired potential, especially in electrochemical cells with low values of uncompensated resistance(9,74). Low values are encountered when a Luggin capillary tip is used in conjunction with the reference electrode to decrease the effective distance between the reference and working electrodes.

If the surface area of the working electrode is reduced, the (Faradaic) cell current will also be reduced by a proportionate amount. Using the values given above and an electrode area of $10^{-5} \text{ cm}^2$ the potential error appearing across the cell will be less than 60
Table 1. Cell Currents and iR Errors for Different Electrode Areas and Cell Resistances, Calculated With Equations (1)-(2).

<table>
<thead>
<tr>
<th>Electrode Area, cm²</th>
<th>1.0</th>
<th>10⁻³</th>
<th>10⁻⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>100 ns</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i_F)</td>
<td>1.2 A</td>
<td>1.2 mA</td>
<td>12 µA</td>
</tr>
<tr>
<td>(i_{Cl , \text{ohm}})</td>
<td>0.5 A</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(i_{Cl , 500 , \text{ohms}})</td>
<td>-</td>
<td>1 mA</td>
<td>0.37 mA</td>
</tr>
<tr>
<td>(i_R)</td>
<td>850 V</td>
<td>1.1 V</td>
<td>0.19 V</td>
</tr>
<tr>
<td><strong>1 µS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i_F)</td>
<td>370 mA</td>
<td>0.37 mA</td>
<td>3.7 µA</td>
</tr>
<tr>
<td>(i_{Cl , \text{ohm}})</td>
<td>0.48 A</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(i_{Cl , 500 , \text{ohms}})</td>
<td>-</td>
<td>0.9 mA</td>
<td>50 nA</td>
</tr>
<tr>
<td>(i_R)</td>
<td>425 V</td>
<td>0.64 V</td>
<td>1.9 mV</td>
</tr>
<tr>
<td><strong>10 µS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i_F)</td>
<td>120 mA</td>
<td>0.12 mA</td>
<td>1.2 µA</td>
</tr>
<tr>
<td>(i_{Cl , \text{ohm}})</td>
<td>0.30 A</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(i_{Cl , 500 , \text{ohms}})</td>
<td>-</td>
<td>0.37 mA</td>
<td>0</td>
</tr>
<tr>
<td>(i_R)</td>
<td>210 V</td>
<td>0.25 V</td>
<td>0.6 mV</td>
</tr>
<tr>
<td><strong>100 µS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i_F)</td>
<td>37 mA</td>
<td>37 µA</td>
<td>370 nA</td>
</tr>
<tr>
<td>(i_{Cl , \text{ohm}})</td>
<td>3.4 mA</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(i_{Cl , 500 , \text{ohms}})</td>
<td>-</td>
<td>50 nA</td>
<td>0</td>
</tr>
<tr>
<td>(i_R)</td>
<td>20 V</td>
<td>19 mV</td>
<td>0.19 mV</td>
</tr>
<tr>
<td><strong>1 mS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i_F)</td>
<td>12 mA</td>
<td>12 µA</td>
<td>120 nA</td>
</tr>
<tr>
<td>(i_{Cl , \text{ohm}})</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(i_{Cl , 500 , \text{ohms}})</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(i_R)</td>
<td>6 V</td>
<td>6 mV</td>
<td>60 µV</td>
</tr>
<tr>
<td><strong>10 mS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i_F)</td>
<td>3.7 mA</td>
<td>3.7 µA</td>
<td>37 nA</td>
</tr>
<tr>
<td>(i_{Cl , \text{ohm}})</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(i_{Cl , 500 , \text{ohms}})</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(i_R)</td>
<td>1.9 V</td>
<td>1.9 mV</td>
<td>19 µV</td>
</tr>
</tbody>
</table>
microvolts (t = 1 ms). This amounts to an insignificant error in a diffusion-controlled potential step experiment. Indeed, even after only 1 microsecond, the potential error is less than 2 millivolts. Therefore, the need for a potentiostat is eliminated. An advantage to this approach, besides its simplicity, is that active circuitry is no longer required to maintain the potential, which eliminates the speed and instability problems mentioned above. Cell currents and IR errors for different electrode areas, under the conditions mentioned above, are given in Table 1.

*Conditions given in text. IR assumes that diffusion controlled redox potential has been attained. For the 1 cm² electrode, IR indicates the degree of potential compensation necessary with a potentiostatic control system. For the microelectrodes, IR exists between the reference and working electrodes and is the total potential error. R = 1 ohm case is for reference electrode/potentiostat used with large area electrode and Luggin capillary. iC for this case will be current drawn by cell for potentiostatic double-layer charging; this current will be dropped across the cell resistance of 500 ohms. Capacitive currents included in IR calculation.
2. Calculation of Optical Absorbance Signal

As shown in Figure 4, two practical configurations for spectroelectrochemistry with microelectrodes are cylindrical and disc geometry. An electrode with cylindrical geometry (MCE) may be constructed by sealing the wire into a glass capillary so that it protrudes a few millimeters from the tip of the capillary. The optical beam is then reflected from the side of the electrode. Electrical contact is made to the electrode inside the capillary with carbon powder or mercury. Such electrodes, made of platinum, gold, or carbon(75) fibers were used for initial experiments.

The absorbance at a planar electrode for an external reflection spectroelectrochemistry experiment at a normal incidence angle based on the expression derived by Kuwana(76) is given by

$$A = \frac{4}{\pi^{1/2}} \epsilon_p C_r b (D_r t)^{1/2}$$

in which Kuwana's original expression has been multiplied by a factor of two to account for the assumed use of external reflection geometry.

When the incident beam does not impinge on the electrode surface at a normal angle of incidence, the absorbance will be accentuated by a factor that is dependent on the incident angle:
Figure 4. Two practical geometrical configurations for spectroelectrochemistry with microelectrodes. A, cylinder, B, disk.
Figure 5. Geometry of cylindrical electrode with respect to optical probe beam. $\Theta_1$, $\Theta_2$ is the beam incidence angle as defined in the text, $a$ the electrode radius, and $\delta$ a parameter related to the diffusion layer thickness.

\[ A(\theta) = A(n) / \cos(\theta/2) \]  \hspace{1cm} (4)

where $A(n)$ is the absorbance observed for a normal incidence probe beam, and the incidence angle as defined in Figure 5. $\theta$ was defined in this manner to simplify the visualization of the incident angle on a curved surface, as in the case of a cylindrical electrode. Alternatively, defining the incidence angle as the angle of the beam with respect to the electrode surface results in a similar expression to Equation 4, except $\cos(\theta/2)$ is replaced with $\sin(\theta)$. 

The absorbance for MCEs and microdisk electrodes (MDEs) will be equal to that calculated by the equation, provided the diffusion layer thickness is small compared to the electrode radius. When \((Dt)^{1/2}/r_0\) is appreciable, the absorbance for an MCE must be calculated by alternative means to ensure accuracy.

The first approach that was taken involves the double integration of an equation that describes heat transfer from a cylindrical surface. The heat transfer case is exactly analogous to the diffusion of electrogenerated species from the electrode surface. The concentration profile for an electrogenerated species is given by (77)

\[
C_p(r,t) = C_R \left[ \left( \frac{a}{r} \right)^{1/2} \text{erfc} \left( \frac{r - a}{2(Dt)^{1/2}} \right) + \frac{r - a}{4a^{1/2} \tau_{3/2}} + \frac{(9a^2 - 2ar - 7r^2)Dt}{32a^{3/2} \tau_{3/2}} \text{erfc} \left( \frac{r - a}{2(Dt)^{1/2}} \right) + ... \right]
\] (5)

The absorbance vs. time curve may be obtained by substitution of Equation (5) into Equation (6)

\[
A(t) = 2 \int_0^t \int_a^r e_p C_p(r,t) \, dr \, dt
\] (6)

and performing the integration with Simpson's rule. This approach has limited value, however, because the integration converges very slowly at long \(t\), and will yield anomalous concentration values (e.g.,
negative concentrations near the electrode surface). At large t, the higher order terms in Equation (5) contribute more to the integral, and these terms cause the poor convergence.

A more rigorous approach, valid for all t pertinent to these experiments, uses a Laplace transform approach to the heat transfer problem. The solution to the cylindrical case was performed by Carslaw and Jaeger(77) and modified for spectroelectrochemical calculations by McCurdy(78).

The absorbance for a cylindrical electrode can be compared to that for a large planar electrode for various values of the dimensionless parameter \((Dt)^{1/2}/r_o\). Such a comparison is useful to obtain insight into when cylindrical diffusion begins to affect the response for a particular diffusion layer thickness. At short times the thickness of the diffusion layer is still small relative to the size of the electrode, and essentially planar diffusional behavior should be observed. At longer times, the diffusion layer thickness becomes a significant fraction of the electrode radius, and the increasing contribution of cylindrical diffusion becomes apparent. Table (2) gives the absorbance for a cylindrical electrode normalized to that for the planar case, for various values of normalized diffusion layer thickness. It can be seen that a 5% deviation from the planar case exists when the diffusion layer thickness is 10% of the electrode radius. This occurs at a time of 0.49 ms for an electrode radius of 5 microns \((D = 5\times10^{-6}\text{cm}^2/\text{s})\); a 51% deviation would be observed with the same electrode at \(t = 18.8\) s. For a larger electrode radius, the same deviation would be expected at longer times. Figure 6
is a plot of the normalized absorbance vs. normalized diffusion layer thickness data listed in Table 2.

Table 2. Absorbance for a Cylindrical Electrode, Normalized to Calculations Using Equations in Reference 78.

<table>
<thead>
<tr>
<th>$(Dt)^{1/2}/r_o$</th>
<th>$A/A_{\text{planar}}$</th>
<th>$(Dt)^{1/2}/r_o$</th>
<th>$A/A_{\text{planar}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0222</td>
<td>0.993</td>
<td>3.02</td>
<td>0.677</td>
</tr>
<tr>
<td>0.0237</td>
<td>0.975</td>
<td>5.78</td>
<td>0.607</td>
</tr>
<tr>
<td>0.0692</td>
<td>0.959</td>
<td>10.4</td>
<td>0.547</td>
</tr>
<tr>
<td>0.102</td>
<td>0.949</td>
<td>19.4</td>
<td>0.488</td>
</tr>
<tr>
<td>0.165</td>
<td>0.931</td>
<td>30.2</td>
<td>0.450</td>
</tr>
<tr>
<td>0.203</td>
<td>0.922</td>
<td>44.6</td>
<td>0.420</td>
</tr>
<tr>
<td>0.329</td>
<td>0.893</td>
<td>60.0</td>
<td>0.398</td>
</tr>
<tr>
<td>0.365</td>
<td>0.885</td>
<td>74.0</td>
<td>0.384</td>
</tr>
<tr>
<td>0.531</td>
<td>0.856</td>
<td>88.9</td>
<td>0.372</td>
</tr>
<tr>
<td>0.993</td>
<td>0.798</td>
<td>194</td>
<td>0.327</td>
</tr>
<tr>
<td>1.036</td>
<td>0.794</td>
<td>381</td>
<td>0.296</td>
</tr>
<tr>
<td>1.939</td>
<td>0.727</td>
<td>600</td>
<td>0.279</td>
</tr>
<tr>
<td>2.54</td>
<td>0.697</td>
<td>873</td>
<td>0.266</td>
</tr>
</tbody>
</table>

For a microdisk electrode, the calculation of absorbance deviation is considerably more complicated. Deviation from linearity would be expected to occur first at the edge of the electrode, and then progress towards the axis of the disk. Because of the finite diameter of the optical probe beam, some "smearing" of response deviation would be expected because both the central and edge portions of the electrode are monitored simultaneously. For a rigorous theoretical examination of the response, it would therefore not only be necessary to integrate the effect of the electrode edge on the diffusional flux, but also the effect of the transition from planar to spherical diffusion over the radius of the probe beam. This would be
Figure 6.

Plot of normalized absorbance versus normalized diffusion layer thickness for a cylindrical electrode (data from same source as that listed in Table 2).
Normalized Absorbance

Normalized Diffusion Layer Thickness

Figure 6
impractically difficult because of the nonexistence of a closed-form solution to microdisk diffusional behavior which could be successfully integrated to obtain the absorbance vs. time response.

Obviously, careful aiming of the beam at the electrode surface and use of the smallest possible beam radius will allow longer operation under conditions of planar diffusional behavior. This is especially desirable for kinetic studies, because the modeling of kinetic systems is simplest under planar conditions. Because of the complexity of the requisite calculations, a rigorous solution to the microdisk problem was not attempted; the experimental conditions were adjusted empirically to ensure operation under planar conditions.

3. Cell Electrical Parameters

The cell resistance of a two-electrode configuration has contributions from two sources: the solution resistance and the resistance of the electrodes and connecting leads. The resistance of the electrodes can be calculated from the resistivity of the electrode material and the electrode geometry. The solution resistance may be calculated by integration of the resistivity expression (Equation 7) from the working electrode radius to the counter electrode radius, assuming symmetrical placement of these two electrodes, and a cylindrical current field, as shown schematically in Figure 7. A cylindrical working electrode is surrounded by a ring of wire that serves as the counter electrode.
Figure 7. Geometry of cylindrical ring counter electrode with respect to the cylindrical working electrode. Model used for calculation of cell resistance, Equation 7. a, ring counter electrode; b, working electrode. Arrows denote flow of cell current between electrodes.

The total cell resistance is given by Equation (8). The first term arises from the resistivity of the working electrode itself, and is simply the resistivity of the electrode material times its length divided by its cross-sectional area.

$$\rho_s \int_{r_0}^{r_1} \frac{1}{2\pi r_0 h} \, dr$$  \hspace{1cm} (7)

The first term in the expression assumes that the electrode's total length is large relative to both its radius and the length exposed to the solution. The second term in Equation (8) is Equation (7), after integration. This expression assumes that the resistivity of the
counter electrode is negligible compared to the working electrode because of its larger size.

\[ R_{\text{cell}} = \frac{\rho_e L}{\pi r_0^2} + \frac{\rho_s}{2\pi h} \ln \frac{r_1}{r_0} \quad (8) \]

in which \( \rho_e \) = electrode resistivity, ohm-cm; \( L \) = total working electrode length, cm; \( h \) = length of working electrode exposed to solution, cm; and \( \rho_s \) = resistivity of solution, ohm-cm.

The time constant of the cell, \( \tau \), is

\[ \tau = (2\pi r_0 h c^0) R_{\text{cell}} \quad (9) \]

where \( c^0 \) is capacitance per unit area. The above expression assumes the contribution from the exposed end of the electrode to be negligible. Substitution of (8) into (9) gives

\[ R_{\text{cell}} c_{d1} = \frac{2\rho_e L c^0 h}{r_0} + c^0 \rho_s r_0 \ln \frac{r_1}{r_0} \quad (10) \]
Figure 8 is a plot of both RC and R versus electrode radius for a cylindrical electrode. The values were calculated based upon those encountered in a typical experiment \( (\rho_e = 9.8 \times 10^{-4} \text{ ohm-cm (platinum)}, \ h = 0.1 \text{ cm, } L = 1 \text{ cm, } \rho_S = 2.8 \text{ ohm-cm (1M H}_2\text{SO}_4)) \). A minimum in the calculated values for the cell time constant occurs at \( r_0 = 2.5 \) microns, because the increasing resistivity of smaller diameter Pt wires increases the time constant for smaller diameter wires. Since the ohmic potential error increases at smaller radii, the optimum electrode radius would be slightly larger than that value. For the fastest cylindrical microelectrode experiments, platinum wire of 10 microns diameter was used, because of the mechanical strength limitations of platinum.

To minimize its contribution to the total cell resistance, the counter electrode consisted of a saturated calomel reference electrode (SCE) connected in parallel to a platinum wire which was AC coupled to the SCE. The reason for using the dual shunt/reference electrode rather than only a reference electrode (as is the practice in polarography), is that the Pt shunt acts as a low impedance path for the transient current generated immediately after the potential step. A single reference electrode would have degraded the transient response because of its high resistance. After the first few microseconds the cell current is divided roughly equally between the reference electrode and the shunt.

Figure 9 is a simplified equivalent circuit representation of the dual reference electrode. \( C_{18} \) is the isolation capacitor for the shunt; because its value is much larger than the shunt's double layer
Plot of cell time constant and cell resistance vs. working electrode radius. Data calculated from Equation 8, assuming platinum working electrode ($\rho_e = 9.8 \times 10^{-4}$ ohm-cm). Other parameters are: $h = 0.1$ cm, $L = 1$ cm, $\rho_s = 2.8$ ohm-cm (1M H$_2$SO$_4$).
Figure 8: Graph showing Time Constant (μsec) vs. Radius (x 10^4 cm). The graph includes two curves labeled $R_{cell}$ and $R_{cell}C_{dl}$. The y-axis represents Time Constant in microseconds, ranging from 0 to 1.6, and the x-axis represents Radius multiplied by 10^4 centimeters, ranging from 0 to 10.
Figure 9. Simplified equivalent circuit of electrochemical cell used for microelectrode experiments. $E_{app}$, source of applied potential; $E_{ref}$, reference electrode equilibrium potential; $R_{ref}$, reference electrode effective internal resistance; $C_{is}$, isolation capacitor for platinum shunt electrode; $R_{Pt}$, internal resistance of platinum shunt electrode; $C_{Pt}$, double-layer capacitance of shunt electrode; $R_{g}$, sum of total common series resistances of cell (comprised mostly of solution resistance and working electrode internal resistance); $R_f$, working electrode Faradaic pseudoresistance; $C_{dl}$, working electrode double-layer capacitance.

capacitance, its presence does not affect the operation of the circuit. Its purpose is to prevent discharge of the reference electrode through the shunt in the event that a spontaneous redox process could occur at zero volts at the shunt electrode. Because the shunt's internal resistance $R_{Pt}$ (less than 1 ohm) is low compared to the solution resistance, its presence also does not affect the operation of the circuit. $R_{ref}$ is the internal resistance of the reference electrode, and represents the combination of its Faradaic and internal resistances. The emf source of the reference electrode, $E_{ref}$, is shown connected in series with $R_{ref}$. $R_s$ represents the total of the cell's series resistances, mostly arising from the resistances of the solution and the working electrode. $R_f$ is the Faradaic pseudoresistance, and $C_{dl}$ the double layer capacitance of the working electrode.
During the passage of electrolysis current and charging of $C_{d1}$, a charge will begin to accumulate on $C_{pt}$. This will be slowly discharged by $E_{ref}$ through $R_{ref}$. Most of the charge deposited on $C_{pt}$ will be neutralized by the passage of reverse current upon stepping the applied potential to its rest value. Any charge not dissipated immediately after the return step because of diffusion of product from the working electrode will be eliminated by $E_{ref}$. The only constraint placed upon this system is that $t_{wait} > R_{ref}C_{pt}$ during extensive signal averaging, otherwise charging of $C_{pt}$ will occur, impeding proper operation of the circuit.

To prevent reference electrode fatigue, the amount of electrolysis current supplied by the reference electrode in discharging the shunt polarization must be small relative to its capacity as a "battery". This means that the surface area of the working electrode must be small, as in the case of the electrodes used here. The number of moles electroactive species electrolyzed in a typical microelectrode experiment is on the order of a few hundred femtomoles, using the values mentioned above. Taking into account signal averaging, the burden placed upon the reference electrode is approximately several nanomoles. This is easily accommodated by the reference electrode, considering the amount of $\text{Hg/HgCl}_2$ in a typical saturated calomel reference electrode.

Because the area of the Pt shunt is thousands of times greater than the working electrode, the polarization of the shunt will amount to only a few millivolts, which will not degrade cell performance (the degree of polarization of the shunt will be directly proportional to
the magnitude of the potential step times the area of the working electrode divided by the area of the shunt, and would be equal to the polarization of the working electrode if the areas of the two electrodes were equivalent).

As $C_{dl}$ becomes charged and the Faradaic current decays, the effective impedance of the working electrode will increase. As time progresses, $R_{ref}$ drops, and more current will flow through the reference electrode. It should be noted that at the time this occurs, the cell current has decayed to a negligible value, and that the greater proportion of the cell current flows through the shunt, as long as its double layer is relatively unpolarized.

This electrode arrangement differs from that used by Pilla (79) in that it is designed to conduct higher currents, and that complete decoupling of current from the shunt electrode does not occur during the experiment. The value of $C_{ls}$ used by Pilla, 0.01 uF, assures that current flow through the shunt is terminated shortly after the potential step.

Microdisk electrodes may be prepared by sealing electrode wire in a capillary, cutting off the end of the capillary, and polishing the resulting electrode surface. Microdisk electrodes are mechanically more robust than MCEs. They may also be reused after polishing of the electrode surface. For a given electrode radius, the surface area is smaller than that of an MCE. The optical efficiency of an MDE is also greater, because most of the beam reflected from an MCE is scattered and cannot be collected. This becomes important when light sensitive systems are studied and the optical intensity must be kept to a
minimum. Because the optical intensity requirements are relaxed, for most experiments a less intense but more versatile xenon arc source may be used in place of a laser. The desired wavelength is selected by simply inserting a narrow bandwidth interference filter into the optical path.

The cell resistance between a microdisk and distant reference electrode is (80)

\[ R_{\text{cell}} = \frac{p_s}{4r_0} \]  

(11)

Given that the capacitance of the disk electrode is \( r_o^2 C^0 \) where \( C^0 \) is the integral double-layer capacitance per unit area, the cell time constant is therefore

\[ R_{\text{cell}}C_{\text{d1}} = \frac{\pi p_s C^0 r_0}{4} \]  

(12)

In contrast to the cylindrical case, the cell time constant is linearly dependent upon the electrode radius (provided the internal resistance of the wire is negligible). Decreasing the electrode radius should therefore lead to an improvement in cell time constant, for any radius of microdisk electrode considered.
4. Further Improvements in Cell Transient Response

Obviously, there exists a practical limit to electrode miniaturization. Rather than carry this aspect of electrode design to an extreme, a sophisticated potential control system for improving transient response was devised. The circuit is based upon the technique introduced by Bewick and Fleischmann(9), and implemented by Davis and Winograd(22). It consists of a small capacitor which is charged to a high voltage. The charge stored by the capacitor is dumped into the cell with a fast electronic switch(81,82) (Figure 10). The intended result is charging of the electrode double layer on a nanosecond time scale, much faster than the "natural" risetime of the electrode potential predicted by 3RC (dotted curve in Figure 11).

After charging of the electrode double layer is accomplished by the injected charge, the potential is maintained at the desired value and electrolysis current supplied by the pulse generator. The time constant of an electrochemical cell assisted by charge injection is(22)

\[ \tau = R_{\text{cell}} C_{\text{inj}} \]  

(13)
Figure 10. Block diagram/simplified schematic of charge injection circuit. Pulse generator supplies electrolysis potential to cell and triggers switch used to connect injection capacitor across the cell.
Figure 11. Representation of working electrode potential vs. time. Dotted line is potential rise in absence of charge injection; curve shape is determined by product of cell resistance and capacitance. Spike-shaped curve is potential waveform produced by charge injection circuit and applied to cell; square-edged curve is desired working electrode potential versus time response.

where $C_{\text{inj}}$ is the value of the injection capacitor. For complete double-layer charging, the charge stored by $C_{\text{inj}}$ ($Q_{\text{inj}} = C_{\text{inj}} E_{\text{inj}}$) must be equal to the charge required to charge the working electrode double layer to the desired potential ($Q_{\text{cell}} = C_{\text{dl}} E_{\text{step}}$). The approach taken in this work was to use the maximum possible value for $E_{\text{inj}}$ (determined by the breakdown voltage of the switching transistor, $Q_1$) and adjust $Q_{\text{inj}}$ by varying the value of $C_{\text{inj}}$. This will give the best possible time constant for the circuitry employed. Typical values for $C_{\text{inj}}$ when used with microelectrodes are between 0.25 and 150 pF. If

$$Q_{\text{cell}} = Q_{\text{inj}} \quad (14)$$

then

$$C_{\text{dl}} E_{\text{step}} = C_{\text{inj}} E_{\text{inj}} \quad (15)$$

and
The cell rise time, $3 \tau$, is therefore

$$3 \tau = 3R_{cell}C_{dl}E_{step}/E_{inj}$$  \hfill (17)

The improvement in rise time anticipated with charge injection is therefore $E_{inj}/E_{step}$. For $E_{inj} = 200$ volts and $E_{step} = 0.5$ volts, the risetime would be improved by a factor of 400. The actual improvement observed can be significantly less than this, because of mismatches in injection circuit/cell impedances, and the fact that cell capacitance does not exhibit ideal capacitive behavior. This will be particularly severe at short times (less than 100 ns). The effects of $Q_1$ switching time in this circuit and transmission line capacitance must also be taken into account. Also, the inductance of the cell wiring will result in a high cell impedance at high frequencies, greatly increasing the apparent cell time constant. The inductance and therefore high frequency impedance can be reduced by coaxial working/counter electrode geometry, which will improve the transient response of the cell.
Chapter 3
EXPERIMENTAL SECTION

1. Cylindrical Microelectrodes

Microelectrodes with cylindrical geometry were prepared from carbon fibers, platinum, or gold wires. Carbon fiber microelectrodes were constructed by inserting a fiber into the small end of a disposable pipet so that it protruded about 1 mm from the end of the pipet. The fiber was rinsed with acetone (Eastman electronic grade) to remove the layer of sizing, and sealed into the pipet with jeweler's wax. Electrical contact to the fiber was made with mercury.

Fibers from two sources were used for experiments. 12 micron fibers ("Thornel 32") were obtained from Union Carbide, and 9 micron fibers ("Rigilor AGT") from Serofim (Gennevilliers, France). The latter fibers swelled to 12 microns after electrochemical experiments, and this diameter was used for calculations.

Construction of metal microelectrodes was similar, except a small amount of graphite powder was placed in the pipet to prevent contact of the wire with mercury, which would result in amalgamation and dissolution of the wire. It was found preferable to trim the wire length before mounting because the electrode was very sensitive to
mechanical damage after mounting.

The wires obtained from Goodfellow Metals Ltd. (U.K.) were gold wire of 60 microns diameter, platinum (1, 10, 25, 50, and 125 microns diameter), Pt87/Rh13, and Pt87/Ir10 (both 50 microns diameter). 12.8 micron gold wire was purchased from Consolidated Refining Co. (Mamaroneck, NY). Platinum (225, 300, and 826 microns) and Pt87/Ir10 (405 microns) were obtained from VWR Scientific Co. (Columbus, OH).

The operational amplifier/voltage follower used as a potentiostat for cylindrical and the slower (greater than 100 mS) disk microelectrode experiments was a Tektronix AM501 amplifier (maximum output ± 40 V at 50 ma, unity gain bandwidth 5 MHz). The reference electrode (SCE, used for all spectroelectrochemical experiments) was connected to the inverting input of the amplifier. The auxiliary electrode (20 gauge X 4 cm Pt wire) was connected to the output, and the amplifier stabilized by a 50 pF capacitor connected between the output and inverting input. The DAC of the computer (Hewlett-Packard 21MX1000) applied potential pulses to the noninverting input. A schematic of the potentiostat is shown in Figure 12.

For the high speed cylindrical microelectrode experiments, the cell was connected directly across the output of the computer DAC (Datel VR12B3C). The DAC settling time (1%) was less than 2 microseconds, and its risetime (90%) was 250 ns. The working electrode was a 10 micron X 1mm platinum wire. The counter electrode consisted of an SCE connected in parallel to a 20 gauge X 4 cm platinum wire which was AC coupled to the SCE with a 20 microfarad capacitor, as described in Chapter 2. No special attention was paid to electrode
placement, because it has little effect on cell resistance. A diagram of the experimental setup for the direct electrode connection used with microcylindrical electrodes is shown in Figure 13.

![Diagram of operational amplifier potentiostat](image)

**Figure 12.** Schematic of operational amplifier potentiostat used for some electrochemical experiments. Amplifier used was Tektronix AM501 (+ 40V at 50 mA); $E_{\text{applied}}$ = source of applied potential. Capacitor in amplifier feedback loop assures stability of amplifier by compensating stray reactances.

The optical arrangement is shown in Figure 14. The focused laser beam was collected by a fiber optic light guide after reflection from the working electrode. The guide was placed in the solution to minimize refractive index mismatch and light loss. The cell was
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Figure 13.

Apparatus for spectroelectrochemistry with cylindrical microelectrodes with a two-electrode configuration.
Figure 13. Apparatus for spectroelectrochemistry with cylindrical microelectrodes with a two-electrode configuration.
Figure 14. Experimental arrangement used with cylindrical microelectrodes, all components mounted on optical table.
constructed of 1/16 inch Pyrex. Two adjacent sides of the cell were oriented at the Brewster angle to ensure that light scattered randomly by the electrode exited the cell without being collected by the light guide. Light exiting the fibers was collimated with a 12mm focal length lens and directed onto a 1P28 photomultiplier. Scattered light entering the light guide accounted for less than 1% of the total input, as assessed by moving the electrode out of the path of the beam. The fiber was positioned 1 cm away from the electrode, a distance which represented a good compromise between angular discrimination and light input. The output of the photomultiplier was processed by an operational amplifier (Analog Devices 40J) current to voltage converter (Figure 15). Filtering of input noise was accomplished by selection of the appropriate filtering capacitor with switch S1. Unfortunately, it was discovered that the 10 pF capacitor caused instability of the operational amplifier, probably because of the stray capacitances presented to the inverting input of the amplifier. The use of that position of S1 was therefore avoided.

The light source was an argon ion laser (Spectra-Physics 164-09) operated at 514.5 nm, or in broadband mode when pumping the dye laser (Spectra-Physics Model 375/376). The lasing medium used in the dye laser was rhodamine 6G dissolved in ethylene glycol, which allowed stable lasing at wavelengths from 568 to 650 nm. An etalon in the cavity of the dye laser decreased its linewidth to a rated 0.05 nm(83). The wavelength of operation of the dye laser was determined by directing a small portion of the beam into a monochromator (J-Y, bandpass 0.2 nm). A Spectra-Physics Model 120, 5 mW helium-neon laser
Figure 15. Schematic diagram of current to voltage converter used for processing of signal from photomultiplier in experiments with cylindrical microelectrodes. S1 selected capacitor for desired amount of filtering; diodes were for amplifier (Analog Devices 40J) protection.
was also used.

The laser beam was focused on the electrode by a 267 mm focal length lens. The beam waist at the focal point was approximately 180 microns. The beam intensity was controlled by adjustment of the light intensity control of the laser power supply. The laser was operated in the optical feedback light control mode to minimize beam noise. Large attenuations of the beam intensity were accomplished with the use of neutral density filters (Melles-Griot, optical density (O.D.) 0.5 to 3.0, and Ealing Optical, O.D. 2.0 high power laser filter).

The laboratory computer was used for potential control and data acquisition in all cylindrical electrode experiments reported here. The maximum data acquisition rate was 5 microseconds per point, with the first point being taken after 4 microseconds. For spectroelectrochemical runs, the duty cycle \( T_{\text{step}}/T_{\text{wait}} \) was 1%. The duty cycle was randomized over the period of one line voltage cycle to prevent synchronization with AC line noise.

The test reactions included o-dianisidine (O-D), benzyl viologen (BV), and methyl viologen (MV). Other possible systems included o-tolidine (O-T) and trianisylamine (TAA). O-T was not used because of its limited solubility, and TAA was inferior to the other systems in the context of this experiment because it required a nonaqueous electrolyte; solutions of TAA in acetonitrile also discolored quickly, indicating a short useful lifetime. O-D has a diffusion coefficient of \( 0.44 \times 10^{-5} \text{ cm}^2/\text{s} \) and a molar absorptivity of 22700 M\(^{-1}\) cm\(^{-1}\) at 515 nm in 1M H\(_2\)SO\(_4\)\(^{(85)}\). An absorbance vs. wavelength curve (bandpass 0.5 nm) was determined for O-D after oxidation by stoichiometric (1:2)
Ce(IV) (respectively). The absorbance at 505 nm was 4 percent greater
than that at 515 nm. The O-D (Sigma Chemical Co. anhydrous grade
510-50) was used without further purification. Other grades of O-D
gave inconsistent results. MV dichloride (Aldrich, D = 0.86 x 10^-5
cm^2/s(86)) was dried and purified by recrystallization from a
saturated solution in methanol by addition of acetone(86).
Electrochemical experiments with methyl and benzyl viologen were
performed in pH 7.0 phosphate buffer. For routine experiments the
buffer concentration was 0.3M, but 2M buffer was used for high speed
runs owing to its lower resistance. This concentration represents a
nearly saturated solution. The buffer was prepared by dissolving the
desired amount of K_2HPO_4 in distilled water and adjusting the pH with
phosphoric acid while monitoring the pH with a pH meter. The molar
absorptivity of MV was reported to be 12400 M^-1cm^-1 at a wavelength of
605 nm(86,87). This value could not be replicated, the experimental
results indicating a lower molar absorptivity, especially in the 2M
buffer. The concentration dependence of viologen spectra reported by
Van Dorn and Ponjee(88) could be partly responsible for the lower
absorptivity observed here, because the concentrations employed for
the studies in (86) were 5 to 10 times lower than in this work.
Despite the lower absorptivity obtained here, methyl viologen
exhibited good absorbance vs. t^{1/2} response. Therefore, the absorbance
vs. time response of a given run was judged empirically by comparison
with a longer run, when necessary. Benzyl viologen (molar absorptivity
10100 M^-1cm^-1 at 595 nm, diffusion coefficient 4.3 x 10^-6 cm^2/s(86),
ICI) was used without further purification.
2. Microdisk Electrodes

For the initial experiments with microdisk electrodes, the rectangular (3x3x5 cm) glass cell was glued to an aluminum support (Figure 16). A hole at the rear of the cell allowed insertion of the electrode, with sealing accomplished by a rubber O-ring glued to the inside cell wall. The Pt counter electrode was inserted through another hole in the rear of the cell and sealed with epoxy. Connection to the electrode was made via BNC connector. The working electrode was soldered to a BNC connector, sealed in 8mm OD glass or acrylic tubing with epoxy resin (Buehler Castolite), and polished with sandpaper (200 to 600 grit), diamond compound (15 to 1.0 micron) and alumina (particle size 1.0 to 0.05 microns). The wire electrode materials used were the same types and sizes used for the cylindrical microelectrode experiments. The Castolite did not dissolve appreciably in the supporting electrolytes used, and exhibited fairly good adhesion and sealing to the electrode. This cell was used for the non-coaxial electroreflectance experiment, and the initial high speed MV spectroelectrochemical run.

An improved version of the cell was constructed. The working electrode was sealed into a 7/25 ground glass standard taper joint, which mated with a corresponding female joint on the cell. The new cell featured a water jacket for thermostating of the cell, allowing precise temperature control for kinetic experiments. A Textronix DM
Figure 16. Diagram of cell (top view) used with non-coaxial microdisk electrodes. A: BNC connectors; B: cell wall (1/16" Pyrex); C: Platinum shunt/counter electrode; D: optical probe beam; E: microdisk working electrode; F: aluminum support.
A digital multimeter/thermometer was used to monitor the temperature of the water circulated in the water jacket; a Braun Thermomix 1420 heater/circulator controlled the water temperature. The temperature of the water could be maintained within ± 0.1°C for a 24 hour period without adjusting the circulator. A temperature of 25.0°C was used for kinetic experiments.

The cell was constructed of Pyrex tubing. Two 2-cm lengths of 50 and 60 mm ID Pyrex tubing were positioned concentrically, the interstitial space serving as the water jacket after sealing the ends of the tubing together. Four female joints were sealed to a glass plate which was sealed to the cell and served as the back wall of the cell. Working, reference and counter electrodes were inserted into the joints, the fourth joint serving as a connection for purging of the cell. The front Pyrex window was glued to the cell with epoxy (Torr-Seal, Varian, Inc.). The internal volume of the cell was approximately 100 ml. A smaller version of the cell, shown schematically in Figure 17, was constructed entirely of Pyrex and designed for use with coaxial working electrodes. The inside diameter of this cell was 20 mm, and the internal volume 6 ml. A joint concentric with the cell was used for working electrode mounting, and the reference electrode was mounted in a second joint which entered the cell on an axis perpendicular to that of the other joint, penetrating and extending through the water jacket. After initial optical alignment, the electrode could be removed for polishing or changing solutions and easily replaced and returned to the original alignment with a minimum of effort. This is impressive, considering the degree
Figure 17.

Diagram of cell (side view) used for experiments with coaxial microdisk electrodes.

Figure 18.

Diagram of face of coaxial electrode.
Figure 17

Coaxial electrode Face

Figure 18
of mechanical precision required to consistently bring a 50 micron
diameter electrode and focused optical beam into alignment. A
schematic of the face of a coaxial microdisk electrode used with the
cell is shown in Figure 18.

Light sources included the lasers already mentioned, and a xenon
arc lamp. The lamp housing (Kratos LH 150/1) and power supply (Model
LPS251HR) were used with 75 and 150 watt lamps. The 75 watt lamp gave
the most stable output because the smaller size of the arc made it
less susceptible to wander. A Kratos Model 1144 optical feedback
amplifier reduced output beam line frequency noise by approximately 50
percent. The beam was collimated with the manufacturer's pinhole (40
micron) collimator. The desired wavelengths were selected by filtering
the resulting beam with bandpass interference filters (Edmund
Scientific, bandpass 10 nm).

A schematic of the cell's optical arrangement is shown in Figure
19. The laser or arc lamp beam was focused on the electrode with a 30
mm f.1. lens, after preliminary focusing with a 267 mm f.1. lens. When
the beam was properly focused on the electrode, the reflected beam
produced a well-defined circular image when projected on a flat
surface. This beam was collimated with a 30 mm f.1. lens, and directed
to the 1P21 photomultiplier. The collimated beam could be directed
over a distance of several meters without appreciable loss of
intensity. The fiber optic light guide was not used for the microdisk
electrode experiments, to maximize light throughput. This allowed the
source intensity to be kept as low as possible to minimize thermal
beam absorption effects.
Figure 19. Experimental arrangement used with coaxial microdisk electrodes, all components mounted on optical table.
The photomultiplier housing for the high speed microdisk experiments was a specially-designed RF-shielded unit (Pacific Photometric Model RF-50B). This eliminated the pickup by the photomultiplier of RF spikes produced by the charge injection circuit. To illustrate the effect of RF noise, the a spectroelectrochemical experiment was performed with the working electrode disconnected, and a dummy cell \( (R = 100 \text{ ohms}, C = 0.47 \text{ nF}) \) connected in place of the electrochemical cell. The PMT housing was a standard (non-shielded) unit. Figure 20 is the result of such an experiment. The apparent absorbance change is due to RF interference. A similar effect of smaller magnitude was observed when a simple potential step without charge injection was used (which produced less RF interference). The false signal was completely eliminated when the shielded housing was substituted for the standard housing.

The operational amplifier potentiostat described earlier was used with microdisk electrodes of diameters greater than 225 microns, and for experiments longer than 160 mS with all electrodes. For the faster experiments with smaller electrodes, the charge injection circuit described in Chapter 4 was used. A block diagram of the microdisk electrode/charge injection/data acquisition system is shown in Figure 21. The pulse generator applied potential steps to the cell, and triggered the charge injection unit. The duty cycle of the pulses was controlled by adjustment of the pulse generator. For slower runs, it was desirable to vary the duty cycle over the period of one line voltage cycle to minimize the effects of line frequency noise on the measurements. To accomplish this, a second pulse generator with a
Figure 20.

False signal recorded when PMT was mounted in standard housing. Working electrode disconnected and output of charge injection connected to dummy cell (100 ohms in series with 0.47 nF). Experimental conditions same as for high speed (non-coaxial) microdisk electrode runs; 3.16 million runs were averaged.
Figure 20

TIME

ABSORBANCE X 10^4
Figure 21.

Block diagram of experimental apparatus used with high speed (non-coaxial) microdisk electrode experiments. Pulse generator triggered data acquisition system and applied potential steps to electrochemical cell. Not shown is 3rd order lowpass filter for signal from photomultiplier, and second pulse generator used for setting duty cycle.
Reference CELL

POWER SUPPLY

SOURCE
(Collimated and filtered Xe arc, laser)

[Collimated and filtered Xe arc, laser]

PHOTOMULTIPLIER

Pt Shunt

Working Electrode

2N6661

CHARGE INJECTION CIRCUIT

0.25-150pF

20 μF

E_{cell}

PULSE GENERATOR

Trig. Generator

Trig. out

APPLE II
MICROCOMPUTER

IEEE 488 BUS

Trig. Signal

WAVEFORM PROCESSOR

LH0033C

R_{load}

PMT SUPPLY

Figure 21
frequency sweep capability was used to trigger the pulse generator used to supply pulses to the cell. The frequency sweep varied the duty cycle because the experiment repetition rate depended upon the output frequency of the second pulse generator. The use of the second pulse generator also allowed the pulses to the working electrode to be interrupted during the time when the oscilloscope was performing the absorbance calculation. This minimized the total number of pulses applied to the electrode in a given experiment, in the interest of prolonging electrode life. A DIP solid state relay was used to interrupt the trigger pulses from the second pulse generator to the cell's pulse generator, which was set for external triggering. The relay was closed by a TTL voltage output from the oscilloscope. The TTL voltage was programmed to go into the "low" state when data was not being collected. Simply connecting the relay to the TTL output resulted in an extreme amount of noise being imposed on its output; decoupling of the TTL signal with a lowpass network (R = 50 ohms, C = 10 uF) essentially eliminated the noise.

To take advantage of the improved transient response afforded by the reduced surface area of the microdisk electrode, a Tektronix 7854 waveform processing oscilloscope with the capability of nanosecond time resolution was used for data acquisition and processing for all microdisk electrode experiments. The oscilloscope was programmed (program listing in Appendix) to calculate the optical absorbance from the averaged data. The pulse generator used for potential control was adjusted for a time delay between triggering of the oscilloscope and application of potential to the cell. Data points obtained during the
delay period were used to determine \( I_0 \) for calculation of absorbance. 10 to 50 data points (depending on the points used per waveform) prior to the potential step were averaged for this purpose. Data from the oscilloscope was transferred (program listed in Appendix) to an Apple II computer via 488 interface for storage and further processing.

Cyclic voltammetry was performed with a BAS Model CV-1B function generator and Houston Instruments Model 2000 X-Y recorder.

3. Kinetic Studies With Microdisk Electrodes

The investigations of reaction kinetics of chlorpromazine radical cation were carried out with microdisk electrodes. Several buffer systems were used to cover the pH range from 1.6 to 7.5. The general procedure in making the buffers was to weigh out enough acid to give a concentration of 0.2M acid. The pH was adjusted by adding enough KOH to produce a concentration of KOH between 0.06 and 0.18M. The ionic strength was then adjusted to a value of 1.8 by adding an appropriate amount of KCl. This concentration represents nearly a saturated solution of KCl/buffer in the working solution; high ionic strengths were used to minimize solution resistance. Appropriate amounts of the above chemicals were dissolved in distilled water to make a concentrated stock buffer solution. The stock buffer solution was combined with an equal volume of methanol. After mixing and cooling to 25\(^\circ\)C, the resulting solution was brought up to a volume equal to twice the original volume of methanol added, with distilled water. The
initial mixing was accomplished with the stream of argon bubbled through the solution for deaeration. More vigorous methods of mixing caused rapid heating of the solution and boiling of the methanol, resulting in violent ejection of solution from the flask. The concentrations mentioned above refer to the final resulting concentrations in the working solution. The composition and pH of buffers used for experiments are given in Table 3.

Table 3. Composition and pH of Buffers.

<table>
<thead>
<tr>
<th>Acid</th>
<th>(KOH), M</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₂COOH</td>
<td>0.00</td>
<td>1.58 ± 0.01</td>
</tr>
<tr>
<td>CHCl₂COOH</td>
<td>0.06</td>
<td>1.885 ± 0.03</td>
</tr>
<tr>
<td>CHCl₂COOH</td>
<td>0.18</td>
<td>2.695 ± 0.01</td>
</tr>
<tr>
<td>CH₂ClCOOH</td>
<td>0.06</td>
<td>3.090 ± 0.01</td>
</tr>
<tr>
<td>CH₂ClCOOH</td>
<td>0.10</td>
<td>3.475 ± 0.01</td>
</tr>
<tr>
<td>CH₂ClCOOH</td>
<td>0.18</td>
<td>4.145 ± 0.03</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>0.10</td>
<td>5.31 ± 0.03</td>
</tr>
<tr>
<td>(CH₃)₂AsO₂H</td>
<td>0.10</td>
<td>6.79 ± 0.03</td>
</tr>
<tr>
<td>(CH₃)₂AsO₂H</td>
<td>0.18</td>
<td>7.53 ± 0.03</td>
</tr>
</tbody>
</table>

The reactions of chlorpromazine with dopamine, hydroquinone, and ascorbic acid were studied. Kinetic runs had equimolar concentrations of chlorpromazine and the other reactant; the concentration used for all runs, unless otherwise noted, was 2 millimolar. The wavelength monitored was 520 nm, selected by filtering the beam from the arc
source with an interference filter. Platinum microdisk electrodes were used for all kinetic experiments. The size of the disk was chosen to provide maximum absorbance linearity over the time scale of the experiment. This meant selecting the largest radius disk which would still give acceptable transient response.

For the kinetic experiments occurring on the fastest time scales, the beam was directed at a small angle with respect to the electrode surface for sensitivity enhancement. This also minimized the background absorbance and its contribution to the total signal. The angles employed were approximately 23 and 15 degrees, determined empirically by calculation of the angle from the observed absorbance enhancement. The range of angles employed were limited by the difficulty of focusing the beam on the microelectrode at glancing incidence. As the incidence angle decreased, the size of the "footprint" of the beam on the electrode increased. At a certain point the edge of the beam began to spill off the edge of the microelectrode, and it became difficult to discriminate from such scattered light and the light which was reflected only from the electrode. Therefore, for maximum accuracy, a 125 micron diameter electrode and (calculated) incidence angle of 23 degrees was employed for all glancing incidence kinetic experiments.

All kinetic runs employing dopamine and hydroquinone were performed with a potential step from 0.0 to 0.82 volts vs. SCE. The experiments with ascorbic acid used a rest potential between -0.25 to -0.30 volts, rather than 0.0 volts. This was done to ensure that this compound was not being oxidized at the rest potential, because its
oxidation potential lies at a more negative value than that of the other two systems. Additionally, the duty cycle was 0.1% for ascorbic acid experiments, because its oxidation is irreversible on the time scale of these experiments and a longer time must therefore be allowed to re-establish the initial conditions of the experiment.

Calculation of kinetic information from the data was facilitated by the use of the digital sampling oscilloscope. Reference and kinetic runs were stored in memory and divided point by point to obtain the normalized absorbance vs. time curve used for rate constant calculation. A computer program (listing in Appendix) written in Basic for the Apple II microcomputer was then used to calculate rate constants from the data after transfer to the Apple. The working curve used for calculation of rate constants was Case 2 from Reference 53.
Since the instrumentation required for fast potential control and signal processing was not available commercially, the design and construction of circuitry suitable for fast spectroelectrochemistry was undertaken. This chapter discusses the design goals and philosophy of such circuitry, as well as a description of pertinent circuit configurations. A discussion of the interfacing of this circuitry with the experiment will also be given.

1. Potential Control Circuitry

Two methods of potential control were used for the experiments performed in this work. A schematic of the operational amplifier potentiostat used for some of the experiments is shown in Figure 22. The amplifier was a Tektronix AM501 plug-in operational amplifier module, with easily accessible binding-post terminals for the connection of electronic components. The reference electrode connected to the inverting input senses the solution potential and applies a correction potential if the solution potential is different from the
Figure 22. Schematic of operational amplifier potentiostat used for some electrochemical experiments. Amplifier used was Tektronix AM501 (+ 40V at 50 mA); $E_{\text{applied}}$ = source of applied potential. Capacitor in feedback loop assures stability of amplifier by compensating stray reactances.

applied potential. Since the inverting input operates at a virtual potential equal to that applied at the noninverting input, any difference in solution potential and the applied potential will cause current flow through the feedback loop until the two potentials are equalized. Since the cell is normally some distance away from the control amplifier, stray capacitances and inductances are present
which will cause instability in the control amplifier. This instability is dampened by the installation of a small (50 pF) capacitor into the feedback loop of the amplifier. The capacitor selected should be as small-valued as possible, as overcompensation of stray reactance will result in loss of speed in the control amplifier. The component values used result in a transient response of the potentiostat of 10 to 50 microseconds, when driving an electrochemical cell. This potential control method should therefore be used only for experiments requiring a time resolution of greater than a few tens of microseconds.

The rationale for eliminating the potentiostat in microelectrode experiments was discussed in Chapter 2. The circuits depicted in Figures 24 and 25 may be divided into two main parts, the charge injection circuit and the potential control/protection circuit. A simplified schematic/block diagram of the charge injection circuit is depicted in Figure 23.

The charge injection circuit consists of an electronic switch which is used to switch a small-valued capacitor charged to a high voltage across the cell. The primary consideration in the design of the circuit is the selection of the switch. The switch must possess fast (less than 10 ns) switching time, have a sufficiently high (100 V) breakdown voltage, and low (less than 20 ohms) "on" resistance. These requirements are satisfied by a power field effect transistor, such as a 2N6658 or 2N6661. Such transistors have a turn-on time of under 5 ns, "on" resistance of 3 ohms, and breakdown voltage of
Figure 23. Block diagram/simplified schematic of charge injection circuit. A small capacitor charged to a high voltage was used to quickly charge the double-layer of the working electrode. Capacitor was switched across cell by a fast electronic switch triggered by the pulse generator.
90V(81). It was determined experimentally that the latter parameter was somewhat conservatively rated, at least for the present application, and the FET could be operated at voltages of up to 230 volts without apparently sustaining damage.

The capacitor selected should possess a sufficiently high voltage rating and fairly low inductance and dissipation factor. These requirements are best met by fixed value capacitors, for example polystyrene (best)(89,90) or silvered mica (more values available). Because the optimum value of this capacitor is dependent upon cell parameters (cell capacitance, magnitude of potential step, cell resistance), a variable capacitor was used because of the greater convenience of capacitance adjustment. Large changes in the value of the injection capacitor were made by parallel connection of fixed polystyrene or mica capacitors, with subsequent fine-tuning done by adjustment of the variable capacitor. This approach did not exhibit any noticeable performance loss over the use of fixed capacitances, and the convenience of capacitance trimming was a significant time saving advantage. Trimmer capacitors used included a Teflon dielectric trimmer (0.25-1.5 pF), and ceramic and film trimmers (6-25 pF, 0.8-10 pF, 6-60 pF). The smaller-valued trimmers were obtained from Mouser Electronics (California), and the 6-60 pF from Radio Shack.

High voltage power supplies included a Kepco Model BOP 36-1.5M high voltage operational amplifier (0-65V), and a KH 11HR-220 tube power supply (0-500V). The supply isolation resistor, R15, prevented large amounts of current from being drawn from the supply during FET
switching. The maximum repetition rate of the charge injection circuit is set by the value of this resistor and the size of the injection capacitor.

The two versions of the charge injection circuit shown schematically in the figures above differ principally in that the circuit in Figure 24 incorporates features to make its operation more convenient. The toggle switches were used to verify the operation of the various sections of the circuit, and to make cell polarity changes easier. Cell current could be measured by opening the \( R_M \) bypass switch, and observing the \( iR \) drop across \( R_M \). The circuit shown in Figure 25 is a no-compromise version of the circuit in Figure 24, and special attention was paid to circuit layout. All circuitry not essential to the performance of the circuit was eliminated. Toggle switches were not used because of the possible contribution to stray capacitance and inductance. The cell was connected to the circuit with a length of RG58U cable soldered directly to the circuit board; polarity changes therefore required the use of a soldering iron.

The following description of the operation of the circuit in Figure 25 may also be generally applied to that in Figure 24.

Complementary pulses from the dual-output function generator are applied to the terminals designated as \( E_{CELL} \) IN and TRIG. Since the resolution of the pulse amplitude controls of the pulse generator did not permit the precision in voltage adjustment necessary for an electrochemical experiment, large amplitude pulses from the pulse generator were divided down to the desired value with precision
Figure 24.

Schematic diagram of first prototype charge injection circuit. Toggle switches enabled activation of special features of circuit. Pulse generator rectification circuit could be disabled by closing the switch labeled "PG PROTECT". Crude chronoamperometry experiments could be performed by opening the $R_M$ BYPASS switch, and monitoring the voltage appearing across $R_M$. The charge injection circuit could be easily disabled by opening the high voltage switch. Other circuit details explained in text.
Figure 24
Figure 25. Schematic diagram of charge injection circuit used with coaxial microdisk electrodes. Operation explained in text.
potentiometers $R_5$ and $R_{13}$. This also effectively reduces the Thevenin output resistance of the pulse generator, which is desirable. The lower output resistance allows faster switching of $Q_1$ because $Q_1$ can not turn on until its stray gate capacitance of approximately 65 pF is charged.

Variable capacitor $C_{\text{inj}}$ was charged to between 60 and 200 volts. The charge was switched across the cell when $Q_1$ was triggered by a positive-going pulse from the pulse generator. The saturation voltage of $Q_1$ is approximately 5 volts; the pulse amplitude at the gate of $Q_1$ must therefore exceed this value. The gate of $Q_1$ was isolated from DC offsets in the pulse generator by film capacitors $C_4$ and $C_5$. $R_{13}$ was adjusted while observing the waveform at point A until a waveform was produced which had maximum peak value with a minimum of ringing. Attempts at increasing the breakdown voltage of $Q_1$ through a totem pole arrangement of two transistors were abandoned because a single transistor produced a cleaner output waveform.

The pulse generator was protected from the negative-going injection transient by diode $D_1$. $D_1$ allows negative-going pulses from $E_{\text{CELL}}$ IN to be applied to the cell. $R_9/R_4$ minimize $D_1$'s "on" impedance and risetime by insuring that $D_1$ is properly biased when there are no pulses present. $C_1$ and $C_2$ are low dissipation factor electrolytics (shunted by film capacitors for improved high frequency performance), used to prevent DC current from flowing through the cell from the bias supply. They also serve to decouple the reference electrode from the platinum shunt electrode. $E_{\text{CELL}}$ was measured at the connection to the
reference electrode, and adjusted by R5. For reductions, the reference electrode was grounded, the working electrode connected to point A, and the Pt shunt connected to ground through a film bypassed 330 microfarad electrolytic capacitor. The circuit was installed in a thick-walled cast aluminum box, and connections were made via BNC connectors mounted directly on the circuit board.

A few comments are in order concerning the selection of R4 in this application. R4 must provide sufficient bias current (on the order of a milliampere) to D1. The combination of R4/C1 is a highpass filter whose time constant determines the maximum duration of the experiment that may be performed with this circuit (the time constant determined by $R_s C_1 C_2/(C_1+C_2)$ is less important because current flow through this portion of the circuit at long times is insignificant, compared to current flow through R4). If the output of the circuit is observed during a potential step whose duration approaches $R_4 C_1$ seconds, the output of the circuit begins to droop; the change in voltage is of sufficient magnitude to cause problems in an electrochemical experiment. Increasing the value of R4 will increase the time constant, but at the expense of transient response. The time constant may also be increased by increasing C1, but this can be impractical because of the physical size of the large-value capacitor required. Because the emphasis in this work was on experiments of short duration, this performance limitation was judged insignificant. However, caution is warranted for experiments longer than $R_4 C_1/10$ seconds (in this case, approximately 200 ms).
2. Photometry Circuitry

For submicrosecond and routine work a new photomultiplier interface circuit was constructed (Figure 26). The output of the PMT is dropped across load resistor $R_L$. The voltage appearing across $R_L$ is determined by Ohm's law. Large values of $R_L$ will give the highest output voltage, but for high speed experiments the load resistor must be as small as possible to minimize the RC time constant of the load resistor with the stray capacitance of the PMT and connecting cable. The optimum value of $R_L$ for high speed response is 50 ohms, which properly terminates the 50 ohm coaxial cable used to connect the circuit to the PMT. The voltage appearing across $R_L$ is buffered by IC1, a fast operational amplifier. IC1 and IC2 are hybrid buffer amplifiers (National Semiconductor LH0033C) capable of 1.4 V/ns slew rate and 100MHz bandwidth. The National LH0066C, 200 MHz buffer amplifier was also considered for this application but the phase response and amplitude flatness were considered inferior to the LH0033C(92).

To process the PMT signal and extract the maximum performance from the PMT/amplifier circuit, a 3rd order Bessel low pass filter was designed. The sharper cutoff slope of the filter greatly improves the signal to noise ratio over that which would be obtained with a simple 1st order RC filter. The sharper cutoff slope also minimizes the
effects of high frequency aliasing when digital data acquisition systems are used. There is also less signal degradation as the Bessel filter function offers a linear phase (constant time delay for all frequencies below the cutoff frequency) characteristic. The disadvantages of the use of such a circuit are that a more complicated circuit is required, and the selection of the cutoff frequency for a given experiment is more critical. The latter is circumvented by the circuit in Figure 26. The values of R4-R6 are changed conveniently via DIP switches S1-S8. The values of R4-R6 are arranged in a power-of-three sequence (Figure 27). Intermediate values may also be arrived at by parallel combinations of appropriate values. The range of adjustment is over frequencies from 315 Hz to 3.2 MHz. The important parameter in selection of proper cutoff frequency is the time delay of the circuit for a given cutoff frequency. The delay of the filter was measured at a frequency near the cutoff frequency of the filter for different filter cutoff frequencies, and can be described by the relation \( T_d = 0.31/F_c \) where \( T_d \) is in microseconds and \( F_c \) in megahertz. Negligible observable transient distortion is assured if the time delay of the filter is equal to or less than the time resolution of the data acquisition system. Optimal filtering is obtained by selecting a cutoff frequency producing a delay equal to the resolution of the data acquisition system. The correction for the delay is then accomplished by simply offsetting the data by one data point. The cutoff frequency of the filter is given by
Schematic diagram of 3rd order lowpass filter circuit used for photometric processing. Adjustable resistances R4-R6 are represented in Figure 27. Capacitors are 2.5% polystyrene, resistors metal film type. Metal cases of amplifiers tied to their outputs to lower their stray input capacitance.

Resistor array used for tuning 3rd order filter of Figure 26. Switches S1-S8 are miniature DIP switches. Resistors are 1% tolerance, metal film type.
Figure 26

Figure 27
\[ F_c = \frac{1}{2} \pi R C_{\text{equiv}} \quad (18) \]

where \( C_{\text{equiv}} \) for the above circuit is 1014 pF. The values of \( F_c \) and \( T_d \) for various values of \( R4-R6 \) are given in Table 4.

Table 4. Photomultiplier Amplifier Cutoff Frequencies.

<table>
<thead>
<tr>
<th>Switch</th>
<th>( F_c ), kHz</th>
<th>( T_d ), ( \mu )S</th>
<th>( R_{\text{equivalent}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>0.315</td>
<td>980</td>
<td>499 k</td>
</tr>
<tr>
<td>1</td>
<td>1.28</td>
<td>240</td>
<td>123 k</td>
</tr>
<tr>
<td>2</td>
<td>3.18</td>
<td>98</td>
<td>49.5 k</td>
</tr>
<tr>
<td>3</td>
<td>8.93</td>
<td>35</td>
<td>17.6 k</td>
</tr>
<tr>
<td>4</td>
<td>26.3</td>
<td>12</td>
<td>5.97 k</td>
</tr>
<tr>
<td>5</td>
<td>79.0</td>
<td>3.9</td>
<td>1.99 k</td>
</tr>
<tr>
<td>6</td>
<td>231</td>
<td>1.3</td>
<td>680</td>
</tr>
<tr>
<td>7</td>
<td>696</td>
<td>0.45</td>
<td>226</td>
</tr>
<tr>
<td>8</td>
<td>2100</td>
<td>0.15</td>
<td>75</td>
</tr>
<tr>
<td>1-8</td>
<td>3140</td>
<td>0.099</td>
<td>50.1</td>
</tr>
</tbody>
</table>

The performance of the PMT interfacing circuit was tested by observing the output of an LED pulsed by the charge injection circuit. The LED was placed directly in front of and approximately 1 cm away from the photomultiplier (1P21). The circuit was monitored at the output of IC1.

Figures 28-29 illustrate the signal delay of 40 ns accumulated in the PMT (electron transit time) and interface circuitry. The fast-rising pulse was obtained by monitoring the voltage appearing across the LED, and it is displayed next to the output of the PMT interface circuit, operated at its full bandwidth. Data collected during experiments must be corrected for this delay, if it is
Figure 28.

Response of photomultiplier to pulsed LED, showing time delay of photomultiplier (100 nS full scale). Curve A is the voltage step applied to the LED, Curve B the output of the photomultiplier processing circuit operated at full bandwidth ($E_{PMT} = 800$ V, $R_L = 50$ ohms). LED was prebiased by a DC potential which was increased until maximum LED pulse output was observed. Delay of 40 nS caused by sum of photomultiplier electron transit time and delays in photomultiplier processing circuit.
Figure 29.

Response of photomultiplier to pulsed LED showing time delay of photomultiplier (900 nS full scale). same conditions as Figure 28. Curve A is voltage applied to LED, Curve B the response of LED.
significant on the time scale of the experiment.

Figure 30 demonstrates the risetime of the PMT for different power supply voltages. A higher voltage clearly improves the risetime, at the cost of increased noise. The pre-pulse noise is due to pickup of RF noise by the cable connecting the PMT interface circuit and the oscilloscope. The noise was greater for lower voltages because of the proportionately smaller signal at lower voltages. All measurements of the circuit reported below were made at a PMT voltage of 800 V, which represents a good compromise between risetime and PMT shot noise.

Figures 31-32 illustrate the change in risetime of the circuit when the value of $R_1$ is changed. It is clear that for optimum transient response a value of 50 ohms should be used. For experiments on a longer time scale $R_1$ can be larger for greater sensitivity.

Figure 33 is the response of the filter circuit at its maximum bandwidth setting. Although the pulse is badly distorted, the rise time and amplitude of waveforms intended to be processed by the filter are much less than the pulse used here. The large amplitude high frequency components present in the pulse are somewhat challenging to the amplifier when used in such a filter configuration, and probably drive the amplifier into nonlinear operation. For proper operation of the filter circuit the amplifier used must have a unity gain bandwidth of at least 100 times the maximum filter cutoff frequency(93). This constraint is somewhat relaxed in this case because the amplifier is a hybrid type designed for unity gain operation. Additionally, the $1/f$ nature of the amplitude spectrum of shot noise present with the
Figure 30.

Change in photomultiplier risetime with different supply voltages. Load resistor was 50 ohms, maximum bandwidth. Prepulse noise greatest for lower voltages.
Figure 31.

Change in photomultiplier risetime with different load resistors. PMT voltage 800 volts, maximum bandwidth. Curve a, 50 ohms; b, 225 ohms; c, 1000 ohms.
LED OUTPUT (ARBITRARY UNITS)

Figure 31

TIME $\times 10^7$ seconds
Figure 32.

Change in photomultiplier risetime with different load resistors. 
PMT voltage 800 volts, maximum bandwidth. Curve a, 50 ohms; b, 225 ohms; c, 1000 ohms; d, 10000 ohms; e, $10^5$ ohms.
Figure 33.

Comparison of response of PMT circuit to fast rising pulse at full bandwidth with response at 3.14 MHz bandwidth (R4-R6 50.1 ohms). R_L = 50 ohms, 800 volts. Curve A, output of LED, full bandwidth; Curve B, output at 3.14 MHz bandwidth.
signals encountered during spectroelectrochemical experiments assures that high frequency signals reaching the amplifier are relatively small in magnitude. This is verified by Figure 34, in which the lower repetition rate pulses used to generate the data apparently cause the circuit less distress, as witnessed by the improved pulse shape. The other curves demonstrate the operation of the filter at different cutoff frequencies, and the effect of the 5 MHz filter of the oscilloscope vertical amplifier on the pulse.

Finally, Figure 35 is the response of the LED with the charge injection circuit disabled. The slow risetime is caused by the diode's junction capacitance; the PMT/circuit response delay is also visible in the figure.
Figure 34.

Effect of lowpass filtering and filter cutoff frequency on shape of square pulse from photomultiplier. $R_L$ 50 ohms, 800 volts. Curve a, full bandwidth; b, response of 5 MHz filter on oscilloscope plug-in; 3rd order filter set at 3.14 MHz(c), 696 kHz(d), 231 kHz(e), 79 kHz(f).
Figure 34

TIME X 10^6 seconds

0

LED OUTPUT (ARBITRARY UNITS)
Figure 35.

Response of LED without charge injection assist. Full bandwidth, PMT 800 volts. Curve A, voltage pulse applied to LED; B, LED response.
AMPLITUDE (ARBITRARY UNITS)

Figure 35

TIME X 10^7
Chapter 5

RESULTS AND DISCUSSION

1. Cyclic Voltammetry of Test Systems

Cyclic voltammetry was performed with microelectrodes to characterize the spectroelectrochemical test systems used in this work with regards to their redox potentials. This ensured that the proper potentials were used for the generation of chromophore under diffusion controlled conditions, and that the electrodes demonstrated normal electrochemical behavior. Figure 36 is a scan taken at 100 mV/sec in a solution of 3 mM O-D in 1M H$_2$SO$_4$. The electrode used was a carbon fiber microelectrode. The sigmoidal shape(60,61) of the voltammogram is due to the large diffusional flux present when experimental conditions favor the formation of a diffusion layer thickness of comparable magnitude to the size of the electrode radius. The cyclic voltammogram of methyl viologen in Figure 37 shows the expected sigmoidal shape at potentials up to -800 mV. The lower trace is a cyclic voltammogram of the same system, carried out to more negative potentials. The second peak is due to the two-electron reduction of MV to an insoluble film(91,92). Cyclic voltammetry performed with 12.8 micron diameter gold microcylindrical electrodes at a scan rate of 400 mV/sec exhibits similar behavior (Figures 38-39).
Figure 36.

Cyclic voltammogram of ortho-dianisidine using carbon fiber working electrode. Scan rate 100 mV/S, concentration 3 mM in 1M H₂SO₄.

Figure 37.

Cyclic voltammetry of methyl viologen using carbon fiber working electrode. Scan rate 500 mV/S, 5 mM, 0.45M pH 7 phosphate buffer.
Figure 38. Cyclic voltammetry of methyl viologen using 12.8 micron gold cylindrical electrode. 400 mV/S, 5 mM, 0.45 M pH 7 phosphate buffer. Upper curve, 0.0 to -0.85 volts; lower curve, 0.0 to -1.1 volts.
Figure 39. Cyclic voltammogram of ortho-dianisidine using 12.8 micron gold cylindrical electrode. Scan rate 400 mV/S, 6.6 mM, 1M H$_2$SO$_4$. 
Figure 40 is a cyclic voltammogram of 5 mM MV on a platinum microcylindrical electrode in 1.5M pH 7 phosphate buffer, 500 mV/sec. The large background current at negative potentials is due to reduction of $H^+$. Curiously, the hydrogen evolution wave of the cyclic voltammogram in Figure 41, on a 300 micron diameter Pt electrode, was displaced to more negative values, allowing resolution of the first MV reduction wave. This characteristic is desirable from both electrochemical and spectroelectrochemical standpoints because it extends the useful operating potential range and minimizes background currents. The platinum for this electrode was obtained from VWR Scientific. Possible causes of this behavior are impurities in the platinum or the crystal structure of the platinum surface, caused by the method of fabrication of the wire. Likely impurities in Pt are other noble group metals such as iridium, palladium, or rhodium.

A cyclic voltammogram of the same system on 405 micron diameter Pt/Ir (90%/10%, VWR, Figure 42, lower traces) shows similar behavior, with appreciable hydrogen evolution not occurring until a potential of $-1000$ mV. The upper trace is for the same system, but restricting the negative limit of the scan to $-800$ mV. Cyclics performed on 50 micron diameter Pt/Ir (90/10, Figure 43) and Pt/Rh (87/13, Figure 44) electrodes from Goodfellow Metals show only slightly better performance than the 50 micron platinum, however; crystallographic structure or some unknown surface property which varies with the crystallographic structure of the Pt surface must therefore be responsible for the shift in the hydrogen wave. Of the three 50 micron
Figure 40.

Cyclic voltammogram of methyl viologen using 50 micron platinum cylindrical electrode. 500 mV/S, 4 mM, 1.5M pH 7 phosphate buffer.

Figure 41.

Cyclic voltammogram of methyl viologen using 300 micron platinum cylindrical electrode. 200 mV/S, 5 mM, 0.45 M pH 7 phosphate buffer.
Figure 42.

Cyclic voltammogram of methyl viologen using 405 micron platinum-iridium cylindrical electrode. 100 mV/S, 4 mM, 2M pH 7 phosphate buffer.
Figure 43.

Cyclic voltammogram of methyl viologen using 50 micron platinum-iridium cylindrical electrode. 400 mV/S, 4 mM, 2M pH 7 phosphate buffer.

Figure 44.

Cyclic voltammogram of methyl viologen using 50 micron platinum-rhodium cylindrical electrode. 400 mV/S, 4 mM, 2M pH 7 phosphate buffer.
Figure 43

Figure 44
Pt electrodes, the Pt/Ir showed the best performance. The first scan of the cyclic voltammogram in Figure 42 also exhibited the shoulder present in Figure 39. The shoulder is probably due to the formation of a reduced viologen film, which is insoluble\(^{(47)}\).

Cyclic voltammograms obtained with 60 micron diameter gold microdisk electrodes are shown in Figures 45-48. Figure 45 is 10 mM MV in 1.5M phosphate buffer. The scan rate is 200 mV/sec. Figure 46 shows the voltammetric response of the gold microdisk electrode after initial polishing with 600 grit sandpaper (scan rate 500mV/sec). The shoulder on the return sweep disappears if the electrode is subjected to further polishing with diamond compound and alumina (Figure 47). Figure 48 is a cyclic voltammogram of O-D in 1M H\(_2\)SO\(_4\). The degradation of the response after 15 minutes of scans (Curve C) is probably due to polymerization of oxidized O-D and passivation of the electrode surface. The spectroelectrochemical response also was degraded after many experiments were performed using O-D, probably for the same reasons. The cyclic voltammetric behavior of the above chemical systems on gold MDEs are essentially identical to those obtained with gold MCEs.

The hydrogen overvoltage of a 50 micron Pt microdisk electrode was improved by the electrodeposition of a mercury film, using the procedure described by Hartley\(^{(48)}\). The film was deposited galvanostatically for 5 minutes at 60 nA from 0.1M Hg(NO\(_3\))\(_2\). The mercuric nitrate solution was prepared from metallic mercury and nitric acid. The excellent cathodic performance is demonstrated in
Figure 45.

Cyclic voltammogram of methyl viologen using 60 micron gold microdisk electrode. 500 mV/S, 10 mM, 1.5M pH 7 phosphate buffer.

Figure 46.

Cyclic voltammogram of methyl viologen on gold after rough polishing. 500 mV/S, 10 mM, 1.5M pH 7 phosphate buffer.

Figure 47.

Cyclic voltammogram of methyl viologen on gold after final polishing. 500 mV/S, 10 mM, 1.5M pH 7 phosphate buffer.
Figure 48.

Cyclic voltammogram of ortho-dianisidine on gold after repetitive scans. 300 mV/S, 5mM, 1M H₂SO₄.
Figure 49.

Cyclic voltammogram of methyl viologen on mercury-coated platinum microdisk electrode. 500 mV/S, 3 mM, 1.5 M pH 7 phosphate buffer.

Figure 50.

Cyclic voltammogram of methyl viologen on mercury-coated platinum after 7000 1-mS spectroelectrochemical runs. 500 mV/S, 3 mM, 1.5 M pH 7 phosphate buffer.
Figure 49. The scans were performed in 1.5M pH 7 phosphate buffer; MV concentration was 3 mM and scan rate 500 mV/sec. Negligible hydrogen evolution is observed in the top scans, even at -1100 mV. The scans in the middle curve were performed after the first four scans, and show that the electrochemical properties of the electrode were not altered appreciably after the negative potential excursions employed in the bottom curve. Figure 50 demonstrates that Hg film degradation occurs after extensive use in spectroelectrochemical experiments (seven thousand runs of millisecond duration, for the reduction of MV in pH 7 phosphate buffer). The use of Hg-coated electrodes would therefore necessarily be limited to experiments where extensive signal averaging is not required (e.g. experiments on longer time scales).
2. Spectroelectrochemistry- Cylindrical Microelectrodes

A. Carbon Fiber Microelectrodes

An initial reaction to an attempt at the use of microelectrodes for a spectroelectrochemical experiment is understandably one of skepticism. Because of their microscopic size, intuition dictates that the resulting optical signal must also be small. While the optical signal in a typical reflection spectroelectrochemical experiment is indeed quite small, the optical response (to a first approximation) has nothing to do with the size of (physically realizable) electrodes, but is controlled by the properties of the electrochemical system under consideration. The important parameter affecting the optical response with microelectrodes, as discussed in the theory chapter, is the relative sizes of the diffusion layer thickness and the electrode. Because the diffusion layer thickness in a typical spectroelectrochemical experiment lasting less than one second is on the order of a few tens of microns or less, the optical response observed in experiments with microelectrodes does not differ greatly from that of an experiment employing a conventionally-sized electrode. As will be shown, differences in optical responses become negligible as the duration of the experiment is reduced to the millisecond or submillisecond time scale.
Carbon fiber microcylindrical electrodes were used for the initial spectroelectrochemical experiments. An absorbance versus time transient, shown in Figure 51, has the expected shape, as predicted by Equation 3. The test system was O-D in 1M H₂SO₄.

Because the size of the electrode radius is within an order of magnitude of the wavelength of visible light, it is possible that the wave nature of light may cause anomalous behavior in the context of these experiments. If this is the case, such effects should become more pronounced as the wavelength or incident angle of the optical beam is changed. Experiments were therefore performed to determine if the ray optic approximation was valid.

Methyl viologen was reduced at -0.85 volts vs. SCE, stepping from a potential of -0.2 volts, and the radical cation monitored at 632.8 nm. The absorbance of a run at normal incidence after 100 ms was compared to that for other runs made at different observation angles. The result of this experiment is depicted in Figure 52. The solid line is the absorbance calculated from the geometric arrangement of the beam/detector: $A(\theta) = A_0/\sin(\theta)$, where $A_0$ is the absorbance at 100 ms at a normal angle of incidence (90 degrees). The points are data from experiment. Large angles were avoided because of anomalous scattering and diffraction from the electrode. An absorbance vs. wavelength spectrum was also recorded by measuring the absorbance after 100 ms at different wavelengths. The wavelength region between 568 and 650 nm was obtained with the dye laser; the emission lines of the Ar⁺ laser were used for the other wavelengths. The upper curve in
Figure 51.

100 mS absorbance vs. time transient, 2.7 mM ortho-dianisidine in 1M H$_2$SO$_4$ on carbon fiber electrode. Potential was stepped from 0 to +1.0 V vs. SCE, observation angle 10°, 514.5 nm.
Figure 52. Dependence of absorbance at t = 0.1 S on the angle between input laser beam and fiber optic probe. Points are experimental and line is calculated from ordinary reflection, as discussed in text.
Figure 53 is the spectrum thus obtained; the lower curve is a spectrum from Reference 49 for comparison. No significant distortion of the spectrum is observed. As shown above, the angular dependence on absorbance also agreed with the expected values. Therefore, the MCE can be considered to exhibit simple ray-optic behavior.

Because of the increase in diffusional flux to a microcylindrical electrode, as demonstrated by the cyclic voltammetry discussed earlier, the re-establishment of initial conditions in a spectroelectrochemical experiment would be expected to occur more quickly than for a large planar electrode. The faster rate of diffusion of electrogenerated product away from the electrode should permit the use of a higher duty cycle for spectroelectrochemical experiments. The advantage of this would be a shorter total experimental time when many runs are signal averaged. This could be of possible value in kinetic experiments, because the rapid diffusion of electrogenerated reactants away from the electrode would slow the rate of fast second order reactions because of product dilution. The maximum absorbance of 100 mS runs with different duty cycles were compared. The absorbance was independent (within 10%) of duty cycles for duty cycles less than 0.1. At higher duty cycles, the absorbance decreased. For carbon fiber spectroelectrochemical runs, the duty cycle employed was therefore 10%.

The maximum absorbance at 100 mS for experiments such as those depicted in Figure 51 was dependent upon the step potential, even for potential steps considerably beyond the diffusion limited potential
Figure 53.

A bsorbance at t = 0.1 S as a function of wavelength for the reduction of methyl viologen to its cation radical. Curve A is from this work; Curve B is a literature spectrum(48) (observation angle 10°).
Figure 53
determined from cyclic voltammetry. Figure 54 illustrates this effect. There are three possible explanations for this effect. Passivation of the electrode surface by O-D polymerization(76) would slow the rate of radical generation, requiring a higher potential. The appearance of iR errors across the cell during the potential step would also necessitate a higher potential for diffusion-controlled O-D oxidation. Alternatively, the reflectance of the electrode may be potential dependent, a possibility supported by the fact that the curves shown in Figure 54 for different step potentials are separated by a roughly constant value for the duration of the run. Also, if mechanical stresses induced in the electrode in the presence of a large electric field caused a distortion in its shape, the amount of light reaching the detector would be affected, producing an effect similar to that observed if the reflectance of the electrode material were potential dependent.

An absorbance vs. $t^{1/2}$ transient for a 1 second experiment is shown in Figure 55. The linear behavior to 1 second is unexpected, because the primary mode of diffusion for electrodes of this diameter at an elapsed time of 1s is cylindrical, rather than linear diffusion. It is possible that the high surface roughness factor of carbon fiber MCEs (up to 500(66,97)) contributed to the increased absorbance. The effects of optical beam absorption must also be considered; for a 10% reflective carbon fiber, the absorption of 90% of the probe beam, if sufficiently high in intensity, will cause heating of the surface of the electrode, especially in the case of a carbon electrode with its
Figure 54.

Effect of potential step on response, ortho-dianisidine oxidation on carbon fiber microelectrode. From top to bottom, curves represent potential steps from 0 to 1.2, 0 to 1.0 and 0 to 0.8 volts vs. SCE, respectively. ( ) = 10°, 514.5 nm.
Figure 55.

1 s absorbance versus time$^{1/2}$ transient, carbon fiber microelectrode. Points are experimental data, solid line is best straight line through points. Experimental conditions are as in Figure 51.
Figure 55

Absorbance

$\frac{1}{2} (\text{sec}^2)$
low thermal conductivity. The primary means of heat transfer from the electrode would therefore be into the solution surrounding the electrode, which would affect the diffusion of electroactive species to the electrode surface in an unpredictable fashion.

Such an optical power density effect was observed for carbon fiber microelectrodes. The curves in Figure 56 demonstrate the effects of different probe beam power. Above a power of 60 mW (corresponding to a power density at the electrode surface of \(1 \text{ W/cm}^2\)) the absorbance observed in a 100 mS spectroelectrochemical experiment increased with increasing laser power. The beam power was therefore held to less than 60 mW for all spectroelectrochemical experiments with carbon fibers. Thermally-induced optical effects were also observed for metal microelectrodes and noted below; the effects on optical response would be expected to be different for metal electrodes because of their higher thermal conductivity and reflectance.

The transient response of the carbon MDE for the O−D oxidation is shown in Figure 57. The absorbance signal begins to rise after an elapsed time of 30 microseconds. While the behavior falls quite short of the theoretical response, it is impressive for a three-electrode potentiostat with no IR compensation. The high resistance of these electrodes (greater than several thousand ohms\((63,66,97)\)) will produce a significant IR potential error at short times. The resistance of these electrodes is also effectively greater for the configuration used here; the radial resistance to current flow (e.g. in a cylindrical electrode) is many times greater than the axial resistance
Figure 56.

Effect of laser beam power density on response, carbon fiber microelectrode. Laser beam (595 nm) was focused with 267 mm focal length lens. Test system was 4.85 mM benzyl viologen in 0.3M pH 7 phosphate buffer; potential was stepped from 0.0 to -0.65 V vs. SCE. From top to bottom, curves represent power densities of 12 W/cm$^2$, 6 W/cm$^2$, 3 W/cm$^2$, respectively. Power density of 1.5 W/cm$^2$ gave same result as lowest curve.
Figure 57.

Transient response of carbon fiber microelectrode for o-dianisidine oxidation. Conditions same as Figure 51.
Absorbance $\times 10^4$

Figure 57

Time ($\mu$sec)
(disk electrode case) because of the atomic/molecular orientation of the carbon atoms which results from the method of "growing" of the fibers(63). Also, the high roughness factor greatly increases the double layer capacitance of such electrodes over that predicted from the geometrical area, increasing the time constant of the cell.

B. Metallic Microcylindrical Electrodes

a. Electrical Characteristics

The electronic transfer characteristics of the cell depicted in Figures 12-13 are illustrated in Figure 58. The cell impedance vs. frequency was determined by measuring the ratio of rms potential applied across the cell to the rms current through the cell. The current was measured as a voltage drop across a resistor in series with the cell. The impedance minimum at 2.3 MHz indicates that the solution resistance is no larger than 38 ohms. This agrees with the calculated $R_{\text{cell}}$ of 35 ohms for a 10 micron radius electrode in 1M H$_2$SO$_4$, and indicates that there is no unexpected source of series or shunt resistance. If the Pt pseudoreference electrode is disconnected, the minimum impedance increases to 400 ohms at 600 KHz (see Figure 71). In this case, all cell current must flow through the high resistance SCE, which increases the cell impedance; the lower impedance obtained with the shunt is indicative of its excellent
Figure 58. Electrochemical cell impedance vs. frequency, 10 micron platinum cylindrical electrode in 1M H₂SO₄, 4 mM Cl⁻. Cell configuration same as shown in Figure 13.
electrical coupling to the solution. The rapid rise in cell impedance is due to the inductance of the cell's connecting wires; this will affect cell performance at short times and will limit the cell's time constant, depending upon the experimental conditions employed. The cell capacitance may also be estimated from the plot, because the reactance of a capacitance, \( Z_c \), is equal to \( 1/2\pi fC \) (98), where \( f \) is the frequency of interest. The variation of capacitance/unit area calculated from this relation is listed in Table 5. The capacitance of a 5 micron radius Pt MCE was also measured by observing the response to a triangular potential waveform centered at 0.4 V vs. SCE (\( C_{dl} = i_{cell}/4f\Delta E \)) (99). In the frequency range from 10 to 10^6 Hz, the capacitance per unit area varied from 20-60 \( \mu F/cm^2 \). The range of capacitance observed is reasonable for platinum(26,34,38,100), indicating no pronounced surface roughness or other sources of capacitance. Additionally, the cell inductance calculated from the data in Figure 58 (in the region where impedance increases with frequency) with the relation \( Z_L = 2\pi fL \) (101) is approximately 3 \( \mu H \), increasing at higher frequencies (Table 5). For \( C_{dl} = 20 \mu F/cm^2 \) and \( R_{cell} = 40 \) ohms, the cell potential risetime, \( 3RC \), is 0.9 \( \mu S \). A plot of \( \ln i \) vs. \( t \) for a potential step was nonlinear, but the slope indicated a risetime in the range of 1.2 to 4.2 \( \mu S \). The observed time constant (0.6 \( \mu S \)) and risetime (less than 4 \( \mu S \)) for the cell are comparable with those expected from the calculated (Equations 8-10) resistance (0.53 \( \mu S \) and 1.59 \( \mu S \), respectively). The calculated risetime indicates that the double layer will be at least 95% charged 4 \( \mu S \) after the
potential step.

Table 5. Variation in Cell Inductance and Capacitance With Frequency, 10 Micron Cylindrical Platinum Microelectrode

<table>
<thead>
<tr>
<th>Frequency, MHz</th>
<th>Impedance</th>
<th>Capacitance, nF</th>
<th>Inductance, nH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>1200</td>
<td>4.4</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>420</td>
<td>3.8</td>
<td>-</td>
</tr>
<tr>
<td>0.30</td>
<td>150</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>48</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>3.0</td>
<td>49</td>
<td>-</td>
<td>2.6</td>
</tr>
<tr>
<td>6.3</td>
<td>114</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td>10.0</td>
<td>270</td>
<td>-</td>
<td>4.3</td>
</tr>
<tr>
<td>15.1</td>
<td>1000</td>
<td>-</td>
<td>10.5</td>
</tr>
<tr>
<td>20.0</td>
<td>5600</td>
<td>-</td>
<td>44.6</td>
</tr>
</tbody>
</table>

The cell current for a potential step to 1.1 V vs. SCE from a rest potential of 0.3 volts in a 2.4 mM O-D solution was 300 μA, 4 μS after the potential step. For the experiment depicted in Figure 59, the resulting iR error at 4 μS after the potential step would be 11 mV, easily compensated by an increase in potential.

b. Spectroelectrochemistry

Absorbance vs. time$^{1/2}$ transients for 100 mS runs with a 25 micron diameter Pt electrode in a solution containing 3.5 mM O-D are shown in Figure 59. The solid line in Figure 59 was obtained with a three-electrode potentiostatic arrangement; the open circles are a run made with a two-electrode arrangement, and the solid circles are the
theoretical response calculated from the equation in Appendix 1. The two-electrode arrangement exhibits the best transient response, and confirms that potentiostatic potential control is unnecessary when cell currents are small, as encountered with microelectrodes. The agreement with theory for both runs is excellent, indicating that uncomplicated cylindrical diffusion occurs for at least 100 mS. The diffusion layer thickness for a 10 micron diameter electrode at 100 mS was 1.3 times the electrode radius.

The maximum value of the dimensionless parameter \((Dt)^{1/2}/r_0\) for which theory and experiment agreed was 1.7, corresponding to a time of 300 mS for the 12.8 micron diameter gold electrode used. This case is interesting because the diffusion layer thickness is nearly twice the electrode radius; as such, cylindrical diffusional behavior of the system would be expected to dominate over planar diffusion. For larger electrode radii, a longer experiment would be necessary for observation of the same behavior. The maximum values of \((Dt)^{1/2}/r_0\) for agreement of theory with experiment for other electrode radii were also measured. For a 50 micron diameter platinum electrode, \((Dt)^{1/2}/r_0_{\text{max}}\) was 0.52 \((t = 420 \text{ mS})\); for \(r_0 = 280\) microns, the value was 0.23 \((t = 10 \text{ S})\). The smaller attainable values of \((Dt)^{1/2}/r_0\) with the larger electrodes are not unexpected. For a larger electrode, a longer run is necessary to attain the same value of \((Dt)^{1/2}/r_0\). At longer times, the system is more susceptible to the effects of convection. The larger absorbances obtained at longer times also increase the rate and integral thermal absorption of the optical beam,
Figure 59.

Absorbance vs. $t^{1/2}$ transients for a 25 micron diameter platinum electrode in 1M $\text{H}_2\text{SO}_4$ containing 3.5 mM o-dianisidine. Open circles, theoretically predicted response; solid line, experimental response for a conventional three-electrode potentiostatic arrangement, average of 100 runs; solid circles, response for the two-electrode configuration shown in Figure 13, average of 60 runs. $E_{\text{app}}$ was stepped from 0.3 to 1.1 V vs. SCE. Laser power 20 mW/cm$^2$. 
Figure 59
which can cause heating effects which will disrupt normal diffusional processes. Figure 60 depicts a comparison of theory vs. experiment for different electrode radii. The larger electrodes would be expected to be more immune from the effects of convection, and this is reflected in the data. As noted above, however, the effective normalized diffusion layer thickness is less than that for the smaller electrodes.

As the power of the probe beam was increased, optical heating effects became apparent. The optical response and maximum time for negative deviation from theory were strongly dependent upon laser power, with good agreement between theory and experiment at power densities at the electrode surface of less than 50 mW/cm², corresponding to a beam power of approximately 0.1 mW. The power density dependence is depicted in Figure 61 for three different power densities at the surface of a 280 µm radius Pt electrode. There are at least three possible causes of deviation at high laser power. First, the absorption of the beam by the electrode will heat up the electrode and produce local heating. The rate of heating will be proportional to beam power, and for an incident power density of 0.2 W/cm², the rate of heating for a 90% reflective platinum electrode will be 2°C/s. Second, absorption of the beam by electrogenerated chromophore will cause heating of the solution at the same rate at this power density when the absorbance is 10⁻². Third, high laser powers can cause bleaching of chromophore if it is photolytically unstable. This would account for the negative deviations observed at longer times. It
Figure 60.

Absorbance vs. \( t^{1/2} \) transients for different electrode radii. Theoretical curves calculated from Equations 5-6 as described in text, with \( A_{\text{planar}} \) given by Equation 3. Experimental conditions as in Figure 59 with a conventional three-electrode configuration. Solid line is the linear planar response, others as indicated: \(--\), theory, \( r_0 = 280 \) microns; \( \cdots \cdots \), theory, \( r_0 = 25 \) microns; \( \cdots\cdots \), theory, \( r_0 = 6.4 \) microns. Open circles, experimental, 280 micron radius platinum electrode, 2.6 mM, single run, 5 mW/cm\(^2\); solid circles, experimental, 25 micron radius platinum electrode, 2.8 mM, 10 runs averaged, 35 mW/cm\(^2\); squares, experimental, 6.4 micron radius gold electrode, 2.2 mM, 100 runs, 700 mW/cm\(^2\).
Absorbance vs. $t^{1/2}$ as a function of laser power for 2.6 mM O-D on a 280 micron radius platinum wire: line is theory; circles are for laser power = 5 mW/cm$^2$; triangles, 20 W/cm$^2$; squares, 360 W/cm$^2$. 
Figure 61
should be noted that high power densities caused a positive deviation from theory at short times, but a much larger negative deviation as the experiment progresses. Fortunately, these deviations, whether resulting from photolytic, thermal, or convective effects, may be avoided with the use of laser power densities of less than 50 mW/cm$^2$ or experimental runs of less than 300 mS. For faster runs, higher power densities are permissible because the run is completed before the appearance of thermal or bleaching effects. Higher beam powers are desirable for short experiments from the standpoint of improving the available light intensity and therefore the signal to noise ratio.

The transient response of a 10 micron diameter platinum MCE is shown in Figures 62-63. The test system was O-D/1M H$_2$SO$_4$. Figure 62 shows the absorbance vs. time response for the first 200 microseconds of the run depicted in Figure 63. Curve A is the response for a solution containing O-D; Curve B is a blank containing 4.4 mM HCl. The blank absorption of about 7 x 10$^{-4}$ will vary with metal, medium, potential, wavelength, and probe beam incident angle. The absorbance is composed of electroreflectance effects(21) combined with surface oxide formation or any other changes in the electrode surface. For experiments of short duration and/or with weak chromophores the blank absorption can be a significant fraction of the total absorbance and blank runs should be recorded and subtracted when necessary.

The absorbance vs. $t^{1/2}$ plot in Figure 63 is the entire 1 mS run, the first 200 uS of which was shown in Figure 62. The run shown in Figure 63 was corrected for background absorbance by simple
Figure 62.

Absorbance vs. time transients for first 200 microseconds of the 1 mS run shown in Figure 63: 5 micron radius Pt electrode, two-electrode configuration, laser power = 280 mJ/cm², 514.5 nm; upper curve, average of 2700 runs with $E_{\text{app}}$ stepped from 0.3 to 1.1 V vs. SCE in 2.2 mM O-D in 1M H₂SO₄; lower curve, same conditions in 1M H₂SO₄ and 4.4 mM HCl, 5700 runs.
Figure 62

Absorbance $\times 10^3$ vs. Time, $\mu$sec

- 2.2 mM OD
- Blank

Time, $\mu$sec

Values:
- 5.0
- 4.0
- 3.0
- 2.0
- 1.0
- 0.0
Figure 63.

Absorbance vs. $t^{1/2}$ for entire $1 \text{ mS}$ run of which Figure 6 is first 20%. Absorbance is background corrected by subtraction of blank. Line is theoretical and exhibits a 5% deviation from linearity at $1 \text{ mS}$ due to cylindrical diffusion.
Figure 63

Absorbance $\times 10^3$

$1\text{ms}$

$300\mu\text{s}$

$100\mu\text{s}$

$20\mu\text{s}$

$4\mu\text{s}$

$t^{\frac{1}{2}} (s^{\frac{1}{2}})$
subtraction of the blank run. The transient response of 4 microseconds is a direct result of the low time constant and small iR error resulting from the small electrode area. The results compare favorably with those obtained with the best competitive method, internal reflection spectroscopy. It should be noted, however that the peak power required for charging of the double layer (1.4 mW) is thousands of times less than that required for the IRS experiment (200-300W). The fine tuning and sophisticated circuitry required of the IRS experiment are replaced with a simple, passive two-electrode cell design requiring no elaborate adjustments. Furthermore, the A vs. t response can be predicted with existing theoretical treatments, not requiring the use of IRS' empirically adjustable penetration parameter(46) which can lead to uncertainty in the interpretation of results.
3. Microdisk Electrodes

A. Spectroelectrochemistry - General

The surface area for a given radius is smaller for a disk electrode than a cylindrical electrode. The transient response with a disk electrode will therefore be improved, because of the lower capacitance (reduced RC) and smaller cell currents (less iR error). The planar geometry of such electrodes should also prove to be an advantage in predicting the theoretical response and minimizing nonlinear diffusional behavior.

Figure 64 is an absorbance vs. \( t^{1/2} \) transient for a 160 mS experiment with a 50 micron diameter platinum electrode. The oxidation of 2.14 mM O-D was monitored at 505 nm. The solid line in the plot is the theoretical response, based on a molar absorptivity value of 23600 \( M^{-1}cm^{-1} \) for O-D, which was corrected for the measured absorbance at 505 nm. This experiment could be used to determine the conditions under which the transition from planar to spherical diffusional behavior occurred. The point at which the absorbance showed a 5% deviation from planar behavior was determined by plotting \( At^{-1/2} \) vs. \( t \) (Figure 65). The \( y \)-intercept of such a plot is the "ideal" planar slope for an absorbance vs. \( t^{1/2} \) plot, extrapolated to \( t = 0 \). The solid line in Figure 65 is a linear least-squares fit, and represents a good approximation to the data. From the slope and \( y \)-intercept of
Absorbance vs. $t^{1/2}$ for the generation of oxidized O-D (2.14 mM) at a 50 micron diameter coaxial Pt microdisk electrode in 1M H$_2$SO$_4$. The potential was stepped from 0.2 to 1.1 V vs. SCE (two-electrode potential control system), and 10 runs were averaged. The straight line is that calculated from an independent measurement of the diffusion coefficient; electroreflectance background absorbance was negligible on this time scale.
Figure 64
Figure 65.

Determination of linear response region, 50 micron microdisk electrode. Data is displayed as plot of $A/t^{1/2}$ vs. $t$, same run as Figure 64. The straight line is the result of a linear least-squares fit. Y-intercept corresponds to slope of an $A$ vs. $t^{1/2}$ plot of data, extrapolated to $t = 0$ (ideal planar behavior). Linear response region is defined as the point where the value of the line deviates by more than 5% from the y-intercept value, and represents the point where the response deviates from planar behavior by 5%.
ABSORBANCE / ROOT (TIME)
Determination of linear response region, 125 micron coaxial Pt microdisk electrode. Conditions same as Figures 64-65, except for use of potentiostatic potential control system.
Figure 66

TIME (SECONDS)

ABSORBANCE / ROOT (TIME)
Figure 67.

Determination of linear response region, 405 micron platinum-iridium microdisk electrode. Conditions same as Figure 66.
the line, the time for 5% deviation from planar behavior can be calculated to be 120 mS. Figures 66-67 are similar plots for 125 and 404 micron diameter electrodes. The noise in the data presented in Figures (65-67) is accentuated because of the expansion of the y-axis. The least-squares data from these experiments and calculated $t_{5%}$ are listed in Table 6.

### Table 6. Maximum Experimental Times for Deviation From Planar Behavior, Microdisk Electrodes

<table>
<thead>
<tr>
<th>Disk Diameter, Microns</th>
<th>Slope</th>
<th>Y Intercept</th>
<th>$T_{max}$</th>
<th>$(Dt)^{1/2}/r_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-0.098</td>
<td>0.245</td>
<td>120 mS</td>
<td>0.29</td>
</tr>
<tr>
<td>125</td>
<td>-0.027</td>
<td>0.272</td>
<td>500 mS</td>
<td>0.24</td>
</tr>
<tr>
<td>405</td>
<td>-0.006</td>
<td>0.247</td>
<td>2.1 S</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The maximum normalized diffusion layer thickness for planar behavior for the microdisk case, 0.29, is nearly three times that observed for the cylindrical case (0.099, for a 12.8 micron diameter gold electrode). Empirically, the microdisk case follows planar diffusional behavior for a longer period of time than the cylindrical case. Both the total experimental time and normalized diffusion layer thickness for planar behavior are greater for the microdisk case than the cylindrical case, when comparing the smallest electrodes used. The shielding of the electrode edge by the surrounding glass will extend the effective planar area "seen" by the electrode, and certainly will delay the onset of spherical diffusional behavior and minimize convective effects. Whether or not this is the reason for the longer
Figure 68.

Electroreflectance risetime, 60 micron gold microdisk electrode, corrected for time delay of circuit in Figure 26 (no lowpass filtering). Wavelength was 514.5 nm, solution 1M H₂SO₄. Potential was stepped from 0.0 to 0.8 V vs. SCE, and 80,000 runs were averaged. Charge injection circuit shown in Figure 24 was used to apply potential step.
Figure 68

Optical Absorbance vs. Time [Microseconds]
Figure 69.

50 microsecond absorbance vs. time transient, 60 micron gold microdisk electrode. 8.17 mM methyl viologen, 1M pH 7 phosphate buffer, 632.8 nm, potential step from -0.4 to -0.8 V vs. SCE. Charge injection circuit shown in Figure 24 was used to apply potential step, and 30000 runs were averaged. The run was corrected for background by subtraction of a blank made in buffer solution containing 16 mM Cl\(^-\) (6000 averaged runs).
Figure 69

OPTICAL ABSORBANCE $\times 10^3$

TIME [MICROSECONDS]

891
Figure 70.

Absorbance vs. $t^{1/2}$ plot of run from Figure 69.
Figure 70

ABSORBANCE X 10^4

TIME^{1/2} X 10^3 (SECONDS^{1/2})
than expected existence of planar behavior, the linearity of the data is supported by two other pieces of information. First, the sigmoidal shape of the cyclic voltammograms obtained with cylindrical microelectrodes is not as apparent with microdisk electrodes, despite the latter's smaller surface area and therefore greater likelihood of experiencing spherical diffusional behavior. This indicates that the onset of spherical diffusion effects may be delayed. Second, the conclusion of planar behavior is supported, perhaps more strongly, by the digital simulation of edge effects performed by Flanagan and Marcoux(102). The concentration profiles obtained by the simulation indicate that a significant perturbation of the concentration profile occurs only directly over the edge of the disk, even for diffusion layer thicknesses on the order of the electrode radius. On this basis, spectroelectrochemically planar behavior would be expected to occur even for longer runs. The deviation at longer times would therefore be of thermal or convective origin.

The transient response of a 60 micron Au MDE is shown in Figure 68. The electroreflectance of the electrode was monitored at 515 nm for a potential step of 0.2 to 0.8 V vs. SCE. For the best possible transient response, the potential was applied with the pulse generator/charge injection circuit of Figure 24 (experiments whose time resolution approached the predicted risetime of the cell, as in this case, were performed with the assistance of charge injection). The spectroelectrochemical transient response for the one-electron reduction of methyl viologen is shown in Figure 69. The first point in the figure was taken 780 ns after the potential step, and a plot of
Figure 71.

Impedance vs. frequency plots for various electrode configurations in 1M H$_2$SO$_4$. Impedance was measured as the ratio of rms applied potential to rms current without regard to phase. Curve 1 is an SCE vs. a large Pt wire; 2 is a 1 mm long, 10 micron diameter Pt cylinder vs. a Pt wire/SCE dual reference electrode; 3 is a 60 micron diameter Au microdisk vs. a Pt wire/SCE dual reference; 4 is a 60 micron Au microdisk vs. a coaxial Pt tube/SCE dual reference. 3 and 4 differ at low frequency due to differences in the Au/glass (Curve 4) and Au/epoxy (Curve 3) seal.
Figure 71
the data vs. $t^{1/2}$ shows good linearity (Figure 70). However, even with the charge injection circuit, the transient response of 160 nS shown in Figure 68 (corrected for PMT delay, see Chapter 4) does not attain the level of performance predicted by the theoretical risetime of 57 ns ($R = 100$ ohms, $C = 5.7 \times 10^{-10}$ uF). At such high speeds, the inductance of the cell wiring limits the current that can be drawn by the cell at short times. Further improvements in transient response therefore dictate that coaxial geometry be maintained from the charge injection circuit to the electrochemical cell.

B. Coaxial Microdisk Electrodes

a. Electrical Characteristics

The coaxial microdisk electrode shows no signs of inductive behavior, as evidenced by the impedance vs. frequency plot of Figure 71. For purposes of comparison, the data for the cylindrical case (Figure 58) are also shown in the plot. Curve 2 is $Z$ vs. $f$ for the cylindrical case. Curves 3 and 4 were obtained with the circuit shown in Figure 25, by measuring the voltage drop across a series connected 50 ohm resistor. Curve 3 is $Z$ vs. $f$ for the conventional (non-coaxial) microdisk electrode, and shows the inductive rise at high frequencies. The inductive rise is due only to the inductance contributed by the electrochemical cell, because a coaxial cable was used to connect the electrode to the circuit. This is in contrast to the data presented in
Curve 2, where separate wires were used to connect working and counter electrodes to the circuit. If this were done for the case depicted in Curve 3, its inductive rise would have the appearance of Curve 2. Disconnecting the platinum shunt increased the cell impedance (Curve 1). The capacitance and inductance (non-coaxial electrode) versus frequency for the microdisk electrodes was calculated using the procedure in Section a for the cylindrical case and are shown in Table 7.

Table 7. Cell Capacitance and Inductance at Different Frequencies, Microdisk Electrodes

<table>
<thead>
<tr>
<th>Frequency (MHz)</th>
<th>Z_{coax} (ohms)</th>
<th>Z_{normal} (ohms)</th>
<th>C_{coax} (nF)</th>
<th>C_{normal} (nF)</th>
<th>L_{normal} (nF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4700</td>
<td>2500</td>
<td>0.34</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>1760</td>
<td>1080</td>
<td>0.30</td>
<td>0.49</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>680</td>
<td>425</td>
<td>0.23</td>
<td>0.37</td>
<td>-</td>
</tr>
<tr>
<td>3.0</td>
<td>280</td>
<td>200</td>
<td>0.19</td>
<td>0.27</td>
<td>-</td>
</tr>
<tr>
<td>10.0</td>
<td>124</td>
<td>118</td>
<td>0.13</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>13.2</td>
<td>100</td>
<td>95</td>
<td>0.12</td>
<td>0.13</td>
<td>1.1</td>
</tr>
<tr>
<td>14.1</td>
<td>-</td>
<td>104</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>15.8</td>
<td>-</td>
<td>124</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>20.0</td>
<td>-</td>
<td>150</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>21.0</td>
<td>69</td>
<td>-</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50.0</td>
<td>12</td>
<td>-</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The lower capacitance of the coaxial electrode is apparently due to the method of insulation of the "sides" of the electrode. The coaxial electrode was sealed in glass, whereas the other microdisk was sealed with epoxy resin. The epoxy allows a small amount of solution creeping to occur, increasing the effective surface area, and therefore the capacitance, of the electrode.
The rapid drop in impedance of the coaxial MDE between 20 and 50 MHz is anomalous in light of the linearity of the impedance at other frequencies. The impedance value at 50 MHz of 11 ohms is much less than that expected based on the calculated cell resistance. The difficulty of making measurements at such high frequencies may have caused some imprecision in the data. Stray capacitances are a likely cause of the drop in impedance. The impedance of the transmission line comprised of the Pt shunt, glass dielectric, and Au wire may be calculated from the relation \( Z = \frac{138}{k} \log(b/a) \) where \( k \) is the dielectric constant of the dielectric material, \( a \) the MDE radius, and \( b \) the spacing between the Pt tube and MDE. The dielectric constant of the Corning 0120 glass is 6.65(104), which gives an impedance of 30.3 ohms. This value can be considered to be in parallel with any stray capacitances, reducing the impedance at high frequencies.

b. Transient Response of Coaxial Microdisk Electrodes

Figure 72 demonstrates that the reflectivity of the electrode is dependent upon the applied potential. The smooth curve is a plot of the applied potential, and the noisy curve, which follows the applied potential, is the electroreflectance response. The slight lag in response is caused by the lowpass filter used to minimize the noise. Because the purpose of this experiment was to demonstrate that the response tracked the applied potential, extremely fast transient response was not required. The wide signal bandwidth required for fast
Electroreflectance change at 505 nm (noisy curve) and $E_{\text{app}}$ (smooth curve) for a complex waveform applied to an Au microdisk/coaxial dual reference cell, 1M $\text{H}_2\text{SO}_4$. Potential step was from -0.03 volts to 0.85 V vs. SCE, assisted by the charge injection circuit of Figure 25 ($E_{\text{inj}} = 230 \text{ V}, C_{\text{inj}} = 2 \text{ pF}$). Electroreflectance curve is an average of 65,000 pulses, and the photodetection circuit cutoff frequency was 2 MHz.
Figure 72: Time (μsec) vs. $E_{app}$ (volts)
The initial setup of the electroreflectance experiment was performed using phase-sensitive detection techniques. A PAR Model 186A lock-in amplifier at its maximum bandwidth setting was used to detect the signal from the experiment. The signal was lowpass filtered at 2 MHz, and the trigger pulse from the pulse generator used as the reference signal for the lock-in. This method of adjusting the experiment for maximum performance was preferable to using direct signal averaging because the results of an adjustment were apparent in a few seconds, rather than the several hours necessary for signal averaging. The applied potential was varied until the signal was maximized. After a few hours of averaging, the lock-in signal decreased by about 25%. This method also allowed for the easy checking of the presence of phantom signals (see Chapter 3, Figure 20). Blocking the optical beam caused the signal to vanish, as expected; this was further checked by illumination of the photomultiplier with a floating DC light source (flashlight). At the illumination level corresponding to that used in the experiment, the signal was zero,
ensuring that any signal observed was not due to electronic interference from the high speed circuitry.

The transient response of the Au coaxial MDE, corrected for electronic delay, is shown in Figure 73. The plot confirms that complete double-layer charging is achieved in under 28 ns. This is close to the limit of both the charge injection circuit (approximately 15 ns) and the photomultiplier processing circuit (10 ns). The results of a crude chronoamperometry experiment indicates that current flow to the cell is essentially complete in under 35 ns (the response is slowed slightly by the 50 ohm resistor used for current measurements in series with the cell).

If the duty cycle of the electroreflectance experiment is reduced until relaxation of the double layer has insufficient time to occur, the apparent transient response of the experiment is improved. Figure 74 demonstrates a reduction in double layer charging time to 11 ns. This experiment is of value in indicating the ultimate response time of the charge injection circuit under low-demand conditions. The response delay observed here is probably due to the switching time of the charge injection transistor.

The spectroelectrochemical transient response is depicted in Figures 75-76, 78, and 79. Figure 75 is the result of an experiment monitoring the product of the oxidation of O-D in 1M H$_2$SO$_4$. Linearity of the plot was maintained down to a time of 3 μS. The rapid increase in absorbance at short times is due to the background absorbance. The presence of O-D affected the blank absorbance, because the absorbance of a blank run (lower curve, beginning emphasized as the heavy trace)
Figure 73.

Electroreflectance risetime, 60 micron gold coaxial electrode. Bandwidth of photodetection circuit 100 MHz. Plot corrected for 40 ns delay (Figure 28), 380,000 averaged runs.
Figure 73
Figure 74.

Electroreflectance risetime of 60 micron gold coaxial microdisk electrode with incomplete double-layer relaxation. Conditions same as Figure 73, except duty cycle of waveform was increased by 50%, and $E_{\text{inj}} = 230$ V, $C_{\text{inj}} = 0.5$ pF.
Spectroelectrochemical transient response of 125 micron platinum coaxial microdisk electrode. Absorbance vs. $t^{1/2}$ plot (upper curve) is a result of potential step from 0.3 to 1.2 V vs. SCE with charge injection assist ($E_{inj} = 230$ V, $C_{inj} = 175$ pF) in 2.31 mM O-D in 1M H$_2$SO$_4$, 505 nm. Straight line is theory for disk electrode, based on a molar absorptivity of 23600 at 505nm. The slope of the line is 3 percent lower than the slope of a linear regression line (0.266, correlation 0.995) through the data. Lower curve (emphasized line) is a blank taken under the same conditions, containing 4.62 mM HCl (5000 runs averaged).
Figure 75

ABSORBANCE $\times 10^3$

TIME $^{1/2} \times 10^3$ (SECONDS $^{1/2}$)
was larger at short times than the corresponding run containing 0-D (upper curve in Figure 75). Simple subtraction of the blank to correct for background absorbance caused the response to be depressed at short times. A similar effect was noted in kinetic experiments performed with chlorpromazine, which will be discussed later. That the presence of electroactive species affected the blank is not entirely surprising, because electroreflectance effects are very strongly dependent upon the surface properties of the electrode(57). Changes in the refractive index or adsorbed layers at the surface of the electrode, or any surface oxide layer(54,55,105) mediated by other species in close proximity to the surface, could certainly be expected to alter the electroreflectance behavior of the electrode. What is surprising is that simple subtraction of the blank in correcting for background absorbance was sufficient in the microcylindrical case. However, the experimental conditions employed in the two experiments were not identical. The wavelength used in the disk experiment (505 nm) was different from that used in the cylindrical case (514.5 nm). The polishing of the surface of the disk would also change its properties (Pt wire for the cylindrical electrodes was used as supplied by the manufacturer; polishing or similar surface preparation was impossible). Because the electroreflectance effect is strongly angle dependent, a small change in observation angle could greatly affect the background signal observed, as well as the effect of the presence of electroactive species. Since the beam incidence and observation angles, wavelength of observation, and surface preparation in the microdisk and microcylindrical cases were not identical, it is
not possible to directly compare the results from the two experiments, and no conclusions may be drawn from the differences in the results.

Experiments with a test system whose background absorbance was apparently immune from the above effects are shown in Figures 76, 78 and 79. The electrode used was a 60 micron diameter coaxial gold electrode, and the formation of the one-electron reduction product of MV$^{2+}$ in 2M pH 7 phosphate buffer was monitored at 632.8 nm. Figure 76 is the raw data from blank and spectroelectrochemical runs of 200 microseconds duration. Curve A is the blank run, and Curve B was obtained in the presence of chromophore. The absorption from generation of chromophore is nearly swamped by the blank absorbance. The response glitch at 175 microseconds is due to pickup of radio frequency noise by the 15 cm length of connecting cable between the photomultiplier amplifier and the oscilloscope. The radio frequency noise was generated by the charge injection circuit.

The output of the photomultiplier was filtered by the third order filter described in Chapter 4. The cutoff frequency of the filter was 3.14 MHz. Additional filtering was provided by the 5 MHz lowpass filter on the vertical amplifier of the oscilloscope. The system was not operated at full bandwidth because any observable improvement in transient response would have been swamped by the increased noise present with the wider bandwidth, making the small absorbances present here nearly impossible to separate from the noise. FFT spectrum analysis of a theoretically generated absorbance vs. time transient with the same time resolution and duration of the fast run shown here indicates that 99.9% of the power spectrum of the transient lies at
Figure 76.

Absorbance vs. time curves for the generation of methyl viologen cation radical (concentration 5.59 mM, Curve B) and a blank containing 11.2 mM KCl; 2M pH 7 phosphate buffer, 60 micron diameter coaxial gold electrode, potential step (charge injection assisted, $E_{\text{ind}} = 230 \text{ V}$, $C_{\text{ind}} = 1.25 \text{ pF}$) from -0.3 to -0.85 V vs. SCE. Laser beam (632.8 nm) power density 1.8 W/cm². Curve A represents 60,000 runs, the blank 22,000. The photodetection circuit lowpass filter was set at 3.14 MHz; the spike at 175 microseconds apparently originated in the acquisition electronics. Time resolution 1 microsecond per point.
frequencies below 3.14 MHz, justifying the selection of the cutoff frequency of the filter for this experiment. Such filtering would have been unacceptable for transient response determination by monitoring electroreflectance, as indicated in Figure 77. A plot of the amplitude of the energy distribution with frequency of an absorbance vs. time transient is compared to that for a step waveform. The curves in the plot have been normalized so that the total energy of both curves is equivalent, and the frequency axis is normalized to the case where the temporal resolution of the data acquisition system is 1 second per point. Therefore, to obtain the true frequency for a given temporal resolution, the normalized frequency axis is multiplied by the reciprocal of the actual temporal resolution. The absorbance vs. time curve clearly has a larger percentage of its energy distributed at lower frequencies. If the high speed electroreflectance transient of Figure 73 (resolution 2 ns) were processed with the 3.14 MHz filter, over 40% of the high frequency signal would have been rejected. Filtration of such a signal would therefore have caused an unacceptable amount of distortion of the signal waveform. The full bandwidth of the amplifier (100 MHz) passes 98% of the electroreflectance signal, however.

In addition to the MV spectroelectrochemical runs shown in Figure 76, a separate high resolution run was made to determine the best spectroelectrochemical transient response. The total duration of the high resolution run was only 6 microseconds, although the entire observation window comprised 20 microseconds. The duration of the run was limited in the interest of minimizing the wait time between runs,
Figure 77.

Frequency spectrum analysis of absorbance vs. time and step transients. Spectrum analysis was the result of Fourier transforms of 512-point theoretically generated curves. The first 256 points of the data were set to a value of zero; the remaining points constituted the theoretically generated waveform. The edge of the step waveform was rounded slightly with an $e^{-0.0}$ power function to simulate the risetime of the experimentally generated electroreflectance signal, resulting in a 10%-90% risetime of three data points. The two waveforms were normalized so that their areas were equal. A vs t transient, Curve a; step waveform, Curve b.
NORMALIZED AMPLITUDE (ARB. UNITS)

Figure 77
because the extensive signal averaging required would otherwise have made the duration of the experiment prohibitively long (days). Increasing the time resolution for this run by adjusting the timebase would have further increased the duration of the experiment, because the oscilloscope is forced into the equivalent-time sampling mode when the time resolution is better than a few microseconds per data point. Higher resolution runs then require several pulses to acquire an entire waveform. A blank high resolution run was also performed; both runs are shown in Figure 78.

A plot of the 200 μS run from Figure 76, and the high resolution 6 μS run vs. time\(^{1/2}\), after subtracting the blanks, is shown in Figure 79. The solid line is a least-squares fit to the data, and has a slope of 0.0532 s\(^{-1/2}\) (correlation 0.994). This is in agreement with the slope for a 5 ms run (0.0552 s\(^{-1/2}\), correlation 0.995). The absorbance observed in these experiments was less than that for similar experiments performed in a supporting electrolyte of lower concentration. The y-intercept of the curve is 1.1 x 10\(^{-6}\). The first data point at 150 ns is in good agreement with the line, and is an improvement in spectroelectrochemical transient response by a factor of 27 over the previous state of the art. The electroreflectance change observed with a gold electrode in the red region of the spectrum is much smaller than that at shorter wavelengths. The sign of the electroreflectance background would also be expected to be opposite to that observed in the transient response measurement above, because the direction of the potential step is different. The most striking, and unexpected, difference in the two electroreflectance
Figure 78.

6 microsecond absorbance vs. time transients, methyl viologen reduction and blank. Conditions same as Figure 76, except time resolution 150 nS per point. Run corrected for 40 nS signal delay. Curve A, run containing 2.8 mM methyl viologen, 150,000 runs; Curve B, blank with 5.6 mM KCl, 30,000 runs. Period before and after run is shown; point where potential was stepped to rest value denoted by arrow.
Figure 79.

The difference (dashed line) of curves A and B in Figure 76 plotted vs. $t^{1/2}$ after a moving average smooth with a window of 1.5 microseconds. Solid curve is unsmoothed difference of Curves A and B from Figure 80. The solid line is a linear regression line fit to both data sets.
Figure 79
curves (Figures 74 and 76) is the time needed to attain a steady-state value. In the case of the reduction in phosphate buffer, the blank absorbance continues to change, even after complete charging of the double layer. Since the electrode has become fully charged, the blank absorbance change must be due to bulk diffusional processes or the slow formation of surface oxides, rather than processes which are intrinsic to the electrode material itself. It is possible that such processes were occurring during the electroreflectance transient response experiment, but their presence would have been masked by the larger electroreflectance at the wavelength employed in that experiment.
4. Investigation of Chlorpromazine Reaction Kinetics

The investigation of the kinetics of the reduction of chlorpromazine radical cation was then attempted. In the spectroelectrochemical approach to this kinetic study, a solution containing chlorpromazine and the other reactant (for example, dopamine) is oxidized at a platinum electrode. The oxidation potential selected is one where both chlorpromazine and the other reactant are oxidized. Therefore, after the potential step, at the electrode surface dopamine is present in its oxidized quinone form, and will not react with the chlorpromazine radical. The radical must diffuse away from the working electrode before reaction with dopamine may occur. The decay of the radical is monitored at 520 nm, where the absorptivity of both dopamine and dopamine ortho-quinone is low. A run is made with a solution containing only chlorpromazine. Dividing the curve from the run containing dopamine and chlorpromazine by the curve from the chlorpromazine run results in a curve which resembles a conventional kinetic decay curve. This curve is compared with a decay curve obtained from a computer simulation, to obtain rate constant and mechanistic information. Absorbance vs. time transients for oxidation of CPZ by itself and in the presence of dopamine are shown in Figure 80. The working electrode was an 810 micron diameter Pt disk, and the probe beam was reflected at normal incidence. The corresponding normalized absorbance vs. time plot is shown in Figure 81. The data
from Figure 80 was divided point by point in the waveform processing oscilloscope to obtain Figure 81.

First, attempts were made to replicate earlier results for the rate constant for the reaction of dopamine with CPZ+* obtained by Mayausky and McCreery(53). The rate constant of $1.593 \pm 0.046 \times 10^5$, obtained with an 820 micron diameter platinum electrode at pH 1.5 and an ionic strength of 0.2, is 25 percent lower than the earlier value of $2.12 \pm 0.25 \times 10^5$. Changing the size of the electrode to 225 microns diameter decreased the rate constant slightly to $1.506 \pm 0.029 \times 10^5$. The experiment was repeated at a reactant concentration of 1 mM, resulting in a rate constant of $1.416 \pm 0.030 \times 10^5$. The method of rate constant calculation used by Mayausky and McCreery was slightly different from that used in this work, and could account for some of the difference. Rate constants in this work were calculated based upon the entire data set, rather than selecting points which were judged to represent the average value of the kinetic decay curve, as was the case in the earlier work. Additionally, Mayausky and McCreery used a glancing incidence technique for kinetic experiments, which may account for some of the difference in the rate constant obtained. Whatever the cause of the difference, it was judged insignificant for these experiments because the purpose of this investigation is to examine trends in rate constants. Therefore, any differences in absolute rate constants are unimportant so long as the differences are internally consistent, which is a reasonable assumption in this case. Increasing the ionic strength of the solution to 1.8 to improve transient response caused the rate constant to decrease. The effect
Figure 80.

Absorbance vs. time transients for oxidation of chlorpromazine (upper curve) and chlorpromazine in the presence of dopamine (lower curve). Platinum electrode was stepped from 0.0 to 0.82 V vs. SCE; generation of CPZ radical was monitored at 520 nm. Solution contained 0.2M pH 1.58 dichloroacetic acid / 42% methanol buffer, 2mM CPZ or CPZ and DA. Ionic strength of buffer was 1.8 (KCl added); 100 runs were averaged in each case.
OPTICAL ABSORBANCE vs TIME [MILLISECONDS]

Figure 80
Figure 81.

Normalized absorbance vs. time curve from kinetic run of Figure 80. First data point was set to value of 1.0.
Figure 81

OPTICAL ABSORBANCE (NORMALIZED)

TIME [MILLI SECONDS]

Figure 81
was assumed to be the result of ionic strength effects (107).

As the pH of the supporting electrolyte was increased, the rate of reaction also increased. For maximum precision in determination of the rate constant, the time scale of the experiment must be shifted so that normalized absorbances in the range of 0.7 to 0.4 are observed. At higher speeds the absorbance from chromophore decreases, and background absorbances become an increasing problem. A blank run in pH 1.6 buffer for a potential step of 0.0 to 0.82 volts is shown in Figure 82 (lower curve). For a 4 ms kinetic run, this can represent as much as 20% of the total signal, which will seriously affect the calculated value of the rate constant. Increasing the magnitude of the potential step by decreasing the rest potential to -0.25 volts (used for ascorbic acid runs), causes a significant increase in blank absorbance. Normally, subtraction of blank will correct this problem. Unfortunately, the presence of CPZ or dopamine reduces the blank absorbance, because simple subtraction of the blank causes nonlinearity in the absorbance vs. time$^{1/2}$ transient; the y-intercept of a chlorpromazine absorbance vs. time$^{1/2}$ also indicated a lower blank. A similar effect was noted earlier in connection with experiments involving O-D (also an oxidation with a platinum electrode). The blank was also reduced by the presence of dopamine, hydroquinone, ascorbic acid, and 6-hydroxydopamine. Figure 83 is a plot of two runs made at pH 2.7. The upper curve is the absorbance obtained from a solution containing only buffer; the lower curve is a blank from the same buffer, containing 2 mM dopamine. As mentioned earlier, the absorbance of dopamine at the wavelength used is
Figure 82.

Absorbance vs. time transient for a blank in pH 1.6 buffer. Conditions same as in Figure 80. Potential step 0.0 to 0.82 V (lower curve); -0.25 V to 0.82 V (upper curve). 300 runs averaged.
negligible. Increasing the dopamine concentration above 2 mM caused no further reduction in blank. Hydroquinone, ascorbic acid, and 6-hydroxydopamine produced similar results. Figures 84 and 85 are blanks from similar experiments, but at pH values of 3.5 and 5.3, respectively. In all cases, increasing the pH caused an increase in blank, and addition of reactant caused the blank to decrease (lower curves in Figures 84 and 85). It is possible that the blank may be due to the formation of oxidized Cl\textsuperscript{−} species from adsorbed Cl\textsuperscript{−}, because the potentials employed are near the Cl\textsuperscript{−} oxidation potential. This possibility is supported by the fact that the presence of a reducing agent (i.e. DA or HQ), and the fact that the concentrations of oxidized species formed from Cl\textsuperscript{−}, such as ClO\textsubscript{3}\textsuperscript{−}, are lowered at the electrode surface under acidic conditions\textsuperscript{(108)}. Given the large variation in background absorbance over the range of experimental conditions employed, the most prudent action in dealing with the blank is decreasing the blank absorbance and/or increasing the signal, rather than attempting to correct the experimental data for each experiment.

By varying the duty cycle, the blank could be reduced or eliminated. Figure 86 shows absorbance vs. time transients for blanks at duty cycles of 10%, 1%, 0.1% and 0.01%. As the duty cycle was reduced, the blank was also reduced. This indicates that some relatively slow adsorption or other surface process is connected with the blank absorbance. Eliminating the methanol in the supporting electrolyte also reduced the blank (Figure 87). However, eliminating the methanol will decrease the pH of the buffer, and the reduction in
Figure 83.

Absorbance vs. time transients in pH 2.7 buffer, same conditions as Figure 80. Upper curve, blank only; lower curve, buffer containing 2 mM dopamine.
Figure 83

ABSORBANCE X 10^4

TIME X 10^3 (SECONDS)
Figure 84.

Absorbance vs. time transients in pH 3.5 buffer, same conditions as Figure 80. Upper curve, blank only; lower curve, buffer containing 2 mM dopamine.
Figure 84

**ABSORBANCE X 10^4**

**TIME X 10^3 (SECONDS)**
Figure 85.

Absorbance vs. time transients in pH 5.3 buffer, same conditions as Figure 80. Upper curve, blank only; lower curve, buffer containing 2 mM dopamine.
Figure 85

TIME X 10^3 (SECONDS)

ABSORBANCE X 10^4
blank absorbance may be due to a reduction in pH because of the pH
dependence of the background signal.

An attempt was made to use KNO₃ to increase the ionic strength of
the supporting electrolyte rather than KCl, under the assumption that
modulation of electrode coverage by Cl⁻ was responsible for the
background absorbance. Unfortunately, the solubility of KNO₃ was lower
than KCl in the methanol solution. Reducing the ionic strength to
accommodate this factor would have increased the resistance of the
supporting electrolyte, which was undesirable, and would also have
made direct comparison with previous results difficult.

While the two methods mentioned above may be used to reduce the
blank, they have somewhat undesirable consequences. Obviously,
reducing the duty cycle may be impractical from the standpoint of
increasing the total time needed for an experiment. While the nearly
100% reduction in blank absorbance with the smallest duty cycle is
attractive, the increase in experimental time of a factor of 100 is
unacceptable. The additional factor of long-term stability of the
xenon arc and electronics must be considered for long experiments. It
was also not worthwhile to trade the loss in precision from electronic
drift and the longer experimental time for a mere 30% improvement (or
less) in blank absorption afforded by the 0.1% duty cycle. Reduction
of the methanol concentration, while also attractive from the blank
absorbance standpoint, will cause problems with CPZ adsorption(53),
affecting data taken at short times. Unfortunately, this is exactly
the region where blank reduction is most desirable. Therefore, an
alternative means of improving the quality of the data for fast
Figure 86.

Absorbance vs. time transients in pH 5.3 buffer, same conditions as Figure 80. Curve A, 10% duty cycle ($T_{\text{wait}}/T_{\text{step}}$ 10:1), 5000 runs; B, 1% duty cycle, 3000 runs; C, 0.1% duty cycle, 2000 runs; D, 0.01% duty cycle, 2000 runs.
Figure 86

Absorbance $\times 10^3$ vs. Time $\times 10^4$ (seconds)

Graph showing absorbance over time for different conditions labeled a, b, c, and d.
Figure 87.

Absorbance vs. time transients in pH 5.3 buffer, same conditions as Figure 80. Methanol was not added to buffer; as a result, the pH would be slightly lower than the buffer solution containing methanol. Curve A, 10% duty cycle, 3000 runs; B, 1% duty cycle, 2000 runs; C, 0.1% duty cycle, 1000 runs.
Figure 87
Experiments must be found.

Experiments at glancing incidence were successful in improving the signal and therefore minimizing the contribution of the blank to the total absorbance. Additionally, because the blank absorbance arises mostly from processes occurring at the electrode surface, they will be strongly angle dependent. This was observed in the runs made at glancing incidence, with the blank absorbance contributing less to the total absorbance (smaller values of the y-intercept for plots of absorbance vs. time$^{1/2}$). The angle of incidence was determined empirically by comparing the slope of an absorbance vs. time$^{1/2}$ plot of a run made at glancing incidence to that of a run made at a normal incidence angle. A plot of absorbance vs. time$^{1/2}$ showing runs obtained at normal and glancing incidence angles is shown in Figure 88. Both runs were made with the same concentration of CPZ. The upper, glancing incidence curve has a slope of 0.2151 and a y-intercept of $-1.00 \times 10^{-5}$; the values for the normal incidence curve were 0.0807 and $9.67 \times 10^{-4}$, respectively. Dividing the slopes of the runs gives an enhancement factor of 2.6. An enhancement of 2.6 corresponds to an incidence angle of 22.7 degrees (Equation 4, see text). The incidence angle was not measured directly because it was difficult to determine the exact orientation of the electrode surface with respect to the beam. An exact value for this parameter was not needed anyway, because the use of the normalized absorbance parameter for kinetic calculations is not affected by enhancements in absorbance, as long as both runs in an experiment are made under the same conditions and show linear diffusional behavior. A kinetic run made at glancing incidence
Figure 88.

Absorbance (520 nm) vs. t^{1/2} transients for the oxidation of 2 mM CPZ at normal (lower curve) and glancing (upper curve) incidence. Upper curve: 125 micron coaxial Pt electrode, 350 averaged runs; linear regression line fit to data has y-intercept of $-1.00 \times 10^{-5}$, slope 0.2151 (correlation 0.9998). Lower curve: 225 micron diameter Pt electrode, 500 runs; linear regression line y-intercept 9.67 x 10^{-4}, slope 0.0807 (correlation 0.991).
Figure 89.

Absorbance vs. time transients at glancing incidence for oxidation of chlorpromazine (upper curve) and chlorpromazine in the presence of dopamine (lower curve). Conditions same as Figure 80, except 125 micron coaxial platinum electrode was used; pH was 6.79 (dimethylarsenic acid buffer). CPZ run represents 3000 averaged runs; DA, 1120 runs (smoothed with 6 microsecond window).
Figure 89

Absorbance x 10^3

Time (μsec)
is shown in Figure 89.

Attempts at operation at smaller incidence angles were mostly unsuccessful. For a given beam diameter, the area of the beam on the electrode surface increases as the enhancement factor increases. At smaller angles, the beam begins to be reflected from the glass surrounding the MDE, and the resulting stray light affects the data. The poorer transient response observed at a calculated incidence angle of 15 degrees may be a result of incidence angle, or a result of scattered light. In the latter case, the use of a light source with a smaller effective source size (a laser, or a smaller pinhole in the arc collimator) will allow focusing of the beam to a smaller size, eliminating scattered light and improving the transient response. This will be particularly true in the case of the 50 micron MDE.

The rate constants were calculated from the data with the computer program in the Appendix (working curve was kinetic case 2, Equation 2, Reference 53). The fit of normalized data from experiments to this working curve is demonstrated in Figure 90. The data are for kinetic runs with dopamine at pH 1.5 ($Z = 0.2$), and represent data from 13 experiments. The data for each run was fit to the working curve using the rate constant calculated from the data in that particular run. The plot shows that most of the kinetic information in the runs used here is concentrated over the normalized absorbance range from 0.38 to 0.55. The maximum time of the plot, corresponding to the average rate constant of $1.6 \times 10^5$, is 140 mS full scale (concentration = $2.0 \times 10^{-3}$ M).
The computer program used for the calculation of the rate constant compared each data point to the working curve used in Reference 53, and calculated the rate constant corresponding to the normalized absorbance and time values of that particular point. Intermediate values not corresponding to points on the working curve were interpolated using either a simple average, or the derivative method. Both methods of interpolation resulted in essentially the same rate constant; the former method was therefore incorporated into the program because of its lower complexity and concomitant increase in computational speed. Any points lying outside the normalized absorbance range of 0.31 to 1.0 were not used in the kinetic calculation. This was repeated for each data point in the normalized absorbance vs. time range of approximately 0.9 to 0.4 (the fastest runs extended the lower limit to 0.3). The average of these rate constants and its standard deviation was calculated, and represents the rate constant for the entire run. The fit of the rate constant obtained to the working curve was checked by plotting the calculated rate constant for each point vs. time. A perfect fit should give a line with a slope of zero (no variation in rate constant over the duration of the run). This method of determining mechanistic shifts was more sensitive than a comparison of normalized absorbance vs. time data with the working curve (Figure 90), because any variation is enhanced by the expansion of the y-axis, and it is easier to observe conformity of the data to a straight, rather than curved, line. The result of such a plot is shown in Figure 91; the case is the reaction of dopamine with CPZ$^{+*}$ at pH 6.79, resulting in a calculated rate
Plot demonstrating fit of normalized absorbance data to working curve. Data is normalized absorbance values from 13 runs (3246 data points) for CPZ/DA at pH 1.5 (ionic strength 0.2). Data from each run was fit to normalized absorbance curve based upon the calculated rate constant for that data set. For $k_{obs} 1.6 \times 10^5$ the full scale time for the plot would be 140 mS.

Plot of rate constant vs. time for each point for data from Figure 89. Horizontal line is average of all points and has a value of 5.126 $\pm$ 0.915 $\times$ 10^7. Rate constants calculated from computer program described in text.
Figure 90

LOG (kct)

Figure 91
constant of $5.12 \times 10^7$ (the absorbance vs. time transients used for this run are the same as those shown in Figure 89). The straight line in the figure corresponds to the average of all rate constant data points in the plot.

Rather than calculating a rate constant for each experiment and then averaging the result to obtain the average rate constant, the normalized absorbance vs. time curves were averaged; the resulting curve was used for calculation of the rate constant, improving the accuracy of the calculation.

The calculated average rate constants are shown in Table 8. The ascorbic acid data is of limited value because of the imprecision in the calculated rate constants. The large imprecision in the results is due to the fact that a 0.1% duty cycle was used in ascorbic acid kinetic runs, because the irreversible oxidation of ascorbic acid results in a longer time necessary for initial conditions to be re-established. The poor long-term noise performance of the xenon arc lamp used resulted in exceedingly noisy data, which is reflected in the poor precision of the rate constants.

Because the runs made with dopamine and hydroquinone employed a 1% duty cycle, the precision in the rate constants for those systems is better. Figure 92 is a plot of $\log(k_{\text{obs}})$ vs. pH for these two systems. The pH dependence of these two systems is quite different. The rate of reaction of hydroquinone with CPZ$^{+\cdot}$ increases by about a factor of ten over the pH range studied, while the rate of reaction of dopamine with CPZ$^{+\cdot}$ increases by nearly three orders of magnitude.
Figure 92. Plot of log(observed rate constant) vs. pH for reaction of chlorpromazine radical cation with dopamine and with hydroquinone.
Table 8. Rate Constants for Reduction of Chlorpromazine Radical Cation as a Function of pH and Substrate

$K_{obs}, \times 10^{-6}$

<table>
<thead>
<tr>
<th>Substrate:</th>
<th>Dopamine</th>
<th>Hydroquinone</th>
<th>Ascorbic Acid</th>
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</thead>
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<tr>
<td>pH</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1.60</td>
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<td>1.09 ± 0.145</td>
<td>-</td>
</tr>
<tr>
<td>1.90</td>
<td>0.146 ± 0.035</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>1.84 ± 0.110</td>
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</tr>
<tr>
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<td>0.273 ± 0.058</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.47</td>
<td>0.592 ± 0.151</td>
<td>3.62 ± 1.60</td>
<td>12.20 ± 12.9</td>
</tr>
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<td>102.8 ± 49.2</td>
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</table>
5. Miscellaneous Experiments

Two other types of experiments were performed that are worth discussing. Attempts at diffractive spectroelectrochemistry experiments with microelectrodes (cylindrical and ribbon) were made. Experiments designed to determine if artificial diffusional enhancement with laser heating would increase the allowable spectroelectrochemical duty cycle were also performed.

A. Diffractive Spectroelectrochemistry

A typical diffraction pattern produced by intercepting the central portion of a laser beam with a cylindrical electrode of small diameter, using the experimental configuration shown in Figure 93, is shown in Figure 94. Because the diffraction pattern produced depends upon the diameter of the fiber and the wavelength of light used, the layer of chromophore produced during electrolysis should effectively increase the electrode "diameter" seen by the beam. There should therefore be a shift in the pattern of maxima and minima in the diffraction pattern as chromophore is generated (i.e. as the "diameter" of the electrode changes). If one were to monitor the intensity of the beam at the appropriate position on the diffraction pattern, one should see an absorbance enhancement as the position of the pattern shifts. This is depicted in Figure 94. As generation of
Figure 93.

Experimental configuration for diffractive spectroelectrochemistry from a microelectrode. Electrodes used were 12.8 micron gold diameter cylindrical and 25 x 500 micron gold ribbon. Electrode was placed at focal point of lens; position of electrode was adjusted until equal amounts of diffraction from both sides of the electrode was obtained. With the ribbon electrode, alignment of the long axis of the electrode with the beam was changed until the highest quality diffraction pattern was obtained.

Figure 94.

Diagram of diffraction pattern obtained with focused laser beam. A, before potential step; B, during spectroelectrochemical run. Shrinkage of pattern was accompanied by a general loss of intensity of the pattern and blooming of the undiffracted portion of the beam. 1: position of detector during experiment depicted in Figure 99; 2: detector position for experiment depicted in Figure 98; 3: detector position for experiments depicted in Figures 95, 96, 97, and 100.
chromophore commences, the shift of the position of the minimum at point 3 to a smaller angle will cause a pseudoabsorbance to be superimposed upon the absorbance due to chromophore. If the shift is great enough, it should be possible to track the traversing of several maxima and minima across observation point 3. The rate of the traverse could be indicative of the rates of processes occurring in the diffusion layer and/or near the electrode surface.

The results of an experiment using the diffraction of the beam of an Ar+ laser (514.5 nm) is shown in Figure 95. The electrode was a 12.8 micron gold cylinder. The position of the detector for this and other diffraction experiments is denoted in Figure 94. The absorbance is enhanced over the value that would be expected in a reflection experiment. If the beam was focused (lens f.l. 267 mm), the maximum absorbance increased (Figure 96).

Some far more interesting results are shown in Figures 97-100. The working electrode in this case was a 25 x 500 micron gold ribbon electrode. The focused probe beam was passed at parallel incidence to the long electrode axis. The absorbance enhancement of about a factor of 10 (compared to a normal reflection experiment) shown in Figure 97 arises from a visibly large shift in the diffraction pattern. To enhance the linear shift in the pattern, the selected minima was projected over a distance of approximately 4 m. For a given angular shift in the pattern, the resulting radial shift will increase as the distance from the electrode is increased. A pinhole aperture was used on the PMT housing for spatial discrimination. When this was done, it was possible to observe the traversal of a diffractive maximum over
Figure 95.

1 s absorbance vs. time transient for diffraction from 12.8 micron gold cylindrical electrode, unfocused probe beam. 3.52 mM O-D, 0.0 to 0.8 V vs. SCE, beam power density 2.8 W/cm², 7 runs averaged.

Figure 96.

1 s absorbance vs. time transient for diffraction from 12.8 micron gold cylindrical electrode, focused probe beam. 3.52 mM O-D, 0.0 to 0.8 V vs. SCE, beam power density 50 W/cm², 4 runs averaged.
Figure 97.

1 s absorbance vs. time\(^{1/2}\) transient for diffraction from gold ribbon electrode. 2.81 mM O-D, 0.0 to 0.8 V vs. SCE, beam power density 50 W/cm\(^2\), 7 runs averaged.
the detection point, reducing the absorbance after 300 mS (Figure 98). This effect was observed to increase with increasing laser power; the enhancement at high powers was therefore due to a thermal effect. This might indicate the contribution of thermal lensing to the absorbance enhancement through establishment of a refractive index gradient at the electrode surface. This is supported by the data presented in Figure 99. The detector was positioned so that the housing's pinhole aperture was located at the first diffractide minimum. As the experiment progressed, the heating of the solution from beam absorption caused blooming of the portion of the beam projected near the detector, because the beam was defocused by the thermal refractive index gradient. The result was overload of the photomultiplier amplifier, shown as the clipped portion of the curve after 400 mS.

The transient response of the refractive index effect was approximately 2 mS (Figure 100), which represents a diffusion layer thickness corresponding to approximately twice the wavelength of the light used (514.5 nm). Therefore, the diffusion layer thickness must apparently be equal to the light wavelength if it is to interact with the beam and produce enhancements, at least in the geometrical orientation of the electrode with respect to the beam used in this experiment.

When the laser was unfocused, the distance between maxima/minima in the diffraction pattern was smaller, which is the same direction the pattern shifted during a diffractive spectroelectrochemistry experiment with a focused beam. Movement of the pattern was not observed when an unfocused beam was used. This may indicate that the
Figure 98.

1 s absorbance vs. time transient for diffraction from gold ribbon electrode, illustrating movement of diffraction pattern. 2.81 mM O-D, 0.0 to 0.8 V vs. SCE, beam power density 50 W/cm², 10 runs averaged.

Figure 99.

1 s absorbance vs. time transient for diffraction from gold ribbon electrode, illustrating blooming of probe beam. 2.81 mM O-D, 0.0 to 0.8 V vs. SCE, beam power density 50 W/cm², 6 runs averaged.
**Figure 98**

![Graph showing absorbance over time.](image)

**Figure 99**

![Graph showing absorbance over time.](image)
Figure 100.

100 ms absorbance vs. time$^{1/2}$ transient for diffraction from gold ribbon electrode. 2.81 mM O-D, 0.0 to 0.8 V vs. SCE, beam power density 1.4 W/cm$^2$, 20 runs averaged.
Figure 100  \[ \text{TIME}^{1/2} \text{ (SECONDS}^{1/2} \text{)} \]
shifts in the pattern resulting in absorbance enhancement were caused by the defocusing of the beam by the formation of a thermal lens which effectively defocuses the beam. The conclusion, at least as far as this experiment is concerned, is that the absorbance enhancement is due mostly to thermal lens formation, rather than an apparent increase in electrode "diameter" from the formation of a diffusion layer containing a chromophore.

B. Laser Enhancement of Duty Factors

The utility of signal averaging in an electrochemical experiment would be greatly enhanced if it were possible to operate under experimental conditions where the allowable duty factor were significantly greater than the normally used value of 1%. The reason for this limit is that sufficient time must be allowed for electrolysis of chromophore and diffusion of electroactive species to the surface of the electrode to re-establish the initial conditions of the experiment. In the case of an irreversible charge transfer reaction, the time necessary for re-establishing initial conditions would be greater.

If the layer of chromophore near the surface of the electrode were illuminated with a high power laser pulse of the appropriate wavelength immediately after the spectroelectrochemical experiment, absorption of the beam will cause the generation of a thermal pulse causing local heating of the diffusion layer and rapid convectional
mixing and ejection of chromophore. In the case of an irreversible
charge transfer reaction, this could be of advantage during signal
averaging, as the mixing of the solution during the pulse will allow
the initial conditions to be established more rapidly. This can
shorten the duration of a spectroelectrochemical experiment where
signal averaging is required, particularly in those cases where long
experiments and/or extensive averaging are required.

To determine the feasibility of this hypothesis, a 60 micron gold
MDE was used in the spectroelectrochemical monitoring of the one
electron reduction of MV$^{1+}$ to its monocation radical. The generation
of chromophore was monitored at 632.8 nm. After the
spectroelectrochemical run, the electrode was illuminated by a focused
pulse from a dye laser at a wavelength of 580 nm. The power density of
the focused beam was 320 W/cm$^2$. The duration of the pulse was 0.12 ms,
which represents a 2% duty cycle compared to the length of an entire
experimental cycle. The PMT was protected from the intense beam in two
ways: two Wratten #25 (deep red) photographic filters were inserted
between the reflected beam and the PMT (an interference filter tuned
to 632.8 nm would have provided superior rejection of the high power
beam, but was not available at the time); and the angle of incidence
of the pulsed beam was adjusted so that the beam's reflection was
directed away from the PMT. The wavelength of the pulsed beam was
selected to be as close as possible to the visible absorption maximum
of reduced methyl viologen (605 nm), but sufficiently far away from
the observation wavelength to avoid interference with the data
acquisition system.
The dye laser beam was pulsed with the use of a chopper (Laser Precision, Inc.) equipped with a 2% duty cycle blade. The spectroelectrochemical experiment was triggered with the synchronization clock signal from the chopper. Although the relative timing of the pulse with respect to the spectroelectrochemical experiment could be adjusted somewhat by mechanical positioning of the chopper and adjustment of the trigger threshold of the oscilloscope, ideal positioning of the pulse (coincident with the spectroelectrochemical return step) could not be achieved.

The results of the experiment are shown in Figure 101. The absorbance vs. time response for MV" reduction with a 30% duty cycle is shown both with and without the laser pulse. The position of the pulse is indicated by the arrows in the figure. The laser illumination spike actually swamped the detection system, and is truncated here for clarity. The laser pulse appears somewhat broader than its actual duration because of the time taken by the photomultiplier to recover from the momentary optical and electronic overload. The results indicate that for the experimental conditions employed here, laser pulsing has no effect on the response. If increased diffusional mixing were occurring, a drop in absorbance should be observed immediately after the laser pulse. It should be noted, however, that the experimental conditions employed in this experiment are not optimum for observation of the desired effect, and the use of an electrochemically irreversible system and/or longer runs to test the hypothesis may give significantly different results. The larger absorbances present with longer runs would cause greater absorption of
Figure 101.

Absorbance vs. time transients for methyl viologen reduction, 60 micron gold electrode illuminated with 120 microsecond duration, 320 W/cm², 580 nm laser pulse during return step. Methyl viologen concentration was 8.78 mM in 2M pH 7 phosphate buffer; potential step was -0.4 to -0.85 V vs. SCE, and charge injection was used. Probe beam power density was 20 mW/cm². Transients both with and without high power laser pulse are superimposed. Arrows indicate position of laser pulse.
the beam, enhancing any thermal stirring effect. Also, the high power pulse could concievably have a duration approaching $T_{\text{wait}}$, maximizing the heating effect. Before the possible utility of thermally-induced mixing is dismissed, an experiment with a more flexible timing arrangement and/or an irreversible system should be performed.
Chapter 6

GENERAL DISCUSSION

1. Microelectrodes for Spectroelectrochemistry

A. Comparison of Techniques

The low surface area of microelectrodes results in a significant advantage over the use of electrodes of conventional size in terms of the low demands upon the driving electronics. Additionally, the improved transient response observed with microelectrodes is of considerable value in expanding the scope of the technique. The faster transient response results in an improvement in the total temporal dynamic range attainable in a spectroelectrochemical experiment.

In all cases, the metallic microelectrodes were superior to carbon fiber microelectrodes in terms of longevity, ease of fabrication, availability of different sizes, and transient response. The best overall performance was obtained with electrodes of disk configuration; the ease of theoretical modeling of the absorbance was a significant advantage over cylindrical electrodes. The best transient response was obtained with microdisk electrodes of small radii. Reductions in surface area always resulted in an improvement in
transient response, but the inductance of the wiring of a conventional electrochemical cell configuration caused the transient response to be much worse than that predicted from the simple RC model of cell risetime. The product of cell resistance and capacitance does not account for any reactive circuit elements other than the cell capacitance, such as inductance, which can strongly affect the cell performance on the submicrosecond time scale, as was shown.

The coaxial microdisk design eliminated the problems from stray inductive reactances, reducing the inductance to an immeasurably low value, at least at frequencies below the measurement limit of 50 MHz. This allowed the advantages of the low surface area microelectrode to be fully realized. Additionally, the fact that the working and counter electrodes are housed in the same assembly simplified the overall cell design and resulted in optimum placement of counter electrode with respect to the working electrode, namely, a symmetrical, cylindrical current field during electrode charging and electrolysis.

Background absorbance from electroreflectance and other sources was the major problem encountered when using the technique. However, the selection of proper electrode materials and wavelengths can reduce the magnitude of this problem. The most effective method of reducing its influence on the experiment would seem to be tuning the optical beam incidence angle to minimize the blank absorbance and/or increase the total signal. The horizontally and vertically polarized components of the light show different behavior regarding electroreflectance(57). There are angles of incidence where the magnitudes of electroreflectance are equal but opposite in sign for perpendicularly
and parallel polarized light. For randomly polarized light this would cause the electroreflectance signal to be cancelled or minimized. This was indicated in the glancing incidence kinetic experiments, which reduced the blank to an insignificant proportion of the signal. The y-intercept of a regression line drawn through absorbance vs. time$^{1/2}$ plots of data from chlorpromazine oxidation experiments indicates the amount of background absorbance. This was reduced in magnitude by as much as a factor of 100 in experiments at glancing incidence, compared to a similar experiment at normal incidence. Because the background absorbance represented the major limitation in the use of microdisk electrodes for high speed kinetic studies, reduction of this problem was a significant step in the improvement of this technique.

The total temporal dynamic range of microelectrode techniques are listed in Table 9, where the dynamic ranges of various microelectrode configurations are compared. The dynamic range is defined here as the length of the longest run where planar conditions are followed (within 5%) divided by the fastest usable transient response in a spectroelectrochemical experiment (monitoring of an electrogenerated chromophore). For a cylindrical electrode, the widest dynamic range is exhibited by an electrode of 10 microns diameter. While the poorer transient response of a larger electrode is offset by its ability to operate for a longer period under planar conditions, the longer runs are more susceptible to convective and thermal heating effects, causing a reduction in the actual dynamic range. A smaller cylinder is mechanically more difficult to realize, in addition to having higher resistivity, as demonstrated by Figure 8, which will reduce the
transient response improvement anticipated by the reduction of electrode area. The dynamic range of the 10 micron cylinder is 0.49 ms/4 us, or 123.

Table 9. Dynamic Range of Different Electrode Configurations

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<thead>
<tr>
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<th>Usable Time Scale</th>
<th>Dynamic Range</th>
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<tr>
<td>( r = 5 ) microns cylindrical</td>
<td>4 us - 490 us</td>
<td>123</td>
</tr>
<tr>
<td>( r = 25 ) microns disk</td>
<td>150 ns - 110 mS</td>
<td>( 7.3 \times 10^5 )</td>
</tr>
<tr>
<td>( r = 25 - 202 ) microns disk</td>
<td>150 ns - 2.1 s</td>
<td>( 1.4 \times 10^7 )</td>
</tr>
</tbody>
</table>

The maximum duration of the experiment for linear operation reported here may limit the use of microelectrodes in kinetic studies to systems with rate constants much slower than those studied here, i.e. slower than about \( 10^4 \). Fortunately, this is the temporal range where techniques such as stopped-flow methods and "ordinary" spectroelectrochemistry are applicable, and can be employed for such systems.

The widest dynamic range was exhibited by the coaxial microelectrodes. With a 50 micron diameter disk, the usable spectroelectrochemical temporal range was determined to be 150 ns to 110 ms, or a dynamic range of \( 7.3 \times 10^5 \). This exceeds the temporal dynamic range of presently available digital data acquisition systems; a 110 ms experiment with a time resolution of 1 part in 4096 would
have the ability to resolve events with a precision of 27 microseconds, which does not approach the transient response of the microdisk electrode. Fortunately, spectroelectrochemical experiments rarely require such wide dynamic range in a single experiment. Therefore, the upper limit of the dynamic range may be extended by selecting larger diameter electrodes. For example, a 405 micron disk was found to exhibit linear behavior to at least 2.1 s. This limit could probably be extended by further reductions in probe beam intensity. The use of larger electrodes for experiments not requiring high time resolution will extend the total temporal dynamic range to at least $1.4 \times 10^7$. It should also be pointed out that there is a very small number of techniques that possess a dynamic range of this magnitude.

The dynamic range of over $10^7$ can be compared to that of $2 \times 10^5 (20\text{s}/100\text{us})$ for a typical reflection spectroelectrochemical experiment with a large surface area electrode. Besides having a greater dynamic range, the microelectrode has the additional advantages of not requiring the elaborate fine tuning required of fast potentiostatic control systems, and the ability to examine electrode and solution processes occurring on faster time scales. While solution kinetic reactions may be slowed by the reduction of reactant concentrations, there is an obvious limit to this practice because reducing the concentration also reduces the available signal, and the problems of background processes (e.g. electroreflectance) become more important. Microelectrodes therefore can be used to advantage in the examination of reactions whose rates are dependent on concentration in a nonlinear
manner.

The work reported here made exclusive use of aqueous electrochemical systems. Because of the generally high resistivity of nonaqueous systems, the performance of this technique, as measured by the transient response, will decrease due to the larger RC time constant and greater IR errors. Although the transient response of an electrochemical experiment with microelectrodes will be worse with nonaqueous supporting electrolytes, an experiment performed with conventional electrodes and potential control circuitry will be affected to the same or greater extent. The higher IR errors encountered with nonaqueous solvents will require greater voltage compliance from an active potential control system, which will further expose any limitations of such apparatus. The performance of an electrochemical cell using microelectrodes will therefore always be superior to conventional equipment for the experiments conducted here, regardless of solvent or solution resistivity.

B. Selection of Experimental Conditions for Optimum Performance When Using Microelectrodes

With electrodes of surface areas of greater than $10^{-3}$ cm$^2$ it is generally prudent to adhere to conventional potentiostatic potential control for all spectroelectrochemical experiments. The selection of an electrode of smaller surface area for an experiment presents other possibilities of potential control, such as those discussed in this work.
For all spectr electrochemical experiments, the high slope
lowpass filter used for photometric processing was superior to a
conventional single-pole passive RC filter for improving the
signal-to-noise performance of the experiment. An added feature of
this system that is often overlooked is the reduction in aliased
information when digital data acquisition systems are employed;
aliasing can affect the quality of data collected in an experiment,
particularly with signals containing appreciable high frequency noise.

Knowledge of the approximate values of the solution resistivity
and electrode double-layer capacitance for a given electrochemical
system are necessary in selecting the proper microelectrode/potential
control system for optimum results. Generally, the first consideration
is the maximum time resolution required in the experiment. The surface
area of the electrode selected should give a time constant of less
than 10 times the fastest time response required. For electrodes with
a time constant approaching this value, charge injection is required.
If all electrodes under consideration possess time constants well
below the prescribed value, the largest electrode should be selected,
in the interests of maximizing the linearity of response at longer
times. The larger electrodes are also more convenient from the optical
standpoint: it is easier to focus the optical beam on a larger
electrode, and the total light throughput for a given beam power
density is increased, improving the quality of the signal. Thermal
effects from beam absorption by the solution will decrease the
duration of linearity in an experiment for a given electrode size. The
beam power should therefore be as low as possible (with microdisk
electrodes power densities of 100 uW/cm² or less were used for longer experiments).

For runs where optimum transient response is not required (time resolution of experiment is greater than 100RC), the charge injection circuit may be disabled, which will allow for simpler operation of the electrochemical cell (no adjustments required other than setting of the applied potential).

Compared to the circuitry employed in this work, potentiostatic control will improve the linearity of runs longer than 200 ms, particularly for larger electrodes. The charge injection circuit was optimized for faster runs, as mentioned earlier in the discussion of that topic in Chapter 4. However, if desired, this problem may be eliminated by modification of the circuit. This was not done in this work, because the emphasis on faster experiments.

C. The Question of Diffusion Layer Thickness vs. Probe Beam Wavelength

For reflection spectroelectrochemical experiments occurring on a submillisecond timescale, the agreement of experiment with theory may be surprising after considering that on this time scale, the wavelength of the photons used in the observation of electrogenerated chromophore can be much larger than the thickness of the layer of chromophore. The most extreme case of this occurs in the fastest spectroelectrochemical runs, where agreement with theory was observed 150 nanoseconds after the initiation of electrolysis. At this point in
the experiment, over 70% of electrogenerated species is within 100 Angstroms of the electrode surface. The wavelength of light employed in the absorbance measurement was over 60 times longer than this distance. Furthermore, a given photon has the opportunity to interact with only a few tens of molecules of chromophore in a diffusion layer of this thickness. Electric field calculations (57) at and near the surface of the electrode would seem to imply that data collected at such short times would exhibit anomalous behavior, because of the variations in the mean electric field near the electrode surface. This was not demonstrated to any great extent by the data from the experiment, although caution should be exercised in drawing conclusions until data of higher quality are obtained. It can be said, however, with a fair amount of certainty, that the data obtained on the microsecond time scale are completely free from any anomalous behavior; the diffusion layer thickness at these times remains a small fraction of the wavelength of the light employed.

A possible explanation may be advanced in support of these observations. The electric field calculations mentioned above assume an electrode surface smooth on the dimensions of the wavelength of the light used (rms roughness less than 10% of the wavelength). While such smoothness is fairly simple to realize when experiments concerning infrared wavelengths are concerned, it becomes more of a problem at visible wavelengths. The roughness of the electrode surface used in this work was greater than 1000 Angstroms (twice the particle size of the smallest polishing compound used). Such surface roughness would disrupt any structure in the spatial distribution of the electric
field at and near the electrode surface. The net effect is that the
importance of anomalous electric field effects near the electrode
surface would be diminished. The behavior of the system would
necessarily approach that of a simple ray-optic (non-wavelike)
representation. The extent to which this occurs in these experiments,
if at all, is uncertain, but is strongly suggested by the experimental
results.
2. Possible Mechanism of pH Dependence of the Reaction of Chlorpromazine Radical Cation With Dopamine and Hydroquinone

The increase in the reaction rate of dopamine (DA) with chlorpromazine radical cation with increasing pH observed by Mayausky and McCreery(53) is supported by the rate constant data obtained in this work. Also, at low pH, the relative rates of reaction of DA and hydroquinone (HQ) correlate roughly with their oxidation potentials, as put forth by Mayausky and McCreery(53). This correlation was also demonstrated for several other reactive substrates. What is unexpected, however, is the shift in the relative rates of DA and HQ with increasing pH, DA actually reacting with CPZ+* faster than HQ above a pH of 6.0. The hypothesis of reaction rate being solely dependent upon oxidation potential therefore loses its validity.

If structural effects are brought into consideration, the reasons for the different pH dependences become clearer. The initial removal of one electron from the ring system of DA or HQ is followed by the formation of a cationically charged species. The nature of the species formed in the cases of DA and HQ differ greatly, because of the orientation of the hydroxy groups in each case. The hydroxy groups in dopamine, being ortho to one another, increase the stability of the radical species formed after ejection of one proton, through bridging of the remaining proton between the hydroxy groups. Such bridging is impossible in the case of hydroquinone. The net result is that the pH of the first proton ejected would be expected to be lower in the case of DA than HQ, because of the greater stability of the resulting radical species in the dopamine case. Obviously, result of this will
have no effect on the reaction kinetics below the pK$_a$ of the first proton.

The initially oxidized species before proton ejection would be destabilized in the case of DA, because it must exist as a dication at low pH because of the protonation of the amine group on the side chain. Above pK$_{a1}$, the radical will be more stable than the corresponding HQ radical, because of the bridging of the remaining proton. Therefore, the oxidation of DA at low pH would be expected to be more facile than HQ at high pH, whereas the oxidation of DA would become more difficult because of the necessity of the initial formation of a dication, a step which will possess a higher activation energy than the similar step in hydroquinone.

This hypothesis is supported by the data in Reference 53. The reaction rate of 4-methylcatechol (4MC) was 6 times greater than that of hydroquinone at the same pH. The formation of the radical species would be easier in the case of 4MC because of the bridging effect, and this is reflected in the data. The methyl group of 4MC is weakly electron donating to the ring, a factor which will also stabilize the formation of the initially oxidized species.

The above hypothesis could be examined in more detail, if data from a pH study of catechol and its structural analogs with and without amine side chains were available. The compounds with amine side chains would be expected to react more slowly than analogous compounds without the side chains because of the positive charge present on the protonated amino group. The side chain compounds would also be expected to show a stronger pH dependence because of the
effect of the deprotonation of the charged hydroxy species. The effect of deprotonation would be less pronounced in analogs with para-hydroxy groups because of the lower stability of the deprotonated radical.
Conclusion

The low capacitance, low impedance coaxial microelectrode represents a significant step forward in techniques useful for the observation of fast electrochemical processes. After an elapsed time of 150 ns, over 70% of an electrogenerated species is within 100 Angstroms of the electrode surface. Therefore the spectroscopic probe can be used to observe events constrained to molecular dimensions. The coaxial microdisk electrode is also of potential value in the studies of electrode surface properties with impedance methods. At a driving frequency of 50 MHz, the diffusion layer thickness is only 20 Angstroms. This can be of value as a probe of processes occurring at and near the electrode surface, uncomplicated by the properties of the bulk solution. Further studies may be performed in exploring the possible value of impedance studies at high frequencies.

The fast transient response has also been demonstrated to be valuable in studies of fast solution kinetics. The selectivity of electrochemistry for the generation of reactants in solution is a valuable asset of the technique, and therefore represents an alternative if not more accurate method than radiolytic techniques for solution kinetic studies. Operation at glancing incidence optical geometry improves the sensitivity and reduces problems caused by background absorbances, and may allow the observation of reactions whose rates approach diffusion-controlled limits.
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APPENDIX

Computer Programs
PROGRAM TEK.BR

Data Transfer From and Program Dump To Tektronix 7854 Oscilloscope
BASIC Program For Data Transfer From Oscilloscope

100 LOMEM: 16384:SLX = 3:DT$ = "SCAPE:03":RS$ = "":FS$ = "":CI$ = "":PAZ = 1
150 DIM A(1024)
200 SN = 49168 + 256 * SLX
300 CALL 49184 + 256 * SLX: CALL 49152 + 256 * SLX
350 REM LAST MOD 12/17/82 VZR CORRECTION STMT 3050/060/130
400 FOR L = 1 TO 80:RS$ = RS$ + " ": NEXT
450 CI$ = "S,SCAPE":FS$ = "CALL EXECUTE": CALL SN
500 D$ = CHR$(4)
600 TEXT : HOME : PRINT "APPLE – TEKTRONIX 7854 UTILITIES
650 VTAB 3: PRINT "1. SAVE PROGRAM FROM SCOPE":
               PRINT "2. LOAD PROGRAM TO SCOPE
700 PRINT "3. SAVE DATA TO TEXT FILE
710 PRINT "4. DISPLAY PROGRAM FROM DISK ON SCREEN
720 PRINT "5. DISPLAY PROGRAM FROM DISK ON PRINTER"
730 PRINT "6. EXIT PROGRAM
800 PRINT "YOUR CHOICE:";
900 GET AS$: PRINT AS$:
               ON VAL (AS$) GOTO 1000,1800,3000,4000,5000,6000: GOTO 900
1000 INPUT "FILE NAME: ";FS$
1100 CI$ = "S,SCAPE": CALL SN
1200 PRINT D$"OPENTK."FS$: PRINT P$"WRITETK."FS$:
1300 PRINT D$"CLOSE":  GOTO 900
1400 ONERR GOTO 2300
2050 PRINT D$"CLOSE":  GOTO 900
2000 ONERR GOTO 2300
2050 PRINT D$"CLOSE":  GOTO 600
2100 PRINT D$"OPENTK."FS$: PRINT D$"READTK."FS$:
2200 INPUT FS$: CALL SN: GOTO 2200
2300 POKE 216,0: IF PEEK (222) = 6 THEN
               PRINT "FILE NOT FOUND...";
               IF ASC (LEFT$ (RS$,1)) < 128 THEN PRINT RS$;: GOTO 1400
2350 IF PEEK (222) = 6 THEN PRINT "FILE NOT FOUND...";
               IF ASC (LEFT$ (RS$,1)) < 128 THEN PRINT RS$;
               IF PEEK (222) > 5 THEN PRINT "ERROR " PEEK (222)" IN READING..."; GET A$:
2400 PRINT D$"CLOSE":  GOTO 600
3000 INPUT "FILE NAME: ";FS$:QT = 0
3003 INPUT T$: PRINT D$"IN\0"
3050 CI$ = "S,SCAPE":FS$ = "VZR VSCL * SENDX": CALL SN:
               CI$ = "R,SCAPE":  CALL SN: A$ = RS$:
3060 VZ = 2.0 * VAL (AS$)
3099 CI$ = "S,SCOPE":FS$ = "O WFM SENDX": CALL SN
3100 CI$ = "R,SCOPE": CALL SN:A$ = RS$:P = 1: GOSUB 5100:A = V
3110 GOSUB 5100: GOSUB 5100:T = V
3120 GOSUB 5100;YZ = V: GOSUB 5100:VS = V
3130 FOR L = 1 TO A: GOSUB 5100:A(L) = V * VS - VS - YZ: NEXT
3540 PRINT : PRINT D$"OPEN"F$: PRINT D$"WRITE"F$
3550 PRINT A: PRINT T * 1000: PRINT 0: PRINT 0: PRINT 0:
3560 FOR L = 1 TO A: PRINT A(L): NEXT
3700 GOTO 600
4000 FL = 0
4005 INPUT "FILE NAME: ":F$
4006 IF FL THEN PRINT D$"PR#1": PRINT "FILE NAME: ";F$: PRINT
4010 ONERR GOTO 4900
4020 L = 0: PRINT D$"VERIFYTK."F$
4030 PRINT D$"OPENTK."F$: PRINT D$"READTK."F$
4040 INPUT A$: IF LEN (A$) - 5 < 1 THEN 4920
4050 A$ = LEFT$ (A$, LEN (A$) - 5)
4500 PRINT MID$ ("00", LEN (STR$ (L)))L"A$
4510 L = L + 1: GOTO 4040
4900 POKE 216,0: IF PEEK (222) = 6 THEN
4910 IF PEEK (222) < > 5 THEN PRINT "ERROR ";
4920 PRINT D$"CLOSE": PRINT D$"PR#0": GET A$: GOTO 600
5000 FL = 1: GOTO 4005
5100 Q$ = MID$ (A$,P,1): IF Q$ = "0" AND Q$ < = "9" OR
5110 Q$ = "-" THEN 5200
5120 P = P + 1: GOTO 5100
5200 IF P > LEN (A$) - 10 THEN CALL SN:
5210 V = VAL (MID$ (A$,P)):P = P + LEN (STR$ (V)): V = P
5220 IF P > LEN (A$) - 10 THEN CALL SN:
5300 Q$ = MID$ (A$,P,1): IF Q$ = ";" OR
5310 Q$ = CHR$ (13) THEN RETURN
5320 P = P + 1: GOTO 5300
6000 END
PROGRAM ABSORBANCE2TTL.BR

Data Acquisition Program For Tektronix 7854
For Spectroelectrochemistry Experiments
Program Written In RPN For Tektronix 7854 Oscilloscope
For Data Acquisition And Calculation Of Absorbance.

Modified As Necessary To Suit Experimental Conditions.

LNN 00 VMDL HMDB CRS2-1 HSCL 1.0 * >HCRD 512 >P/W 2.5 ENTER 8 >CNS
500 ENTER 5 >CNS 1 ENTER 4 >CNS .1 ENTER 11 >CNS .3 CHS ENTER 12 >CNS
SCOPE VSCL 3 * 14 > CNS VSCL CHS 2 * 16 >CNS BOTH 100 ENTER 15 >CNS
SWH 15 CNS AVG SWL 0 WFM 2 >WFM CRS1
0 >HCRD CRS2-1 0 >HCRD
HSCL 1.0 * >HCRD
CRS1> CRS1> CRS1> CRS1> CRS1> CRS1> CRS1> CRS1> CRS1> CRS1>
CRS2> CRS2> CRS2> CRS2> CRS2> CRS2> CRS2> CRS2> CRS2> CRS2>
2 WFM MEAN 6 >CNS 2 WFM 6 CNS - 8 CNS + 8 CNS X<Y / LN 2.303 /
0 WFM MEAN - 2 >WFM .12 SMOOTH .12 SMOOTH P-P 3 >CNS 3 CNS PAUSE
PAUSE

LNN 02 SWH 15 CNS AVG SWL 0 WFM 1 >WFM CRS1 0 >HCRD CRS2-
10 >HCRD HSCL 1.0 * >HCRD
CRS1> CRS1> CRS1> CRS1> CRS1> CRS1> CRS1> CRS1> CRS1> CRS1>
CRS2> CRS2> CRS2> CRS2> CRS2> CRS2> CRS2> CRS2> CRS2> CRS2>
1 WFM MEAN 6 CNS - 8 CNS + 7 >CNS 1 WFM MEAN - 7 CNS + 7 CNS X<Y /
LN 2.303 / 0 WFM 1 >WFM .1 SMOOTH .1 SMOOTH 4 LBL GOTO P-P 10 >CNS
3 CNS 10 CNS - 3 CNS / 13 >CNS 13 CNS 11 CNS IFY>X 3 LBL GOTO 12 CNS
13 CNS IFY>X 3 LBL GOTO

LNN 04 8 CNS 7 CNS - 14 CNS 7 LBL GOTO IFY>X 3 LBL GOTO 8 CNS 7 CNS -
16 CNS X<Y IFY>X 3 LBL GOTO

LNN 07 1 WFM MEAN - 0 WFM 2 WFM + 2 >WFM 4 CNS 1 + 4 >CNS
5 CNS 4 CNS IFX=Y 3 LBL GOTO 4 CNS 15 CNS * 4 CNS 15 CNS * 2 LBL GOTO

LNN 03 2 WFM 4 CNS / 1 >WFM 1 WFM MEAN - 4 CNS 15 CNS *
STOP
PROGRAM CPZKIN512.BR

Calculation of Rate Constants From Normalized Absorbance Data
BASIC Program For Calculation Of Rate Constants
From Normalized Absorbance Data

1 LOMEM: 16385
3 FOR L = 1 TO 16:RS$ = RS$ + " ": NEXT
4 CI$ = "S,PLOTTER"
10 DIM A(190)
11 DIM B(190)
12 DIM TK(512)
14 DIM D(512)
50 INPUT "INPUT CONCENTRATION";C
55 INPUT "WRITE K FILE TO DISK? ";W1$
56 IF W1$ = "N" GOTO 101
57 INPUT "FILENAME FOR K FILE: ";H$

* Working Curve (Statements 101-290) Are Listed At End Of Program *

Set Up kct Array

400 FOR J = 1 TO 100
410 B(J) = J / 10.0
420 NEXT
430 FOR J = 101 TO 190
440 B(J) = J - 90.0
450 NEXT

Input Data File

700 D$ = CHR$(4): TEXT : PRINT D$"PR#0
750 PRINT D$"CATALOG,D1"
800 INPUT,"FILENAME?";F$
810 PRINT D$"RENAME"F$","F$": GOTO 860
820 ONERR GOTO 830
830 IF PEEK (222) » 4 OR PEEK (222) - 10 THEN 860
840 IF PEEK (222) - 6 THEN PRINT "FILE NOT FOUND": GOTO 800
850 PRINT "ERROR"; PEEK (222): GOTO 800
860 POKE 216,0: PRINT D$"OPEN"F$: PRINT D$"READ"F$
870 INPUT A,T,G,R,I0,E1,E2,B,T$
880 IF A > 4100 THEN A = 4100
890 FOR L = 1 TO A: INPUT D(L)
893 NEXT : PRINT D$"CLOSE
895 PRINT "## OF POINTS =";A
896 INPUT "USE POINTS FROM -- TO -- FOR RATE CONSTANT CALCULATION";
900 IF MI > D(N1): FOR L = N1 TO N2
901 IF MI < D(L) THEN MI = D(L)
902 NEXT
920 NEXT
921 NF = N2 - N1 + 1
925 C1 = C * T
970 PRINT " YMIN= ",MI
980 PRINT " YMAX= ",MA
Calculate Rate Constant (TK)

990  J1 = 21
995  A = 0
996  N4 = 0
1100  FOR L = N1 TO N2
1104  IF D(L) > .9664 GOTO 1106
1105  IF D(L) > .3153 GOTO 1110
1106  NP = NP - 1:N4 = N4 + 1: NEXT L
1107  IF L > N2 GOTO 1450
1110  IF A(J1 - 19) < D(L) THEN J1 = 20
1112  FOR J = J1 - 19 TO 190
1115  IF A(J) - D(L) GOTO 1150
1120  IF A(J) < D(L) GOTO 1200
1130  NEXT J
1150  TK(L) = B(J) / (Cl * (L - 1)): GOTO 1275
1200  B1 = B(J) - (B(J) - B(J - 1)) * (D(L) - A(J)) / (A(J - 1) - A(J))
1220  TK(L) = B1 / (Cl * (L - 1))
1275  L$ = STR$ (TK(L))
1280  PRINT L, LEFT$ (L$,4), T * (L - 1)
1285  A = A + TK(L)
1286  AW = AW + TK(L) / LOG (L)
1290  IF J > 20 THEN J1 = J
1291  W3 = 1 / LOG (L) + W3
1292  A4 = TK(L) * TK(L) + A4
1295  W4 = TK(L) * TK(L) / LOG (L) + W4
1296  W5 = TK(L) / LOG (L) + W5
1298  IF L = N2 GOTO 1450
1300  NEXT L
1450  PRINT "COMPUTING STD DEV" 1460 PRINT " "
          AW1 is Weighted Average Rate Constant; A1 is Unweighted
1530  A1 = A / NP
1535  AW1 = AW / W3
1540  SW = SQR ((W4 - W5 * W5 / W3) / (W3 - W3 / NP))
1545  PW = SW * 100 / AW1
1546  PRINT "PERCENT STD.DEV.(WEIGHTED)= ";PW
1547  WW$ = STR$ (AW1)
1548  PRINT "K(WEIGHTED)= "; LEFT$ (WW$,5);" STD.DEV.= ";SW
1550  S = SQR ((A4 - A * A / NP) / (NP - 1))
1555  PD = S * 100 / A1
1556  PRINT "PERCENT STD.DEV.= ";PD
1557  W$ = STR$ (A1)
1560  PRINT "K(XE06)= "; LEFT$ (W$,5);" STD.DEV.= ";S
1590  R1 = TK(1):R2 = TK(1)
1595  FOR I = N1 TO N2
1596  IF R1 > TK(I) THEN R1 = TK(I)
1597  IF R2 < TK(I) THEN R2 = TK(I)
1598  NEXT
Print Out Results Of Calculations

1600 PRINT D$"PR#1"
1610 PRINT "FILENAME ";FS
1615 PRINT "CONCENTRATION (MMOLAR)= ";C
1620 PRINT "K (X10E06)= ";A1
1630 PRINT "STD. DEVIATION= ";S
1640 PRINT "PERCENT STD. DEV.= ";PD
1641 PRINT "WEIGHTED: "; LEFTS (WW$,5)
1642 PRINT "STD. DEVIATION= ";SW
1643 PRINT "PERCENT STD. DEV.= ";PW
1650 PRINT "1ST POINT= ";N1;"LAST POINT= ";N2
1660 PRINT "TIME OF FIRST POINT= ";(N1 - 1) * T" MILLISECONDS"
1670 PRINT "ANORM FROM ";MA;" TO ";MI
1680 IF W1$ = "N" GOTO 1700
1690 GOSUB 5000

Plotting Routine

1700 HGR
1705 POKE - 16302,0
1710 HCOLOR= 3
1805 YS = 191 / ((A1 * .2) + R2 - R1):XS = 279 / ((L - 1) * T)
1810 FOR I = N1 TO N2
1820 KX = (I - 1) * T * XS:KY = (TK(I) + .1 * A1 - R1) * YS
1830 HPLOT KX,191 - KY
1840 NEXT
1850 Y = R1 - .1 * A1:Z = R2 + .1 * A1
1860 Y$ = STR$ (Y):Z$ = STR$ (Z)
1865 U$ = STR$ (R1):V$ = STR$ (R2)
1870 PRINT "DATA RANGE "; LEFTS (U$,4);" TO "; LEFTS (V$,4)
1880 PRINT "YRANGE= "; LEFTS (Y$,4);" TO "; LEFTS (Z$,4)
1900 KY = (1.1 * A1 - R1) * YS
1910 KW = (1.1 * AW1 - R1) * YS
2000 HPLOT 0,191 - KY TO 279,191 - KY
2100 HPLOT 0,191 - KW TO 279,191 - KW
2200 HPLOT 0,0 TO 279,0 TO 279,191 TO 0,191 TO 0,0
2300 PR# 1
2300 PRINT "FULL SCALE TIME= "T * (N2 - 1)"MILLISECONDS"
2310 IF PEEK (- 12506) = 183 THEN 2330
2320 IF PEEK (- 12506) = 183 THEN 2330
2320 PR# 1: PRINT : PR# 0
2330 POKE - 12524,0: POKE - 12529,255: PR# 1
2340 PRINT ""
2350 POKE - 12529,0
2360 PR# 0
2370 PRINT D$"PR#0
2390 TEXT
4000 GOTO 1
Write Rate Constant File To Disk

5000 PRINT D$"IN#0": PRINT D$"PR#0"
5100 PRINT : PRINT D$"OPEN"H$: PRINT D$"WRITE"H$
5200 PRINT NP + N4: PRINT T: PRINT Al: PRINT PD:
       PRINT AW1: PRINT PW: PRINT 1: PRINT F$
5300 FOR L = Nl TO N2: PRINT TK(L): NEXT
5400 PRINT : PRINT D$"CLOSE"
5500 RETURN
20000 END

Working Curve Follows

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