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ELECTROCHEMICAL PROCESSES MONITORED
BY OPTICAL DIFFRACTION
AT AN ELECTRODE EDGE

DISSERTATION

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

By
Paula Rossi, B.S.

* * * * *

The Ohio State University
1982

Reading Committee:
Richard L. McCreery
Theodore Kuwana
Alan Marshall

Approved By

Adviser
Department of Chemistry
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VITA

August 19, 1955  Born—Columbus, Ohio

1977  B.S., University of Cincinnati, Cincinnati, Ohio

1977-1979  Teaching Assistant, Department of Chemistry, The Ohio State University, Columbus, Ohio

1979-1982  Research Associate, Department of Chemistry, The Ohio State University, Columbus, Ohio

PUBLICATIONS


FIELD OF STUDY

Major Field: Chemistry
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CHAPTER I

INTRODUCTION

Spectroelectrochemistry, the combination of optical and electrochemical techniques, is an effective approach in the study of electrochemical processes. In most applications, some event is initiated by applying a potential or passing current at the electrode, and a beam of light is used as a probe to monitor the solution adjacent to the electrode surface. With the proper choice of wavelength, information can be obtained about any absorbing species which is generated, whether it is the primary product of the electrochemical reaction or the product of a succeeding homogeneous chemical reaction. Mechanisms of reactions involving an electrogenerated species and the rates at which those reactions proceed can also be elucidated. The principle advantage of spectroelectrochemical techniques is that they provide a degree of selectivity not available using purely electrochemical methods since the species of interest must be electroactive at the applied potential and also must absorb light at the frequency of the incident beam.

Many optical methods have been successfully combined with electrochemistry. Absorption spectroscopy (UV, visible, IR) has long been used to monitor the appearance or disappearance of a chromophore, and much effort in the past has been directed towards characterizing the relationship between the observed intensity changes and the electrochemical
events taking place. In recent years, many other optical methods have been combined with electrochemistry, making available a wide range of tools with which an electrochemical system can be examined. Structural information can be provided by the combination of Raman, Resonance Raman, NMR, and even Mass Spectroscopy with electrochemistry.

Despite recent developments, however, absorption spectroscopy remains the most frequently used spectroelectrochemical technique, probably due to the fact that the method is applicable to a wide variety of inorganic, organic, and biological redox systems, and the required experimental equipment is of relatively low cost and is readily available. The primary emphasis in the development of this technique has been spectral characterization of electrogendrated chromophores and reaction intermediates and examination of the kinetics of reactions involving these species. Absorbance measurements can currently be made via the four optical geometries shown in Figure 1.

Transmission spectroelectrochemistry involves passing a beam of light directly through an optically transparent electrode (OTE) and the solution contained in the electrochemical cell as shown in Figure 1. The beam will be attenuated in the presence of chromophore, and absorbance can be monitored as a function of time, \( t \), after initiation of electrolysis. The effective optical pathlength for absorbance is determined by the width of the diffusion layer. For a stable electrogendrated chromophore, absorbance can be described by the following equation:

\[
A = \frac{2}{\pi} \epsilon C_{\text{bulk}} D t^{\frac{1}{2}}
\]  
(1)
Figure 1. Four optical geometries for absorption spectroelectrochemistry. Top left: transmission. Top right: internal reflection. Bottom left: specular reflectance. Bottom right: parallel geometry
Figure 1

electrode solution
electrode solution
electrode solution
electrode solution
where $\varepsilon$ is the molar absorptivity of the chromophore, $C_{\text{bulk}}$ is the bulk concentration, and $D$ is the diffusion coefficient of the precursor. In addition to the conventional cell shown in Figure 1, an optically transparent thin-layer cell (OTTLE) can be used$^6$. The most significant advantage of the OTTLE is that, due to the small volume of the cell, it is possible to completely electrolyze the species of interest in 10-20 seconds. Standard reduction potentials can be determined, and absorbance measurements can be made even when both reactant and product absorb, since the reactant is consumed within seconds.

An OTE is also used for Internal Reflection Spectroelectrochemistry (IRS), where the light beam is again directed at the back of the electrode (opposite the solution side) but at an angle greater than the critical angle so that most of the beam is reflected (Figure 1). Due to the wave nature of the light, a small volume of the solution near the electrode surface is sampled by the incident beam, and the presence of a chromophore will be indicated by attenuation of the reflected beam. Absorbance is then measured as a function of time after initiation of electrolysis.$^5$ Because only a small volume of solution is sampled, the absorbance change due to generation of chromophore is rapid, and a steady state is achieved in only a few milliseconds. The degree to which the beam penetrates the solution side ($\delta$) is dependent upon the wavelength of the incident beam as well as the angle of incidence and the material from which the OTE is constructed. The optical pathlength for absorbance is defined by $\delta$ and is usually on the order of 1000 A. Some control over the pathlength is possible since $\delta$ can be varied over an order of magnitude simply by changing the angle of incidence.
Both transmission spectroelectrochemistry and IRS have been extensively used to detect the products of electrochemical reactions and intermediates of reactions which precede or follow the electrochemical step. The mechanism and rates of these reactions can be determined using finite difference methods provided the concentration of the species is known as a function of time and many mechanisms have been worked-out in detail. A chromophore with a half life of only one millisecond can be observed using transmission spectroelectrochemistry and, in conjunction with a rapid-scanning spectrophotometer, complete spectra of reactive intermediates can be obtained. With signal averaging, absorbance measurements using IRS can be made at times as short as four microseconds.

Because the electrode must be transparent within the frequency range of interest, much attention has been directed towards the construction of optically transparent electrodes. A variety of conductive materials (for example, gold, platinum, and tin oxide) can be vapor deposited onto the surface of a transparent substrate, forming a suitably thin transparent film. Mercury can be electrodeposited onto platinum and carbon films. However, these thin films typically have a high resistance to current flow, and it can be difficult to ensure an equal distribution of potential over the entire surface. A recent development has been a polyester sheet covered with a thin film of electrode material which displays low resistivity and high transparency and is highly flexible. Alternatively, for transmission-mode spectroelectrochemistry, an OTE can be constructed from thin wire mesh (referred to as a minigrid electrode), which results in an electrode with good conductivity and transparency. Such
electrodes can be constructed from any conductive material for which the grid is available and are very well suited for use in OTTLE cells.

Another geometry which can be used for absorption spectroscopy is shown in Figure 1, where the incident beam is directly towards the electrode from the solution side and reflected at the surface. This method is referred to as Specular Reflectance, and absorbance of the reflected beam is measured as a function of time. Using such a geometry, a smooth flat electrode surface is still required for best quantitative results but the electrode no longer need be transparent at the frequency of the incident beam. This allows the use of solid electrodes, such as glassy carbon or platinum sheets, materials which are both highly conductive and reflective. The pathlength for absorbance will again be determined by the width of the diffusion layer and can be easily varied over an order of magnitude simply by changing the angle of incidence of the beam.

Although the techniques discussed above have been invaluable in the observation of chromophores in the diffusion layer and in elucidation of the kinetics of reactions, they suffer from an inherent lack of sensitivity due to the limited optical pathlength for absorbance. The maximum absorbance which can be provided is ultimately determined by the width of the diffusion layer, which can be quite small at short times after initiation of electrolysis. For example, for a species with a diffusion coefficient of $1.0 \times 10^{-5}$ cm$^2$/sec, the width of the diffusion layer is only about 0.003 cm at 1 sec. As a result, analysis of a species which is present at very low concentrations or which is a weak absorber can become quite difficult even with extensive time averaging.
Also, no information about the distribution of chromophore within the diffusion layer is provided by use of these methods since they are basically integrative in nature, and absorbance is measured over the entire width of the portion of solution that is sampled. Such information would be useful not only in the study of complex reaction mechanisms but also in the investigation of other processes as well, such as mass transport of the electroactive species to the electrode.

Several attempts have been made to increase the sensitivity of these methods. Multiple reflections at the electrode surface have been used with some success for both IRS and Specular Reflectance,\textsuperscript{15} but the resulting measurement can be noisy and difficult to quantitate. Glancing Incidence Reflection (GIR), where the beam is directed at the electrode from the solution side at a very small angle of incidence (less than 0.5°),\textsuperscript{16-18} results in an improvement in sensitivity of a factor of about 100. Somewhat higher sensitivity could be observed using even smaller angles, but reproducible results were not obtained.

An alternative geometry which results in improved sensitivity is also shown in Figure 1, where the incident beam is now oriented parallel to the electrode surface so that the maximum pathlength for absorbance will be determined by the length of the electrode along the optical axis. Tyson and West\textsuperscript{19} utilized this geometry by passing a narrow light beam at an angle of "grazing incidence" to the electrode surface and monitoring absorbance of the entire beam as a function of time. As expected from theoretical calculations for electrolysis under conditions of semi-infinite linear diffusion, absorbance was found to be a linear function of $t^{\frac{1}{2}}$ and linear with concentration of the electroactive species, and concentrations
as low as $10^{-8}$ M of $\sigma$-Toluidine were detected. However, the absorbance response was very slow (on the order of minutes) due to the time required for a significant amount of diffusion of the chromophore into the beam to occur. Also, the shape and position of the beam relative to the surface were difficult to determine exactly, so quantitative agreement with theory was not obtained.

Better results have been obtained by utilizing the same geometry, but where the region monitored by the beam is defined by a slit.\textsuperscript{20} In this manner, only a portion of the diffusion layer was sampled, but increased sensitivity was still obtained due to the longer pathlength for absorbance. By positioning the slit at various distances from the electrode surface, concentration could be determined as a function of distance, and fairly good agreement with theory (within 20%) was achieved at distances within 20 $\mu$m of the surface. However, regions closer to the electrode could not be sampled due to interferences resulting from diffraction by the electrode. Therefore, the absorbance response was not particularly fast, and use of this method was limited to the observation of species with lifetimes of more than about 100 milliseconds. Also, for best results, this geometry required that the beam, electrode, and slit be oriented exactly parallel to each other, conditions which could be quite difficult to fulfill, especially with relatively short electrodes.

Aside from absorption spectroelectrochemical methods, several interferometric techniques are currently available\textsuperscript{21} which make use of refractive index measurements to elucidate the concentration vs. distance profile of an electroactive species. In these methods, the light beam is passed parallel to the electrode surface and the phase shift introduced by
the presence of a local refractive index gradient is measured. For a binary system, i.e., where the refractive index gradient is due to only one species in solution, this phase shift can be quantitatively related to changes in concentration, and concentration profiles in transient diffusion layers have been determined. Under certain circumstances, concentration changes of $10^{-5} \text{M}$ can be detected, and resolution within the diffusion layer to $10^{-4} \text{cm}$ has been obtained. However, methods based on refractive index changes suffer from an inherent lack of selectivity, and only reactions involving electrodeposition of a single metal ion have been examined in detail. In addition, since the refractive index gradient generated must be fairly large in order to be measured, these methods are rather insensitive and therefore would be unsuitable for concentrations at or below the millimolar level. Distances within more than about 100 microns of the electrode cannot be sampled; as a result, the measurement must be made on a fairly long time scale, and detection of relatively short-lived species would not be possible.

In the present work, the development of a new technique involving the combination of electrochemistry with a completely different optical phenomenon is discussed. When the incident beam is oriented parallel to the electrode surface and is bisected by the edge of the electrode, diffraction by the edge will scatter some of the light away from the main beam. Diffracted intensity will appear both above and below the main beam. A schematic diagram of such an experimental configuration is shown in Figure 2. Since light must pass very close to the electrode to be diffracted, the diffracted light should contain much information about electrochemical events occurring at the surface. For example, formation
Figure 2. General experimental configuration for monitoring light diffracted by the electrode. Diffracted intensity is symmetrically distributed above and below the undiffracted beam.
laser beam

D

electrode

diffusion layer

screen

diffracted light

undiffracted beam

diffracted light

Figure 2
of an absorbing species as the product of the electron-transfer step should result in attenuation of the diffracted intensity. High sensitivity should be provided since the pathlength for absorbance will be determined by the length of the electrode along the optical axis. Also, the diffracted light is expected to contain spatial information about the distribution of chromophore in the diffusion layer in much the same way as X-ray diffraction contains information about molecular structure.

In the case where a chromophore is generated electrochemically, this method would combine the high sensitivity of a parallel geometry with faster time response, since regions within a few wavelengths of the electrode surface are sampled by light which is then diffracted. Even at short times, when the width of the diffusion layer is small, it should be possible to monitor an absorbing species.

The objective of the present work is to examine the analytical utility of the combination of diffraction and electrochemistry. A theoretical description of the effect of an electrogenerated chromophore on the intensity of diffracted light is discussed in detail in Chapter II. The distribution of the diffracted intensity (the diffraction pattern) before and after initiation of electrolysis can be predicted, and absorbance in the diffraction pattern can also be calculated as a function of time. Use of the technique in the study of other electrochemical processes is discussed. In Chapter III, experimental methods are presented. Experimental results are presented and discussed in Chapter IV, and comparisons with theoretical calculations are made where appropriate. Experimental and theoretical diffraction patterns in the absence of chromophore are compared, and experimental absorbance as a function of time for several well
characterized chemical test systems is compared to that predicted from theory. The dependence of the absorbance response on concentration, electrode length, and wavelength of the incident light is discussed, and the effect of adsorption of the electroactive species onto the electrode surface is examined. Use of this technique for observation of an electro-generated reaction intermediate and in the observation of the absorbing product of a homogeneous chemical reaction is illustrated.
CHAPTER II

THEORETICAL CALCULATIONS AND DISCUSSION

Introduction

Light does not always travel in a straight line but will be affected by obstacles placed in its path. There are two distinct approaches to the problem of describing the propagation of a beam of light through a particular region of space. Light can be treated as a wave, the magnitude and phase of the wave at a particular point in space and time being determined by a set of characteristic equations (Maxwell's equations). This "wave optics" approach provides a complete description of the wave but can become quite complicated except for the simplest cases. Another description of light propagation is provided by representing the beam of light as being composed of rays traveling in a direction perpendicular to the wavefront. Such an approach is termed "geometrical optics" and in many cases results in a quite accurate description of the interaction of the light beam with objects in its path.

When a parallel beam of light impinges on an electrode edge as shown in Figure 2, light passing close by the edge is scattered, this scattering phenomenon being referred to as diffraction. An explanation of this event can be based on either system of optics. Wave optics will provide a complete description of the interaction of the light wave with the surface as a mathematical boundary value problem, and the solution to this problem is
an equation describing the diffraction pattern viewed on the screen. Alternatively, the range of geometrical optics can be extended to include diffraction via the Fresnel-Kirchoff formulation of Huygen's principle. In this approach, light is considered to be diffracted at an infinite number of angles at the electrode edge, and the combination of all these rays at the screen produces a diffraction pattern.

In either method of analysis, light must pass close to the surface in order to interact with it at all, and so the diffracted light will be very sensitive to any changes taking place in the solution adjacent to the electrode. If an absorbing species is being generated electrochemically at the surface, the diffraction pattern should be modified in a predictable manner.

This chapter presents a theoretical analysis of the dependence of diffracted light on the presence of an electrogenerated chromophore. The use of Maxwell's equations is found to introduce a high degree of mathematical complexity into the analysis. However, the Fresnel-Kirchoff approach results in a description of the diffraction pattern as the Fourier transform of the cross section of the incident beam at the electrode edge. The intensity at each point in this cross section is found to be attenuated in an amount related to the concentration of chromophore present at that point; therefore, the shape of the diffraction pattern is affected in some characteristic manner by the concentration vs. distance profile of the chromophore in solution. The results of theoretical calculations show that the intensity distribution in the diffraction pattern is also a function of time. The potential advantages of the diffraction technique in the examination of experimental systems are discussed.
Derivation of Equations Describing Diffraction
at an Infinitely Thin Edge

In the most basic analysis, the behavior of light can be understood by
description of it as an electromagnetic wave. Maxwell's equations of electro­
magnetism exactly describe the propagation of light in free space. In these
equations, light waves are described as vectors consisting of sinusoidally
varying electric (\( \vec{E} \)) and magnetic (\( \vec{B} \)) fields. Maxwell's equations can be
used to derive the three-dimensional wave equation,

\[
\nabla^2 \vec{E} - \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} = 0,
\]

where \( \nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \) and \( c \) is the velocity of light in a vacuum. The
solutions to the three-dimensional wave equation give the electric field \( \vec{E} \) as
a function of \( x, y, z, \) and \( t \), allowing the electric field at a particular point
and time to be determined mathematically. An expression analogous to
equation 2 can be derived from Maxwell's equations for \( \vec{B} \).

Both the electric field and the magnetic field must obey the three-
dimensional wave equation but are not independent of each other and are
related by Maxwell's equations. In the presence of matter, the situation
becomes even more complicated, since Maxwell's equations are modified by
the existence of charge and currents in the material through which the light
is traveling. In a situation such as that described by Figure 2, where the
diffracting object is an edge of finite thickness along the optical axis, fur­
ther complexity will result from reflection and absorption effects due to the
electrode as well as the surrounding media. Boundary conditions must be
imposed at the interface between the edge and surrounding media for the
vectors \( \vec{E} \) and \( \vec{B} \). When the macroscopic properties involved and
relationships between them are known, then a solution to the wave equation can be found using Maxwell's equations, and this case has been examined in detail.24

It can be seen that an attempt to describe wave propagation in three-dimensions with Maxwell's equations can become very complex even with the simplest geometries. Fortunately, completely rigorous solutions of the wave equation are not necessary to describe quantitatively many of the phenomena associated with diffraction. There exists an extremely useful description of wave propagation in the form of Huygen's principle,25 itself an approximate consequence of the wave equation, which can be used to examine the process of diffraction.

Huygen's principle simply describes each point on the plane at the diffracting edge ($z = 0$ in Figure 2) as a radiator which is reradiating the incident beam in spherical waves, giving rise to an expanding wavefront. The intensity distribution viewed on the screen at $\hat{z}$ will be the summation of the contribution from all of these spherical radiators. Huygen's principle contains two important rules about the way the waves should be combined. First, the waves originate at each point on the surface $\sigma$, where $\sigma$ is determined by the tangent at $\hat{z} = 0$ to an infinite number of rays from the original light source. Figure 3 illustrates $\sigma$ for the case in which a plane wave is incident on an edge. Second, light is assumed to travel straight outward from $\sigma$, so the region between the rays $\tilde{A}$ and $\tilde{B}$ in Figure 2 is illuminated while the region outside is not. Only the waves contained within this region will be included in the summation to produce the intensity at some distance $\hat{z}$ from the edge.
Figure 3. Schematic diagram of an expanding wavefront resulting from plane parallel light incident on an edge located at \( z = 0 \). Rays \( \hat{A} \) and \( \hat{B} \) are constructed assuming light travels straight outward, the position of \( \hat{A} \) being determined by the position of the edge along the x axis, \( \hat{B} \) determined by the width of the incident beam along the x axis.
It is important to realize that the above formulation of Huygen's principle actually gives rise to the basic rules of geometrical optics in which diffractive effects are neglected. It is the contribution from the waves in the shadow region, i.e., that region outside \( \bar{A} \) and \( \bar{B} \) in Figure 3, which gives rise to diffraction. In order to examine diffraction, the Fresnel-Kirchoff formulation of Huygen's principle\(^{26}\) may be used. In this formulation, the intensity at a viewing screen positioned at \( z' \) includes the contribution from all the waves, including those in the shadow region in Figure 3.

In order to sum up the intensity of all the waves at some distance \( z \) from the diffracting edge, the spatial and time dependence of each must be described. The electric field \( \tilde{E} \) at a particular distance and time can be written

\[
\tilde{E}(r,t) = \text{Re}\tilde{E}(r) \exp (2\pi ivt),
\]

(3)

where \( \tilde{E}(r) \) is a complex, spatially dependent, time independent wave function, and \( v \) is the frequency of the wave. The variable \( r \) is the spherical coordinate describing the position of the wave. The variable \( v \) can be dropped as an explicit variable for convenience, and if \( \tilde{E}(r,t) \) is substituted into equation 2, the result is a time independent form of the wave equation, called the Helmholtz equation,

\[
\nabla^2 \tilde{E} + k^2 \tilde{E} = 0,
\]

(4)

where \( k = 2\pi v/c \).

The equation for a spherical wave,
is a solution to this equation and thus can be used to describe the electric field at a particular distance \( \mathbf{r} \) from any position \( \mathbf{r'} \) on \( \sigma \). Figure 4 describes the coordinate system in detail. The origin \((z = 0)\) is at \( x' = y' = 0 \) and in this case is contained in the same plane as \( \sigma \). \( A' \) is a complex coefficient describing the value of the amplitude and the phase of the wave.

Since Huygen's principle states that the radiator at \( \mathbf{r'} \) is reradiating the incident wave, \( A' \) is proportional to the amplitude of the incident wave as well as to \( \Delta \sigma \), where \( \Delta \sigma \) is the incremental area from one radiator to another and should be small enough that the intensity of the incident beam does not vary significantly over this distance. The proportionality factor \( B \) between \( A' \) and \( \Delta \sigma \) is a slowly varying function of the angle between the normal to the incident wavefront and the normal to the edge. If this angle is small, \( B = \frac{ik}{2\pi} \). Equation 5 becomes:

\[
A(\mathbf{r}) = \frac{A'}{|\mathbf{r} - \mathbf{r'}|} \exp \left[ -ik|\mathbf{r} - \mathbf{r'}| \right],
\]

where the amplitude of the incident beam has been described by the square root of its intensity.

The total electric field at \( \mathbf{r} \) is given by the summation of contributions from all the radiators, and in the limit, as \( \Delta \sigma \) approaches zero, this result becomes the integral

\[
A(\mathbf{r}) = \frac{ik}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I_0^{\frac{1}{2}}(x', y') \frac{\exp \left[ -ik|\mathbf{r} - \mathbf{r'}| \right]}{|\mathbf{r} - \mathbf{r'}|} \, dx' \, dy'.
\]
Figure 4. Coordinate system used in theoretical analysis. \( |\mathbf{r} - \mathbf{r}'| \) is the propagation distance of light originating in the diffusion layer and arriving at some arbitrary point on the screen.
The equation above describes the amplitude of the electric field at \( \vec{r} \) when the magnitude of the electric field at \( \vec{r}' \) is simply determined by the amplitude of the incident beam. However, the magnitude of the incident intensity at the edge can be attenuated in the presence of chromophore. The absorbance, defined as the base 10 logarithm of initial intensity relative to final intensity, can be determined from Beer's law,

\[
\log \frac{I_0}{I} = A = \varepsilon bc(x',y').
\] (8)

In the equation above, \( \varepsilon \) is the extinction coefficient of the species of interest at the frequency of the incident beam, \( c \) is its concentration, and \( b \) is the pathlength for absorbance. Since the chromophore is being generated electrochemically at the electrode, the pathlength \( b \) is just equal to the length of the electrode along the optical axis. The concentration will be a function of distance from the electrode, since electrolysis generates a concentration gradient extending from the electrode surface into the solution. The exact nature of the relationship between concentration and distance will be discussed later.

Solving equation 8 for \( I \) and taking the square root yield a function which describes the amplitude of a wave at the electrode surface,

\[
\psi(x',y') = I_0^{\frac{1}{2}}(x',y')10^{-\varepsilon bc(x',y')/2}.
\] (9)

Note that the amplitude function \( \psi \) could represent any two dimensional shape with arbitrary optical density created by the concentration vs. distance profile of chromophore. The function \( \psi \) then replaces \( I_0^{\frac{1}{2}} \) in
equation 7, and the resulting expression for the amplitude at \( \mathbf{r} \) in the presence of chromophore is

\[
A(\mathbf{r}) = \frac{ik}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi(x', y') \exp \left( -ik|\mathbf{r} - \mathbf{r}'| \right) \frac{dx'dy'}{|\mathbf{r} - \mathbf{r}'|}. \tag{10}
\]

In order to derive the above equation, the only assumption that has been made is that the edge is short enough along the optical axis that it can be assumed to act as an infinitely thin edge. This means that surface effects and diffractive effects associated with the finite thickness of the edge are neglected.

Through use of the above equation, the diffracted intensity at a screen at any distance \( r \) from the electrode plane could be calculated. In order to evaluate the integral in equation 10, \( |\mathbf{r} - \mathbf{r}'| \) must be expressed in terms of \( x, x', y, \) and \( y' \). If the dimensions of \( x' \) and \( y' \) are small compared with \( r \), and \( |x - x'| \ll z \) and \( |y - y'| \ll z \), then \( |\mathbf{r} - \mathbf{r}'| \) can be expanded in a Taylor series:

\[
|r - r'| = z + \frac{1}{2} \left( \frac{(x - x')^2 + (y - y')^2}{z} \right) + \ldots \tag{11}
\]

The above restrictions on relative distances allow higher order terms in the expansion to be neglected. This expression for \( |\mathbf{r} - \mathbf{r}'| \) can be substituted into equation 10,

\[
A(\mathbf{r}) = \frac{ik}{2\pi z} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi(x', y') \exp \left[ -ik \left( z + \frac{1}{2z} ((x - x')^2 + (y - y')^2) \right) \right]. \tag{12}
\]

Depending on the distance from the electrode to the viewing screen, equation 12 can be treated by one of two simplifying assumptions. The Fresnel approximation is used when the diffraction field is close enough
that the quadratic terms in \( x' \) and \( y' \) in the exponential must be considered. Physically, this means that the distribution of intensity in the diffraction pattern (i.e., the shape) is dependent upon distance from the electrode edge. The resulting integral can be evaluated numerically.

The Fraunhofer approximation is an even more useful one, both mathematically and experimentally. In the Fraunhofer region the screen is sufficiently far from the electrode so that \( x'^2 \) and \( y'^2 \) in the exponential in equation 11 can be neglected. The result is the following equation:

\[
A(r) = \frac{ik}{2\pi^2} \exp \left[-ik\left(z + \frac{x'^2 + y'^2}{2z}\right)\right] \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi(x', y') \exp \left[i\left(\frac{kx}{z}\right)x' + i\left(\frac{ky}{z}\right)y'\right] dx' dy'.
\]

In the Fraunhofer region, the size of the diffraction pattern increases with increasing \( z \), but the shape does not change.

Notice that the integral above is just an ordinary Fourier transform of the function \( \psi(x', y') \). It is true in general that the diffraction pattern at the screen in the Fraunhofer region is the Fourier transform of the amplitude function which generated it. This is the feature that makes the Fraunhofer region convenient to use mathematically. Experimentally, the Fraunhofer region is convenient because the diffracted light has been scattered significantly away from the main beam, while in the Fresnel region, it would be necessary to monitor small changes in the main beam intensity.

All that is necessary to calculate the integral in equation 13 and thus to predict the diffraction pattern is to determine the incident intensity \( (I_0) \) and the concentration of the chromophore as functions of \( x' \) and \( y' \). In the case in which the beam incident on the electrode surface is a Gaussian-shaped laser beam, the incident intensity can be described by the following equation:\textsuperscript{28}
\[ I_0(x', y') = \exp \left\{ -\frac{(x'^2 + y'^2)}{r_0^2} \right\}, \]  

(14)

where \( r_0 \) represents the distance from the axis at which \( I_0 \) has decreased to \( 1/e^2 \) of its maximum value. Note that \( I_0 \) is easily factored into a product of functions of \( x' \) and \( y' \). This incident intensity is attenuated in the presence of chromophore in an amount determined by Beer's law (equation 8). In a single-edge geometry, it can be assumed that the concentration of chromophore at a particular \( x' \) will be constant for all \( y' \), since diffusion is occurring perpendicular to the electrode edge. For the case in which the chromophore is the stable product of a reversible oxidation or reduction at the electrode, concentration as a function of \( x' \) at a time \( t \) after initiation of electrolysis can be calculated from standard linear diffusion equations, which are a result of Fick's laws. The necessary parameters for this calculation are the diffusion coefficient of the species of interest, the initial concentration of the precursor to the chromophore, and time after initiation of electrolysis.

It can be seen from the above that the total amplitude function \( \psi(x', y') \) can be expressed as the product of two independent functions.

\[ \psi(x', y') = \phi(x') \rho(y') \]  

(15)

The result of the integration over all \( y' \) can be collected together with the other \( y \) dependent factors into a single function, \( a(y) \), which is a constant for a particular set of \( y \) and \( y' \) coordinates. The equation describing the Fourier transform can then be written

\[ A(\mathbf{r}) = \frac{i k a(y)}{2 \pi z} \exp \left\{ -i k z - \frac{ikx^2}{2z} \right\} \int_{-\infty}^{\infty} \phi(x') \exp\left[i \left(\frac{kx}{z}\right) x'\right] dx', \]  

(16)
where \( \phi(x') \) is given by

\[
\phi(x') = I_0(x') 10^{-\varepsilon bc(x')/2}.
\]  

(17)

\( A(r) \) from equation 16 can be converted to intensity by multiplying the amplitude by its complex conjugate, and the term preceding the integral becomes a constant, independent of the \( x \) coordinate on the screen. When only relative intensities are required, as in absorbance measurements, the pre-exponential term need not even be calculated, since it will remain the same regardless of the concentration of chromophore. Therefore, intensity as a function of \( x \) at the screen can be calculated. In addition, the absorbance observed at the screen for a particular screen coordinate \( x \) can be predicted as a function of time after initiation of electrolysis.

Strictly speaking, the limiting case of Fraunhofer diffraction is achieved only when the point of observation is at infinity from the diffracting object. However, proper placement of a lens after the diffracting edge results in observation of the Fourier transform in the focal plane of the lens.\(^{29}\)

If \( \phi'(x) \) is the wave form directly before the lens, then \( \phi(x) \) directly after is

\[
\phi(x) = \exp[-i(k f)(r^2 - x^2)] \phi'(x).
\]  

(18)

This equation describes the focusing action of the lens, where \( r \) is the radius of the lens, \( x \) is the \( x \) coordinate of the wave form at the lens, and \( f \) is the focal length of the lens. An analogous equation can be written for \( \phi(y) \). If the electrode is effectively at the lens, then the coordinates \( x \) and \( y \) can be replaced by \( x' \) and \( y' \). Substituting the resulting expression
for $\Psi(x',y')$ into equation 12, and again collecting the results of the $y'$
integration in $a(y)$,

$$A(r^+) = \frac{i k a(y)}{2 \pi z} \int_{-\infty}^{\infty} \phi(x') \exp \left[ -i \frac{k}{2f} (r^2 - x'^2) \right] \exp \left[ -i k [z + \frac{1}{2z} (x - x')^2] \right] dx'. \quad (19)$$

When $z = f$, the final result, after algebraic manipulation, is

$$A(r^+) = \frac{i k a(y)}{2 \pi z} \int_{-\infty}^{\infty} \phi(x') \exp \left[ -i k \left( f + \frac{r^2 + x'^2}{2f} \right) \right] \exp \left[ -i \frac{kx}{f} x' \right] dx'. \quad (20)$$

It should be noted that the quadratic terms in $x'^2$ in the exponential dis­
appear in the focal plane, where $z$ equals $f$. This ensures that the dif­
fraction pattern viewed in the focal plant of the lens is indeed the Fraun­
hofer diffraction pattern, and in fact, equation 20 is essentially identical

to equation 16 except for an unimportant phase factor in the term pre­
ceding the integral.

From a physical perspective, the above result can be understood by
realizing that light focused at a particular point $x$ in the focal plane is
composed of light rays which were parallel to each other before the lens.
This situation is illustrated graphically in Figure 4. At each point $x'$ in
the electrode plane, light is diffracted at all angles, and light from each
angle is focused by the lens at a particular point $x$ in the focal plane.
Compare this to the situation in the absence of a lens, where the viewing
screen is at infinity from the diffracting object. The pathlength from all
points $x'$ to a particular point $x$ can be considered to be equal, since the
distance $z$ is so much greater than the $x'$ dimension. This is illustrated
in Figure 6 in which the rays diffracted from all $x'$ at a particular angle are
Figure 5. Schematic diagram showing the path of diffraacted rays when the screen is placed in the plane of geometric focus of a lens. Only two representative points on the screen plane are shown. (top figure)

Schematic diagram showing the path of diffracted rays when the screen is at infinity from the diffracting object. Only a few representative rays are shown. (bottom figure) They are not drawn on the same scale.
Figure 5
so close together relative to the size of the diffraction pattern that they can be considered to lie on the same point \( x \) on the viewing screen.

An important result of the transform relationship between the diffraction pattern in the focal plane and the amplitude function in the electrode plane is that each point \( x \) can be regarded as a particular spatial frequency and \( A(\mathbf{r}) \) at that \( x \) as a sinusoidal component of the Fourier transform. In theory, any real physical quantity can be described by the summation of an infinite number of sine waves of various frequencies, and both the amplitude function at the edge and the diffraction pattern in the focal plane can be described in this manner. Each can be obtained from the other by summing all the Fourier components from the known function to produce the desired one. Thus, not only can the diffraction pattern be calculated by Fourier transform of the amplitude function in the electrode plane, but also the amplitude function itself can theoretically be obtained directly from the diffraction pattern by inversion of equation 20. Inversion of equation 20 and solving for \( \phi(x') \) result in

\[
\phi(x') = \frac{2\pi z}{ik\alpha(y)} \exp\left[\frac{i k}{2f} \left( r^2 + x^2 \right) \right] \int_{-\infty}^{\infty} A(\mathbf{r}) \exp\left[-i \left( \frac{kx}{f} \right) x \right] dx. \tag{21}
\]

It is important to point out that in order to accomplish the inversion, the amplitude function in the electrode plane must be centrosymmetric. For such functions, the phase shift upon Fourier transformation is zero; that is, the equation describing the transform does not contain a phase factor. Examination of equations 20 and 21 reveals that a phase factor is present in the form of the complex exponential term preceding the integral. Note that when the amplitude is multiplied by its complex conjugate to obtain the intensity, this term disappears, and the phase information is lost. It
is, of course, the intensity that is experimentally measured, and devices used to measure this quantity, such as a photomultiplier tube, are insensitive to phase. Only in the special case of a centrosymmetric input function is it strictly true that the amplitude is equal to the square root of the intensity, and so only in this case would the inversion be easily accomplished. An example of an experimental geometry fulfilling this requirement would be a very thin electrode, positioned in the center of the laser beam, where identical amplitude profiles exist on both sides of the electrode. This geometry was not used in the present work but is only pointed out here for clarification.

**Results of Theoretical Calculations**

Using the present geometry, the diffraction pattern for a particular amplitude function at the electrode surface can be calculated from equation 20. Figure 6 shows $\phi(x')$ at several different times. The amplitude curves in the figure are normalized to give a maximum intensity of 1.0 at $x' = 0$ for the unattenuated beam. At $t = 0$, the amplitude function is just the cross section of a Gaussian-shaped laser beam truncated at its center by the opaque electrode. Generation of chromophore at times greater than zero results in attenuation of the incident beam, with greatest effects seen at small $x'$. In the theoretical situation which Figure 6 illustrates, it has been assumed that in the electrochemical reaction,

$$A \pm ne = B,$$

the precursor $A$ is converted quantitatively to $B$, the chromophore, at the electrode surface. This is apparent from the graph, in which the curves at $t = 1\text{ sec.}$ and $t = 10\text{ sec.}$ intersect at $x' = 0$. It can also be seen from Figure 6
Figure 6. Theoretical profile of the amplitude of the incident beam as a function of distance from the electrode surface \( \phi(x') \) for the times indicated after initiation of electrolysis. A Gaussian beam of radius 0.044 cm is bisected exactly in half by an opaque electrode. Tris-(p-bromophenyl)-amine (TBA) is the precursor to the chromophore and is present at a bulk concentration of 2.0 mM. The chromophore has an extinction coefficient \( (c) \) equal to 15100 M\(^{-1}\) cm\(^{-1}\) and diffusion coefficient \( (D) \) equal to \( 1.6 \times 10^{-5} \) cm\(^2\)/sec. The electrode length is equal to 0.027 cm.
that even at fairly long times \((t = 10 \text{ sec.})\), the tailing portion of the incident beam has not been significantly affected in the presence of chromophore. This is the expected result, since the width of the laser beam is typically much greater than the width of the diffusion layer.* For example, at 10 sec., the width of the diffusion layer, calculated using the same parameters as are used to construct Figure 6, is 0.0063 cm compared with a beam radius of 0.044 cm.

The Fourier transform of the amplitude functions of Figure 6 can be easily calculated by use of a commonly available fast Fourier transform routine. A detailed explanation of how the routine is used in this case is presented in Appendix A. The intensity of the diffraction pattern is plotted as a function of screen coordinate, \(x\), in Figure 7. Intensity rather than amplitude was plotted to permit experimental comparison and is arrived at by squaring the modulus of the Fourier transform in equation 20.

It can be seen from Figure 7 that the intensity at relatively large \(x\) is attenuated proportionately more and that this effect is most pronounced at the shorter time of 1 sec. Also notice that even at 10 sec., the intensity at large \(x\) has not decreased more than at 1 sec. after initiation of electrolysis. This result is reasonable since the larger \(x\) values represent the higher spatial frequencies of the Fourier transform. Since the original amplitude function at the electrode can be expressed as the summation of these Fourier components, the higher frequency components would be

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*The width of the diffusion layer is equal to \(\sqrt{Dt}\), where \(D\) is the diffusion coefficient of the species of interest.
Figure 7. Intensity on the screen as a function of screen coordinate (x) for the amplitude profiles of Figure 6 at the times indicated after initiation of electrolysis. The diffraction pattern is symmetric about x = 0. The focal length of the lens is 1 m, the wavelength of the light incident on the electrode is 632.8 mm. The total width in the electrode plane transformed is 0.15 cm. The number of points used in the FFT routine is 512.
Figure 7

INTENSITY VS X

INTENSITY

X (cm)

Figure 7

1.0

0.8 10s 1s 0s

0.6

0.4

0.2

0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
necessary to describe the sharp edge of the electrode, while lower frequencies would, for the most part, describe the more gradual fluctuation of the Gaussian-shaped beam. When chromophore is generated at the electrode surface, the edge quickly becomes less sharp, and the magnitude of the intensity at the higher frequencies is attenuated. In contrast, the lower frequency components are attenuated more slowly, since the width of the beam is relatively large and it takes a long time for chromophore to diffuse a significant distance into the beam.

This effect is better illustrated by a plot of absorbance as a function of \( x \), which is shown in Figure 8. In this figure, absorbance has been calculated from the data plotted in Figure 7. Examination of the figure reveals that at 1 sec. after initiation of electrolysis, larger angles* have been attenuated more. It is also important to note that at sufficiently large angles, absorbance remains constant with increasing angle and that at longer times (10 sec.) most angles have been attenuated equally. In fact, at an infinite time the same absorbance would be obtained at all angles, and its value is the same as that which would be calculated from Beer's law, where \( b \) is the length of the electrode along the optical axis, \( \varepsilon \) is the extinction coefficient of the chromophore, and \( c \) is the bulk concentration of chromophore. This is reasonable since after initiation of electrolysis, chromophore is diffusing out into solution and thus into the

*For convenience in the following discussion, the \( x \) coordinate on the screen may be described as the sine of an angle, where the cosine of that angle is the focal length of the lens. This allows a particular point on the screen to be described as being at a particular angle to the horizontal, undiffracted portion of the laser beam, which is a convenient reference, since it has coordinates \((z, 0)\), where \( z \) is the focal length of the lens.
Figure 8. Absorbance as a function of screen coordinate x. Dashed line is 1 sec. after initiation of electrolysis, solid line is 10 sec. Absorbance was calculated from intensity data of Figure 7.
Figure 8

ABSORBANCE VS X

X (cm)
beam. At very long times, the entire beam would be filled with chromophore equal in concentration to the bulk concentration of precursor. This situation would be analogous to one of placing a cuvette of length $b$, containing a homogeneous concentration of chromophore, between the laser beam and the edge. It is easy to see that absorbance in this case would indeed be equal to the Beer's law absorbance. From Figure 8, it can be seen that even at short times, higher frequency components of the Fourier transform are experiencing the same situation, even though only a very small amount of chromophore has been generated.

Close attention to the absorbance traces in Figure 8 reveals that certain spatial frequencies exhibit absorbance larger than the value which would be calculated from Beer's law. This behavior can more readily be seen from Figure 9 which shows absorbance plotted as a function of time for a range of diffraction angles. This plot was calculated by evaluating the Fourier transform in equation 20 for a series of amplitudes, $\phi(x')$, each corresponding to the concentration profile at 100 equally spaced times within the desired time range. The absorbance plotted is the log of the ratio of intensity before to that after electrolysis began. In Figure 9, higher frequencies peak and then level off to a value equal to that which would be predicted by Beer's law. In Figures 10 and 11, the same type of plot is shown for higher (Figure 10) and lower (Figure 11) concentrations. Comparison of these figures with Figure 9 illustrates that when the concentration of chromophore is relatively high, the spatial frequencies represented by large angles are affected in the presence of chromophore to a much greater degree than when the concentration is relatively low. This is a reasonable result, since the shape of the incident beam is affected to
Figure 9. Theoretical absorbance plotted as a function of time after
initiation of electrolysis for the angles indicated. The electrode length is 0.027 cm. The bulk concentration of tris-(p-
 bromophenyl)-amine (TBA) is 2.6 mM. The chromophore has
an extinction coefficient ($\varepsilon$) equal to 15100 M$^{-1}$ cm$^{-1}$ and dif-
fusion coefficient (D) equal to $1.6 \times 10^{-5}$ cm$^2$/sec. The focal
length of the lens is 1 m, and the wavelength of the incident
light is 632.8 nm. The total width of the electrode plane
transformed is 0.15 cm. The total number of points used in
the FFT routine is 2048.
Figure 9
Figure 10. Theoretical plot of absorbance vs. time for the same conditions as Figure 9 with the exception that the concentration of TBA is 4.0 mM.
Figure 11. Theoretical plot of absorbance vs. time for the same conditions as in Figure 9 with the exception that the concentration of TBA is 0.5 mM.
Figure 11
a much greater degree at high concentrations of chromophore, and this is reflected in the large angle response. Figure 12 shows the shape of the incident beam as a function of concentration of chromophore. The attenuation of the beam is shown at a time of 60 msec., chosen to correspond closely to the appearance of the peak in the absorbance-time trace at an angle of 1.16 degrees in the diffraction pattern.

Several important features which indicate the value of the diffractive technique are illustrated by Figures 8-11. First, the absorbance response is very fast, particularly at large angles. For example, for the conditions specified in Figure 9 for chromophore and electrode length, an absorbance of more than 1.1 a.u. is obtained in roughly 60 msec. Second, the absorbance at longer times reaches a constant value, regardless of the angle examined. The absorbance is dictated by Beer's law for the species of interest, at a concentration equal to the bulk concentration of precursor, for an electrode of a particular length. For example, for the parameters used to construct the absorbance-time curves in Figure 9, a Beer's law calculation would give an absorbance of 0.825 units which corresponds very well with the level value of the figure. Higher observation angles reach this value faster, which is a result of the fact that higher angles correspond to higher spatial frequencies. These frequencies are greatly affected by events close to the electrode surface since, as mentioned above, these Fourier components are required to describe the sharpness of the edge. This result illustrates a third important feature: the diffracted light contains spatial information since the absorbance time transient is highly dependent on angle. Therefore, it would be possible to distinguish different concentration vs. distance profiles by their different absorbance-time curves.
Figure 12. Theoretical profile of the amplitude as a function of distance from the electrode surface [$\phi(x')$] for TBA present in the bulk concentration indicated. Other conditions are the same as in Figure 7.
Figure 12

\[ \phi(x') \]

- 0.0 mM
- 0.5 mM
- 2.0 mM
- 4.0 mM

AMPLITUDE

\[ x'(cm) \]

52
Last, the diffraction technique is potentially quite sensitive. The pathlength for absorbance is determined entirely by the length of the electrode along the optical axis, which in theory can be made arbitrarily long. In addition, since the time-independent value of absorbance is related to concentration by Beer's law, a plot of absorbance vs. concentration will be linear as long as the value is taken off the level portion of the absorbance-time curve. Figure 13 illustrates such a plot for a point on the rising portion of the curve (0.25 sec.) and also for a point corresponding to the level portion (1 sec.). This plot was obtained by transforming the amplitude function $\psi(x')$ at the appropriate time for a series of concentrations and calculating the change in intensity at the angle desired (in this figure, 0.542 degrees). Notice that as expected, the plot is linear at 1 sec. but not at 0.25 sec. For this electrode length (0.027 cm) a concentration range from 10 $\mu$m to 4 mm gives minimum and maximum values for absorbance between the limits of 0.004 and 1.6. It would theoretically be possible to fit any concentration range between these experimentally convenient limits simply by adjusting the electrode length. This flexibility provided by the diffraction technique would be very useful in the observation of weakly absorbing chromophores or measurement of low concentrations. Even at 0.25 sec., absorbance does increase with concentration, though not linearly, showing good sensitivity even at much shorter times than that necessary to obtain absorbance corresponding to Beer's law.

The theoretical results discussed above apply to the case in which the chromophore is the stable product of the electrochemical reaction. However, the diffraction technique should also be useful in cases in which more
Figure 13. Theoretically predicted plot of absorbance as a function of concentration. Concentration range is from 10 μM to 4.0 mM tris-(p-bromophenyl)-amine (TBA). Absorbance is calculated at an angle of 0.582 degrees at times equal to 0.25 sec. and 1 sec., using ε = 15100 M⁻¹ cm⁻¹, D = 1.6 × 10⁻⁵ cm²/sec., and electrode length = 0.027 cm.
Figure 13
complicated mechanisms are involved. The absorbance vs. time behavior should be characteristic of the mechanism since the intensity at each point in the diffraction pattern is highly dependent on the concentration vs. distance profile at the electrode surface. Calculation of absorbance-time plots for cases such as these would involve simulating the concentration vs. distance profile by commonly used digital simulation techniques, followed by transforming the resulting amplitude function. Or, more conveniently, the diffraction pattern could be inverted as in equation 21 to give the concentration vs. distance profile directly. Of course, this would have to be accomplished using the proper electrode geometry but has the very great advantage of producing the concentration vs. distance profile at the electrode without the use of digital simulation.

Even without theoretically predicting the absorbance-time behavior, the diffraction technique can be extremely useful for monitoring any species present in the diffusion layer. For example, deviation from the predicted absorbance-time behavior for a particular chromophore would indicate that it was being consumed in a follow-up reaction of some sort. Even relatively fast reactions could be examined since solution very close to the electrode is being sampled. An absorbing species generated in a homogeneous reaction subsequent to the electrochemical reaction could also be monitored. The special features of diffraction would make the technique most useful when a significant amount of chromophore is generated relatively close to the electrode, i.e., when the reaction is quite fast.
Conclusions

Theoretical calculations indicate that the diffraction technique has several characteristics which make it well suited for the observation of an electrogenerated chromophore. Since light must pass very close to the surface in order to interact with it at all, the light which is diffracted is very sensitive to the presence of an absorbing species in the diffusible layer. Although the equations for predicting the diffracted light intensities initially appear quite complicated, several conditions can be imposed to yield the following simple result: when the electrode is closely followed by a lens and the diffracted light is monitored in the focal plane of that lens, the diffraction pattern is the Fourier transform of the amplitude function (or beam cross section) at the electrode edge. This amplitude function is simply the Gaussian-shaped laser beam attenuated by the concentration of chromophore in an amount predicted by Beer's law.

This relationship between absorbance and Beer's law has several important results. First, at large angles, an absorbance dictated entirely by Beer's law is obtained at relatively short times (1 sec.), and the only two parameters which need to be known are the extinction coefficient of the species of interest and the length of the electrode, both of which can be easily measured experimentally. This is in contrast to other spectroelectrochemical techniques, in which the diffusion coefficient of the species under examination is usually necessary and often other geometrical properties of the experiment as well. Also, absorbance measured via other spectroelectrochemical methods is usually time dependent, while the diffraction technique results in a time-independent value obtained only a short time after initiation of electrolysis.
Second, absorbance measured a short time after initiation of electrolysis is linear with concentration over a wide range. In addition, since the pathlength for absorbance is the length of the electrode, this length can be made arbitrarily long, resulting in greatly enhanced absorbance. This presents an advantage over many currently used spectroelectrochemical techniques, in which the pathlength for absorbance is dependent on the width of the diffusion layer. In the case of a weakly absorbing chromophore or very low concentrations, the pathlength enhancement obtained with the diffraction technique would be quite useful for accurate measurement. In cases where the electrochemical reaction of interest is chemically irreversible, only a single run would be necessary using diffraction where, in many cases, extensive time averaging might be necessary with other techniques.

The high sensitivity of diffraction also makes it useful in situations in which more complex reaction mechanisms are involved. Observation of any absorbing species present in the solution close to the electrode surface is easily accomplished by monitoring the diffracted light.

Finally, an important result of the transform relationship between the concentration-vs.-distance profile at the electrode and the diffraction pattern is that spatial information is contained in the variation of the diffracted intensity with angle. The distribution of diffracted light changes with the shape of the diffusion layer. With the proper electrode geometry, it should be possible to directly invert the diffraction pattern and to obtain the distribution of chromophore as a function of distance from the electrode. This could provide much information about mass transport and reaction mechanisms. Although the inversion would be the most convenient way to
determine the concentration vs. distance profile, the same result could be accomplished by the combination of digital simulation techniques with the Fourier transform in the forward direction.
CHAPTER III

EXPERIMENTAL

Optics

The optical configuration for a typical experiment is shown in Figure 14. A laser was the light source of choice because it provided an intense, monochromatic beam of light which produced a distinct diffraction pattern in the focal plane of the lens. The diffraction pattern was wavelength dependent, so diffraction of light of more than one frequency at the electrode would result in "blurring" of the pattern, introducing more complexity into the data analysis than was desired in the present set of experiments. A coherent, highly collimated beam such as that emitted by a laser was required in order to obtain the Fraunhofer pattern.

The single wavelength sources used were a Spectraphysics 5 mwatt Helium-Neon laser (632.8 nm) and a Liconix 10 mwatt Helium-Cadmium laser (422 nm). These lasers produced a fairly quiet light signal, and the shape of the cross section of the beam was Gaussian.

A multiwavelength source was provided by use of dye laser. The optics became slightly more complicated when the dye laser was used, and the optical configuration is shown in Figure 15. The 514.5 nm line of an Argon ion laser (Spectraphysics, Model #164) was used to pump the dye laser (Spectraphysics, Model #375). Part of the beam was reflected into a monochromator as shown so that the wavelength could be accurately
Figure 14. Experimental configuration for diffraction experiments using single wavelength lasers. Reference and auxiliary electrodes were placed in the bulk solution below the working electrode compartment, and solution was drawn up into the capillary cell formed by the glass shields. The focal length of the lens was 1 m. The photomultiplier tube (PMT) was placed in the focal plane of the lens, and the aperture preceding the photomultiplier was a 0.8 mm diameter pinhole. The angle $\beta$ illustrates the angle that the PMT made with the horizontal. Diffraeted rays are not shown. (Figure not drawn to scale)
Figure 14
Figure 15. Optical configuration for diffraction experiments using dye laser. Components are not drawn to scale. Only the electrode edge is shown, but the complete electrochemical cell used was identical to that illustrated in detail in Figure 14. The angle $\beta$ illustrates the angle that the PMT made with the horizontal. Diffracted rays are not shown.
Figure 15
determined. The dye used in the present experiments was Rhodamine 6G, which provided a wavelength range of 630-575 nm. Careful tuning of both the Argon ion laser and the dye laser itself was required to decrease the noise of the signal and, most importantly, to properly select the cavity mode producing a Gaussian-shaped beam (the TEM$_{00}$ mode).

A plano-convex spherical glass lens (Melles Griot) of focal length equal to one meter was placed as closely as possible after the electrochemical cell. Any focal length could be used, but since the lateral size of the diffraction pattern was proportional to this parameter, a longer focal length resulted in better resolution in the diffraction pattern. The detector, positioned in the focal plane of the lens, was a 1P28 photomultiplier tube (PMT) which was mounted on a micrometer stage to allow precise positioning at the desired angle in the diffraction pattern. The PMT was fitted with a pinhole 0.8 mm in diameter to allow only a small piece of the diffraction pattern to be sampled at one time which results in an angular resolution of 0.05°. The entire apparatus was mounted on a vibration isolated optical table.

Proper alignment of the electrode edge in the beam was critical to the success of the experiment, and a reliable means of aligning electrodes of various widths was necessary. The edge must be horizontally positioned so as to bisect the cross section of the incident beam, and the surface must be parallel to the direction of propagation of the beam. With other components of the optical configuration in place (Figure 14), the electrode was moved from a position above the beam down along the x axis and into the beam until the intensity of the diffraction pattern, monitored at the PMT, went through a maximum. The position of the
electrode producing maximum intensity at any point in the diffraction pattern was that position which exactly bisected the Gaussian shaped laser beam. The electrode was then rotated along an axis perpendicular to the yz plane until the intensity monitored at any point in the diffraction pattern went through a minimum. The rotation producing minimum intensity was that position in which the electrode surface was oriented parallel to the beam. This conclusion was verified by comparing this orientation to that found using a reflection method described previously. The intensity minimum method was initially devised because the reflection method was difficult with thin electrodes, and the minimum method was subsequently found to be a more sensitive means of alignment for electrodes of all sizes. Fine tuning was accomplished by alternately moving the electrode slightly up and down and rotating slightly until the same electrode position gave both maximum intensity along the x axis and minimum intensity in the yz plane.

**Electrodes**

Electrodes of lengths of 0.014, 0.027, and 0.050 cm were constructed from platinum sheets of the above widths purchased from Matthey Bishop, Inc. A highly polished electrode surface was required to achieve maximum optical and electrochemical performance. A mechanical polisher (Buehler minimet) was used to polish the electrode surface. The electrode substrate was imbedded in "castolite" resin (Buehler) before polishing, and the castolite was surrounded by a Pyrex cylinder. The cylinder prevented the resin from being rounded off during polishing when care was taken to ensure that the platinum edge, the resin, and
the Pyrex cylinder formed a very flat, smooth surface. The following series of abrasives (Buehler products) were used: silicon carbide paper (180, 240, 320, 400, 600 grit), "Metadi" diamond (15u, 6u, 1u), alumina A (0.05 u), and alumina B (0.03 u). At each step, the electrode was polished only until the surface was uniform in appearance and was well cleaned and rinsed after each successive polishing step. The resin was then dissolved with "strip solve" (Cargille Laboratories), and the electrode was ready for use.

Sheets of glassy carbon were purchased from Atomergic and machined to the desired width to construct larger electrodes. Edges of 0.161, 0.63, and 1.1 cm were made, and the same polishing procedures were followed as for the platinum electrodes. Electrical contact was made with the carbon in the following way: a small indentation was made on the side opposite the polished surface, and then a piece of glass tubing was sealed in place over this indentation and filled with roughly 0.25 in. mercury. Contact was made with a platinum wire placed in the mercury.

The lifetime of both the platinum and carbon electrodes was found to be dependent on several factors. For most test systems, electrodes polished by the procedure discussed above would have a lifetime of at least two months of everyday use. For maximum lifetime, care should be taken to avoid scratching the electrode surface and to keep the edges from rounding off. A surface of poor optical quality was indicated when the electrode could not be aligned properly in the light beam. Formation of a film on the surface of the electrode, which could occur upon sitting in some solutions, shortened the lifetime. The presence of a film could result in slow charge transfer, and this yielded an experimental
absorbance-time transient which was sluggish in comparison with that exhibited by a clean, newly polished electrode.

For the thin platinum electrodes, a capillary cell was constructed by placing the platinum edge between two microscope slides held together by rubberbands. Electrical contact was made with the platinum at the top, and solution was drawn up into the cell from a reservoir positioned below. The cell illustrated in Figure 14 was of this design. The reference electrode used in this case, as for all test systems, was a saturated calomel electrode (SCE), and the auxiliary electrode consisted of a platinum wire. Both were positioned in the bulk solution as shown.

The size of the carbon electrodes made them unsuitable for a thin-layer cell of this type so they were placed directly into the bulk solution as shown in Figure 16. This experimental design resulted in a noisier signal, since the pathlength of the light beam through solution was greatly increased and convection disturbed the diffraction pattern. However, this design placed the working electrode in close proximity to the reference, which had the advantage of decreasing the uncompensated resistance of the electrochemical system.

In the actual experiment, the phase boundary between the solvent and air would result in a phase shift at the interface. However, it could be shown theoretically that no net change in direction occurred between the electrode edge where the diffraction took place and the angle \( \beta \) (Figure 14) measured at the focal plane of the lens. The theoretical diffraction pattern was calculated through use of a Fast Fourier transform routine (see Appendix A), which produced a set of coefficients describing the intensity, but these intensities were oriented along the x axis in the
Figure 16. Experimental configuration for diffraction experiments utilizing glassy carbon as the working electrode. a) glassy carbon square, b) mercury, c) platinum wire for connection to potentiostat. The focal length of the lens was 1 m, and the photomultiplier tube (PMT) was placed in the focal plane of the lens. The aperture preceding the PMT was a 0.8 mm diameter pinhole. The angle $\beta$ illustrates the angle that the PMT makes with the horizontal. Diffracted rays are not shown. (Figure not drawn to scale)
focal plane of the lens. The spacing depends on the focal length of
the lens and the wavelength of incident light and is determined by means
of the following equation (derived in detail in Appendix A):

\[ \sin \alpha = \frac{x}{zf_s} = \frac{n\lambda_s}{2L}. \]  

(23)

In the equation above, \( \alpha \) is the scattering angle within the solvent of
refractive index RI, \( \lambda_s \) is the wavelength of the incident light within the
solvent \( (= \lambda_{\text{air}}/RI) \), \( f \) is the focal length of the lens, and \( 2L \) is the physi-
cal width of the input to the Fourier transform algorithm. The integer \( n \)
is the component of the numerical transform. This equation will place
the predicted intensity of the \( n \)th component at the angle \( \alpha \) in the dif-
fraction pattern.

The above equation assumes the entire diffraction process occurs in
a medium of constant refractive index. In the actual experiment, the
scattered light passed into air, the observed angle \( \beta \) being larger than \( \alpha \)
according to Snell's law:

\[ \sin \alpha = \sin \frac{\beta}{RI}. \]  

(24)

Substitution into equation 23 yields:

\[ \sin \beta = \frac{x}{f} = \frac{n\lambda_{\text{air}}}{2L}. \]  

(25)

Note that equation 25 is identical to equation 23, except the parameters
now refer to those measured in air.
Three well-characterized, electrochemically reversible test systems were used to obtain experimental results which could be compared to theoretical predictions. Table 1 contains a list of these three systems and indicates other pertinent experimental parameters. Other test systems were used in order to investigate specific electrode or chemical processes. Chlorpromazine was used to examine the effect of adsorption on the results obtained by diffraction. Chlorpromazine and Adrenaline were both examined in various media to determine the feasibility of using diffraction to investigate mechanistically complex systems. Finally, N,N,N',N'-tetramethyl-ρ-phenylenediamine was used for the purpose of obtaining an absorbance vs. wavelength spectrum using diffraction since it has a distinct absorbance maximum within the wavelength range provided by the dye laser.

Trianisylamine (TAA) was obtained as gifts from R. N. Adams (University of Kansas) and Robert Walters (University of Illinois, Chicago Circle). The reversible one-electron oxidation of TAA at 0.6 volts vs. SCE produced a blue cation radical with molar absorptivity (ε) of 10750 M⁻¹ cm⁻¹ at 632.8 nm.³²

Tris-(ρ-bromophenyl)-amine (TBA) was synthesized in this lab following a published procedure.³³ TBA undergoes a reversible one-electron oxidation at 1.05 volts vs. SCE.³⁵ The molar absorptivity of the cation radical formed was determined to be 15100 M⁻¹ cm⁻¹ at 632.8 nm by a transmission spectroelectrochemical technique using a gold minigrid in a thin-layer cell.³⁶ Chronoamperometry was used to determine the
Table 1. Chemical Systems*

<table>
<thead>
<tr>
<th>Electroactive Species</th>
<th>Solvent</th>
<th>( \lambda ) (nm)</th>
<th>Electrode Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trianisylamine</td>
<td>Acetonitrile</td>
<td>632.8</td>
<td>Platinum, Carbon</td>
</tr>
<tr>
<td>Tris-(p-bromophenyl)-amine</td>
<td>Acetonitrile</td>
<td>632.8</td>
<td>Platinum, Carbon</td>
</tr>
<tr>
<td>Ferrocyanide</td>
<td>1 M KNO₃</td>
<td>442.0</td>
<td>Platinum</td>
</tr>
</tbody>
</table>

*Three of the test systems employed in diffraction experiments. The electroactive species were oxidized at the electrode, and the chromophore produced was monitored at the wavelength \( \lambda \) indicated. Tetraethylammonium perchlorate (TEAP) (0.1 M) was present as the inert electrolyte in Acetonitrile solutions.
diffusion coefficient \((1.6 \times 10^{-5} \text{ cm}^2/\text{sec})\), and the results were verified by a large-angle reflection experiment.\(^{17}\)

The solvent for both the TAA and TBA test systems was reagent-grade acetonitrile. Tetraethylammonium perchlorate (TEAP) at a concentration of 0.1 M was present as the inert electrolyte. TEAP purchased from Eastman Kodak was polarography grade (#X8617) and was used without purification.

The ferrocyanide/ferricyanide redox couple was a well-behaved electrochemical system in which an inorganic ion was oxidized in an aqueous medium. The potassium ferrocyanide used in diffraction experiments was purchased from Baker Chemical Co. and was used without further purification. Ferrocyanide, \(\text{Fe(}\text{CN})_6^{4-}\), underwent a one-electron oxidation at 0.35 volts vs. SCE\(^{37}\) to form ferricyanide, \(\text{Fe(}\text{CN})_6^{3-}\), which has a diffusion coefficient in 0.1 M KNO\(_3\) of \(0.632 \times 10^{-5} \text{ cm}^2/\text{sec}\).\(^{38}\) Ferricyanide weakly absorbed at 442 nm, having a molar absorptivity of \(554 \text{ M}^{-1} \text{ cm}^{-1}\), determined from a wavelength spectrum obtained through use of a Cary 15 spectrophotometer. Potassium ferricyanide (Fisher Scientific) was used to obtain the absorbance spectrum.

In diffraction experiments performed with ferrocyanide, it was necessary to isolate the auxiliary electrode from the bulk solution to prevent interference due to products of reactions occurring at the auxiliary. This was accomplished by using a piece of vycor glass tubing, sealed at one end, as a compartment for the auxiliary electrode.

Chlorpromazine (CPZ) in acidic aqueous media, underwent a reversible one-electron oxidation at 0.66 volts vs. SCE.\(^{39}\) The cation radical formed \((\text{CPZ}^{+})\) had a molar absorptivity of approximately \(2200 \text{ M}^{-1} \text{ cm}^{-1}\),
as determined from a spectrum obtained using a Cary 15 spectrophotometer. The chlorpromazine perchlorate salt used in determination of the molar absorptivity was generated by controlled potential coulometry. Adsorption of CPZ was observed on solid electrodes but was greatly reduced in the presence of methanol, and in diffraction experiments, both 0.1 M HCl and a mixture of 50:50 0.1 M HCl/methanol were used as solvents. Both platinum and carbon working electrodes were used. The cation radical, although quite stable in acidic solutions, became very reactive in the presence of certain nucleophilic buffers. The behavior of the cation radical was examined in both phosphate and citrate buffers under the experimental conditions listed in Table 2. The pH of the

<table>
<thead>
<tr>
<th>Buffer</th>
<th>[NaCl]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025 M Phosphate</td>
<td>0.25 M</td>
<td>4.13, 5.16,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.33, 7.08</td>
</tr>
<tr>
<td>0.109 M Citrate</td>
<td>0.52 M</td>
<td>5.04</td>
</tr>
<tr>
<td>0.200 M Citrate</td>
<td>0.52 M</td>
<td>5.08</td>
</tr>
</tbody>
</table>

solution was adjusted by addition of either a few drops of 1 M H₂SO₄ or a small amount of solid NaOH. Platinum was the working electrode material used in diffraction experiments with the above buffer solutions.

Adrenaline was oxidized to the open-chained quinone (adrenalinequinone) in a reversible two-electron step at 0.7 volts vs. SCE in 1 M H₂SO₄. However, at pH greater than 2.5, the electrochemical reaction was followed by two subsequent chemical reactions (ECC mechanism), and the final products were adrenochrome and the starting material,
adrenaline. Adrenalinequinone and adrenochrome had maximum absorbance ($\lambda_{max}$) at 390 nm and 500 nm, respectively.

Adrenaline, in the form of L-epinephrine bitartrate, was purchased from Sigma and used without further purification. Solutions of adrenaline in both 1 M H$_2$SO$_4$ and pH 5 McIlvaine (citrate-phosphate) buffer were examined by diffraction at 442 nm, where the adrenochrome absorbed approximately five times as strongly as the adrenalinequinone. A platinum electrode was used for all experiments, and the solution in the capillary cell was changed after each single run for experiments performed in pH 5 McIlvaine buffer.

N,N,N',N'-Tetramethyl-ρ-phenylenediamine (TMPD) was oxidized reversibly at 0.22 volts vs. SCE to form the cation radical (TMPD$^{\cdot+}$). Because the cation radical exhibited maximum absorbance at 612 nm ($\varepsilon$ = 13000), diffraction experiments at a range of wavelengths, including $\lambda_{max}$, could be performed using the dye laser. A spectrum was obtained in this manner, absorbance being measured every 5 nm from 630 to 575 nm.

TMPD was converted from the dihydrochloride salt (Sigma) to the free base according to a published procedure, but the product was used directly after recrystallization from benzene, without sublimation. The solvent was reagent grade acetonitrile with 0.1 M TEAP as supporting electrolyte. The working electrode was a platinum edge in a capillary cell. The auxiliary electrode was isolated from the working electrode by a medium-porosity glass frit.
Experimental Methods and Data Acquisition

A typical diffraction experiment was performed in the following manner: the detector (PMT) was positioned at an angle $\beta$ (see Figure 14), the desired potential was applied at the working electrode, and intensity was monitored as a function of time. This procedure was repeated for a range of angles (0.07° to 1.45°) for a particular set of experimental conditions. Since the diffracted intensity was distributed symmetrically about the undiffracted portion of the beam ($\beta = 0.0^\circ$), the detector was placed in the geometric shadow region of the electrode to minimize stray light from reflection or other non-diffractive scattering.

All diffraction experiments were performed with computer control of potential and data acquisition. For all electrochemical systems, a potentiostat (Princeton Applied Research), interfaced to a lab minicomputer (Hewlett Packard), was used to provide the desired potential step. The step was at least 200 millivolts greater than the peak potential to ensure complete conversion of the electroactive species to product at the electrode surface. IR compensation was provided by a current follower (Princeton Applied Research). The level of IR compensation required was determined by setting the electrode at the initial potential (where Faradaic processes do not occur) and increasing the amount of compensation until the potentiostat oscillated. Then the level was decreased about 10% below this point so that stability was restored to the system.

Data acquisition was accomplished by interfacing the photomultiplier tube to the minicomputer. Absorbance as a function of time was defined to be the base 10 logarithm of the ratio of the initial intensity to the intensity at time $t$ and was computed at 1000 points within the chosen time
interval. Since the PMT was interfaced to the minicomputer, the maximum initial intensity was limited to 4.5 V, and the minimum intensity which could be reliably measured by the PMT was about 0.05 V. This limited the maximum absorbance which could be determined to less than 2 a.u. TIME6^38 was the computer program used for all single potential step experiments and provided measurement of absorbance as a function of time. TIME5^32 was used when a double potential step was required.
CHAPTER IV

RESULTS AND DISCUSSION
Comparison of Experimental Results with Theoretical Predictions

The exact manner in which diffracted light is attenuated by generation of chromophore can be predicted by theoretical calculations that have been discussed in detail in Chapter II. The important characteristics are the following: 1) absorbance, monitored as a function of time, varies with the observation angle, and the absorbance which is observed at larger angles rises faster with time than that at smaller angles; 2) at sufficiently long times after initiation of electrolysis, a time independent value for absorbance is obtained at all angles that can be related to the concentration of chromophore by Beer's law (equation 8), where \( \varepsilon \) is the extinction coefficient of the chromophore, \( b \) is the length of the electrode along the optical axis, and \( c \) is the bulk concentration of precursor to the chromophore.

One of the most important assumptions made in arriving at a theoretical description of diffraction at an electrode edge was that the diffracting edge acts as though it were infinitely thin along the optical axis. This means that any reflection or other types of non-diffractive scattering along the surface as well as any physical imperfections in the surface itself, such as scratches or lack of a sharp edge, were neglected.
A comparison of theoretical and experimental diffraction patterns is informative in view of this assumption and is illustrated in Figure 17, where the theoretically calculated intensity is plotted as a function of x on the same scale as the intensity obtained experimentally from diffraction by a 0.027 cm platinum electrode. The experimental diffraction pattern is that for the bare edge placed in a capillary cell without solution, and the experimental configuration was as shown in Figure 14, with an incident beam of wavelength equal to 632.8 nm. The theoretical diffraction pattern was calculated by transforming a Gaussian shaped beam of radius equal to the actual radius of the laser beam (equals 0.044 cm, the distance where the initial intensity has decreased to \(1/e^2\) of its maximum value) and with the maximum intensity arbitrarily set equal to 1.0. Since only relative intensity as a function of x was measured experimentally, the magnitude of the experimental intensity was then scaled until the best fit with theory was obtained.

From Figure 17, it can be seen that a very good fit is obtained for x coordinates between 1.14 cm and 1.11 cm. (Since the focal length of the lens is 1 m and the sine of the observation angle is equal to x/f, these x coordinates correspond to observation angles of 0.65° and 1.3°, respectively.) At x coordinates less than 1.14 cm, the diffracted intensity increases with decreasing x more rapidly than predicted. As x becomes larger than 2.22 cm, the diffracted intensity decreases faster than expected. Both these effects probably can be attributed to the finite length of the edge. For example, it is reasonable that some of the light propagating along the surface is subject to various types of non-diffractive interactions, such as reflection, which might result in a loss of
Figure 17. Intensity in the diffraction pattern as a function of $x$. Dashed line is the result of a theoretical calculation using 1024 points in the FFT routine. The solid line is the relative intensity obtained by diffraction at 0.027 cm platinum electrode. The wavelength of the incident light is 632.8 nm, and the beam radius is equal to 0.044 cm.
Intensity vs X

Figure 17
total intensity near the edge. In the diffraction pattern, this effect would be most evident at large angles since, as explained in detail in Chapter II, intensity at these angles is mostly the result of light which has passed very near the surface of the electrode. If light is reflected at very small angles, it may not only decrease the apparent intensity very near to the surface but may increase the intensity at distances farther away from the electrode but still within the radius of the incident beam. In the diffraction pattern, this would result in an increase in intensity at small angles over that predicted theoretically, since diffracted light measured at small angles contains large contributions from the entire beam. The net effect is a flattening of the Gaussian shape of the cross section of the incident beam.

Nondiffractive interactions would of course become greater in magnitude in the presence of any surface imperfections, such as scratches or rounded edges. These types of interactions would also be expected to increase as the length of the electrode along the optical axis increased. The diffraction pattern obtained from a 0.63 cm carbon electrode in the absence of any solution is shown in Figure 18, and for ease of comparison, the theoretical diffraction pattern calculated for an infinitely thin edge is also shown. The experimental measurement was made using the experimental configuration shown in Figure 16, and the wavelength of the incident beam was again equal to 632.8 nm. No fit could be found on any portion of the curve with the theoretical diffraction pattern so the intensity was simply scaled by a constant to the same order of magnitude as the predicted intensity. The relative intensity for a 0.63-cm edge at any x coordinate is at least three orders of magnitude less than that for the
Figure 18. Intensity in the diffraction pattern as a function of x. Dashed line is the result of a theoretical calculation using 1024 points in the FFT routine. The solid line is the relative intensity obtained by diffraction at a 0.63-cm carbon electrode. The wavelength of the incident light is 632.8 nm, and the beam radius is equal to 0.044 cm.
Figure 18
0.027-cm electrode over the range of x coordinates plotted in the figures. In order to compare the results for both electrode lengths on the same intensity scale, the scaling factor required in Figure 18 is $10^3$ larger than that used for the results shown in Figure 17.

A comparison of Figures 17 and 18 clearly indicates that as the real electrode length increases, the distribution of intensity in the diffraction pattern can be less well described by diffraction at an infinitely thin edge. A portion of the experimental curve obtained by diffraction at a 0.027-cm electrode corresponds quite well to the theoretically predicted one, but when the electrode length is increased to 0.63 cm, the experimentally obtained intensity decreases much more rapidly with increasing x than theory predicts. It is important to realize that since these results are obtained in the absence of chromophore, the results are a direct indication of the influence of the finite width of the edge on diffracted intensity.

To determine the effect of the presence of chromophore on the diffracted intensity, the entire diffraction pattern could be recorded at a particular time after initiation of electrolysis. However, with the present experimental configuration, it is simpler to monitor the change in intensity at any angle in the diffraction pattern as a function of time. Absorbance can then be calculated from the log of the ratio of diffracted intensity before to that after initiation of electrolysis.

Experimental absorbance-time transients obtained using a 0.027-cm platinum electrode are shown in Figure 19 for the angles indicated, where the electroactive species is tris-(p-bromophenyl)-amine (TBA) at an initial concentration of 2.619 mM. The wavelength of the incident light was 632.8 nm, where the cation radical (TBA$^{+}$) generated by electrolysis has
Figure 19. Experimental absorbance as a function of time for the angles indicated. The bulk concentration of TBA is 2.619 mM, and the electrode is a 0.027 cm platinum edge placed in a thin-layer cell.
an extinction coefficient of 15100 M$^{-1}$ cm$^{-1}$. The experimental configuration is shown in Figure 14.

Comparison of Figure 19 with Figure 10 shows that the experimental absorbance-time transients agree quite well, in a qualitative sense, with theoretical predictions. As expected, the absorbance measured at larger angles increases faster than that measured at relatively small angles. This can be understood by realizing that initiation of electrolysis establishes a steep concentration gradient extending from the electrode into the bulk solution, with the largest concentration of chromophore (TBA$^{+}$) present at the surface. The incident intensity at the edge, represented at large angles in the diffraction pattern, is therefore attenuated in a substantial amount in only milliseconds even though the total amount of chromophore which has been generated in this time is small. As time increases after initiation of electrolysis, the concentration gradient becomes less steep as more chromophore is produced and diffuses out into the bulk solution. This results in attenuation of a larger portion of the incident beam, which will be indicated by a significant absorbance of diffracted light even at relatively small angles in the diffraction pattern.

The angular variation in the absorbance-time transients indicates that the shape of the diffraction pattern changes as the concentration vs. distance profile of the chromophore in solution changes. This shows that the diffractive process is sensitive to spatial features within the diffusion layer.

The absorbance response at large angles is quite fast. For example, an absorbance of more than 1.2 absorbance units (a.u.) is obtained in less than 100 msec at an angle of 1.16°, even though the diffusion layer is only 0.013 cm in width at this time. Finally, it can be seen from Figure 19
that the absorbance at angles of 0.58° or larger reaches the same time independent value in less than one second, and at longer times than shown, it was found that the absorbance measured at all the angles shown levels off to this value. This value of absorbance corresponds very well to the value of 1.07 a.u. which would be calculated from Beer's law for this set of experimental conditions. This is an extremely advantageous result, since the only parameters that would then be necessary to determine an unknown concentration of an electroactive species in solution would be the length of the electrode along the optical axis and the extinction coefficient of the product chromophore.

Even though Figure 19 verifies many conclusions drawn from theoretical considerations, there are some differences between results obtained experimentally and those obtained from theoretical calculations. In Figures 20 and 21, the absorbance-time transients shown in Figure 19 have been plotted individually (solid line) together with the theoretical result predicted for each angle (dashed line). It can be seen that the experimental absorbance response at small angles (0.29°, for example) is faster and peaks higher than that predicted theoretically. Experimental absorbance monitored at 0.58° levels off to a time independent value within one second, while the theoretical absorbance-time transient is still decreasing slightly with time. However, at 0.87° and 1.16°, the rise time of the experimental absorbance-time transients corresponds well to the theoretical response. In fact, good agreement is consistently obtained in the region between 0.65° and 1.16°, and the experimental and theoretical absorbance-time transients for 0.65° and 1.02° are given as further examples in Figure 22.
Figure 20. Theoretical (dashed line) and experimental (solid line) absorbance as a function of time for an observation angle of 0.29° (top) and 0.58° (bottom). The theoretical calculation is made using 2048 points in the FFT routine. The bulk concentration of TBA is 2.619 mM and the electrode is a 0.027-cm platinum edge placed in a thin-layer cell. The wavelength of the incident beam is equal to 632.8 nm.
Figure 20
Figure 21. Theoretical (dashed line) and experimental (solid line) absorbance as a function of time for an observation angle of 0.87° (top) and 1.16° (bottom). Other parameters are the same as for Figure 20.
Figure 21
Figure 22. Theoretical (dashed line) and experimental (solid line) absorbance as a function of time for an observation angle of 0.65° (top) and 1.01° (bottom). Other parameters are the same as for Figure 20.
Figure 22

ABSORBANCE

TIME (s)

0.2 0.4 0.6 0.8 1.0

0.0 0.2 0.4 0.6 0.8 1.0

ABSORBANCE

TIME (s)

0.2 0.4 0.6 0.8 1.0 1.2

0.0 0.2 0.4 0.6 0.8 1.0
The difference between the experimental and theoretically predicted results at short times is probably due to a combination of factors. First, even in the absence of chromophore, the diffraction pattern produced by an edge of finite width deviates from that calculated for an infinitely thin edge, as can be seen in Figure 17. In fact, it can be seen from a comparison of Figure 17* and the absorbance-time transients in Figures 20-22 that small angles show the most deviation from the predicted result whether chromophore is present or not. It seems reasonable to conclude that the finite length and the quality of the surface of the electrode, which affect the diffraction pattern in the absence of chromophore, will also affect the shape of the diffraction pattern as chromophore is generated and thus will have an effect on the absorbance measured as a function of time.

Second, the design of the electrochemical cell used in the present work is not an ideal one for electrolysis. Thin-layer cells of this type typically present a high resistance to conductivity, with the result that the real potential at the working electrode is less than the applied potential by an amount that is equal to the resistance times the amount of current passed in the cell ($\Delta E = iR$). In a thin-layer cell, $R$ can be quite large, which results in a substantially lower potential at the working electrode. In the case of TBA in acetonitrile, this was found to result in an extremely slow absorbance response. Some correction was obtained by the use of IR compensation, which basically consists of a current follower,

*Although the intensity in Figure 17 is plotted as a function of $x$, the angle corresponding to a particular $x$ coordinate is simply that angle with sine equal to $x/f$, where $f$ is the focal length of the lens used to focus the diffraction pattern (1 m).
connected to the potential control system of the potentiostat, which feeds back a certain fraction of the real potential at the working electrode. However, positive feedback systems of this type tend to overcompensate, primarily due to time lag in the potential sensing and application circuits. This can result in potential overshoot and ringing, which would have an unknown effect on the concentration vs. distance profile of the chromophore in solution and therefore on the absorbance measured in the diffraction pattern at a particular time after initiation of electrolysis. Any effects due to IR compensation would be most pronounced at short times, when the largest current is flowing in the electrochemical cell.

It should be emphasized, however, that regardless of deviation from theory at short times, the time independent value of absorbance corresponds very closely to the expected result. In addition, both theoretical and experimental values are in good agreement with that which would be predicted by Beer's law, theory agreeing to within 0.5% and experimental to within 3.0% for all angles shown.

Similar results are obtained from diffraction experiments using ferrocyanide as the electrochemical test system. Ferrocyanide in 1 M KNO₃ undergoes a reversible oxidation to produce ferricyanide, which is a weak absorber at 442 nm, with an extinction coefficient of only 554 M⁻¹ cm⁻¹. Experimental (solid line) and theoretical (dashed line) absorbance-time transients for several angles are shown in Figures 23 and 24 for electrolysis of a 30.11 mM solution of ferrocyanide at a 0.027-cm platinum electrode. Again, it can be seen that experimental absorbance rises faster and peaks higher than predicted at smaller angles (0.29°, 0.58°), but better agreement is obtained at larger angles (0.80°, 0.87°). The
Figure 23. Theoretical (dashed line) and experimental (solid line) absorbance as a function of time for an observation angle of 0.29° (top) and 0.58° (bottom). The theoretical calculation is made using 2048 points in the FFT routine. The bulk concentration of ferrocyanide is 30.11 mM, and the electrode is a 0.027-cm platinum edge placed in a thin-layer cell. The wavelength of the incident beam is equal to 442 nm.
Figure 24. Theoretical (dashed line) and experimental (solid line) absorbance as a function of time for an observation angle of 0.80° (top) and 0.87° (bottom). Other parameters are the same as for Figure 23.
absorbance obtained from the level portion of the experimental absorbance-time transient at larger angles is within 5% of the value predicted by theoretical calculations.

The differences between experiment and theory at short times appear to be more pronounced than those observed for TBA. Also, a longer time than predicted is required for the absorbance to reach a constant value. In the case of the ferro/ferricyanide redox couple, it was found experimentally that absorbance at all angles was substantially higher than expected unless the auxiliary electrode was isolated from the bulk solution. This was necessary because highly colored products are formed by electrochemical reactions occurring at the auxiliary during the course of the experiment. Even when the auxiliary was isolated from the solution, angles less than 0.80° continued to exhibit an apparently constant value of absorbance that was as much as 15% higher than the Beer's law value, even when monitored for as long as five seconds after initiation of electrolysis. This result was obtained for a range of concentration from 2 to 60 mM.

It is thought that the discrepancy between the experimental and theoretical absorbance is due to electrolysis of a low-level impurity in solution for the following reasons. The percentage error decreases with increasing concentration of ferrocyanide, as would be expected since the absorbance due to an impurity becomes less noticeable as the absorbance of the species of interest increases. Also the percentage difference from Beer's law consistently decreases with increasing angle in the range of angles between 0.58° and 0.80°. This implies that as the observation angle increases, which effectively amounts to preferential sampling of
regions in solution nearer to the electrode, the relative absorbance due to the impurity decreases, i.e., the concentration of the impurity decreases relative to the concentration of ferricyanide. This type of angular variation in the time independent value of absorbance might be expected in the presence of a small amount of electroactive impurity, since, although electrolysis results in the formation of a concentration gradient for both species, the absorbance due to the impurity will be a smaller fraction of the total absorbance very near to the electrode surface, where the concentration of ferricyanide is greatest. The exact relationship between the absorbance due to each species at a particular distance from the electrode would, of course, be dependent upon their respective diffusion coefficients, as well as the applied potential, since the concentration of each chromophore relative to its electroactive precursor at the electrode surface is that ratio determined by the Nernst equation.

Regardless of the origin of the increased absorbance, the effect on the time independent measurement at observation angles greater than or equal to 0.80° appears to be negligible, since good agreement with Beer's law can be obtained for a wide range of concentration of ferrocyanide.

The effect of increasing the length of the electrode along the optical axis can be seen in Figure 25, which shows both experimental and theoretical results for an electrode of length equal to 1.12 cm. Experimental (solid line) and theoretical (dashed line) absorbance-time transients at an angle of 0.73° are shown for the electrolysis of an 11-μm solution of trianisylamine (TAA) at a glassy carbon edge. The large size of the electrode made it necessary to use the experimental configuration shown in Figure 16, and the wavelength of the incident beam was 632.8 nm. At
Figure 25. Theoretical (dashed line) and experimental (solid line) absorbance as a function of time for an observation angle of 0.73°. The theoretical calculation is made using 2048 points in the FFT routine. The bulk concentration of TAA is 11.2 μm, and the electrode is a 1.12-cm carbon edge placed directly into the bulk solution. The wavelength of the incident beam is equal to 632.8 nm.
Figure 25
this wavelength, the chromophore \((\text{TAA}^{\bullet+})\) has an extinction coefficient equal to \(10750 \text{ M}^{-1} \text{ cm}^{-1}\).

It can be seen that good agreement with theory is not observed at short times (less than about 0.5 seconds), even within a region of the diffraction pattern that shows good agreement when a 0.027-cm electrode is used. This is not surprising since, as discussed in reference to Figure 18, the intensity in the diffraction pattern obtained with longer electrodes decreases much more rapidly with increasing angle than expected, and the magnitude of the intensity is much lower than that observed with a 0.027-cm edge. Since the loss of intensity is probably due to non-diffractive interactions with the surface of the electrode, the shape of the incident beam will be most disturbed near the edge, and the effect will be most pronounced in the measurement of absorbance at short times, when the width of the diffusion layer is small. As time increases after initiation of electrolysis, the width of the diffusion layer increases, resulting in absorbance of the incident beam in regions farther away from the electrode, where any unexpected interactions with the surface are probably negligible, and the absorbance measured in the diffraction pattern more closely resembles that predicted theoretically. The slow rise time may also be due to inadequate IR compensation, even though the electrode is placed directly in the bulk solution, since the area of the electrode is quite large, and therefore, a relatively large amount of current is required at initiation of electrolysis. Also, it is difficult to achieve an equal distribution of potential along the surface with electrodes of this size, a factor which could contribute to a slow absorbance response.
It should be noted, however, that the time independent value is in good agreement with both theoretical diffraction calculations and the value of 0.135 a.u. which would be calculated from Beer's law for these experimental conditions.

Analysis of the absorbance-time transients obtained in diffraction experiments using a 0.027-cm platinum electrode show that good agreement with theory is obtained even at relatively short times for observation angles between 0.58° and 1.16°. Results obtained with a much longer electrode show that the rise time of the absorbance is much slower than expected, even in this region of the diffraction pattern. In order to obtain the best possible agreement with theory for both electrodes, the cell design should be such that the amount of IR compensation which is required is minimal. Any remaining disagreement with theory would then probably be due simply to differences between the diffractive process predicted for an infinitely thin edge and that actually observed at a real edge of finite length. Despite some disagreement at short times, the constant absorbance value obtained at both electrodes is in very good agreement with that which would be predicted by a Beer's law calculation.

**Absorbance as a Function of Concentration**

The simple relationship between the time independent absorbance value observed in a diffraction experiment and Beer's law can be of great analytical utility. The value obtained from the level portion of the absorbance-time transient \(A_{\text{exp}}\) over a wide range of concentrations of TBA is listed in Table III. Similar data are shown in Tables IV and V for
<table>
<thead>
<tr>
<th>[TBA] (mM)</th>
<th>Electrode</th>
<th>Length (cm)</th>
<th>$A_{\text{exp}}$</th>
<th>Angle</th>
<th>$A_{\text{exp}}/\text{bc}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.719</td>
<td>platinum</td>
<td>0.014</td>
<td>1.14</td>
<td>0.58°</td>
<td>14238</td>
<td>15100</td>
<td>5.7</td>
</tr>
<tr>
<td>6.035</td>
<td></td>
<td>1.21</td>
<td></td>
<td>0.73°</td>
<td>14321</td>
<td></td>
<td>5.2</td>
</tr>
<tr>
<td>0.012</td>
<td>platinum</td>
<td>0.027</td>
<td>0.049(50)</td>
<td>0.58°</td>
<td>15187</td>
<td></td>
<td>0.6</td>
</tr>
<tr>
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<td></td>
<td>0.023(20)</td>
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<td></td>
<td>14393</td>
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<td>4.7</td>
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<td>0.598</td>
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<td>0.250</td>
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<td></td>
<td>15494</td>
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<td>2.6</td>
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<tr>
<td>2.619</td>
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<td>1.09</td>
<td></td>
<td></td>
<td>15414</td>
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<td>2.1</td>
</tr>
<tr>
<td>3.329</td>
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<td>1.38</td>
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</tr>
<tr>
<td>0.144</td>
<td>carbon</td>
<td>0.16</td>
<td>0.296(20)</td>
<td>0.58°</td>
<td>12811</td>
<td></td>
<td>15.2</td>
</tr>
<tr>
<td>0.115</td>
<td></td>
<td>0.260(20)</td>
<td></td>
<td></td>
<td>14081</td>
<td></td>
<td>6.7</td>
</tr>
<tr>
<td>0.0157</td>
<td>carbon</td>
<td>0.63</td>
<td>0.143(20)</td>
<td>0.58°</td>
<td>14430</td>
<td></td>
<td>4.4</td>
</tr>
<tr>
<td>0.0160</td>
<td></td>
<td>0.151(20)</td>
<td></td>
<td>0.58°</td>
<td>14887</td>
<td></td>
<td>1.4</td>
</tr>
</tbody>
</table>

*Experimental absorbance ($A_{\text{exp}}$) obtained by the electrolysis of TBA in acetonitrile with 0.1 M TEAP as inert electrolyte. Platinum electrodes are placed in a capillary cell, and the applied potential is 1.3 V vs. SCE. Carbon electrodes are placed directly into the bulk solution, and the applied potential is 1.1 V vs. SCE. Absorbance is for a single run, except in the cases where the number of time averaged runs is indicated by the number in parentheses after $A_{\text{exp}}$. The extinction coefficient ($\varepsilon$) is that obtained by a transmission spectro-electrochemical technique using a gold minigrid in a thin-layer cell.
Table 4. Absorbance as a Function of [TAA]*

<table>
<thead>
<tr>
<th>[TAA] (mM)</th>
<th>Electrode</th>
<th>Length (cm)</th>
<th>$A_{\text{exp}}$</th>
<th>Angle</th>
<th>$A_{\text{exp}}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2530</td>
<td>Carbon</td>
<td>0.16</td>
<td>0.462(20)</td>
<td>0.58°</td>
<td>11342</td>
<td>10750</td>
<td>5.5</td>
</tr>
<tr>
<td>0.0075</td>
<td>Carbon</td>
<td>0.63</td>
<td>0.043(10)</td>
<td>0.58°</td>
<td>9137</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>0.049</td>
<td>Carbon</td>
<td>1.12</td>
<td>0.054(50)</td>
<td>0.73°</td>
<td>9992</td>
<td>7.0</td>
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</tr>
<tr>
<td>0.0112</td>
<td>Carbon</td>
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<td>0.136(20)</td>
<td></td>
<td>10861</td>
<td>1.0</td>
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</tr>
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</table>

*Experimental absorbance ($A_{\text{exp}}$) obtained by the electrolysis of TAA in acetonitrile with 0.1 M TEAP as inert electrolyte. Carbon electrodes are placed directly into the bulk solution and the applied potential is 0.80 V vs. SCE. The number of time averaged runs is indicated by the number in parentheses after $A_{\text{exp}}$. The extinction coefficient ($\varepsilon$) is from the literature.
Table 5. Absorbance as a Function of [Ferrocyanide]*

<table>
<thead>
<tr>
<th>[Ferrocyanide] (mM)</th>
<th>Electrode</th>
<th>Length (cm)</th>
<th>$A_{exp}$</th>
<th>Angle (°)</th>
<th>$A_{exp}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.164</td>
<td>Platinum</td>
<td>0.027</td>
<td>0.0343(5)</td>
<td>1.02°</td>
<td>587</td>
<td>554</td>
<td>6.0</td>
</tr>
<tr>
<td>2.680</td>
<td></td>
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<td>0.0401(5)</td>
<td></td>
<td>554</td>
<td></td>
<td>0.0</td>
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<tr>
<td>4.744</td>
<td></td>
<td></td>
<td>0.0718</td>
<td></td>
<td>560</td>
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<td>1.1</td>
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<td>4.933</td>
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<td></td>
<td>0.0717</td>
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<td>0.1474</td>
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</tr>
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<td>10.09</td>
<td></td>
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<td>0.151</td>
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<td>19.99</td>
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<td>528</td>
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<td>26.81</td>
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<td>39.75</td>
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<td>0.744</td>
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<td>544</td>
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<td>1.8</td>
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<td>61.62</td>
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<td>0.850</td>
<td></td>
<td>511</td>
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<td>7.8</td>
</tr>
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</table>

*Experimental absorbance ($A_{exp}$) obtained by the electrolysis of ferrocyanide is 1 M KNO$_3$. The electrode is placed in a capillary cell and the applied potential is 0.55 V vs. SCE. Absorbance is for single runs except in the cases where the number of time averaged runs is indicated by the number in parentheses after $A_{exp}$. The extinction coefficient ($\varepsilon$) is obtained from the literature.
TAA and ferrocyanide, respectively. As indicated in the tables, carbon and platinum electrodes of various lengths were used, and the measurement was made at the observation angle listed for each set of experimental conditions. The only criterion which was used for selecting the observation angle in a particular set of data was that the absorbance-time transient be apparently level at the time the measurement was made. In the case of ferrocyanide, the observation angle was not less than 0.800° for reasons which have been discussed above.

For convenience in comparison of results obtained with electrodes of length b, and for concentration c, the apparent value of the extinction coefficient for each species, determined from Beer's law to be equal to \( \frac{A_{exp}}{bc} \), is listed along with the value which is expected for each species, \( \varepsilon \), determined by conventional means. The per cent difference between these two values is also indicated in the tables. It can be seen from the results listed in Tables 3, 4, and 5 that constantly good agreement with Beer's law is observed for a wide range of electrode lengths and concentrations. Using all the data listed in each table, the average value of \( \frac{A_{exp}}{bc} \) differs from the expected value of \( \varepsilon \) by 3.3%, 3.9%, and 0.0% for TBA, TAA, and ferrocyanide, respectively.

Due to the nature of the experimental configuration, only one diffraction angle can be monitored at a time, and the experiment must be repeated several times using the same solution in order to examine a large portion of the diffraction pattern. The variation in the time independent value obtained as the result of each run can be used to provide an indication of the reproducibility of the response. Table 6 lists the average value of the extinction coefficient obtained at each angle for the
Table 6. Angular Variation (TBA)*

<table>
<thead>
<tr>
<th>Angle</th>
<th>$A_{\text{exp}/bc}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>% $\sigma$</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58°</td>
<td>15168 (5)</td>
<td>2.5</td>
<td>15100</td>
<td>2.5</td>
</tr>
<tr>
<td>0.66°</td>
<td>15928 (5)</td>
<td>7.7</td>
<td></td>
<td>5.8</td>
</tr>
<tr>
<td>0.73°</td>
<td>15737 (7)</td>
<td>8.9</td>
<td></td>
<td>4.2</td>
</tr>
<tr>
<td>0.80°</td>
<td>16386 (6)</td>
<td>9.9</td>
<td></td>
<td>8.5</td>
</tr>
<tr>
<td>0.87°</td>
<td>18846 (8)</td>
<td>22.8</td>
<td></td>
<td>24.8</td>
</tr>
<tr>
<td>1.02°</td>
<td>15862 (6)</td>
<td>5.9</td>
<td></td>
<td>5.0</td>
</tr>
</tbody>
</table>

*Average value of $A_{\text{exp}/bc}$ for electrolysis of solutions containing from 0.011 to 3.3 mM TBA. The electrode is a 0.027-cm platinum edge placed in a capillary cell, and the wavelength of the incident beam is 632.8 nm. The relative standard deviation (% $\sigma$) is calculated for the data set for each angle. The number of runs in each data set is indicated by the number in parentheses after the value of $A_{\text{exp}/bc}$. The extinction coefficient ($\varepsilon$) is that obtained by a transmission spectroelectrochemical technique using a gold minigrid in a thin-layer cell. The percent difference between this value and the average value obtained by diffraction for each angle is also listed.
electrolysis of TBA at a 0.027-cm platinum electrode placed in a capillary cell. In order to calculate the average value, the results of diffraction experiments over a range of concentrations from 11 um to 3.3 mM were collected, and the standard deviation (\% \sigma) within the set of data for each angle was calculated, as well as the percent difference of the experimental value from the expected value of the extinction coefficient.

It can be seen from the data in Table 6 that 0.58° gives the most precise results, as well as the best agreement with Beer's law. The larger \% standard deviation found at larger angles is probably the result of the following two factors: 1) as the measurement angle increases, the magnitude of the diffracted intensity decreases, and the effect of stray light becomes more important, and 2) the diffracted intensity as the angle increases contains larger contributions from light passing closer to the edge and will be more affected by imperfections in the electrode surface. Although measurements at all angles are not as consistent as those made at 0.58°, good agreement with the expected value of the extinction coefficient is obtained at all angles with the exception of 0.87°. The large percent difference of the measurements made at this angle is the result of one discordant absorbance measurement which differs from the value nearest to it in the set of data for that concentration of TBA by more than one standard deviation. If the Q test is applied to the entire set of data for TBA, this measurement can be discarded with 90\% confidence that it was subject to some factor which did not affect the other results. Using all the rest of the data (36 values in all), the overall average value of \( A_{\text{exp}}/bc \) is found to be 15874 M\(^{-1}\) cm\(^{-1}\), with a standard deviation of
8.8%. This value is within 5.1% of the expected value for the extinction coefficient.

In Table 7 are presented similar data for ferrocyanide, obtained over a concentration range from 2 to 60 mM. Note that the results at 0.87° are now consistent with the results obtained at other angles. Again using all the data from all angles, the average value of $A_{\text{exp}}/bc$ is calculated to be $573 \text{ M}^{-1} \text{ cm}^{-1}$, with a per cent standard deviation of 8.2%. The difference between the average value obtained from diffraction experiments and the expected value of the extinction coefficient is 3.5%.

In general, the results obtained with electrodes of longer length showed more variation from run to run. This is probably due to the increased importance of stray light in the measurement of intensity before and after the initiation of electrolysis, since the intensity of diffracted light decreases with increasing electrode length. Also, longer electrodes were placed directly into the bulk solution, and even when the solution volume in the cell was minimal, solution convection resulted in a large amount of noise in the measurement of light intensity at the PMT. As a result, time averaging was necessary at all angles, and measurements at observation angles greater than 0.80° became quite difficult even when several runs were averaged. The number of time-averaged runs is indicated by the number in parentheses after the experimental absorbance for a particular concentration for all the entries in Tables 3 and 4. The value obtained for the extinction coefficient is still seen to be in fairly good agreement with the expected value, although the difference in a few cases is as high as 15%.
Table 7. Angular Variation (Ferrocyanide)*

<table>
<thead>
<tr>
<th>Angle</th>
<th>$A_{\text{exp}}/bc$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$% \sigma$</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80°</td>
<td>579 (13)</td>
<td>8.6</td>
<td>554</td>
<td>4.5</td>
</tr>
<tr>
<td>0.87°</td>
<td>578 (13)</td>
<td>7.9</td>
<td></td>
<td>4.3</td>
</tr>
<tr>
<td>0.95°</td>
<td>582 (12)</td>
<td>8.9</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>1.02°</td>
<td>554 (13)</td>
<td>7.2</td>
<td></td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Average value of $A_{\text{exp}}/bc$ for electrolysis of solutions containing from 2 to 60 mM ferrocyanide. The electrode is a 0.027-cm platinum edge placed in a capillary cell, and the wavelength of the incident light is 442 nm. The relative standard deviation ($\% \sigma$) is calculated for the data set for each angle. The number of runs in each data set is indicated by the number in parentheses after the value of $A_{\text{exp}}/bc$. The extinction coefficient ($\varepsilon$) is obtained from the literature. The per cent difference between this value and the average value obtained by diffraction for each angle is also listed.
The dynamic range of the diffractive technique is illustrated in Figure 26 where the absorbance is plotted as a function of concentration. All measurements were made at an observation angle of 0.58° using a 0.027-cm platinum electrode positioned in a capillary cell. Time averaging was necessary for concentrations below 0.12 mM, and the number of runs averaged was 50 or less. It can be seen from Figure 26 that the plot is linear when the absorbance is measured at a time corresponding to the level portion of the absorbance-time transient (1 second or less), for a range of concentrations from 11 μM to 3.3 mM, a dynamic range of 300. When the measurement is made at shorter times (0.25 seconds), corresponding to the rising portion of the absorbance-time curve, the plot of absorbance vs. concentration is non-linear, but it should be noted that good sensitivity is shown over this concentration range. It can be seen from reference to Figure 12 that theoretical absorbance as a function of concentration is also linear at one second, but non-linear at 0.25 seconds. (The parameters of electrode length, diffusion coefficient, etc., used to construct Figure 12 are identical to the experimental conditions for Figure 26).

With the detector used in the present experimental configuration (a PMT interfaced to a lab minicomputer), the maximum absorbance which could be reliably measured was limited to less than 2.0 a.u. With a 0.027-cm edge, the measurement of absorbance in the diffraction pattern up to this limit presented no difficulty. The minimum limit on the dynamic range was imposed by background absorbance, that is, the absorbance measured in a diffraction experiment when a potential was applied to the electrode in the absence of TBA. This background can be appreciable,
Figure 26. Absorbance as a function of concentration for TBA at a bulk concentration ranging from 0.011 to 3.3 mM. Solid line is absorbance measured on the level portion of the absorbance-time transient, and the time after initiation of electrolysis is 1 second or less. The dashed line is absorbance measured at 0.25 seconds. The electrode is a 0.027-cm platinum edge placed in a thin-layer cell, and the incident beam is 632.8 nm. The observation angle is 0.58°.
Figure 26
especially at short times, and an example of the absorbance as a function of time is shown in Figure 27. The solvent was acetonitrile with 0.1 M TEAP as the inert electrolyte, and the observation angle was 0.58°. Due to the magnitude of the background absorbance, concentrations lower than about 11 µm were found to give inconsistent results not only from experiment to experiment, but even in subsequent runs on the same solution.

In comparison to that of a 0.027-cm electrode, the dynamic range of longer electrodes is found to be relatively small. The maximum absorbance which can be determined with longer electrodes is now limited by stray light, which becomes a more important part of the total intensity as the intensity of diffracted light decreases. For example, using a 0.63-cm carbon electrode, an absorbance of more than 0.25 a.u. was not observed, even when the concentration of TBA was increased to 0.034 mM, which from Beer's law would be expected to yield an absorbance of 0.32 a.u..

The same type of background that is observed with the shorter electrode also limits the minimum absorbance which can be measured at electrodes of longer length.

It can be seen that background imposes a limitation on the dynamic range of the diffractive technique, and the subject deserves further discussion here. The source of the background observed in acetonitrile/TEAP solutions is unclear but was observed to increase with increasing electrode length. Also, the size of the background was potential dependent, increasing with the size of the potential step. Regardless of electrode length or the applied potential, the background absorbance consistently returns to a near zero level in less than 0.5 seconds. During
Figure 27. Absorbance as a function of time observed in acetonitrile with 0.1 M TEAP present as the inert electrolyte. The electrode is a 0.027-cm platinum edge placed in a thin-layer cell. The potential step is from 0.0 to 1.3 V vs. SCE. The wavelength of the incident beam is 632.8 nm, and the observation angle is 0.58°. Twenty consecutive runs are time averaged.
Absorbance

CH$_3$CN/TEAP

Figure 27
background runs in solvents other than acetonitrile, the absorbance measured was of very low magnitude and relatively flat over the entire duration of the potential step. An example of the background observed in 1 M KNO₃ is shown in Figure 28.

The origin of the background in acetonitrile was not investigated further in the present work. However, in relation to results discussed below, it is important to emphasize that the background decreases to near zero in at least 0.5 seconds, and therefore reliable measurements can be made at times longer than this.

Detection Limit

Despite the limited dynamic range of longer electrodes, the longer pathlength for absorbance allows accurate measurement of very low concentrations of chromophore. A detection limit of 1.18 um TAA was established using a 1.12-cm carbon electrode. The absorbance as a function of time after initiation of electrolysis is shown in Figure 29 (solid line) along with the background absorbance (dotted line). The level value of absorbance which would be predicted from Beer's law is also indicated (dashed line). The absorbance-time transient was measured at an angle of 0.80°, and 100 runs were time averaged. Similar results were obtained at other angles within the range from 0.58° to 0.80°. Measurements made at angles greater than 0.80° were greatly affected by noise, probably caused by solution convection and stray light; therefore, a reliable value for absorbance could not be determined.

The average absorbance measured on the level portion of the experimental absorbance-time transient (0.5 to 1.0 seconds) is 0.015 and agrees
Figure 28. Absorbance as a function of time observed in 1 M KNO$_3$.

The electrode is a 0.05-cm platinum edge placed in a thin-layer cell. The potential step is from 0.0 to 0.55 V vs. SCE. The wavelength of the incident beam is 442 nm, and the observation angle is 0.58°. Twenty consecutive runs are time averaged.
Figure 28
Figure 29. Absorbance as a function of time. Solid line is for a 1.18-μm solution of TAA. The electrode is a 1.12-cm carbon edge placed directly into the bulk solution. The wavelength of the incident beam is 632.8 nm, and the observation angle is 0.80°. One hundred consecutive runs are time averaged, and the potential step is from 0.0 to 0.80 V vs. SCE. Dotted line is a typical background run for these experimental conditions. Dashed line indicates the predicted value of the time-independent absorbance measurement (calculated from Beer's law).
Figure 29
with the predicted value of 0.014 a.u. to within 7%. It is interesting to note that the peak height observed at about 100 milliseconds is greatly enhanced in the presence of TAA. As will be discussed in a later section, this may be due to adsorbed neutral which is released as chromophore after initiation of electrolysis.

Absorbance as a Function of Wavelength

Since the time-independent value of absorbance is equal to that which would be calculated from Beer's law, the molar absorptivity of an electrogenerated chromophore can be determined as a function of wavelength when the concentration of the precursor and the electrode length are known. A spectrum of the tetramethylphenylenediamine cation radical (TMPD') which was obtained in this manner is shown in Figure 30. Solutions approximately 1 mM in TMPD were analyzed in typical diffraction experiments where the working electrode was a 0.027-cm platinum edge placed in a capillary cell. The solvent was acetonitrile with 0.1 M TEAP present as the inert electrolyte. The light source was a carefully tuned dye laser, and an absorbance measurement was made every 5 nm from 630 to 570 nm and also at 612 nm, the wavelength of maximum absorbance. At each wavelength, a potential step from -0.200 V to 0.55 V was applied, and absorbance was monitored as a function of time at an angle of 0.73°. The molar absorptivity of TMPD' at each wavelength was then calculated from the absorbance-time transient. The spectrum shown is the average of six complete spectra. TMPD air oxidizes in reagent-grade acetonitrile so a bulk solution was stored under argon, and the solution in the capillary cell and the reservoir below were replaced with fresh solution approximately every 45 minutes.
Figure 30. Absorbance as a function of wavelength for the electrolysis of TMPD at a concentration of approximately 1 mM in acetonitrile with 0.1 M TEAP as inert electrolyte. The electrode is a 0.027-cm platinum edge placed in a capillary cell. The points shown are the average molar absorptivities calculated from Beer's law for six separate runs, and a smooth curve is drawn between the points to construct the spectrum.
Figure 30

$\text{TMPD} \rightarrow \text{TMPD}^+ + e^-$
The amount of IR compensation which is applied to the electrochemical cell was found to be a critical factor in obtaining reproducible results. Inadequate compensation resulted in an absorbance-time transient which rose slowly and did not level off to a time-independent value. Overcompensation resulted in an absorbance-time transient which was sharply peaked at short times, dipped down and then continued to rise, all during a time of only one second after the initiation of electrolysis. In order to determine the proper amount of IR compensation required, the current follower was "tuned" until a level absorbance-time transient was obtained. No further adjustments in the amount of IR compensation were required until fresh solution was placed in the electrochemical cell, at which point the above procedure was repeated.

The spectrum obtained is in good agreement with a published spectrum\(^1\) which was obtained in a conventional spectrophotometer. The value of the molar absorptivity at each wavelength agrees with the expected value to within 8%, with the exception of the value at 630 nm, which differs by 19%. (This probably due to the fact that 630 nm is at the upper extreme of the range of this dye laser when it is pumped in the manner described in Chapter III). It is important to realize that the spectrum obtained via diffraction has the advantage of simultaneous generation of chromophore and measurement of absorbance.

The spectrum shown in Figure 30 is also important because no anomalous effects are seen near the wavelength of maximum absorbance ($\lambda_{\text{max}}$). The molar absorptivity of the chromophore describes the attenuation of the light beam as it propagates through a medium of refractive index $n_s$. The refractive index of an absorbing medium can be described as a
complex number, where the molar absorptivity is related to the imaginary component \( n_1 \), and the real component \( n_r \) is a measure of how much the light is bent as it passes through the medium. In a homogeneous medium, the refractive index is a constant, and there is no net effect on the direction of the diffracted light, as explained in Chapter III. However, the initiation of electrolysis results in a concentration gradient extending from the electrode into the bulk solution, and the refractive index, being a function of the amount of each species present in the medium, is no longer constant but also varies with distance from the electrode. If the refractive index gradient which is generated is sufficiently large, the distribution of intensity in the diffraction pattern will be quite different before and after initiation of electrolysis, and absorbance measurements will reflect this influence.

In general, the real component of the refractive index is relatively small and increases with decreasing wavelength in a gradual manner. In this case, the difference in the refractive index before and after initiation of electrolysis would be small and have a negligible effect on the measurement of absorbance. However, in the region on either side of \( \lambda_{\text{max}} \), \( n_r \) takes on maximum and minimum values, and any refractive index effect would be expected to be most evident in this region of the spectrum, probably resulting in a discontinuity at the absorbance maximum.

It can clearly be seen from Figure 30 that the spectrum obtained by monitoring diffracted light is well behaved in the region of \( \lambda_{\text{max}} \), as evidenced by the smooth curve in this region. In addition, the values for the molar absorptivity near \( \lambda_{\text{max}} \) are in good agreement with those obtained by conventional means. These results indicate that, at least
when the concentration is not greater than millimolar, the absorbance measured on the time-independent portion of the absorbance-time transient is not affected by the presence of any refractive index gradient, even in regions near the absorbance maximum. This is not surprising in view of the fact that the absorbance is equal to that which would be predicted from Beer's law, indicating that the concentration of chromophore in this region is equal to the bulk concentration of precursor; therefore, the concentration of precursor is essentially zero. This alone requires that the concentration of chromophore be nearly homogeneous in this portion of solution because the laws of mass balance must be obeyed. In addition, the fact that the absorbance becomes independent of time indicates that the solution being sampled is essentially homogeneous since diffusion would result from the presence of any concentration gradient, and this would be reflected in further changes in absorbance.

However, absorbance measured directly after initiation of electrolysis, on the rising portion of the absorbance-time transient, may be affected by the refractive index gradient. If refractive index effects are negligible, the rise time of the curve would be expected to be the same regardless of the wavelength of the incident beam and the relative magnitude of the absorbance at a particular time would increase as the wavelength approached $\lambda_{\text{max}}$ from either side. Therefore, the shape of a plot of absorbance vs. wavelength should have the same shape as the spectrum shown in Figure 30, although the absorbance would increase with time.

The absorbance obtained at times corresponding to points on the rising portion of the absorbance-time transient (0.1, 0.3, and 1.0 seconds) is plotted as a function of wavelength in Figure 31. The
Figure 31. Absorbance as a function of wavelength for the electrolysis of 0.950-mM solution of TMPD. The time at which the absorbance measurement is made is indicated for each curve. The electrode is a 0.027-cm electrode placed in a capillary cell.
Figure 31
distortion which can be seen at 612 nm, especially at 0.3 seconds, appears to indicate that refractive index does have some effect on absorbance measurements made at short times. These results, however, are not conclusive due to other factors which complicate the analysis of TMPD. As mentioned previously, the absorbance-time transient was very dependent upon the amount of IR compensation used in the electrochemical cell. This is probably due to the fact that TMPD undergoes two successive oxidation steps, the first resulting in formation of the cation radical \( E_p = 0.138 \text{ V} \), and the second resulting in formation of the dication \( E_p = 0.715 \text{ V} \). With the use of IR compensation, at relatively short times, the real potential applied at the working electrode may be substantially positive of the applied potential (0.55 V) and into the potential range where the second oxidation will occur. The presence of the dication in the diffusion layer would undoubtedly affect the measurement of absorbance. Also, certain characteristics of the absorbance-time transient appear to indicate that TMPD may adsorb onto the surface of the platinum electrode. A negative dip in absorbance was often observed at short times (less than 0.20 seconds) after which the absorbance would begin to rise as expected. And, as mentioned above, a large fluctuation of the absorbance with time was observed when the level of IR compensation was too high. These features are similar to those seen in the case of chlorpromazine, a compound which is known to adsorb under certain conditions, and which will be discussed in detail in a later section. If, however, neutral TMPD does adsorb onto the surface and is released as the cation radical after the potential step, the concentration of chromophore would be much larger than expected near the surface, and the
resulting refractive index gradient could be of sufficient magnitude to have an effect on absorbance measurements, especially in regions near the absorbance maximum.

It is clear from Figure 30 that, although absorbance measurements at short times do not yield expected results, perhaps due to refractive index effects, at sufficiently long times (2 seconds or longer), the absorbance measured as a function of wavelength compares very well with published spectra. This indicates that through use of Beer's law, absorbance measurements made at times corresponding to the level portion of the absorbance-time transient can be used to construct a spectrum. This would allow an electrogenerated species to be produced and analyzed as a function of wavelength in one experimental step. Also, the diffractive technique would be useful in obtaining the spectra of rather short-lived species, since the absorbance measurement can be made within seconds after the product is generated.

Absorbance measurements made at very short times after initiation of electrolysis would be necessary in order to obtain spectra of an extremely reactive electrogenerated species. The results obtained using TMPD do indicate, however, that refractive index effects may present a problem at short times, but there is reason to believe that this may be peculiar to the TMPD test system. Although not attempted in the present work, the short time behavior would be best studied in a cell designed to minimize the amount of IR compensation required and with a well-behaved electrochemical test system.
Double Potential Step Experiments

In all the diffraction experiments discussed in previous sections, the potential applied to the working electrode has simply been sufficient to convert precursor to chromophore at a diffusion controlled rate, and the appearance of the chromophore has been observed by monitoring absorbance as a function of time. The application of a double potential step should allow both the appearance and disappearance of the chromophore to be observed.

Results of diffraction experiments performed using a double potential step are shown in Figures 32 and 33. The working electrode was a 0.027-cm platinum edge placed in a capillary cell. The electroactive species present in solution was ferrocyanide at a concentration of 13.9 mM. The wavelength of the incident beam was 442 nm at which ferricyanide, the absorbing product of the oxidation, has a molar absorptivity of 554 M\(^{-1}\) cm\(^{-1}\), and the observation angle was 1.02°. The initial potential step was from 0.0 to 0.55 V vs. SCE, sufficient to oxidize the ferrocyanide to ferricyanide, and the second step was back to 0.0 V, which will result in reconversion of the product to ferrocyanide.

For the results shown in Figure 32, the total time of the experiment was 10 seconds, and the time at which the potential was switched from 0.55 back to 0.0 V was 5 seconds. The absorbance exhibits the expected behavior as a function of time, obtaining a time independent value in less than 0.5 seconds and returning to zero in the same amount of time when the potential is returned to 0.0 V. In fact, the second half of the absorbance-time curve shown in Figure 32 is virtually identical to the
Figure 32. Absorbance as a function of time for a double potential step. The first step is from 0.0 to 0.55 V vs. SCE and occurs at time equal to 0.0 seconds. The second step is back to 0.0 V and occurs at 5.0 seconds. The bulk concentration of ferrocyanide is 13.9 mM, and the electrode is a 0.027-cm platinum edge in a capillary cell. The wavelength of incident light is 442 nm, and the observation angle is 1.02°.
Figure 32
Figure 33. Absorbance as a function of time for a double potential step. The first step is from 0.0 to 0.55 V vs. SCE and occurs at time equal to 0.0 seconds. The second step is back to 0.0 V and occurs at 0.10 seconds. Other experimental conditions are the same as for Figure 31.
Figure 33

Absorbance vs. Time

Ferrocyanide
Double Potential Step
first, except that it is inverted on the absorbance axis. An experiment such as this can be imagined as analogous to one in which an extremely small-volume cell, equal in length to that of the electrode, is placed up against the surface and is alternately filled with chromophore and then dumped as a function of the applied potential.

When the switching time is shorter than the time required to obtain a time-independent absorbance value, an absorbance peak such as that shown in Figure 33 is observed. In this example, the absorbance was monitored for a total time of 3 seconds, but the second potential step was applied only 0.1 second after the initial step. It should be noted that the absorbance as a function of time after the second potential step, although inverted, again has the appearance of a typical absorbance-time transient.

Double potential step experiments of this type serve to emphasize that at times corresponding to the level portion of the absorbance-time transient, the attenuation of light in the diffraction pattern is due to the presence of an essentially homogeneous concentration of chromophore in the solution very near the electrode surface. The results of such experiments provide a graphic illustration of the analogy which can be made to a conventional spectrophotometric experiment where absorbance is measured using a cell filled with a homogeneous concentration of chromophore. Since a level value of absorbance is reached in at most 0.5 seconds, when the width of the diffusion layer (equal to $\sqrt{D\tau}$) is equal to 0.0018 cm, the dimensions of the corresponding spectrophotometer cell would be $0.0018 \times 0.027$ cm (the length of the electrode along the optical axis). Because of the fast time response, a diffraction experiment has
the additional advantage in that the cell can be quickly filled and dumped simply by changing the potential.

Double potential step experiments of this type may also prove to be useful as a means of determining the degree of reversibility of an electrochemical reaction. For example, in the case of a "quasi-reversible" electrochemical reaction, where the anodic and cathodic peak potentials are widely separated, the absorbance-time transient would vary as a function of the size of both the initial and second potential steps, and the rise time could provide information about the rate at which the electron transfer occurs. This relationship may be quite complex, and this discussion is presented here only to point out the potential usefulness of double step experiments on less well-behaved electrochemical systems.

Absorption

It has already been shown that the intensity distribution in the diffraction pattern is dependent on the concentration vs. distance profile of an electrogenerated chromophore in solution. In the simplest case, the electroactive species is assumed to undergo electrolysis at a diffusion controlled rate, and therefore the concentration as a function of distance from the electrode can be determined using Fick's laws. However, in the case of an electroactive species that adsorbs onto the surface of the working electrode, the concentration vs. distance profile of the chromophore would be quite different, since upon initiation of electrolysis, the adsorbed neutral would be converted to product and released as a pulse of material into the solution directly adjacent to the electrode surface. This would create a regionally high concentration of chromophore, since before a
significant amount of diffusion can occur, the concentration of chromophore near the electrode surface may be greater than the bulk concentration of precursor.

It might be expected that increased sensitivity could be obtained in this case since adsorption can be considered to be equivalent to a pre-concentration step in the analysis, and in fact, it has been noted that in the case of TBA at micromolar concentrations, absorbance measured at short times was considerably larger than predicted. However, the release of a large amount of material into the solution upon initiation of electrosis may also generate a large refractive index gradient since the density near the surface will be greater than that of the bulk solution.

Chlorpromazine (CPZ) is well-suited for use in investigating the effect of adsorption since the neutral species adsorbs onto the surface of both platinum and carbon electrodes in solutions of 0.1 M HCl but adsorbs to a greatly reduced degree in HCl solutions to which 50% by volume of methanol has been added, while other characteristics of the electrochemical system remain approximately the same. In Figure 34 are shown the results obtained in diffraction experiments with CPZ as the electroactive species at a 0.53-cm carbon electrode. The wavelength of incident light was 442 nm, where the cation radical (CPZ+) has a molar absorptivity of approximately 2200 M⁻¹ cm⁻¹, and ten runs were time averaged for each plot shown. The observation angle was 0.58°.

In the top plot in Figure 33 is shown the absorbance-time transient observed for a solution where the bulk concentration of CPZ is 0.315 mM, and the solvent is 0.1 M HCl. The level absorbance value obtained in less than 1 second is 36% higher than the value of 0.37 a.u. predicted
Figure 34. Absorbance as a function of time for electrolysis of CPZ at a 0.53-cm carbon electrode placed directly into the bulk solution. The wavelength of the incident beam is 442 nm, and the observation angle is 0.58°. Top plot: the bulk concentration of CPZ is equal to 0.315 mM, and the solvent is 0.1 M HCl. Bottom plot: the bulk concentration of CPZ is equal to 0.377 mM, and the solvent is a 50:50 mixture of 0.1 M HCl and methanol.
Figure 34

ABSORBANCE vs TIME (s) for HCl and HCl/Methanol solutions.
from Beer's law, and the absorbance at short times shows a pronounced dip in the negative direction. The addition of 50% methanol to the solvent results in a well-behaved absorbance-time transient such as that shown in the bottom plot in Figure 34 for the same electrode where the bulk concentration of CPZ was 0.377 mM. The time independent absorbance value (0.41 a.u.) is within 6.8% of the absorbance which would be predicted by a Beer's law calculation (0.44 a.u.). In addition, there is no sign of the negative dip in absorbance which is observed at short times in the absence of methanol.

It is clear from comparison of these results that adsorption of the neutral CPZ has an effect on the intensity observed in the diffraction pattern after initiation of electrolysis. When the problem of adsorption is alleviated by addition of 50% methanol to the solvent, the absorbance-time transient becomes similar in appearance to that routinely observed for a well-behaved electrochemical system.

In Figure 35 are shown the absorbance-time transients observed for a 0.027-cm platinum electrode with CPZ present as the electroactive species. For the results shown in the top plot in Figure 35, the solvent was 0.1 M HCl with a bulk concentration of CPZ equal to 1.52 mM. In the bottom plot in Figure 35, the solvent was a 50:50 mixture of 0.1 M HCl and methanol, and the bulk concentration of CPZ was 1.98 mM. For both plots, the observation angle was 0.58°. Comparison of the two figures shows that results obtained with and without methanol are quite similar. Absorbance measured on the level portion of both the top and bottom curves is in good agreement with the predicted absorbance value of 0.093 and 0.12 a.u., respectively.
Figure 35. Absorbance as a function of time for electrolysis of CPZ at a 0.027-cm platinum electrode placed in a capillary cell. The wavelength of the incident beam is 442 nm, and the observation angle is 0.58°. Top plot: the bulk concentration of CPZ is 1.52 mM, and the solvent is 0.1 M HCl. Bottom plot: the bulk concentration of CPZ is 1.98 mM, and the solvent is a 50:50 mixture of 0.1 M HCl and methanol.
Figure 35

HCl / Methanol

TIME (s)
Similar experiments indicated that when the bulk concentration of CPZ was less than 5 mM, the absorbance-time transients observed in 0.1 M HCl using a 0.027-cm electrode were nearly identical to those observed in solutions where 50% by volume of methanol had been added. [Longer electrodes (see Figure 34) are affected by adsorption at smaller bulk concentrations of CPZ.] At approximately 6 mM, although no unusual features were noticed in the absorbance-time transient, the absorbance observed in a 0.1 M HCl solution was 26% higher than expected. When the concentration of CPZ was increased to 8.7 mM, severe distortions are observed in the absorbance-time transient when the solvent is 0.1 M HCl and the effect became more pronounced with increasing concentration. This can be seen in Figure 36 where the concentration of CPZ is equal to 8.76 for the top plot and 9.20 mM for the bottom plot. These effects are reproducible from run to run, and similar results are obtained at all observation angles. However, the result obtained for a 9.43 mM solution of CPZ in a mixed HCl/methanol solvent is normal in appearance, as can be seen in Figure 37, although the time independent absorbance is 14.3% lower than the expected value.

These results indicate that adsorption of neutral CPZ onto the surface of both carbon and platinum electrodes can greatly affect the absorbance of diffracted light. The appearance of the absorbance-time transients at relatively high concentrations of CPZ are probably due to a combination of two factors. First, the presence of adsorbed material on the working electrode makes available at the surface a larger than expected amount of CPZ to be converted to chromophore. This would be expected to result in enhanced absorbance and, in fact, at moderately high
Figure 36. Absorbance as a function of time for electrolysis of CPZ at a 0.027-cm platinum electrode placed in a capillary cell. The solvent is 0.1 M HCl. The wavelength of the incident beam is 442 nm, and the observation angle is 0.58°. Top plot: the bulk concentration of CPZ is equal to 8.76 mM. Bottom plot: the bulk concentration of CPZ is equal to 9.20 mM.
Figure 36

876 mM CPZ HCl

920 mM CPZ HCl

Figure 36
Figure 37. Absorbance as a function of time for electrolysis of CPZ at a 0.027-cm platinum electrode placed in a capillary cell. The solvent is a 50:50 mixture of 0.1 M HCl and methanol. The bulk concentration of CPZ is equal to 9.43 mM. The wavelength of the incident beam is 442 nm, and the observation angle is 0.58°.
Figure 37

943 mM CPZ
HCl/ Methanol
concentrations of CPZ an unexpectedly large absorbance is observed for electrolysis at both carbon and platinum electrodes. Second, electrolysis will result in the release of the adsorbed material as a pulse of chromophore into the solution directly adjacent to the working electrode, creating a local concentration that may be high enough to change the refractive index by a nonnegligible amount. The experimental results are consistent with this explanation since, as is expected in the case of a refractive index gradient, more distortion of the absorbance-time transient is observed as the concentration of CPZ is increased.

The contribution of refractive index effects can be verified by monitoring the intensity of diffracted light at a frequency where the cation radical does not absorb. While it is true that, as described in a previous section, the refractive index varies gradually with wavelength, results obtained at wavelengths sufficiently far from the absorbance maximum of CPZ (525 nm) should be similar in appearance.

In the top plot in Figure 38, absorbance as a function of time observed for a 9.1 mM solution of CPZ in 0.1 M HCl is shown where the wavelength of the incident beam is now equal to 632.8 nm. In the bottom plot in Figure 38, the result is shown for identical conditions, except that the solvent is a 50:50 mixture of HCl and methanol. Since no absorbance due to the cation radical or any other species in solution is expected at 632.8 nm, the observed "absorbance" can be attributed to refractive index effects. It can be seen by comparison of the two plots in Figure 38 that the addition of 50% methanol to the solvent greatly decreases the effect. The negative absorbance which can be observed upon close
Figure 38. Absorbance as a function of time for electrolysis of CPZ at a 0.027-cm platinum electrode placed in a capillary cell. The wavelength of the incident beam is 632.8 nm, and the observation angle is 0.58°. Top plot: the bulk concentration of CPZ is 9.10 mM, and the solvent is 0.1 M HCl. Bottom plot: the bulk concentration of CPZ is 9.08 mM, and the solvent is a 50:50 mixture of 0.1 M HCl and methanol.
Figure 38

Absorbance vs. Time for HCl and HCl/Methanol solutions at 632.8 nm.
examination of the bottom graph in Figure 38 indicates that some adsorption of CPZ may occur even in the presence of methanol.

The negative values which are often obtained for absorbance in the presence of an adsorbing species can be explained in the following manner. As explained in Chapter III, in a homogeneous medium there is no net effect on the distribution of light in the diffraction pattern due to the refractive index of the solution. However, if a large refractive index gradient is created by electrolysis, there can be a differential phase shift within the beam, and the intensity distribution in the diffraction pattern can be shifted. Under these conditions, the intensity at a particular point in the diffraction pattern could increase after initiation of electrolysis, and the absorbance, defined as the log of the initial intensity relative to the final intensity, would then be a negative number.

The results discussed above for chlorpromazine indicate that, at least at wavelengths removed from $\lambda_{\text{max}}$, the refractive index gradient has no noticeable effect on the measurement of absorbance when the concentration of CPZ is relatively small (less than 5 mM), even when adsorption of the neutral occurs. In view of the fact that the refractive index gradient in the case of such an adsorbing species would be expected to be much greater than any generated by the smaller concentration gradient resulting from diffusion controlled electrolysis, it seems reasonable to conclude that the effect of the refractive index in most cases will be negligible, especially at concentrations at or below the millimolar level. However, it is still possible that when the wavelength of the incident beam approaches $\lambda_{\text{max}}$, effects due to the refractive index gradient may become nonnegligible at short times.
Observation of an Electrogene-rated Reaction Intermediate

It has been shown that diffraction can be used to detect the presence of a stable electrogene-rated chromophore in the diffusion layer. Because of the high sensitivity provided by the diffractive technique, it should also be possible to monitor a species which is generated electrochemically and then consumed in a follow-up homogeneous chemical reaction.

Chlorpromazine (CPZ) is a convenient species to examine in this respect since the cation radical (CPZ$^{+}$) produced by electrolysis is relatively stable in acidic solutions, but becomes quite reactive in the presence of certain nucleophilic buffers. The mechanism of the reaction with nucleophile B$^{-}$ is as follows:

\[
\begin{align*}
\text{CPZ}^{+} + \text{B}^{-} & \rightleftharpoons \text{(CPZB)$'} \quad (26) \\
\text{(CPZB)$'} + \text{CPZ}^{+} & \rightleftharpoons \text{(CPZB)$}^{+} + \text{CPZ} \quad (27) \\
\text{H}_2\text{O} + \text{(CPZB)$}^{+} & \longrightarrow \text{CPZO} + \text{HB} + \text{H}^{+} \quad (28)
\end{align*}
\]

Previous studies$^{44-46}$ have shown that reaction 27 is the rate-determining step for phosphate and citrate buffers and that the overall reaction is first order in buffer. Therefore, increasing the concentration of buffer is expected to increase the rate of reaction. Also, the rate of the reaction is pH dependent since deprotonation of the buffer increases the concentration of free B$^{-}$ available for reaction and results in an increased rate. For polyprotic acids, the rate of reaction at a certain pH is dependent upon the identity of the nucleophilic species present. The pH dependence can be analyzed through use of an observed rate constant,
which is determined by the sum of individual rate constants for each of the anionic species present. For example, for triprotic acid H$_3$B,

$$k_{obs} = \alpha_1 k_{H_2B^-} + \alpha_2 k_{HB^-} + \alpha_3 k_{B^-}$$  \hspace{1cm} (29)$$

where $\alpha$ is the fractional concentration of the anionic species, and $k$ is the individual rate constant for nucleophilic attack on CPZ$^+$ by that species without deprotonation.$^{40}$ The value of the observed rate constant can be used to compare relative rates of reaction for a nucleophilic buffer as a function of pH.

In order to determine if the results of diffraction experiments could be used to indicate the rate of reaction, solutions of CPZ in 0.10 and 0.20 M citrate solutions were examined using the technique. The pH of both solutions was equal to 5.0, and both solutions contained 50% by volume of methanol to reduce the amount of adsorption of CPZ onto the surface of the working electrode. Since the rate of the reaction is first order in buffer, the rate in 0.20 M citrate should be twice that in 0.10 M, if all other factors are held constant.

The reaction is dependent on pH as well as buffer concentration, so solutions of CPZ in phosphate buffers of pH equal to 4.13, 6.33, and 7.08 were also examined. The concentration of phosphate was 0.025 M, and solutions were again 50% by volume in methanol. The working electrode in all cases was a 0.027-cm platinum edge, positioned in a capillary cell. The wavelength of the incident beam was 442 nm, where the cation radical has a molar absorptivity equal to approximately 2200 M$^{-1}$ cm$^{-1}$. Results can be compared using normalized absorbance ($A_n$), defined as
the ratio of the observed absorbance to that expected* in the absence of nucleophile, adjusted for relative concentrations.

The normalized absorbance is plotted as a function of time for pH 5 buffer solutions of 0.10 and 0.20 M citrate in Figure 39. The small value of the normalized absorbance indicates that the rate of reaction is fast. Absorbance is dependent on the concentration of CPZ⁺⁺ remaining in the diffusion layer and as the rate of reaction increases, A₀ at a particular time after initiation of electrolysis will decrease. It can be seen in Figure 39 that A₀ in the case of the 0.20 M citrate solution is just about half that of the 0.10 M citrate at times longer than 1.0 second, which is consistent with the fact that the rate of disappearance of CPZ⁺⁺ in 0.20 M citrate should be twice that in 0.10 M.

The results shown in Figure 39 were obtained at an observation angle in the diffraction pattern of 1.16°. Some angular variation in the absorbance response was observed, with absorbance at larger angles being somewhat higher at short times and decaying with time faster than at small angles.

The normalized absorbance obtained for CPZ⁺⁺ in the presence of phosphate is plotted as a function of time after initiation of electrolysis in Figure 40. The pH of each solution is as indicated in the figure. It can clearly be seen from the curves shown in Figure 40 that, as the rate of reaction increases with increasing pH, the normalized absorbance decreases. For electrolysis of CPZ in phosphate buffer solutions, the same type of angular variation of absorbance was observed as was the case with citrate.

*This value was determined from the experimental absorbance obtained for electrolysis in 0.1 M HCl/methanol.
Figure 39. Normalized absorbance ($A_n$) as a function of time for electrolysis of CPZ in buffer solutions of 0.10 and 0.20 M citrate, adjusted to pH 5.0. The wavelength of the incident beam is 442 nm, and the observation angle is 1.16°. The electrode is a 0.027-cm platinum edge placed in a capillary cell.
Figure 39

$A_n$ vs. TIME (s)

Citrate buffer

0.1 M

0.2 M
Figure 40. Normalized absorbance ($A_n$) as a function of time for electrolysis of CPZ in 0.025 phosphate buffer solutions of the indicated pH. The wavelength of the incident beam is 442 nm, and the observation angle is 1.16°. The electrode is a 0.027-cm platinum edge placed in a capillary cell.
Figure 40

PHOSPHATE buffer

pH 5.13

pH 6.33

pH 7.08

$A_n$

TIME (s)
The results shown in Figures 39 and 40 illustrate that an electro-generated reaction intermediate can be observed using diffraction and, in addition, that the normalized absorbance can be used to provide an indication of relative rates of reaction. The exact relationship between the absorbance measured at a particular time and the concentration of chromophore has not yet been determined. Since the results showed some variation with observation angle, even at times as long as 5 seconds, the concentration of CPZ⁺⁺ in the sampled region is not expected to be homogeneous; therefore, the relationship between absorbance and concentration is probably not a simple one as was observed to be the case for a stable electrogenerated chromophore. However, the absorbance as a function of time could be calculated for various values of \( k_{\text{obs}} \) through the use of digital simulation techniques and could be used to provide more concrete information about the rate of the reaction.

It is worth emphasizing that diffraction can be used to monitor an electrogenerated species even when it is being consumed in a follow-up reaction that proceeds at a fast rate. For example, the half life of CPZ⁺⁺ in pH 7 phosphate buffer is only about 100 milliseconds. Due to the fast rate of nucleophilic attack by citrate anion, buffer solutions of 0.10 and 0.20 M citrate have not yet been examined by conventional spectroelectrochemical techniques, such as glancing incidence reflection, but the disappearance of the radical cation can be easily monitored using diffraction. In view of the results discussed above for both citrate and phosphate buffer solutions, it appears that diffraction may prove to be a very useful tool in the observation of reaction intermediates. As a result of the increased pathlength for absorbance provided by this technique,
the concentration of the chromophore does not need to be large. This would be advantageous in the examination of second-order processes where, for convenience in the analysis, the rate of reaction could be slowed down simply by decreasing the concentration of the species of interest.

Observation of the Product of a Homogeneous Reaction

It has been shown that diffracted light will be attenuated due to the presence of chromophore in the diffusion layer. Although in all the cases discussed so far the chromophore has been the product of an electrochemical reaction, it should also be possible to detect the presence of a species which has been generated as the product of a homogeneous chemical reaction.

Adrenaline can be oxidized in a reversible two-electron step to form adrenalinequinone, which is stable in 1 M H₂SO₄, but in solutions of pH greater than about 2.5, undergoes subsequent chemical reaction with the final products being adrenochrome and a stoichiometric amount of the initial species, adrenaline. The reaction sequence is shown in Figure 41. Adrenalinequinone loses a proton and cyclizes to form leucoadrenochrome (reaction 3) which is more easily oxidized than adrenaline itself, so it is oxidized by adrenalinequinone to form adrenochrome (reaction 4). The deprotonation is the rate-determining step.

Since adrenochrome is the product of homogeneous electron transfer from adrenalinequinone to leucoadrenochrome, it should be possible to electrochemically reduce the adrenochrome back to the leuco form. As expected, the cyclic voltammogram of adrenaline in pH 3 Mac buffer⁴¹
Figure 41. Mechanism for conversion of adrenaline to adrenochrome
shows a fairly reversible wave at approximately -0.20 V vs. SCE for the adrenochrome/leucoadrenochrome couple.

In order to both observe the formation of the adrenochrome and examine its electrochemical behavior, a double potential step experiment was carried out. The initial step was to 1.0 V vs. SCE, sufficient to oxidize adrenaline, and the second step was to -0.30 V, which should result in reduction of adrenochrome to the colorless leuco form. The absorbance as a function of time is shown in Figure 42. The total time for the experiment was 20 seconds, and the potential was switched from 1.0 to -0.30 V at 5 seconds. It can be seen that the absorbance increases with time as expected for the formation of adrenochrome, but when the potential is stepped to -0.30 V, the absorbance decreases rapidly and then begins to level off at about 12 seconds after the second potential step. In fact, the absorbance-time curve for the disappearance of adrenochrome is similar to that obtained in a double potential step experiment performed using ferrocyanide (Figure 32). The rising portion of the absorbance-time transients observed at angles from 0.44° to 1.16° were practically superimposable, indicating that the concentration gradient of adrenochrome is very small. This is not surprising since adrenochrome is the product of a homogeneous chemical reaction, and the chromophore in this case would be expected to be distributed more evenly throughout the diffusion layer.

These results show that the absorbing product of a homogeneous chemical reaction can be observed by monitoring the absorbance of diffracted light. The relatively flat concentration vs. distance profile produced by the specific reaction which was investigated results in little variation of the absorbance-time transient with angle. Reactions in which
Figure 42. Absorbance as a function of time for a double potential step.

The bulk concentration of adrenaline is 6.22 mM, and the solvent is pH 5.0 Mac buffer. The first potential step is from 0.0 to 1.0 V vs. SCE and occurs at time equal to 0.0 seconds. The second step is to -0.30 V and occurs at 5.0 seconds. The electrode is a 0.027-cm platinum edge in a capillary cell. The wavelength of incident light is 442 nm, and the observation angle is 0.73°.
Figure 42
the electrochemical step is rate determining would probably result in a more complicated angular dependence. Application of a double potential step allows the investigation of the electrochemical behavior of the chromophore.
CHAPTER V

CONCLUSION

The process of diffraction can be employed as a sensitive probe of the diffusion layer. Using the present experimental configuration, absorbance due to the presence of a chromophore in solution can be conveniently monitored in the diffraction pattern as a function of time and exhibits several features which are of analytical utility.

The most useful feature of the diffractive technique is the simple relationship between the time independent value of absorbance and the concentration of the electroactive species in solution. Absorbance is linearly related to concentration by the electrode length and the extinction coefficient of the chromophore, two parameters which are easily measured experimentally. In contrast to many spectroelectrochemical techniques, it is not necessary to know the diffusion coefficient of the chromophore.

A variety of electrochemical systems, both organic and aqueous, can be examined using diffraction, even when the product is a weak absorber like ferricyanide. Also, absorbance as a function of concentration is linear over a range of concentrations of TBA from 0.011 to 3.3 mM, a dynamic range of 300. At times less than about 0.5 seconds after initiation of electrolysis, good sensitivity is shown over this concentration range, even though a plot of absorbance vs. concentration is not linear.
Since the optical pathlength for absorbance is determined by the length of the electrode along the optical axis, sensitivity can be enhanced by simply increasing this parameter. Absorbance measurements made using longer electrodes are more susceptible to interferences from solution convection and stray light but are useful when the concentration of electroactive species is small. Micromolar concentrations of TAA can be determined with good accuracy using a 1.12-cm electrode. For electrodes of all lengths, the lower limit on the dynamic range in acetonitrile/TEAP solutions appears to be determined by background absorbance, which can become quite large with the use of longer electrodes. Fortunately, background does not appear to present a problem in aqueous solutions.

The relationship between the time independent absorbance value and Beer's law also allows the molar absorptivity of a chromophore to be determined as a function of wavelength. Using a variable wavelength source, the spectrum of an electrogenerated chromophore can be obtained. Since the measurement can be made within seconds, fairly short-lived species can be examined. Any change in the refractive index of the solution due to the initiation of electrolysis does not appear to affect measurements made on the time independent portion of the absorbance-time transient, even near the absorbance maximum of the chromophore, but does seem to interfere at short times in the analysis of TMPD. This is unfortunate because measurements at short times would be necessary to obtain the spectrum of a very reactive species. However, due to other complicating factors in the analysis of TMPD, reliable conclusions cannot be drawn from the present work, and further study is warranted. At wavelengths removed from $\lambda_{\text{max}}$, refractive index changes do not appear
to present a problem except in the case of a relatively high concentration of an adsorbing species.

Another analytically useful feature of the diffractive technique is the fast time response for absorbance when the measurement is made at large angles in the diffraction pattern. Using a 0.027-cm electrode, an absorbance of more than 1.2 a.u. can be obtained for a 2.6 mM solution of TBA in less than 100 milliseconds. For the same experimental conditions, a spectroelectrochemical experiment using an OTE would yield an absorbance of only 0.056 a.u. The increased absorbance obtained in a diffraction experiment is not surprising due to the increased pathlength for absorbance over that of a typical transmission experiment.

Perhaps the two techniques can be more easily compared by comparing the optical pathlength provided by each. The absorbance in a transmission experiment using an OTE is given in Equation 1. In analogy to Beer's law, the effective pathlength, $L$, for absorbance will be

$$L = \frac{2}{\pi^2} t^{\frac{3}{2}} D^{\frac{1}{2}}$$

(30)

where $D$ is the diffusion coefficient of the precursor, and $t$ is the time after initiation of electrolysis. For a chromophore with a diffusion coefficient of $1.6 \times 10^{-5}$ cm$^2$/sec, it would take 36 seconds to obtain the same pathlength provided in a diffraction experiment by a 0.027-cm electrode.

By contrast, using diffracted light monitored at relatively large observation angles, absorbance equal to that calculated by Beer's law can be obtained in less than 1 second.

Diffraction shows promise of becoming a versatile method of analysis. Double potential step experiments allow the appearance and the
disappearance of a species to be observed as a function of potential. Both an electrogenerated reaction intermediate and the product of a homogeneous chemical reaction can be easily observed. In addition, absorbance monitored as a function of time is dependent upon the rate of reaction. The use of digital simulation techniques to predict the concentration vs. distance profile as a function of rate may allow the rate constants to be determined. Since the concentration vs. distance profile of the chromophore depends on the mechanism of the reaction, it may also be possible to distinguish between reaction mechanisms by the behavior of the absorbance-time transient. Since diffraction is sensitive to spatial features in the diffusion layer, it is potentially more useful in this respect than typical spectroelectrochemical techniques which are basically integrative in nature, i.e., they measure absorbance over the entire width of the diffusion layer.

In fact, the most exciting feature of the diffractive technique is this ability to spatially resolve the diffusion layer. Thus far, theoretical predictions have been made by predicting the concentration vs. distance profile of the chromophore and Fourier transforming this to produce the expected intensity distribution in the diffraction pattern. This can be referred to as the "forward" transform. By repeating this process for a large number of times after initiation of electrolysis, theoretical absorbance-time transients can be constructed for observation angles within the diffraction pattern and compared to those obtained experimentally. Good agreement between theory and experiment is obtained for a range of angles using a 0.027-cm electrode. Thinner electrodes and improved design of the electrochemical cell in order to minimize the
amount of IR compensation required may result in even better agree-
ment.

In theory, the diffraction pattern obtained experimentally could be
inverted by Fourier transformation to directly produce the concentration
vs. distance profile. The degree of success obtained with the forward
transform indicates that the inversion may eventually be possible with the
proper choice of electrode geometry. This would allow direct observation
of the concentration vs. distance profile of a chromophore in solution.
Reaction mechanisms as well as reaction rates could then easily be deter-
mined without the necessity of using digital simulation. In addition to
mechanistic studies, the concentration vs. distance profile produced by
modes of mass transport other than diffusion could be examined, and
fundamental questions about these processes could be addressed.
APPENDIX A

USE OF A FAST FOURIER TRANSFORM ROUTINE
Almost any function $f(x')$ can be represented as an expansion of a suitable set of basis functions, $\psi(x')$, in the following manner:

\[
f(x') = C_1 \psi_1(x') + C_2 \psi_2(x') + \ldots = \sum_{n=-\infty}^{\infty} C_n \psi_n(x')
\]

where $C_n$ is a complex valued coefficient that properly weights each term in the summation. Many functions $\psi(x')$ can be used as long as they satisfy certain requirements of completeness and orthogonality. The set of complex exponentials,

\[
\psi(x') = \exp(-2\pi i n \nu_0 x')
\]

satisfies these conditions and also is an extremely useful set of equations for describing optical systems.\textsuperscript{47} The coefficients in the series are then found to be equal to

\[
C_n = \frac{1}{T} \int_{0}^{T} f(x') \exp(-2\pi i n \nu_0 x') dx'
\]

where $T = \nu_0^{-1}$, the period of the function. An expansion of this type is called a Fourier series and can be used to represent many periodic functions. Note that since $n$ has only integer values in the equations above, the series representation of the function $f(x')$ will be a set of discrete values.

In order to use a Fourier series to represent a nonperiodic function, the same coefficients are used as though the function were periodic. However, the summation is not valid everywhere but only over the
interval \( x - L \leq x \leq x + L \), where \( 2L \) is the length of the nonperiodic function. Also, the period \( T \) of the periodic function must be \( > 2L \).

A Fourier transform can be used to represent a nonperiodic function everywhere in space. If \( f(x') \) is again the function in question, then,

\[
f(x') = \int_{-\infty}^{\infty} F(x) \exp (2\pi i v x') dx \tag{34}
\]

and the transform of the function \( f(x') \) is

\[
F(x) = \int_{-\infty}^{\infty} f(x') \exp (-2\pi i v x') dx' \tag{35}
\]

\( F(x) \) weights each term in the integral expansion, just as \( C_n \) does in the Fourier series, but the integer \( n \) has been replaced with the variable \( v \) which now can take on any real value.

The Fourier transform of the amplitude function \( [\phi(x')] \) in Equation 16, however, must be calculated by numerical means because the attenuation due to the presence of chromophore does not lend itself to an explicit formula but must be calculated numerically as a function of distance \( (x') \) and time. A digital computer is used to sample the function \( \phi(x') \) at equally spaced intervals, perform complex multiplication and addition operations on these values, and return a set of complex Fourier series coefficients, which is the transform representation of the amplitude function. For a large number of samples, the number of complex calculations required is quite large, and the calculation time can be very long. The computer programs referred to as Fast Fourier transform routines (FFT) minimizes the number of calculations necessary by requiring the total number of samples, \( N \), to be the number 2 raised to an integer power. This
significantly reduces the computer time even for a small number of samples. Both the forward transform and the inversion can be performed.

For the transform in the forward direction, the FFT routine actually computes a summation of the following form:

\[
Y_n = \sum_{j=0}^{N-1} X_j \exp \left(-\frac{2\pi i nj}{N}\right) \tag{36}
\]

where \( n \) is an integer from 0 to \( N - 1 \), \( X_j \) is the function sampled, and \( Y_n \) is the complex coefficient of the Fourier series representation of the transform. In order to use the FFT routine, \( \phi(x') \) must be put in the form \( X_j \exp \left(-\frac{2\pi i nj}{N}\right) \). The following mathematical treatment was derived by C. W. McCurdy (The Ohio State University) for this purpose.

The basic finite transform of any function \( f(q) \) on the interval \( 0-2\pi \) is

\[
C_n = \frac{1}{2\pi} \int_0^{2\pi} f(q) \exp(-ipq) dq \tag{37}
\]

Comparison of this equation with Equation 33 shows that \( p = 2\pi n v_0 \).

The integral is approximated by the summation

\[
C_n = \frac{1}{2\pi} \sum_{j=0}^{N-1} f(q_j) \exp(-ipq) \Delta q \tag{38}
\]

To produce a symmetric distribution of points over the width to be transformed, let

\[
q_j = j2L/N - \lfloor (N - 1)/N \rfloor L
\]

then

\[
\Delta q = q_{j+1} - q_j = 2L/N
\]
Substituting into Equation 38 gives

\[ C_n = \frac{L}{n\pi} \sum_{j=0}^{N-1} f(j2L/N - [(N - 1)/N]L) \exp (-ip[j2L/N - [(N - 1)/N]L]) \]

The complex coefficients \(C_n\) arrived at through use of the above equation are actually those for a periodic function with period \(2\pi\) and are valid for the nonperiodic function only over the width of the actual function. If the width of the function is \(2L\), then \(T = 2L = v_0^{-1}\) and \(p = n\pi/L\). Substituting this expression for \(p\) into the summation results in:

\[ C_n = \frac{L}{n\pi} \exp [in\pi(N-1)/N] \sum_{j=0}^{N-1} f(j2L/N - [(N - 1)/N]L) \exp (-2\pi jn/N) \]

The summation is \(Y_n\) from the FFT routine, and the parameters involved in the terms preceding the summation are known. The expression for \(C_n\) is the amplitude of the nth component of the transform, and intensity is arrived at by multiplication of \(C_n\) by its complex conjugate.

In order to construct the theoretical diffraction pattern, the component \(n\) of the Fourier transform routine must be related to the \(x\) coordinate of the diffraction pattern in the focal plane of the lens. Comparison of Equation 37 with Equation 16 shows that \(p = kx/f\). It has also been shown above that \(p = n\pi/L\). Therefore,

\[ \frac{kx}{f} = \frac{n\pi}{L} \]

and

\[ \frac{x}{f} = \frac{n\pi}{Lk} \]

(41)
Solving for \( x/f \) (remembering that \( k = 2\pi/\lambda \)) yields

\[
\frac{x}{f} = \frac{n\lambda}{2L}
\]  

(42)

Note that \( x/f \) is the tangent of the angle \( \beta \) that the \( x \) coordinate makes with the horizontal, measured from the center of the lens. When \( f \) is much larger than \( x \), \( \tan \beta \) can be assumed to be equal to the sine of the angle. It is important to realize that the focal length of the lens, \( f \), determines the lateral size of the diffraction pattern for light of wavelength \( \lambda \). This can readily be seen from the fact that \( x \), the position on the focal plane of a particular \( C_n \) coefficient, is directly proportional to \( f \). Equation 42 above is a completely general equation, which can be used for any set of experimental variables, \( f \) and \( \lambda \).

Appendix B contains a listing of the program FT2 which performs the overall calculation for the amplitude function in the electrode plane, calls the FFT routine (called CFT, and also listed in Appendix B) which transforms the function, and calculates the absorbance in the focal plane of the lens as a function of time after initiation of electrolysis.

The total number of points (\( N \)) used in the FFT routine is a critical factor in the results obtained, especially at short times after initiation of electrolysis. For example, using 512 points and letting \( 2L \) equal 0.15 cm, the incremental distance (Inc) between each point is \( 2.93 \times 10^{-4} \) cm (Inc = 0.15 cm/512). Relative to the Gaussian profile of the laser beam (the radius is defined to be equal to the distance where the intensity has decreased to \( 1/e^2 \) of its maximum value, usually about 0.05 cm), which is the function to be transformed, Inc is small enough to ensure adequate
resolution. The presence of chromophore, however, results in attenuation of the incident beam near to the electrode surface and to obtain adequate resolution within the portion of the beam which will be attenuated, Inc must be small relative to the size of the diffusion layer (equals \sqrt{D t}, where D is the diffusion coefficient of the chromophore, and t is the time after initiation of electrolysis). At times of one second or more after initiation of electrolysis, for a chromophore with D equal to \(1.6 \times 10^{-5}\) cm\(^2\)/sec, (\(\sqrt{D t}\) equals \(4.0 \times 10^{-3}\) cm), it was found that less than 5% difference was obtained in the value of absorbance calculated using 512 points compared to that calculated using 1024 points. At shorter times, it was necessary to use up to 2048 points (Inc = \(7.3 \times 10^{-5}\) cm) in the summation to achieve a reliable result. This number of points seemed to be adequate at least for times of 10 milliseconds or longer.
APPENDIX B

COMPUTER PROGRAMS

This appendix contains programs used in Fourier transform calculations. Four2 was written by R. L. McCreery (The Ohio State University, Columbus, Ohio) to calculate the theoretical intensity as a function of distance in the diffraction pattern. FT4 and subroutine Gaus, written by this author, were used to calculate absorbance at an angle in the diffraction pattern as a function of time. The subroutine CFT, used in both the above programs, is also listed in this appendix.
0056 104 FORMAT('X12.4')
0057 25 WRITE(1,115)
0058 115 FORMAT('PLOT INPUT TO FT?')
0059 READ(1,12)I
0060 IF(I.AN.EQ.1318)GO TO 20
0061 DO 20 1=1,N
0062 20 X(i)=A(i)
0063 YMIN=0.
0064 YMAX=0.
0065 XMAX=0.
0066 CALL GRAPH(XMIN,XMAX,YMIN,YMAX,0.1,N,1,1,1,1,1,XDATA,YDATA)
0068 20 CALL CF'T(A,B,N,SH)
0069 DO 30 I=1,N
0070 TMAX =EXP((1.0-I-1)*PI/(N-1))
0071 LCMPMX(A(I),B(I))=XLT/(1+PI)
0072 YDATA(I)=(EMP*|CUNJG|TEMP)
0073 A(I)=XMAX/(TEMP)
0074 30 B(I)=A1MAG(TEMP)
0075 IF(I.AN.S.EQ.1318)GO TO 50
0076 WRITE(1,105)
0077 105 FORMAT('WRITE RESULT OF FT?')
0078 READ(1,106)IANS2
0079 IF(IANS2.NE.1318)GO TO 50
0080 WRITE(6,107)T,ALPHA,F BICK,DT
0081 107 FORMAT(16.2E15.6)
0082 IF(0.5.<=|KDT|) WRITE(6,108)T,ALPHA,F BICK,DT
0083 DO 40 I=1,N/2
0084 J=I+N/4
0085 DO 40 I=1,N/2
0086 40 WRITE(6,106)T,A(I),B(I),J,A(J),B(J)
0087 50 XDELT=XDLAM*1.0-8/(2.*XLT)
0088 DO 60 I=1,N
0089 60 XDATA(I)=I-1)*XDELT
0090 IF(I.AN.S.EQ.1318)GO TO 40
0091 WRITE(1,111)
0092 111 FORMAT('WRITE SCREEN INTENSITY?')
0093 READ(1,112)IANS2
0094 IF(IANS2.NE.1318)GO TO 30
0095 WRITE(6,109)T,W,A,ALPHA,F BICK,DT
0096 109 FORMAT('WRITE SCREEN INTENSITY?')
0097 IF(0.1.<=T) WRITE(6,108)T,A,ALPHA,F BICK,DT
0098 108 FORMAT('WRITE SCREEN INTENSITY?')
0099 DO 70 I=1,N/2
1000 J=I+N/4
1001 DO 70 I=1,N/2
1002 70 WRITE(6,109)XDATA(I),YDATA(I),XDATA(J),YDATA(J)
1003 109 FORMAT('WRITE SCREEN INTENSITY?')
1004 DO 110 I=1,N/2
1005 110 WRITE(6,109)T,A,ALPHA,F BICK,DT
1006 IF(I.AN.S.EQ.1318)GO TO 70
1007 XMIN=-9.
1008 YMIN=-9.
1009 XMAX=-9.
1010 YMAX=-9.
CALL GKF(XMIN,XMAX,YMIN,YMAX,0,1,XP,1,1,1,1,XDATA,YDATA)
STOP
END

FTN4 COMPILER: HP9204-16192 REV. 1726

** NO WARNINGS ** NO ERRORS ** PROGRAM = 09373 COMMON = 00000
SUBROUTINE GAJS(NTOT, TW, XZERO, AMP, BMP)
REAL NVC, AMP(8192), XDIS(8192), BMP(8192)
REAL TW
REAL AL
COMMON T(100), YDATA(100), IDATA(100)
PI = 3.1415926546
ALPHA = 397.83
DO 100 I = 1, NTOT
100 XDIS(I) = 0.0
DO 400 I = 1, NTOT
XDIS(I) = (I - 1) * TW / NTOT - (((Ntot - 1) / NTON) * TW / 2)
IF (XDIS(I) .LT. 0.0) GO TO 200
GO TO 300
200 AMP(I) = 0.0
GO TO 400
300 AL = ALPHA / PI
AL = -AL
AL = AL * (XDIS(I) * 2.)
AMP(I) = AZERO * EXP(AL)
400 BMP(I) = 0.0
600 CONTINUE
RETURN
END
DIMENSION A(T), AT(2), B(T), SK(2)

THE FOLLOWING TWO CONSTANTS SHOULD AGREE WITH THE ARRAY DIMENSIONS:

DIMENSION A (T), AT (2), B (T), SK (2)

THE FOLLOWING CONSTANTS ARE ADJUSTED.

-American-Cold War

-American-Nuclear Proliferation

-American-Intervention in Middle East

-American-Intervention in Latin America

-American-Intervention in Southeast Asia

-American-Intervention in Afghanistan

-American-Intervention in Iraq

-American-Intervention in Libya

-American-Intervention in Syria

-American-Intervention in Iran

-American-Intervention in North Korea

-American-Intervention in Korea

-American-Intervention in Japan

-American-Intervention in Taiwan

-American-Intervention in China

-American-Intervention in India

-American-Intervention in Pakistan

-American-Intervention in Afghanistan

-American-Intervention in Pakistan

-American-Intervention in India

-American-Intervention in China

-American-Intervention in Japan

-American-Intervention in Taiwan

-American-Intervention in Korea

-American-Intervention in North Korea

-American-Intervention in Iran

-American-Intervention in Afghanistan

-American-Intervention in Pakistan

-American-Intervention in India

-American-Intervention in China

-American-Intervention in Japan

-American-Intervention in Taiwan

-American-Intervention in Korea

-American-Intervention in North Korea

-American-Intervention in Iran

-American-Intervention in Afghanistan

-American-Intervention in Pakistan

-American-Intervention in India

-American-Intervention in China

-American-Intervention in Japan

-American-Intervention in Taiwan

-American-Intervention in Korea

-American-Intervention in North Korea

-American-Intervention in Iran

-American-Intervention in Afghanistan

-American-Intervention in Pakistan

-American-Intervention in India

-American-Intervention in China

-American-Intervention in Japan

-American-Intervention in Taiwan

-American-Intervention in Korea

-American-Intervention in North Korea

-American-Intervention in Iran

-American-Intervention in Afghanistan

-American-Intervention in Pakistan

-American-Intervention in India

-American-Intervention in China

-American-Intervention in Japan

-American-Intervention in Taiwan

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-American-Intervention in Iran

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-American-Intervention in India

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-American-Intervention in Japan

-American-Intervention in Taiwan

-American-Intervention in Korea

-American-Intervention in North Korea

-American-Intervention in Iran

-American-Intervention in Afghanistan

-American-Intervention in Pakistan

-American-Intervention in India

-American-Intervention in China

-American-Intervention in Japan

-American-Intervention in Taiwan

-American-Intervention in Korea

-American-Intervention in North Korea

-American-Intervention in Iran

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-American-Intervention in Pakistan

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-American-Intervention in Afghanistan

-American-Intervention in Pakistan

-American-Intervention in India

-American-Intervention in China

-American-Intervention in Japan
J = 2
1014  IF (MOD(K, J), NE. 0) GO TO 70
1015  M = M + 1
1016  NFAC(M) = J
1017  M = M + 1
1018  IF (J, LE. K) GO TO 100
1019  J = J - 1
1020  M = M + 1
1021  NFAC(M) = NFAC(J)
1022  J = J - 1
1023  IF (J, LE. 0) GO TO 90
1024  COMPUTE FAST FOURIER TRANSFORM
1025  GO TO 100
1026  SD = RADF*PLAT (KSPAN)
1027  SD = RINEQjSD*SD
1028  KK = 1
1029  IF (NFAC(I), NE. 2) GO TO 400
1030  C
1031  TRANSFORM FOR FACTOR OF 2 (INCLUDING ROTATION FACTOR)
1032  C
1033  C
1034  KSPAN = KSPAN/2
1035  K1 = KSPAN + 2
1036  K2 = KK + KSPAN
1037  AA = A(K2)
1038  BB = B(K2)
1039  A(K2) = A(KK) + AK
1040  B(K2) = B(KK) + BK
1041  A(KK) = A(KK) + AK
1042  B(KK) = B(KK) + BK
1043  KK = K2 + KSPAN
1044  IF (KK, LE. NN) GO TO 210
1045  KK = KK - NN
1046  IF (KK, LE. IC) GO TO 210
1047  IF (KK, GT. KSPAN) GO TO 900
1048  C
1049  C
1050  C
1051  C
1052  C
1053  C
1054  C
1055  C
1056  C
1057  C
1058  C
1059  C
1060  C
1061  C
1062  C
1063  C
1064  C
1065  C
1066  THE FOLLOWING THREE STATEMENTS COMPENSATE FOR TRUNCATION
197

C   ERROR. IF ROUNDED ARITHMETIC IS USED, THEY MAY BE DELETED.
C   Cl=0.5/(K*K+1.*S+1.) + 0.5
C   S1=Cl*Cl
C   C1=C1*K
C   NEXT STATEMENT SHOULD BE DELETED IF NON-ROUNDED ARITHMETIC IS Y:
C 1.1 Cl=Cl
C 1.2 K=K + JC
C 1.3 IF (KK.LT. K2) GO TO 230
C 1.4 K1=K1+K+HL
C 1.5 (K*K-(KSPAN)/2 + JC
C 1.6 IF (K .LT. KLE) GO TO 230
C 1.7 GO TO 100
C 1.8 C   TRANSFORM FOR FACTOR OF 3(OPTIONAL CODE)
C 1.9 320 K1=KK*KSPAN
C 1.10 K2=K1 + KSPAN
C 1.11 AK = A (KK)
C 1.12 BK=B(KK)
C 1.13 AJ=A(K1)*A(KK)
C 1.14 B1=B(K1)*B(KK)
C 1.15 AK=AK-0.5*AT+BK
C 1.16 B1=BT-K1
C 1.17 IF (K*K .LE. KL+JC) GO TO 220
C 1.18 K = K - NN
C 1.19 IF (KK .LE. KSPAN) GO TO 320
C 1.20 GO TO 100
C 1.21 C   TRANSFORM FOR FACTOR OF 4
C 1.22 400 IF (NFAC(T) .NE. 4) GO TO 600
C 1.23 KSPAN=KSPAN/4
C 1.24 410 C1=1.0
C 1.25 420 K1=KK*KSPAN
C 1.26 K2=KK*KSPAN
C 1.27 K3=K2*KSPAN
C 1.28 AK=A(KK)*A(K2)
C 1.29 AJ=A(K1)*A(K3)
C 1.30 A1=A(K2)*A(K1)
C 1.31 B1=B(K1)*B(K2)
C 1.32 B2=B(K2)*B(K1)
C 1.33 B3=B(K1)*B(K2)
C 1.34 B4=B(K2)*B(K1)
C 1.35 B5=B(K2)*B(K3)
C 1.36 B6=B(K1)*B(K2)
C 1.37 B7=B(K1)*B(K2)
C 1.38 B8=B(K1)*B(K2)
C 1.39 B9=B(K1)*B(K2)
C 1.40 B10=B(K1)*B(K2)
C 1.41 B11=B(K1)*B(K2)
C 1.42 B12=B(K1)*B(K2)
C 1.43 B13=B(K1)*B(K2)
C 1.44 B14=B(K1)*B(K2)
0221  IF (ISH .LT. 0) GO TO 450
0222  AKP=AKM-BJM
0223  BKP=IKM-AJM
0224  BKM=IKM-AJM
0225  IF (S1 .LT. 0.0) GO TO 460
0226  AKP=A(K1)-AIJ+KK
0227  B(K1)=AKM+B(K1)+BJM
0228  B(K2)=AJM+B(K2)+B(K1)
0229  B(K3)=AKM+B(K3)+B(K1)
0230  B(K4)=AKM+B(K4)+B(K1)
0231  B(K5)=AKM+B(K5)+B(K1)
0232  B(K6)=AKM+B(K6)+B(K1)
0233  KK=KK+KK
0234  IF (KK .LE. N1) GO TO 420
0235  440 C2=C1-(CD+C1+C1)*S1
0236  S1=(S2*S1-C1+C1)*S1
0237  THE FOLLOWING THREE STATEMENTS COMPENSATE FOR TRUNCATION.
0238  C ERROR. IF ROUNDED ARITHMETIC IS USED, THEY MAY ALL BE DELETED.
0239  C CI=0.5/(C2+C2+C2)*S1*S1
0240  C CI=C2*S1+C2
0241  C NEXT STATEMENT SHOULD BE DELETED IF NON-ROUNDLD ARITHMETIC IS USED.
0242  C CI=C2
0243  C2=C1+C1*C1*C1
0244  S2=2.0*C1*C1
0245  C3=C2*C2*C1*C1
0246  S3=2.0*C1*C1
0247  KK=KK+KK
0248  IF (KK .LE. KSPAN) GO TO 420
0249  C KK=KK+KK
0250  IF (KK .LE. KK+KK) GO TO 420
0252  C KK=KK+KK
0253  GO TO 100
0254  450 AKP=AKM+BJM
0255  BKP=IKM-AJM
0256  BKM=IKM-AJM
0257  IF (S1 .LT. 0.0) GO TO 460
0258  460 A(K1)=AKP
0259  B(K1)=BKP
0260  A(K2)=AJP
0261  B(K2)=B(KP)
0262  A(K3)=AKM
0263  B(K1)=B(KP)
0264  B(K3)=AKM
0265  B(K5)=AKM
0266  IF (KK .LE. N1) GO TO 420
0267  GO TO 440
0268  C TRANSFORM FOR FACTOR OF Y(OPTIONAL CODE)
0269  510 C2=C2*C2+C2*C2
0270  S2=2.0*C2*C2
0271  KK=KK+KK
0272  K2=K1+K1
0273  K1=K1+K1
0274  K4=K4+K4
0275  AKP=A(K1)+A(K4)
<table>
<thead>
<tr>
<th>Line</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>0276</td>
<td>( A(K+1) = A(K) - A(K4) )</td>
</tr>
<tr>
<td>0277</td>
<td>( B(K) = B(K1) + O(K4) )</td>
</tr>
<tr>
<td>0278</td>
<td>( B(M) = B(K1) - O(K4) )</td>
</tr>
<tr>
<td>0279</td>
<td>( A(J) = A(K2) + A(K3) )</td>
</tr>
<tr>
<td>0280</td>
<td>( A(M) = A(K2) - A(K3) )</td>
</tr>
<tr>
<td>0281</td>
<td>( D(J) = B(K2) - B(K3) )</td>
</tr>
<tr>
<td>0282</td>
<td>( D(J) = B(K2) - B(K3) )</td>
</tr>
<tr>
<td>0283</td>
<td>( M = M(K) )</td>
</tr>
<tr>
<td>0284</td>
<td>( B(K) = B(K) )</td>
</tr>
<tr>
<td>0285</td>
<td>( B(K) = B(K) )</td>
</tr>
<tr>
<td>0286</td>
<td>( B(K) = B(K) + B(J) )</td>
</tr>
<tr>
<td>0287</td>
<td>( A(K) = A(K) + A(K) )</td>
</tr>
<tr>
<td>0288</td>
<td>( B(K) = B(K) + B(J) )</td>
</tr>
<tr>
<td>0289</td>
<td>( A(K) = A(K) + A(K) )</td>
</tr>
<tr>
<td>0290</td>
<td>( B(K) = B(K) + B(J) )</td>
</tr>
<tr>
<td>0291</td>
<td>( A(K) = A(K) + A(K) )</td>
</tr>
<tr>
<td>0292</td>
<td>( B(K) = B(K) + B(J) )</td>
</tr>
<tr>
<td>0293</td>
<td>( B(K1) = B(K1) + A(K) )</td>
</tr>
<tr>
<td>0294</td>
<td>( B(K4) = B(K4) - A(K) )</td>
</tr>
<tr>
<td>0295</td>
<td>( A(K1) = A(K1) + A(K4) )</td>
</tr>
<tr>
<td>0296</td>
<td>( B(K) = B(K) - B(J) )</td>
</tr>
<tr>
<td>0297</td>
<td>( A(K1) = A(K1) - A(K4) )</td>
</tr>
<tr>
<td>0298</td>
<td>( B(K) = B(K) - B(J) )</td>
</tr>
<tr>
<td>0299</td>
<td>( A(K1) = A(K1) - A(K4) )</td>
</tr>
<tr>
<td>0300</td>
<td>( A(K1) = A(K1) - A(K4) )</td>
</tr>
<tr>
<td>0301</td>
<td>( B(K1) = B(K1) + B(J) )</td>
</tr>
<tr>
<td>0302</td>
<td>( B(K1) = B(K1) + B(J) )</td>
</tr>
<tr>
<td>0303</td>
<td>( B(K1) = B(K1) + B(J) )</td>
</tr>
<tr>
<td>0304</td>
<td>( \text{IF} (K &lt; L, N) \text{ GO TO } 539 )</td>
</tr>
<tr>
<td>0305</td>
<td>( \text{IF} (K &lt; L, N) \text{ GO TO } 539 )</td>
</tr>
<tr>
<td>0306</td>
<td>( \text{IF} (K &lt; E, K) \text{ GO TO } 520 )</td>
</tr>
<tr>
<td>0307</td>
<td>( \text{GO TO } 700 )</td>
</tr>
<tr>
<td>0308</td>
<td>( \text{TRANSFORM FOR ODD FACTORS} )</td>
</tr>
<tr>
<td>0309</td>
<td>( \text{IF } )</td>
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<tr>
<td>0310</td>
<td>( \text{IF } )</td>
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<td>0311</td>
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<td>0320</td>
<td>( \text{IF } )</td>
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<td>0321</td>
<td>( \text{IF } )</td>
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<tr>
<td>0322</td>
<td>( \text{J} = 1 )</td>
</tr>
<tr>
<td>0323</td>
<td>( \text{J} = 1 )</td>
</tr>
<tr>
<td>0324</td>
<td>( \text{J} = 1 )</td>
</tr>
<tr>
<td>0325</td>
<td>( \text{J} = 1 )</td>
</tr>
<tr>
<td>0326</td>
<td>( \text{J} = 1 )</td>
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<tr>
<td>0327</td>
<td>( \text{J} = 1 )</td>
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<tr>
<td>0328</td>
<td>( \text{IF } )</td>
</tr>
<tr>
<td>0329</td>
<td>( \text{IF } )</td>
</tr>
<tr>
<td>0330</td>
<td>( \text{IF } )</td>
</tr>
</tbody>
</table>
0331  \( K_2 = K + K_{SPAN} \)
0332  \( A_K = A(K) \)
0333  \( B = B(K) \)
0334  \( A = A \)
0335  \( B = B \)
0336  \( J = 1 \)
0337  \( K_1 = K_1 + K_{SPAN} \)
0338  \( 650 \) GO TO 650
0339  \( 0 \) J = 1
0340  \( \) AT(J) = A(K1) + A(K2) \)
0341  \( \) AK = AT(J) + AK \)
0342  \( \) BT(J) = B(K1) + B(K2) \)
0343  \( \) BK = BT(J) + BK \)
0344  \( \) J = J + 1
0345  \( \) AT(J) = A(K1) - A(K2) \)
0346  \( \) BT(J) = B(K1) - B(K2) \)
0347  \( \) K1 = K1 + KSPAN \)
0348  \( \) IF (K1 .LT. K2) GO TO 650
0349  \( \) A(KK) = AK \)
0350  \( \) B(KK) = BK \)
0351  \( \) K1 = K \)
0352  \( \) K2 = KK + KSPAN \)
0353  \( \) J = 1
0354  \( \) 660 K1 = K1 + KSPAN \)
0355  \( \) K2 = K2 - KSPAN \)
0356  \( \) JF = J \)
0357  \( \) AK = AA \)
0358  \( \) BJ = B \)
0359  \( \) AJ = 0.0 \)
0360  \( \) UJ = 0.0 \)
0361  \( \) K = 1
0362  \( \) 670 K = K + 1 \)
0363  \( \) AK = AT(K) * CK(JJ) + AK \)
0364  \( \) BK = BT(K) * CK(JJ) + BK \)
0365  \( \) JJ = JJ + 1 \)
0366  \( \) AJ = AT(K) * CK(JJ) + AJ \)
0367  \( \) BJ = BT(K) * CK(JJ) + BJ \)
0368  \( \) JJ = JJ + 1 \)
0369  \( \) IF (JJ .GT. JF) GO TO 670 \)
0370  \( \) IF (K1 .LT. JF) GO TO 670 \)
0371  \( \) K = JF - J \)
0372  \( \) AK1 = BK - BT \)
0373  \( \) BK1 = BK + AJ \)
0374  \( \) AK2 = BK + BJ \)
0375  \( \) BK2 = BK - AJ \)
0376  \( \) J = J + 1 \)
0377  \( \) IF (J .LT. K) GO TO 660 \)
0378  \( \) K = KK + KSPAN \)
0379  \( \) IF (KK .LE. NN) GO TO 640 \)
0380  \( \) KK = KK - NN \)
0381  \( \) IF (KK .GT. NN) GO TO 640 \)
0382  \( \) IF (KK .LE. NN) GO TO 640 \)
0383  \( \) GO TO 700 \)
0384  \( \) CC = + 1 \)
0385  \( \) CC = - 1.0 - CD
0306   S1=S0
0307   S2=S1
0308   K1=AC(KK)
0309   KK=K1+KSPAN
0310   A(KK)=C2*A(KK) - C2*C2 + C2*K(KK)
0311   KK=KK + KSPAN
0312   IF (KK .LE. NT) GO TO 730
0313   A(KK)=C2*
0314   S2=SI*C2 + SI*S2
0315   C2=CI*C2 - AK
0316   KK=KK - NT + KSPAN
0317   IF (KK .LE. KSPAN) GO TO 730
0318   C2=C1*(CD*C1 + SI*S1)
0319   SI=SI + (SI*C1 - C0*SI)
0320   CTHE FOLLOWING THREE ESTATEMENTS COMPENSATE FOR TRUNCATION
0321   IF ROUNDED ARITHMETIC IS USED THEY MAY
0322   BE DELETED.
0323   CI=0.5/((C1**2 + S1**2)*0.5
0324   C2=C1*C1
0325   C2=C1*C1
0326   KK=KK - KSPAN + JC
0327   IF (KK .LE. KSPAN) GO TO 720
0328   KK=KK - KSPAN + JC + INC
0329   IF (KK .LE. JC+INC) GO TO 710
0330   GO TO 100
0331   C PERMUTE THE RESULTS TO NORMAL ORDER --- DONE IN TWO STAGES
0332   PERMUTATION FOR SQUARE FACTORS OF N
0333   800 NP(I)=K(I)
0334   IF (K.T.EQ. 0) GO TO 996
0335   K=K+K+1
0336   IF (M .LT. K) K=K-1
0337   J=1
0338   NP(K+1)=JC
0339   B10 NP(J+1)=NP(J)+NFAC(J)
0340   NP(K+1)=NP(K+1)*NFAC(J)
0341   J=J+1
0342   K=K-1
0343   IF (J .LT. K) GO TO 810
0344   K=NP(K+1)
0345   KSPAN=NP(2)
0346   N(A)+1
0347   K=KSPAN+1
0348   J=1
0349   IF (M .NE. NTOI) GO TO 659
0350   C PERMUTATION FOR SIMULTANEOUS-VARIATE TRANSFORM (OPTIONAL CODE)
0351   820 PK=PK(KK)
0352   K(KK)=RP
0353   A(KK)=AH
0354   M=KH
0355   B(KK)=BH(KK)
0356   RK2+1
0357   RK2+1
0358   RK2+1
0359   RR=KH+INC
0360   K2=KSPAN+K2
0441 IF (K2, LT, K3) GO TO 310
0442 830 K2=K2-NP(J)
0443 J=J+1
0444 820 IF (K2, Gt, NP(J)) GO TO 830
0445 J=1
0446 840 K2=K2+INC
0447 IF (K2, LT, K5) GO TO 840
0448 K2=SPAN + K2
0449 IF (K2, LT, K9) GO TO 840
0450 IF (K2, LT, K5) GO TO 840
0451 J=K3
0452 GO TO 640
0453 845 PERMUATION FOR MULTIVARIATE TRANSFORM
0454 850 K'=K + JG
0455 860 AK=A(K)
0456 870 K=K+1
0457 880 IF (K2, LT, K3) GO TO 860
0458 890 K2=K2+INC
0459 900 IF (K2, LT, K5) GO TO 890
0460 K2=K2+INC
0461 910 GO TO 640
0462 IF (K2, LT, K9) GO TO 810
0463 K2=K2+INC
0464 IF (K2, LT, K5) GO TO 840
0465 K2=K2+INC
0466 IF (K2, LT, K9) GO TO 840
0467 K2=K2-INC + NP(J)
0468 K2=K2+INC + NP(J)
0469 K2=K2+INC + NP(J)
0470 IF (K2, LT, K5) GO TO 840
0471 970 K2=K2-NP(J)
0472 J=J+1
0473 K2=K2-NP(J) + K2
0474 IF (K2, GT, NP(J)) GO TO 870
0475 J=1
0476 880 IF (K2, LT, K2) GO TO 890
0477 K2=K + JG
0478 890 K2=K+INC
0479 IF (K2, LT, K5) GO TO 890
0480 IF (K2, LT, K5) GO TO 890
0481 J=3
0482 900 IF (C(K1+1).GE. N) RETURN
0483 910 K2=K2+INC + NP(J+1)
0484 C PERMUATION FOR SQUARE-FREE FACTORS OF N
0485 J=M-KT
0486 NFAC(J+1)=1
0487 920 NFAC(J+1)=NFAC(J) * NFAC(J+1)
0488 J=J+1
0489 930 IF (J, .GE. KT) GO TO 900
0490 KT=KT+1
0491 N=NFAC(KT-1)
0492 IF (N, .GE. K2) GO TO 930
0493 J=1
0494 J=0
0495 GO TO 640
0501 IF (J, GE, K2) GO TO 902
0502 NP(J)=J
0503 956 K2=MAXF(K)
0504 K=K2
0505 IF (J,LT, NP(J)) GO TO 904
0506 C DETERMINE THE PERMUTATION CYCLES OF LENGTH GREATER THAN 1
0507 J=0
0510 GO TO 914
0511 910 K=KK
0512 KK=NP(K)
0513 NP(K)=KK
0514 IF (KK, LE, J) GO TO 910
0515 K=KK
0516 914 J=J+1
0517 KK=NP(J)
0518 IF (KK, LT, 0) GO TO 914
0519 IF (KK, LE, J) GO TO 910
0520 NP(J)=-J
0521 IF (J, NE, NN) GO TO 914
0522 MAXF=INC+MAXF
0523 C REORDER A AND B, FOLLOWING THE PERMUTATION CYCLES
0524 GO TO 954
0525 924 J=J-1
0526 IF (NP(J), LT, 0) GO TO 924
0527 J=J
0528 926 KSPAN=MJ
0529 IF (J,J, LT, MAXF) KSPAN=MAXF
0530 IF (J=K2, KSPAN) S=NP(J)
0531 IF (J,LT, IT + J) J=J + 1
0532 K1=KK + KSPAN
0533 K2=0
0534 920 K2=K2 + 1
0535 IF (K1, NE, KK) GO TO 930
0536 K1=K1+1
0537 IF (K1, NE, K2) GO TO 930
0538 K1=K1+1
0539 K2=K2+1
0540 IF (K1, NE, K2) GO TO 930
0542 K2=K2+1
0543 932 K1=K1+1
0544 K2=K2+1
0545 K2=K2+1
0546 K2=K2+1
0547 IF (K1, NE, KK) GO TO 916
0548 K2=K2
0549 IF (K, NE, J) GO TO 972
0550 K1=K1+1
0551 K2=K2+1
0552
IF (K1 .NE. 0) GO TO 940
IF (JJ .NE. 0) GO TO 956
IF (J .NE. 1) GO TO 954
IF (K .NE. 1) GO TO 950
IF (J1 .NE. 1) GO TO 924
RETURN
C ERROR FINISHED, INSUFFICIENT ARRAY STORAGE
970 ISN=0
STOP
999 FORMAT(44I0) ARRAY BOUNDS EXCEEDED WITHIN SUBROUTINE CFT"
END
BIBLIOGRAPHY


24. Ref. 1a, p. 553.

25. Ref. 1b, p. 19.

26. Ref. 1b, p. 293.


28. Ref. 1b, p. 634.

29. Ref. 5, p. 132.

30. Appendix B, this text.


