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Diffusion layer imaging and the related electrochemistry studied by optical absorption spectroscopy

Wu, Huan Ping, Ph.D.
The Ohio State University, 1990
Diffusion Layer Imaging and The Related Electrochemistry
Studied by Optical Absorption Spectroscopy

Dissertation

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

By
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The Ohio State University
1990

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Dedicated to the memory of my Uncle

Sun Sam Wong
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Chapter I
Introduction

Spectroelectrochemistry

Electrochemical methods have been major analytical tools for many years. These methods are based on the measurement of electrical responses in the form of current, charge or potential. They may be used for solution analysis, such as the analysis of trace amounts of metal ions or organic species, or may be used to generate unstable intermediates such as radical ions, which are then studied for their spectroscopic properties or for reactions following heterogeneous electron-transfer. Electrochemical methods may also be used for obtaining quantitative and thermodynamic information about an electrochemical system. The variety of information obtained with this analytical technique is particularly useful because electrochemistry is very sensitive and in some cases can be selective.

Recent years have witnessed the introduction of spectroscopy into electrochemistry. The combination of spectroscopy and electrochemistry, in which a spectroscopic technique is used to study electrochemical events in situ, is commonly referred to as spectroelectrochemistry (SEC). The direct coupling of spectroscopy and electrochemistry has been driven mainly by the following motivations. First, spectroelectrochemistry provides ways for obtaining information about electrochemical systems that could not be gathered in pure electrochemical experiments, thus enhancing the information content. Second, electrochemistry usually lacks selectivity and specificity because of the low resolution of electrochemical measurements, while spectroscopy is known for specificity and selectivity in providing qualitative information about electrochemical products. Third, electrochemistry
often suffers from background electrochemical events, the most notable of which is the charging current. Spectroelectrochemistry is superior in background rejection, and thus reduces interferences from background events.

Closely related to spectroelectrochemistry are two groups of techniques which involve combinations of optical and electrochemical phenomena. The first group includes off-line spectroscopic methods in which conventional spectroscopic techniques such as IR and NMR are used to characterize the products of an electrochemical reaction. The second group, known as photoelectrochemistry, involves monitoring of a photochemical process by an electrode, often at a semiconductor electrode. These two groups of techniques will not be discussed here.

Spectroelectrochemistry can be further classified into surface and solution SEC. Surface SEC involves spectroscopic techniques which provide information about the electrode surface itself. Solution SEC probes species within the diffusion layer or nearby solution, providing information about the identities or concentration of molecules generated or consumed by electrochemical processes in the diffusion layer.

Since the initial development of UV-vis absorption spectroelectrochemistry in 1964 by Kuwana [1], many spectroscopic techniques have been coupled with electrochemistry. In general, there are three geometries used to couple spectroscopic techniques with electrochemistry. They are transmission, reflection and parallel geometries, as shown in Fig.1. In transmission geometry, a light beam transmits through an optically transparent electrode(OTE), probing electrochemical products in the diffusion layer. Absorption spectroscopic techniques have been the most successful in this geometry. In external reflection geometry, reflects form an electrode surface, detecting species in the diffusion layer as well as on an electrode surface. Signals could result from reflection off the surface or Raman scattering. In parallel geometry, a light beam passes parallel to the electrode surface. Different rays of a light beam probe different regions in the diffusion layer.
Fig. 2-1. Electrode geometries for spectroelectrochemistry
Spectroelectrochemical techniques and their relative strengths and weaknesses have been discussed and reviewed [2-3].

UV-vis absorption spectroscopic methods coupled with OTE transmission geometry [4-7] represent the most commonly encountered SEC techniques. The popularity of these SEC methods is partly due to the optical transmission characteristics of the solvents commonly used in electrochemistry and partly due to the simplicity of implementing these experiments. In its simplest form, thin layer OTE spectroelectrochemistry consists of a light beam transmitted through the electrode and solution. Spectra of reactants and products can be obtained, although the ability to resolve mixtures is usually low. This technique relies on stable components of the electrochemical system. Under appropriate conditions, equilibrium parameters such as \( n \) (number of electrons transferred) and \( E^\circ \) (formal reduction potential of a redox couple) can be determined, even for non-nernstian couples. A good example is the measurement of \( n \) and \( E^\circ \) for cytochrome-c [8]. UV-vis OTE spectroelectrochemical techniques can also be used to study heterogeneous charge-transfer kinetics [9-10] and homogeneous reactions kinetics [11-12].

Over the years, high-resolution spectroscopic methods have been coupled with electrochemistry to obtain more structural information about electrochemical products. Vibrational spectroscopic methods such as IR and Raman are among the most popular [13-14]. IR absorption SEC has not been as successful as UV-vis absorption SEC for quantitative solution analysis because of difficulties with electrode and solvent properties. The primary interest in IR SEC techniques results from the need for identification of electrochemical products and monitoring of electrochemical processes. In particular, IR reflectance spectroelectrochemistry has been successfully applied for analysis of the electrode/solution interface and has provided much useful information about the orientations of adsorbed molecules on the electrode surface [15-17], as well as about mechanisms of surface electrochemical processes [18,19]. Raman spectroelectrochemistry
has also been actively involved in probing both surface and solution processes of electrochemical experiments [18,20-24]. Surface enhanced Raman spectroelectrochemistry has become one of the most sensitive techniques for examining electrode surfaces [25]. Raman spectroscopy has recently been used ex situ to study the mechanism of laser activation of carbon electrode, through the correlation of Raman spectral bands with the microstructure of carbon electrode surfaces [26-28]. Both IR and Raman SEC have proved to be dynamic techniques in providing information about electrochemical systems.

Other high-resolution spectroscopic techniques such as electron spin resonance (ESR) [26-32], nuclear magnetic resonance (NMR) [33], and mass spectrometry (MS) [34-35] have also been coupled with electrochemistry. Due to its high sensitivity for radical species, ESR is substantially more amenable to studying electrochemical intermediates and products and has been developed extensively. Information available from ESR spectroelectrochemical techniques is usually qualitative, highly selective and specific. However, ESR is not a very quantitative technique and has very limited use for quantitative analyses. NMR is inherently a highly selective but insensitive technique which provides structural information with high specificity but requires a high concentration of spinning sample. Coupling this technique directly with electrochemistry is rare because of technical difficulties. MS spectroelectrochemistry has demonstrated its potential usefulness in providing structural information. However, development of MS electrochemistry is limited by the instrumental constraints of the solution-vacuum interfacing.

**Spatially resolved absorption spectroelectrochemistry**

Of particular interest in this thesis is the quantitative analysis of solution species. Parallel geometry is employed in these analyses in which a monochromatic light beam of UV-visible wavelength passes parallel by the electrode surface, as shown in Fig.1. Since the parallel geometry is resolved along the \( x_e \) axis in this thesis, it is referred to as spatially
resolved SEC. A common feature among previously mentioned Spectroelectrochemical methods is that optical signals for solution analysis are integrated over the entire diffusion layer, which is heterogeneous in concentration distribution. This is a weak feature of all other SEC techniques because they can only obtain averaged information about electrochemical reactants and products over the diffusion layer. On the other hand, rays of a light beam in spatially resolved SEC probe different regions in the diffusion layer. Specifically, the primary interest of spatially resolved absorption spectroelectrochemistry (SRAS) is the concentration gradient (profile). Shown in Fig. 1-2, a concentration profile is plotted as a function of distance and time for a case of linear diffusion. The significance of SRAS can be fully appreciated by looking at the information content provided from a concentration profile. First of all, the slope of the concentration profile at the electrode surface is proportional to current, which is the information from amperometric methods. Secondly, the area underneath the profile is proportional to absorbance, which is in turn proportional to the signal obtained by OTE, reflection and Raman SEC. Thirdly, SRAS provide three-dimensional information, that is, concentration profile as a function of distance and time. This is not available from conventional electrochemical or other SEC methods. Therefore, all of the information from amperometric and absorption methods is in principle obtainable from a spatially resolved absorption spectroelectrochemical technique.

Accurately determining concentration profiles in the diffusion layer is the best way to quantify electrochemical processes in the solution phase. First, concentration profiles are important to describe the mass transport associated with heterogeneous charge transfer. Any abnormal behaviors in current could be understood with help from concentration profiles provided by SRAS. Second, intermediates which might be formed away from the electrode may hardly cause any changes in electrochemical signals, and may perturb the integrated absorbance slightly, but may be monitored selectively with SRAS. Third, since
Parallel Absorption: $A_i \propto C(x)$

$X_0 \ X_1 \ X_2 \ldots$

Absorbance $\propto \int_{0}^{\infty} C(x) \, dx$

OTE, Reflection, Raman

Fig. 1-2. Information content from SRAS. Concentration profile as a function of distance and time.
a concentration profile is a representation of distribution of an electrochemical product, any follow-up reactions in the diffusion layer can alter concentration profiles. Therefore, spatially resolved techniques in principle can be used to study homogeneous reactions initiated electrochemically by monitoring concentration profiles at different wavelengths. However, SRAS with multi-wavelength monitoring has not been applied for kinetic study and much can be learned about homogeneous reactions with SRAS. Fourth, ultramicroelectrodes have become more and more popular in modern electroanalytical chemistry. The behavior of these modern electroanalytical devices, ultramicroelectrodes and arrays, is directly related to diffusion processes. Thus, it is important to know how molecules diffuse in and out in the diffusion layer. Spatially resolved techniques can be used to understand different diffusion processes by providing concentration profiles of different types of microelectrodes and arrays.

To date, spatially resolved absorption spectroelectrochemical experiments have been conducted by passing a laser beam parallel to the electrode surface. Lasers have several salient properties for these experiments such as high power density and high collimation. Concentration profiles with high spatial resolution (4 μm) have been obtained by SRAS with a laser source [36]. This method is superior over the methods based on double beam interferometry [37], thermal deflection spectroscopy [38-39], and UV-vis absorption spectroscopy [40], which have at most a spatial resolution of about 20 μm with the concentration as high as 0.1 M. However, this method has been limited to a few wavelengths and a narrow range of wavelength, and thus to a small number of chemical systems.

Research objectives

The initial objective of this research project was to broaden the utility and versatility of the spatially resolved absorption spectroelectrochemical technique, by adapting a
continuum light source. This technique was then used to study different electrochemical systems, and study diffusion processes at different electrode geometries.

Chapter 2 describes in detail the adaptation of a xenon arc lamp broad band source to give wavelength tunability. The performance of SRAS equipped with the new light source is evaluated against that of the laser-based SRAS. Features of multi-wavelength monitoring and spectrum acquisition by SRAS are demonstrated. The technique is then used to study diffusion processes at planar electrodes with different electrode orientations.

In Chapter 3, SRAS is applied, in combination with Abel inversion, to obtain cylindrical concentration profiles at micro-cylindrical electrodes. Since diffusion is no longer planar, cylindrical concentration profiles cannot be obtained by directly applying SRAS to the problem. Abel inversion is used to invert lateral absorbance profiles into radial concentration profiles. The effect of solution convection on voltammetric currents is also explored to reveal the unexpected diffusion dynamics in micro-cylindrical electrodes.

Chapter 4 gives an example of a kinetic study, in which SRAS is used to study the electrochemically initiated homogeneous cross reaction between chlorpromazine (CPZ) cation radical and dopamine initiated electrochemically. The study is used to determine if the reaction of CPZ« and DA is a step-wise mechanism or a disproportionation mechanism. Because of the dilution effect in microelectrodes, the reaction is studied at a micro-wire electrode (d = 25 μm) to provide more kinetic data by further perturbing the concentration distribution. The power of spatially resolved SEC for kinetic study of homogeneous reactions is demonstrated.

In Chapter 5, the spatially resolved imaging technique is further expanded into two-dimensional imaging experiments, using a charge-couple-device (CCD) detector. Two-dimensional as well as three-dimensional diffusion problems in ultramicroelectrodes and arrays are examined. The adaptation of the CCD detector has made the imaging technique a two-dimensional imaging system. Three imaging modes can be used. They are the
transmission mode, electrogenerated chemiluminescence (ECL) imaging mode, and normal incident reflection imaging mode. Examples are given to demonstrate the capability of the two-dimensional imaging system for obtaining heterogeneous surface electrochemical activities and two-dimensional as well as three-dimensional information in modern electroanalytical chemistry.
Chapter II
Spatially Resolved Absorption Spectroelectrochemistry Equipped
with a Continuum Light Source for Imaging Experiments
at Planar Electrodes

Background

The magnitude of the current for an electrochemical process involving an electrode in solution is determined in part by mass transport resulting from diffusion [41,42], convection [43,44], and migration [45,46]. For finite current processes involving either diffusional or convective mass transport, there are concentration gradients in the solution near the electrode surface that provide the driving force for mass flow. The involvement of mass transport in electrochemistry is widespread in the areas of electrosynthesis, electroanalysis, biological electrochemistry and electrochemical engineering. Due to the fundamental importance of mass transport to electrochemical processes, significant theoretical and experimental efforts have been expanded to study the shape and dynamics of concentration vs. distance profiles. Observing the shapes and behavior of concentration profiles experimentally is challenging because the electrochemical boundary layer is thin, usually about 100 μm for electroanalytical and hydrodynamic systems. Therefore, it is important to determine concentrations in the diffusion layer accurately with a spatial resolution of 10 μm or less.

Existing spectroelectrochemical techniques for spatially determining the diffusion layer of an electrochemical system involve a light beam passing parallel to the active surface of
a planar electrode. There are two groups of methods, based on the measured variables -- index of refraction and absorption. Interferometry is the technique developed earlier wherein the change of refractive index is monitored during an electrochemical reaction [47-54]. The electrogenerated concentration gradient produces a corresponding refractive index gradient near electrodes which creates an interference pattern after the beam passes by the electrode. The major drawbacks of this technique are that it is nonselective, and low in spatial resolution and sensitivity. The other group of techniques, based on light absorption by electrochemical products, is usually more selective and sensitive. The absorption method, developed in our laboratory earlier, is based on a mechanical slit with a resolution of 25 µm [55,56]. Other absorption methods including the focal cylinder method of Ikeshoji [57], and photothermal deflection spectrometry [58,59], achieved spatial resolution no better than 20 µm. While other methods are being developed, such as the imaging method by Kondo et al [40], based on absorption and refractive index effects, and the thermal deflection method [38,39], based solely on refractive index effect, none can selectively observe concentration profiles at high resolution.

Spatially resolved optical methods and their relative merits have been reviewed extensively [2,47,60]. The major performance criterion for a spatially resolved probe of the electrochemical diffusion layer is resolution, defined as the minimum distance increment of the axis normal to the electrode surface for which a concentration may be determined accurately [61]. For the common case of an optical beam passing parallel to a planar electrode surface, the resolution is determined by gradients of index of refraction, the electrode length and the aperture of an optical system [61]. Most optical methods involving long electrode length (10 mm along the optical axis), and high concentrations (about 0.1 M) suffer from diffraction effects and the fact that light beams tend to bend in refractive index gradients, it is no surprise that the resolutions of these methods is no better than 50
Concentration profiles with high resolution (a few \( \mu \text{m} \)) had not been observed experimentally until the imaging method was developed in our laboratory. The imaging technique, developed by Jan [61], is based on magnification of the light beam passing parallel to the electrode followed by imaging on an array detector. Each pixel on the detector corresponds to a particular 1.25 \( \mu \text{m} \) segment of the dimension perpendicular to the active electrode surface. There is a one-to-one correspondence between the observed absorbance and the concentration in the diffusion layer of a planar electrode, and most importantly, the spatial resolution is high, sometimes < 5 \( \mu \text{m} \).

Since the imaging method is an absorbance-based technique, it has the additional advantage of selectivity and sensitivity, thus permitting analytical applications [62] or the examination of multi-component reaction mechanisms [63]. A recent report by Engstrom discusses a microelectrode-based probe of electroactive species in the diffusion layer with a resolution of a few micrometers [64,65], (a major achievement of electrochemical methods in obtaining concentration profiles.) The optical spatially-resolved imaging method has the advantage of being "noninvasive", with the probe having no effect on the diffusion layer. In addition, the optical imaging method can provide a complete concentration profile in a single experiment. The laser used in Jan's studies [61] provides excellent collimation and sufficient intensity requirements important to perform SRAS, but it is expensive and constrains the choice of wavelength to a few values or a narrow range of values. If broad wavelength selection were available, the potential application of SRAS would be broadened to a wider range of chemical systems. The objectives of the present work include the expansion of SRAS to the entire visible wavelength range using a continuum rather than a laser source. In addition, SRAS equipped with continuum source is applied to different electrode geometries, including a twin working electrode configuration, to study the
diffusion process under electrolytic conditions, (one of the fundamental processes in 
 electrochemistry.)

Experimental

Source and Optics.

Requirements of light beam. The optical configuration, using both a laser and a xenon arc lamp for imaging experiments, is shown in Fig. 2-1. All components were mounted on a 4 x 8 ft. optical table with pneumatic vibration isolation (RS - series, Newport Research Company, Fountain Valley, CA). The magnifying lens (L4 and L5) and array detector were identical to those described previously [61,66]. The magnification was calibrated with a "minigrid" electrode. The source was a 150 W compact xenon arc (Model 02-150X, USH10, Japan) in a f/4.5 lamp housing and LPS 200 power supply (Photon Technology International, Princeton, New Jersey). In order to maintain spatial resolution and signal-to-noise ratio comparable to a laser, a continuum source must include three important qualities of the laser source: low divergence, high irradiance (W/cm²) and a small diameter beam spot. The divergence must be low to avoid resolution degradation by light passing non-parallel to the electrode surface. If the half divergence angle is less than 1°, then a worst case input ray will sample a 3.5 μm section of the diffusion layer while traveling across a 200 μm electrode. In other words, this divergence yields a spatial resolution of less than 4 μm. Since this value is comparable to the diffraction limit [61], a half divergence angle of less than 1° is acceptable. High irradiance is necessary to assure that the light passing through the diffusion layer is intense compared to stray light from solution scatter, dust, etc. Experience with laser sources indicated that a 1 mW/cm² irradiance over a 0.6 mm diameter beam at the electrode was sufficient. A small beam spot (diameter/area) further assures that the stray light problem is minimal. Thus the source design must achieve
1. Xenon arc lamp.
2. Heat absorbing glass.
3. Pinhole.
4. Interference filter.
5. Iris 1.
6. Iris 2.
7. Pt strip electrode.
8. Array detector.

$L_1$: $f_1=31$ mm, $d_1=17$ mm (achromatic).
$L_2$: $f_2=60$ mm, $d_2=30$ mm (achromatic).
$L_3$: $f_3=-5$ mm, $d_3=6$ mm.
$L_4$: $f_4=100$ mm, $d_4=31.5$ mm (achromatic).
$L_5$: $f_5=380$ mm, $d_5=76$ mm.
$f_6=86.7$ mm.

Fig. 2-1 Optical apparatus for spatially resolved imaging experiments.
<1° half divergence angle and 1 mW/cm² irradiance, with a beam cross section at the electrode of less than 1 mm. All three of these specification are critical to maintaining resolution and minimizing stray light.

Selection of proper optical components is based on the following calculations. Assume that the focused light spot on the pinhole from the lamp is 3 mm in diameter. Then, according to the manufacturer's claim that there is 2 mW/nm power output from the light source, a 150 W lamp will give an irradiance of (2 mW/nm)/(0.07 cm²) = 28.3 mW/cm²-nm at the pinhole. After going through a 100 μm pinhole, the power is only (28.3 mW/cm²-nm)x(7.85x10⁻⁵ cm²) = 2.22 μm/nm. A 10 nm bandwidth and 50% transmittance interference filter will give an energy of 11 μW and an irradiance of 3.93 mW/cm² at the electrode, if the beam spot is 600 μm, assuming 100% transmission of all optical components. Given the f/4.5 of the lamp housing, the half convergence angle before the pinhole is tanθ = 1/(2f/d), or θ = 6.34°, which is the same as the half divergence angle after the pinhole. In order to achieve a beam of < 1° half divergence angle by using a single lens for collimation after a 100 μm pinhole, the image distance (i) has to be at least 6 times the object distance (o) of the collimating lens (since θ₂ = θ₁(o/i)). Furthermore, because of the space constraint, the lamp housing cannot be closer to the cell than 25 cm. Taking magnification into consideration, the light beam is greater than 1.0 mm in diameter after traveling a distance of 50 cm. As a result of this arrangement, the beam diameter is large and the irradiance is inevitably low, although the beam satisfies the required collimation. Therefore a single lens optical arrangement does not give satisfactory beam qualities for imaging experiments. A final design uses a telescopic lens system (a combination of a positive and a negative lens) [67] in front of the electrode. The telescopic lens system functions to reduce the beam diameter. As will be shown later, the beam generated by a telescopic lens system gives the required qualities.
Optical alignment. With the present optical arrangement shown in Fig. 2-1, the following alignment procedures were used. The xenon arc lamp was focused onto a pinhole by adjusting the three set screws on the back of the lamp housing. A pinhole of 100 µm was built on a 5x5 cm² stainless steel bracket, positioned at 288.4 mm from the front of the lamp housing. Lens 1 (d₁=17 mm, f₁=31 mm, achromatic doublet, Melles Griot, CA) was positioned approximately 31 mm away from the pinhole bracket. The height and left-right position of lens 1 was adjusted to give a nearly perfect visual image of the arc source. A carpenter square was used to check the height of the beam along the optical axis to make sure the light beam traveled straight. Occasionally, the orientation of the lamp housing had to be adjusted to correct the traveling course of the light beam. By focusing at the detector (adjusting the position of lens 1) the light beam was directed with the aid of a carpenter square to go through the center of a rotational stage (which is the center of the imaging electrode), and then to the array detector. Lens 2 (d₂=30 mm, f₂=60 mm, achromatic doublet, Melles Griot, CA) was then put into the optical train about 9 cm away from the electrode supporter in such a way that the center of the beam did not change after lens 2 was introduced. Lens 3 was so positioned that it was about 5 cm away from the rotational stage (the electrode supporter) in order to have a small beam spot at the electrode. Lenses 1 and 2 were adjusted, in combination, to achieve the best beam spot. The traveling course of the light beam was checked after lens 3 with a carpenter square to make sure that the beam was directed toward the detector. Any one of the five axes of the lens 3 holder was adjusted if necessary to accomplish the goal. Finally, lens 4 and lens 5 were positioned into the optical train according to the procedure outlined by Jan [66].

There were two irises between the two mirrors, separated by about 15 cm. Under normal operating conditions, the light beam went through the centers of these two irises. Their function was to assist in adjusting the traveling course of the beam after each
replacement of the lamp. When a laser source was needed, it came from the back of mirror 1, then traveled through the centers of the two irises. Infrared radiation was filtered out by a heat-absorbing glass (d=60 mm, thickness=6 mm, Cord Camera, Columbus, OH) positioned at one-third of the distance between the pinhole and lamp housing. Wavelength selection was accomplished by interference filters (Edmund Scientific, MA) placed after lens 1. Since lenses 1, 2 and 4 are achromatic doublets, little or no adjustment was needed when changing interference filters of different wavelengths. Final optimization of the beam intensity was accomplished by adjusting the focusing of the xenon arc lamp, lens 1 and lens 2, to achieve the highest intensity of the light beam shown on the detector screen.

**Preparation of Imaging Electrodes and Electrochemical Cells**

Having a good imaging electrode is an important part of an imaging experiment because a smooth electrode and a sharp edge will give a good image of the electrode edge. Polishing procedure was not ordinary. A detailed description of preparation of an imaging electrode has been given by Jan [66]. A brief outline is given here. As shown in Fig. 2-2, a stainless steel clamp was used to fix a platinum strip electrode. Starting from about 400 grit sand paper, the whole stainless steel block was pushed gently against the polishing wheel (Material Sciences Lab, OSU). After about 10 min of polishing, the stainless steel block was rinsed with water and then examined under a microscope. It was ensured that scratches were even over the electrode surface before going on to the next finer polishing material. After 600 grit sand paper, the electrode was polished with diamond compounds, starting from particle size of 15 μm and moving to 6, 3, 1, and 0.25 μm. Lapping oil was used for lubrication during polishing with diamond compounds. After each polishing, the surface was covered with a layer of soap before rinsing, to protect the smoothness of the surface. The soap and the polishing material were then thoroughly rinsed with water before examining the surface under a microscope. A final polishing was performed with 0.05 μm alumina
Fig. 2-2. Stainless steel clamp for polishing imaging electrodes.
polishing material on microcloth, lubricated with slow dripping of water. When the polishing was finished, the electrode was carefully taken out of the stainless steel block. The electrode was rinsed thoroughly with water.

Before each experiment, the platinum strip electrode and two microscope slide glasses were cleaned with concentrated sulfuric acid. The container was covered with a watch-glass and the acid heated for 15 min on a hot plate. After the acid was cooled to room temperature, the electrode and two glasses were rinsed thoroughly with nanopure water. The electrode and two glasses were dried with Kimwipe tissues. Care was taken not to touch the imaging edge of the electrode, and the electrode and two glasses were blown dry with high purity nitrogen or argon gas.

Three working electrode geometries were employed in this work. The cell thickness along the optical axis was measured spectrophotometrically to be 210 μm, by filling it with known concentrations of Fe(CN)$_6^{3-}$ solutions. Electrodes were oriented relative to the optical beam as shown in Fig. 2-3. A "vertical diffusion" configuration refers to the geometry employed previously with a laser source [61], with the diffusion downward. In the "horizontal diffusion" configuration, the light beam strikes on the vertical edge at the electrode and diffusion is horizontal. In the twin electrode geometry, the beam passes between two opposing parallel faces spaced 750 μm apart. Construction of the electrochemical cell and the assembly of the electrode holder are shown in Fig. 2-4 (b). The working electrode was sandwiched between two microscope slides. The electrode and thin layer cell assembly was mounted on a custom stage, as pictured in Fig. 2-4 (a), to provide movements along the y-direction. (Movements along the y-direction were important to experiments with horizontal diffusion and twin electrode geometries.) This custom stage was then mounted to two rotational stages and one translational stage. (Newport Corp. Fountain Valley, CA). A thin layer cell was formed inside the slides when they were dipped into solutions.
Vertical Diffusion Orientation

Horizontal Diffusion Orientation

Twin Electrode Orientation

Light Beam

Fig. 2-3. Electrode orientations with respect to incoming light beam for imaging experiments
Fig. 2-4 (a) Custom translational stage for movements of imaging electrodes along y direction. (b) Imaging electrode and thin layer cell assembly, which is mounted onto the stage shown in (a).
For the reduction of Fe(CN)$_6^{3-}$, the potential was stepped from 0.55 V to 0.00 V vs. SCE, while for the oxidation of Fe(CN)$_6^{4+}$, the potential was stepped from 0.00 V to 0.55 V vs. SCE. For twin electrode experiments, the potential was controlled with a conventional potentiostat, with one electrode acting as the working electrode, the other the auxiliary. All twin electrode experiments involved equimolar solutions of ferri- and ferrocyanide to avoid any undesirable products at the auxiliary electrode. The potential was set at $E^\circ = 0.22$ V before electrochemical experiments, and stepped to 0.55 V vs. SCE for oxidation at the anode. Because ferri- and ferrocyanide were in equimolar concentration, an equal amount of Fe(CN)$_6^{3-}$ was expected to be reduced at the cathode when Fe(CN)$_6^{4+}$ was oxidized at the anode. Potential controlled over the CPZ system needed closer attention because CPZ$^+$ is the product of only the first electron transfer. The electrochemical and subsequent chemical behavior of the CPZ system have been studied extensively [68-70]. The well known behavior of CPZ and our interest in studying reaction mechanisms dictated choice of this system. CPZ cation radical is stable up to 20 sec in acidic medium (below pH 0.3). As shown in Fig. 2-5, there are two one-electron transfer processes. The first electron transfer is a reversible process, corresponding to the formation of the cation radical. The second electron transfer corresponds to the formation of the dication, which rapidly hydrolyses to sulfoxide [69]. Therefore, the potential had to be accurately controlled, especially in the thin layer cell. A cyclic voltammogram of CPZ in a thin layer cell with the imaging electrode was obtained to determine the proper potential range, as shown in Fig. 2-5 (b). The potential was stepped from 0.20 to 0.90 Volt vs. SSCE. Since the auxiliary electrode was remote from the thin layer region probed by the optical beam for single working electrode experiments, any electrolysis products formed at the auxiliary electrode will not interfere with the observations. The reference electrode was located outside of the solution region formed by the microscope slides for all electrode geometries.
Fig. 2-5. Cyclic voltammograms of CPZ, $v = 100$ mV/sec, 1 M HClO$_4$, 42% MeOH/H$_2$O. (a) CV with BAS electrode. (b) CV with imaging electrode in thin layer cell.
Chlorpromazine HCl (CPZ), K$_4$Fe(CN)$_6$ and K$_2$Fe(CN)$_6$ were used as received. CPZ solutions were prepared in 42% (W/W) methanol/water containing 1 M HClO$_4$ (doubly distilled, GFS Chemical Company, Columbus, Ohio), spectral grade methanol was used for all experiments. After the 42% MeOH/H$_2$O, 1 M HClO$_4$ solvent was prepared, it was usually set aside for several hours or overnight to let it equilibrate. Due to the heat of solvation, freshly mixed MeOH/H$_2$O solvents generate air bubbles, which will upset imaging experiments. Before preparing CPZ solutions, the MeOH/H$_2$O solvent was degassed with Ar gas, which was presaturated with methanol. The oxygen content in air equilibrated solvents is usually high enough to oxidize the CPZ. In order to assure complete dissolution, one ml of pure methanol was added to dissolve the CPZ before adding the bulk solvent. All Fe(CN)$_6^{3/-4}$ solutions were prepared in 1 M KCl with nanopure water. The temperature of the solutions was checked periodically in the electrochemical cell and equaled the ambient temperature of 22°C. The cell design and need for optical access prevented thermostatic operation.

Timing between the electrochemical and spectroscopic experiments was provided by an XT compatible Computer. The control diagram is shown in Fig. 2-6. Before an electrochemical experiment, the computer sent out a 10 ms pulse from the digital I/O Port to trigger the controller of diode array detector (Tracor Northern) for obtaining an I$_0$ beam profile (the reference beam). After a delay of 20 ms, depending on the time needed for taking the I$_0$ profile, the computer sent out another 10 ms pulse from the D/A channel to trigger the potentiostat for a chronoamperometric experiment. A few seconds later (this is the actual time of an electrochemical experiment), the computer sent out a second digital I/O pulse to trigger Tracor Northern for taking the I beam profile. The potential was triggered back to the initial value by the computer. The absorbance profile was calculated with the software provided by Tracor Northern to view the result of an experiment. Instead
Fig. 2-6. Timing-control diagram for imaging experiments.
of transferring the absorbance profile, the two beam profiles were transferred from Tracor
Northern to an IBM compatible personal computer. The two beam profiles were then
processed according to Beer's law and any necessary manipulations by Hyperplot software
(JHM International, Columbus, Ohio).

Results and Discussion

Performance of the xenon arc lamp as a light source for imaging experiments.

In order to thoroughly understand the behavior of the lamp, beam profiles of different
optical arrangements were recorded, as shown in Fig. 2-7, to compare the quality of beams
under different conditions. As would be expected, there is a fundamental trade-off between
divergence and intensity. A beam of lower intensity has smaller divergence, as is the case
when only lens 1 was used to collimate the beam after a 100 μm pinhole, as pictured in Fig.
2-7(a). Using lenses 2 and 3, the beam divergence is bigger (but still within the
requirements), but the irradiance is increased by a large amount because the energy is
packed into a smaller area. This effect can be seen in Fig. 2-7 (b). Given the interference
of stray light from a wide beam, a 220 μm FWHM beam diameter at the electrode was a
good compromise, with a divergence of 0.6°. A larger pinhole leads to a brighter beam, but
greater divergence and beam width. This effect is shown in Fig. 2-7(c). The 100 μm
pinhole and 520 μm FWHM beam width yielded the required divergence and irradiance for
a 10 nm interference filter band width. Experience shows that a beam of at least 1500
counts at the center of a beam profile detected by the photodiode array detector will give
results with good signal-to-noise ratio. This corresponds to about 3 μW over a 520 μm
FWHM beam width. Spectral distribution of the light beam at the present optical setup is
another aspect of the beam performance. Fig. 2-8 (a) shows a typical transmittance curve
of an interference filter with a spectral bandwidth of 8 nm. The selectivity of wavelengths
Fig. 2-7. Beam intensity profiles from xenon arc lamp recorded by photodiode array detector.

(a) 100 μm pinhole, collimated by lens 1 only. Half divergence angle $\theta = 0.20^\circ$, FW = 2 mm.

(b) 100 μm pinhole, collimated by lens 1, then reduced by telescopic lenses 2 and 3. Half divergence angle $\theta = 0.60^\circ$, FWHM = 520 μm.

(c) 150 μm pinhole, collimated by lens 1, then reduced by telescopic lenses 2 and 3. Half divergence angle $\theta = 0.86^\circ$, FWHM = 700 μm.
Fig. 2-8. (a) Transmission curve of interference filter at 520 nm (obtained spectrophotometrically).
(b) Wavelength selectivity by interference filters in 400-700 nm range.
was available with interference filters over the visible range, as shown in Fig. 2-8 (b). The spectral intensity of the light beam over the visible range is the product of the spectral emission curve of the arc lamp (Fig. 2-9 (a)), the transmittance curve of the heat absorbing glass (Fig. 2-9 (b)), the percent transmittance of different interference filters (Fig. 2-8 (c)) and the spectral sensitivity curve of the detector (Fig. 2-9 (c)), assuming a flat optical transmission of all other optical components. The relative intensity of the light beam over the visible range was estimated, by multiplying different spectral curves of the major optical components in the optical train. As can be seen from Fig. 2-10, the measured relative intensity follows the same trend as the estimated intensity. The low intensity of the light source in the blue end is due largely to the low quantum efficiency of the detector. Taking source output and the transmission of optical components into account, the measured overall signal strength at 400 nm is 24% that at 575 nm, resulting in somewhat reduced signal-to-noise ratio in the blue.

Performance of SRAS equipped with the xenon arc source

A detailed description of a well focused electrode edge has been given by Jan [66]. A check of the beam quality for imaging experiments is to look at the image of an electrode edge. As stated by Jan [66], the beam profile of a well-focused electrode edge should have four diodes on the rising portion. The Tracor photodiode array detector has a photodiode every 25 μm and four diodes occupy 100 μm on the image, which implies a spatial resolution of less than 5 μm when taking the consideration of 20 times magnification. Though this image is also related to the quality of the electrode edge, four diodes along the rising portion on the transition from dark to bright implies a spatial resolution about 4 μm. The image obtained by a light beam from the xenon lamp also gives four diodes along the rising portions, as shown in Fig. 2-11, indicating that the light beam from the xenon arc lamp is comparable to a laser. The performance of the continuum source SRAS apparatus for the
Fig. 2-9.  (a) Spectral emission curve of xenon arc lamp (data from xenon arc literature, (b) Transmittance curve of heat absorbing glass. (c) Spectral sensitivity of silicon photodiode array detector (data from Tracor literature).
Fig 2-10. Relative spectral intensity of SRAS system.
Closed circles: estimated by multiplying curves of Fig 2-8 (b) and Fig 2-9 (a), (b), (c) together. Normalized to highest intensity.

Open circles: Peak counts(power) of beam profiles measured at different wavelengths by diode array detector. Normalized to highest intensity.
Fig. 2-11. Image of a well-focused electrode edge by a light beam from xenon arc lamp. There are four diodes along the rising portion in the transition from low to high intensity.
case of an electrogenerated absorber is shown in Fig. 2-12. The slightly poorer performance of the continuum source compared to a laser [61] at short distances from the electrode and short times results from the larger divergence and low irradiance of the arc source. The lower irradiance (W/cm²) of the arc source leads to a slightly noisier concentration profiles compared to the laser-based experiments. A double potential step chronoamperometric experiment was also performed to test the spatial resolution of SRAS equipped with the continuum source, with results plotted in Fig. 2-13 (a). The region shown in Fig. 2-13 (b), with expanded abscissa demonstrates a deviation of experiment from theory for x_e < 5 μm, indicating that the actual spatial resolution for describing concentration profiles is less than 5 μm [61].

It was pointed out in the beginning that the initial motivation of adapting a continuum source for imaging experiments is to provide a light source for multi-wavelength monitoring of electrochemical processes and products, since a laser source is limited to a few wavelengths. Though concentration profiles are slightly noisier as compared to those in reference [61], the value of the wide wavelength range of the arc source will greatly outweigh the price of higher noise in many experiments. The wavelength tunability of the continuum source is demonstrated in Fig. 2-14, which shows a spatially resolved absorbance spectrum of electrogenerated CPZ•+. By changing the interference filter shown in Fig. 2-1, absorbance profiles at various wavelengths were obtained. As can be seen from the figure, the spectrum (triangles) acquired by SRAS technique closely follows that (circles) obtained by thin layer OTE spectroelectrochemical technique. The number and spacing of data points for the SRAS experiments will depend on the choice of interference filters. In this case, eight filters were employed which unevenly covered the 450-550 nm wavelength range. The absorbance at several distances and t = 2 sec are also plotted vs. wavelength in Fig. 2-14. The SRAS spectrum could be obtained at any distance from the electrode. This feature
Fig. 2-12. Absorbance profiles of CPZ$^+$ at 540 nm. Solid lines are experimental. Dotted lines are theoretical. Experimental times are: (a) 0.3 sec, (b) 0.5 sec, (c) 1.0 sec, (d) 2.0 sec, (e) 3.0 sec, (f) 4.0 sec.
Fig. 2-13. (a) Absorbance profiles of CPZ•+ as results of double-step potential experiments. Potential was stepped to 0.9 V vs. SSCE for 4 sec, then returned to 0.3 V. (A) 1.0 sec after the second potential step, (B) 3.0 sec, (C) 6.0 sec. (D) 15.0 sec.
(b) Expanded plot of profile (B) above. [CPZ] = 2.0 mM, 1 M HClO₄, 42% MeOH/H₂O.
Fig. 2-14. Spatially resolved absorbance spectrum of CPZ•+, 2.0 sec after a diffusion limited potential step.

Triangles (▲): at $x_c = 0$ μm.
diamonds (♦): at $x_c = 26$ μm.
Pluses (+): at $x_c = 39$ μm.
Open circles (○) are a conventional spectrum obtained with a UV-visible spectrophotometer and an optically transparent thin layer cell. Due to the decay of CPZ•+ during the time required for generation in the OTTLE cell, the ordinate of the conventional absorbance spectrum was adjusted to equal the spatially resolved absorbance at $x_c = 0$ μm and wavelength $\lambda = 520$ nm.
raises the prospect of obtaining spectra of intermediates which might be formed away from the electrode.

Access to wavelengths in the whole visible range (and perhaps in the UV region) is another objective to be achieved in this work, particularly in the blue region since wavelengths in the blue region are difficult to obtain. The availability of blue lights make it possible to study diffusion processes in an electrochemical system such as Fe(CN)$_6^{3-/4}$, a classic example of reversible systems. Since the SRAS light beam passes only through solution which is affected by the diffusion process, it is possible to monitor either the reactants or products of the electrochemical reaction, assuming suitable absorption characteristics. Fig. 2-15 shows concentration profiles for Fe(CN)$_6^{3-}$ both as reactant and as product. Profiles of Fig. 2-15(a) have the classical shape predicted by Fick's laws [153] for a diffusion controlled process below of 10 sec. Experimentally determining diffusion profiles by SRAS has several points of significance. One of them is to provide a way to measure the diffusion coefficient of an electrochemical product, which is not available by any other methods. Eq (2.1) below describes the processes in Fig. 2-15(a), while the profiles of Fig. 2-15(b) are governed by eq (2.2) which assumes diffusion limited generation of Fe(CN)$_6^{3-}$ from bulk Fe(CN)$_6^{4-}$.

\[
C_R(x,t) = C_R^b \text{erf} \left[ \frac{x}{2\sqrt{D_R t}} \right] \\
C_p(x,t) = C_R^b \left[ \frac{D_R}{D_p} \right]^{1/2} \left\{ 1 - \text{erf} \left[ \frac{x}{2\sqrt{D_p t}} \right] \right\} 
\]

where R stands for reactant, and p for product. Note that $D_R$ affects the magnitude of $C_p$ in eq (2.2), while the depth of the profile is determined by $D_p$. In contrast, the integrated concentration profile, as measured by normal incidence chronoabsorptometry [62] depends
Fig. 2-15. Concentration profiles of Fe(CN)$_6^{3-}$ obtained under vertical diffusion conditions at 420 nm wavelength.

(a) Concentration profiles of 9.50 mM Fe(CN)$_6^{3-}$ consumed by reduction at the electrode. The experimental times are (from left to right): 1, 2, 4, 6, 8, 10, 20, 30, 40, 50 sec, and 3, 5, 10, 15 min. The dotted lines are simulated profiles at 10, 20, and 50 sec.

(b) Concentration profiles of Fe(CN)$_6^{3-}$ generated by oxidation of Fe(CN)$_6^{4-}$. The experimental times are (from left to right): 1, 2, 4, 6, 8, 10, 20, 40, 60 sec, and 5, 10, 15 min.
Fig. 2-15.
on $D_R$. Thus SRAS provides a means to determine the product diffusion coefficient from the depth of the observed SRAS profile. For comparison, neither the forward or reverse absorbance for single- or double-step chronoabsorptometry depends on the product diffusion coefficient [71], nor does the forward or reverse current for double-step chronoamperometry [153]. Double step methods are insensitive to the product diffusion coefficient because the rate of diffusion of the product away from the electrode equals the rate of diffusion back to the electrode, regardless of the magnitude of the diffusion coefficient. However, concentration profiles measured by SRAS are fundamentally dependent on the diffusion coefficient of either the reactant or the product, in this case the product diffusion coefficient. Since Fe(CN)$_6^{3-}$ is being monitored in both experiments as a reactant and a product, the diffusion coefficients from these processes should be the same. Rearranging eq (2.1) gives eq (2.3)

$$\frac{C_R(x,t)}{C^b} = \text{erf}\left[\frac{x}{2\sqrt{D_Rt}} \right] = \text{erf}[Z]$$  \hspace{1cm} (2.3)

At $x = (D_Rt)^{1/2}$, the inverse error function at $Z=0.5$ gives $C_R(x,t)/C^b=0.522$, or $C_R(x,t) = 0.522C^b$. That is, at one diffusion layer thickness, the concentration of reactant is 0.522 that of the bulk concentration. In this way, the diffusion coefficient of Fe(CN)$_6^{3-}$ as a reactant was determined to be $(6.79 \pm 0.04) \times 10^{-6}$ cm$^2$/sec. By curve-fitting eq (2) to the profiles in Fig.2-15 (b), the diffusion coefficient of Fe(CN)$_6^{3-}$ as a product was determined to be $(6.8 \pm 0.10) \times 10^{-6}$ cm$^2$/sec. These values are 11% lower than the literature value [72]. According to Meites, lowering of the experimental temperature has a large effect on diffusion coefficients. The temperature coefficient of diffusion coefficients is given below [73]:
\[
\frac{1}{D^°} \frac{dD^°}{dT} = \frac{dD^°/D^°}{dT} = \frac{1}{\lambda^°} \frac{d\lambda^°}{dT} + \frac{1}{T} \tag{2.4}
\]

where, \(\lambda^°\) and \(D^°\) are the equivalent conductance and diffusion coefficient at infinite dilution. The temperature coefficient of equivalent conductance is

\[
\frac{1}{\lambda^°} \frac{d\lambda^°}{dT} = \frac{d\lambda^°/\lambda^°}{dT} = 0.02 \text{ /degree} \tag{2.5}
\]

This relationship is exactly true only at infinite dilution, but it does not appear to be seriously in error under polarographic conditions [73]. For most ions the temperature coefficient of the equivalent conductance is very close to +0.02 per degree. Therefore, for a three degree decrease in temperature in these experiments, the diffusion coefficient of \(\text{Fe(CN)}_6^{3-}\) is expected to decrease by 7% from \(7.63 \times 10^{-6} \text{ cm}^2/\text{sec}\) [72] to \(7.10 \times 10^{-6} \text{ cm}^2/\text{sec}\).

The higher concentration of both analyte (9.5 vs. 4 mM) and supporting electrolyte (1.0 M vs. 0.8 M) would further lower the value determined by this method [74].

It is not the purpose of this work to question the literature value for the diffusion coefficient of \(\text{Fe(CN)}_6^{3-}\), nor do the current results justify doubt of the accepted value. However, several points about determination of diffusion coefficients by SRAS need to be addressed. First, diffusion coefficients of both reactant and product may be determined with SRAS, which is not the case in chronoamperometry and chronoabsorptometry. Second, the SRAS determination of diffusion coefficient based on curve fitting of Fig. 2-15(b) depends only on the accuracy of the \(C\) vs. \(x\) profile, with errors in \(C^b\), \(D_r/D_p\), and path length being unimportant. In contrast to chronoamperometry and chronoabsorptometry, the variables of electrode surface area, concentration, molar absorptivity, absorbance, number of electrons, and current do not enter into the calculation of diffusion coefficients in SRAS.

One of the important questions in electroanalytical chemistry is the determination of the time at which diffusion reaches virtual steady state in a controlled potential experiment.
Perhaps this question can be answered from concentration profiles at long times. Plotted in Fig. 2-15 are concentration profiles of Fe(CN)$_6^{3-}$ as a reactant and a product. In Fig. 2-15 (a) concentration profiles are plotted in roughly three time ranges: 1 to 10 sec, 20 to 50 sec, and 3 to 15 min. In the 1 to 10 sec time range, concentration profiles basically follow that predicted by Fick's diffusion laws. That is, eq (2.1) can be used to describe diffusion processes under potential step conditions. This can be seen by a good agreement between the dotted profile and the solid line of the 10 sec experiment. In the 20 to 50 sec time range, the diffusion process falls behind that predicted by theory. Two dotted profiles at 20, and 50 sec are plotted in comparison with the experimental profiles. As the time increase, deviation between theory and experiment becomes larger. Finally, the diffusion process slows down more and more, and eventually the diffusion reaches virtual steady state after 5 min. In Fig. 2-15 (b) concentration profiles at 10, 15 min even fall below that of 5 min, indicating that the diffusion front is being pushed backward, presumably by the natural convection. For the cell and aqueous solutions used here, the diffusion layer half-thickness (which is defined as the thickness $x$ when $C(x, t) = 0.522C^b$, or $(Dt)^{1/2}$ for well-behavior diffusion) reached a limit of 200-300 $\mu$m at steady state (Fig. 2-16). Based on these observations, mass transport is said to reach steady state when the increase of the diffusion layer half thickness is less than 0.05 $\mu$m over a time period of 1 sec.

Several reports have appeared regarding convective effects induced by density gradients during electrochemical experiments[75-77]. For instance, unusual potential fluctuations occur when a more dense layer of Fe$^{3+}$ is electrogenerated at constant current above a bulk solution of Fe$^{2+}$ for a vertical diffusion case [76]. The oscillations were attributed to density driven convection as the Fe$^{3+}$ solution was pulled downward by gravity. If this effect is present for Fe(CN)$_6^{3-/4+}$ system, the observed profiles should be dependent on electrode orientation and the direction of any density gradients. Fig. 2-16 shows the time course of
Fig. 2-16. Plots of diffusion layer half-thickness (defined as $(Dt)^{1/2}$) vs. $t^{1/2}$. Open circles($\circ$), consumption of 9.50 mM Fe(CN)$_6$$_3$ with horizontal diffusion; squares($\square$), generation of Fe(CN)$_6$$_3$ from 20 mM Fe(CN)$_6$$_4$ with vertical diffusion; triangles($\triangle$), consumption of 9.50 mM Fe(CN)$_6$$_3$ with vertical diffusion. (a) is an expanded plot of (b).
the observed diffusion layer thickness for the Fe(CN)$_6^{3/4}$ system. The growth of the diffusion layer was independent of diffusion direction or the sign of the electrochemical current at least up to 20 sec, although the diffusion process slows down after 10 sec, as can be seen in Fig. 2-16 (a). At longer times, while the diffusion layer of vertical diffusion reaches steady-state at 200-300 μm after 5 min, the diffusion layer of horizontal diffusion became erratic after about one min. If there is anything different at all, this erratic diffusion layer can be viewed as diffusion-direction-dependent. While the Fe(CN)$_6^{3/4}$ concentration (9 mM) is high by normal electroanalytical standards, the difference in density between the Fe(CN)$_3^-$ and Fe(CN)$_6^{4-}$ is still low (Fe(CN)$_6^3^-$ solution is more dense by about 0.1%) [78]. This density difference is less than that present when Rayleigh-Benard convection was observed for Fe$^{2+/3+}$ (0.4%) [76]. Thus, conditions used here are more relevant to electroanalytical experiments than to studies of Rayleigh-Benard convection. The absence of orientational effects on diffusion layer thickness implies that the conditions employed here are not conducive to density driven convection. A high degree of vibration isolation certainly can prevent the initiation of orientation-dependent convection. Equally important are the small cell volume and thin solution layer in preventing the start of orientation-dependent convection. The effects of small cell volume and thin solution layer are more apparent in the twin electrode cell and will be explained later.

The twin electrode thin layer geometry differs significantly from experiments discussed thus far not only because of restricted diffusion but also because of the presence of two working electrodes. This geometry has been known for many years [79-80], but has come into prominence recently in the form of microelectrode arrays [81-83] and layered modified electrodes [84]. More recently, people have used the twin electrode-based interdigitated microelectrode arrays for analytical applications [85-87]. The current behavior of the twin electrode geometry has long been studied, yet the diffusion aspect of the twin electrode
geometry thin layer cell has not been studied. Using the geometry of Fig. 2-5 (c), SRAS method was used to examine transient and steady-state diffusion in the twin electrode thin layer geometry.

Experimental absorbance profiles of the twin electrode thin layer geometry are shown in Fig. 2-17. At short times, two independent profiles are observed, corresponding to Fe(CN)$_6^{3-}$ generation at the anode and Fe(CN)$_6^{3-}$ depletion at the cathode. As time progresses, a linear steady-state absorbance profile is reached. Upon closer look at the profiles, several things need to be further examined. First, absorbance at cathode are greater in absolute values than those at anode. Second, the profile corresponding to Fe(CN)$_6^{3-}$ (anode branch) reaches a linear steady state at 60 sec while that corresponding to the depletion of Fe(CN)$_6^{3-}$ (cathode branch) still has some curvature. Third, all profiles cross over from positive to negative absorbance at the same point, but the crossing point of the profile at 300 sec (5 min) shifts to the left by a small distance. Are these findings simply the experimental errors or can something else account for them?

The diffusion process at the twin electrodes in this system (equimolar concentrations of Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4+}$) can be described by eq (2.6) and (2.7), and the following boundary conditions.

\[
\frac{\partial C_{\text{red}}(x,t)}{\partial t} - D \frac{\partial^2 C_{\text{red}}(x,t)}{\partial x^2} = 0 \quad (2.6)
\]

\[
\frac{\partial C_{\text{ox}}(x,t)}{\partial t} - D_{\text{ox}} \frac{\partial^2 C_{\text{ox}}(x,t)}{\partial x^2} = 0 \quad (2.7)
\]

\[
c^b_{\text{red}}(x,0) = c^b_{\text{ox}}(x,0) = c^b \quad (2.8)
\]
Absorbance profiles from a twin electrode thin layer cell resulting from a diffusion-limited potential step to a solution of 8.00 mM Fe(CN)$_6^{3-}$ and 8.00 mM Fe(CN)$_6^{4-}$. Times progresses from bottom to top on left side of figure (and reverse on right side). Times after the potential step are 2, 4, 6, 8, 10, 20, 30, 40, 60, 300 sec.
Due to the complexity of the problem, Laplace transfer was not attempted and the problem was solved by digital simulation. Because the molar concentrations of ferro- and ferricyanide are equal, it was assumed that equal amounts of \( \text{Fe(CN)}_6^{3-} \) and \( \text{Fe(CN)}_6^{4+} \) are being oxidized and reduced at the anode and cathode respectively, even though the potential was stepped to 0.55 V vs. SCE and controlled at the anode only. The digital simulation aspect is explained in the appendix A and the simulation program (PROGRM3.FOR) is listed in appendix B. Simulation profiles are plotted in Fig. 2-18 (a) using the model diffusion coefficients in the ratio of \( D_{\text{ox}}/D_{\text{red}} \) of the Fe(CN)\(_6^{3-}/4^+\) system. Simulation profiles of equal model diffusion coefficients of ox and red are also plotted in Fig. 2-18 (b). It is clear that the asymmetry of concentration profiles is due to different diffusion coefficients of the two species in the redox couple. Using the diffusion coefficient of \( \text{Fe(CN)}_6^{3-} \) (6.8 x 10\(^{-4}\) cm\(^2\)/sec), the diffusion coefficient of \( \text{Fe(CN)}_6^{4+} \) was found to be 5.05 x 10\(^{-4}\) cm\(^2\)/sec by fitting experimental profiles with simulated profiles.

Experimental profiles from 2 sec up to 300 sec, fitted with simulated profiles, are shown in Fig. 2-19 (A) and (B). Several points are apparent from Fig. 2-19. First of all, it does not appear that there is any convection in the twin electrode thin layer cell because

\[
c_{\text{red}}^b(0,t) = 0
\]

\[
c_{\text{ox}}^b(0,t) = 0
\]

\[
D_{\text{red}} \frac{\partial C_{\text{red}}(x,t)}{\partial x} \bigg|_{x=0} = -D_{\text{ox}} \frac{\partial C_{\text{ox}}(x,t)}{\partial x} \bigg|_{x=0}
\]

\[
D_{\text{red}} \frac{\partial C_{\text{red}}(x,t)}{\partial x} \bigg|_{x=L} = -D_{\text{ox}} \frac{\partial C_{\text{ox}}(x,t)}{\partial x} \bigg|_{x=L}
\]
Fig. 2-18. Simulated profiles of Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ at twin electrode separated by 750 μm, using finite differences method. Assumed $C_{ox}^m = C_{red}^m = 1.0$. Times (from center of the figure to the top on left side) are 2, 4, 6, 8, 10, 20 30, 40, 60 sec.

(a) $D_{MB} = 0.45$, $D_{MA} = D_{MB}(D_{red}/D_{ox}) = 0.334$, where

$D_{red} = 5.05 \times 10^{-6}$ cm$^2$/sec, $D_{ox} = 6.8 \times 10^{-6}$ cm$^2$/sec are measured by curve-fitting for the system used under conditions of the imaging experiments ($D_{ox} = 6.8 \times 10^{-6}$ cm$^2$/sec has been known from the single electrode imaging experiments.)

$D_{red}/D_{ox} = 0.743$ is close to the literature value of 0.828 [72] so that qualitative explanation of the experimental results is valid.

(b) $D_{MA} = D_{MB} = 0.45$. 

Fig. 2-18.
Fig. 2-19  (A) Concentration profiles of Fe(CN)$_6^{3-}$, fitted with simulated profiles with $D_{MB} = 0.45$, $D_{MA} = D_{MB}(D_{red}/D_{ex}) = 0.334$, where $D_{red} = 5.05 \times 10^{-8}$ cm$^2$/sec, $D_{ex} = 6.8 \times 10^{-9}$ cm$^2$/sec (see text for explanation). Experimental times are (from bottom to top on the left side of the figure): 2, 4, 7, 10 20, 30, 60 sec.

(B) Concentration profiles. (a) linear profile predicted by eq (2.26); (b) simulated profile at 300 sec, using $D_{MB} = 0.45$, $D_{MA} = 0.334$; (c) experimental profile at 300 sec; (d) experimental profile at 60 sec; (e) simulated profile at 2 sec, $D_{MA} = 0.334$, $D_{MB} = 0.45$. 

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Fig. 2-19.
the fitting between simulated and experimental is so consistent for such a large time range, from 2 sec up to 60 sec. Second, concentration profiles at the twin electrodes are better for determining both coefficients at once because two branches, independent of each other, needed to be fitted separately. No good fitting can be found for both branches until two coefficients are right. Third, results from both the single electrode experiments (page 41) and the twin electrode experiments give $6.8 \times 10^{-6}$ cm$^2$/sec as the diffusion coefficient, which implies this value is indeed a good number at least for this system. Because of the difference in diffusion coefficients for this system, there is a "diffusion-lag" effect at the anode region when Fe(CN)$_6^{4-}$ diffuses into the electrode and diffuses out after being converted into Fe(CN)$_6^{3-}$ at the anode. The effect of "diffusion-lag" is manifest in such a way that concentration profiles at the anode region is lower than would be if the two diffusion coefficients were equal. The simulated profiles of Fe(CN)$_6^{4-}$ at the cathode, plotted in Fig. 2-18 (a), can then be viewed as the "diffusion delay". Materials are built up in the cathode region, as a result of the difference in diffusion coefficients. Since the branches at the anode are lower in absolute values, diffusion reaches a linear profile before the branch at the cathode. Consequently, a small curvature is seen in the experimental profile of 60 sec at the cathode, even though the section at the anode has become linear. Finally, the section of profile at the cathode slowly approached linearity, until the entire profile became linear. It is in this process that the zero crossing point of the profile slowly shifted away from that of those profiles at short times.

The behavior of concentration at steady state can be understood in the following way. Consider a case where two planar electrode are oriented parallel to each other, one at $x_e = 0$, one at $x_e = L$, with the solution between them containing initial concentrations of Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$ ($C_{red}^b$), plus supporting electrolyte. $C_{ox}$ is the absorbing species in the Fe(CN)$_6^{3/4}$ case, and the absorbance is defined in a usual way, according to eq (2.13).
\[ A(x_e, t) = \log \left[ \frac{I_{\text{init}}(x_e)}{I(x_e, t)} \right] \]  

(2.13)

where \( I_{\text{init}}(x) = \) initial transmitted intensity (as attenuated by \( C_{\text{ox}}^b \)) and \( I(x, t) = \) transmitted intensity at time \( t \) after electrolysis is initiated. Suppose that a diffusion limiting potential is applied across the cell, such that \( C_{\text{red}}(0, t) = 0 \), and \( C_{\text{ox}}(L, t) = 0 \). At \( t = \infty \), a steady state will be reached where linear concentration profiles for \( C_{\text{ox}}(x) \) and \( C_{\text{red}}(x) \) should exist, and eq (2.14) - (2.16) apply.

\[ C_{\text{ox}}(x, \infty) = C_{\text{ox}}(0, \infty) \left[ 1 - \frac{x}{L} \right] \]  

(2.14)

\[ C_{\text{red}}(x, \infty) = C_{\text{red}}(L, \infty) \left[ \frac{x}{L} \right] \]  

(2.15)

\[ C_t = C_{\text{ox}}^b + C_{\text{red}}^b \]  

(2.16)

Equations (2.14) - (2.15) are based on the assumption of constant flux of ox and red for all \( x_e \) at steady state. Assuming that the sum of \( C_{\text{ox}} \) and \( C_{\text{red}} \) remains constant in the cell throughout the experiment, the following equation is obtained.

\[ \int_0^L C_{\text{ox}}(x) \, dx + \int_0^L C_{\text{red}}(x) \, dx = C_t \]  

(2.17)

Substituting eq (2.14) and (2.15) into eq (2.17) gives

\[ \int_0^L C_{\text{ox}}(0, \infty) \left[ 1 - \frac{x}{L} \right] \, dx + \int_0^L C_{\text{red}}(L, \infty) \frac{x}{L} \, dx = C_t \]  

(2.18)

Upon integration of eq (2.18), eq (2.19) is obtained:
At any time of the experiment, the following conditions hold:

\[ \frac{i_a}{nFA} = -D_{red} \left[ \frac{\partial C_{red}}{\partial x} \right]_{x=0} = -D_{red} \frac{C_{red}(L,\infty) - C_{red}(0,\infty)}{L} \]  \tag{2.20}

\[ i_c \]

\[ \frac{i_a}{nFA} = D_{ox} \left[ \frac{\partial C_{ox}}{\partial x} \right]_{x=L} = D_{ox} \frac{C_{ox}(L,\infty) - C_{ox}(0,\infty)}{L} = -D_{ox} \frac{C_{ox}(0,\infty)}{C_{ox}} \]  \tag{2.21}

Combining eq (2.20) and (2.21) gives:

\[ \frac{|i_a|}{nFA} = \frac{|i_c|}{nFA} \]  \tag{2.22}

After substituting eq (2.23) into eq (2.18), \( C_{ox}(0,\infty) \) is solved in terms of \( C_t \) and diffusion coefficients:

\[ C_{ox}(0,\infty) = \frac{2C_t}{1 + \frac{D_{red}}{D_{ox}}} \]  \tag{2.24}
Thus, eq (2.26) may be derived for the concentration profiles:

\[ C_{\text{ox}}(x,\infty) = \frac{2(L - x)/L}{1 + D_{\text{ox}}/D_{\text{red}}} \cdot C_t \]  

(2.26)

If only \( C_{\text{ox}} \) absorbs light at the wavelength employed, eq (2.13) may be combined with eq (2.14) to yield eq (2.27).

\[ A(x,\infty) = \varepsilon b \left[ C_{\text{ox}}(x,\infty) - C_{\text{ox}}^b \right] \]  

(2.27)

Where \( \varepsilon \) is the molar absorptivity of \( \text{ox} \) and \( b \) is the optical path length perpendicular to the diffusion direction in this case. In general, both \( \text{ox} \) and \( \text{red} \) may absorb, but must have different molar absorptivities. In this case, \( \varepsilon \) in eq (2.27) becomes \( \Delta \varepsilon \).

Shown in Fig. 2-19 (B) are the experimental profiles and simulated profiles at long times. For comparison, a simulated profile at 2 sec is also plotted. As can be seen, profiles c (300 sec) and d (60 sec) near the anode are practically overlapping. However, the crossing points of profiles c and d with e are not the same, indicating that c is approaching a straight line while d still has a larger curvature. Also in Fig. 2-19 (B) the simulated profile at 300 sec is approaching the linear profile predicted by eq (2.26), but there is still a small curvature near the cathode. Both a and b profiles predict that the concentrations at the anode decrease at infinity. This result does not agree with profile c at 300 sec, in which concentrations at the anode stay much higher. At this point, no further experimental data are available for explanation. However, a small amount of fresh \( \text{Fe(CN)}_6^{3/4} \) diffusing
slowly into the region near the electrode surface could contribute a large effect on the concentration profile over a long period of experimental time.

In the early discussion of convection, it was shown that there is no evidence of density-driven convection in the Fe(CN)$_6^{3/4-}$ system under the experimental conditions here and that there is no obvious dependence on diffusion direction at least for times up to 50 sec. At longer times (after 1 min), the diffusion layer thickness became erratic for horizontal diffusion. If the effects of small cell volume and thin solution layer prevent the initiation of solution convection, then these effects are more pronounced in the twin electrode thin layer geometry. Because the solution was confined in a small volume and thin layer, solution convection was vanishingly small. Further stabilization is provided by the action of electrolysis at both electrodes. Therefore, even though the electrodes are oriented vertically with horizontal diffusion, the diffusion layers were neither pushed backward nor erratic as was the case discussed in page 45. There was also no evidence of solution convection when molecules of different species were mixing at the center of the cell.

**Conclusion**

The high resolution spatially resolved absorption spectroelectrochemistry equipped with a continuum source has shown promising results. The combination of xenon broad band source and SRAS can provide concentration profiles of both reactants and products, though the concentration profiles are slightly noisier than those obtained with a laser source. Spatial resolution of SRAS with the xenon source is the same as that achieved with a laser. It broadens SRAS to many more redox systems than could be observed with a laser source. In addition, multi-wavelength monitoring of electrochemical processes and products is demonstrated to obtain absorption spectra of electrogenerated species at any distance away from the electrode if desired, within the limits of resolution and photometric sensitivity.
Concentration profiles are observable for a variety of electrode geometry and orientations, including the thin layer twin electrode case.

SRAS equipped with a continuum source is subsequently used to study the diffusion and convection aspects in electroanalytical chemistry. Concentration profiles behave in the way predicted by Fick's diffusion laws. There does not seem to be density driven convection in the time scale and concentration range relevant to electroanalytical chemistry. As time gets longer, diffusion of both reactants and products slows down and eventually reaches a virtual steady state, with a diffusion half-thickness of about 200-300 μm in the system employed here. There is no observed dependence of concentration profiles on the electrode orientation and diffusion-direction at least for times up to 50 sec, though concentration profiles are erratic at longer times in horizontal diffusion. A high degree of vibration isolation contributes significantly to the prevention of the start of convection, but equally important are the small cell volume and thin solution layer in these experiments. The effects of small cell volume and thin solution layer on the prevention of the initiation of solution convection is more evident in the twin electrode thin layer cell experiments. Concentration profiles agree with the simulated profiles consistently from 2 sec to 60 sec, with no profiles falling below the simulated ones.
Chapter III
Observation of Concentration Profiles at Cylindrical Microelectrodes
by a Combination of Spatially Resolved Absorption Spectroscopy
and Abel Inversion

Background

A variety of advantageous features have stimulated a broad research effort into the behavior of very small voltammetric electrodes [88-91]. These unusual properties include steady state diffusion-limited current, high mass flux of solution species, rapid dilution of electrogenerated products, low ohmic potential error, low cell time constant, and applications in very small volumes of electrolyte. Microelectrodes were used initially in understanding electrode mechanisms under conditions of high current density [92]. Meanwhile, miniature electrodes were being developed for use as in vivo probes [93,94]. It is clear now that many new areas which were inaccessible to electrodes of larger size can be explored with very small electrodes. After a decade of intensive study, use of microelectrodes has increased, producing dramatic improvements in the quality of electrochemical data. Directly related to the properties of microelectrodes, these improvements include increased temporal resolution (because of the reduced cell time constant), increased current density (because of the convergence of materials to the electrode surface), and decreased sensitivity to the effects of solution resistance (due to the reduced magnitude of current). New areas of research made possible by microelectrodes include submicrosecond electrochemistry [95,96], electrochemistry in gases [97], and
electrochemistry under time-independent conditions [98]. Microelectrodes have made in vivo measurement of chemical concentration possible.

Electrochemical responses at microelectrodes differ greatly from those at conventional electrodes. As pictured in Fig. 3-1, diffusion to a shielded planar electrode is one-dimensional, but in microelectrodes, molecules converge from a much larger area into a smaller area at the electrode surface and the product molecules diverge out into the bulk solution area. Consequently, special properties such as steady state current and rapid dilution of electrochemical products are obtained when the electrode size becomes small relative to \((D\tau)^{1/2}\), where \(D\) is the diffusion coefficient of the electroactive species and \(\tau\) the time scale of the experiment. Effects of these properties are pictured in Fig. 3-2, where a set of cylindrical concentration profiles is plotted in comparison with a 10 sec profile of planar electrode diffusion. Two things can be seen from the figure. First, the slopes of concentration profiles at the surface do not change much from experimental times of 0.2 sec to 10 sec, implying a virtual steady state current. Second, the concentration profile of the planar electrode at 10 sec in a distance around 40 \(\mu\)m from the electrode is about 0.8 unit, while that at a 10 sec profile of the micro-cylindrical electrode is only about 0.4 unit, implying that the concentration in the cylindrical field is diluting much faster than in one-dimensional diffusion field.

Types of microelectrodes and their general behavior, as well as their utilities and applications, have been reviewed and discussed thoroughly by others [99-101]. Of particular relevance, however, is the diffusion behavior associated with a free standing micro-cylinder electrode, such as a carbon fiber or fine metal wire electrode [91,102-104]. It is important to realize that the area of a micro-wire electrode depends not only on its radius but also on its length. Therefore, one can achieve the high mass flux characteristics at the electrode surface without requiring the measurement of small current signal against noisy background by adjusting microwire electrodes to desired lengths. Micro-cylindrical electrodes, however,
Fig. 3-1  Linear diffusion at a planar electrode and convergent diffusion at a microcylindrical electrode
Fig. 3-2  Comparison between theoretical concentration profiles of linear diffusion and cylindrical diffusion for an absorbing product generated at \( r_0 = 6 \, \mu \text{m} \) cylinder, assuming \( D = 7.63 \times 10^{-6} \, \text{cm}^2/\text{sec} \). Solid lines are for 0.2, 1, 3, 6, 10 sec after electrolysis began (counting from bottom); dotted line is for a planar electrode at 10 sec. Concentrations are relative to bulk value for reactant.
have not been used as working electrodes as extensively as other microelectrode geometries (e.g. disks, lines, spheres, etc.)

An initially unrelated effort was the development and enhancement of spatially resolved absorption spectroscopic probes of planar electrochemical diffusion layers, which has been discussed in Chapter 2, with the objective of providing time resolved concentration vs. distance profiles for both electrogenerated and electroconsumed optical absorbers. The work to be discussed in this chapter was stimulated by two interests. First, can the spatial resolution of SRAS be increased by going from a finite length electrode to micro-cylindrical electrodes 10 times smaller in diameter? Second, can the spatially resolved absorption spectroelectrochemical technique be applied to the convergent diffusion to provide information similar to that from planar electrode diffusion? Conventional electrochemical methods fail to provide information such as the shape and behavior of concentration vs. distance profiles. For mainly practical reasons, the case of a free standing microwire electrode was chosen to be studied by SRAS, with the optical beam passing perpendicular to the wire axis. The diffusion equations for the microwire have not been solved analytically because of the difficulties of a mathematical treatment of the cylindrical diffusion problem, and concentration profiles for the microwire have never been observed experimentally. In this chapter, SRAS is used in combination with Abel inversion to observe concentration vs. distance profiles of an absorber generated at a micro-cylindrical electrode. The method is subsequently used to reveal unexpected mass transport effects present during potential step experiments at the microwire.

Theory

Spectroelectrochemistry of a microwire electrode diffusion case presents two substantial theoretical problems: prediction of radial concentration profiles and inversion of an observed lateral absorbance profile to an experimental C(r) profile. The classical problem
of cylindrical diffusion was solved first by Jaeger in 1942 for the case of heat transfer from a cylindrical rod with a constant surface temperature [105,106]. The cylindrical diffusion equation of heat transfer problem is:

$$\frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} - \frac{1}{\kappa} \frac{\partial v}{\partial t} = 0 \quad (3.1)$$

where $v$ is the temperature as a function of distance $r$ and time $t$. The solution of the above partial differential equation is given by:

$$v = V + \frac{2}{\pi} \int_0^\infty e^{-\kappa u t} \left\{ \frac{J_0(ur)Y_0(ua)}{J_0^2(au) + Y_0^2(au)} \right\} \frac{du}{u} \quad (3.2)$$

where $J_0$ and $Y_0$ are Bessel functions of the first and second kind of order zero. The flux at the surface of a cylinder $r = a$ is:

$$f = -K \left[ \frac{\partial v}{\partial r} \right]_{r=a} = \frac{4VK}{\pi a^2} I(\Phi) \quad (3.3)$$

where:

- $V$ -- Constant temperature at the surface $r = a$.
- $\kappa = K/\rho c$, conductance coefficient, cm$^2$/sec.
- $K$ -- Thermal conductivity, cal/°K-cm-sec.
- $\rho$ -- Density of the medium, g/cm$^3$.
- $c$ -- Specific heat per unit mass cal/°K-g.
- $\Phi = \kappa t/a^2$.

and
The integrated result of $I(\phi)$ had been tabulated as a function of $\phi[106]$. The partial differential equation for diffusion at a cylindrical electrode is:

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} - \frac{1}{D} \frac{\partial c}{\partial t} = 0$$

(3.5)

Because of the similarities in the form of partial differential equations and boundary conditions between the heat transfer problem and the mass transfer problem in cylindrical diffusion of electrochemistry for a potential step experiment, the solution of eq (3.5) has been cast into the following form according to reference [107], with the concentration as a function of $r$ and $t$:

$$c_p(r, t) = c_R^b + \frac{2c_R^b}{\pi} \int_0^\infty \frac{e^{-\theta x^2} J_0(\tau x/r_0)Y_0(x) - Y_0(\tau x/r_0)J_0(x)}{J_0^2(x) + Y_0^2(x)} \frac{du}{u}$$

(3.6)

and the flux at the electrode surface:

$$J = \frac{i}{nFA} = -D \left[ \frac{\partial c_R}{\partial r} \right]_{r=r_0} = \frac{4c_R^b D_R}{r_0^2} \frac{I(\theta)}{\pi}$$

(3.7)

where $C_R^b$ is the bulk concentration of the reactant, $p$ and $R$ stand for product and reactant respectively, and $\theta = D_R r_0^2$, with $I(\theta)$ being:

$$I(\theta) = \int_0^\infty \frac{e^{-\theta x^2} dx}{x[J_0^2(x) + Y_0^2(x)]}$$

(3.8)
Eq (3.8) can be related to the tabulated values in reference [106] to obtain current values for chronoamperometric experiments. Others have used analytical expressions for current responses of a microcylindrical electrode [101,102,108]. For a cylinder with a radius of $r_0$ and a length $l$, and surface area $A = 2\pi r_0 l$, the unitless current is:

$$i = \frac{8}{\pi} I(\theta) = 2\pi f(\theta)$$

where $f(\theta)$ is related to the $I(\theta)$ function by the following equation:

$$f(\theta) = \frac{A}{\pi^2} I(\theta) = \frac{A}{\pi^2} \int_0^\infty e^{-\theta x^2} \frac{dx}{x [J_0^2(x) + Y_0^2(x)]}$$

An approximated analytical expression of current has been given [102] for eq (3.10)

$$f(\theta) = \frac{e^{-\sqrt{\pi \theta}/10}}{\sqrt{\pi \theta}} + \frac{1}{\ln \left[ \left[ 4\theta e^{-\gamma} \right]^{1/2} + e^{5/3} \right]}$$

so that

$$i = \frac{8}{\pi} I(\theta) = 2\pi \left\{ \frac{e^{-\sqrt{\pi \theta}/10}}{\sqrt{\pi \theta}} + \frac{1}{\ln \left[ \left[ 4\theta e^{-\gamma} \right]^{1/2} + e^{5/3} \right]} \right\}$$

where $\gamma = 0.5772156...$ is the Euler's constant.

The present work requires the calculation of concentration $C(r)$ as a function of time and distance after a potential step. Direct integration of eq (3.6) to provide $C(r,t)$ is a tedious task. Instead, digital simulation is used for calculating $C(r)$, and $i(t)$. The simulation is complicated by the usually large ratio of $(Dt)^{1/2}$ to wire radius $(r_0)$ so that a standard explicit finite difference simulation [109] is unacceptably slow to produce sufficient
accuracy. Here the expanding box algorithm and implicit approach is used to simulate \( C(r) \) [110]. Details of this algorithm are given in the appendix A. The simulated current takes the form of Fick's first law.

\[
J = \frac{i}{nFA} = \frac{D}{R} \left[ \frac{\partial C}{\partial r} \right]_{r=R_0} = D \frac{C}{R} \frac{\Delta C}{\Delta R_0} = D \frac{C}{R} \frac{C_R (1)}{\Delta R_0}
\]  
(3.12)

After making the proper substitutions into eq (3.12), the following equation is obtained (see appendix A for details)

\[
\frac{i}{nFA} \frac{b}{R} \frac{C_R (1)}{\Delta R_0} = \frac{2\pi}{\int d\tau / \tau_0} \frac{C_R (1)}{\Delta R_0}
\]  
(3.13)

where \( C_R (1) \) is the dimensionless concentration in the simulation and \( \Delta R_0 \) the increment of the dimensionless radius at the surface (which is related to the simulation parameters—see appendix A). Results of current calculations by the approximate analytical expression of eq (3.9) and (3.11), the simulated currents (3.13), and Jaeger's tabulated values using eq (3.9), are listed in Table 3-1 and plotted in Fig. 3-3. As can be seen from Table 3-1, while the analytical expression of eq (3.11) gives positive deviations in the whole time range, the simulated currents agrees with Jaeger's currents excellently with deviations from Jaeger's currents being less than 1% except for the first few points. It is clear from eq (3.11) that the simulated current may give better results by decreasing the \( \Delta R_0 \) value. The accuracy and adequacy of the digital simulation are thus verified and approved. Since the algorithm is implicit, it has the advantage of being stable even with \( \lambda \) (the model diffusion coefficient in the digital simulation) much greater than 0.5.

Since the diffusion is two-dimensional, the absorbance profile obtained by SRAS can no longer be directly related to concentration profile. This is because the absorbance along
Fig. 3-3  Theoretical current for microwire electrode, calculated from simulation (pluses), from Jaeger's approach (circles), and from twice the value for a hemicylinder electrode (triangles).
Table 3-1
Comparison of cylindrical current calculations using different methods.

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Jaeger's Current</th>
<th>Simulated Current</th>
<th>Relative to Jaeger's(%)</th>
<th>Current by Eq (3.12)</th>
<th>Relative to Eq (3.12)(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000667</td>
<td>34.24</td>
<td>32.45</td>
<td>-5.23</td>
<td>35.11</td>
<td>2.54</td>
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<tr>
<td>0.001500</td>
<td>22.97</td>
<td>22.74</td>
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<td>8.88</td>
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<td>0.006000</td>
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<td>12.82</td>
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<td>0.010667</td>
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<td>-0.10</td>
<td>11.95</td>
<td>16.1</td>
</tr>
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<td>7.702</td>
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<td>9.099</td>
<td>18.1</td>
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<td>6.139</td>
<td>-0.05</td>
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<td>5.764</td>
<td>17.7</td>
</tr>
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<td>4.460</td>
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<td>2.22</td>
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</tr>
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</table>
the x axis is the integration of the absorbance in each box in the diffusion field along the y axis, as diagrammed in Fig. 3-4. The problem of calculating C(r) from the lateral absorbance profile A(x) determined at the diode array is an example of a general class of inversion problems faced in tomography. The case of a cylindrically symmetric source of light has been addressed by spectroscopists studying inductively coupled plasma (ICP) emission sources [111-114]. The approach, known as Abel inversion, has been discussed in the ICP literature. The basic idea behind the approach is to divide the diffusion field into concentric rings and lateral zones. If the division is in such a way as depicted in Fig. 3-4 and fine enough, then each absorbance point along x axis can be approximated by adding the absorbance in each region along y axis, assuming that the Beer's law holds in each box. Consider a case of four rings and four lateral zones. Apparently, the radial concentrations are related to lateral absorbances through the areas confined by lateral zone i and radial ring j, symbolized as S_{ij} [114]. As pictured in Fig. 3-4, S_{ij} is the area bounded by two circles, one of radius j and one of radius j-1, and further bounded in a direction perpendicular to, and co-planar with, the viewing direction by zonal boundaries at lateral displacements i and i-1 from the optical axis. Calculations of all areas follow the steps below[114]:

(1) When i > j, there is no overlap between j ring and i zone, therefore

\[ S_{ij} = 0, \quad i > j \]  \hspace{1cm} (3.14)

(2) For those segments with i = j, one edge is along the diameter perpendicular to the optical axis, the area is given by:

\[ S_{ij} = \int_{x_{i-1}}^{x_i} dx \int_{0}^{\sqrt{r_j^2 - x^2}} dy, \quad i = j \]  \hspace{1cm} (3.15)
Abel Inversion Geometry

Fig. 3-4 Abel inversion applied to absorbance at microwire electrode. S values are the areas of irregularly shaped sections of the cylindrical diffusion profile; \( \Delta r \) is the radius increment, which equals the detector pixel \( \Delta x \) divided by the magnification.
(3) For those segments with \( i < j \) condition, the area is given by the following formula:

\[
S_{i,j} = \int_{x_{i-1}}^{x_i} \sqrt{\frac{x^2}{r_j^2 - x^2}} \, dx, \quad i < j
\]  

(3.16)

Take eq (3.15) as an example for calculation. After the first integration, eq(3.15) becomes:

\[
S_{i,j} = \int_{x_{i-1}}^{x_i} \frac{x^2}{r_j^2 - x^2} \, dx, \quad i = j
\]  

(3.17)

This integration can be evaluated by substituting \( x = r_j \cos(t) \), and \((r_j^2 - x^2)^{1/2} \, dx = -r_j^2 \sin^2(t) \) 

\[-(r_j/2)(1 - \cos^2 t) \, dt, \text{ so that}
\]

\[
S_{i,j} = \int_{x_{i-1}}^{x_i} \frac{x^2}{r_j^2 - x^2} \, dx, \quad i = j
\]  

(3.17)

\[= -\frac{r_j^2}{2} \int_{x_{i-1}}^{x_i} (1 - \cos 2t) \, dt
\]

\[= -\frac{r_j^2}{2} \left[ t - \frac{1}{2} \sin(2t) \right]_{x_{i-1}}^{x_i}
\]

\[
S_{i,j} = -\frac{r_j^2}{2} \left[ \cos^{-1} \left( \frac{x_{i-1}}{r_j} \right) - \left( \frac{x_{i-1}}{r_j} \right)^2 \right]^{1/2}
\]  

(3.18)

Since \( r_j = j \Delta r \), \( x_{i,1} = (i-1) \Delta x \), and \( \Delta x = \Delta r \), eq (3.18) becomes:
Similarly, eq (3.16) can be integrated to give:

\[
S_{ij} = \frac{1}{2} \left\{ \cos^{-1}\left[ 1 - \frac{j - 1}{j} \right] - \frac{j - 1}{j} \sqrt{1 - \left( \frac{j - 1}{j} \right)^2} \right\} \Delta x^2
\]  

Similarly, eq (3.16) can be integrated to give:

\[
S_{ij} = \frac{1}{2} \left\{ \cos^{-1}\left[ 1 - \frac{j - 1}{j - 1} \right] - \frac{j - 1}{j - 1} \sqrt{1 - \left( \frac{j - 1}{j - 1} \right)^2} \right\} \Delta x^2 - \frac{(j-1)^2}{2} \left\{ \cos^{-1}\left[ 1 - \frac{j - 1}{j - 1} \right] - \frac{j - 1}{j - 1} \sqrt{1 - \left( \frac{j - 1}{j - 1} \right)^2} \right\} \Delta x^2
\]

The absorbance obtained at the detector for a four element case is approximated by eq (3.21) - (3.24)

\[
A_1 = 2\epsilon L_{11} C_1 + 2\epsilon L_{12} C_2 + 2\epsilon L_{13} C_3 + 2\epsilon L_{14} C_4
\]  

\[
A_2 = 2\epsilon L_{22} C_2 + 2\epsilon L_{23} C_3 + 2\epsilon L_{24} C_4
\]  

\[
A_3 = 2\epsilon L_{33} C_3 + 2\epsilon L_{34} C_4
\]  

\[
A_4 = 2\epsilon L_{44} C_4
\]

or by a matrix equation of \(2\epsilon L C = A\):

\[
2\epsilon \begin{bmatrix}
L_{11} & L_{12} & L_{13} & L_{14} \\
0 & L_{22} & L_{23} & L_{24} \\
0 & 0 & L_{33} & L_{34} \\
0 & 0 & 0 & L_{44}
\end{bmatrix}
\begin{bmatrix}
C_1 \\
C_2 \\
C_3 \\
C_4
\end{bmatrix}
= \begin{bmatrix}
A_1 \\
A_2 \\
A_3 \\
A_4
\end{bmatrix}
\]

(3.25)
where $C_1...C_4$ denote the concentrations at four radial increments from the wire, and $\varepsilon$ is the molar absorptivity of the cylindrically distributed absorber. $L_\gamma$ denotes an effective path length obtained by dividing the area $S_\gamma$ of the appropriate sector by the lateral zone width $\Delta x$. Thus $A(x)$ may be obtained from $C(r)$ by matrix multiplication by a matrix $L$ which is calculated from the $S$ matrix. The Abel inversion can be stated as eq (3.26)

$$C(r) = \frac{1}{2\varepsilon} L^{-1} A(x)$$  \hspace{1cm} (3.26)

where $L^{-1}$ is the inverse matrix of $L$. For the geometry of the experiment depicted in Fig. 3-4, the increments $\Delta x$ in $r$ and $x$ are 1.25 $\mu$m, with the resulting effective path lengths being of the same order. An implicit assumption in the analysis is the constancy of concentration across each $L_\gamma$ element, an assumption that becomes valid when $(Dt)^{1/2} >> 1.25$ $\mu$m.

A technical problem arises when one tries to convert a large matrix $L$ (250 x 250) into $L^{-1}$. It is more efficient in both time and computer memory to use a back-substitution approach. Consider eq (3.25), elements below the diagonal line are all zeros in the $L$ matrix, so that $C_4$ can be directly obtained by back-substitution:

$$C_4 = \frac{A_4}{2\varepsilon L_{44}}$$  \hspace{1cm} (3.27)

$$C_3 = \left[ \frac{A_3}{2\varepsilon} - C_4 L_{34} \right] \frac{1}{L_{33}}$$  \hspace{1cm} (3.28)

$$C_2 = \left[ \frac{A_2}{2\varepsilon} - \left[ C_3 L_{23} + C_4 L_{24} \right] \right] \frac{1}{L_{22}}$$  \hspace{1cm} (3.29)

$$C_1 = \left[ \frac{A_1}{2\varepsilon} - \left[ C_2 L_{12} + C_3 L_{13} + C_4 L_{14} \right] \right] \frac{1}{L_{11}}$$  \hspace{1cm} (3.30)
In general

\[ c_i = \frac{A_i}{\max_{i \max} 2 \pi L_i \max_{i \max}} \]  

(3.31)

and

\[ c_i = \left[ \frac{A_i}{2 \pi} - \sum_{j=i+1}^{j_{\max}} c_j L_{ij} \right] \frac{1}{L_{ii}} \]  

(3.32)

A final calculation arises when predicting an \( A(x) \) profile from a simulated \( C(r) \) profile. The theoretical \( C(r) \) profiles have varying \( \Delta r \) as a result of the expanding box simulation. Subsequently the scheme based on Fig. 3-4 cannot be used for prediction of \( A(x) \) because in Fig. 3-4, equal increments in both \( r \) and \( x \) are assumed. In order to calculate \( A(x) \) from a profile of \( C(r) \) with expanding \( \Delta r \), \( S_{ij} \) and thus \( L_{ij} \) values have to be calculated on the basis of the expanding increments in \( r \) and \( x \). Details of the scheme are explained in the appendix A along with the expanding box implicit solution algorithm for diffusion simulation. When one is inverting experimental \( A(x) \) profiles, \( \Delta x \) is determined by detector pixel size and is constant. Thus the experimental \( C(r) \) and \( A(x) \) used herein always have equal-sized distance increments, while the theoretical \( C(r) \) and \( A(x) \) always involve an expanding distance increment.

**Experimental**

**Electrochemical cell and electrode preparation.**

The optical apparatus was identical with that described in Chapter 2. However, the electrochemical cell and the electrode for imaging experiments are drastically different. Although there are a few existing methods for making microcylindrical electrodes [103,115],
none of these is suitable for imaging experiments. A custom electrode holder and cell body is shown in Fig. 3-5. A microwire was mounted vertically between a larger platinum wire and a glass rod secured with heat-shrinkable Teflon tubing. Fig. 3-6 shows the step-wise procedures for electrode preparation. A 5-50 μm diameter wire was secured onto a glass rod of 3 mm diameter by heat-shrinkable Teflon tubing. The wire and the glass rod were then inserted into the bottom hole in the Teflon electrode holder. The other end of the microwire was inserted into a smaller heat-shrinkable Teflon tubing. The tubing was then put on the large platinum wire (about gauge 18). A physical contact between the large platinum wire and microwire was obtained when the Teflon tubing shrunk under heating from a soldering iron. The glass rod was slowly and carefully pulled from the bottom of the electrode holder to make the microwire vertically straight while stabilizing the bottom part of the holder by hand. The glass rod stayed in that position for quite a long time because the Teflon tubing kept it snugly fitted in the bottom hole. Care was taken not to break the wire by pulling it too hard. A small curvature was usually assumed when preparing the electrode. The bottom end of the large platinum wire was protected from contacting solutions by torr seal. Since the 5 μm microwires are coated with a layer of silver (for protection of the microwire when shipping), the electrode holder with the already fixed microwire was soaked in a 20% of nitric acid for overnight to dissolve the silver coating. After the silver coating was stripped off, extreme care was taken to conduct imaging experiments.

Before each experiment, the microwire electrode was straightened with a final pulling. Occasionally the glass rod crept up by a small distance, curving the microwire after the electrode was put into the solution. If the curvature was large, the electrode was taken out of the solution, and straightened by pulling the glass rod again. Problems were encountered sometimes when the microwire broke after 3-4 adjustments. Acceptable results were obtained when 2-3 diodes appeared on the edge. The whole electrode holder was put into a standard 1-cm photometric cuvette with a silver wire of gauge 16 as the reference
Fig. 3-5 Schematic of electrode holder, which was placed in a conventional 1 cm path length cuvette for wire-imaging experiments.
Fig. 3-6  Diagrams showing the stepwise preparation of a microwire electrode for imaging experiments.
electrode and a 20 gauge Pt wire as the auxiliary electrode. The solution came in contact with both the auxiliary and reference from the holes on each side of the cell body. Another hole in the bottom of the Teflon body allowed solution to flow up and down when the holder was put in and taken out of the cuvette. The holder size from the bottom up to the shoulder was about the same as the cuvette so that movements of the holder inside the cuvette were kept at a minimum. Approximately 7 mm of wire was exposed to the solution and the wire was at least 2 mm from cell walls or other objects, with a set crew being used to tie up the upper part of the electrode. The electrode surface treatment was provided by soaking the microwire in concentrated sulfuric acid for one minute for newly prepared electrodes. If the microwire survived an experiment, the electrode was soaked in acid for about 5 minutes before each experiment to provide cleaning and surface treatment. The electrode holder was then rinsed with nanopure water thoroughly and dried with Kimwipe tissues, with the water inside the holes blown out by dry nitrogen or argon gas. A small amount of water in the holes was a source of solution convection especially when the solvent was a 42% MeOH/H₂O mixture. This is because the water, when introduced into the MeOH/H₂O solvent, caused solution inhomogeneity, which causes convection.

**Optical alignment of wire-imaging experiments**

**Light source.** Because of the small diameters of microwire electrodes, diffusion layers were expected to be very thin. Therefore, the optical path length in absorption spectrometric measurements would be very small. A laser source was first used in an effort to obtain absorbance profiles with a better signal-to-noise ratio because of the laser's higher intensity. However, this idea was hindered by the fact that the image of a microwire electrode by a laser source was superimposed by many fringes, as shown in Fig. 3-7 (a). This apparent interference effect on microwire images is presumably due to the inherent coherent nature of lasers and the absorbance profiles obtained with a laser source have many fringes. On the other hand, images of microwire electrodes by xenon source do not
Fig. 3-7  One-dimensional images of a 25 µm diameter wire obtained (a) by a laser, with an interference pattern on top of the image, and (b) by the xenon arc lamp.
have such fringes, as shown in Fig. 3-7 (b). The xenon arc lamp is inherently incoherent and the interference problem is not expected to be seen in the images of microwire electrodes. Thus, the xenon arc lamp as a continuum source for imaging experiments has another advantage over a laser source.

**Optical alignment of wire imaging experiments.** The optical beam was directed horizontally through the cell and was centered on the microwire by adjusting the custom stage shown in Fig. 2-4(a) of chapter 2. Taking magnification into account, each detector element sampled a 125 x 1.25 μm portion of the beam cross section, with the long dimension parallel to the wire axis. As diagramed in Fig. 3-8, this geometry results in integration of the cylindrical diffusion profile along a linear path to produce an absorbance profile at the detector. Stated differently, each detector element measures an absorbance proportional to the integral of concentration along the path of the light at discrete distances lateral of the wire axis. The beam alignment was the same as that described in Chapter 2. However, procedures as well as the criteria for focusing were different from that for the planar electrode. The orientation of the photometric cell was adjusted by turning the post-mount holding the imaging assembly to make sure that the cell wall was perpendicular to the incoming beam so that the cell did not introduce any displacement of the beam. The electrode orientation was adjusted by turning the rotational stage holding the cell assembly and by looking at the image of the microwire at a plane near the detector to make sure that the microwire was vertically straight. A well-focused image of a microwire electrode should have two diodes along the rising portions from dark to bright on each side, with the bottom diodes being flat, as shown in Fig. 3-9. Positions of lenses 4 and 5 were moved along the optical axis if necessary to achieve a well-focused image.

**Control of imaging experiments.** The timing-control was the same as that described in Chapter 2 by a PC-compatible computer. The magnified beam cross section was first recorded by the photodiode array to provide an initial lateral intensity profile (the reference
Fig. 3-8  Orientation of microwire (cross hatched), diffusion and detector. Magnification was accomplished with a two-element simple magnifier.
Fig. 3-9 One-dimensional images of microwire electrodes with 2 diodes along the rising portion on each side, (a) $r_0 = 6 \mu m$, (b) $r_0 = 12.5 \mu m$. 
beam). At some specified time after a potential step, a second beam profile was taken. These two beam profiles were then processed according to Beer's law with the software provided by Tracor Northern to provide a lateral absorbance profile. Because any negative noise in the absorbance profile was taken as a very large positive number causing the profile to be buried in the bottom as noise after the absorbance profile was transferred, two beam profiles were transferred to a PC-compatible computer instead of transferring the absorbance profile. 520 nm was selected with an interference filter from the xenon arc lamp. The molar absorptivity of CPZ was measured to be \( (10620 \pm 100) \text{ cm}^{-1}\text{M}^{-1} \) at 520 nm by chronoabsorptometry while that of CPZ was negligible. Because the reference electrode was a Ag/AgCl wire, the oxidation potential of CPZ tended to shift to more positive values with time, making close potential control of experiments necessary. Before each chronoamperometric experiment, a cyclic voltammogram was obtained to determine oxidation potential and correct for slow reference electrode drift.

**Chemicals and Solutions.** Chlorpromazine (CPZ) was obtained from Sigma as the hydrochloride salt, and the platinum microwire was obtained from Good fellow Metals (Cambridge, England). Precautions described in Chapter 2 were taken to prepare solutions of CPZ. Three electrolyte solutions, 1 M the HCl in \( \text{H}_2\text{O} \), 1 M \( \text{HClO}_4 \) in 42% MeOH/H\( _2\text{O} \), and 0.3 M tetra-n-butylammonium perchlorate (TBAP) in \( \text{CH}_3\text{CN} \) were employed in order to vary solution viscosity. Diffusion coefficients for CPZ were determined by chronoamperometry at a 0.022 cm\(^2\) platinum electrode to be \( 1.3 \times 10^{-5} \text{ cm}^2/\text{sec} \) in \( \text{CH}_3\text{CN} \) and \( 3.2 \times 10^{-5} \text{ cm}^2/\text{sec} \) in 42% MeOH/H\( _2\text{O} \). Diffusion coefficient of CPZ were taken to be \( 3.2 \times 10^{-6} \text{ cm}^2/\text{sec} \) assuming that it is the same as that of CPZ and shown to be so in chapter 2. Solutions of Fe(CN)\(^{6-}\) were prepared in 1 M KCl for testing the performance of microwire electrodes.
Results and Discussion

Electrochemical performance of micro-cylindrical electrodes.

Assessment of the electrochemical performance of microwire electrodes was necessary because of the way these electrodes were made. There was neither any silver epoxy between the big platinum wire and the microwire, nor any soldering. The contact between the large platinum wire and microwire was only physical. A set of cyclic voltammograms is shown in Fig. 3-10 (a) at scan rates from 10 mV/sec to 100 mV/sec, with a linear plot of $i_p$ vs. $\nu^{1/2}$ shown in Fig. 3-10 (b). The voltammograms behave normally. Due to the nature of cylindrical diffusion at microwire electrodes, a true steady-state is never obtained. Instead, the current reaches only a virtual steady-state when $(D\tau)/r^2 > 10$ and decreases very slowly (logarithmically) with time [91,102,104,108]. While the physical contact between the large platinum wire and microwire electrodes did not show any signs of bad connections, cyclic voltammograms do show relatively large peak separations. This is probably because the connection between the large Pt wire and the microwire was only by a surface contact. Surface contact gives a larger resistance than would exist if there were a layer of silver epoxy or solder around the whole microwire surface. However alternative methods of contact proved impractical. Furthermore, the primary concern in these experiments was not electrochemical activity. The larger resistance in the microwire electrodes did not create any error in the spectroelectrochemical experiments.

Surface treatment of microelectrodes was achieved by soaking microwire electrodes in concentrated sulfuric acid. Other researchers have reported the use of nitric acid for surface treatment [116]. The practice of surface treatment by concentrated sulfuric acid was the extension of treatment of the platinum strip imaging electrodes discussed in Chapter 2. The effect of treatment by concentrated sulfuric acid can be seen in the cyclic voltammograms shown in Fig. 3-11. Voltammogram (a) shows a very sluggish electron transfer activity, presumably because of the surface deposits from the solutions. After
Fig. 3-10  (A) Cyclic voltammograms of a 25 μm diameter microwire electrode. Scan rates are: (a) 10 mV/sec, (b) 20 mV/sec, (c) 50 mV/sec, (d) 100 mv/sec. (B) Peak current $i_p$ vs $v^{1/2}$. 
3-11. Cyclic voltammograms of a microwire electrode showing the effect of acid treatment, (a) after three to four times usage but before soaked with concentrated sulfuric acid, (b) after acid treatment.
soaking the microwire electrode in concentrated sulfuric acid for 5 minutes, the electrochemical activity (current) increased by approximately a factor of eight (CV (b) in Fig. 3-11). The surface deposits were most likely dissolved by acid.

Cyclic voltammograms often showed severe sloping, as seen in Fig. 3-12(a). It was found later that this is due to solution resistance in the microspace between the torr seal and the microwire electrode. After putting a thin layer of silicone sealant on top of the torr seal, especially in the region where the microwire is in contact with the torr seal, the sloping problem in the cyclic voltammograms was corrected. A second cyclic voltammogram, shown in Fig. 3-12 (b), has no such problem and has relatively small background. The silicone sealant is more resistant to a moderate acidic medium, while torr seal attaches to Teflon tubing better.

Performance of SRAS for wire imaging experiments

As pointed out in the beginning of the chapter, spatial resolution of SRAS is expected to increase with use of a microwire electrode because smaller objects will reduce the diffraction effect. A well-focused image of a microwire electrode should give only two diodes along the rising portions on each side, as shown in Fig. 3-9. The fact that there are only two diodes along the rising portion empirically implies that the spatial resolution has increased, given the fact that 4 µm spatial resolution has 4 diodes along the rising portion discussed in Chapter 2. Also seen in Fig. 3-9 is the diffraction effect of the light beam by a microwire electrode, producing a big spike and small fringes near the electrode surface. A perfect image of a microwire electrode should show two big spikes, one on each side of the image. The origin of the asymmetry of the spikes is unclear, but it was a constant for an experiment and did not affect absorbance. Another problem in the wire-imaging experiments was the electrode vibration which interfered with the imaging experiments. However, the magnitude of the vibration did not exceed 2 µm because the shifting of edge diodes of an image before and after an electrochemical experiment was never larger than
Fig. 3-12 Cyclic voltammograms showing the effect of a bad sealing between the wire and the torr seal, (a) severe sloping before applying a layer of silicone sealant, (b) after application of such a layer.
one diode. The effect of the edge vibration is shown in Fig. 3-13. When the image of a microwire shifted to the right because of vibration, the edge diode and the next few diodes on the right side were lower in intensity while those on the left side were higher in intensity than would have been with no vibration. Wire vibration caused the largest errors in absorbance near the wire surface, where vibration induced intensity fluctuation were the greatest. As a result of this, the absorbance profile showed a spike near the surface on right side and a negative spike on the left side. The edge diodes on the image profile of a vibration-free microwire should lower their intensities in proportion to their initial intensities as shown in Fig. 3-14. A vibration free profile is difficult to obtain. That is why absorbance profiles usually show unequal values of the edge points and the next few points on both sides. However, the uncertainties in these edge points due to vibration of a microwire electrode should not be confused with that due to the optical resolution of the imaging system. A spatial resolution of 2 μm is intrinsic to the optical system while the uncertainty due to a vibration is mechanical, and could be larger or smaller, depending on the severity of a vibration. Closer attention of vibration for imaging experiments, such as closing the door of the cabinet, could usually yield better results.

Experimental absorbance profiles for diameters of 50, 25, 12 and 5 μm are shown in Fig. 3-15 to 3-18 for single potential step experiments, compared with theoretical simulated profiles in solid lines. The simulated A(x) profiles were calculated from independent measurements of r₀, D and ε, with no adjustable parameters. In general, stable and symmetrical absorbance profiles are obtained with a larger diameter microwire for longer electrochemical experimental times. For example rather symmetrical profiles for wires of 25 and 50 μm diameter can be obtained at times up to 60 sec. The agreement between theory and experimental is quite close even for such long times. On the other hand, stable and symmetrical profiles can be obtained only for times up to 10 sec with 12 μm wire, and even shorter at 6 sec with 5 μm diameter wire. Over these time ranges, the agreement of
Fig. 3-13 (a) Intensity profiles of reference and sampling beams as a result of microwire vibration, (b) the absorbance profile calculated from the two profiles with microwire vibration.
Fig. 3-14 (a) Intensity profiles of reference and sampling beams of a vibration-free microwire electrode, (a) the profile calculated from the two profiles obtained in (a).
Fig. 3-15  Raw lateral absorbance profiles for diffusion-limited generation of CPZ•⁺ at 50 μm diameter microwire, compared with simulated profiles. Experimental times are: (a) 0.2, 0.5, 2, 4, 6, 8 sec, (b) 20, 40, 60 sec. The dotted lines are experimental, the solid lines are simulated.
Fig. 3-15
Fig. 3-16 Raw lateral absorbance profiles (dotted lines) for diffusion-limited generation of CPZ at 25 μm diameter microwire, compared with simulated profiles (solid lines). Experimental times are: (a) 0.2, 0.5, 1, 2, 4, 6, 8, 10 sec; (b) 20, 30, 40, 60 sec.
Fig. 3-16
Fig. 3-17 (a) Raw lateral absorbance profiles for diffusion-limited generation of CPZ$^{+}+$ at 12 μm diameter microwire; (b) Comparison of simulated (lines) and observed (points) A(x) profiles for half of (a) plot. Simulated curves were calculated from line integrals of theoretical C(r) and independent values of ε, D and $r_p$. Experimental times are: 0.2, 0.5, 1, 2, 4, 6, 10 sec.
Fig. 3-17

**a**

Absorbance vs. Distance From Electrode (µm)

**b**

Absorbance vs. Distance From Center of Electrode (µm)

- ... Experimental.
- --- Simulated.
Fig. 3-18  (a) Raw lateral absorbance profiles for diffusion-limited generation of CPZ$^+$ at 5 μm diameter microwire. Times: 0.5, 1, 2, 4, 6, 8 sec. (b) Comparison of simulated (lines) and observed (points) A(x) profiles for half of (a) plot. Simulated curves were calculated from line integrals of theoretical C(r) and independent values of $\epsilon$, D and $r_p$. Experimental times are: 0.5, 1, 2, 4, 6 sec.
Fig. 3-18
theory and experiment supports using a line integral of absorbance of rays passing through a cylindrical field of absorbers (eq 3.21 - 3.24). The results also indicate that any diffraction or optical aberration introduced by the microwire is negligible and that a ray optic description of beam propagation is sufficient for this work. Stated differently, the agreement of theory and experiment supports the approximation that each detector element monitors a flat layer of solution with a thickness of about 1.25 μm along the axis perpendicular to and lateral of the wire axis (as depicted in Fig. 3-7). The microwire certainly produces diffraction and reflection, but most such scattered light is not imaged at the detector. Given the fairly small collection angle of the imaging optics and the thin diffusion layer, a given ray can deviate only very slightly from linearity and still be detected.

The minimum observation time after initiation of electrolysis was determined by sensitivity, because short times lead to short path lengths for absorption. For example, the diffusion layer at 100 ms is about 7 μm thick, and its maximum absorbance is about 0.02 for CPZ⁺⁺. At an absorbance lower than 0.02, the profile is unacceptably noisy. In addition, the assumption of constant concentration across the zone width is no longer valid. As the diffusion layer grows with time, the effective path length increases, and the absorbance continues to increase, as shown in Fig. 3-15 through 3-18. A rough analogy is a double-sided optically transparent electrode (OTE), with solution accessible to both sides of the transparent electrode. Light passing through the OTE would be absorbed by two expanding diffusion layers, and the absorbance would be proportional to 2(Dt)½. For the case of a ray passing close to the microwire, the light is absorbed by the cylindrical profile, with the effective path length being twice the diffusion layer thickness. At the limit of large (Dt)½, the absorbance of a ray passing next to the microwire should equal that of one reflected by the wire.

There are several technical problems presented by Abel inversion affecting the accuracy of the inversion. Abel inversion itself is a disintegration process, and thus the resulting
profile after Abel inversion is inherently noisier than the lateral absorbance profile. Therefore, necessary smoothing (7-15 pts) has been applied to all absorbance profiles before Abel inversions in order to achieve a reasonable signal-to-noise ratio. This was accomplished by first extrapolating a profile from \( r_0 \) to the wire center, smoothing the absorbance profile, and inverting it. Second, the size of the profile that can be inverted accurately is controlled by the size of the computer memory. A matrix of 261 x 261 with double precision is the maximum size for the area \( S \) and thus the \( L \) matrix. Data files larger than 261 data points exhibited error in the back-substitution, with larger error for larger arrays. The effect of having a data file greater than 261 points is shown in Fig. 3-19. The rising tail in concentration profiles for longer experimental times is due to this effect. For most experiments lasting 20 sec or less, Abel inversion should give accurate results, even though the 20 sec profile may have exceeded the maximum points. The third technical problem comes from inverting absorbance profiles of very small diameter wires. Going from 50 \( \mu \)m to 5 \( \mu \)m diameter wire, Abel inversion becomes technically more difficult. The 12 \( \mu \)m diameter microwire is probably the limit of Abel inversion with a 1.25 \( \mu \)m mechanical resolution. The assumption of Abel inversion is that the division of the diffusion field by the concentric rings and lateral zones is fine enough so that concentration within each segment area are relatively constant. However, because of the large dilution effect present with a microwire of small diameter, the concentration profile near the electrode is so steep (large concentration gradient) that 1.25 \( \mu \)m resolution is no longer fine enough for accurate inversion. This technical problem is more pronounced for short time experiments when the concentration profile is very steep. The effect is shown in Fig. 3-20 where an open-circle line is shown to be lower than the solid, simulated profile. The good agreement between simulated profiles and the absorbance profiles gives more support of this argument because the section of a profile near the electrode has many more points and much finer resolution (remember, concentration profiles are simulated with the expanding box algorithm.)
Fig. 3-19 A 60 sec radial concentration profile (261 points) of CPZ* at 25 μm diameter wire, compared with the simulated profile.
Fig. 3-20 2 sec radial concentration profiles (after Abel inversion) at 5 μm diameter wire. Open circles, Abel inversion with a resolution of 1.25 μm determined by the detector resolution; closed circles, the lateral absorbance profile has been interpolated before Abel inversion, with a resolution of 0.625 μm. The solid line is simulated.
Therefore, in order to extract the information from absorbance profiles of a 5 \( \mu \)m diameter wire, points equal to the average of two nearby data points have been added along the whole absorbance profile to increase the mechanical resolution from 1.25 to 0.625 \( \mu \)m for 5 \( \mu \)m diameter microwire. This approach seems to improve the accuracy of Abel inversion. A best result of this approach is shown in Fig. 3-20 where the dotted line is the result of Abel inversion after interpolation. All concentration profiles for 5 \( \mu \)m diameter wire were obtained this way.

Results of an Abel inversion of \( A(x) \) to produce \( C(r) \) are shown in Fig. 3-21 through 3-24 for microwires of 50, 25, 12, and 5 \( \mu \)m in diameter, along with simulated profiles. The back-substitution approach was used in all cases presented here. An internal check of the calculations was made by inverting an experimental \( A(x) \) profile with the use of back-substitution and then transforming the resulting \( C(r) \) profile with the matrix \( L \) to reproduce the original \( A(x) \) profile. Going from 50 \( \mu \)m to 5 \( \mu \)m diameter, it is clear that the effect of rapid dilution is more obvious when the microwires become smaller, but the current behavior of micro-cylindrical electrodes can never attend steady-state. The behavior of current is more complicated than one would expect. The relationship between current behavior and molecules diffusion and perhaps solution convection is examined further below.

At times longer than a few seconds, it was noted that the \( A(x) \) profiles often become asymmetric about the wire axis. Changes in optics, cell design, etc., did not remove the asymmetry, and the asymmetry became more severe as the microwire diameter was decreased (Fig. 3-15 through Fig. 3-18). A simple change in experimental design revealed the unexpected source of the problem. After 5 sec of electrolysis in the usual way, the microwire electrode was disconnected and the \( A(x) \) profile was recorded at several subsequent times. With the electrode off, the absorbance profiles often moved away from the wire by a distance much greater than the wire diameter (Fig. 3-25). This motion varied
Fig. 3-21  Radial concentration profiles of 50 μm diameter microwire determined by Abel inversion of experimental profiles A(x) shown in Fig. 3-15. Dotted curves are experimental; solid lines are simulated. Experimental times are: 0.2, 0.5, 1, 2, 4, 6, 10 sec.
Fig. 3-22 Radial concentration profiles of 25 μm diameter microwire determined by Abel inversion of experimental profiles A(x) shown in Fig. 3-16. Dotted curves are experimental; solid lines are simulated. Experimental times are: 0.2, 0.5, 1, 2, 4, 6, 8, 10 sec.
Fig. 3-23 Radial concentration profiles of 12 μm diameter microwire determined by Abel inversion of experimental profiles A(x) shown in Fig. 3-17. Dotted curves are experimental; solid lines are simulated. Experimental times are: 0.2, 0.5, 1, 2, 4, 6, 10 sec.
Fig. 3-24 Radial concentration profiles of 5 μm diameter microwire determined by Abel inversion of experimental profiles A(x) shown in Fig. 3-18. Dotted curves are experimental; solid lines are simulated. Experimental times are: 0.5, 1, 2, 4, 6 sec.
Fig. 3-25 Behavior of observed A(x) profiles for CPZ in 1 M HClO₄ (42% MeOH/H₂O) following disconnection of working electrode. In all cases, CPZ⁺⁺ was generated for 5 sec. Then absorbance was recorded at 5 (curve a), 10 (b), and 15 (c) sec after the microwire was open circuited. The vibration isolation system was active, and 5 min has elapsed between solution stirring and initiation of electrolysis.
in magnitude and direction, but often occurred on a time scale of a second or so. Clearly the entire cylindrical diffusion field is moving relative to the wire, presumably because of convection. When the electrode is not disconnected and the electrolysis time increases, the diffusion field moves laterally, leading to asymmetry in the $A(x)$ profile. The open circuit experiment of Fig. 3-25 makes this motion obvious by interrupting the generation of absorber.

The drift of the electrogenerated absorber field varied greatly from run to run and with time during an experimental session. In many cases, the behavior of Fig. 3-25 was observed, with a stable diffusion layer occurring for only a few hundred milliseconds after initiation of electrolysis. In other cases, experimental profiles that agreed with theory for up to 20 sec were observed but were often difficult to reproduce. The drift was significantly less severe for the 25 and 50 μm diameter wires than 5 and 12 μm diameter wires. In addition, more stable profiles were observed in water than in acetonitrile, presumably because of the significantly lower viscosity of acetonitrile. Given the random nature of the observed drift, no attempt was made to quantitatively correlate drift and viscosity. Unstable diffusion layers are expected for natural or vibration-induced convection, so possible sources of vibration were investigated further.

The entire experiment was constructed on an air-suspended optical table shielded from air current (Newport RS grade) and should have substantially better vibration isolation than that of a conventional electrochemical apparatus. Vibration of electrode was assessed by observing its motion on the array detector, as was discussed earlier and shown in Fig. 3-13. The electrode never moved more than 1 pixel ($< 3 \mu m$), a distance much smaller than the several hundred micrometers often observed for the diffusion field drift. Thus electrode motion is unlikely to be responsible for the convection. After all obvious sources of vibration had been addressed, three factors were found to have large effects on convection. First, mixed solvents such MeOH/H$_2$O and solutions needed a time to equilibrate after
mixing to allow thermal and density gradients to relax. Second, it was necessary to wait 5 - 10 min after solution stirring before initiating electrolysis. This waiting period is longer than normally recommended for ordinary electrochemical experiments, but serious drift was usually observed at times of 1 - 5 min after stirring. Third, the diffusion field was more stable if the air suspension legs were turned off. Vibration isolation systems, including that used here, often have reduced damping at very low frequencies (< 1 Hz). In addition, the active pressure control on the air suspension legs can lead to slow, minute table motion on a several second time scale. Any small or transient source of vibration disturbed the solution, requiring a several minute wait to restore stability. Stable profiles were more easily attainable in water compared to acetonitrile due to higher viscosity, with good profiles observed for 20 sec with proper care.

The effect of convection on the current is shown in Fig. 3-26 and 3-27 for voltammetry, and chronoamperometry. Curve 3-26 (a) is a voltammogram obtained under the conditions of Fig. 3-23, with little drift observed. The scan rate was fast enough to show a small peak on top of a near steady-state current, and a small reverse peak rather than a simple sigmoid. Curve 3-26 (b) was obtained with convection present (as in Fig. 3-25). The steady-state oxidation current is too high (by 10% in this case) and the reverse peak too small, because of the removal of CPZ* by convection. The convective effects are confirmed by Fig. 3-27, in which a positive deviation from theory is observed for chronoamperometric experiments when convection is present. Several investigators have related the positive current deviations to natural convection. For example Osteryoung et al. have recently reported the observed positive current in chronoamperometric experiments at micro-cylinder electrodes [104]. This optical probe provides the first observation of convection at microelectrodes which correlates well with the current behavior at convection. The small reverse peak for cyclic voltammetry at a micro-cylinder reported by Wightman [91] may be caused by the same convection effect.
3-26. Cyclic voltammograms on a 12 μm diameter microcylinder for 3 mM CPZ in 0.3 M TBAP in acetonitrile. Curve (a) was obtained when optical monitoring exhibited a stable profile over a 10 sec period. Curve (b) is same experiment when optical monitoring showed convection similar to that in Fig. 3-25. Scan rate was .10 V/sec.
3-27. Chronoamperometry at 12 μm diameter microcylinder in presence and absence of convection. Solution conditions are the same as in Fig. 3-26. Points are simulated current, $D = 1.3 \times 10^5$ cm$^2$/sec. Solid line is experimental current with minimal convection. Dashed line is Observed current with convection present.
Both optical and amperometric results indicate that convection is a much more serious problem with a free-standing microwire electrode than with a "large" planar electrode. Very well behaved profiles were observed for a planar electrode, with Fick's law behavior routinely observed up to at least 20 sec, as discussed in Chapter 2. Yet a 12 \( \mu \)m diameter microwire exhibits convective effects at times as short as 100 ms, with the severity of such effects being highly unpredictable. An explanation of the increased sensitivity of the microwire electrode is based on viscous drag at the surface. For a planar electrode or a microelectrode embedded in a large plane, the solution velocity must be zero at the surface, and convection of nearby solution will be dampened. In addition, the diffusion layer is thin compared to the dimension of the plane, so viscous drag can dampen motion of the entire diffusion field. As has been reported by others, microelectrodes embedded in a large plane are relatively immune to convective effects, such as in flowing streams [117]. For a free-standing wire, however, there is no large plane to dampen solution motion. The diffusion field is large relative to the wire and may more easily move relative to the wire. Because convection itself is dependent on viscosity, vibrations, and measurement time, these variables will affect microwire behavior. If particular care is taken to reduce vibrations and at least 5 min are allowed to elapse after solution stirring, solution convection appears minimal even in acetonitrile. Without these precautions, deviations from theory of 20 percent or more are likely.

Conclusions

The high resolution spatially resolved absorption spectroelectrochemical technique equipped with a continuum source has broadened the utility and versatility of SRAS. In this chapter, another application of this method has been described. The microwire electrode has been shown to be amenable to spatially resolved absorption methods. The
xenon arc lamp has proved to be a superior light source for wire imaging experiments over a laser because of the lack of an interference pattern superimposed on the wire image. Spatial resolution of SRAS improves from ca. 4 μm to ca. 2 μm when the dimension of imaging objects is reduced down to micrometer size.

The diffusion and current behaviors of micro-cylinder electrodes has been studied with SRAS. The C(r) profile for cylindrical diffusion was observed experimentally for the first time. The Abel inversion was successfully applied to inversion of a lateral absorbance profile to a C(r) profile with good accuracy for microwires of diameters greater than 10 μm. The experimental profiles agreed with theory in the absence of convection. Natural solution convection of unusual severity has been observed experimentally for the first time. Due to the absence of viscous drag, a free-standing microwire electrode is extremely sensitive to solution convection induced by vibration or stirring. Such convection causes serious deviation of the observed C(r) profiles from theory and causes a positive deviation of current from calculated values in the absence of convection. The high sensitivity of the free-standing wire is due to the lack of a large plane to impede motion. With proper attention to vibrations and a long waiting period following solution stirring, convection can be reduced enough to permit 10 - 20 sec experiments.
Chapter IV

Kinetic Study of Homogeneous Reaction Between
Chlorpromazine Cation Radical (CPZ•⁺) and Dopamine (DA)
by Spatially Resolved Absorption Spectroelectrochemistry

Background

Spatially resolved absorption spectroelectrochemistry (SRAS) has been shown to be a useful technique with high sensitivity and high spatial resolution in quantifying electrochemical processes in the diffusion layer near an electrode surface [60]. The utility and versatility of the technique has been broadened by adapting a continuum light source for imaging experiments, as discussed in chapters 2 and 3. For the planar electrode case, SRAS has been used for observing profiles of reactants and products for potential step and cyclic voltammetry experiments [60], for trace analysis [61], and in twin working electrode cells (chapter 2). By passing a light beam parallel to a microwire electrode, SRAS has also been applied to a convergent diffusion case for observing radial concentration profiles of 5 - 50 μm diameter wires. The diffusion properties of microwire electrodes, such as the virtual steady state of mass transport, the dilution effect of electrochemical products and the unexpected solution convection, have been examined thoroughly by SRAS. Since the diffusion layer of an electrochemical product in a microwire electrode is much thinner than that in a planar electrode (Fig. 3-2 in chapter 3) for the same experimental time, the rapid dilution effect is relevant in the study of the reaction mechanism between CPZ•⁺ and DA in the joint effort with Deputy.
The initial effort by Deputy with SRAS at planar electrodes was to examine the reaction mechanism of CPZ•+ oxidation of DA. The overall reaction is given by eq (4.1):

\[
2 \text{CPZ}^+ + \text{DA} \rightleftharpoons \text{K}_{eq} \rightarrow 2 \text{CPZ} + \text{DOQ} + 2\text{H}^+ \quad (4.1)
\]

where DOQ denotes dopamine orthoquinone. Using normal or glancing incident absorption spectroelectrochemistry(SEC), it was concluded[117] that the CPZ•+ oxidation of DA was first order in both reactants and followed the rate law:

\[
\frac{d[\text{DOQ}]}{dt} = -\frac{1}{2} \frac{d[\text{CPZ}]}{dt} = k_2 [\text{CPZ}^+][\text{DA}] \quad (4.2)
\]

Where \(k_2 = 2.1 \times 10^5 \text{M}^{-1}\text{s}^{-1}\) at pH 1.5. Since DA is oxidized by two electrons to the quinone, the complete mechanism must involve two or more steps. Possible mechanisms include a second electron transfer to CPZ••+ (scheme I) or disproportionation of the DA semiquinone (DA••+) intermediate (scheme II).

**Scheme I:**

\[
\begin{align*}
\text{CPZ}^+ + \text{DA} & \rightleftharpoons k_3 \rightarrow \text{DA}^{+•} + \text{CPZ} \\
\text{CPZ}^+ + \text{DA}^{+•} & \rightleftharpoons k_4 \rightarrow \text{CPZ} + \text{DOQ}
\end{align*}
\]

**Scheme II:**

\[
\begin{align*}
\text{CPZ}^+ + \text{DA} & \rightleftharpoons k_3 \rightarrow \text{DA}^{+•} + \text{CPZ} \\
2\text{DA}^{+•} & \rightleftharpoons k_5 \rightarrow \text{DA} + \text{DOQ}
\end{align*}
\]

Note that reactions 4.3 - 4.5 ignore the involvement of protons, and that DA••+ may in fact be neutral or anionic. Because reactions (4.4) and (4.5) occurred after the rate limiting step
using previous conditions, it was not possible to determine which scheme is operative using the glancing incidence spectroelectrochemical technique.

After applying SRAS to the CPZ•+/DA system at a planar electrode, Deputy found [118] that the overall reaction mechanism is described by scheme I, and that the reaction rate law is dependent on the local concentrations of the species in the diffusion layer, with the rate law (4.2) being a special case of the overall reaction mechanism (scheme I). Because the concentration profiles at microwire electrodes are very much different from that at planar electrodes, it is worthwhile to examine the reaction mechanism under the rapid dilution condition at a microwire electrode, thus enhancing the kinetic complication and perhaps providing additional kinetic data.

The reaction of CPZ•+ and DA is an example of redox catalysis reactions that have been studied for the last twenty years by Kuwana [119-121], Savèant [122-127] and McCreery [117, 128]. These studies were driven by the widespread use of phenothiazine derivatives, such as chlorpromazine (CPZ) in psychopharmacology [129], as well as a general interest in phenothiazine cation radical reactions [130,131]. Much of the work in this area has centered around investigating the formation of sulfoxides and hydroxylated metabolites. A detailed mechanism of sulfoxide formation has been elucidated [132, 133]. The close association of phenothiazine antipsychotic activity with the neurotransmitter dopamine (DA) prompted research into CPZ•+ oxidation of DA [134,135]. The excess formation of neuromelanin and the occurrence of tardive dyskinesia in patients undergoing long term CPZ therapy may be related to DA oxidation.

The CPZ•+ oxidation of DA represents a class of reactions in which the reduced forms of two redox couples are oxidized at their diffusion controlled rates at the electrode surface. The optical probe serves to monitor perturbations to the diffusion layer caused by the redox cross reaction. The reaction mechanism is complicated by the second electron transfer. Conventional amperometric methods have provided much kinetic information for
simple coupled homogeneous reactions. However, amperometric methods only monitor the surface flux of electroactive species, and give no information on homogeneous reactions which occur away from the electrode surface. These methods are certainly insufficient for deducing complex reaction mechanisms like the CPZ•+/DA system because the homogeneous reaction may have minor or negligible effects on the observed current [126]. Studies of coupled homogeneous reactions have benefitted from spectroelectrochemical techniques such as OTE transmission [2,4,7], reflection/absorption [117,128,133] and Raman spectroscopy[20,24,59]. Compared to conventional kinetic techniques such as stopped-flow or pulse radiolysis, spectroelectrochemistry has the advantages of generating reactive species at the electrode without requiring mixing of reactants, wider experimental time scales, and precise control over reactant generations under controlled-potential conditions[2].

Despite the improvements brought about by the previous SEC methods in diagnosis of reaction mechanisms, the information obtained with these methods is only proportional to the integrated concentration profile of the species being monitored over the entire diffusion layer (Fig. 1-2). With the development of spatially resolved absorption SEC (SRAS), the dimensionality of complete concentration vs. distance profiles of electrogenerated absorbers was added to the previous SEC experiments [60,136-138], with the electroactive absorbers allocated in the diffusion layer instead of getting averaged information. In two recent publications, is was demonstrated that SRAS can be used to monitor a simple redox catalysis mechanism to reveal its stoichiometry and equilibria [137,138]. The fact that signals from glancing incident SEC are averaged over the entire diffusion layer (Fig. 1-2 in chapter 1) has limited its application to more complex reaction mechanisms where local concentrations of different species are important. The inability of glancing incidence SEC to determine the second step mechanism of CPZ•+ reaction is an example of such a limitation. SRAS is distinct from previous approaches such as amperometry and chronoabsorptometry (see chapter one for explanation) in several ways, which may be appreciated upon consideration of Fig. 4-1 (a). Amperometric methods monitor the
Simulated concentration profiles for the diffusion limited oxidation of a 1:1 mixture of DA and CPZ. (a) All curves were calculated from equation (4.13) with $\gamma = k_C^{\text{CPZ}} t = 600$. $x_i$ is the distance from a planar electrode. (b) All curves were calculated from equation (4.9) with $k_A C_{\text{CPZ}}^{\text{b}} = 0.04$. $r$ is the distance from a microwire electrode.
Fig. 4-1
concentration gradients of oxidizable species at $x_e = 0$ and the observed current is insensitive to reaction (4.1) unless the diffusion coefficients of DA and CPZ are very different [126]. Normal or glancing incidence SEC monitors the integral of CPZ$\cdot^+$ profile and leads to the rate law of eq (4.2). However, the overlap between CPZ$\cdot^+$ and DA profiles at $x_e = 0.7(Dt)^{1/2}$ is where the reaction principally occurs, and neither amperometry nor normal incident SEC are sensitive to this region. The profile slope at $x_e = 0$ and its integral are dominated by the large CPZ$\cdot^+$ concentration accumulated by the reaction, and are relatively unaffected by concentrations in the region where the reaction is occurring. With SRAS, however, the entire CPZ$\cdot^+$ profile is monitored, simultaneously acquiring kinetic data over a wide range of local CPZ$\cdot^+$ concentrations including the overlap region. A single SRAS experiment thus provides the equivalent information of a series of kinetic runs at different concentrations, some of which would be difficult due to limited dynamic range in time or observable concentration.

In his initial effort, Deputy has outlined the reaction mechanism of CPZ$\cdot^+$ and DA by SRAS at a planar electrode [118]. Because of the dilution effect of electrochemical products in a cylindrical diffusion field, SRAS at a microcylindrical electrode was used to further modify the concentration distribution. On the basis of the determination of the reaction mechanism by SRAS at a planar electrode, the reaction between CPZ$\cdot^+$ and DA is examined with SRAS at a microwire electrode, in an effort to further confirm the mechanism and to provide additional kinetic data. The performance of SRAS at microwire electrodes for studying homogeneous reactions was first tested by a known system of CPZ$\cdot^+$/MPZ (methoxypromazine.) These studies permit diagnosis of rates and mechanisms at a level of detail which was previously unavailable.
Experimental

Spectral properties of molecules. Microwire SRAS with a 25 μm diameter wire was performed as described in Chapter 3, with the wavelength of 520 μm being selected for monitoring CPZ•+ concentration profiles. For the testing system of CPZ•+/MPZ, the wavelength of 600 nm was selected for monitoring MPZ•+. Molecular structures of CPZ, MPZ and DA are pictured in Fig. 4-2. Spectral properties of cation radicals of the phenothiazine derivatives and dopamine orthoquinone are shown in Fig. 4-3. As can be seen from the spectra, there is no overlap between the absorption bands of CPZ•+ and MPZ•+ at 600 nm (molar absorptivity of CPZ•+ at 600 nm is negligible), and those of CPZ•+ and DOQ at 520 nm. Therefore spectral monitoring of MPZ•+ at 600 nm for CPZ•+/MPZ•+ system and CPZ•+ at 520 nm for CPZ•+/DA system have no absorption contribution from other electroactive species in the electrochemical systems. The molar absorptivity of CPZ•+ at 520 nm was measured to be (10620±100) cm⁻¹M⁻¹ and that of MPZ•+ at 600 nm to be 4000 cm⁻¹M⁻¹. All precautions mentioned in Chapter 3 for wire-imaging experiments were taken to avoid vibrations for microwire experiments as verified by the observation of expected profiles in the absence of reaction convection.

Solution preparations. MPZ, DA and CPZ reagents were available commercially and used as received. Solutions were prepared in constant ionic strength (0.8 M) mixtures of HClO₄ and NaClO₄ in 42% MeOH/H₂O (W/W) with a pH between 0.1 and 1.5. These conditions were the same as those reported previously for glancing incidence SEC experiments [117]. The equilibrium constant Keq for reaction (4.1) was calculated from E°' values determined from the average of the anodic and cathodic peak potentials of CPZ and DA in the relevant medium. These Keq values are: pH 0.1, 150; pH 0.5, 1000; pH 1.3, 1.5 x 10⁶; pH 1.5, 5 x 10⁴.

Potential control of experiments. Potential control of imaging experiments was critical. In general, potentials were fairly constant over relatively long experimental times, even
Fig. 4-2  Molecular structures of dopamine (DA), chlorpromazine (CPZ) and methoxypromazine (MPZ).
Fig. 4-3  UV-vis absorption spectra of DOQ, CPZ$^{+}$ and MPZ$^{+}$. 
though the reference electrode was a Ag/AgCl wire. The performance of this reference electrode has been discussed in Chapter 3, and found to be shifting positive with time. Therefore, the potential range was checked by running a cyclic voltammogram periodically. A typical cyclic voltammogram of the CPZ\textsuperscript{+}/MPZ reaction is shown in Fig. 4-4. Four distinct peaks are seen in this redox catalysis system, corresponding to MPZ and CPZ oxidations ($i_1$, $i_2$) and CPZ\textsuperscript{+} and MPZ\textsuperscript{+} reductions ($i_3$, $i_4$). Several cyclic voltammograms for the CPZ\textsuperscript{+}/DA reaction are shown in Fig. 4-5. Depending on the pH values at which reaction of CPZ\textsuperscript{+} and DA occurs, there is only one forward peak and the reverse peak may or may not be observed. At pH 0.1 the reverse peak is not seen at all and it is barely seen at pH 1.3, indicating the complexity of the CPZ\textsuperscript{+}/DA reaction.

**Simulation of reactions under diffusion conditions.** Simulations of concentration profiles were performed with standard finite difference techniques on an AT personal computer. Details of simulation are explained in the appendix A. Necessary parameters included $\gamma = k_3 C_{\text{CPZ}}$, $\omega = k_4/k_3$, and $\beta = C_{\text{DA}}/C_{\text{CPZ}}$. Although the parameter of $k_4 C_{\text{CPZ}} t$ was included in the kinetic simulation, it is not independent of $\gamma$ and $\omega$, since $K_{eq}$ is known from voltammetric data. However, $k_4$ has been adjusted around the value determined from $k_3$, $\omega$, and $K_{eq}$ to achieve the best fits during simulation, given the fact that $K_{eq}$ measured is not highly accurate. One of the advantages of SRAS at a microwire for kinetic study is that $k_4$ is made meaningful in a concentration profile. Since $\beta$ is fixed by the experiment, the majority of cases involved a fit of simulation and experiment by varying $\gamma$ and $\omega$ (the only two independent parameters). No curve fits involved more than two adjustable parameters and it was verified that these parameters were invariant with $\beta$ and $t$. In all cases, $\omega$ was found to be very close to 1.0.
Fig. 4-4 Cyclic voltammogram of CPZ$^{••}$ and MPZ reaction. $i_{o1}$ and $i_{o2}$ are due to CPZ and MPZ oxidations, while $i_{a2}$ and $i_{a1}$ are due to CPZ$^{••}$ and MPZ$^{••}$ reductions respectively.
Fig. 4-5  Cyclic voltammograms of CPZ•+ and DA reaction initiated electrochemically at pH of (a) 0.1, (b) 0.5, (c) 1.3. β = 1 for all three pH values. scan rate ν = 100 mV/sec.
Results and Discussion

Performance of SRAS at microwire electrode for homogeneous reactions

The redox catalysis system of CPZ\(^{\ast}\)/MPZ is a one electron cross-reaction and has been studied thoroughly by Deputy using planar electrode SRAS [137]. Both CPZ and MPZ are oxidized to cation radicals at the electrode surface according to eq (4.6) and (4.7) at a controlled potential.

\[
\begin{align*}
\text{CPZ} & \rightarrow \text{CPZ}^{\ast} + e^- & E_0 = 0.605 \text{ Volt vs. SSCE} \\
\text{MPZ} & \rightarrow \text{MPZ}^{\ast} + e^- & E_0 = 0.475 \text{ Volt vs. SSCE}
\end{align*}
\] (4.6) (4.7)

CPZ\(^{\ast}\) is a stronger oxidant in the system and oxidizes MPZ when it diffuses away from the electrode

\[
\text{CPZ}^{\ast} + \text{MPZ} \rightleftharpoons K_{eq} \rightarrow \text{CPZ} + \text{MPZ}^{\ast}
\] (4.8)

Once the reaction is initiated, MPZ is consumed at some distance away from the electrode as if the electrode surface were expanding into the diffusion layer. Due to the finite equilibrium constant of the system, the reaction is dominated by equilibrium with \(K_{eq}\) equal to 159[137]. Since CPZ\(^{\ast}\)/MPZ is a one electrode catalytic reaction, no kinetic complication is expected by going from planar to microcylindrical electrode and yet the reaction provides a good test for the performance of SRAS at microwire electrode to study homogeneous reactions.

Lateral absorbance profiles and concentration profiles of MPZ\(^{\ast}\) (after Abel inversion) obtained at 600 nm wavelength are shown in Fig. 4-6 (a) and (b) compared with the solid simulated profiles. The agreement between experiment and theory with \(K_{eq} = 159\) indicates that SRAS at a microcylindrical electrode is as good for studying homogeneous reactions as SRAS at a planar electrode. The concentration near the electrode surface at a microwire electrode decreases slowly because of the dilution effect in the cylindrical diffusion. This
Fig. 4-6  
(a) Raw lateral absorbance profiles of MPZ•*, which are obtained at 600 nm as the results of the reaction between CPZ•* and MPZ initiated electrochemically.  
(b) Radial concentration of MPZ•* (determined by Abel inversion) at a 25 μm diameter microwire electrode. Experimental times (from the bottom to the top) are: 0.5, 1, 2, 4, 6, 10 sec.
Fig. 4-6
is an obvious difference as compared to those of the planar diffusion case where MPZ:: near the electrode surface at a planar electrode has a constant concentration near the electrode surface.

**Theoretical Consideration.**

After applying a steady state approximation for DA:: and ignoring protons, the rate law for scheme I is given by eq (4.9), and that for scheme II by eq (4.10)

\[
\frac{d\text{[DOQ]}}{dt} = \frac{k_3 k_4 \text{[CPZ]}^2 \text{[DA]} - k_3 k_4 \text{[DOQ]}[\text{CPZ}]}{k_3 \text{[CPZ]} + k_4 \text{[CPZ]}}
\]  \hspace{1cm} (4.9)

\[
\frac{d\text{[DOQ]}}{dt} = \frac{k_3 k_5 \text{[CPZ]}^2 \text{[DA]}^2 - k_3 k_5 \text{[DA]}[\text{DOQ}][\text{CPZ}]}{k_3 \text{[CPZ]}^2 + k_5}
\]  \hspace{1cm} (4.10)

At equilibrium, when \( d\text{[DOQ]}/dt = 0 \), both equations reduce to the equilibrium constant for the overall reaction,

\[
K_{eq} = \frac{k_3 k_4}{k_3 k_4} = \frac{\text{[CPZ]}^2 \text{[DOQ]}}{\text{[CPZ]}^2 \text{[DA]}}
\]  \hspace{1cm} (4.11)

\[
K_{eq} = \frac{k_3 k_5}{k_3 k_5} = \frac{\text{[CPZ]}^2 \text{[DOQ]}}{\text{[CPZ]}^2 \text{[DA]}}
\]  \hspace{1cm} (4.12)

As mentioned earlier, the rate limiting step and the observed rate law depend on local CPZ:: concentration, which may lead to different results from different techniques. For example, if \([\text{CPZ}^+\cdot^+]\) is large relative to \([\text{CPZ}]\) (as will be the case near the electrode during oxidation), eq (4.9) but not eq (4.10) reduces to eq (4.2), the confirmed rate law [117], and reaction 4.3 is rate limiting. If \(k_4\) is negligible and both terms in the denominator of eq (4.9) are comparable, the rate law of eq (4.13) is obtained.
\[
\frac{d[\text{DOQ}]}{dt} = \frac{k_3 \omega [\text{CPZ}^+]^2 [\text{DA}]}{[\text{CPZ}] + \omega [\text{CPZ}^+]} \tag{4.13}
\]

where \( \omega = k_4/k_3 \) is set as a single constant in simulation. Finally, in regions of small \([\text{CPZ}^+\ast]\) and high \([\text{DOQ}]\), the reverse of reaction (4.4) is important, and equilibrium is attained. Thus the observed kinetics may depend strongly on where in the diffusion layer the reaction is monitored. Since the SRAS experiment monitors all relevant distances from the electrode, a range of kinetic cases is observed.

The fact that the rate law (4.10) cannot be reduced to (4.2) argues against the disproportionation mechanism, and the kinetic study may thus be concluded. However, several issues remain. First, the disproportionation mechanism cannot be ruled out just because rate law (4.10) cannot be reduced to (4.2), and further experimental confirmation is needed. Second, reexamination of \text{CPZ}^+/\text{DA} reaction by SRAS is to distinguish the rate law (4.9) from (4.2) even though (4.2) can be reduced from (4.9) and has been confirmed under the conditions of glancing incident SEC. Furthermore, additional kinetic parameters may be extracted out from experiments by SRAS. Since the observed kinetics is strongly dependent on local concentration, they should be perturbed significantly by a change in electrode geometry which will give a different concentration distribution. Diffusion of electrogenerated \text{CPZ}^+ from a microwire electrode will lead to a lower concentration far from the electrode compared to the case of diffusion from a planar electrode. The determination of radial concentration profiles by SRAS and Abel inversion and the dilution effect have been thoroughly discussed in Chapter 3, and the application of SRAS at a microcylindrical electrode to a redox catalysis system of \text{CPZ}^+/\text{MPZ} has also been demonstrated. SRAS at a microwire electrode is used to confirm the reaction mechanism that has been already outlined by Deputy.
Fig. 4-7 (a) shows $\text{CPZ}^\ast$ concentration profiles at a planar electrode for three cases of eq (4.9) which are relevant to the experimental results. Case A (dashed line) assumes $k_3 << k_4, k_5$, so that eq (4.2) applies, Case B (solid line) assumes comparable values for $k_4$ and $k_5$, but negligible $k_4$, yielding eq (4.13). Finally, case C (dotted line) illustrates the case where $k_4$ is not negligible and the entire eq (4.9) applies. Note that the $\text{CPZ}^\ast$ profile extends further into solution due to a comparatively small equilibrium constant which results from a finite $k_4$. Fig. 4-7 (b) shows the effect of rate law on the $C(r)$ profiles for $\text{CPZ}^\ast$ at a planar electrode case, in the same format as Fig. 4-7 (a). One obvious differences is that the thickness of the $C(r)$ profiles is smaller than that of the planar electrode case, as would be expected for rapid dilution. It is based on these considerations that a kinetic study of $\text{CPZ}^\ast$ was conducted using microcylindrical electrodes in an effort to further distinguish rate law (4.9) from (4.10) and (4.2).

Experimental Confirmations and Discussion

Experimental profiles of $\text{CPZ}^\ast$ at a planar electrode conducted in pH 1.5 have been shown to be fitted to scheme I [118], with the $k_4$ being neglected from the rate law because of the large $K_{eq}$ for the overall reaction. It has been also shown that neither the simple first order law of eq (4.2) nor the disproportionation mechanism of eq (4.10) fits the observed $\text{CPZ}^\ast$ profile, with the two kinetic parameters of $k_3 = 2.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ and $k_4/k_3 = 1.0$ being extracted from the fitting. The fit was quite sensitive to $k_3$ and $k_4/k_3$, implying reasonable quantitative accuracy. Based on the determinations of the rate constant $k_3$ and the multi-step mechanism of reaction (4.1) by SRAS at a planar electrode, SRAS is applied to the convergent diffusion case occurring at a microcylindrical electrode in order to enhance the kinetic complications in the region of low $\text{CPZ}^\ast$ concentration. Fig. 4-8 shows the agreement between the $C(r)$ profiles calculated from eq (4.9) and observed profiles. Although small, the inclusion of $k_4$ accounts for the longer tail of the radial $C(r)$ profile. Fig. 4-9 shows the poor agreement between alternative mechanisms and the
Fig. 4-7  
(a) Simulated CPZ•+ profiles at a planar electrode for equation (4.9), cases A-C as described in the text. Dashed line, case A, \( \gamma = 750, \beta = 1, \omega >> 1 \). Solid line, case B, \( \gamma = 570, \beta = 1, \omega = 1 \). Dotted line, case C, \( \gamma = 570, \beta = 1, \omega = 1, k_A C_{CPZ} = 1.0 \).
(b) Simulated CPZ•+ profiles at a microcylindrical electrode, same parameter for three cases.
Fig. 4-7
Fig. 4-8  Radial concentration profiles (points) of CPZ<sup>•</sup> at a 25 μm diameter microwire electrode fitted with simulated profiles (lines) for the CPZ<sup>•</sup>/DA reaction based on equation (4.9), all at pH 1.3. Curve (a), 1 sec; curve (b), 3 sec; curve (c) 10 sec. In all cases, β = 1; k<sub>3</sub> = 2.0 x 10<sup>4</sup>; ω = 1.0
Fig. 4-9  Fits of alternative mechanisms to cylindrical CPZ\textsuperscript{+} concentration profile for the DA reaction at pH 1.3. Points are experimental, solid line was calculated from equation (4.9) for $k_3 = 2.0 \times 10^3$ and $k_4 = 13$. Lower curve was simulated for scheme I, Case a, $k_3 = 2.0 \times 10^3$. Dashed curve is scheme II, $k_3 = 2.0 \times 10^3$, $t = 6$ sec.
observation, thus confirming scheme I for the radial diffusion field near a microwire. Finally, Fig. 4-10 shows the effect of $\omega$ on the agreement between experiment and simulation. Both the shape and depth of the simulated profile vary with $\omega$, and a value of 1.0 provides the best fit.

Lateral absorbance profiles are shown in Fig. 4-11 to 4-13 with the shapes ranging from moderately thin at pH 0.1 to very thin at pH 1.3. The reaction of $\text{CPZ}^{++}/\text{DA}$ is governed by equilibrium at pH 0.1 and kinetics at pH 1.3 respectively as can be seen by the rather close fits consistently from time 1 sec to 10 sec in Fig. 4-11 and 4-13. However, the attempt to account for the reaction at pH 0.5 with an equilibrium model provide rather poor fits of the lateral profiles, as shown in Fig. 4-12, where $K_{eq} = 1000$ only fits the tails of absorbance profiles with the curving portions being poorly fitted. The kinetic model of scheme I could not either fit the lateral profiles from the heads to tails, indicating that the reaction at pH 0.5 may not be governed by either equilibrium or kinetics alone. The complexities of determining equilibrium and kinetics have been addressed by others [137,138]. At a small equilibrium constant, cross reactions are dominated by equilibrium, with the kinetic effects being buried under the equilibrium effects. The case of $\text{CPZ}^{++}/\text{MPZ}^{++}$ is an example. However, the case of $\text{CPZ}^{++}/\text{DA}$ at pH 0.5 can be accounted for neither by equilibrium nor by kinetics. Instead, kinetics accounts for the head of the profile and equilibrium the tail, as shown in Fig. 4-14 (a). The solid line, simulated by rate law (4.9), fits the head portion of the concentration profile, while the dashed line, simulated by equilibrium (4.11), fits the tail of the concentration profile. These two simulated profiles cross over with each other, and as a result of this, the absorbance profiles of Fig. 4-14 (b) are obtained. Based on this observation, the following algorithm for simulation was proposed: in each iteration during a simulation, correction factors due to kinetics by rate law (4.9) and equilibrium by (4.11) are calculated. The smaller one of the two was used to correct the reaction effect on a concentration profile. The concentration profile such simulated is surprisingly well-fitted to the experimental
Fig. 4-10 Comparison of observed (points) and simulated profiles for CPZ$^+$/DA under cylindrical diffusion. $K_{eq} = 1.5 \times 10^4$ and $k_3 = 2.0 \times 10^5$ in all cases. Points are experimental. Solid line, simulated for $\omega = 1.0$, $k_4 = 13 \text{ M}^{-1}\text{s}^{-1}$. Lower dashed curve, $\omega = 10$, $k_4 = 130$; upper dashed curve, $\omega = 0.2$, $k_4 = 2.6$. 
Fig. 4-11 Lateral absorbance profiles (dotted lines) of CPZ•+ at a 25 μm diameter microwire electrode for CPZ•+/DA reaction at pH 0.1, fitted by simulated profiles with an equilibrium constant $K_{eq} = 150$. 
Fig. 4-12 Lateral absorbance profiles (dotted lines) of CPZ$^{\cdot +}$ at a 25 $\mu$m diameter microwire electrode for CPZ$^{\cdot +}$/DA reaction at pH 0.5, fitted by simulated profiles with an equilibrium constant $K_{eq} = 1000$. 
Fig. 4-13  Lateral absorbance profiles (dotted lines) of CPZ·+ at a 25 µm diameter microwire electrode for CPZ·+/DA reaction at pH 1.3, fitted by simulated profiles with kinetic parameters of \( k_3 = 2.0 \times 10^5 \), \( \beta = 0.97 \) and \( k_d = 13 \).
Fig. 4-14  (a) At pH 0.5, the equilibrium model (dashed line) only fits to the tail of the 1 sec radial concentration profile, while the kinetic model (solid line) only fits to the head of that profile.  (b) The simulated absorbance profile based on the equilibrium model fits to the tail while the kinetic model to head of the experimental absorbance profile.
**Fig. 4-14**

(a) Concentration (mM) vs. Distance From Center of Electrode (µm)

(b) Absorbance vs. Distance From Center of Electrode (µm)
concentration profile (after Abel inversion), as shown in Fig. 4-15 (A). Details of profiles can be seen in the expanded profiles in the upper corner of Fig. 4-15 (A). Profile (a) and (b) of equilibrium and kinetics are shown to be out of fit in the head and tail portions respectively with the experimental profiles, but profile (c) overlaps perfectly with the head portion of profile (b), the tail portion of profile (a) and with the experimental profile. Fig. 4-15 (B) shows the nearly perfect fit of the new simulation with the experimental absorbance profile. This new approach of simulation may perhaps be used to illustrate a principle of "the smallest correction" for homogeneous cross reactions. The significance of this principle can be appreciated as followings. The rate of a homogeneous reaction is governed by a rate constant, while the extent of the reaction is governed by an equilibrium constant. The final result, however, is determined by the process yielding the smallest concentration change. Examples of homogeneous cross reactions at two extremes of both equilibrium and kinetics have been studied, and often they are treated independently. What has not been seen and is yet more general, however, is the case between the two extremes. Experimental results at pH 0.1, pH 1.3 and 1.5 of the CPZ⁺⁺/DA reaction can all be explained by "the smallest correction" principle. At the low pH of 0.1, the equilibrium constant is fairly small so that the reaction of relatively fast rate is finally governed by the equilibrium process (the process yielding the smaller effect on concentrations). Thus the effect of equilibrium is observed under such a condition. On the other hand, the equilibrium constants at pH 1.3 and 1.5 are fairly large so that the final result of the reaction within a particular time interval is governed by the rate of reaction (the process yielding the smaller effect on concentrations again). Since only one process dominates in each of the two extreme cases, the smallest correction principle has been easily ignored in simulations and fits between experimental and simulations tend to be heads and tails under the conditions between two extremes. With "the smallest correction" principle incorporated in the simulation, only the correction factor yielding the smallest concentration change is used to correct the concentrations. Results such obtained better reflect closer to the real situation of cross reactions.
Fig. 4-15  (A) The simulated concentration profile based on the smallest correction principle (see text for explanation) fits to the experimental concentration profile (the dotted line). Curve (a) is the profile with $K_{eq} = 1000$. Curve (b) is the profile with $k_3 = 2.0 \times 10^5$, $\beta = 0.97$, $k_4 = 13$. In curve (c) (the solid line), $K_{eq} = 1000$, $k_3 = 2.0 \times 10^5$, $\beta = 0.97$, and $k_4 = 13$ are used. (B) The absorbance profile is fitted by the three cases mentioned in (A), with the solid line fitting well to the experimental absorbance profile (dotted line).
Fig. 4-15
The pH dependence of scheme I is likely to be complex, since as many as 4 pKs of DA and DA\textsuperscript{++} may be involved. In addition, the time scale accessible with SRAS is fairly small, ranging from about 500 msec to several seconds for the CPZ\textsuperscript{++}/DA reaction. Therefore, there is a limit on the variation in rates for which useful profiles may be obtained. Nonetheless, several pH values from 0.1 to 1.5 were investigated for the microwire case. The kinetic parameters extracted from experimental profiles are listed in Table 4-1. The \( k_3 \) values shown in Table 4-1 were simply derived from the measured values of \( \gamma = k_3 C_{CPZ}^b \). \( k_4 \) was determined from \( k_3 \), the experimental values of \( \omega = k_4/k_3 \) and the known values of \( K_{eq} \) via eq (4.8). Since reaction (4.1) generates H\textsuperscript{+}, its equilibrium will be shifted toward the reactants at lower pH. The lower pH experiments show a greater tail on the C(t) profile, so that the integration of this tail by optical experiments gives thicker absorbance profiles at 0.1 pH as opposed to thin at pH 1.3. Table 4-1 summarizes kinetic results from the various experimental condition, including pH.

Scheme I and eq (4.9) are validated experimentally from observed concentration profiles with varying \( \beta \), time and diffusion geometry. Table 4-1 demonstrates consistent values of \( k_3 \) determined from curve fits under a variety of conditions. Furthermore, alternative mechanisms are inconsistent with the observations and can be rejected for the conditions employed. All attempts to vary \( \gamma \) and \( \omega \) to fit scheme II did not lead to consistent values of \( k_3 \) with varying \( \beta \).

As mentioned earlier, the observed rate law depends strongly on local concentrations and therefore on the distance from the electrode surface. This fact make SRAS a particularly appropriate probe of the reaction, and provides new information not available with conventional amperometry or glancing incidence chronoabsorptometry. Amperometry is insensitive to the redox cross reaction, and reveals only the sum of the two bulk concentrations of CPZ and DA. Glancing incidence absorption experiments measure the integral of the CPZ\textsuperscript{++} concentration profile, and are dominated by a region of high CPZ\textsuperscript{++}
Table 4-1

Kinetic parameters determined from CPZ•+ profiles

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>β</th>
<th>( k_3 \times 10^{-5} ) (M²s⁻¹)</th>
<th>( k_4 ) (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPZ•+ /DA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar** Electrode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 1.5</td>
<td>2.18</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.47</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>pH 0.1</td>
<td>1.0</td>
<td>(0.1)⁷</td>
<td></td>
</tr>
<tr>
<td>Cylindrical Diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 1.3</td>
<td>1.0</td>
<td>2.0</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>0.48</td>
<td>2.0</td>
<td>13</td>
</tr>
<tr>
<td>pH 0.5</td>
<td>0.97</td>
<td>1.8</td>
<td>180</td>
</tr>
<tr>
<td>pH 0.1</td>
<td>1.0</td>
<td>(1.6)⁷</td>
<td>(1070)⁷</td>
</tr>
</tbody>
</table>

a. See text for details of \( k_4 \) determination.
b. Kinetic data at planar electrode are from reference [118].
c. Too close to equilibrium for accurate fit.
concentration. Thus conventional SEC is consistent with eq (4.2) for the CPZ\(^{++}\)/DA case and does not reveal reactions (4.4). The perturbation on the integral caused by the overlap region is slight, amounting to only a few percent of the integrated CPZ\(^{++}\) concentration.

The SRAS experiment provides complete concentration profiles rather than their integral, and the region where the CPZ\(^{++}\) profile meets the DA profile can be monitored distinctly from the majority of the CPZ\(^{++}\) concentration near the electrode. Not surprisingly, it is this region which is most sensitive to mechanistic nuances. Stated differently, the low CPZ\(^{++}\) concentration in this region decelerates the reaction rate enough to observe the multi-step reaction. SRAS at microwire electrode makes the region of low CPZ\(^{++}\) concentration extend further relative to the bulk CPZ\(^{++}\) concentration near the electrode to that mechanistic nuances are more pronounced. Furthermore, the involvement of microwire electrode SRAS in kinetic study of CPZ\(^{++}\)/DA reaction makes \(k_4\), which was neglected from the rate law because of its small values, a significant part in eq (4.9). At pH 1.3 and 1.5, the experimental profiles could not be fitted well without the involvement of \(k_4\). The fact that \(k_4\) can be neglected from the rate law (4.9) to give (4.12) at a planar electrode and not at a microwire electrode owes its origin to the extended tail in the microwire electrode case. The greater accuracy of the SRAS experiment thus permits the conclusion that scheme I mechanism (4.6) if favored over eq (4.2).

Given the normally rapid disproportionation of semiquinones in acidic solution, it may be surprising that DA\(^{++}\) reacts with a second CPZ\(^{++}\) rather than another DA\(^{++}\). This occurrence may be a simple matter of local concentration. Even in the region where CPZ\(^{++}\) and DA meet, the CPZ\(^{++}\) concentration is presumably much higher than DA\(^{++}\). Thus \(k_5\) would have to be much larger than \(k_4\) for disproportionation to be operative. The rate constants in Table 4-1 lead to several conclusions about the kinetics of scheme I. First, \(k_5\) is weakly pH dependent, varying by less than a factor of two from pH 0.5 to 1.5. Deakin and Wightman have reported that heterogeneous oxidation of catechols involves electron
loss before proton loss at low pH [140], implying that the forward step of reaction (4.3) should not depend on [H⁺]. This finding is consistent with earlier work based on eq (4.2) [117]. Second, the observed $k_4$ is strongly pH dependent, as it must be to explain the observed values of $K_{eq}$. Since $k_3$ and $k_4/k_3$ vary only slightly with pH, the variation $K_{eq}$ with pH must be due primarily to $k_4$. Although only a limited range of pH values were studied, the results are consistent with the reverse of reaction (4.4) involving at least one proton [140].

**Conclusions**

SRAS has been applied to study the reaction of $\text{CPZ}^{+*}/\text{DA}$ reaction and has been shown to be informative about homogeneous reactions following electrochemical reactant generation, providing new information about redox mechanisms. In particular, SRAS at microwire electrodes is used to obtain more kinetic data by further perturbing the concentration distribution of electroactive species as a result of the convergent diffusion at the microcylindrical electrode. The normal incident SEC experiment was shown to lead to a limiting case of the overall mechanism and provide a subset of the conclusions available from SRAS. The mechanisms and kinetics of the $\text{CPZ}^{+*}/\text{DA}$ redox cross reaction have been studied in some detail. The stepwise mechanism of cross electron transfer reaction is supported strongly by experimental data with the rejection of the disproportionation mechanism. With SRAS, kinetic rate laws are shown to be strongly dependent on the local concentrations of electroactive species in the diffusion layer, information which is not available from any other SEC techniques.

Due to the involvement of $\text{H}^+$ in the $\text{DA}/\text{DOQ}$ redox couple, the reaction of $\text{CPZ}^{+*}/\text{DA}$ is strongly dependent on pH, with kinetic data of $k_3$, $k_4/k_3$, and $k_4$ being extracted from experimental results at pH 0.1, 0.5, 1.3, and 1.5. At the lower pH of 0.1, the reaction is totally governed by equilibrium (the slower process compared to kinetic) and is
governed by kinetics at higher pH values of 1.3 and 1.5, (again the slower process compared to equilibrium). Instead of trying to explain the concentration profile using a single factor of either equilibrium or kinetics, the principle of the smallest correction was shown to be applicable in the reaction at pH 0.5. This principle has been shown to give good simulation results for the reaction at pH 0.5, where neither equilibrium nor kinetics alone, but the process yielding the smallest correction is operating at any particular time.
Chapter V

Two-dimensional Imaging of Diffusion fields at Micro-disk Electrodes and Microelectrode Arrays by Charge-Coupled-Device (CCD) Detector

Background

Two-dimensional imaging methods such as optical microscopy and scanning electron as well as scanning electron tunneling microscopy are very powerful techniques for surface analysis and microanalysis, providing surface structure and topographic information. However, there are only a few two-dimensional imaging techniques for in situ electrochemical analysis. Two-dimensional imaging of electrode surface activity enhanced by electrogenerated chemiluminescence (ECL) has been a useful method for examining the heterogeneity of electrode surfaces [142]. For example, the difference in electron transfer kinetics between basal plane and edge plane has been demonstrated on a highly ordered pyrolytic graphite (HOPG) surface by two-dimensional imaging enhanced with ECL [143]. Scanning electrochemical microscopy is another two-dimensional imaging technique that has recently been developed and has demonstrated the ability for characterizing electrode surfaces and topography [144-146]. While these imaging methods have provided a great deal of information regarding the surface conditions and heterogeneous electron kinetics, diffusion fields of modern analytical electrodes have never been observed. Diffusion fields have much information analogous to the topography of solid surfaces which may have been ignored due to the fact that they are not a part of the solid electrode per se. Part of the reason for not observing diffusion fields is the lack of proper detectors and enhancement
of diffusion fields by the existing two-dimensional imaging techniques. As microelectrode-based electroanalytical devices become more popular in electrochemistry, studies of electrochemical processes of many electroanalytical devices and microelectrodes can benefit from two-dimensional imaging of diffusion fields.

In the development of the spatially resolved imaging technique, SRAS has been used to provide one-dimensional mass transport information. Specifically, SRAS has been applied to obtain concentration profiles and reveal unexpected mass transport processes. Examples of unexpected mass transport include solution convection in one-dimensional diffusion cases at different electrode geometries in chapter 2, and of two-dimensional but radial symmetrical diffusion cases at microcylindrical electrodes in chapter 3. Spatial resolutions of 4 μm at planar electrodes of finite electrode length and 2 μm at microcylindrical electrodes have been obtained. It is a natural step to study the three-dimensional diffusion problem at electrodes such as a microdisk embedded in a large plane, or the end of a microwire and a microdisk electrode array. With the availability of two-dimensional array detectors such as charge-coupled-device (CCD), a new form of SRAS is possible in which the diffusion field of a microdisk electrode is imaged.

Owing to the small size of microdisk electrodes in comparison to \((Dt)^{1/2}\), two-dimensional diffusion will be established rapidly so that special properties such as steady state diffusion-limited current and high mass flux at the electrode surface may be observed, as has been discussed in chapter 3 in conjunction with the discussion of micro-cylindrical electrodes. Although much has been learned about the diffusion and current behavior of micro-cylindrical electrodes in terms of the shape and dynamics of concentration vs. distance profiles, there is still much to be learned about the diffusion behavior of microdisk electrodes arrays. As an early type of microelectrode, microdisk electrodes have been the most popular partly because of the higher mass flux to microdisk, compared to a microwire electrode. In addition, microdisk electrodes are easily pre-treated.
In spite of its more common usage, the mathematical treatment of the diffusion problem of microdisk electrodes is even more difficult than that of microcylindrical electrodes, although the diffusion process in microdisk electrodes can be approximated by a hemispherical diffusion at times near steady state. Most previous efforts on microdisk electrodes have been based on attempts to solve and interpret the time-dependent diffusion problem of eq (5.1) in the cylindrical coordinate system [90].

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2} \right) \quad (5.1)
\]

Numerical calculations of the time-dependent response (digital simulation of the diffusion process at microdisk electrode) represent a major effort in solving the diffusion problem of eq (5.1), and have yielded many useful results [89]. Recently, Pons and Fleischmann have reported solving the time-independent problem of eq (5.2), a steady state solution of eq (5.1)[90].

\[
\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2} = 0 \quad (5.2)
\]

For a boundary condition of a microdisk electrode with a radius \( r_0 \), and experimental conditions of a diffusion-limited potential step experiment, the following solution was obtained:

\[
C = C_b - \frac{2}{\pi} C_b \int_0^\infty e^{-\lambda z} \sin(\lambda r_0) J_0(\lambda r) \frac{d\lambda}{\lambda} \quad (5.3)
\]

with the total flux to the surface of the disk being:

\[
F = 2\pi D \int_0^\infty \left[ -\frac{\partial C}{\partial z} \right]_{z=0}^\infty r dr = 4DC_b r_0 \quad (5.4)
\]
where $J_0$ is a Bessel function of the first kind of order zero. The initial interest of this solution was in the study of fast heterogeneous electron transfer reactions under steady state diffusion conditions [147,148]. While the two important solutions of eq (5.2) may have helped in understanding the diffusion and current behavior at steady state, the following questions arise: When does mass transport reach steady state and how does the mass transport of microdisk electrodes at steady state differ from hemispherical diffusion?

Microelectrode arrays are attractive because they can retain certain characteristics of microelectrodes such as high mass flux at the electrode surface and steady state current without requiring measurements of small signals against noisy background. Depending on the size of each microspot and the separation between spots, their effects on the voltammetric current behavior of microdisk electrode arrays created by a nitrogen laser has been studied [149]. As this study may lead to a better understanding of the microelectrode arrays in terms of the spot size and separation, a knowledge of how and when the fields of nearby spots are overlapping would be beneficial because these factors essentially affect the voltammetric current behavior such as lowering the mass transport rate. Furthermore, a closer examination of the electrochemical performance of each individual spot on a microdisk electrode with an in situ technique such as ECL imaging would add further support to the already existing regular image of a microelectrode array examined under a microscope. These and the questions mentioned earlier about the steady state of microdisk electrodes may be resolved by spatially resolving the diffusion layer to quantify the diffusion processes at microdisk electrodes and arrays.

In this chapter, the capabilities of the two-dimensional imaging system equipped with a CCD detector are investigated and demonstrated with three imaging modes: transmission mode, ECL imaging mode and normal incidence reflection mode. The transmission mode is used to image the diffusion field at the tip end of a microwire and the mass transport processes at minigrid electrodes. The ECL imaging mode is used for studying the surface
activity of microelectrodes and arrays, and the normal incidence reflection mode is used to reveal the three-dimensional information of mass transport in microelectrodes and arrays.

**Experimental**

**Optical arrangement and imaging modes.** The optical arrangement for the two-dimensional imaging experiments with the CCD is shown in Fig. 5-1 with (A) showing the overall layout of the imaging apparatus and (B) specifically showing the optics for the ECL and normal incidence reflection imaging experiments. The photodiode array detector was replaced with a charge-coupled-device detector, with the detector chip being in the same focal plane. For transmission mode imaging experiments, the rest of the optical components were in the same positions as discussed in Chapter 3. For ECL and normal incidence reflection imaging modes, the light was directed to the back of two collection lenses 4 and 5 by two mirrors and a beam splitter. The light beam was used for illumination for pre-focusing before ECL imaging experiments, and the ECL emission light was detected by the CCD during an ECL process with the illumination light turned off (or blocked off). In the normal incidence reflection imaging mode, the light beam came in through the two collection lenses 4 and 5 to strike on and reflect off the electrode surface (traversing twice the diffusion layer perpendicularly), and went straight to the CCD detector. The beam splitter was a pellicle type (d = 25.4 mm, Melles Griot, CA) with a thickness of only 5 μm which causes little direction displacement and minimal ghost images after beam passage.

**Electrode Preparations.** For transmission mode imaging experiments, two kinds of electrodes were used: microwire electrodes and minigrid electrodes. Preparation of a microwire electrode for wire-end-imaging was the same as that described in Chapter 3 except that after the wire was pulled straight, it was trimmed with a pair scissors at a length of 3 mm. Preparation of a minigrid electrode was lengthy. Two microscope slide glasses with a size of 1 x 2 cm² were drilled near one end, one with a slot of 3 x 5 mm² the other...
Fig. 5-1 Optical arrangement for two-dimensional imaging experiments. (a) Overall optical layout for three imaging modes. (b) Optics for ECL and normal incidence reflection imaging modes.
other with a slot of 3 x 10 mm². After the two glasses were roughened with sand paper on one side, a thin layer of silicone sealant was applied on the roughened surface of each glass. A 6 x 8 mm² piece of gold minigrid was put on the glass, with the smaller 3 x 5 mm² slot being completely covered. The glass with a bigger slot was then put on top of the first glass, with the gold minigrid piece being sandwiched in between the two glasses. A gentle pressure was applied to the two glasses until the silicone sealant was dry. The minigrid electrode with the glass substrate was then inserted into the slots in a Teflon holder similar to the one in Chapter 3. A piece of copper wire was used to make an electrical connection from the gold minigrid to a large platinum wire. After the silver epoxy between the copper wire and the gold minigrid was dry and hardened, a layer of silicone sealant was put on top of them to protect the copper wire and silver epoxy from contacting the solution. The preparation of the microdisk electrode array is described in detail in reference [149]. A brief outline is given here: A glassy carbon disk of 5 mm diameter was polished using a standard electrode polishing procedure (1, 0.3, 0.05 μm alumina). A layer of organic thin film (indelible felt-tipped marker pen which is based on proprietary chemistry [149]) was then applied to the surface of glassy carbon disk. After this layer dried, the disk was put into an electrode holder and connector, which was then screwed into an assembly suitable for fabrication of microelectrode arrays by a nitrogen laser. After the array fabrication, the electrode holder was then screwed into an electrochemical cell horizontally. The Teflon electrochemical cell was bolted onto a rotational stage, which was on top of two translational stages.

**Beam alignment.** Beam alignment for transmission imaging experiments was the same as described in Chapters 2 and 3. However, the beam alignment for ECL and normal incidence reflection experiments was very different. Procedures below were followed for beam alignment. After the beam was aligned with the procedures for transmission experiments, it was directed by two mirrors (M1 and M2) into the beam splitter (assisted
with a carpenter square), as shown in Fig. 5-1(B). Positions of lenses 4 and 5 were never moved so that the light collection optics were kept in alignment. The beam splitter was orientated at 45° with respect to the incoming beam, and was positioned approximately 10 cm after lens 5. With the position of the beam splitter adjusted, the beam reflected off the splitter was directed through the centers of lenses 4 and 5. The beam direction was checked with a carpenter square before and after the two lenses to insure alignment. A mirror was then put in a position close to the expected position of the working electrode to reflect the beam going back through the collection lenses and then to the detector. After putting the solution into the cell and the working electrode into the imaging position, the beam was adjusted to image onto the CCD by turning the rotational stage holding the cell and the rotational stage holding the beam splitter (slightly if necessary).

**Image focusing.** Procedures as well as the criteria for fine-focusing of the two-dimensional imaging experiments were totally different from one-dimensional imaging experiments. First, there was no such a criterion as how many diodes are along the rising portion of the intensity profile of an image because of the way a profile is displayed by CCD. Second, the readout and display processes were not instantaneous which are different from the readout and display processes of the photodiode array detector with the Tracor Northern controller. It took at least 7 sec to see the effect of changes in positions of the collection lenses. The host computer of CC200 was programmed to control the CC200 system to take a picture and display it continuously while an object was being focused. Since imaging objects were small (usually microwires), for transmission imaging experiments, the quality of focusing was judged by looking at the image of the object during a coarse tuning and by looking at sharpness of the beam profile displayed on the monitor screen during a fine tuning. A well-focused image should have a nearly flat bottom across the object image (microwire) in the beam intensity profile, with the transitions from dark (low intensity) to bright being as sharp as possible. For ECL and normal incidence reflection
imaging experiments, the quality of focusing was judged visually by how good the image of the glassy carbon electrode surface was, such as the sharpness of a small scratch or a small hole. Instead of tuning the positions of lenses 4 and 5, the position of the object was tuned for ECL and normal incidence reflection imaging experiments. It was noticed that the front glass of the electrochemical cell also reflected light and gave a ghost image on the CCD chip. This image was easily taken as the image reflected off the electrode surface. If the glass was parallel with the electrode surface plane, the two images were overlapping, otherwise they were not. It was sure that the image detected by the CCD detector was reflected off the electrode surface.

**CCD operation.** CCD detectors represent the latest advancement of modern technology in optical sensors. Advantages of these detectors over others include their higher quantum efficiency towards radiation in the visible and near IR range, low readout noise and low dark counts when operating at -110°C cooled by liquid nitrogen. The CCD detector used is made by Photometrics company (Tucson, AZ), and has 516 x 516 elements. The timing-control by an XT computer for CCD and the potentiostat was similar to that described in Chapter 2. However, the camera head was controlled by the host computer with the following command strings: "1 ci trig 1 obs 2 ci trig 1 obs qshow" (see Table 5-1 for comments of each command, also see the CCD manual for a complete description of the CCD commands.) At "1 ci", the CC200 computer was told to go to cache 1 (fast access memory location) for storage of the first image data. The CCD detector was put on a waiting status by the "trig" command. When the CC200 computer received a negative pulse from the XT computer, the detector was ready to expose and was triggered to do so when the triggering pulse went from logic low to logic high. The command "1 obs" was executed to open the shutter for an exposure of 1 unit time (1 is one unit time length. The default length is 1 dsec) and to read out the data on the chip after the shutter was closed. Depending on the system gain, it took at least 5.5 seconds at zero cgain for the CC200
Table 5-1

Summary of CCD commands used in imaging experiments

<table>
<thead>
<tr>
<th>commands</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ci</td>
<td>The CCD is directed to go to cache 1 (a cache is a fast access storage memory location) for storage of the first set of image data.</td>
</tr>
<tr>
<td>trig</td>
<td>The CCD detector is waiting for a triggering signal (5 ms, 5 Volt negative pulse) at this command.</td>
</tr>
<tr>
<td>1 obs</td>
<td>The CCD detector is directed to expose for 1 unit time, and then reads out the electrons stored in each pixel element. The default length of unit time is 1 dsec. This length can be changed, however, to as small as 1 msec, or as long as 1 minute by another command &quot;tscale n&quot;. The readout times may vary, depending on the CCD format, such as binning and the size of the picture frame. For example, for a full frame picture with zero binning and zero cgain, it takes about 5.5 sec for the CCD to read all 516 x 516 pixel elements.</td>
</tr>
<tr>
<td>2 ci</td>
<td>The CCD computer is directed to go to cache 2 for storage of a new image data.</td>
</tr>
<tr>
<td>qshow monitor.</td>
<td>The CCD computer displays the latest image obtained on the monitor. The brightness and contrast of the picture is automatically determined by the CCD computer. For a better view of the picture, a windowing command can be used (see CCD manual for detailed description of the windowing method).</td>
</tr>
</tbody>
</table>
computer to read all 516 x 516 elements out. At "2 ci" command, CC200 quickly switched to cache 2 and waited for another negative pulse upon receiving the command of "trig". After a certain time (a few seconds), the XT computer sent out a second negative pulse to trigger the CCD detector. The detector followed the same sequence to obtain a second beam image. It was necessary for the timing-control computer to wait at least 6 seconds (the time for the CC200 computer to read all data out) before sending a second negative pulse to CCD. Otherwise, the CC200 system would wait for a triggering pulse to come forever when this pulse had actually been sent out but had not been received by CC200 at a proper time. Thus the whole system would be stuck on waiting. The second image was finally displayed on the monitor by the command "qshow".

For absorption experiments (transmission and normal incidence reflection imaging), the exposure time of the CCD detector was no longer than 0.5 sec, depending on the actual experimental time and the intensity of the beam. For ECL imaging experiments, the CCD detector was exposed to the ECL emission light immediately after the oxidation of luminol (it was actually 0.01 sec after) and the emission light was collected for 5 to 10 sec under the assumption that electrochemical experiments were at least as long. Because of the high sensitivity of the CCD detector, an exposure time of 10 sec resulted in collection of much stray light on the ECL image. In order to compensate for this, the CCD detector was open to the same environment (except no ECL) for the same length of exposure time before an ECL experiment. This background image was then subtracted from ECL image. Exposure time was an important experimental parameter. The CCD can detect much lower light levels than the photodiode array detector. In transmission imaging experiments, an exposure time of 10 ms should be long enough to give a bright image. However, since the shutter action was mechanical and took about 10 to 20 ms to mechanically open and close, an exposure time shorter than 50 ms was not very accurate and reliable. Another factor which limited the use of short exposure time was the "ghost" image of a shutter blade.
When the exposure time was shorter than 30 ms, the shutter blades were not being opened completely before they were forced to close again. As a result of this, part of the image was covered by one of the blades, and a "ghost" image was thus formed. Therefore, the shortest time for SRAS experiments was limited to 0.1 sec with an exposure time of 50 ms, which was already long enough to challenge the accuracy of the true electrochemical experimental time.

**Chemicals and solution preparation.** Chlorpromazine (CPZ) for absorption imaging experiments and Luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) for ECL experiments were purchased from Sigma and Kodak chemical companies respectively and were used as received. CPZ solutions were prepared in 42% MeOH/H2O (W/W) in 0.5 M HClO4, taking all precautions mentioned in Chapters 2 and 3. Luminol solutions of 5 mM in a 50 ml flask were prepared in 0.05 M Sodium Borate (NaB₄O₇•10H₂O), adjusted to pH 10. After the solution was degassed, a drop of 30% hydrogen peroxide was added to the flask (a drop of H₂O₂ weighed 0.025 g), making the concentration of H₂O₂ 4.4 mM in 50 ml. For transmission imaging experiments, since a Ag/AgCl wire was used for the reference electrode the potential control was the same as the imaging experiments in Chapter 3. For ECL imaging experiments, the oxidation potential of luminol was stepped to 1. volt vs. SEC to make sure that luminol was oxidized at a maximum rate. Since mechanisms of ECL generation from luminol have been studied and discussed thoroughly in the literature, no attempt was made to study the electrochemical behavior of luminol, but the ECL emission phenomena was simply utilized to enhance images.

**Results and Discussion**

Examination of small objects by microscope has been a common practice for analytical chemistry. However, imaging of diffusion fields of electrogenerated products is still rare, especially the diffusion fields from microelectrodes. The image of a dropping mercury
electrode and the diffusion field have been reconstructed from holographic interferograms with relatively low spatial resolution [49]. The combination of the already existing imaging optics and the CCD two-dimensional detector makes SRAS a potentially useful technique. Given the dimensions of 20 μm per pixel element, the 20x magnification of the collection optics by lenses 4 and 5 gave a mechanical resolution of 1 μm, that is, one pixel in the detector represents 1 μm in the diffusion field. With the CCD size of 516 x 516 elements, the maximum size of object observable was 500 μm squared. Plate 5-I shows an image of a gold minigrid with 200 grids/in, with the intensity profile of the center row extracted from the image shown in Fig. 5-2. As can be seen from the figure, there are only two pixels along the rising portions from dark to bright, indicating that the spatial resolution is 2 μm.

The minigrid electrode was one of the early types of optical transparent electrodes used for thin layer OTE spectroelectrochemistry. SEC with minigrid electrodes offers simplicity and convenience for probing electrochemical processes and has contributed a wealth of useful information to electrochemistry [4,7]. However, the mass transport process from the minigrid electrodes has not been studied in detail at this point. SRAS with two-dimensional imaging was used to examine the diffusion process at a minigrid electrode. With the grid-plane oriented perpendicular to the optical axis, the diffusion field is traversed by the light beam with the absorbance at each pixel being proportional to the integration of concentration. Since the cylindrical diffusion process has been studied thoroughly in chapter 3, no attempts were made to resolve the single wire diffusion case. Instead, the behavior of the minigrid electrode as a whole was examined. Shown in Plate 5-II are four images of diffusion fields from a minigrid electrode for experimental times ranging from 0.1 sec to 2 sec. Because of the limitations in the CC200 computer, images could be displayed only as differences between reference images and sample images, not as absorbances. Nonetheless, the diffusion field is shown to grow with time. The squares are shown to be filled with electrogenerated product at 2 sec. The diffusion process at a minigrid electrode
Plate 5-I.

An image of a minigrid electrode (transmission mode) by CCD detector.
Fig. 5-2  Intensity profile of a minigrid electrode with approximately two pixels along the rising portions of the grid wires. With the pixel size being 20, $\mu$m, a 20 times magnification makes the mechanical resolution 1 $\mu$m.
Plate 5-II. Images of diffusion fields of a minigrid electrode at experimental times: (a) 0.1, (b) 0.5, (c) 1, and (d) 2 sec.
Plate 5-II
can be seen better in Fig. 5-3, where absorbance profiles of 0.1 sec to 8 sec are the results of external calculation from the reference and sample beam profiles of the center rows extracted from the reference and sampling beam images. Diffusion layer from adjacent wires are shown to start overlapping at time of about 1.0 sec. However, as the space between two wires was filled by more and more electrogenerated product, the diffusion layer did not become flat even at time of 8 sec. After 8 sec of electrolysis, the diffusion layer half-thickness was \((3.2 \times 10^6 \text{ cm}^2/\text{sec}) (8 \text{ sec})^{1/2} = 50.6 \mu\text{m}\), which was half of the dimension between the two wires (the separation between two wires is about 112 \(\mu\text{m}\).) Although experimental data for times longer than 8 sec were not available, it is predicted that the diffusion layer would not become flat until at least 40 sec after initiation of electrolysis at which time the diffusion layer thickness is about the same as the separation distance between wires (112 \(\mu\text{m}\)). Shown in Fig. 5-4 is a plot of absorbance at the center between two wires of the profile vs. \(t^{1/2}\). The slope of 0.0733 is smaller than twice the slope of the plot expected for diffusion of OTE experiments at a planar electrode for the same solution conditions, indicating that the diffusion was not long enough for a minigrid electrode to behave as a planar electrode.

Imaging of the diffusion field at the end of a microwire was the extension of SRAS at planar and microwire electrodes using a one-dimensional photodiode array detector. Two motivations have prompted to this research effort. First, the diffusion process at a microdisk electrode should be expected to be one-dimensional at short times and spherical at long times. What are the time scales for one-dimensional and spherical diffusion respectively? What should the intermediate states look like? Second, when will the mass transport at a microdisk electrode reach steady state and how close is the diffusion field to a spherical diffusion field at steady state? Using the same optical setup described in Chapter 3 with the light beam pointing to the wire-end, images of the diffusion field of a wire-end of a 25 \(\mu\text{m}\) diameter were obtained and are shown in Plates 5-III for experimental
Fig. 5-3  Absorbance profiles (across the central row of the minigrid) vs. minigrid dimension. Experimental times from bottom to top are: 0.1, 1, 2, 3, 4, 6, 8 sec.
Fig. 5-4  Absorbance (the center point between two wires) vs. $t^{1/2}$.

Slope = 0.733

$R = 0.9988$
Plate 5-III. Images of diffusion fields of a microwire-end at experimental times: (a) 0.1 sec, (b) 1 sec, (c) 2 sec, (d) 4 sec, (e) 8 sec, (f) 12 sec, (g) 16 sec, (h) 20 sec.
times of 0.1 sec to 20 sec. Scattering of dust particles can also be seen from these images. Due to the problem of exposure time described in the experimental section, the shortest reliable time of potential step experiment was 0.1 sec. As can be seen from the plate, even at 0.1 sec, the diffusion field has started demonstrating some spherical diffusion characteristics. At a 4 sec experimental time, the spherical diffusion cone is rather pronounced. Although the diffusion field becomes more spherical at longer times, at the experimental time of 20 sec it exhibits a non-spherical field. This view of non-spherical diffusion field may have been caused by two things. First, the diffusion process at the side is only two-dimensional, while at the bottom the diffusion process is three-dimensional and the dilution effect is faster, making the diffusion field look flat. Second, the diffusion process is probably under strong influence from solution convection at this time. While the two-dimensional images provide qualitative information about the diffusion process at the wire-end, spatially resolved profiles provide direct quantitative information about the diffusion layer as a function of distance from the electrode surface. Using the model diagrammed in Fig. 5-5, the diffusion field at the end of a microwire electrode is modelled as spherical at long times. It is assumed that there is no net mass transport across the x-y plane so that the diffusion cone is due to the end of a microwire only. Because of spherical symmetry, the central slice is shown to be taken out from the diffusion field for analysis. If the diffusion process has progressed to the extent that spherical diffusion can be assumed, then analysis of spherical diffusion can be approximated by applying the Abel inversion to the geometry in Fig. 5-5 (b), with the light beam being along the y axis. Thus, a strategy for obtaining a spherical concentration profiles is outlined as follows: The center column data along the wire axis is extracted out from a two-dimensional image. This absorbance vs. distance profile is compared with the simulated absorbance profile of a pure spherical diffusion case to see the difference between pure spherical diffusion and diffusion from the end of a microwire (an approximation of a microdisk electrode). Absorbance
Fig. 5-5 Schematic of the spherical diffusion at a virtual steady state of mass transport at the end of a microwire electrode.
Fig. 5-6  Absorbance profiles of the central slice of a diffusion field at the end of a microwire. Experimental times are: 2, 4, 8, 12, 16, and 20 sec (from the bottom to the top), where the solid lines are experimental and the dashed lines are simulated using spherical diffusion model.
profiles of a 25 μm wire end obtained according to the scheme outlined above are shown in Fig. 5-6 along with the simulated absorbance profiles of 25 μm pure spherical diffusion for comparison. The absorbance profiles at experimental times of 1 to 4 sec fall below the simulated ones for pure spherical diffusion. After 8 sec, the diffusion geometry at the wire-end appears to be spherical to 16 sec. The absorbance profile at 20 sec falls below the simulated profile again at the tail which is consistent with this qualitative view of the image. The diffusion front after 16 sec is probably being pushed back by solution convection.

What has been observed is that the diffusion process slows down after about 16 sec as compared to a theoretical model of the true hemispherical diffusion, which may eventually leads to a virtual steady state of mass transport. Virtual steady state mass transport is shown to form about 20 sec for 25 μm micro-disk electrode. While 20 sec of electrolysis may be considered a long time for chronoamperometry at microelectrodes ((Dt)^1/2 = 80 μm with D = 3.2 x 10^-6 cm^2/sec), it may not be long enough for a true steady state of mass transport (a steady state that is governed by eq (5.3) under ideal conditions without convection) to be established for microdisk electrode of 25 μm diameter. In reality, such an ideal condition may not be attainable because solution convection usually sets the final virtual steady state of mass transport, although the diffusion process at the end of a microwire is only an approximation of a microdisk electrode of the same diameter.

Two-dimensional imaging has long been used for surface examination and has recently been used to examine the heterogeneous activities of an electrode surface enhanced with the electrogenerated chemiluminescence (ECL) [142]. The applicability of this feature with a CCD detector is demonstrated in Plates 5-IV to 5-V, where one microwire electrode gives bright ECL emission while only a small portion of the other microwire gives ECL emission as a result of long time usage without cleaning. One of the problems discussed in Chapter 3 was the surface treatment of a microwire electrode. It was shown that soaking a microwire electrode in concentrated sulfuric acid could regenerate electrochemical activity, resulting in an increase in current by a factor of eight after acid treatment. While it was
Plate 5-IV.
(a) ECL, and (b) normal images of a microwire electrode which demonstrated a high electrochemical activity (high current response)
Plate 5-V.

(a) ECL, and (b) normal images of a microwire electrode which demonstrated a low electrochemical activity (low current response)
postulated that surface deposits may have blocked the electrode surface, it is worthwhile to examine the surface conditions in an *in situ* condition such as ECL imaging. Plate 5-IV shows the ECL image of a microwire electrode which has been treated by sulfuric acid and has shown large voltammetric current. On the other hand, Plate 5-V shows the image of a microwire electrode which has been used for three to four times without acid treatment and has shown very low current. As can be seen from the image, only a small portion of the surface gives ECL emission (For comparison, a full image of the same electrode is shown by the ECL image.) Although the identity of the surface deposits could not be revealed by this method, the reason for low electrochemical activity and the usefulness of the acid treatment have been verified by the ECL imaging method.

The procedure of examining surface activity by ECL imaging was used for the examination of the electrochemical performance of a microdisk electrode array created by a nitrogen laser on a glassy carbon disk covered by an organic film. The voltammetric behavior of a microdisk electrode array has been studied quite thoroughly [149]. Although the image of a microdisk electrode array has been given by microscopy and shows the spots being spread out regularly on a supposedly inactive background of a glassy carbon disk, the electrochemical activities of the laser spots and the rest of the surface were not obtainable from regular microscopy. A normal image of such an electrode array obtained by CCD is shown in Plate 5-VI. The ECL imaging method was used to further examine the performance of each individual spot and to see if the background was really inactive. Using the geometry shown in Fig. 5-1, a microdisk electrode array ($d_s = 45 \mu m$, separation between spots = 110 \mu m) was subject to the ECL imaging by CCD, with the ECL image shown in Plate 5-VII. The first thing seen from the image is that only the spots fired by the laser are active (shown by ECL emission); the rest of the electrode surface is inactive. Another important observation from the ECL image is that some laser spots show a small inactive region, approximately in the center of the laser spot. The laser action on the organic thin
Plate 5-VI.

A normal image of a microdisk electrode array with $d_0 = 45 \, \mu m$ and separation of $110 \, \mu m$, which is obtained by the CCD detector.
Plate 5-VII.

An ECL image of the same array in Plate 5-VI
film was apparently to remove the thin film and perhaps activate the glassy carbon surface. However, since the intensity at the center of a laser beam is usually higher (assuming a Gaussian distribution of the intensity), the small central inactive regions may have been damaged by laser action. Although simple, ECL imaging has been shown to provide important information about the structure and performance of each individual spot in a microdisk electrode array.

Imaging experiments by the normal incidence reflection geometry differ greatly from the previously imaging experiments in geometry and the information provided. The initial use of the normal incidence reflection geometry was to prefocus an object for an ECL imaging experiment. It was soon realized that an absorbance measurement can be made when a light beam traverses the diffusion layer by striking on and bouncing off the electrode surface, provided that the spots as well as the inactive regions are reflective towards the incoming light. The experiment was accomplished in the following way. A reference beam image was taken with the light beam striking on and bouncing off the electrode surface when there was no electrolysis. Then a sampling beam image was obtained a few seconds after a potential step experiment the same way as earlier SRAS experiments. Instead of calculating the absorbance image from the two, the difference image of the two (subtracting A from B) was obtained to enhance the diffusion field. Images obtained in this way with experimental times from 0.1 to 5 sec are shown in Plate 5-VIII for a single spot of radius about 30 µm. As the time gets longer the diffusion field gets larger with a bigger dark spot due to absorption. The diffusion process from a microdisk electrode can be seen better with a three-dimensional plot. That is, the absorbance as a function of x-y pairs, as shown in Fig. 5-7.

The three-dimensional profiles of the diffusion images are processed by extracting data points from the two original images with a resolution of 10 µm, which is appropriate for a proper 3-D representation of the diffusion images. (Too many points, or too fine a resolution would only make the plots darker without any visual improvements.) One very
Plate 5-VIII. Images of diffusion fields of a single microdisk electrode
Experimental times are: (a) 0.1 sec, (b) 0.5 sec, (c) 1 sec.
(d) 5 sec.
Plate 5-VIII

a

b

30 μm

c

d
Fig. 5-7  Three-dimensional profiles of the diffusion field at a microdisk electrode \((r_0 = 15 \, \mu m)\) obtained by the normal incident reflection imaging method. Experimental times are: (a) 0.1 sec, (b) 0.5 sec, (c) 1 sec, (d) 5 sec.
Fig. 57

MICROMETER

MICROMETER

300

300

ABSORBANCE

ABSORBANCE

0

0

0.10
noticeable aspect of the plots is that these plots are very noisy. Two factors have contributed to the low signal-to-noise ratio. First, the images were read out without any binning which usually gives higher readout noise. Second and more important, the electrode surface was not smooth, giving noisy images of the surface itself. A glassy carbon surface is usually quite shiny and a smooth beam image of the surface would be expected. However, the circumference and the center-laser damaged region of a laser spot were less reflective and little light was reflected from these areas. Furthermore, noisy images arise from the small holes at the glassy carbon surface which also reflected little light, as can be seen from Plate 5-IX. Nonetheless, these 3-D profiles provide very useful information about the diffusion process at a single microdisk and a microdisk electrode array.

One of the initial interests in designing such an experiment as this was to see the overlap of diffusion layers from adjacent microdisk electrodes. By shining a light beam on to a group of spots spaced within several hundred μm squared, the same experiment was repeated to image diffusion fields from more than one spot. Such images are shown in Plate 5-X, for experimental times of 1.0 and 2.0 sec. Again, because these are difference images and not the true representations of diffusion fields, better views of the diffusion process can be seen in the three-dimensional plots shown in Fig. 5-8 with experimental times from 0.1 to 10 sec. With a diameter of 20 μm and separation of 150 μm, the diffusion fields are shown to be restricted to the immediate vicinity of each individual microdisk electrode at times from 0.1 sec to 1 sec, and the fields begin to coalesce at a time of about 2.0 sec, when the characteristic parameter for diffusion layer half thickness \((Dt)^{1/2}\) is 25 μm. The diffusion fields from different microdisk electrodes overlap significantly at 5.0 sec and overlap completely at 10.0 sec, with the three microdisk electrodes and the inactive areas acting as a single large electrode.

Although imaging the diffusion field by the normal incidence reflection imaging method is an extension of SRAS, the method provides different and more information about the diffusion process at the electrode surface. The horizontal spatial resolution is about 2 μm,
Plate 5-IX.

A normal image of a single microdisk electrode and the surface features (many holes) on a gassy carbon electrode surface.
**Plate 5-X.** Images of diffusion fields of three microdisk electrodes with $r_0 = 10 \mu m$ and a separation of $150 \mu m$. Experimental times are: (a) 1 sec, (b) 2 sec.
Fig. 5-8 Three-dimensional profiles of the diffusion field at three microdisk electrodes \( r_0 = 10 \, \mu m \) separated by 150 \( \mu m \). Experimental times are: (a) 0.1 sec, (b) 1 sec, (c) 2 sec, (d) 5 sec, (e) 10 sec.
the same or better than that of SRAS for wire imaging experiments because there is no
diffraction effect in the imaging process of the normal incidence reflection mode, while the
vertical resolution is expected to be the same as the horizontal resolution or even better.

The information available about the diffusion field is truly spatially three-dimensional, with
the absorbance being a function of points \((x, y)\) on the electrode surface. For a linear
diffusion case, the absorbance for an OTE experiment is given by eq (5.5)[2].

\[
A = \log \frac{I_0}{I} = \int_{0}^{\infty} e^{\frac{C(x,t)dx}{\epsilon_{ox}}} = \frac{2}{\sqrt{\pi}} \int_{\epsilon_{ox}}^{\epsilon_{red}} \frac{C_{red}(Dt)^{1/2}}{D_{Red}t} \tag{5.5}
\]

The absorbance obtained in a normal incidence reflection imaging experiment should be
proportional to twice the value of \(2(\pi)^{1/2} \epsilon_{ox}C_{red}b(D_{Red}t)^{1/2}\) because the normal incidence
light beam travels twice through the diffusion layer of a three-dimensional diffusion field.

Although the absorbance is proportional to the integration of concentration over the
diffusion layer along the optical axis perpendicular to the electrode surface and the true
meaning of SRAS along the optical axis may be considered lost, the three-dimensional
information available from this measurement is real, with the information along two
directions still being spatially resolved. Since absorbance is proportional to \((Dt)^{1/2}\) which
has a dimension of distance, the diffusion front at \((Dt)^{1/2}\) as a function of points \((x, y)\) can
be seen moving with time \(t\), which is the significance of the normal incidence reflection
imaging method.

Since this method relies on the smoothness and reflectivity of an electrode surface, it
is no surprise that the three-dimensional profiles are noisy, depending on the experimental
conditions of the glassy carbon electrode surface and the laser fired spots. However, the
normal incidence reflection imaging experiment can be improved with better surface
conditions. The potential implications of this method can be appreciated with the following
considerations. Because the information content of two-dimensional SRAS with a CCD
detector has been enriched by the three-dimensional representation of the diffusion field, many experiment can now be performed. For example, the steady state problem of mass transport on a microdisk electrode is expected to be seen better with this method on a flat, smooth and reflective electrode and substrate surface. As the solution convection problem is expected to be minimized at a microdisk electrode, electrolysis can be carried out to the point of steady state of mass transport. Under these conditions, the steady state diffusion field could be seen as a cone on top of the microdisk electrode. Imaging of the diffusion process of interdigitated electrodes could be another good example of applications of this method. The typical size of one filar electrode is about 50 µm with a separation of 50 µm. The amperometric behavior of filar electrodes has been studied by simulation and experimental verification [149], but it would be worthwhile to examine the diffusion process experimentally. Imaging of the diffusion field in filar electrodes is within the capability of the normal incidence reflection imaging method because both the electrode (gold) and substrate (ceramic) surface are smooth and reflective enough to carry out the experiment. Finally, the normal incidence reflection imaging method could provide more information for diagnosis of mechanisms of homogeneous reactions because of the three-dimensional information available from this method, although the kinetic modelling by simulation may be more complicated due to the two-dimensional diffusion problem. The normal incidence reflection imaging method with a CCD detector takes the spatially resolved absorption spectroelectrochemistry to a higher level of sophistication.

Conclusions
The utility and versatility of the two-dimensional imaging system with a CCD detector is fully demonstrated with three modes: the transmission, the ECL imaging and the normal incidence reflection imaging modes. In the transmission mode, the diffusion process of a minigrid electrode under potential step electrolysis was studied, and showed filling of the
grid-holes 1 sec after electrolysis. In particular, the diffusion process at the wire-end of a 25 \( \mu \text{m} \) diameter microwire was studied in the transmission mode. Spherical diffusion is partly formed at the wire-end (an approximation of a microdisk electrode) as early as 0.1 sec. The spherical diffusion cone is quite pronounced at time of 4 sec and reaches virtual steady state of mass transport at time of 16 sec. The diffusion front was seen to be pushed back presumably by solution convection.

In the ECL imaging mode, the heterogeneity of the electrochemical activity at an electrode surface was detected with the enhancement of electrogenerated chemiluminescence (ECL). Under \textit{in situ} conditions, the electrochemical performance of each individual spot in a microdisk electrode array created by firing nitrogen laser pulses on a glassy carbon surface was examined. While the vast area covered by an organic film was shown to be inactive (such information was not available from ordinary microscopy), small regions in the centers of some laser spots are also inactive due probably to the laser damages.

The normal incidence reflection imaging mode is shown to be an extension of SRAS with a two-dimensional detector and to provide spatially three-dimensional information about the diffusion field. The absorbance is a function of points \((x, y)\) on the electrode surface which essentially depicts the movements of the diffusion front at \((\text{Dt})^{1/2}\) along the \(x, y, z\) axes, although a direct concentration vs. distance profile may not be available from this imaging mode. The imaging method was used to image the diffusion fields at a single spot as well as a multi-spot microdisk electrode, and diffusion fields are seen to grow and overlap in a truly spatially three-dimensional space. The normal incidence reflection imaging method with a CCD takes SRAS to a higher level of sophistication.
LIST OF REFERENCES


42. Adams, R.N. "Electrochemistry at Solid Electrodes," Marcel Dekker: New York, 1968; Ch. 3.


46. Reference 42, Ch. 4.


152. Reference 151, p 34.

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Appendix A

This appendix presents algorithms used in the digital simulation of electrochemical diffusion problems, Abel inversion and data analyses. Computer programs will be listed in appendix B. Emphasis in this section is given to the algorithms for diffusion problems and the associated digital simulation of diffusion under various experimental and boundary conditions. Abel inversion and data analysis processes are discussed in more general terms. The order of presentation is as follows:

1) A general description of the finite difference method for the digital simulation of diffusion problems is given, including examples of simulations of diffusion at a microcylindrical electrode for single potential step experiments, at a planar electrode for double potential step experiments and at twin electrodes for single potential step experiments.

2) Expanding box algorithm with implicit solution is explained in terms of uneven spacing and implicit solution. A comparison will be given between the finite difference method and the expanding box algorithm with implicit solution for spherical diffusion. The current simulation problem is also discussed.

3) A description of Abel inversion with algorithms of equal increments in x and r, and expanding box increments for calculating A(x) from expanding box C(r) associated with the digital simulation in microcylindrical diffusion.

4) Routines for modeling of homogeneous reactions coupled with electron transfer reactions are given for equilibrium-control, kinetics-control as well as equilibrium and kinetics combined control.

5) Routines for analysis of two-dimensional imaging data are discussed.

There are a variety of problems existing in the field of electrochemistry that are described by partial differential equations. Some of these equations, often simple ones, can be solved analytically in closed form. However, many others must be solved by numerical methods because these equations are too difficult to solve analytically. In particular, digital simulation has become a standard method for solving mass transport or kinetic problems in electrochemistry. Although simple, the method of finite differences has been the basic tool for digital simulations and has been explained thoroughly by others[109,110,150]. The example to be given here is a diffusion problem in a microcylindrical electrode because the partial differential equation (A.1) of cylindrical diffusion has no analytical solution and the problem is quite common in electrochemistry.

\[
\frac{\partial C(r,t)}{\partial t} = D \frac{\partial^2 C(r,t)}{\partial r^2} + \frac{D}{r} \frac{\partial C(r,t)}{\partial r} \tag{A.1}
\]

Eq (A.1) can be expanded into the finite-differences form of eq (A.2) and further into eq (A.3):

\[
\frac{C(r,t+\Delta t)-C(r,t)}{\Delta t} = \frac{D}{(\Delta r)^2} \left[ \frac{C(r+\Delta r,t)+C(r-\Delta r,t)}{2} - 2C(r,t) \right] + \frac{\Delta r}{2r} \frac{C(r+\Delta r,t)-C(r-\Delta r,t)}{2r} \tag{A.2}
\]

\[
C(r,t+\Delta t)=C(r,t)+\frac{D\Delta t}{(\Delta r)^2} \left[ \frac{C(r+\Delta r,t)+C(r-\Delta r,t)}{2} - 2C(r,t) \right] + \frac{\Delta r}{2r} \frac{C(r+\Delta r,t)-C(r-\Delta r,t)}{2r} \tag{A.3}
\]
An awkward situation arises when one wants to make \( r \) a dimensionless parameter which is necessary for the algorithm format. Since the diffusion starts from the electrode surface, the reference is naturally at \( r = r_0 \). However, the boundary condition of \( r = r_0 + r' \) needs to be incorporated into the simulation algorithm, and this is accomplished by substituting \( r = r_0 + r' = (Z + j)\Delta r \) into the denominator of the second term in eq (A.3), where \( r_0 = Z\Delta r \) and \( Z \) is the number of \( \Delta r \) within \( r_0 \) for a particular set of simulation parameters.

Using the notations in reference [150]:

\[
\Delta t = \frac{t_v}{L}
\]
\[
t = k\Delta t = \frac{kt_v}{L}
\]
\[
\Delta r = \left( \frac{D_{t_v}}{D_M L} \right)^{1/2}
\]
\[
D_M = \frac{D\Delta t}{(\Delta r)^2}
\]
\[
f = \frac{C}{C^b}
\]

and the boundary condition notation \( Z \) for a cylinder of radius \( r_0 \):

\[
Z = \frac{r_0}{\Delta r} = \frac{r_0}{\int_{r_s}^{L} D_M L} = \text{RE} \int_{r_s}^{L} D_M L \quad (A.4)
\]

where \( \text{RE} = \frac{r_0}{(D_{t_v})^{1/2}} \). Thus, eq (A.3) can be expressed in terms of the dimensionless parameters listed above.

\[
f(j,k+1) - f(j,k) + D_M \left\{ f(j+1,k) - 2f(j,k) + f(j-1,k) + \frac{1}{2(j+Z)} \left[ f(j+1,k) - f(j-1,k) \right] \right\}
\]

\[
- f(j,k) + D_M \left\{ 1 + \frac{1}{2(j+Z)} \left[ f(j+1,k) + f(j-1,k) - 2f(j,k) \right] \right\} \quad (A.5)
\]

where \( j, k \) are distance and time parameters in the algorithm respectively, and \( L \) is the total iteration number. \( D_M \), the model diffusion coefficient, must be less than 0.5 for explicit solution of the algorithm if a stable simulation is desired. \( \text{RE} = \frac{r_0}{(D_{t_v})^{1/2}} \) is a parameter.
that describes the diffusion character. When \( RE \) is small, the diffusion has more cylindrical character; when \( RE \) is large, the diffusion has less cylindrical character and is closer to a linear diffusion. The program is listed as \texttt{PROGRM1.FOR} in appendix B.

**Digital simulation for double potential step experiments.** Digital simulation for a double potential step at planar electrode needs only minor modifications to the program in reference [150]. The forward step simulation is the same except for a few additions. The reverse step can be viewed as another forward step except that the initial concentration arrays are not \( C_A(x,0) = C_A^0 \) and \( C_B(x,0) = 0 \), but have some initial distributions which have been determined in the forward step simulation. Another difference is that the diffusion layer thickness continues to grow on the basis of the diffusion layer in the forward step. Thus the followings are the changes:

1) Forward step: \( t_1, t_2, D \) and \( L_1 \) (the iteration number for forward step).

2) Reverse step:
   i) \( L_2 = L_1 t_2 / t_1 \) (the iteration number for the reverse step).
   ii) Diffusion layer thickness: \( J_{\text{max}} = 4.2(L_1 + K) \).
   iii) Faradaic conversion:

   \[
   \text{FANEW}(1) = \text{FANEW}(1) + \text{FBNEW}(1) \\
   \text{FBNEW}(1) = 0
   \]

3) Store data to disk: \( X = (D(t_1 + t_2)^{1/2} J - 1)/(D_M(L_1 + L_2))^{1/2} \)

The program is listed as \texttt{PROGRM2.FOR} in appendix B.

**Simulation for the twin-electrodes diffusion problem.** The partial differential equations for the twin electrodes geometry take the following forms and boundary conditions:

\[
\frac{\partial C_{\text{red}}(x,t)}{\partial t} = D \frac{\partial^2 C_{\text{red}}(x,t)}{\partial x^2} \quad (2.6)
\]
\[
\frac{\partial C_{ox} (x,t)}{\partial t} = D \frac{\partial^2 C_{ox} (x,t)}{\partial x^2}
\]

(2.7)

\[
C_{red}^b (x,0) = C_{ox}^b (x,0) = C^b
\]

(2.8)

\[
C_{red}^b (0,t) = 0
\]

(2.9)

\[
C_{ox}^b (L,t) = 0
\]

(2.10)

\[
D_{red} \left[ \frac{\partial C_{red} (x,t)}{\partial x} \right]_{x=0} - D_{ox} \left[ \frac{\partial C_{ox} (x,t)}{\partial x} \right]_{x=0}
\]

(2.11)

\[
D_{red} \left[ \frac{\partial C_{red} (x,t)}{\partial x} \right]_{x=L} - D_{ox} \left[ \frac{\partial C_{ox} (x,t)}{\partial x} \right]_{x=L}
\]

(2.12)

Instead of applying a Laplace transform to solve the partial differential equations (though whether or not they are solvable is still a question), digital simulation may be used to solve the problem. Since the separation between the two cofacial electrodes is 0.075 cm, the number of boxes between the two boundaries is:

\[
N = 0.075 \left[ \frac{D M L}{D t_s} \right]^{1/2} = 1
\]

(A.6)

where \(D\), \(t_s\) and \(L\) are the diffusion coefficient, time and iteration number respectively, and are entered before simulation. Since \(D_{MA}/D_A = D_{MA}/D_B\), \(N_A\) is equal to \(N_B\). It is assumed that both \(A\) and \(B\) are driven to their diffusion-limit so that \(C_A(0,t) = 0\) and \(C_B(L,t) = 0\). Therefore, the algorithm should be very similar to the one in reference [150] except for the following changes:
1) Diffusion beyond the first and the last boxes:

\[
\begin{align*}
\text{DO 20 } & J = 2, \text{ JMAX} \\
& \text{FANEW}(J) = FAOLD(J) + DMA*(FAOLD(J-1) - 2*FAOLD(J) + FAOLD(J+1)) \\
& \text{FBNEW}(J) = FBOLD(J) + DMB*(FBOLD(J-1) - 2*FBOLD(J) + FBOLD(J+1)) \\
& I = N - J + 2 \\
& \text{FANEW}(I) = FAOLD(I) + DMA*(FAOLD(I-1) - 2*FAOLD(I) + FAOLD(I+1)) \\
& \text{FBNEW}(I) = FBOLD(I) + DMB*(FBOLD(I-1) - 2*FBOLD(I) + FBOLD(I+1)) \\
20 & \text{CONTINUE}
\end{align*}
\]

2) Diffusion into the first and the last boxes:

\[
\begin{align*}
& \text{FANEW}(1) = FAOLD(1) + DMA*(FAOLD(2) + FAOLD(1)) \\
& \text{FBNEW}(1) = FBOLD(1) + DMB*(FBOLD(2) + FBOLD(1)) \\
& \text{FANEW}(N+1) = FAOLD(N+1) + DMA*(FAOLD(N) + DAOLD(N+1)) \\
& \text{FBNEW}(N+1) = FBOLD(N+1) + DMB*(FBOLD(N) + FBOLD(N+1))
\end{align*}
\]

Minor change is: IF (JMAX .GT. N) THEN JMAX = N.

In most of the simulations, the model diffusion coefficients \( D_{MA} \) and \( D_{MB} \) are set to be equal. In this simulation, however, the ratio of the two model diffusion coefficients is set to be equal to the ratio of the real diffusion coefficients of A and B, that is, \( D_{MA}/D_{MB} = D_A/D_B \) where A and B here are Fe(CN)_6^4^- and Fe(CN)_6^3^- respectively. Faradaic conversion at the anode, the potential of which was controlled by the potentiostat, is the same as that in reference [150], but there was no control over the potential of the cathode. There are a couple of possible schemes for faradaic conversion at the cathode.

At anode:

\[
\begin{align*}
& \text{FBNEW}(1) = \text{FANEW}(1) + \text{FBNEW}(1) \\
& \text{FANEW}(1) = 0
\end{align*}
\]

At cathode, Scheme I:

\[
\begin{align*}
& \text{FANEW}(N+1) = \text{FANEW}(N+1) + \text{FBNEW}(N+1) \\
& \text{FBNEW}(N+1) = 0
\end{align*}
\]

At cathode, Scheme II:

\[
\begin{align*}
& \text{FANEW}(N+1) = \text{FANEW}(N+1) + \text{FANEW}(1) \\
& \text{FBNEW}(N+1) = \text{FBNEW}(N+1) - \text{FANEW}(1)
\end{align*}
\]

Scheme I simply assumes that A and B are driven to their diffusion limit so that \( \text{FANEW}(1) \) is totally converted into \( \text{FBNEW}(1) \) and itself \( \text{FANEW}(1) = 0 \) at anode, and \( \text{FBNEW}(N+1) \)
is also totally converted into FANEW(N+1) at cathode. Since the initial concentrations of A and B are the same, this assumption is reasonable. Scheme II takes into consideration the fact that equal amounts of A and B are being converted at the anode and cathode respectively. That is why FANEW(1) is added to FANEW(N+1) instead of FBNEW(N+1). If FBNEW(N+1) is greater than FANEW(1), there will be some B left over in box N+1 and FBNEW(N+1) = FBNEW(N+1) - FANEW(1). However, if FBNEW(N+1) is less than FANEW(1), then something else in the solution will be reduced at cathode. In actuality, the simulated profiles by Scheme II could not account for the experimental profiles, while Scheme I gave almost perfect fits to the experimental profiles. These results indicate that the system behaves as if the anode and the cathode were being controlled independently. The entire program is listed as PROGRM5.FOR in appendix B.

A.2. Expanding box algorithm with implicit solution.

There are three problems associated with the finite differences algorithm for cylindrical diffusion. First, the algorithm is unstable at $D_M > 0.5$ because the algorithm is explicit. Second, the algorithm requires a large number of iterations for large $(Dt)^{1/2}/r_0$ in order to have accurate results. Third, the large number of iterations essentially gives many points which are usually out of the limit for forward step Abel inversion when predicting $A(x)$ from $C(r)$. Therefore, other algorithms are explored for the simulation. The particular one used for simulation of cylindrical diffusion is the expanding box with implicit solution. Use of the expanding box algorithm and implicit solution results in a faster convergence rate along with unconditional stability and increased accuracy. These procedures together provide efficiency and accuracy for simulations and thus much improvement over the finite differences method.

Expanding box, or unequal intervals algorithm is based on a transformation function that converts the evenly spaced boxes (points) into an unevenly and expanding spacing.
Consider for a moment a concentration profile. One prominent feature in a concentration vs. distance profile is that the greatest changes of C with respect to x take place very close to the electrode surface. This change slows down away from the electrode and finally the change stops practically in the bulk solution. This situation is more pronounced in cylindrical and spherical diffusions. Therefore, it would be logical to use wider point-spacings in the region away from the electrode, and finer-spacings at small distances near the electrode surface. This procedure is accomplished by a transformation function which converts the evenly spacing y variable into a variable of unevenly and expanding box spacing. The transformation function should look roughly like the concentration profile so that the points near the electrode surface in the simulation stay close together while those away from the electrode are spread out in a way closely associated with a concentration profile. Such a transformation is shown in Fig. A-1, where the evenly spacing points in domain y is shown to be a function of the unevenly spacing points in domain x. On reverse, the unevenly spacing points in x domain can be governed by the evenly spacing points in the y domain. The function of (A.7) shown in Fig. A-2 (a) has a shape close to that of an error function and has been used by others to implement the expanding box algorithm[110]. The transformation functions shown in Fig. A-2 (b) are for simulations of cylindrical and spherical diffusions which will be discussed later.

\[
y = \frac{2x}{2x + 1} \tag{A.7}
\]

An implicit numerical solution of a partial differential equation refers to whether the difference is forward or backward, or somewhere in between. Two things associated with the degree of implicitness are the stability of a numerical method and the accuracy. Digital simulation of diffusion problems by the finite differences method may be more generally described as a procedure based on a numerical solution of a parabolic partial-differential equation (A.8) [151].
Fig. A-1  A general transformation function of $y = f(x)$. The unevenly, expanding spaced points in the $x$ domain can be governed by the evenly spaced points in the $y$ domain by the reverse function of $x = g(y)$. 
Fig. A-2  (A) Comparison between the error function and the transformation function of (A.7) for planar diffusion case. (B) Comparison between a spherical diffusion profile and the transformation function of (A.17). Curve (a), \( r_\theta = 5 \mu m \), \( D = 5 \times 10^4 \text{ cm}^2/\text{sec} \), and \( \tau = 2 \text{ sec} \). Curve (b), the constant \( A = 5 \), \( R_\theta = r_\theta/(D\tau)^{1/2} = 0.16 \). Curve (c), \( A = 2 \), \( R_\theta = 0.16 \).
Error Function

\[
\frac{2x}{2x + 1}
\]

\[C(x,t)/C^p\]

\[x^o/(Dt)^{1/2}\]

\[C(r,t)/C^p\]

\[(r - r^o)/(Dt)^{1/2}\]

Fig. A-2
subject to the conditions:

\[ U(0,t) = 0, \ U(1,t) = 0, \ t > 0 \]  \hspace{1cm} (A.9)

\[ U(x,0) = f(x), \hspace{1cm} 0 \leq x \leq 1 \]  \hspace{1cm} (A.10)

The method to approximate the solution to this problem involves finite differences, and the two mesh constants selected for the calculation are h and k. The grid points for this situation are \((x_i, t_j)\), where \(x_i = ih\), for \(i = 0, 1, ..., m\), and \(t_j = jk\), for \(j = 0, 1, ..., \) with the stipulation that \(m = 1/h\). According to reference [151], the general form for the approximate solution is given by

\[
\frac{w_{i,j+1} - w_{i,j}}{k} = \alpha^2 \frac{w_{i+1,j} - 2w_{i,j} + w_{i-1,j}}{h^2}
\]  \hspace{1cm} (A.11)

where \(w_{i+1,j}\) is an approximation of \(U\) at iteration \(j+1\). Since \(w_{i,j+1}\) is calculated for the previous solutions \(w_j\) in the numerical iterations, the method is called forward-difference method, meaning that the approximation is projected forward with respect to \(t\) from a previous value. It has been proved mathematically that in order for the numerical solution to be stable, the constant \(\lambda = \alpha^2(k/h^2)\) has to meet the following requirement [151]:

\[
\lambda = \alpha^2 \frac{k}{h^2} < 0.5
\]  \hspace{1cm} (A.12)

Thus, this method is called conditionally stable and the method converges to the solution of eq (A.9) with a rate of convergence \(O(k + h^2)\) provided that requirement (A.12) is met.

In order to obtain a method that is unconditionally stable, an "implicit-difference" method, which results from using the backward-differences, is considered. In the backward-differences method, the finite difference form of eq (A.8) is:
This method is unconditionally stable and it converges to the solution of eq (A.9) with rate of convergence $O(k + h^2)$. The backward difference method is totally implicit.

Another finite difference method is called Crank-Nicolson method, and is an averaged difference method with the finite difference form eq (A.8) being

$$\frac{w_{i, j} - w_{i, j-1}}{k} = \alpha^2 \frac{w_{i+1, j} - w_{i, j} + w_{i-1, j}}{h^2} \quad (A.13)$$

$$\frac{w_{i, j+1} - w_{i, j}}{k} = \alpha^2 \left( \frac{w_{i+1, j+1} - 2w_{i, j} + w_{i-1, j}}{h^2} + \frac{w_{i+1, j} - 2w_{i, j} + w_{i-1, j} + w_{i+1, j+1}}{h^2} \right) \quad (A.14)$$

The Crank-Nicolson method is unconditionally stable and has order of convergence $O(k^2 + h^2)$. The accuracy of this method over the forward-difference and the backward-difference can be appreciated by considering Fig. A-3. The time projection of $w$ (U) in the forward-difference method is based on $w_{i,j}$ and the slope at $w_{i,j}$. The larger the time step $k$ taken in the numerical method, the more the tangent line deviates from the curve. If the step $k$ is too large, the projection is to such an extent that convergence may be difficult. On the other hand, the time-projection of $w$ in the backward-difference method is based on the $w_{i,j+1}$ value and the slope at $w_{i,j+1}$. Although large error will be involved in the projection when a large time step $k$ is taken, convergence is not a problem because the final result with respect to time is controlled by boundary conditions and this result is projected backward with a recursive action. Therefore, the backward-difference method is unconditionally stable. The time projection in the Crank-Nicolson method takes the averaged slope of forward and backward difference. The accuracy of the projection is improved, as shown by line 3 in Fig. A-3. Since half of the time projection is taken from the backward-difference projection, there will be no convergence problem because each time projection is tied with the final result through recursions. Stabilization of the numerical calculation through a series of backward recursion may be appreciated also by comparing this method with the
Fig. A-3  Schematic diagram showing the concentration projection with respect to time. Line (1), forward differences projection. Line (3), backward differences projection. Line (2) is the average of (1) and (3).
stabilization of an operational amplifier by a feed-back loop, where the backward recursion is to compared with the feed-back loop. Therefore, as long as there is a small degree of implicitness in the algorithm, the calculation will be stabilized and large $\lambda (\alpha^2 k/h^2 > 0.5)$ can be used for simulation.

The expanding box algorithm with implicit solution (Crank-Nicolson method) and the associated recursive formula for a linear diffusion case have been given in reference [110]. The problem to be solved here is the diffusion at a microcylindrical (or microspherical) electrode which is described by (A.15). The digital simulation of cylindrical diffusion must overcome the problems of accuracy, stability and efficiencies both in time and storage space.

\[
\frac{\partial C(r,t)}{\partial t} = D \frac{\partial^2 C(r,t)}{\partial r^2} + \frac{D}{r} \frac{\partial C(r,t)}{\partial r} \quad (A.15)
\]

In order to numerically solve eq (A.15) by expanding box algorithm with implicit solution, a transformation function must be chosen, with the shape being close to that of a cylindrical concentration profile. First, the partial differential equation is expressed in terms of unitless parameters $T$ and $R$:

\[
\frac{\partial C(R,T)}{\partial T} = \frac{\partial^2 C(R,T)}{\partial R^2} + \frac{1}{R} \frac{\partial C(R,T)}{\partial R} \quad (A.16)
\]

where $T = t/\tau$ and $R = r/(Dt)^{1/2}$ are two unitless parameters. Second, a transformation function of (A.17) is chosen, the shape of which is in Fig A-2 (b) in comparison with a theoretical profile of a spherical diffusion.

\[
Y = \frac{A(R - R_0)}{A(R - R_0) + 1}, \quad R_0 \leq R \leq RLIM = 6 \quad (A.17)
\]

and $YLIM$ is given by:
where a value between 2 and 5 is usually taken for A. This function is similar to eq (A.7) plotted in Fig A-2 (a). The boundary condition at \( r = r_0 \) is built in the function by the constant \( R_0 = r_0/(D \tau)^{1/2} \). At A = 5, the transform function is very close to the shape of the spherical profile. Since the shape of a cylindrical profile is not expected to be as steep as that of a spherical profile, an A value between 2 and 5 should give a transform function close to cylindrical profiles. The inverse function of (A.17) is given by:

\[
R = \frac{Y}{A(1 - Y)} + R_0, \quad 0 \leq Y \leq Y_{\text{LIM}} < 1.0 \quad (A.19)
\]

According to Fig. A-1, if points are evenly spaced in Y domain, points in R domain will be spaced unevenly so that the unevenly spaced simulation can be controlled by a set of evenly spaced points. Thus, the partial differential equation can be written in terms of the transformation function Y. According to reference [110], eq (A.20) is obtained by using the chain rule of differentiation:

\[
\frac{\partial C}{\partial \tau} = \frac{\partial Y}{\partial R} \frac{\partial C}{\partial R} + \frac{1}{R} \frac{\partial C}{\partial R} - \frac{\partial Y}{\partial R} \left[ \frac{1}{\partial Y} + \frac{1}{\partial R} \frac{\partial Y}{\partial R} \right] + \frac{1}{R} \frac{\partial Y}{\partial R} \frac{\partial C}{\partial Y} + \frac{1}{R} \frac{\partial Y}{\partial R} \frac{\partial C}{\partial Y}
\]

\[
= \left[ \frac{\partial Y}{\partial R} \right]^2 + \frac{\partial Y}{\partial R} \frac{\partial^2 C}{\partial Y^2} + \frac{\partial Y}{\partial R} \frac{\partial^2 C}{\partial Y \partial R} + \frac{1}{R} \frac{\partial Y}{\partial R} \frac{\partial C}{\partial Y} \quad (A.20)
\]

where

\[
\frac{\partial Y}{\partial R} = \frac{1}{\partial R/\partial Y} = A(1 - Y)^2 \quad (A.21)
\]
\[
\frac{\partial^2 Y}{\partial Y \partial \tau} = -2A(1 - Y) \quad \text{(A.22)}
\]

Eq (A.20) can be expressed in the finite difference form with (A.21) and (A.22) substituted into the equation:

\[
C_i' - C_i - A^2 (1 - Y_i) \Delta T \left[ \frac{1 - Y}{2A^2 Y} \left[ C_{i-1}' - 2C_i' + C_{i+1}' + C_i' + C_{i-1}' - 2C_i + C_{i+1} \right] \right] \\
- \frac{2}{2(2A^2 Y)} \left[ C_{i+1}' - C_{i-1}' + C_{i+1}' + C_{i-1}' \right] + \frac{C_{i+1}' - C_{i-1}' + C_{i+1}' + C_{i-1}'}{4A^2 Y \left[ Y + AR_0 (1 - Y) \right]} \quad \text{(A.23)}
\]

where \( C \) and \( C' \) are the concentrations at times \( t \) and \( t + \Delta t \) respectively. After a tedious algebraic manipulation of eq (A.23), the following equation is obtained:

\[
C_{i-1}' + a_1 C_i' + a_2 C_{i+1}' = b_i \quad \text{(A.24)}
\]

with coefficients being:

\[
b_i = -C_{i-1} + \text{const}C_i - a_2 C_{i+1} \quad \text{(A.25)}
\]

\[
a_1 = -2 \frac{\Delta Y^2}{A^2 (1 - Y) \Delta T} \left[ \frac{2Y + 2AR_0 (1 - Y) - 1}{2(1 - Y) \left[ Y + AR_0 (1 - Y) \right]} \Delta Y \right] \quad \text{(A.26)}
\]

\[
a_2 = \frac{1 - \frac{2Y + 2AR_0 (1 - Y) - 1}{2(1 - Y) \left[ Y + AR_0 (1 - Y) \right]} \Delta Y}{1 + \frac{2Y + 2AR_0 (1 - Y) - 1}{2(1 - Y) \left[ Y + AR_0 (1 - Y) \right]} \Delta Y} \quad \text{(A.27)}
\]
where $Y$ will be expressed as $i\Delta Y$. The rest of the formulation is the same as that in reference [110] and the formulation of the algorithm could be completed, but for the sake of completeness, the derivation of the recursion formulae of coefficients are given here again. The eq (A.23) can be expanded to a simultaneous equation set:

\[
\begin{align*}
C'_0 + a_1(1)C'_1 + a_2(1)C'_2 &= b_1 \\
C'_1 + a_1(2)C'_2 + a_2(3)C'_3 &= b_2 \\
\vdots \\
C'_{i-1} + a_1(i)C'_i + a_2(i)C'_{i+1} &= b_i \\
\vdots \\
C'_{n-1} + a_1(n)C'_n + a_2(n)C'_{n+1} &= b_n
\end{align*}
\]

(A.29)

However, since $C'_0$ and $C'_{n+1}$ are known from the boundary conditions (which are the surface concentration and concentration at $r=\infty$ in the cylindrical diffusion problem), the equation set (A.29) can be reduced as eq (A.30) following the same formulation in reference [110]:

\[
C'_i + a'_1C'_{i+1} = b'_i
\]

(A.30)

where

\[
a'_1 = \frac{a_2(1)}{a_1(1)}
\]

(A.31)

\[
b'_2 = \frac{b_1(1) - C'_0}{a_1(1)}
\]

(A.32)
and the others are given by the recursion formulae:

\[
a'_i = \frac{a_{2}(i)}{a_{1}(i) - a'_{i-1}} \tag{A.33}
\]

\[
b'_i = \frac{b_{i} - b'_{i-1}}{a_{1}(i) - a'_{i-1}} \tag{A.34}
\]

In general, the diffusion at planar, cylindrical and spherical electrodes is formulated as below, with \(a_1, a_2\) and \text{const} denoted by \(A_1, A_2\) and \(F\):

\[
A_1 = -\frac{2 + D_1/(1 - Y)^4}{1 + D_2} \tag{A.35}
\]

\[
A_2 = \frac{1 - D_2}{1 - D_3} \tag{A.36}
\]

\[
\text{const} = F = \frac{2 - D_1/(1 - Y)^4}{1 + D_2} \tag{A.37}
\]

where

\[
D_1 = 2 \frac{(\Delta Y/A)^2}{\Delta T} \tag{A.38}
\]

\[
D_2 = \frac{\Delta Y}{1 - Y} - D_3 \tag{A.39}
\]

\[
D_3 = \begin{cases} 
0, & \text{linear} \\
\frac{\Delta Y}{2(1 - Y)R_1}, & \text{cylindrical} \\
\frac{\Delta Y}{(1 - Y)R_1}, & \text{spherical}
\end{cases} \tag{A.40}
\]
Based on the derivation above, the program for cylindrical diffusion with expanding box and implicit solution algorithm is listed as PROGRM4.FOR and PROGRM6.FOR.

The performance of the expanding box algorithm with implicit solution has been compared with other methods such as finite difference and hopscotch methods by others [89]. However, because of the importance of the expanding box algorithm with implicit solution, it is worthwhile to discuss the efficiency and accuracy further. The efficiency of the expanding box algorithm results from the smaller number of iterations necessary in comparison to finite differences algorithm. In addition, the efficiency is further improved by the large $\lambda$ values (much greater than 0.5, which is only possible with the implicit solution,) and the effect of this large $\lambda$ may be easily ignored. One important point in the diffusion simulation is that the model diffusion coefficient $\lambda$ is the same for every step of diffusion in the array. In another words, electroactive species diffuse in the same distance at a given time interval throughout the course of diffusion. However, this diffusion manner is no longer true in the expanding box algorithm where species have to diffuse in an increasingly larger distance but still at the same time interval. The only way this can happen is that the model diffusion coefficient change gradually to smaller values. Consider for a moment the model diffusion coefficient $\lambda$, which is defined in the usual way:

$$\lambda = \frac{D\Delta t}{\Delta r^2}$$  \hspace{1cm} (A.42)

where $\Delta r^2$ is determined by the transformation function:

$$\Delta r^2 = \left[\Delta R \sqrt{\Delta r} \right]^2 = \left[\frac{8R}{\alpha_1} \right] \Delta Y^2 (D \tau) - \frac{\Delta Y^2}{A^2 (1 - Y)^2} (D \tau)$$  \hspace{1cm} (A.43)

Substituting (A.43) into (A.42) gives:
\[ \lambda = \frac{D\Delta t}{(D\tau)(\Delta Y)^2/A^2(1 - Y)^2} = \frac{D\tau/NT}{D\tau/(\Delta Y)^2} A^2(1 - Y)^2 - \frac{A^2(1 - Y)^2}{\Delta Y^2 NT} \]  

(A.44)

\[ \lambda_{\text{max}} \text{ is obtained at } Y = 0: \]

\[ \lambda_{\text{max}} = \left[ \frac{A}{\Delta Y} \right]^2 \frac{1}{NT} \]  

(A.45)

where \( \Delta Y = Y_{\text{LIM}}/NY \). It can be seen from eq (A.44) that as \( Y \) gets larger (or the points in \( r \) become further away from the electrode surface), \( \lambda \) becomes smaller. Therefore, when \( \Delta r \) gets larger because of the expanding box, the diffusion process slows down with smaller \( \lambda \). For concentration calculations, the accuracy of a simulation depends on the simulation parameters such as the number of iterations (NT) and the number of points (NY). In order to evaluate the performance of the algorithm, simulation of spherical diffusion is compared with the theoretical solution of a spherical electrode. Simulations with \( (D\tau)^{1/2}/r_{\text{e}} = 6.32 \) (\( \tau = 2 \text{ sec} \)) and 100 (\( \tau = 500 \)) are used to evaluate the performance of the algorithm. The parameters and the results of different simulations are listed in Table A-1 through Table A-4 respectively at spherical diffusion with \( r_{\text{e}} = 5 \mu\text{m} \) and \( D = 5 \times 10^{-6} \text{ cm}^2/\text{sec} \). There are a few comments about the results (only the first several points are listed for each case in the tables) using the expanding box and implicit solution algorithm. First of all, the algorithm is stable for small as well as large \( (D\tau)^{1/2}/r_{\text{e}} \) (up to 100) and also stable for very large values of \( \lambda \) (> 100), as a result of the implicit solution. The \( \lambda_{\text{max}} \) values calculated by eq (A.42) for each set of simulation parameters are many times larger than the value of 0.5 for conditionally stable simulation. Although the first couple of points have errors greater than 1.0% at too large \( \lambda_{\text{max}} \) values, as can be seen from Table A-1 and Table A-3, these deviations quickly reduce to 0.1% and smaller values after the first 4-5 points. This is drastically different from the simulation results using the finite-differences method where
Table A-1
Simulation results with \((D\tau)^{1/2}/r_0 = 6.32\) and \(NY = 20\)

<table>
<thead>
<tr>
<th>Distance (µm)</th>
<th>Theoretical Formula</th>
<th>(\lambda_{\text{max}} = 158) NT = 60</th>
<th>Relative to Formula(%)</th>
<th>(\lambda_{\text{max}} = 95) NT = 100</th>
<th>Relative to Formula(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.765067</td>
<td>0.1445514</td>
<td>0.1510275</td>
<td>4.5</td>
<td>0.1445383</td>
<td>-0.01</td>
</tr>
<tr>
<td>6.607938</td>
<td>0.2650465</td>
<td>0.2604375</td>
<td>-1.7</td>
<td>0.2649713</td>
<td>-0.03</td>
</tr>
<tr>
<td>7.541116</td>
<td>0.3670234</td>
<td>0.3681706</td>
<td>0.3</td>
<td>0.3669516</td>
<td>-0.02</td>
</tr>
<tr>
<td>8.579937</td>
<td>0.4544383</td>
<td>0.4543137</td>
<td>-0.03</td>
<td>0.4543414</td>
<td>-0.03</td>
</tr>
<tr>
<td>9.743417</td>
<td>0.5301913</td>
<td>0.5300235</td>
<td>-0.03</td>
<td>0.5300844</td>
<td>-0.02</td>
</tr>
<tr>
<td>11.05543</td>
<td>0.5964553</td>
<td>0.5963481</td>
<td>-0.02</td>
<td>0.5963383</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

Table A-2
Simulation results with \((D\tau)^{1/2}/r_0 = 6.32\) and \(NY = 50\)

<table>
<thead>
<tr>
<th>Distance (µm)</th>
<th>Theoretical Formula</th>
<th>(\lambda_{\text{max}} = 158) NT = 200</th>
<th>Relative to Formula(%)</th>
<th>(\lambda_{\text{max}} = 95) NT = 250</th>
<th>Relative to Formula(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.297</td>
<td>0.0611503</td>
<td>0.0622102</td>
<td>1.73</td>
<td>0.06121835</td>
<td>0.12</td>
</tr>
<tr>
<td>5.606</td>
<td>0.1177788</td>
<td>0.116692</td>
<td>-0.92</td>
<td>0.1176886</td>
<td>-0.08</td>
</tr>
<tr>
<td>5.929</td>
<td>0.1703693</td>
<td>0.1708832</td>
<td>0.30</td>
<td>0.1704092</td>
<td>0.03</td>
</tr>
<tr>
<td>6.261</td>
<td>0.2193380</td>
<td>0.2192121</td>
<td>-0.06</td>
<td>0.2193032</td>
<td>-0.02</td>
</tr>
<tr>
<td>6.608</td>
<td>0.2650465</td>
<td>0.2650146</td>
<td>0.012</td>
<td>0.2650345</td>
<td>-0.005</td>
</tr>
<tr>
<td>6.969</td>
<td>0.3078093</td>
<td>0.3078023</td>
<td>-0.002</td>
<td>0.3077903</td>
<td>-0.006</td>
</tr>
</tbody>
</table>
### Table A-3
Simulation results with $(D\tau)^{1/2}/r_0 = 100$ and $NY = 100$

<table>
<thead>
<tr>
<th>Distance (µm)</th>
<th>Theoretical Formula</th>
<th>$\lambda_{max} = 190$ NT = 300</th>
<th>Relative to $\lambda_{max} = 95$ NT = 500</th>
<th>Formula(%)</th>
<th>Relative to Formula(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.32919</td>
<td>0.3195907</td>
<td>0.3276608</td>
<td>2.5</td>
<td>0.3196029</td>
<td>0.03</td>
</tr>
<tr>
<td>9.70219</td>
<td>0.4873886</td>
<td>0.4821428</td>
<td>-1.1</td>
<td>0.4873155</td>
<td>0.02</td>
</tr>
<tr>
<td>12.12025</td>
<td>0.5907835</td>
<td>0.5917249</td>
<td>0.16</td>
<td>0.5908205</td>
<td>0.007</td>
</tr>
<tr>
<td>14.58466</td>
<td>0.6608837</td>
<td>0.6612400</td>
<td>0.06</td>
<td>0.6608664</td>
<td>0.003</td>
</tr>
<tr>
<td>17.09678</td>
<td>0.7115411</td>
<td>0.7114536</td>
<td>0.02</td>
<td>0.7115400</td>
<td>0.0002</td>
</tr>
<tr>
<td>19.65798</td>
<td>0.7498591</td>
<td>0.7498030</td>
<td>-0.008</td>
<td>0.7498559</td>
<td>0.0005</td>
</tr>
<tr>
<td>22.26974</td>
<td>0.7798570</td>
<td>0.7798597</td>
<td>0.0003</td>
<td>0.7798532</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

### Table A-4
Simulation results with $(D\tau)^{1/2}/r_0 = 100$ and $NY = 250$

<table>
<thead>
<tr>
<th>Distance (µm)</th>
<th>Theoretical Formula</th>
<th>$\lambda_{max} = 298$ NT = 1000</th>
<th>Relative to $\lambda_{max} = 199$ NT = 1500</th>
<th>Formula(%)</th>
<th>Relative to Formula(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.92650</td>
<td>0.1572086</td>
<td>0.1585131</td>
<td>0.83</td>
<td>0.1572148</td>
<td>0.004</td>
</tr>
<tr>
<td>6.85989</td>
<td>0.2726465</td>
<td>0.2713975</td>
<td>-0.50</td>
<td>0.2726382</td>
<td>-0.003</td>
</tr>
<tr>
<td>7.80025</td>
<td>0.3610902</td>
<td>0.3616085</td>
<td>0.17</td>
<td>0.3610147</td>
<td>-0.002</td>
</tr>
<tr>
<td>8.74766</td>
<td>0.4308223</td>
<td>0.4307754</td>
<td>0.011</td>
<td>0.4308186</td>
<td>-0.0009</td>
</tr>
<tr>
<td>9.70219</td>
<td>0.4873721</td>
<td>0.4873886</td>
<td>0.015</td>
<td>0.4873726</td>
<td>0.0001</td>
</tr>
<tr>
<td>10.66394</td>
<td>0.5341102</td>
<td>0.5341561</td>
<td>0.009</td>
<td>0.5341094</td>
<td>0.0002</td>
</tr>
</tbody>
</table>
a simulated profile usually falls below the theoretical one if the iteration number is too small. A comparison of concentration profiles simulated by the expanding box with implicit solution algorithm and the finite differences algorithm is shown in Fig. A-4. The accuracy and efficiency of the expanding box and implicit solution algorithm can be appreciated more the with following comparisons. The expanding box algorithm uses NT = 500 and NY = 50 and generates points which agree with theoretical values to better than 0.01%, while the finite differences algorithm uses L = 10000 (which results in 420 points in the whole profile) with the concentration points in the center portion falling below the theoretical values. In addition, it only takes 10 sec for the expanding box algorithm to finish the simulation but 24 minutes for the finite differences algorithm to finish the simulation, resulting in an efficiency increase of more than 140 times. While simulation at spherical electrodes is probably the most difficult because steeper concentration profiles require much smaller distance intervals near the electrode, the performance of this algorithm for simulation at cylindrical electrodes should be at least as good as in spherical electrodes. In addition, simulations in Table A-1 and Table A-2 at \((D\tau)^{1/2}/r_0 = 6.32\) as well as Table A-3 and Table A-4 at \((D\tau)^{1/2}/r_0 = 100\) are at different levels of accuracy. At the same value of \((D\tau)^{1/2}/r_0\), simulations can be finished very quickly by using fewer points (NY), but at the cost of not knowing the points near the electrode surface. For example, the first two points in Table A-2 cover the range of the first five points in Table A-1, but values for concentrations closer than 5.765 \(\mu\)m to electrode surface are not obtained. When only less points are desired, a simulation can be finished quicker with data points being spread-out further apart. This fact brings up the problem of current simulations.

Current simulations are carried out on basis of concentrations simulations. According to Fick's diffusion law, the current (flux) is proportional to the concentration derivative with respect to distance at the electrode surface. The Fick's first law can be expressed in terms of simulation parameters:
Fig. A-4 Spherical concentration profiles obtained by three different methods
(a) the solid curve, by the theoretical formula in reference [153].
(b) The points, by the expanding box with implicit solution,
NT (# iteration) = 500, NY (# pts) = 50. (c) The dashed curve, by
finite forward differences method, NT = 10000, NY = 420.
i = nFAD\(_b\) \left(\frac{\partial C}{\partial r}\right)_{r=r_0} - nFAD\(_b\) \frac{C(1) - C(0)}{\Delta r_0} = nFAD\(_b\) \frac{C(1)}{\Delta R_0(D\tau)^{1/2}}

(A.46)

Since the slope at the surface is approximated by the quantity of \(\frac{C(1)}{\Delta R_0(D\tau)^{1/2}}\), the smaller this quantity, the closer the first point to the surface and the more accurate the approximation. As has been seen in the simulation of concentration profiles, the first point in the simulation is prone to have the largest error, with deviations rapidly converged to very small numbers. However, even if the first concentration point agrees with the theoretical value to better than 0.01%, the current simulation may not be as accurate as the concentration simulation. This is because the concentration is recorded as a result of some number of iterations, while the current is recorded as the derivatives of the intermediate simulated concentration values during a simulation. It is very likely that concentration values only converge to their accuracy level in the last several iterations so that the derivatives may very well be fluctuating during a simulation. This is indeed the case when a large \(\lambda_{\text{max}}\) is used to run a simulation, as shown in Fig. A-5. However, the fluctuation can be removed completely by reducing the \(\lambda_{\text{max}}\) value (increasing \(NT\) for given \(NY\)). The effect is shown in the same figure, where curve (b) is a smooth decaying function of time. Therefore, current simulation can not be achieved with the efficiency used to simulate a concentration profile for a same set of conditions.

The simulation of currents is formulated as the follows for a microwire of length \(\ell\) and radius \(r_o\). The theoretical current is given by eq (3.9):

\[
\frac{i}{nFDC^b \ell} = \frac{8}{\pi} I(\phi)
\]

(3.9)

After appropriate substitutions, eq (A.43) can be written in the same format as eq (3.9):
Fig. A-5  Current simulation at spherical electrode by expanding box with implicit solution, assuming $\tau = 0.2$ sec, $r_0 = 5 \mu$m, and $D = 5 \times 10^{-6}$ cm$^2$/sec.  
(a) $NT = 200$, $NY = 20$, $A = 5$.  (b) $NT = 1000$, $NY = 20$, $A = 5$.  
(c) The points, $NT = 5000$, $NY = 20$, $A = 5$.  (d) The dashed line, calculated by the theoretical formula in reference [153].
\[
\frac{i}{nFDc^b_1} = \frac{2\pi}{\sqrt{D\tau/r_0}} \frac{C(1)}{\Delta R_{0}}
\]

where \( \Delta R_{0} \) is the \( R \) increment near the electrode surface and is obtained with the following equation:

\[
\Delta R_{0} = \left[ \frac{\partial R}{\partial Y} \right]_{Y=0} \Delta Y = \left[ \frac{1}{A(1 - Y)} \right]_{Y=0} \Delta Y = \frac{\Delta Y}{A}
\]

The two parameters governing the performance of a current simulation are \( \lambda_{\text{max}} \) and \( \Delta r_{0} = \Delta R_{0}(D\tau)^{1/2} \), which are determined from simulation parameters \( NT, NY, A \) and \( (D\tau)^{1/2} \).

For simulations of cylindrical current, past experience shows that \( \lambda_{\text{max}} \) has to be less than 1.5 to have a stable current simulation. The simulation results shown in Table 3-1 are obtained with the following input parameters: \( D = 7.63 \times 10^{-6} \text{ cm}^2/\text{sec}, t = 5 \text{ sec}, r_0 = 6 \mu\text{m}, NT = 30000, NY = 40, A = 5 \), giving \( \lambda_{\text{max}} = 1.4 \) and \( \Delta r_{0} = 2.99 \times 10^4 \text{ cm} \). It is conceivable that a smaller \( \Delta r_{0} \) will give a better approximation to the real current. Although the number of iterations used in this algorithm may be close to that used for current simulation with finite differences method, smaller number of points used in each iteration can still save much time.


Since the theory of Abel inversion has been discussed in the theory section of chapter 3, only technical problems are considered here. As pointed out in the discussion section of chapter 3, the maximum size of the area matrix is only 261 x 261 because the program needs to be run at double precision \[114\]. However, this requirement may be relaxed to single precision as long as the intervals in \( x \) and \( r \) are small enough. The single precision has been tested and did not seem to give any visible errors. This relaxation of requirement
allows the algorithm to accommodate more data points which are needed to carry out the forward step Abel inversion for concentration profiles of homogeneous reactions. The program is listed as **PORGRM5.FOR** in appendix B.

What will be discussed here is the scheme of Abel inversion for expanding box (uneven spacing) to predict the absorbance profiles from the simulated concentration profiles. For a forward step Abel inversion, the absorbance at $x_i$ point is given by:

$$A_i = 2 \sum_{j=1}^{j_{\text{max}}} e^{L_{ij}} C_j$$

(A.49)

Since $C_j$ is distributed unevenly in the diffusion layer, $L_{ij}$ and thus $S_{ij}$ have to be calculated in the way with points governed by the same transformation function. Let $Z$ and $W$ be the two transformation functions in $x$ and $r$ directions such that:

$$Z = \frac{A(X - Xb)}{A(X - Xb) + 1}$$

(A.50)

$$W = \frac{A(R - Rb)}{A(R - Rb) + 1}$$

(A.51)

Since the spacings in $x$ and $r$ directions have to be the same, they are equivalent functions. In order to calculate the areas by eq (3.19) and (3.20), the following intermediate variables have been defined for the even spacing Abel inversion.

$$B = \frac{X_{i-1}}{R_j}, \quad B_1 = R_j \sqrt{1 - B^2}$$

(A.52)

$$C = \frac{X_i}{R_j}, \quad C_1 = R_j \sqrt{1 - C^2}$$

(A.53)

$$D = \frac{X_{i-1}}{R_{j-1}}, \quad D_1 = D_{j-1} \sqrt{1 - D^2}$$

(A.54)
\[ E = \frac{X_i}{R_{j-1}}, \quad E_1 = E \sqrt{1 - E^2} \]  

\( X_i \) and \( R_j \) are expressed in terms of the transformation functions \( Z \) and \( W \):

\[ X_i = \frac{Z_i}{A(1 - Z_i)} + X_b = \frac{i\Delta Z}{A(1 - i\Delta Z)} + X_b \]  

\[ R_j = \frac{W_j}{A(1 - W_j)} + R_b = \frac{j\Delta W}{A(1 - j\Delta W)} + R_b \]  

Intermediate variables \( B, C, \ldots \) can then be expressed in terms of \( X_i \) and \( R_j \), which have the transformation functions incorporated. The rest of the program is similar to the one with even spacing algorithm. The program is listed as `PROGRM6.FOR` in appendix B, along with the expanding box and implicit solution algorithm. Since spacings away from electrode surface are usually large, errors could result from using this program if too few points are used in the concentration profiles. Therefore a balance has to be made between the efficiency of a concentration simulation and the accuracy of the forward step Abel inversion. At this point, no attempt was made to estimate the performance of the forward step Abel inversion using the expanding box algorithm. Rather, the accuracy of this calculation is assured by using relatively more points in concentration simulations.

### A.4. Kinetic modeling of homogeneous reactions coupled with electron transfer reactions.

SRAS has been shown very sensitive to the follow-up homogeneous reactions because homogeneous reactions perturb the concentration profiles. The way to extract kinetic data is to compare the experimental profiles with profiles simulated with appropriate kinetic or equilibrium models built-in. The method used for simulation here is the forward finite
differences at microcylindrical electrode. Formulations of different algorithms are similar to that discussed in reference [150] except that the correction parts are more complicated. First, the relevant species are allowed to diffuse in the diffusion layers according to:

\[
\mathcal{f}'(j,k+1) - \mathcal{f}(j,k) + D \left\{ \left[ 1 + \frac{1}{2(j-k)} \right] \mathcal{f}(j+1,k) + \left[ 1 - \frac{1}{2(j-k)} \right] \mathcal{f}(j-1,k) - 2 \mathcal{f}(j,k) \right\} \quad (A.5)
\]

Second, a correction factor calculated from the appropriate equilibrium or kinetics is subtracted off the \( \mathcal{f}(j,k+1) \) values:

\[
\mathcal{f}(j,k+1) = \mathcal{f}'(j,k+1) - \text{correction} \quad (A.58)
\]

The algorithm thus goes to the next iteration. Details of derivations of corrections for four different homogeneous reaction cases will be considered here.

1) CPZ\(^+\)/MPZ system with equilibrium.

The reaction between CPZ\(^+\) and MPZ is governed by an equilibrium constant \( K_{eq} \):

\[
\text{CPZ}^+ + \text{MPZ} \rightleftharpoons K_{eq} \text{ CPZ} + \text{MPZ}^+ \quad (4.8)
\]

Let the amount reacted to reach equilibrium be \( x \) so that:

\[
K_{eq} = \frac{[\text{CPZ}][\text{MPZ}^+]}{[\text{CPZ}^+][\text{MPZ}]} = \frac{\mathcal{f}_{\text{cpz}} + x}{\mathcal{f}_{\text{cpz}} - x} \cdot \frac{\mathcal{f}_{\text{mpz}^+} + x}{\mathcal{f}_{\text{mpz}^+} - x}
\]

\[
= \frac{\mathcal{f}_{\text{cpz}} \mathcal{f}_{\text{mpz}^+} + \left[ \mathcal{f}_{\text{cpz}} + \mathcal{f}_{\text{mpz}^+} \right] x + x^2}{\mathcal{f}_{\text{cpz}} \mathcal{f}_{\text{mpz}^+} - \left[ \mathcal{f}_{\text{cpz}} + \mathcal{f}_{\text{mpz}^+} \right] x + x^2} \quad (A.59)
\]

Eq (A.59) can be rearranged to obtain a standard equation of the form:

\[
a x^2 + b x + c = 0 \quad (A.60)
\]
where
\[ a = K_{eq} - 1 \]
\[ b = -\left\{ K_{eq} \left[ f_{cpz} + f_{mpz*} \right] + \left[ f_{cpz*} + f_{mpz} \right] \right\} \]
\[ c = K_{eq} \frac{f}{cpz*} \frac{f}{mpz} - \frac{f}{cpz} \frac{f}{mpz} \]

The correction will be one of the solutions to eq (A.56) so that:
\[ f_{cpz*}(j,k+1) = f'_{cpz*}(j,k+1) - x \] (A.61)
\[ f_{cpz}(j,k+1) = f'_{cpz}(j,k+1) + x \] (A.62)
\[ f_{mpz}(j,k+1) = f'_{mpz}(j,k+1) - x \] (A.63)
\[ f_{mpz*}(j,k+1) = f'_{mpz*}(j,k+1) + x \] (A.64)

The program for modelling of reaction equilibrium between CPZ* and MPZ is listed as PROGRM7.FOR in appendix B.

2) CPZ* / DA system with equilibrium.

The overall reaction between CPZ* and DA is:
\[ 2CPZ^* + DA \underset{eq}{\longleftrightarrow} 2CPZ + DOQ \] (4.1)

Let the amount of CPZ formed at equilibrium be y so that:
\[ K = \frac{[CPZ]^2[DOQ]}{[CPZ^*]^2[DA]} = \frac{[f_{cpz} + y]^2[f_{doq} + 0.5y]}{[f_{cpz*} - y]^2[f_{da} - 0.5y]} \]
Eq (A.64) can be rearranged to give a cubic equation of the form:

\[ ay^3 + by^2 + cy + d = 0 \]  

(A.66)

where

\[ a = 0.5 \left[ 1 + K_{eq} \right] \]

\[ b = f_{cpz} + f_{da} - K_{eq} \left[ f_{cpz} + f_{da} \right] \]

\[ c = 0.5f^2_{cpz} + 2f_{cpz}f_{doq} + K_{eq} \left[ 0.5f^2_{cpz} + af_{cpz}f_{da} \right] \]

\[ d = f^2_{cpz}f_{doq} - K_{eq}f^2_{cpz}f_{da} \]

It is always possible to solve a cubic equation numerically utilizing a number of numerical methods. One such method, the Newton-Raphson method is the most powerful and well-known numerical method and is used here to find a root of eq (A.61). The development of Newton's method has been explained thoroughly[152]. Here, only the formula is given:

\[ y_n = y_{n-1} - \frac{F(y_{n-1})}{F'(y_{n-1})} \]  

(A.67)

where

\[ F(y) = ay^3 + by^2 + cy + d \]

\[ F'(y) = 3ay^2 + by + cy \]
When the algorithm of functional iteration converges to such a point that \( |y_n - y_{n-1}| < \varepsilon \) (\( \varepsilon \) is a tolerance value), \( y_n \) is considered to be the solution of eq (A.61) and is used as the correction so that:

\[
\begin{align*}
 f_{cpz^*}(j,k+1) &= f'_{cpz^*}(j,k+1) - y \\
 f_{cpz}(j,k+1) &= f'_{cpz}(j,k+1) + y \\
 f_{da}(j,k+1) &= f'_{da}(j,k+1) - 0.5y \\
 f_{doq}(j,k+1) &= f'_{doq}(j,k+1) + 0.5y
\end{align*}
\] (A.68)

The program for modelling of reaction equilibrium between CPZ** and DA is listed as PROGRM8.FOR in appendix B.

3) CPZ**/DA system with kinetics.

The overall reaction of eq (4.1) is divided into the step-wise reactions:

\[
\begin{align*}
 &\text{CPZ}^+ + \text{DA} \quad \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} \quad \text{CPZ} + \text{DA}^+ \\
 &\text{CPZ}^+ + \text{DA}^+ \quad \overset{k_4}{\underset{k_{-4}}{\rightleftharpoons}} \quad \text{CPZ} + \text{DOQ}
\end{align*}
\] (4.3) (4.4)

with the following rate law:

\[
\frac{d[\text{DOQ}]}{dt} = \frac{k_3\omega[\text{CPZ}^+]^2[\text{DA}] - k_4[\text{DOQ}][\text{CPZ}]^2}{[\text{CPZ}] + \omega[\text{CPZ}^+]} \] (4.9)

where \( \omega = k_4/k_3 \). The formulation of the dimensionless rate law is outlined as below:

\[
\frac{C' - C}{\Delta t} = \text{(diffusion terms)} + \frac{k_3\omega[\text{CPZ}^+]^2[\text{DA}] - k_4[\text{DOQ}][\text{CPZ}]^2}{[\text{CPZ}] + \omega[\text{CPZ}^+]} \] (A.72)
\[
\frac{C'}{C} = \frac{C}{C} + \left[ \text{diffusion terms} \right] + \frac{1}{C} \left[ \frac{k_3 \omega [CPZ^+]^2 [DA] - k_4 [DOQ][CPZ]^2}{[CPZ] + \omega [CPZ^+]} \right] \]

Take the kinetic term out of eq (A.73) and multiply the numerator and denominator by \(1/(C_{CPZ})^2\).

\[
z = \frac{1}{\left\{ \frac{[CPZ]/C^b + \omega [CPZ^+]/C^b} \right\} \frac{1}{C^b}} \]

\[
- \frac{[k_3 t C_{CPZ}^b] \omega f_{cpz^*}^2 f_{da} - [k_4 t C_{CPZ^*}/L] f_{cpz^*}^2 f_{dpq}}{f_{cpz^*} + \omega f_{cpz^*}} \]

\[
- \frac{\gamma \omega f_{cpz^*}^2 f_{da} - [k_4 t C_{CPZ^*}/L] f_{cpz^*}^2 f_{dpq}}{f_{cpz^*} + \omega f_{cpz^*}} \quad (A.74)
\]

where \(\gamma = k_3 t C_{CPZ}\) and \(L\) is iteration number. Finally, the correction term is added to (or subtracted off) the diffusion terms of each species:

\[
f_{cpz^*}(j,k+1) = f_{cpz^*}'(j,k+1) - z \quad (A.75)
\]

\[
f_{cpz}(j,k+1) = f_{cpz}'(j,k+1) + z \quad (A.76)
\]

\[
f_{da}(j,k+1) = f_{da}'(j,k+1) - 0.5z \quad (A.77)
\]

\[
f_{doq}(j,k+1) = f_{doq}'(j,k+1) + 0.5z \quad (A.78)
\]

The program for modelling of reaction kinetics between \(CPZ^{++}\) and \(DA\) is listed as PROGRM9.FOR in appendix B.
4) CPZ⁺⁺/DA system with both equilibrium and kinetics being operative.

At pH 0.5, the reaction is governed by both equilibrium and kinetics. The slower process of the two is the one that determines the perturbation to a concentration profile. In a simulation algorithm, both eq (A.62) and (A.68) are used to calculate the corrections due equilibrium and kinetics respectively. The smaller of the two is used to make corrections to the concentrations. The program is listed as PORGRM10.FOR in appendix B.

A.5. Routines for data analyses of two-dimensional imaging experiments.

In order to analyze experimental results, a single column (or row) of data or a portion of a 2-D data must be extracted out of the 2-D images followed by any necessary manipulations. Knowledge of the data formats is necessary. A CCD data file is always headed by a header of 160 bytes for documentation of that particular file. One record has two bytes, making the header 80 records. The rest of the data are stored with double precision format so that 516 x 516 elements plus the header uses (516 x 516 x 2 + 160) = 532672 bytes. Furthermore, the data storage starts from row 0 to row 515. Therefore, the header needs to be by-passed when a column or a row of data is extracted from an 2-D image data file. The program, listed as PROGRM11.FOR in appendix B, accounts for the header and the way the data are stored (that is, data are stored by row.) After the reference beam profile and the sampling beam profile are extracted, they are processed with the Hyperplot software.

Constructions of two-dimensional profiles differ greatly from the analysis of one-dimensional profiles. Initially, particular portions of reference and the sample images with an appropriate resolution are extracted from A, B images. These two extracted images are then processed according to the Beer's law to form an absorbance 2-D file which is stored as a function of x, y (or row and column) pair. These two steps are accomplished with
PROGRM12.FOR listed in appendix B. Finally, the three-dimensional data \( (x, y, \text{absorbance}) \) are transferred into a VAX computer. Data points are connected with their neighboring points in space, which is accomplished by PROGRM13.FOR listed in appendix B. The data file such connected is then read by CHEMX software for 3-D plotting.
Appendix B

This appendix contains all the programs discussed in appendix A.

PROGRM1.FOR

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
* *
C  * THIS IS A SIMULATION PROGRAM WHICH GENERATES *
C  * CONCENTRATION PROFILES OF A PRODUCT AND A REACTANT AT *
C  * LINEAR, SPHERICAL AND CYLINDRICAL DIFFUSIONS. THE *
C  * PROGRAM USES THE FINITE-DIFFERENCES METHOD, AND *
C  * FOLLOWS CLOSELY THE PROGRAM LISTED IN BARD'S BOOK *
C  * EXCEPT THAT THE BOUNDARY CONDITION IS DIFFERENT. *
C  * VARIABLES USED ARE DEFINED AS BELOW:
* *
C  * *
C  * RO -- RADIUS OF A MICROCYLINDER OR SPHERE. *
C  * D, DM -- REAL AND MODEL DIFFUSION COEFFICIENTS. *
C  * T, L -- EXPERIMENTAL TIME AND ITERATION NUMBER. *
C  * Z -- NUMBER OF AR WITHIN THE RADIUS RO *
*
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
*
C ******* SET UP ARRAYS AND MODEL VARIABLES ********
C
IMPLICIT REAL*8(A-H,O-Z)
CHARACTER*64 FILE1
DIMENSION FAOLD(700), FANEW(700), FBOLD(700), FBNEW(700)

WRITE(*,900)
900 FORMAT(/' LINEAR(1), SPHERICAL(2), CYLINDRICAL(3) '
READ(*,II)
WRITE(*,'](A)')' ENTER A,B STORAGE FILE NAME: '
READ(*,100) FILE1
100 FORMAT(A)
WRITE(*,'](A)')' ENTER D,RO,T,L- '
READ(*,D, RO, T, L
OPEN(2,FILE=FILE1,STATUS='NEW')
DMB=.45
DMA=DMB
DR=10000*SQRT(D*T)/SQRT(DMA*L)
Z=RO/DR

248
**** INITIAL CONDITIONS ****

DO 10 J-1,1,700
   FAOLD(J)=1.
   FANEW(J)=1.
   FBOLD(J)=0.
   FBNW(J)=0.
10 CONTINUE

**** DIFFUSION BEYOND THE FIRST BOX ****

WRITE(*,'(/A)') ' START CALCULATION....'
K=0
1000 K=K+1
   IF(((K/50)*50).EQ.K) WRITE(*,999) K
999 FORMAT(' K = ',I6)
   JMAX=4.2*SQRT(REAL(K))
   DO 20 J=2,JMAX
      ZJ=REAL(J)
      M=J-1
      N=J+1
      IF (II .EQ. 1) THEN
         Y=1.
         X=1.
      ELSEIF (II .EQ. 2) THEN
         Y=1.+1./(ZJ+Z)
         X=1.-1./(ZJ+Z)
      ELSEIF (II .EQ. 3) THEN
         Y=1.+0.5/(ZJ+Z)
         X=1.-0.5/(ZJ+Z)
      ENDIF
      FANEWCJ)=FAOLD(J)+DMA*(Y*FAOLD(N)-2*FAOLD(J)+X*FAOLD(M))
      FBNW(J)=FBOLD(J)+DMB*(Y*FBOLD(N)-2*FBOLD(J)+X*FBOLD(M))
   20 CONTINUE

**** DIFFUSION INTO THE FIRST BOX ****

IF (II .EQ. 1) THEN
   Y=1.
ELSEIF (II .EQ. 2) THEN
   Y=1.+1./(1.+Z)
ELSEIF (II .EQ. 3) THEN
   Y=1.+0.5/(1.+Z)
ENDIF
   FANEW(1)=FAOLD(1)+DMA*(Y*FAOLD(2)-FAOLD(1))
   FBNW(1)=FBOLD(1)+DMB*(Y*FBOLD(2)-FBOLD(1))

FARADAIC CONVERSION
FBNEW(1)=FBNEW(1)+FANEW(1)
FANEW(1)=0

C
C ******* SET UP OLD ARRAYS FOR NEXT ITERATION *******
C
DO 40 J=1,JMAX
   FAOLD(J)=FANEW(J)
   FBOLD(J)=FBNEW(J)
40 CONTINUE

C
C RETURN FOR NEXT ITERATION IF K<L(TIME PARAMETER)
C
IF (K.LT.L) GO TO 1000

C
C ******* STORE DATA TO DISK *******
C
DO 200 J=1,JMAX
   R = 10000*SQRT(D*T)*(J-1)/SQRT(DMA*L)
   WRITE(2,*) R,FANEW(J),FBNEW(J)
200 CONTINUE
STOP
END
**PROGRM2.FOR**

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

C  * *
C  * THIS IS A SIMULATION PROGRAM THAT GENERATES *
C  * CONCENTRATION PROFILES OF REACTANT AND PRODUCT OF *
C  * DOUBLE POTENTIAL STEP EXPERIMENTS. THE PROGRAM USES *
C  * FINITE DIFFERENCES METHOD FOR SIMULATION. VARIABLES *
C  * USED ARE DEFINED AS BELOW:
C  * *
C  * *
C  * T1, T2 -- TIMES FOR FORWARD AND REVERSE STEPS. *
C  * L1, L2 -- NUMBER OF ITERATIONS FOR FORWARD AND *
C  * REVERSE STEPS. *
C  * D, DM -- REAL AND MODEL DIFFUSION COEFFICIENT. *
C  * *
C  * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

CHARACTER*16 FILE1
DIMENSION FAOLD(700), FANEW(700), FBOLD(700), FBNEW(700)

WRITE(*,'(/A )') ' ENTER A,B STORAGE FILE NAME: '
READ(*,100) FILE1

100 FORMAT(A)
WRITE(*,'(/A )') ' ENTER T1,T2 D,L1- '
READ(*,*)T1, T2, D, L1
OPEN(2,FILE=FILE1,STATUS='NEW')

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

****** INITIAL CONDITIONS ******

DMB=.45
DMA=DMB
L2=L1*T2/T1
DO 10 J=1,700
FAOLD(J)=1.
FANEW(J)=1.
FBOLD(J)=0.
FBNEW(J)=0.
10 CONTINUE

C ************** FORWARD STEP ITERATION **************

WRITE(*,'(/A )') ' FORWARD STEP......'
C

K=0

1000  K=K+1

C

******* DIFFUSION BEYOND THE FIRST BOX *******

C

IF(((K/50)*50).EQ.K)write(*,999)k

999 format('   K = ',I6)

JMAX=4.2*SQRT(REAL(K))

DO 20 J=2,JMAX

    FANEW(J)=FAOLD(J)+DMA*(FAOLD(J+1)-2*FAOLD(J)+FAOLD(J-1))

    FBNEW(J)=FBOLD(J)+DMB*(FBOLD(J+1)-2*FBOLD(J)+FBOLD(J-1))

20 CONTINUE

C

******* DIFFUSION INTO THE FIRST BOX *******

C

FANEW(1)=FAOLD(1)+DMA*(FAOLD(2)-FAOLD(1))

FBNEW(1)=FBOLD(1)+DMB*(FBOLD(2)-FBOLD(1))

C

******* FARADAIC CONVERSION *******

C

FBNEW(1)=FBNEW(1)+FANEW(1)

FANEW(1)=0

C

******* SET UP OLD ARRAYS FOR NEXT ITERATION *******

C

DO 40 J=1,JMAX

    FAOLD(J)=FANEW(J)

    FBOLD(J)=FBNEW(J)

40 CONTINUE

C

RETURN FOR NEXT ITERATION IF K<.L(TIME PARAMETER)

C

IF (K.LT.L1) GO TO 1000

C

****** REVERSE STEP ITERATION ***************

C

WRITE(*,'(/A)') ' REVERSE STEP......'

K=0

1001  K=K+1

C

******* DIFFUSION BEYOND THE FIRST BOX *******

C

IF(((K/50)*50).EQ.K) WRITE(*,999)K

JMAX=4.2*SQRT(REAL(K+L1))

DO 30 J=2,JMAX

    FANEW(J)=FAOLD(J)+DMA*(FAOLD(J+1)-2*FAOLD(J)+FAOLD(J-1))

    FBNEW(J)=FBOLD(J)+DMB*(FBOLD(J+1)-2*FBOLD(J)+FBOLD(J-1))

30 CONTINUE

C

******* DIFFUSION INTO THE FIRST BOX *******
FANEW(1) = FAOLD(1) + DMA*(FAOLD(2) - FAOLD(1))
FBNEW(1) = FBOLD(1) + DMB*(FBOLD(2) - FBOLD(1))

FARADAIC CONVERSION

FANEW(1) = FBNEW(1) + FANEW(1)
FBNEW(1) = 0

******* SET UP OLD ARRAYS FOR NEXT ITERATION *******

DO 50 J = 1, JMAX
   FAOLD(J) = FANEW(J)
   FBOLD(J) = FBNEW(J)
50 CONTINUE

RETURN FOR NEXT ITERATION IF K < L (TIME PARAMETER)

IF (K .LT. L2) GO TO 1001

******* STORE DATA TO DISK *******

DO 200 J = 1, JMAX
   X = 10000*SQRT(D*(T1+T2))*(J-1)/SQRT(DMA*(L1+L2))
   WRITE(2,*), X, FANEW(J), FBNEW(J)
200 CONTINUE
STOP
END
**PROGRM3.FOR**

```fortran
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
* THIS IS A SIMULATION PROGRAM THAT GENERATES *
* CONCENTRATION PROFILES OF REACTANT AND PRODUCT AT *
* TWIN ELECTRODES THIN LAYER CELL. THE PROGRAM USES *
* FINITE DIFFERENCES METHOD. THIS IS ESPECIALLY *
* PROGRAMMED FOR THE TWIN ELECTRODES DIFFUSION *
* PROBLEM OF FERRO/FERRI-CYANIDE SYSTEM. *
* *
* A - FERROCYANIDE, B - FERRICYANIDE. *
* D,DM = REAL AND MODEL DIFFUSION COEFFICIENT. *
* N+1 = NUMBER OF BOXES BETWEEN TWO ELECTRODES. *
* T, L = EXPERIMENTAL TIME AND ITERATION NUMBER. *
* *
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

****** SET UP ARRAYS AND MODEL VARIABLES *******

IMPLICIT REAL*8(A-H,O-Z)
CHARACTER*16 FILEl
DIMENSION FAOLD(1500), FANEW(1500), FBOLD(1500), FBNEW(1500)

WRITE(*,')''ENTER A,B STORAGE FILE NAME: '
READ(*,100) FILEl
100 FORMAT(A)
WRITE(*,')''ENTER Da,Db,T,L - '
READ(*,*)DA, DB, T, L
OPEN(1, FILE=FILEl, STATUS='NEW')

DMB=.45
DMA=DMB*DA/DB
N=0.075*SQR(DMB*L/(DB*T))+1

0.075 mm IS THE ACTUAL SEPARATION OF THE TWIN ELECTRODE.

****** INITIAL CONDITIONS ******

DO 10 J=1,N+1
   FAOLD(J)=1.
   FANEW(J)=1.
   FBOLD(J)=1.
   FBNEW(J)=1.
10 CONTINUE
```
C ******* DIFFUSION BEYOND THE FIRST BOX *******
C
WRITE(*,'(/A)') ' START CALCULATION.....'
K=0
1000 K=K+1
IF(((K/50)*50).EQ.K) WRITE(*,999) K
999 FORMAT(' K = ', I6)
JMAX=4.2*SQRT(REAL(K))
IF (JMAX.GT.N) JMAX=N
DO 20 J=2,JMAX
   FANEW(J)-FAOLD(J)+DMA*(FAOLD(J+1)-2*FAOLD(J)+FAOLD(J-1))
   FBNEW(J)=FBOLD(J)+DMB*(FBOLD(J+1)-2*FBOLD(J)+FBOLD(J-1))
   I=N-J+2
      FANEW(I)-FAOLD(I)+DMA*(FAOLD(I+1)-2*FAOLD(I)+FAOLD(I-1))
      FBNEW(I)-FBOLD(I)+DMB*(FBOLD(I+1)-2*FBOLD(I)+FBOLD(I-1))
20 CONTINUE
C
C ******* DIFFUSION INTO THE FIRST BOX *******
C
FANEW(1)-FAOLD(1)+DMA*(FAOLD(2)-FAOLD(1))
FBNEW(1)-FBOLD(1)+DMB*(FBOLD(2)-FBOLD(1))
FANEW(N+1)-FAOLD(N+1)+DMA*(FAOLD(N)-FAOLD(N+1))
FBNEW(N+1)-FBOLD(N+1)+DMB*(FBOLD(N)-FBOLD(N+1))
C
C ******* FARADAIC CONVERSION *******
C
FBNEW(1)=FBNEW(1)+FANEW(1)
FANEW(1)=0
FANEW(N+1)=FBNEW(N+1)+FANEW(N+1)
FBNEW(N+1)=0.0
C
C ******* SET UP OLD ARRAYS FOR NEXT ITERATION *******
C
DO 40 J=1,N+1
   FAOLD(J)=FANEW(J)
   FBOLD(J)=FBNEW(J)
40 CONTINUE
C
RETURN FOR NEXT ITERATION IF K<L(TIME PARAMETER)
C
IF (K.LT.L) GO TO 1000
C
C ******* STORE DATA TO DISK *******
C
DO 200 J=1,N+1
   X = 10000*SQRT(DB*T)*(J-1)/SQRT(DMB*L)
   WRITE(1,*) X,FANEW(J),FBNEW(J)
200 CONTINUE
STOP
END
**PROGRM4.FOR**

```plaintext
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

C * THIS IS A SIMULATION PROGRAM FOR CONCENTRATION
C * PROFILE OF REACTANT AND CURRENT AT SPHERICAL
C * ELECTRODE. THE PROGRAM USES THE EXPANDING BOX WITH
C * IMPLICIT SOLUTION ALGORITHM. THE TRANSFORMATION
C * FUNCTION USED IS:
C *
C * Y = A(R + RB)/(A(R + RB) + 1)
C *
C * VARIABLES USED ARE DEFINED AS BELOW:
C *
C * RB -- r0/(Dr1)^1/2,
C * NT -- TIME PARAMETER, NUMBER OF ITERATIONS.
C * NYMAX -- NUMBER OF POINTS IN Y DOMAIN.
C * A -- CONSTANT, USUALLY TAKEN AS 2 TO 5.
C * RLIM -- LIMIT IN THE R DOMAIN (RLIM = 6).
C * YLIM -- LIMIT IN THE Y DOMAIN.
C * DT,DR -- ΔT AND ΔR VALUES.
C * DCDRO -- SURFACE DERIVATIVE OF CONCENTRATION.
C *
C * THE PROGRAM CAN BE QUICKLY CHANGED TO SIMULATE LINEAR
C * AND CYLINDRICAL DIFFUSIONS BY USING DIFFERENT D3.
C *
C * D3 = 0, LINEAR DIFFUSION.
C * D3 = DY/2/(1 - Y)/RI, CYLINDRICAL DIFFUSION.
C * D3 = DY/(1 - Y)/RI, SPHERICAL DIFFUSION.
C *
C * CRANK IS THE SUBROUTINE FOR CRANK-NICOLSON ALGORITHM,
C * A1, A2, BA, AD, BDA ARE NECESSARY COEFFICIENTS USED
C * IN THE SUBROUTINE. NECESSARY ARRAYS NEED TO BE
C * DEFINED TO CARRY OUT THE SIMULATION OF PRODUCT.
C *
C * IN ORDER TO ELIMINATE THE UNNECESSARY POINTS IN CURRENT
C * SIMULATION FOR ITERATION LARGER THAN 2000, A ROUTINE IS
C * BUILT IN TO TAKE ONLY THE POINTS WHEN THE SQUARE ROOT
C * OF THE ITERATION NUMBER EQUALS AN INTEGER. THUS THE
C * TOTAL NUMBER OF POINTS IN SIMULATED CURRENTS IS THE
C * SQUARE ROOT OF THE TOTAL NUMBER OF ITERATIONS.
C *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

REVISED 2/7/90
C
C IMPLICIT REAL*8(A-H,O-Z)
```
CHARACTER*16 CURRENT, REACTFIL
DIMENSION CA(301), A1(301), A2(301), F(301)
DIMENSION BA(301), AD(301), BDA(301)
DATA (CA(I), I=1,301)/301*1.0/, RLIM/6.0/

WRITE(*,'(/A\)')' ENTER TIME t, RADIUS R0, AND COEFFICIENT D: '
READ(*,*) T, R0, D
WRITE(*,'(/A\)')' ENTER NT, NYMAX, A: '
READ(*,*) NT, NYMAX, A
WRITE(*,'(/A\)')' ENTER REACTANT FILE NAME: '
READ(*,9) REACTFIL

9 FORMAT(A)
WRITE(*,'(/A\)')' ENTER PRODUCT FILE NAME: '
READ(*,9) PRODFIL
WRITE(*,'(/A\)')' ENTER CURRENT FILE NAME: '
READ(*,9) CURRENT
OPEN(1,FILE=REACTFIL, STATUS='NEW')
OPEN(2,FILE=PRODFIL, STATUS='NEW')
OPEN(3,FILE=CURRENT, STATUS='NEW')
WRITE(*,*) NT, NYMAX, A, RLIM

******* INITIAL VALUES SETUP ******

RDT=10000*SQRT(D*T)
YLIM=A*RLIM/(1.0+A*RLIM)
DT=1.0/REAL(NT)
DY=YLIM/REAL(NYMAX)
DRO=RDT*DY/A/(1.0-DY)
D1=2.0*(DY/A)**2/DT
RB=R0/RDT
R10=R1/R0
PI=3.1415927

******* CALCULATING COEFFICIENTS A1(J), A2(J), F ******

WRITE(*,'(/A\)')' START LOOPPING...
Y=0.0
DO 10 J=1,NYMAX
 Y=Y+DY
 R1=Y+A*RB*(1.0-Y)
 D3=DY/(1.-Y)/R1
 C CYL
 D3=CYL/(1.-Y)/R1/2
 C LIN
 D3=0
 D2=DY/(1.0-Y)-D3
 A1(J)=-2.0+D1/(1.0-Y)**4)/(1.0+D2)
 A2(J)=1.0-D2)/(1.0+D2)
 F(J)=(2.0-D1/(1.0-Y)**4)/(1.0+D2)
10 CONTINUE
TINT=1.0
DO 20 K=1,NT
 C IF (((K/50)*50) .EQ. K) WRITE(*,999) K
C999    FORMAT( ' K= ', I6)
R2=6*SQRT(REAL(K)/REAL(NT))
Y1=A*R2/(A*R2+1.0)
NY=Y1/DY+0.5
IF (NY .GT. NYMAX) NY=NYMAX
CA0=0.0
C    CB0=1.0
CALL CRANK(CA,A1,A2,BA,AD,BDA,CA0,F,NY)
IF (DSQRT(DBLE(K)) .EQ. TINT) THEN
  TT=REAL(K)*DT*T
  DCDRO=CA(1)/DR0
  CI=1/(10000*SQRT(PI*D*TT)) + R1R0
  WRITE(3,*) TT,CI,DCDRO
  TINT=TINT+1.0
ENDIF
20    CONTINUE
WRITE(1,*) R0, CA0
WRITE(2,*) R0, CB0
Y=0.0
DO 25 J=1,NY
  Y=Y+DY
  Rr=R0+RDT*Y/A/(1.0-Y)
  WRITE(1,* ) Rr, CA(J)
  FORMAT(2X,F10.5,2X,F10.8)
  WRITE(2,* ) Rr, CB(J)
25    CONTINUE
STOP
END

C
C ******* SUBROUTINE *******
C
SUBROUTINE CRANK(CA,A1,A2,BA,AD,BDA,CA0,F,N)
  IMPLICIT REAL*8(A-H,O-Z)
  DIMENSION CA(301),A1(301),A2(301),F(301)
  DIMENSION BA(301),AD(301),BDA(301)
  CADO=CA0
C    CBDO=CB0
CA1=CA0
C    CB1=CB0
CA2=CA(1)
C    CB2=CB(1)
DO 30 J=1, N
  CA3=CA(J+1)
C    CB3=CB(J+1)
  BA(J)=-CA1+F(J)*CA2-A2(J)*CA3
C    BB(J)=-CB1+F(J)*CB2-A2(J)*CB3
  CA1=CA2
C    CB1=CB2
CA2=CA3
C    CB2=CB3
30    CONTINUE
AD(1) = A2(1)/A1(1)  
BDA(1) = (BA(1) - CAD0)/A1(1)  
C   BDB(1) = (BB(1) - CBDO)/A1(1)  
DO 40 J = 2, N  
   AD(J) = A2(J)/(A1(J) - AD(J - 1))  
   BDA(J) = (BA(J) - BDA(J - 1))/(A1(J) - AD(J - 1))  
C   BDB(J) = (BB(J) - BDB(J - 1))/(A1(J) - AD(J - 1))  
40 CONTINUE  
DO 50 I = N, 1, -1  
   CA(I) = BDA(I) - AD(I)*CA(I + 1)  
C   CB(I) = BDB(I) - AD(I)*CB(I + 1)  
50 CONTINUE  
RETURN  
END
**PROGRM5.FOR**

```
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C * THIS PROGRAM CALCULATES THE OVERLAP MATRIX FOR ABEL *
C * INVERSION. THE PROGRAM ALSO CALCULATES FORWARD STEP *
C * AND REVERSE STEP ABEL INVERSIONS WITH THE 'A' MATRIX. *
C * A BACK-SUBSTITUTION ROUTINE IS USED FOR REVERSE STEP *
C * ABEL INVERSION. VARIABLES USED ARE DEFINED AS BELOW:
C *
C *
C * A(M,M) -- AREA MATRIX. *
C * W(M) -- DISTANCE ARRAY. *
C * Z(M) -- ABSORBANCE ARRAY. *
C * CON(M) -- CONCENTRATION ARRAY. *
C *
C * IF NECESSARY, DOUBLE PRECISION MAY BE USED, WHICH IS *
C * RECOMMENDED TO DO IN THE ORIGINAL PAPER. HOWEVER, *
C * THE SIZE OF THE AREA MATRIX A(M,M) HAS TO BE REDUCED *
C * TO 261 X 261. THE AREA MATRIX IS CREATED WITH THE *
C * INTERVAL WIDTH EQUAL TO 1. FOR THE REVERSE ABEL *
C * INVERSION, THE INTERVAL WIDTH IS 1.25 µm IF THE DATA *
C * ARE TAKEN BY THE PHOTODIODE ARRAY OF TRACOR NORTHERN. *
C * FOR THE FORWARD ABEL INVERSION, THE INTERVAL WIDTH *
C * MAY VARY, DEPENDING ON SIMULATIONS. *
C * REVISED 1/15/90 *
C *
C * IMPLICIT REAL*8(A-H,O-Z)
C CHARACTER*16 FILE1, FILE2, FILE3, FILE4, FILE5, FILE6
DIMENSION A(366,366), W(366), Z(366), CON(366)
C 10 WRITE(*,'(/A )') ' 1. CREATING AREA MATRIX,'
WRITE(*,'(A )') ' 2. CONVERTING RADIAL TO LATERAL,'
WRITE(*,'(A )') ' 3. CONVERTING LATERAL TO RADIAL,'
WRITE(*,'(A )') ' 4. EXIT.'
WRITE(*,'(/A\ )')' ENTER THE FUNCTION NUMBER: '
READ(*,*)*INT
IF (INT .EQ. 1) GOTO 1
IF (INT .EQ. 2) GOTO 2
IF (INT .EQ. 3) GOTO 3
IF (INT .EQ. 4 ) STOP
C
C ******** CREATE THE A MATRIX ********
```
1 WRITE(*,'(/A/)') 'CREATING THE A MATRIX...' 
   X=0.DO 
   DO 180 I=1,366 
       X=X+1 
       Y=0.DO 
       IF(((I/10)*10) .EQ. I)WRITE(*,999) I 
       999 FORMAT( ' K=', I5) 
       DO 100 J=1,366 
           Y=Y+1 
           IF (I .GT. J) A(I,J)=0.DO 
           IF (I .GT. J) GOTO 100 
           B=(X-1)/Y 
           B1=B*DSQRT(1-B*B) 
           IF(I .EQ. J) THEN 
               A(I,J)=Y**((DACS(B)-B1)/2 
               ELSEIF (I .LT. J) THEN 
               C=X/Y 
               C1=C*DSQRT(1-C*C) 
               D=(X-1)/(Y-1) 
               D1=D*DSQRT(1-D*D) 
               E=X/(Y-1) 
               E1=E*DSQRT(1-E*E) 
               P=DACS(B)-DACS(C)-B1+C1 
               Q=DACS(D)-DACS(E)-D1+E1 
               A(I,J)=Y**P/2-(Y-1)*(Y-1)*Q/2 
           ENDIF 
       100 CONTINUE 
   180 CONTINUE 
   GOTO 10 
C 
C ***** FORWARD STEP ABEL INVERSION ***** 
C 
C IN THIS ROUTINE, THE CONCENTRATION PROFILE IS ASSUMED TO BE 
C UNITLESS, THAT IS, THE MAXIMUM IS 1.0. IF, HOWEVER, THE 
C CONCENTRATION PROFILE IS IN MOLAR UNIT, THE MOLAR CONCENTRATION 
C ENTRY NEEDS ONLY TO BE 1.0. 
C 
C 2 WRITE(*,'(/A/)') 'ENTER MOLAR ABSORPTIVITY E, AND R0:' 
READ(*,*) G, R0 
WRITE(*,'(/A/)') 'ENTER THE CONCENTRATION FILE NAME:' 
READ(*,299) FILE3 
WRITE(*,'(/A/)') 'ENTER THE ABSORBANCE FILE NAME:' 
READ(*,299) FILE4 
299 FORMAT(A) 
WRITE(*,'(/A/)') 'ENTER MOLAR CONCENTRATION:' 
READ(*,*) CONCENT 
OPEN(3, FILE=FILE3, STATUS='OLD') 
OPEN(4, FILE=FILE4, STATUS='NEW') 
C
C  ******* READ DATA FILES *******
C
M=0
M=M+1
IF (M .GT. 366) GOTO 88
READ(3, *, IOSTAT=IOCHECK) W(M), CON(M)
IF (IOCHECK .LT. 0) THEN
  M=M-1
  GOTO 88
ELSE
  GOTO 89
ENDIF
C
C  ******* ABEL INVERSION CALCULATIONS *******
C
88 WIDTH=W(2)-W(1)
  N=1+RO/WIDTH
  IF (M+N .GT. 366) M=366-N
  DO 260 I=1,M
    Z(I)=0.0
    DO 250 J=I,M
      Z(I)=Z(I)+CON(J)*A(I+N-1,J+N-1)*WIDTH*1E-4
    250 CONTINUE
  260 WRITE(4,*) W(I), 2.*Z(I)*CONCENT*G
  CONTINUE
  CLOSE (2)
  CLOSE (3)
  CLOSE (4)
  GOTO 10
C
C  ******* REVERSE STEP ABEL INVERSION (BACK-SUBSTITUTION) *******
C
3 WRITE(*,'(/A \)') ' ENTER MOLAR ABSORPTIVITY, AND RADIUS:'
  READ(*,*) G, RO
  WRITE(*,'(/A \)') ' ENTER ABSORBANCE FILE NAME:'
  READ(*,299) FILE5
  WRITE(*,'(/A \)') ' ENTER RADIAL FILE NAME:'
  READ(*,299) FILE6
  OPEN(3, FILE=FILE5, STATUS='OLD')
  OPEN(4, FILE=FILE6, STATUS='NEW')
C
C  ******* READ DATA FILES *******
C
M=0
M=M+1
IF (M .GT. 366) GOTO 98
READ(3, *, IOSTAT=IOCHECK) W(M), Z(M)
C WRITE(*,*) M, ICHECK, W(M), Z(M)
IF (IOCHECK .LT. 0) THEN
M=M-1
GOTO 98
ELSE
GOTO 99
ENDIF

******* BACK-SUBSTITUTION CALCULATIONS *******

98 WRITE(*,'(/A)')' BACK-SUBSTITUTION...
WIDTH=(W(2)-W(1))
N=1+RO/WIDTH
IF (M+N .GT. 366) M=366-N
CON(M)=Z(M)/(2*G*A(M+N-1,M+N-1)*WIDTH*1E-4)
DO 300 I=M-1, 1, -1
   S=0.DO
   DO 280 J=I+1,M
      S=S+A(I+N-1,J+N-1)*CON(J)*WIDTH*1E-4
   280 CONTINUE
   CON(I)=(Z(I)/(2*G)-S)/(A(I+1,N-1)*WIDTH*1E-4)
300 CONTINUE
DO 400 I=1, M
   WRITE(4,*) W(I), CON(I)
400 CONTINUE
CLOSE (3)
CLOSE (4)
GOTO 10
END
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C * THIS PROGRAM HAS TWO PARTS. THE FIRST PART IS *
C * BASICALLY THE SAME AS PROGRM4.FOR USING THE EXPANDING *
C * BOX ALGORITHM WITH IMPLICIT SOLUTION FOR CYLINDRICAL *
C * DIFFUSION. THE SECOND PART IS A ROUTINE FOR ABEL *
C * INVERSION WHICH IS SIMILAR TO PROGRM5.FOR EXCEPT THAT *
C * THE AREA MATRIX IS CALCULATED USING THE DIVISION OF *
C * DIFFUSION FIELD THAT IS USED IN THE EXPANDING BOX *
C * ALGORITHM FOR FORWARD STEP OF ABEL INVERSION. *
C *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C IMPLICIT REAL*8(A-H,O-Z)
CHARACTER*16 PRODFIL,LTRLFIL
DIMENSION CB(151),BB(151),AL(151),A2(151),F(151)
DIMENSION AD(151),BB(151)
DIMENSION CA(151),BDA(151),BA(151)
DIMENSION AL(151,151),Z(151),Rr(151)
DATA RLIM/6.0/
C
1000 WRITE(*,'(/A)')' 1. SIMULATION OF A CONCENTRATION PROFILE,' WRITE(*,'(A)')' 2. CONVERSION OF RADIAL TO LATERAL,' WRITE(*,'(A)')' 3. EXIT THE PROGRAM.' WRITE(*,'(/A\)')' ENTER THE FUNCTION NUMBER: ' READ(*,*)INT
IF (INT .EQ. 1) GOTO 1
IF (INT .EQ. 2) GOTO 2
IF (INT .EQ. 3) STOP
C
1 WRITE(*,'(/A\)')' LINEAR(1), CYLINDRICAL(2), OR SPHERICAL(3): '
READ(*,*)KK
WRITE(*,'(/A\)')' ENTER T(sec), D AND RO(µm, O FOR LINEAR): '
READ(*,*)T, D, RO
WRITE(*,'(/A\)')' ENTER NT, NYMAX, A: '
READ(*,*)NT, NYMAX, A
WRITE(*,'(/A\)')' ENTER PRODUCT FILE NAME: '
READ(*,9)PRODFIL
9 FORMATA(A)
C WRITE(*,'(/A\)')' ENTER CURRENT FILE NAME: '
C READ(*,9)CURRENT
OPEN(1, FILE=PRODFIL, STATUS='NEW')
C OPEN(3, FILE=CURRENT, STATUS='NEW')
WRITE(*,*) NT,NYMAX,A,RLIM

DO 7 I=1,150
CA(I)=1.0
CB(I)=0.0
CONTINUE

RDT=10000*DSQRT(D*T)
RB=RO/RDT
YLim=A*RLIM/(1.+A*RLIM)
DT=1.0/DBLE(NT)
DY=YLim/DBLE(NYMAX)
DRO=DY/A/(1.0-DY)
Dl=2.0*(DY/A)**2/DT
WRITE(*,'(/A)') 'START LOOPING...
NR=RO-1
Y=0.0
DO 10 J=1,NYMAX
Y=Y+DY
RL=Y+ARB*(1.0-Y)
IF (KK.EQ.1) THEN
D3=0
ELSEIF (KK.EQ.2) THEN
D3=DY/(1.0-Y)/R1
ELSEIF (KK.EQ.3) THEN
D3=DY/(1.0-Y)/R1
ENDIF
D2=DY/(1.0-Y)-D3
A1(J)=-(2.0+D1/(1.0-Y)**4)/(1.0+D2)
A2(J)=(1.0-D2)/(1.0+D2)
F(J)=(2.0-D1/(1.0-Y)**4)/(1.0+D2)
CONTINUE

tINT=1.0
DO 20 K=1,NT
IF (((K/50)*50).EQ. K) WRITE(*,999) K
999 FORMAT( 'K-',I6)
R2=6*DSQRT(DBLE(K)/DBLE(NT))
Y1=A*R2/(A*R2+1.0)
NY=Y1/DY+0.5
IF (NY.GT. NYMAX) NY=NYMAX
CA0=0.0
CB0=1.0
CALL CRANK(CB,A1,A2,BB,AD,BDB,CB0,F,NY)

****** THE ROUTINE BELOW IS FOR CURRENT SIMULATION
IT CAN BE ACTIVATED BY REMOVED THE 'C' IN LINE. ******

IF (DSQRT(DBLE(K)).EQ. TINT) THEN
TT=DBLE(K)*DT*T
DCDRO=CA(1)/DRO/RDT
WRITE(3,*') TT,DCDRO
TINT=TINT+1.
C  ENDIF
20 CONTINUE
Y=0.0
DO 22 J=1,NY
  Y=Y+DY
  RR(J)=RO+RDT*Y/A/(1.0-Y)
22 CONTINUE
CBO=CB0
RR(0)=RO
DO 23 I=0,NR
  WRITE(1,*) DBLE(I),0.0
23 CONTINUE
DO 24 J=0,NY
  WRITE(1,*) RR(J),CB(J)
24 CONTINUE
CLOSE (1)
GOTO 1000
C
****** CREATE THE A MATRIX ******
C
2 WRITE(*,'(A)') ENTER MOLAR ABSORPTIVITY, & CONCENTRATION:
READ(*,*) G, CONCENT
WRITE(*,'(A)') ENTER LATERAL PROFILE NAME:
READ(*,9) LTRLFIL
OPEN(2, FILE=LTRLFIL, STATUS='NEW')
WRITE(*,'(A)') CREATING THE A MATRIX...
D=1/DY
DO 180 I=1,NY+1
  XI1=(DBLE(I)-1.)*DY/A/(1.0-(DBLE(I)-1.)*DY)+RB
  XI=DBLE(I)*DY/A/(1.-DBLE(I)*DY)+RB
  DXI=XI-XI1
  IF(((I/10)*10) .EQ. I) WRITE(*,999) I
  DO 100 J=1,NY+1
    IF (I .GT. J) AL(I,J)=0.0
    IF (I .GT. J) GOTO 100
    RJ=DBLE(J)*D W/A/(1.-DBLE(J)*DW)+RB
    B=XI/RJ
    B1=B*DSQRT(1-B*B)
    IF(I .EQ. J) THEN
      AL(I,J)=(RDT/10000.)*RJ*RJ*(DACOS(B)-B1)/2/DXI
      ELSEIF (I .LT. J) THEN
        C=XI/RJ
        C1=C*DSQRT(1-C*C)
        RJ1=(DBLE(J)-1.)*DW/A/(1.-DBLE(J)-1.)*DW)+RB
        D=XI/RJ1
        D1=D*DSQRT(1-D*D)
        E=XI/RJ1
        E1=E*DSQRT(1-E*E)
        P=DACOS(B)-DACOS(C)-B1+C1
        Q=DACOS(D)-DACOS(E)-D1+E1
        AL(I,J)=(RDT/10000.)*(RJ*RJ*P/2-RJ1*RJ1*Q/2)/DXI
      ENDIF
    ENDIF
  ENDF
ENDIF
100 CONTINUE
180 CONTINUE
DO 260 I=0,NY
   Z(I)=0.0
   DO 250 J=I,NY
      Z(I)=Z(I)+CB(J)*AL(I+1,J+1)
   250 CONTINUE
   Z(I)=2*Z(I)*CONCENT*G
260 CONTINUE
   DO 262 I=0,NR
      WRITE(2,*)(DBLE(I), 0.0)
   262 CONTINUE
   DO 264 J=0, NY
      WRITE(2,*)(Rr(J), Z(J))
   264 CONTINUE
GOTO 1000
END
C
**** SUBROUTINE ****
C
SUBROUTINE CRANK(CB, A1, A2, BB, AD, BDB, CBO, F, N)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION CB(151), BB(151), A1(151), A2(151), F(151)
DIMENSION AD(151), BDB(151)
C
DIMENSION CA(151), BDA(151), BA(151)
C
CA0=CA0
CBO=CB0
C
CA1=CA0
CB1=CB0
C
CA2=CA(1)
CB2=CB(1)
DO 30 J=1, N
   CA3=CA(J+1)
   CB3=CB(J+1)
   BA(J)=CA1+F(J)*CA2-A2(J)*CA3
   BB(J)=CB1+F(J)*CB2-A2(J)*CB3
   CA1=CA2
   CB1=CB2
   CA2=CA3
   CB2=CB3
30 CONTINUE
AD(1)=A2(1)/A1(1)
C
BDA(1)=(BA(1)-CADO)/A1(1)
BDB(1)=(BB(1)-CBD0)/A1(1)
DO 40 J=2, N
   AD(J)=A2(J)/(A1(J)-AD(J-1))
   BDA(J)=(BA(J)-BDA(J-1))/(A1(J)-AD(J-1))
   BDB(J)=(BB(J)-BDB(J-1))/(A1(J)-AD(J-1))
40 CONTINUE
DO 50 I=N,1,-1
C  C A (I)-B D A (I)-A D (I)*C A (I+1)

C B (I)-B D B (I)-A D (I)*C B (I+1)

50 CONTINUE

RETURN

EN D
**PROGRM7.FOR**

* THIS PROGRAM SIMULATES A CHARGE TRANSFER REACTION *
* EQUILIBRIUM BETWEEN CPZ CATION RADICAL AND METHOXY-
* PROMAZINE (MPZ) INITIATED ELECTROCHEMICALLY AT A *
* MICROCYLINDER ELECTRODE. FIRST, DIFFUSION IS CARRIED *
* OUT AS USUAL AT CYLINDRICAL GEOMETRY. EQUILIBRIUM IS *
* CALCULATED BASED ON THE CONCENTRATIONS IN EACH BOX. *
* FINALLY, CONCENTRATIONS ARE CORRECTED BY THE AMOUNT *
* CALCULATED FROM EQUILIBRIUM TO ACCOUNT FOR THE *
* REACTION BETWEEN CPZ CATION RADICAL AND MPZ. *
* *
* THE DIFFUSION PART USES FINITE DIFFERENCES METHOD. *
* VARIABLES DEFINED ARE SIMILAR TO THOSE IN PROGRM1.FOR *
* EXCEPT FOR THE EQUILIBRIUM CONSTANT KEQ. 8 ARRAYS, *
* HOWEVER, TWO FOR EACH SPECIES ARE USED. *

**REAL*4 KEQ**
DIMENSION FANEW(700),FBNEW(700),FAOLD(700),FBOLD(700)
DIMENSION FCNEW(700),FCOLD(700),FDNEW(700),FDOLD(700)
CHARACTER*64 FILA,FILC

***** GET INFORMATION FROM KEYBOARD *****

WRITE(*,'(/A \)') ' ENTER A,B PROFILE STORAGE FILE NAME - ' WRITE(*,11)FILA
11 FORMAT(A)
WRITE(*,'(/A \)') ' ENTER C,D PROFILE STORAGE NAME - ' WRITE(*,20)
20 FORMAT( ' ENTER RO(CM), D, T(SEC), BETA, L, AND KEQ - \)
READ(*,*)RO,D,T,BETA,L,KEQ
OPEN(3,FILE=FILA,STATUS='NEW')
OPEN(4,FILE=FILC,STATUS='NEW')

***** INITIAL CONDITIONS *****

DM = 0.45
Z=R0*SQRT(DM*REAL(L))/SQRT(D*T)
DO 30 I=1,700
   FANEW(I) = 1.0
   DO 30 J=1,700
      FANEW(I+J) = 1.0
30 CONTINUE

...
FAOLD(I) = 1.0
FBNEW(I) = 0.0
FBOLD(I) = 0.0
FCNEW(I) = BETA
FCOLD(I) = BETA
FDNEW(I) = 0.0
FDOLD(I) = 0.0

30 CONTINUE

C  DIFFUSION BEYOND FIRST BOX
C
K = 0
1000 K = K + 1
JMAX = 4.2*SQRT(REAL(K))
DO 40 I=1,JMAX
    M = I + 1
    N = I - 1
    ZI = REAL(I)
    X = 1. + 1./ZI
    Y = 2. + 1./ZI
    FANEW(I) = FAOLD(I) + DM*(X*FAOLD(M) - Y*FAOLD(I) + FAOLD(N))
    FBNEW(I) = FBOLD(I) + DM*(X*FBOLD(M) - Y*FBOLD(I) + FBOLD(N))
    FCNEW(I) = FCOLD(I) + DM*(X*FCOLD(M) - Y*FCOLD(I) + FCOLD(N))
    FDNEW(I) = FDOLD(I) + DM*(X*FDOLD(M) - Y*FDOLD(I) + FDOLD(N))
40 CONTINUE

C  ********** DIFFUSION IN FIRST BOX *******
C
FANEW(1) = FAOLD(1) + DM*((1.+1./Z)*FAOLD(2) - (1.+1./Z)*FAOLD(1))
FBNEW(1) = FBOLD(1) + DM*((1.+1./Z)*FBOLD(2) - (1.+1./Z)*FBOLD(1))
FCNEW(1) = FCOLD(1) + DM*((1.+1./Z)*FCOLD(2) - (1.+1./Z)*FCOLD(1))
FDNEW(1) = FDOLD(1) + DM*((1.+1./Z)*FDOLD(2) - (1.+1./Z)*FDOLD(1))

C  HOMOGENEOUS KINETICS

DO 50 J=1,JMAX
    A1 = FANEW(J)
    B1 = FBNEW(J)
    C1 = FCNEW(J)
    D1 = FDNEW(J)
    E = 1E-6
    IF (A1.LT.E .AND. B1.LT.E .AND. C1.LT.E .AND. D1.LT.E) GO TO 55
    RT1 = 0.0
    A = 1-KEQ
    B = FDNEW(J) + FANEW(J) + KEQ*FCNEW(J) + KEQ*FBNEW(J)
    C = FANEW(J) * FDNEW(J) - KEQ*FBNEW(J)*FCNEW(J)
50 CONTINUE

C  Z2 = B**2-4*A*C
    Z1 = SQRT(Z2)
    RTA = (-1*B +Z1)/(2*A)
    RTB = (-1*B- Z1)/(2*A)
IF (RTA .LT. 0 .AND. RTB .LT. 0) THEN
   WRITE(*,'(/A')' EQUILIBRIUM HAS NO SOLUTION!' STOP
ENDIF
IF (RTA .LT. 0) RT1=RTB
IF (RTB .LT. 0) RT1=RTA
IF (RTA .GT. 0 .AND. RTB .GT. 0) THEN
   IF (RTA .GT. RTB) THEN
      RT1=RTB
   ELSEIF (RTA .LT. RTB) THEN
      RT1=RTA
   ENDIF
ENDIF
FDNEW(J) = FDNEW(J) + RT1
FBNEW(J) = FBNEW(J) - RT1
FCNEW(J) = FCNEW(J) - RT1
FANEW(J) = FANEW(J) + RT1
50 CONTINUE
C
C ******* PARADAIC CONVERSION *******
C
FBNEW(1) = FANEW(1) + FBNEW(1)
FANEW(1) = 0.0
FDNEW(1) = FDNEW(1) + FCNEW(1)
FCNEW(1) = 0.0
C
C ******* SET UP ARRAYS FOR NEXT ITERATION *******
C
DO 60 I=1,JMAX
   FAOLD(I)=FANEW(I)
   FBOLD(I)=FBNEW(I)
   FCOLD(I)=FCNEW(I)
   FDOLD(I)=FDNEW(I)
60 CONTINUE
C
RETURN FOR NEXT ITERATION
C
IF ((K/20)*20 .EQ. K) WRITE(*,*)K
IF (K .LT. L) GOTO 1000
C
C ******* STORE DATA TO DISK FILES *******
C
DO 70 I = 1,JMAX
   X = (I-1)/SQRT(DM*REAL(L))
   WRITE(3,*)X,FANEW(I),FBNEW(I)
   WRITE(4,*)X,FCNEW(I),FDNEW(I)
70 CONTINUE
STOP
END
THIS PROGRAM SIMULATES A CHARGE TRANSFER REACTION
EQUILIBRIUM BETWEEN CPZ CATION RADICAL AND DOPAMINE
(DA) INITIATED ELECTROCHEMICALLY AT A MICROCYLINDER ELECTRODE. FIRST, DIFFUSION IS CARRIED OUT AS USUAL AT CYLINDRICAL GEOMETRY. EQUILIBRIUM IS THEN CALCULATED BASED ON THE CONCENTRATIONS IN EACH BOX. FINALLY, CONCENTRATIONS ARE CORRECTED BY THE AMOUNT CALCULATED FROM EQUILIBRIUM TO ACCOUNT FOR THE REACTION BETWEEN CPZ CATION RADICAL AND DOPAMINE. SINCE THE REACTION IS A TWO ELECTRONS TRANSFER, THE EQUILIBRIUM PROBLEM RESULTS IN A CUBIC EQUATION WHICH IS SOLVED BY THE NEWTON-RAPHSON'S NUMERICAL METHOD.

THE DIFFUSION PART USES FINITE DIFFERENCES METHOD. VARIABLES DEFINED ARE THE SAME AS IN PROGRM7.FOR.

REAL*4 KEQ
DIMENSION FANEW(700),FBNEW(700),FAOLD(700),FBOLD(700)
DIMENSION FCNEW(700),FCOLD(700),FDNEW(700),FDOLD(700)
CHARACTER*64 FILA,FILC

****** GET INFORMATION FROM KEYBOARD *******

WRITE(*,10)
10 FORMAT( ' ENTER A,B PROFILE STORAGE FILE NAME - ' )
READ(*,11)FILA
11 FORMAT(A)
WRITE(*,'(/A\)') ENTER C,D PROFILE STORAGE NAME -
READ(*,11)FILC
WRITE(*,'(/A\)') ENTER RO(CM), D, T(SEC), BETA, L, AND KEQ -
READ(*,*)RO,D,T,BETA,L,KEQ
OPEN(3,FILE=FILA,STATUS= 'NEW')
OPEN(4,FILE=FILC,STATUS= 'NEW')

****** INITIAL CONDITIONS *******

DM = 0.45
Z=RO*SQRT(DM*REAL(L))/SQRT(D*T)
DO 30 1=1,700
    FANEW(I) = 1.0
FAOLD(I) = 1.0
FBNEW(I) = 0.0
FBOLD(I) = 0.0
FCNEW(I) = BETA
FCOLD(I) = BETA
FDNEW(I) = 0.0
FDOLD(I) = 0.0

30
C
C ******* DIFFUSION BEYOND FIRST BOX *******
C
WRITE(*,'(/A)')' START LOOPPING ......'
K = 0
1000 K = K + 1
JMAX = 4.2*SQRT(REAL(K))
DO 50 I=1,JMAX
   M = I+1
   N = I-1
   ZI = REAL(I)
   X = 1. + 1.0/(ZI + Z)
   Y = 2. + 1.0/(ZI + Z)
   FANEW(I)=FAOLD(I)+DM*(X*FAOLD(M)-Y*FAOLD(I)+FAOLD(N))
   FBNEW(I)=FBOLD(I)+DM*(X*FBOLD(M)-Y*FBOLD(I)+FBOLD(N))
   FCNEW(I)=FCOLD(I)+DM*(X*FCOLD(M)-Y*FCOLD(I)+FCOLD(N))
   FDNEW(I)=FDOLD(I)+DM*(X*FDOLD(M)-Y*FDOLD(I)+FDOLD(N))
50 CONTINUE
C
C ******* DIFFUSION IN FIRST BOX *******
C
   X = 1. + 1.0/Z
   FANEW(1)=FAOLD(1)+DM*(X*FAOLD(2)-X*FAOLD(1))
   FBNEW(1)=FBOLD(1)+DM*(X*FBOLD(2)-X*FBOLD(1))
   FCNEW(1)=FCOLD(1)+DM*(X*FCOLD(2)-X*FCOLD(1))
   FDNEW(1)=FDOLD(1)+DM*(X*FDOLD(2)-X*FDOLD(1))
C
C ******* HOMOGENEOUS KINETICS *******
C
DO 55 J=2,JMAX
   CPZ= FANEW(J)
   CPR= FBNEW(J)
   DA = FCNEW(J)
   DOQ = FDNEW(J)
C
C  PICK STARTING GUESS
C
   XO = CPZ
   IF (CPR .LT. XO) XO = CPR
   IF (DA .LT. XO) XO = DA
   IF (DOQ .LT. XO) XO = DOQ
C
C  CALL NEWTON - RAPHSON SUBROUTINE
C
**XSOLN = 0.0**

CALL NEWTON(CPR, DA, CPZ, DOQ, KEQ, XO, XSOLN)

C

******* CORRECT CONCENTRATIONS IN BOX J TO REFLECT EQUILIBRIUM
C

FBNEW(J) = FBNEW(J) - XSOLN
FCNEW(J) = FCNEW(J) - 0.5*XSOLN
FANEW(J) = FANEW(J) + XSOLN
FDNEW(J) = FDNEW(J) + 0.5*XSOLN

C

IF (FANEW(J) .LT. 1E-7) FANEW(J) = 0.0
IF (FBNEW(J) .LT. 1E-7) FBNEW(J) = 0.0
IF (FCNEW(J) .LT. 1E-7) FCNEW(J) = 0.0
IF (FDNEW(J) .LT. 1E-7) FDNEW(J) = 0.0

CONTINUE

******* FARADAIC CONVERSION *******
C

FBNEW(1) = FANEW(1) + FBNEW(1)
FANEW(1) = 0.0
FDNEW(1) = FDNEW(1) + FCNEW(1)
FCNEW(1) = 0.0

******* SET UP ARRAYS FOR NEXT ITERATION *******
C

DO 60 I=1, JMAX
FAOLD(I) = FANEW(I)
FBOLD(I) = FBNEW(I)
FCOLD(I) = FCNEW(I)
FDOLD(I) = FDNEW(I)

CONTINUE

RETURN FOR NEXT ITERATION
C

IF((K/20)*20 .EQ. K) WRITE(*,*) K
IF(K .LT. L) GOTO 1000

******* STORE DATA TO DISK FILES *******
C

DO 70 I = 1, JMAX
X = (I-1.)/SQRT(DM*REAL(L))
WRITE(3,*) X, FANEW(I), FBNEW(I)
WRITE(4,*) X, FCNEW(I), FDNEW(I)

CONTINUE
STOP
END

C

SUBROUTINE NEWTON(CPR, DA, CPZ, DOQ, KEQ, XO, XSOLN)
REAL KEQ, A1, B1, C1, D1, APRIME, BPRIME, CPRIME, F, FPRIME
ERR = 1E-6
A1 = 0.5 * KEQ + 0.5
B1 = -KEQ * CPR - KEQ*DA + CPZ + DOQ
C1 = 2*CPZ*DOQ + 0.5*(CPZ**2) + 2*DA*CPR*KEQ + 0.5*KEQ*(CPR**2)
D1 = (CPZ**2)*DOQ - KEQ*(CPR**2)*DA
APRIME = A1*3
BPRIME = B1*2
CPRIME = C1

C
10 F = A1*(X0)**3 + B1*(X0)**2 + C1*X0 + D1
FPRIME = APRIME*(X0)*(X0) + BPRIME*(X0) + CPRIME
XSO1N = X0 - F/FPRIME
DIFF = X0 - XSOLN
IF (ABS(DIFF) .LE. ERR) THEN
    GOTO 50
ELSEIF (ABS(DIFF) .GT. ERR) THEN
    X0 = XSOLN
ENDIF
GOTO 10

C
20 WRITE(*,20)
20 FORMAT (‘ERROR IN NEWTON LOGIC’)
**PROGRM9.FOR**

```fortran
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
* THIS PROGRAM SIMULATES RADIAL DIFFUSION AT A MICRO-
* CYLINDER ELECTRODE WITH A CHARGE TRANSFER KINETICS *
* BETWEEN CPZ AND DA, USING THE FINITE DIFFERENCES METHOD *
* THE DIFFUSION PART IS THE SAME AS THAT IN PROGRM8.FOR *
* WHILE THE REACTION IS GOVERNED BY A STEP-WISE REACTION *
* MECHANISM. VARIABLES USED ARE DEFINED AS BELOW: *

C

* KTC3 = k_3 \cdot \text{CPZ}, KTC4 = k_4 \cdot \text{CPZ} *

REAL*4 KTC3, KTC4, KTL3, KTL4,
DIMENSION FANEW(700), FBNEW(700), FAOLD(700), FBOLD(700),
DIMENSION FCNEW(1000), FCOLD(700), FDNEW(700), FDOLD(700)
CHARACTER*64 FILA, FILC

C

****** GET INFORMATION FROM KEYBOARD ******

WRITE(*, '(A)') ' ENTER A,B PROFILE STORAGE FILE NAME - '
READ(*, 11) FILA
11 FORMAT(A)
WRITE(*, '(A)') ' ENTER C,D PROFILE STORAGE NAME - '
READ(*, 11) FILC
WRITE(*, '(A)') ' ENTER KTC3, KTC-4, OMEGA, BETA - '
READ(*, *) KTC3, KTC4, OMEGA, BETA
WRITE(*, '(A)') ' ENTER RO(CM), D, T(SEC), L, AND KEQ - '
READ(*, *) RO, D, T, L, KEQ

OPEN(3, FILE=FILA, STATUS='NEW')
OPEN(4, FILE=FILC, STATUS='NEW')

****** INITIAL CONDITIONS ******

DM = 0.45
Z = RO*((DM*Q)**0.5/(D*T)**0.5)
KTL3 = KTC3/Q
KTL4 = KTC4/Q
DO 30 I=1,700
  FANEW(I) = 1.0
  FAOLD(I) = 1.0
  FBNEW(I) = 0.0
  FBOLD(I) = 0.0
30 CONTINUE
```


FDNEW(I) = 0.0
FDOLD(I) = 0.0

****** DIFFUSION BEYOND FIRST BOX ******

K = 0
K = K + 1
WRITE(*,'(/A)') 'START LOOPING .......
JMAX = 4.2*(K)**0.5
DO 50 I=1,JMAX
   M = I+1
   N = I - 1
   ZI = REAL(I)
   X = 1. + 1./ZI
   Y = 2. + 1./ZI
   FANEW(I) = FAOLD(I) + DM*(X*FAOLD(M) - Y*FAOLD(I) + FAOLD(N))
   FBN EW(I) = F B O LD ( I ) + DM *( X * F B O LD ( M ) - Y * F B O LD ( I ) + F B O LD ( N ) )
   FCNEW(I) = FCOLD(I) + DM*(X*FCOLD(M) - Y*FCOLD(I) + FCOLD(N))
   FDNEW(I) = FDOLD(I) + DM*(X*FDOLD(M) - Y*FDOLD(I) + FDOLD(N))
END

DIFFUSION IN FIRST BOX

X = 1. + 1./Z
FANEW(1) = FAOLD(1) + DM*(X*FAOLD(2) - X*FAOLD(1))
FBN EW(1) = FBOLD(1) + DM*(X*FBOLD(2) - X*FBOLD(1))
FCNEW(1) = FCOLD(1) + DM*(X*FCOLD(2) - X*FCOLD(1))
FDNEW(1) = FDOLD(1) + DM*(X*FDOLD(2) - X*FDOLD(1))

DO 55 J=2,JMAX

HOMOGENEOUS KINETICS

D1 = 2*KTL3*OMEGA*FCNEW(J)*FBNEW(J)**2
D2 = 2*KTL4*FDNEW(J)*FANEW(J)**2
D3 = FANEW(J) + OMEGA*FBNEW(J)
DK = (D1 - D2)/D3

FBNEW(J) = FBNEW(J) + DK
FCNEW(J) = FCNEW(J) - 0.5*DK
FANEW(J) = FANEW(J) + DK
FDNEW(J) = FDNEW(J) + 0.5*DK

IF (FANEW(J) .LT. 1E-6) FANEW(J) = 0.0
IF (FBNEW(J) .LT. 1E-6) FBNEW(J) = 0.0
IF (FCNEW(J) .LT. 1E-6) FCNEW(J) = 0.0
IF (FDNEW(J) .LT. 1E-6) FDNEW(J) = 0.0

CONTINUE

55 CONTINUE
FARADAIC CONVERSION

FBNEW(1) = FANEW(1) + FBN(1)
FANEW(1) = 0.0
FDNEW(1) = FDNEW(1) + FCNEW(1)
FCNEW(1) = 0.0

****** SET UP ARRAYS FOR NEXT ITERATION ******

DO 60 I = 1, JMAX
   FAOLD(I) = FANEW(I)
   FBOLD(I) = FBN(1)
   FCOLD(I) = FCNEW(I)
   FDOLD(I) = FDNEW(I)
60

****** RETURN FOR NEXT ITERATION ******

IF((K/20)*20 .EQ. K) WRITE(*,*) K
IF(K .LT. L) GOTO 1000

****** STORE DATA TO DISK FILES ******

DO 70 I = 1, JMAX
   X = (I-1)/(DH*REAL(L))**0.5
   WRITE(3,71)X, FANEW(I), FBN(1)
   WRITE(4,69)X, FCNEW(I), FDNEW(I)
70   CONTINUE
STOP
END
**PROGRM10.FOR**

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

* THIS PROGRAM SIMULATES RADIAL DIFFUSION AT A MICRO-
* CYLINDER ELECTRODE WITH A CHARGE TRANSFER EQUILIBRIUM *
* AND KINETICS BETWEEN CPZ AND DA, USING A METHOD OF *
* FINITE DIFFERENCES. THE DIFFUSION PART IS THE SAME AS *
* THAT IN PROGRM8.FOR, WHILE THE REACTION IS A *
* COMBINATION OF THOSE IN PROGRM8.FOR AND PROGRM9.FOR. *
* *

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

REAL*4 KTC3, KTC4, KTL3, KTL4, KEQ
DIMENSION FANEW(700), FBNEW(700), FAOLD(700), FBOLD(700),
DIMENSION FCNEW(1000), FCOLD(700), FDNEW(700), FDOLD(700)
CHARACTER*64 FILA, FILC

****** GET INFORMATION FROM KEYBOARD ******

WRITE(*,'(A)') 'ENTER A,B PROFILE STORAGE FILE NAME - ' READ(*,11)FILA
11 FORMAT(A)
WRITE(*,'(A)') 'ENTER C,D PROFILE STORAGE NAME - ' READ(*,11)FILC
WRITE(*,'(A)') 'ENTER KTC3, KTC-4, OMEGA, BETA - ' READ(*,*), KTC3, KTC4, OMEGA, BETA
WRITE(*,'(A)') 'ENTER RO(CM), D, T(SEC), L, AND KEQ - ' READ(*,*), RO, D, T, L, KEQ

OPEN(3, FILE=FILA, STATUS='NEW')
OPEN(4, FILE=FILC, STATUS='NEW')

****** INITIAL CONDITIONS ******

DM = 0.45
Z=RO*((DM*Q)**0.5/(D*T)**0.5)
KTL3 = KTC3/Q
KTL4 = KTC4/Q
DO 30 I=1,1700
  FANEW(I) = 1.0
  FAOLD(I) = 1.0
  FBNEW(I) = 0.0
  FBOLD(I) = 0.0
  FCNEW(I) = BETA
  FCOLD(I) = BETA

30 CONTINUE
FDNEW(I) = 0.0
FDOLD(I) = 0.0

****** DIFFUSION BEYOND FIRST BOX ******

K = 0
K = K + 1
WRITE(*,'(/A)')' START LOOPING ......'
JMAX = 4.2*(K)**0.5
DO 50 I=1,JMAX
   M = I+1
   N = I - 1
   ZI =REAL(I)
   X = 1. + 1./ZI
   Y = 2. + 1./ZI
   FANEW(I)=FA0LD(I)+DM*(X*FA0LD(M)-Y*FA0LD(I)+FA0LD(N))
   FBNEW(I)=FBOLD(I)+DM*(X*FBOLD(M)-Y*FBOLD(I)+FBOLD(N))
   FCNEW(I)=FCOLD(I)+DM*(X*FCOLD(M)-Y*FCOLD(I)+FCOLD(N))
   FDNEW(I)=FDOLD(I)+DM*(X*FDOLD(M)-Y*FDOLD(I)+FDOLD(N))
   CONTINUE
50 CONTINUE

DIFFUSION IN FIRST BOX

   X = 1. + 1./Z
   FANEW(1)=FA0LD(1)+DM*(X*FA0LD(2)-X*FA0LD(1))
   FBNEW(1)=FBOLD(1)+DM*(X*FBOLD(2)-X*FBOLD(1))
   FCNEW(1)=FCOLD(1)+DM*(X*FCOLD(2)-X*FCOLD(1))
   FDNEW(1)=FDOLD(1)+DM*(X*FDOLD(2)-X*FDOLD(1))

HOMOGENEOUS KINETICS

   D1 = 2*KTL3*OMEGA*FCNEW(J)*FBNEW(J)**2
   D2 = 2*KTL4*FDNEW(J)*FANEW(J)**2
   D3 = FANEW(J) + OMEGA*FBNEW(J)
   DK = (D1 - D2)/D3

HOMOGENEOUS EQUILIBRIUM

   CPZ = FANEW(J)
   CPR = FBNEW(J)
   DA = FCNEW(J)
   DOQ = FDNEW(J)

PICK STARTING GUESS

   XO = CPZ
   IF (CPR .LT. XO) THEN
      XO = CPR
   ENDIF
IF (DA .LT. XO) THEN
   XO = DA
ENDIF
IF (DOQ .LT. XO) THEN
   XO = DOQ
ENDIF

CALL NEWTON - RAPHSON SUBROUTINE

XSOLN = 0.0
CALL NEWTON(CPR, DA, CPZ, DOQ, KEQ, XO, XSOLN)

C  CORRECT CONCENTRATIONS IN BOX J TO REFLECT EQUILIBRIUM

DE = XSOLN
IF (DK .LT. DE) THEN
   DD = DK
ELSEIF (DE .LT. DK) THEN
   DD = DE
ENDIF
FBNEW(J) = FBNEW(J) - DD
FCNEW(J) = FCNEW(J) - 0.5 * DD
FANEW(J) = FANEW(J) + DD
FDNEW(J) = FDNEW(J) + 0.5 * DD
IF (FANEW(J) .LT. 1E-6) FANEW(J) = 0.0
IF (FBNEW(J) .LT. 1E-6) FBNEW(J) = 0.0
IF (FCNEW(J) .LT. 1E-6) FCNEW(J) = 0.0
IF (FDNEW(J) .LT. 1E-6) FDNEW(J) = 0.0

55 CONTINUE

C  FARADAIC CONVERSION

FBNEW(1) = FANEW(1) + FBNEW(1)
FANEW(1) = 0.0
FDNEW(1) = FDNEW(1) + FCNEW(1)
FCNEW(1) = 0.0

C  ******* SET UP ARRAYS FOR NEXT ITERATION *******

C  DO 60 I=1,JMAX
     FAOLD(I) = FANEW(I)
     FBOLD(I) = FBNEW(I)
     FCOLD(I) = FCNEW(I)
     FDOLD(I) = FDNEW(I)
 60

C  ******* RETURN FOR NEXT ITERATION *******

C  IF((K/20)*20 .EQ. K) WRITE(*,*) K
  IF(K .LT. L) GOTO 1000
**STORE DATA TO DISK FILES**

DO 70 I = 1, JMAX
   X = (I-1)/(DM*REAL(L))**0.5
   WRITE(3,71)X,FANEW(I),FBNEW(I)
   WRITE(4,69)X,FCNEW(I),FDNEW(I)
69   FORMAT(3(2X,F8.6))
70 CONTINUE
STOP
END

SUBROUTINE NEWTON(CFR, DA, CPZ, DOQ, KEQ, XO, XSOLN)

REAL KEQ, A1, B1, C1, D1, APRIME, BPRIME, CPRIME, F, FPRIME

ERR = 1E-6

A1 = 0.5 * KEQ + 0.5
B1 = -KEQ * (CPZ + DA) + CPZ + DOQ
C1 = 2*CPZ*DOQ+0.5*CPZ*CPZ+(2*DA*CFR+0.5*CFR*CFR)*KEQ
D1 = CPZ*CPZ*DOQ-KEQ*CFR*CFR*DA

APRIME = A1*3
BPRIME = B1*2
CPRIME = C1

NEWTON'S FUNCTIONAL ITERATION

NCOUNT = 0
10   F = A1*(X0)**3 + B1*(X0)**2 + C1*X0 + D1
    FPRIME = APRIME*(X0)**2 + BPRIME*(X0) + CPRIME
    XSOLN = X0 - F/FPRIME
    DIFF = X0 - XSOLN

IF (ABS(DIFF) .LE. ERR) THEN
   GOTO 50
ELSEIF (ABS(DIFF) .GT. ERR) THEN
   X0 = XSOLN
ENDIF
NCOUNT = NCOUNT +1
IF (NCOUNT .EQ. 50) THEN GOTO 15
GOTO 10
15 WRITE(*,'(/A\)')' ERROR IN NEWTON LOGIC'
50 CONTINUE
RETURN
END
* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

* THIS PROGRAM IS DESIGNED TO EXTRACT A ROW OR A COLUMN OF DATA FROM A TWO-DIMENSIONAL IMAGE FILE AND STORE IT INTO A DISK FOR FURTHER PROCESSING. VARIABLES ARE DEFINED AS FOLLOWS:

* * CD FORMAT, COL AND ROW -- THE ACTUAL NUMBER OF COLUMNS AND ROWS IN THE IMAGE FORMATTED WHEN THE IMAGE WAS TAKEN.
* IREAD -- THE ADDRESS FOR DIRECT ACCESS TO THE FILE.
* N -- NUMBER OF COUNTS IN EACH PIXEL ELEMENT.
* N1 -- THE SAME NUMBER AS N, BUT HAS ROTATED BY 8 BITS TO CONVERT A BINARY TO A DECIMAL NUMBER.
* REVISED 2/8/90

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

INTEGER*2 N,N1
CHARACTER*16 FILE1,FILE2

OPEN(1, FILE=' ',ACCESS='DIRECT',STATUS='OLD',RECL=2)
OPEN(2, FILE=' ', STATUS='NEW')

WRITE(*, '(A)') ' EXTRACT COLUMN(1), ROW(2) DATA: '
READ (*,*) K
WRITE(*, '(A)') ' ENTER CCD FORMAT, COL AND ROW: '
READ(*,*) COL,ROW
WRITE(*, '(A)') ' ENTER COLUMN, OR ROW NUMBER, L= '
READ (*,*) L

IF (K .EQ. 1) THEN
    M=ROW
ELSEIF (K .EQ. 2) THEN
    M=COL
ENDIF

DO 25 I= 1, M
    IF (K .EQ. 1) THEN
        IREAD = 80 + (I-1)*ROW + L
    ELSEIF (K .EQ. 2) THEN
        IREAD = 80 + L*COL + I
    ENDIF

25 CONTINUE
READ (1,REC=IREAD) N
N1=ISHG(N,8)
WRITE (2,*) I, N1
CONTINUE
STOP
END
**PROGRM12.FOR**

```fortran
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C THIS PROGRAM IS DESIGNED FOR EXTRACTING TWO 2-D PROFILES
C AND CONSTRUCTING A ABSORBANCE PROFILE FROM THE TWO ORIGINAL
C PROFILES. VARIABLES ARE DEFINED AS FOLLOWS:
C *
C *
C CCD FORMAT, COL AND ROW -- THE ACTUAL NUMBER OF COLUMNS AND
C ROWS AS DEFINED IN THE CCD FORMAT.
C *
C *
C STARTING COLUMN AND ROW NUMBER -- COLUMN AND ROW NUMBER AT
C WHICH DATA ARE STARTED TO BE EXTRACTED.
C *
C *
C DATA RANGE AND RESOLUTION -- THE TOTAL NUMBER OF COLUMNS OR
C ROWS TO BE EXTRACTED, AND THE NUMBER OF COLUMNS OR ROWS BY
C WHICH DATA POINTS ARE SEPARATED.
C *
C *
C REVISED 2/8/90
C *
C *
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
C INTEGER*2 N,N1.
C INTEGER*4 COL, ROW, SCOL, SROW
C DIMENSION MA(258,258),MB(258,258),IR(258),JR(258)

OPEN(1, FILE=", ACCESS='DIRECT', STATUS='OLD', RECL=2)
OPEN(2, FILE=", ACCESS='DIRECT', STATUS='OLD', RECL=2)
OPEN(3, FILE=", STATUS='NEW'")

WRITE(*,'(/A\")')' ENTER CCD FORMAT, COL AND ROW: '
READ(*,*) COL,ROW
WRITE(*,'(/A\")')' ENTER STARTING COLUMN AND ROW NUMBER: '
READ(*,*) SCOL, SROW
WRITE(*,'(/A\")')' ENTER DATA RANGE, AND RESOLUTION: '
READ (*,*) M, K

II=0
DO 25 I=SROW, M+SROW,K
   II=II+1
   J1=0
   IR(II)=I
   DO 25 J=SCOL, M+SCOL, K
      J1=J1+1
      JR(J1)=J
      IREAD = 80 + I*COL + J
   25 CONTINUE
```

```
READ (1,REC=IREAD) N
N1=ISHG(N,8)
MA(I1,J1)=N1

25 CONTINUE

C
I1=0
DO 30 I= SROW, M+SROW, K
   I1=I1 +1
   J1=0
   IR(I1)=I
   DO 30 J=SCOL, M+SCOL, K
      J1=J1+1
      JR(J1)=J
      IREAD = 80 + I*COL + J
      READ (2,REC=IREAD) N
      N1=ISHG(N,8)
      MB(I1,J1)=N1
   30 CONTINUE

C
IMAX=I1
JMAX=J1
DO 40 I=1,IMAX
   DO 40 J=1,JMAX
      A=MA(I,J)
      B=MB(I,J)
      ABS=LOG10(A/B)
      ABS=LOG10(A/(B+A))
      WRITE(3,9) IR(I), JR(J), ABS
   40 CONTINUE

9 FORMAT(I4,I4,F10.7)

40 CONTINUE
STOP
END
**PROGRM13.FOR**

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

C  * *
C  * THIS PROGRAM READS IN POINTS OF A 3-D FILE, CONNECTS *
C  * THE NEIGHBORING POINTS FOR PLOTTING A 3-D PROFILE. *
C  * VARIABLES USED ARE DEFINED AS FOLLOWS: *
C  * *
C  * 
C  * # PTS - DATA RANGE/RESOLUTION + 1 *
C  * (DATA RANGE AND RESOLUTION ARE DEFINED IN PROGRM12.FOR) *
C  * CX, CY -- CENTER COORDINATES IN THE PROFILE. *
C  * X, Y, Z -- ARE ROW, COLUMN AND ABSORBANCE. *
C  * MZ -- MULTIPLIER(ABOUT 1000) OF Z COORDINATE. *
C  * *
C  * IN ORDER TO SAVE CPU (VAX) TIME, THE FILE TO BE READ *
C  * HAS TO BE NAMED AFTER FOR001.FOR, AND THE FLIE *
C  * GENERATED WILL BE STORED IN FOR002.FOR IN THE VAX *
C  * SYSTEM. *
C  * *
C  * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

INTEGER CONM1, CONP1, CONMN1, CONNP

TYPE 1

1 FORMAT( ' ENTER #PTS, Z-MULTIPLIER, CX, AND CY: ') READ (5,2) NP, MZ, CX, CY

2 FORMAT (I4)

I = 1

99 READ (1,3,END = 999) IX, IY, Z

3 FORMAT (2$I4,F10.7)

X = IX - CX

Y = IY - CY

Z = M2*Z

IF (2 .LT. 0.0) Z = 0.0

TP = NP * NP

N = I/NP

IPL = 1 + N* NP

CONM1 = I - 1

IF (I .EQ. IPL) CONM1 = 0

CONP1 = I + 1

IF (I .EQ. (N*NP)) CONP1 = 0

CONMN1 = I - NP

IF (CONMN1 .GT. TP) CONMN1 = 0

WRITE(2,4) X, Y, Z, CONM1, CONP1, CONMN1, CONNP

4 FORMAT( 'C',F10.4, 4I6)

I = I + 1
GO TO 99
STOP
END