**Educator's Reference Guide
for Electrochemistry**

**from
Pine Instrument Company
Grove City, Pennsylvania**

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Introduction

Of the three main divisions of analytical chemistry–spectroscopy, chromatography, and electrochemistry–the latter generally receives the least attention in an undergraduate instrumental analysis course, in both the lecture and the laboratory. In many cases, undergraduate students complete their degree without ever having a "hands-on" experience with a modern electroanalytical instrument. This text is an effort to correct this situation by making it as easy as possible for the analytical chemistry instructor to include modern electrochemistry in the instrumental analysis laboratory.

The instructor, faced with a bewildering number of instrumental methods, can perhaps be forgiven for emphasizing the more popular spectroscopic and chromatographic techniques over the less familiar electrochemical methods. Personal undergraduate experience may also cause the instructor to shy away from electrochemistry–perhaps a distant recollection of an old-fashioned polarograph and a clumsy dropping mercury electrode make today's cuvets and columns look much more attractive. But with a little persistence, the instructor will find that things have changed, electrochemical equipment is easier to use these days, and several interesting experiments can be added to the instrumental analysis course with a minimum investment of time and money.

Although its roots can be traced all the way back to Michael Faraday, modern electrochemistry is being applied to a number of current chemical problems. Incredibly small microelectrodes are being used to probe biochemical events on the cellular level. Industrial corrosion processes are being monitored using rotating disk electrodes. Voltammetric methods with amazingly low detection limits are being used to monitor lead levels in the bloodstream. Electrodes coated with special polymers are finding use as glucose detectors for diabetics. The use of electrochemical detection is also expanding the range of analyses that can be performed using liquid chromatography.

In light of all of this recent activity, it is clear that modern electroanalytical techniques should be included in the undergraduate curriculum. The required equipment is quite inexpensive–an institution can now purchase a fully functional potentiostat system for less than the cost of a visible spectrophotometer or a gas chromatograph. Pine Instrument Company offers everything required to start teaching modern voltammetry in the undergraduate laboratory.

Of course, the lab instructor needs to find suitable experiments for undergraduates to perform during a single afternoon lab period. This guide includes several tested procedures, complete with notes for the instructor, that have been successfully used to teach undergraduate level voltammetry. The procedures are mostly designed with an analytical objective in mind, such as determination of an unknown concentration or measurement of a diffusion

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coefficient. It is important to note, however, that there are many non-analytical uses for electrochemistry, and a modern potentiostat can be put to use in the inorganic or physical chemistry laboratory measuring the fundamental thermodynamic properties of chemical systems.

Understanding Voltammetry

Most students in an instrumental analysis course are already familiar with basic electrochemical concepts as taught to them in a high school or introductory college level chemistry course. They have already been exposed to half-reactions, formal potentials, reference electrodes, the Nernst equation, free energy calculations, and simple dual electrode cells. Most of the calculations that students have performed in these early courses deal with the subject of *potentiometry*. That is, they are given stoichiometric and concentration data describing the electrochemical cell and are asked to predict a cell potential. At best, this early emphasis on "number crunching" leaves the student with a very narrow view of electrochemistry. At worst, the students emerge quite confused, worrying far too much about how to tell which electrode is the cathode or which half-reaction gets "flipped." The student rarely ever learns why it might be useful to perform an otherwise mundane redox reaction in that special container known as the electrochemical cell.

Fortunately, the instrumental analysis course provides an opportunity to re-introduce electrochemistry to the student in a more engaging and realistic way. The point should be made (early and often) that the real power behind modern electrochemical techniques derives from a very simple idea: Carrying out a redox process in an electrochemical cell forces electron transfer between reactants to occur through an external electronic circuit. Because the design and control of that external circuit belongs to the electrochemist, the electron flow may be used in whatever way is desired. It can be a source of power, the basis for a chemical measurement, or the driving force for an electrosynthesis reaction. Rather than just passively observing a redox process, the modern electrochemist takes control of the process, adjusting how fast it occurs (by regulating the current) or to what extent it occurs (by regulating the potential).

It should also be emphasized that the current and the potential cannot be controlled simultaneously, and that the electrochemist must choose which experimental variable is to be controlled. This laboratory manual deals exclusively with *voltammetry*, a broad term referring to those techniques where the potential of an electrode is the controlled variable while the current is the observed variable. Techniques where the opposite is true are termed *galvanostatic* methods. As voltammetric methods are more popular than galvanostatic methods, the focus of this laboratory manual is on voltammetry.

To help the student develop a proper understanding of *voltammetry*, it is generally a good idea to begin by contrasting it with potentiometry. Only a few basic concepts need to be discussed to help tie the two together, and a discussion of the Nernst equation and Faraday's Law in each context is probably

sufficient. Then, the student is gently encouraged not to worry about what is happening at every electrode immersed in a test solution, but to focus on what is happening at just one electrode, the *working electrode*. The paragraphs below should provide a useful outline of how to make this transition from potentiometry to voltammetry.

Moving from Potentiometry to Voltammetry

First, the student should be reminded that the Nernst equation describes a relationship between *electrode potential* and *solution concentration*. In the familiar (and rather boring) context of potentiometry, the electrochemist assumes a passive role. This means that the solution concentrations are whatever they are, and the electrochemist just measures the working electrode potential, which, in theory, is the same as that predicted by the Nernst equation. In the more exciting context of voltammetry, things are the other way around, and the electrochemist assumes an active role. By controlling the electrode potential, the electrochemist influences the solution concentrations *in the vicinity of the electrode*.

Of course, the Nernst equation is still useful for predicting the concentrations of species near the electrode surface at a given applied potential. However, it will only give an accurate picture in cases where the redox system responds rapidly to changes in the applied potential. Such kinetically facile redox systems remain in quasi-equilibrium with the electrode surface and are sometimes called "Nernstian" or *reversible* systems for this reason.

The potential of the working electrode determines what, if any, redox processes occur at the surface of the electrode. Extremely positive potentials are likely to oxidize analytes while negative potentials are likely to reduce them. In either case, a current flows through the electrode, and the magnitude of this current is usually proportional to solution concentration. Thus, the current provides the *analytical signal* that can be used as the basis for a calibration curve relating signal to concentration.

This is a good place in the discussion to point out that electrochemical systems are necessarily heterogeneous. All of the interesting chemical and electrochemical events occur at or near the surface of the working electrode. This means that the part of solution very near the electrode is somehow special because it is affected by it. In general, the electrode affects a layer of solution extending just a few micrometers away from the electrode surface. Analyte concentrations in this very small *diffusion layer* can vary widely from those found in the remaining *bulk* of the solution. Compared to the overall volume of solution in the cell, the volume of the diffusion layer is minuscule, and concentration changes caused by the electrode in the diffusion layer rarely affect the bulk solution. Note that students may initially resist these heterogeneous ideas because of their over familiarity with the (well stirred) homogeneous solutions used in spectroscopic and titrimetric analyses.

Next, the student should be reminded that Faraday's Law states that the quantity of charge involved in an electrochemical process is directly related to the underlying half-reaction stoichiometry. Because the majority of half-reactions involve simple one electron transfers, application of Faraday's Law leads to the statement that for every mole of analyte that is oxidized or reduced at an electrode, a mole of electrons, having a charge of 96,485 coulombs, enters or leaves the electrode. For those half-reactions involving two, three or four electrons, the quantity 96,485 C/mole is simply multiplied by the appropriate integer.

Faraday's Law provides the link between the observed current and the analyte concentration. In general, higher concentrations mean higher currents. When the electrode potential is perturbed enough from its equilibrium value, the current is limited only by how fast analyte arrives at the electrode surface. In unstirred solutions, the analyte can only reach the electrode by *diffusing* across the diffusion layer from the bulk solution to the electrode surface. The rate of this diffusion is governed by a concentration gradient–that is, diffusion occurs from a region of high concentration to a region of low concentration, and the greater the concentration difference, the faster the diffusion occurs. (Students are usually already familiar with these ideas from their study of ideal gas behavior.) This means that the current at an electrode is largest when the gradient in analyte concentration (across the diffusion layer) is greatest.

Finally, the student should be told that when Faraday's Law is combined with Fick's First Law of Diffusion, a general expression for the diffusion limited current, i_d, at a working electrode is obtained,

$$i_d = n\,F\,A\,D\,(\mathrm{d}C\,/\,\mathrm{d}x)_0$$

where n is the number of electrons involved in the half-reaction, F is Faraday's constant, A is the electrode area, D is the analyte's diffusion coefficient, and $(\mathrm{d}C\,/\,\mathrm{d}x)_0$ is the concentration gradient at the surface of the electrode. This expression, unlike the Nernst equation, will be new to the student, and it is very important that the proportional relationship between current and concentration gradient be emphasized.

In a sense, all diffusion limited voltammetry techniques (cyclic voltammetry, rotated disk voltammetry, chronoamperometry, etc.) are identical in that they are governed by the equation above. This can be a good unifying concept for students who are learning about more than one kind of voltammetry. Each technique differs only in the way that the concentration gradient, $(\mathrm{d}C\,/\,\mathrm{d}x)_0$, is created and maintained. This is what gives each technique its own unique current response.

Major Techniques and Minor Variations

The dozen or so popular voltammetric techniques can be placed into three general categories: sweep techniques, pulse (or step) techniques, and hydrodynamic techniques. Most of the techniques within a given category are

quite similar but have been given various names by electrochemists concerned with the subtle differences between them. In all cases, the potential of the electrode is varied in some predictable fashion so that the analyte is either oxidized or reduced at the electrode surface, creating a predictable concentration gradient, and thus, a predictable current response. Sweep techniques are preferred for investigating the general electrochemical behavior of the analytes in a solution, while step techniques generally give better quantitative information. Hydrodynamic techniques involve stirring the test solution for reasons described below.

Potential Step and Pulse Methods

The simplest electroanalytical technique is called *chronoamperometry* and involves stepping the electrode potential from an initial potential to some final potential. The initial and final potentials are chosen so that they bracket the formal potential, E^o, for the analyte. At the initial potential, no significant current flows through the electrode. Once the potential is stepped to the final potential, however, the analyte begins to be consumed (via oxidation or reduction) at the electrode surface. This depletes the concentration of analyte near the electrode to such an extent that it is essentially driven to zero at the electrode surface.

The sudden depletion of analyte at the electrode surface creates a very large concentration gradient, so it is not surprising that a very large current is observed immediately after the step. With time, the diffusion layer begins to extend further out into the solution, and the concentration gradient slowly relaxes. This means that the initial surge of current decays away to smaller values as time goes on. The magnitude of the current transient, *i(t)*, is proportional to the analyte concentration, *C*, and its decay with time is described by the Cottrell equation,

$$i(t) \ = \ n \, F \, A \, C \, (D / \pi \, t)^{1/2}$$

In this equation, *n* is the number of electrons appearing in half-reaction for the analyte, *F* is Faraday's constant (96485 C / mol), *A* is the electrode area (cm^2), and *D* is the analyte's diffusion coefficient (cm^2/sec). The experimental data is usually plotted as *i(t)* versus $t^{-1/2}$, yielding a straight line graph called a Cottrell plot. The slope of this line is directly proportional to concentration and may be used as the basis for an analytical determination. For solutions where the analyte concentration is already known, the slope can be used to measure the analyte's diffusion coefficient.

A variation of the simple chronoamperometry experiment that involves stepping back to the initial potential after some period of time is called *double potential step chronoamperometry (DPSCA)*. The principle strength of this experiment is its ability to probe what happens to the analyte after it is oxidized or reduced by the electrode. The oxidized or reduced forms of analytes are often unstable and may undergo various chemical reactions including decomposition. DPSCA provides a way to measure if and how fast these decomposition processes occur.

More complex potential pulse sequences may also be applied to the electrode. Techniques such as *pulse voltammetry* and *differential pulse voltammetry* involve

a series of potential steps to ever larger potentials. These techniques are able to distinguish between currents due to analyte redox processes and currents arising from background processes, and they provide both *current vs. time* and *current vs. potential* data.

Potential Sweep Methods

Rather than suddenly stepping the potential, it is often desirable to gently sweep it at a constant rate from one potential to another. The simplest sweep experiment is called *linear sweep voltammetry* and involves a single sweep from an initial potential to a final potential. As with chronoamperometry, the initial and final potentials are chosen so that they bracket the formal potential, E^o, for the analyte. Initially, the analyte is unaffected by the electrode, but as the potential sweeps by the formal potential, it begins to be oxidized (or reduced) by the electrode. This produces a concentration gradient, and a current transient is observed.

The transient observed in sweep voltammetry is similar to that produced by a chronoamperometry experiment, but it is not as "sharp" because the potential is swept rather than suddenly stepped. Again, the current is proportional to the concentration, and the transient's peak current, i_p, is given by the Randles-Sevcik equation,

$$i_p \ = \ 0.4463 \ n \ F \ A \ C \ (n \ F \ v \ D \ / \ R \ T)^{1/2}$$

In this equation, n is the number of electrons appearing in half-reaction for the redox couple, v is the rate at which the potential is swept (V / sec), F is Faraday's constant (96485 C / mol), A is the electrode area (cm^2), R is the universal gas constant (8.314 J / mol K), T is the absolute temperature (K), and D is the analyte's diffusion coefficient (cm^2/sec). Note that if the temperature is assumed to be 25°C (298.15K), the Randles-Sevcik can be written in a more concise form,

$$i_p \ = \ (2.687 \times 10^5) \ n^{3/2} \ v^{1/2} \ D^{1/2} \ A \ C$$

where the constant is understood to have units (*i.e.*, 2.687×10^5 C mol^{-1} V$^{-1/2}$). The Randles-Sevcik equation applies only when the redox system remains in equilibrium with the sweeping potential of the working electrode. This condition can be satisfied by studying a redox system with rapid kinetics and/or by sweeping the electrode potential at a slow rate.

The experimental results are usually presented as a plot of current versus potential called a *linear sweep voltammogram*. A very popular variation of this experiment, *cyclic voltammetry*, involves repeatedly sweeping the potential back and forth between the initial and final potentials. This technique provides a way to rapidly assess the behavior of an electrochemical system. The cyclic voltammetry experiment begins just like a linear sweep experiment–the analyte is oxidized (or reduced) during the initial sweep–but during the return sweep it is reduced (or oxidized) back to its original form. This causes a typical cyclic voltammogram to exhibit two peaks of equal size but opposite sign because one process is anodic and the other cathodic.

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Much like the DPSCA experiment described above, cyclic voltammetry is sensitive to the fate of the analyte once it is oxidized (or reduced) at the electrode. If it decomposes or undergoes some other chemical reaction after being oxidized (or reduced), then by the time the return sweep begins, there may no longer be a significant concentration of analyte in the diffusion layer, and the return peak will be missing from the cyclic voltammogram. This type of voltammogram is said to be *irreversible*. Irreversible voltammograms, while not as attractive as reversible ones, are still useful for analytical determinations.

A potential sweep is also used in *anodic stripping voltammetry*, which is a variation of linear sweep voltammetry using a mercury working electrode. Mercury electrodes have the unique ability to reduce and then absorb analytes (usually metal cations) from the test solution, concentrating them within the electrode itself. Once a large enough concentration of analytes has been absorbed, the potential of the mercury electrode is slowly swept in a positive (anodic) direction, and the analytes are oxidized and stripped out of the electrode.

Hydrodynamic Methods

In all of the methods described above, the electrode solution is kept as still as possible so that the only way in which the analyte can get to the electrode is by simple diffusion. Methods involving forced convection (that is, stirring) to help the analyte get to the electrode are called *hydrodynamic methods*. When the solution is stirred in a controlled manner, a non-turbulent flow of test solution can be directed toward the working electrode. The most popular way to achieve this effect is to rotate the electrode itself. This sets up a vortex flow within the test solution that sucks the solution up toward the electrode in a manner very similar to a tornado, minus the unwanted side effects. A typical rotating electrode is a long cylindrical rod with a disk electrode mounted concentrically at its end.

The rotating electrode keeps the bulk solution well stirred and homogeneous, but surprisingly, a thin layer of solution immediately adjacent to the electrode surface actually clings to it and rotates with it. Thus, from the perspective of the electrode, the solution in direct contact seems to be stagnant and quiet. While the stirring action of the electrode does bring analyte to the far side of this stagnant layer, in order to actually get to the electrode, the analyte must travel across the stagnant layer by simple diffusion. So even though the analyte is conveyed to the electrode surface by a combination of convection and diffusion, it is the latter vehicle–*diffusion*–that ultimately determines the current observed at the electrode.

The unique characteristic of the diffusion current observed at a rotating electrode is that it does not vary with time. This means that the concentration gradient at the electrode surface remains constant with respect to time. (This is not the case in cyclic voltammetry or chronoamperometry, where the gradient relaxes with time, and observed currents decay with time.) Because the thickness of the diffusion layer is fixed within the stagnant layer, and because the concentration of analyte on the far side of the diffusion layer is held steady by the stirring action of

the electrode, the concentration gradient does not change with time. For this reason, the currents observed using a rotating electrode are called *steady state* currents.

The fundamental equation for *rotating disk voltammetry* is the Levich equation, given below. This equation couples the underlying diffusion process with the hydrodynamic effects that arise from rotating the electrode. As the electrode potential is swept past the formal potential, E^o, for the analyte, the observed current climbs from zero up to a maximum or limiting current that corresponds to the steepest concentration gradient that can be sustained across the fixed-width diffusion layer. The resulting voltammogram (*i.e.*, plot of current versus potential) has a sigmoidal shaped wave centered on the formal potential. The limiting current, i_L, measured from the foot of the wave to its plateau, is given by the Levich equation,

$$i_L = 0.620 \, n \, F \, A \, D^{2/3} \, \omega^{1/2} \, \nu^{-1/6} \, C$$

where $\omega = 2 \, \pi \, f$, with f being the rotation rate in revolutions per second, ν is the kinematic viscosity of the solution, and the other variables have their usual meanings. The limiting current is directly proportional to concentration and can be used as the basis for an analytical determination.

A variation of the rotated disk electrode is the *rotated ring-disk electrode (RRDE)*. This special electrode has a disk electrode with a second ring electrode concentric with the disk. When this electrode is rotated, the vortex flow which brings analyte to the surface of the disk electrode also sweeps it out past the ring electrode after it has been in contact with the disk. Thus the analyte encounters the disk first, then the ring. (This is one of several dual working electrode techniques, all of which require the use of a bipotentiostat.) Just like the DPSCA and cyclic voltammetry experiments described above, the RRDE can be used to discern the fate of an analyte after it has undergone a redox process. If the analyte decomposes or undergoes some other chemical reaction during the time it takes to travel from the disk electrode to the ring electrode, then it will be noticeably absent when the ring electrode attempts to detect it. This so-called RRDE "collection" experiment can provide useful quantitative information regarding the rate of the "follow-up" reactions that occur after the analyte is oxidized or reduced.

Experimental Information

This section is a detailed description of the kinds of equipment needed to perform electroanalytical experiments. It is meant as a general guide to the instructor who is setting up an electrochemical workstation for academic use. As with all instrumental apparatus being used by undergraduates, a lot of time is spent "up front" setting up the equipment. Once this task is complete, however, performing experiments becomes fairly routine, and the instructor need only maintain the workstation.

The basic equipment needed for electrochemistry is a potentiostat, a recording device, and an electrochemical cell. Everything inside the cell is chemistry, and everything outside of it is electronics. A good workstation will have all of the electrical connections pre-wired and in working order so that the student can focus on the chemistry occurring within the cell and the data being generated by the experiment.

The Potentiostat

The principle function of a potentiostat is to control potential and measure current. The conventional *three-electrode potentiostat* is connected to the working, reference, and auxiliary electrodes immersed in the test solution. It controls the potential of the working electrode with respect to the reference electrode while simultaneously measuring the current flowing between the working electrode and the auxiliary electrode. Note that the potentiostat's internal feedback circuits prevent all but a very small current from flowing between the working and reference electrodes.

The more versatile *four-electrode potentiostat* permits the use of two working electrodes, and for this reason is also known as a *bipotentiostat*. The potential of each working electrode is maintained independently of the other and with respect to the reference electrode. The current flows between each individual working electrode and the auxiliary electrode. Only an insignificant current flows through the reference electrode.

Because the very basis of voltammetry is the control of electrode potential, a function generator is required to provide the potential sweep or pulse sequence to be applied to the working electrode. Most modern potentiostats include a built-in sweep and/or pulse generator, and those which are interfaced to a computer usually rely on the computer to generate the desired waveform. An external function generator can also be used by connecting its output to an input on the potentiostat. This latter option is used with potentiostats that have no internal sweep/pulse generator or whenever highly specialized waveforms are required.

The Output Device

The inputs to the potentiostat are the connections to the electrodes in the cell. The outputs from the potentiostat are signal lines reflecting the current and potential of the working electrode(s). If the potentiostat is interfaced to a computer, these signals are read directly by the controlling software, and experimental data is manipulated, displayed, and stored using the computer. This is by far the most convenient way to operate a potentiostat and is highly recommended in an instructional environment.

If, on the other hand, a conventional laboratory output device, such as an X-Y plotter or a digital oscilloscope, is being used to collect data, then the signal outputs are presented on the front panel of the potentiostat at BNC or banana type connectors. These signals must be physically connected to the plotter or oscilloscope using conventional coaxial cables. Such cables are designed to carry voltage signals from one piece of laboratory equipment to another.

The signal line which reflects the working electrode potential represents the voltage between the working and reference electrodes. This signal is used to drive the "X-axis" on the plotter, and the axis sensitivity is typically set between 0.05 to 0.20 volts per centimeter. Because electrode potentials rarely exceed two volts, this range of sensitivities allows entire voltammograms to fit on a single piece of paper. It is important to make a written note of the axis sensitivity directly on the plotter paper so that this information is not lost.

If the North American voltammogram convention is being used, the polarity of the potential signal is reversed so that positive potentials are plotted to the left and negative potentials to the right. The rationale behind this "backwards" convention is that more negative potentials correspond to higher electron energies, hence North American voltammograms are energy spectra with higher energies plotted toward the right.

The working electrode current signal is handled a bit differently. This signal line is also presented as a voltage signal, but the voltage level is actually proportional to the current flowing at the working electrode. The potentiostat has an internal "current converter" circuit that performs the necessary current-to-voltage conversion automatically. The current converter has a number of ranges, and the operator is expected to choose the range most appropriate for the experiment being performed. Each range is associated with a particular proportionality constant, such as "100 mA/V" or "1 µA/V." It is important to note the current converter setting directly on the piece of paper in the plotter just after the experimental data is recorded.

The current signal is usually connected to the "Y-axis" input on the plotter. If the North American voltammogram convention is being used, then cathodic current is plotted "up" in the positive direction, and anodic current is plotted "down" in the negative direction. The sensitivity of the "Y-axis" is adjusted using a control on the plotter, and it usually has units like "1V/cm" or "0.1V/cm." It is important to

note the "Y-axis" sensitivity directly on the piece of paper in the plotter just after the experimental data is recorded. By multiplying the "Y-axis" sensitivity by the current converter setting, one obtains the physical scale used to plot the current in units such as "5 mA/cm" or "10 µA/cm."

The connections described above are adequate for recording just about any voltammogram (*i.e.*, plot of current versus potential) generated by an electrochemical experiment. In pulse and step experiments, like chronoamperometry, the experimental data is often recorded as a plot current versus time. Collecting data in this fashion is very simple using an oscilloscope or a plotter capable of operating as a "strip-chart" recorder. When a dual working electrode experiment is being performed, such as rotated ring-disk voltammetry, the currents flowing at both electrodes are usually monitored. A dual trace digital oscilloscope or a two-pen plotter is required in these cases.

The Electrochemical Cell

When performing electrochemical experiments in the instructional laboratory, the student and instructor must be aware that these lab exercises require a somewhat greater level of care than the average titrimetric, gravimetric, or spectroscopic assay. The glassware is cleaner, the concentrations are smaller, the electrode is polished, and the solvents are purer. Nevertheless, there is no reason why undergraduate students cannot successfully use a variety of electrochemical techniques in their laboratory work. What follows here is a description of the kinds of apparatus and chemical reagents needed for most voltammetric experiments.

Glassware

In its simplest form, the electrochemical cell is a single piece of glassware capable of holding an appropriate volume of a test solution containing one or more electroactive analytes. Immersed in this solution are three electrodes (working, reference, and auxiliary) that are also electrically connected to a potentiostat. Custom glassware designs that include convenient fittings for mounting electrodes, gas inlets and outlets for purging oxygen, temperature jackets, and/or separate chambers for each of the three electrodes are often used in research environments, but common laboratory glassware can also be adapted for use. When choosing glassware for the instructional laboratory, it is important to consider what volume of test solution is to be used, how easily can students "hook up" the cell, and, in the event of an accident, how expensive is it going to be to replace the cell.

The three neck round bottom flask is a readily available and inexpensive piece of glassware that can be used as an electrochemical cell. These flasks can hold a considerable volume of solution, and the neck openings have large enough diameters that most electrodes will fit through them. Each neck on the flask can be used to mount one of the three electrodes. This configuration is well suited for those experiments where the test solution can be safely exposed to oxygen in the air and where isolation of each electrode in a separate compartment is not required.

It is often necessary to eliminate dissolved oxygen from the test solution whenever moderate to quite negative potentials are being applied to the working electrode. At these potentials dissolved oxygen can be reduced, and the resulting undesired cathodic current may interfere with the measurement of interest. A typical benchtop solution to this problem is to use a cell which is airtight except for one or two gas inlets and a single small outlet. An inert gas such as nitrogen is bubbled through the solution to expel any dissolved oxygen. (Usually one of the inlet tubes, designed especially for this purpose, is a capillary tube terminating near the bottom of the solution.) Then, during the course of an experiment, the air space above the solution is blanketed under a positive pressure of inert gas by passing a steady stream of gas through one inlet and then out of the cell through the small outlet.

A four neck round bottom flask can be configured for oxygen removal as follows. Three of the openings are used to mount the three electrodes in an airtight fashion. (Simply sealing the openings with parafilm will usually suffice.) The fourth opening is then sealed using a rubber septum. A small syringe needle is inserted through the septum near the outer edge of the septum. Then, a much longer needle (capable of being pushed through the septum and down into the test solution) is inserted through the center of the septum. Nitrogen gas is passed into the cell through the long needle while the small needle simply serves as the outlet. The long needle is first pushed down into the solution, and nitrogen gas is allowed to bubble through the solution. Then, when it is time to perform an experiment, the long needle is pulled out of the solution (but not all the way out of the cell), and a blanket of nitrogen gas then covers the solution.

A cell is available from Pine Instrument Company that is well suited for use in an instructional laboratory. The cell has a volume of 125 mL and has five openings. Three of these openings have ground glass joints and can be used to mount the working, reference, and auxiliary electrodes. Sleeve mounts made just for this cell are also available that allow popular reference electrodes to be mounted to the cell. The other two openings are screw-thread type and accept 6 mm diameter glass rods mounted using an o-ring seal. These are intended for glass tubing that connects the cell to the inert gas supply. These openings can also be used to mount electrodes fashioned from 6 mm glass tubing.

The Test Solution

The test solution inside the electrochemical cell consists of one or more analytes dissolved in a conductive electrolyte solution. The electrolyte solution usually consists of a (relatively) large concentration of an electrochemically inert salt dissolved in an ultra-pure solvent. The purity of the solvent is very important because the sensitivity of most voltammetric techniques is such that even a trace amount of an electroactive contaminant will show up. Even a cursory reading of the electrochemical literature reveals the great lengths taken by research electrochemists to insure the purity of their chemical systems. It is not uncommon to find them using non-aqueous systems based on HPLC grade

organic solvents that have been rigorously dried and in some cases triply distilled.

The instructor of an academic instructional laboratory, however, is probably more interested in saving as much time and money as possible by using a solvent that is inexpensive and readily available. The obvious choice is to use water, and the experiments in this manual are designed to use aqueous electrolyte solutions. Reagent grade acids and bases, diluted to appropriate concentration levels, make excellent solvents for electrochemistry. Similarly, various buffers and inert salt solutions may also be used. In all cases, however, the solution must be prepared from very pure water and the glassware used must be very clean.

These aqueous electrolyte solutions are in many cases available at the required purity and electrolyte levels directly from major chemical manufacturers. Some instructors (running large laboratory programs) may find that it is easiest simply to order a bulk quantity of the required electrolyte solution and distribute it to the students as needed. In many cases, however, the aqueous electrolyte solutions will have to be prepared "in-house," either by a lab technician or by the students themselves. In these cases, it is very important to have a source of ultra-pure water for making and diluting solutions.

Most undergraduate analytical laboratory programs make extensive use of some kind of purified water source. While this "pure" water from single-stage distillation of the local municipal water supply is quite adequate for spectroscopic and titrimetric experiments, it is generally ill-suited for voltammetry. Water of the highest purity can be obtained from more expensive water filtration systems that make use of ion-exchange columns, and instructors with access to such systems may find this water source most convenient. In smaller academic settings, however, it is probably most cost-effective to simply purchase deionized, ultrafiltered (DIUF) water or HPLC grade water from a major chemical manufacturer. Most manufacturers offer this ultra-pure water in various quantities including 20 liter carboys which are well suited for undergraduate use.

The *supporting electrolyte* present in the electrochemical test solution is put there to increase the conductivity of the solution. This helps diminish the magnitude of the electric field across the (bulk) test solution which, in turn, helps eliminate (undesired) movement of the analyte under the impetus of this field. The potential drop between electrodes in the cell remains the same as it would be for a non-conductive solution, but the added electrolyte causes most of the potential drop to occur within a few nanometers of the electrode surfaces.

The electric field across the bulk of the solution is never entirely eliminated, of course, but it is generally accepted that if the concentration of the supporting electrolyte is at least one hundred (100) times greater that that of the analyte, then the effect of the electric field on the analyte's motion can be safely neglected. In practice, the supporting electrolyte concentration is anywhere between 0.1$\underline{M}$ and 1.0$\underline{M}$, which means that analyte concentrations rarely exceed 0.01$\underline{M}$ in voltammetry experiments.

The choice of supporting electrolyte is generally based on two questions: (1) is it soluble in the solvent being used? and (2), is it electrochemically inert over the range of potentials being used? When using water as a solvent, one of the best choices for supporting electrolyte is potassium nitrate (KNO_3), which is quite soluble and electrochemically inert. Potassium chloride (KCl) may be used, but chloride ion is susceptible to oxidation at more positive potentials. Solutions of strong acids or strong bases in near molar concentrations also make good solvents for electrochemistry due to their high conductivity. The usefulness of acidic solutions is generally limited by the reduction of hydronium ion at negative potentials.

Preparing Dilute Solutions

The laboratory instructor is presented with a bit of a quandary when contemplating how best to supply students with the necessary reagents and pure solvents for an electrochemical experiment. Given the expense and trouble associated with obtaining a pure enough solvent and the cost of hazardous waste disposal, it seems logical to have the students use a minimum volume of solvent when preparing solutions. But because the analyte concentrations in voltammetry experiments are quite dilute (less than 0.01$\underline{M}$), the student who only has access to a milligram resolution balance is forced to use either a large volume of solvent or multiple dilution steps.

An example is offered which illustrates this point. If an experiment calls for the student to quantitatively prepare 100 mL of a 5.0 m$\underline{M}$ solution of an analyte with a formula mass of 300.0 g/mole, then the student and/or instructor may choose one of the following three preparation strategies, each of which has advantages and disadvantages associated with it:

(a)   Accurately weigh 0.1500 grams of the analyte into a 100 mL volumetric flask and then dilute "to the line" using the pure electrolyte solution. A group of ten students, each working alone, would consume only one liter of electrolyte solution using this option.

(b)   Accurately weigh 1.500 grams of the analyte into a 1000 mL volumetric flask and then dilute "to the line" using the pure electrolyte solution. A group of ten students, each working alone, would consume ten liters of electrolyte solution using this option.

(c)   The instructor prepares a "stock" solution by accurately weighing 7.500 grams of the analyte into a 500 mL flask and diluting "to the line" with the pure electrolyte solution. Then each student pipettes 10.00 mL of the stock solution into a 100 mL volumetric flask and dilutes "to the line" using the pure electrolyte solution. A group of ten students, each working alone, would consume only 1.5 liters of electrolyte solution using this option.

The first strategy has the two-fold advantage of using the minimum volume of expensive electrolyte solution while enjoying the precision associated with just

one dilution step. However, in order to prepare the solution with at the required precision, a balance capable of reproducibly measuring to the nearest microgram must be available. The cost of digital microbalances has been dropping in recent years, so that this option may soon be widely available.

The second strategy retains the precision associated with just one dilution step but does not require a microbalance. Unfortunately, if each student prepares a separate solution, this option wastes nine liters of electrolyte solution! Of course, if the entire group of ten students use the same one liter batch of solution, there would be no waste, but there would also be no accountability on the part of each student for the accuracy of the experimental results.

The last strategy is probably the best option when no microbalance is available but the instructor desires to maintain some level of student accountability. It uses an acceptably low volume of electrolyte solution and still requires each student to prepare separate solutions. The primary disadvantage is that the instructor must prepare the stock solution ahead of time.

Choice of Working Electrode

The ideal working electrode is a very clean metal surface with a well-defined geometry that is in direct contact with an electrochemical test solution. Working electrodes intended for general purpose work are usually made from a metal that is electrochemically inert over a wide range of potentials. The most widely used metals are mercury, platinum, gold, and various forms of carbon. Solid metals are typically fashioned into disks surrounded by a chemically inert shroud made from Teflon, glass, or epoxy. Mercury, being a liquid, tends to be used as a spherical droplet in contact with the solution.   There are pros and cons associated with each type of working electrode material, and each is discussed in some detail below.

The size and shape of the electrode surface also has an effect on the voltammetric response of the electrode. The overall current observed at an electrode is directly related to its surface area, and disk shaped electrodes with diameters greater than 100 μm, or *macroelectrodes*, generally produce easily measured currents in the microamp to milliamp range.   Electrodes with dimensions less than 100 μm are generally referred to as *microelectrodes*, and these typically produce currents in the picoamp to nanoamp range. Although the overall currents observed at microelectrodes are small enough to require specialized electrochemical equipment, these electrodes enjoy a greater signal-to-background ratio and, being small, find uses in applications where the sample size is quite small.

Mercury Electrodes

The classic polarography described in most undergraduate textbooks makes use of a liquid mercury as a working electrode. In its most common incarnation, the *dropping mercury electrode*, a reservoir of mercury is allowed to slowly drain through a vertical capillary tube immersed in the electrochemical test solution. As the mercury slowly exits from the capillary, it forms a small drop with a nearly

spherical shape that is in contact with the test solution. Electroactive analytes in the test solution undergo oxidation or reduction reactions at the surface of the drop.

This electrode configuration enjoys quite a few advantages including a very long history of use and an electrode surface that is easily reproducible. Indeed, in the event that the surface of the mercury drop becomes fouled, the drop is simply allowed to fall into the test solution, and a fresh drop is allowed to form at the capillary tube's exit. In aqueous solutions, the mercury electrode can be used at more negative potentials than other metals without interference from the reduction of hydronium ion. Finally, the mercury electrode plays an important role in *stripping voltammetry*-a technique which relies on preconcentrating one or more analytes into a mercury electrode and then separately electrolyzing (or stripping) each individual analyte out of the electrode.

The single biggest disadvantage of the dropping mercury electrode in the undergraduate laboratory is its toxicity. Students must be cautioned ahead of time about the hazards associated with mercury, and provision must be made for proper collection and disposal of the mercury used during an experiment. In addition, undergraduates who find the mercury drop electrode apparatus difficult to operate may lose track of the point of an experiment.

An alternative to the mercury drop electrode is a *mercury film electrode* (MFE). A glassy carbon disk electrode is placed in an electrochemical test solution that contains some mercury(II) nitrate, then by holding the electrode at a sufficiently negative potential, a thin film of mercury will coat its surface. An MFE formed in this fashion is suitable for use in a stripping voltammetry experiment, and the small quantity of mercury involved poses less of a hazard in the undergraduate laboratory.

Platinum Electrodes

Despite the expense associated with this precious metal, platinum is one of the most widely used materials for fabricating working electrodes. Platinum has the advantage of being an easily machined metal that is electrochemically inert. In aqueous solvent systems, the platinum working electrode is a good choice when working with positive potentials, but at negative potentials, interference from the reduction of hydronium ion is a problem. In rigorously anhydrous organic solvent systems, platinum is the best and most popular choice for the working electrode material due to its wide potential window in both the positive and negative directions.

Large diameter platinum macroelectrodes are generally fabricated by welding a thick platinum disk to the end of a brass rod, machining the platinum disk and brass rod so that they are concentric, and then placing a Teflon shroud around the entire assembly. The platinum surface is then ground to a mirror quality finish using a polishing paste that contains sub-micron alumina particles. As with all solid metal electrodes, the surface must occasionally be repolished to remove surface contaminants picked up during experiments.

Smaller diameter platinum disk electrodes and platinum microelectrodes are usually fabricated by shrouding a short length of platinum wire in soft glass. The diameter of the resulting platinum disk is the same as the diameter of the wire used. Because of the hardness of the glass shroud, these electrodes are usually polished to a mirror finish using polishing paste that contains sub-micron *diamond* particles.

The platinum working electrode is an excellent choice for the undergraduate laboratory. Of the solid metal electrodes, it is definitely the most popular due to its applicability to a wide range of electrochemical systems. It is durable and long lasting, and even an undergraduate can be taught how to properly polish it when required. Its primary disadvantage is that it has a limited use at negative potentials in aqueous solutions.

Gold Electrodes

Gold working electrodes are designed along the same lines as platinum working electrodes. Gold is usually less expensive than platinum, but it is not as electrochemically inert. The surface of a gold electrode is subject to oxidation at moderately positive potentials, and so it is not as generally useful as platinum.

Carbon Electrodes

Various forms of carbon are used as working electrode materials. Carbon electrodes are useful over a fairly wide potential window in both the positive and negative directions, and their principle advantage over platinum electrodes is the ability to work at more negative potentials in aqueous solutions. Solid carbon electrodes are usually made from *glassy carbon* or *pyrolytic graphite*, both of which are fairly expensive materials that are more difficult to machine than platinum or gold. The surface of a carbon electrode usually needs to be polished quite frequently, and the surface sometimes has to be "activated" by various empirical methods in order to obtain maximal performance from the electrode.

A less expensive carbon electrode can be fashioned using *carbon paste*. A cylindrical recess is drilled into a Teflon shroud, and an electrical contact is placed in the back of the recess. Each time the electrode is to be used, the recess is packed with a paste that contains carbon particles, and then the paste is carefully polished to a smooth disk-shaped surface. Working with a carbon paste electrode is technically more demanding because the paste can be gouged inadvertently after being polished.

Rotated Electrodes

A special class of electrochemical techniques, known as *hydrodynamic* methods, actually involve the use of spinning working electrodes. Typically, a specially designed glassy carbon or platinum disk electrode is attached to the end of a rigid shaft, and then this shaft is mounted on a high speed motor. These electrodes are immersed in a test solution and rotated at several thousand rotations per minute. A characteristic "vortex-like" solution flow pattern emerges as a result of the electrode's motion.

Because the solution is constantly stirred, fresh analyte solution is always being conveyed to the region near the surface of the electrode. This steady flow of analyte allows what is known as a "steady-state current" to flow at the rotating electrode as analytes are either oxidized or reduced. Steady-state currents are generally quite easy to measure because they remain constant with respect to time. (In most other electrochemical methods, currents tend to decay with time as the supply of analyte near the electrode is depleted.)

When using a rotating electrode, it is important that the cell volume be large enough to sustain a rapidly spinning solution flow. Also, the opening at the top of the cell must be large enough for the shaft of the rotating electrode. This means that the cell contents are open to the air, making oxygen removal difficult. A strong flow of inert gas is required to blanket the solution whenever a rotating electrode is being used to study an air-sensitive electrochemical system.

Electrical contact to a rotating electrode is usually made with brushes that are in mechanical contact with the rotating shaft. If the brushes or the shaft are dirty, experimental results will be obscured by a rapid, but periodic noise source. If this happens, the brushes should be cleaned or replaced, as needed.

Choice of Reference Electrode

The potential of a working electrode in a voltammetry experiment is always controlled with respect to some standard, and that standard is the reference electrode. While the thermodynamic scale of half-reaction potentials found in most textbooks measures electrode potentials against the "standard hydrogen" reference electrode (SHE), in actual practice the SHE is much too cumbersome to use. For this reason, a number of other reference electrodes have been developed. Experimental measurements of potential are made against these alternate reference electrodes, and then the potentials are "corrected" by simple addition or subtraction and reported against the SHE.

One of the most generally available reference electrodes for work in aqueous solutions is the *saturated calomel electrode* (SCE). The half reaction that occurs inside of an SCE reference is given below.

$$Hg_2Cl_2(s) \ + \ 2e^- \ \Longleftrightarrow \ 2\,Hg(l) \ + \ 2\,Cl^-(aq)$$
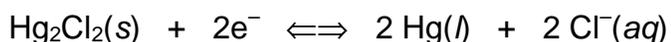
At 25°C, the formal potential for the SCE half reaction lies 0.2415 volts more positive than the SHE reference electrode. A potential measured against using an SCE can be reported versus the SHE simply by adding 0.2415 volts to it.

The SCE electrode must be constructed in an appropriate piece of glassware that can keep a small amount of mercury in direct contact with solid calomel (Hg_2Cl_2) paste while at the same time keeping the paste in contact with a saturated aqueous solution of potassium chloride. The short hand notation for the SCE half cell is as follows:

$$Pt(s) \ / \ Hg(l) \ / \ Hg_2Cl_2(s) \ / \ KCl \ (aq,\ sat'd) \ //$$
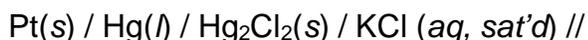
Electrical contact is made by immersing a platinum wire into the liquid mercury, and the potassium chloride solution maintains ionic contact with the test solution in the electrochemical cell via a salt bridge or porous glass frit. Such electrodes can be "home made" or purchased from a variety of manufacturers.

Other useful reference electrodes are based on half reactions involving a silver electrode. For work in aqueous systems, the "silver-silver chloride" or "Ag/AgCl" reference is quite popular. The half reaction for this reference electrode is as follows:

$$AgCl(s) \ + \ e^- \ \mathord{<}\mathord{-}\mathord{-}\mathord{-}\mathord{-}\mathord{-}\mathord{>} \ Ag(s) \ + \ Cl^-(aq)$$
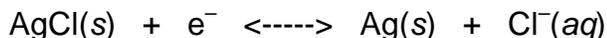
The actual potential assumed by an Ag/AgCl reference depends only on the activity of the chloride anion. (The other two species appearing in the half-reaction are solids which always have unit activity.) To serve as a reference, the chloride activity needs to be held constant. To accomplish this, a silver wire (coated with a layer of silver chloride) is immersed in an internal solution saturated with potassium chloride. The chloride ion concentration remains fixed at the saturation limit. The short hand notation for this reference electrode half cell is given below:

$$Ag(s) \ / \ AgCl(s) \ / \ KCl \ (aq, \ sat'd), \ AgNO_3(aq) \ //$$
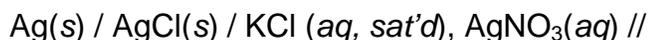
Electrical contact is made by direct connection to the silver wire, and the internal electrode solution is placed in ionic contact with the test solution via a salt bridge or porous glass frit.

The Auxiliary Electrode

In traditional two electrode cells that have only a working electrode and a reference electrode, current is necessarily forced to flow through the reference electrode whenever a measurement is made. If enough current flows through a reference electrode, its internal chemical composition may be significantly altered, causing its potential to drift away from the expected standard value. For this and other reasons, it is desirable to make electrochemical measurements without current flowing through the reference electrode. Modern three and four electrode potentiostats use a feedback circuit to prevent this from happening, but this feedback circuit requires that an additional *auxiliary* electrode be introduced into the electrochemical cell. This auxiliary (or counter) electrode provides an alternate route for the current to follow, so that only a very small current flows through the reference electrode.

The auxiliary electrode can be made from just about any material using any desired electrode geometry. Design choices are usually based on finding a material that is chemically inert in the particular test solution being studied, and it is generally a good idea for the auxiliary electrode to have a large surface area. In most cases, a coil of platinum wire is used, but stainless steel, copper or aluminum wire may work in non-corrosive solutions where metal cation interference is not a concern. If the electrochemical cell is made of metal, then the cell itself might be used as the auxiliary.

Because current flows at the auxiliary electrode, electrochemical processes will also occur there. If the working electrode is reducing something, then the auxiliary electrode must oxidize something, and vice versa. The products generated at the auxiliary electrode, if allowed to diffuse to the working electrode, may interfere with the experimental measurement. When this is a problem, the auxiliary electrode is placed in a separate compartment containing an electrolyte solution that is in ionic contact with the main test solution via a glass frit. In most cases, however, the auxiliary can be placed right in the test solution along with the reference and working electrodes.

Electrical Shielding

The small currents observed in some electrochemical experiments are subject to interference from electrical noise in the laboratory environment. To help shield the experiment from noise, it is a good idea to use coaxial cable to make all connections from the electrodes to the potentiostat, and if using a plotter, the connections between it and the potentiostat should use coaxial cable as well. These simple measures usually reduce noise to an insignificant level.

When using very small electrodes or low analyte concentrations, it is likely that the current observed at the working electrode will on the order of nanoamps to picoamps. When measuring such small currents, it is usually necessary to place the entire cell inside of a metal cage to shield the cell from the noisy laboratory environment. Sometimes called a "Faraday cage," the metal cage should be grounded to the same point that the potentiostat and output device are grounded.

An undue amount of noise can often be traced to the reference electrode. Because the reference electrode is necessarily a high in impedance, it can serve as an antenna for picking up electronic noise. Also, bubbles or clogged frits within the reference electrode are particularly common sources of noise.

Laboratory Procedures

The remainder of this text consists of detailed laboratory procedures in the form of laboratory handouts that can be distributed to students. At the end of each handout are notes with information intended only for the instructor.

The first experiment is the *Introduction to Cyclic Voltammetry* exercise. This experiment has a simple goal–finding the concentration of iron in an unknown test solution–and is a good introduction to working with electrochemical cells, potentiostats, and the Randles-Sevcik equation. The experiment is somewhat lengthy, and the instructor may wish to have students only perform part of it.

The second experiment is the *Determination of Acetaminophen in a Children's Pain Relief Elixir*. This experiment uses cyclic voltammetry to determine the amount of active ingredient in an over-the-counter medication. It exposes students to the use of a carbon electrode and to an irreversible redox couple.

The third experiment is a *Survey of Three Voltammetric Methods*. This experiment introduces students to chronoamperometry and rotated disk voltammetry and builds on their prior knowledge of cyclic voltammetry. Obviously, a rotated disk electrode must be available to complete this experiment. The goal of this experiment is to observe how the responses from three different voltammetric methods are all governed by physical diffusion.

Experiment 1
AN INTRODUCTION TO CYCLIC VOLTAMMETRY

Description

The goal of this experiment is to become familiar with using a modern electrochemical potentiostat, to determine the concentration of iron(III) in an unknown solution, and to measure the diffusion coefficient for iron(III). This procedure illustrates how the current observed in a cyclic voltammetry experiment depends upon experimental parameters such as concentration and sweep rate.

Experimental Apparatus

- Pine Instrument Company AFCBP1 Bipotentiostat
- Pine Instrument Company ASWCV2 **PineChem**™ software package
- Three electrode cell (provision for nitrogen deaeration is optional)
- Platinum disk electrode
- Platinum auxiliary electrode
- SCE reference electrode
- Alumina polishing solution
- Five 100 mL volumetric flasks
- Pipettes (2, 5, 10, 20, and 25 mL)

Reagents and Chemicals

Description	per expt	per 20 expts*
1.0 M hydrochloric acid	600 mL	15 L
250 mM iron(III) chloride in 1.0 M HCl	75 mL	2 L
(40.5 grams $FeCl_3$ per liter of acid solution)		

* includes amounts needed by instructor to prepare stock and unknown solutions for entire group.

Discussion

Cyclic voltammetry is perhaps the most often used electroanalytical technique. A cyclic voltammogram (or CV) is obtained by applying a linear potential sweep (that is, a potential that increases or decreases linearly with time) to the working electrode. As the potential is swept back and forth past the formal potential, E^o, of an analyte, a current flows through the electrode that either oxidizes or reduces the analyte. The magnitude of this current is proportional to the concentration of the analyte in solution, which allows cyclic voltammetry to be used in an analytical determination of concentration.

The equipment required to perform cyclic voltammetry consists of a conventional three-electrode potentiostat connected to three electrodes (working, reference,

and auxiliary) immersed in a test solution. The potentiostat applies and maintains the potential between the working and reference electrode while at the same time measuring the current at the working electrode. (Charge flows between the working electrode and the auxiliary electrode.) A recording device (such as a computer or plotter) is used to record the resulting cyclic voltammogram as a graph of current versus potential.

Figure 1.1 depicts a generic cyclic voltammogram. The potential is graphed along the *x-axis* with more positive (or oxidizing) potentials plotted *to the left*, and more negative (or reducing) potentials *to the right*. The current is plotted on the *y-axis* of the voltammogram, with cathodic (*i.e.*, reducing) currents plotted *up* along the positive direction, and anodic (*i.e.*, oxidizing) currents plotted *down* in the negative direction. (A voltammogram is almost always plotted in this fashion by North American electrochemists, but in Europe, the axes are typically reversed.)
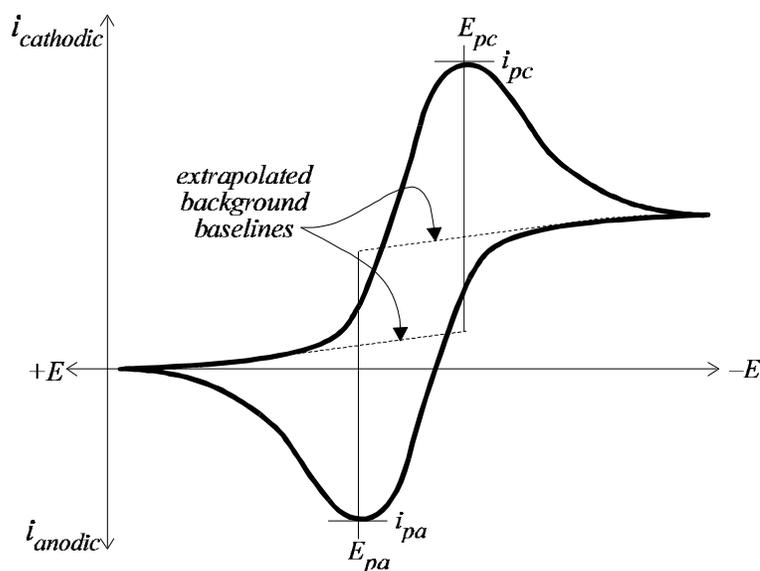

FIGURE 1.1: A TYPICAL CYCLIC VOLTAMMOGRAM

The peaks appearing in a voltammogram are similar to those found in a spectrum or chromatogram. Each peak corresponds to a particular electroactive analyte in the test solution, and the height of a peak is proportional to the concentration of that analyte. The peaks in a cyclic voltammogram are asymmetric, with the leading side being very steep and the trailing side falling off gradually. The peaks observed during the reverse sweep have the same general shape as those seen in the forward sweep, but they are inverted because the direction of current flow is reversed. The first sweep in a cyclic voltammetry experiment may be in either the positive (anodic) direction or in the negative (cathodic) direction.

There is a great deal of quantitative information that can be gleaned from a good cyclic voltammogram. First, it can be a test to see if a redox couple is indeed reversible. The peak potential for the anodic sweep, E_{pa}, and the peak potential for the cathodic peak, E_{pc}, can be directly read from the voltammogram, and the

difference between them, ΔE_{peak}, can be calculated. If the redox couple is reversible, then the relationship,

$$n\,\Delta E_{peak} = 59\text{ mV} \tag{1.1}$$

holds true, where n is the number of electrons involved in the redox couple (usually just one).

In addition, the cyclic voltammogram for a reversible redox couple has an anodic peak current, i_{pa}, that is equal to the cathodic peak current, i_{pc}, so that the relationship,

$$i_{pa} / i_{pc} = 1 \tag{1.2}$$

also holds true. It is important to note that the peak currents are not measured using the *x-axis* as a baseline. Rather, a background current baseline must first be extrapolated out to the peak potential (see Figure 1.1). Then, the peak current is measured (vertically) from the peak down to the extrapolated baseline.

The background current is always present, even in a test solution that contains no electroactive analyte. It is due to a *double layer* of ions in the solution immediately adjacent to the surface of the electrode. This double layer behaves like a capacitor, alternately being charged and discharged as the potential is swept back and forth. Thus, the background current is sometimes referred to as a *charging current*.

The formal potential, E^{o}, for a reversible redox couple is easily determined as the average of the two peak potentials as follows.

$$E^{o} = (E_{pa} + E_{pc}) / 2 \tag{1.3}$$

Formal potentials measured using cyclic voltammetry are usually accurate to within 50 mV of the true value. More accurate values can be obtained using other electrochemical techniques.

Quantitative information regarding analyte concentration can be obtained from the voltammogram using the Randles-Sevcik equation (Eqn. 1.4). This equation specifies the peak current, i_p (either anodic or cathodic), in terms of the analyte concentration, C.

$$i_p = 0.4463\, n\, F\, A\, C\, (n\, F\, v\, D\, /\, R\, T)^{1/2} \tag{1.4}$$

In this equation, n is the number of electrons appearing in half-reaction for the redox couple, v is the rate at which the potential is swept (V / sec), F is Faraday's constant (96485 C / mol), A is the electrode area (cm^2), R is the universal gas constant (8.314 J / mol K), T is the absolute temperature (K), and D is the analyte's diffusion coefficient (cm^2/sec). Note that if the temperature is assumed to be 25°C (298.15K), the Randles-Sevcik can be written in a more concise form,

$$i_p = (2.687\text{x}10^{5})\, n^{3/2}\, v^{1/2}\, D^{1/2}\, A\, C \tag{1.5}$$

where the constant is understood to have units (*i.e.*, $2.687\text{x}10^5$ C mol^{-1} V$^{-1/2}$).

Note that the peak current is directly proportional to the analyte concentration. Also note that if the analyte concentration is a known quantity, then cyclic voltammetry can be used to measure the analyte's diffusion coefficient. The diffusion coefficient is a measure of how fast the analyte moves through the solution as a result of random collisions with other molecules.

Procedure

All glassware used for electrochemistry should be as clean as possible. The solvents and reagents used to make solutions should be as pure as possible. It is a good idea to use deionized, ultrafiltered (DIUF) water or "conductivity water" or "HPLC grade water" for the final rinsing of glassware and for all solution preparation.

A. SOLUTION PREPARATION

1)   These stock solutions should be provided to a group of 20 students:

1.0M hydrochloric acid (15 liters)
Solutions of 1.0 M *hydrochloric acid* available directly from chemical manufacturers are usually well suited for electrochemical experiments. Alternately, a liter of 1.0 M *hydrochloric acid* solution can be prepared by diluting 8.0 mL of *concentrated* hydrochloric acid to a volume of one liter using ultrapure water. Both the water and the concentrated acid must be free of contaminants. Remember to add the acid to the water.

250 mM iron chloride stock solution (2 liters)
This solution can be prepared by dissolving 81.0 grams of $FeCl_3$ in enough 1.0M *hydrochloric acid* to make two liters of solution. The resulting solution has an iron concentration near 250 mM. Note that $FeCl_3$ is quite hygroscopic and is difficult to weigh out as a dry solid. It is much easier to purchase a concentrated solution of ferric chloride directly from a chemical manufacturer and then dilute this solution down to the desired 250 mM concentration.

Unknown solution (2 liters)
To prepare enough unknown solution for twenty (20) students, pipette anywhere from 50 to 500 mL of the *iron stock solution* into a 2000 mL volumetric flask and dilute "to the line" using 1.0$\underline{M}$ hydrochloric acid. Alternately, individual unknowns may be prepared by pipetting anywhere from 2 to 25 mL of the *iron stock solution* into 100 mL flasks and diluting "to the line" with 1.0$\underline{M}$ hydrochloric acid.

2) Each individual student should prepare five standard solutions with various concentrations of iron ranging from 5 to 70 m$\underline{M}$. These solutions can be prepared by pipetting various volumes of the *iron stock solution* into a series of five 100 mL volumetric flasks. When filling each flask "to the line," be sure to use the 1.0$\underline{M}$ *hydrochloric acid* rather than water. The table below is meant to serve as a guide in making these five solutions. The concentrations listed in the table assume that the *iron stock solution* has a concentration of 250 m$\underline{M}$. Students should verify this assumption and recompute the concentrations if needed.

pipette volume (mL)	flask volume (mL)	standard concentration (m$\underline{M}$)
2	100	5.0
5	100	12.5
10	100	25.0
20	100	50.0
25	100	62.5

B. BACKGROUND SCANS

A simple *background* voltammogram of the pure 1.0 $\underline{M}$ *hydrochloric acid solution* is a good way to confirm the purity of the solution, the cleanliness of the glassware, and the preparation of the polished working electrode all in a single step. Electrochemists frequently perform such a background scan before moving on to the main experiment just to make sure everything is okay. Any electroactive impurities from the solvent or dirty glassware will show up as unexplained peaks in the background scan. In addition, a fouled or improperly polished electrode surface usually causes a larger background current. Note, however, that even clean platinum electrodes will exhibit some peaks due to oxide deposition and stripping.

3) Obtain a platinum disk working electrode. Be sure to note the surface area of the disk in square centimeters in your lab notebook. Polish the electrode as needed using an alumina slurry on a polishing cloth. After polishing, wash the electrode with ultrapure water and wipe clean. The electrode surface should be mirror bright and free of defects.

4) Equip a clean electrochemical cell with an SCE reference electrode and a platinum auxiliary electrode. Carefully mount the platinum working electrode in the cell as well.

5) Fill the electrochemical cell with pure 1.0<u>M</u> *hydrochloric acid solution.* If desired, the oxygen in the cell may be purged by bubbling nitrogen through the solution for one or two minutes. Even though oxygen is unlikely to interfere with the chemical system being studied in this experiment, it is still good general practice to remove oxygen from an electrochemical cell.

6) From the INSTRUMENT STATUS panel of the **PineChem** software package, adjust the IDLE CONDITIONS as shown in Figure 1.2. Confirm that the AFCBP1 Bipotentiostat is in DUMMY mode, and then make all necessary electrical connections between the electrodes and the potentiostat. Also, adjust the front panel voltmeter of the AFCBP1 so that it is displaying the working electrode potential (E1). It should confirm that the K1 electrode is idling near zero volts.
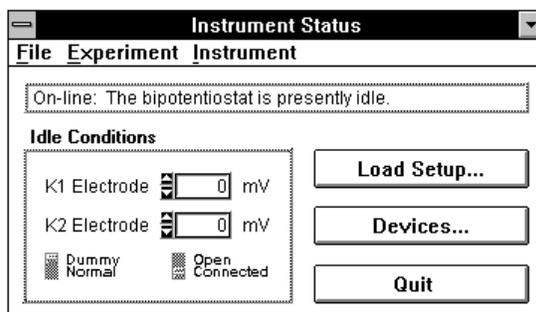
FIGURE 1.2: INITIAL INSTRUMENT STATUS PANEL SETTINGS

7) Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and then enter the experimental parameters shown in Figure 1.3 below. Note that these settings are only suggested starting points for performing a background scan. The ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.

8) Once the experiment settings have been adjusted to match those in Figure 1.3, click on the PERFORM button to initiate the experiment. The resulting cyclic voltammogram should be relatively featureless and exhibit no significant peaks. For a sweep rate of 100 mV/sec, the magnitude of the background current should not exceed 300 μA/cm^2 (that is, 300 times the electrode area in square centimeters). If significant peaks (other than oxide deposition and stripping peaks) are apparent, then the glassware, electrode surface and/or solvent are contaminated. If the background current is too large, the electrode should be polished.
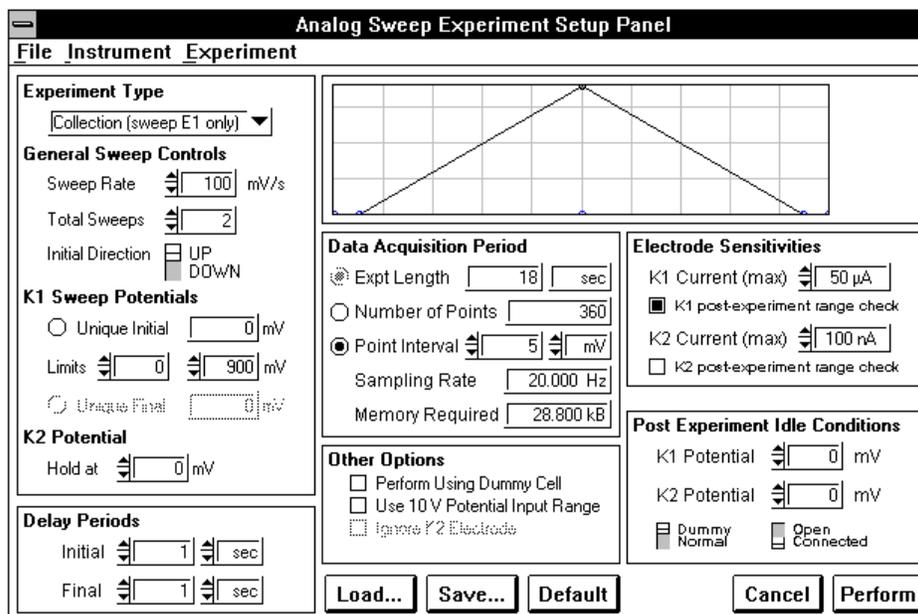
FIGURE 1.3: EXPERIMENTAL SETUP FOR BACKGROUND SCAN

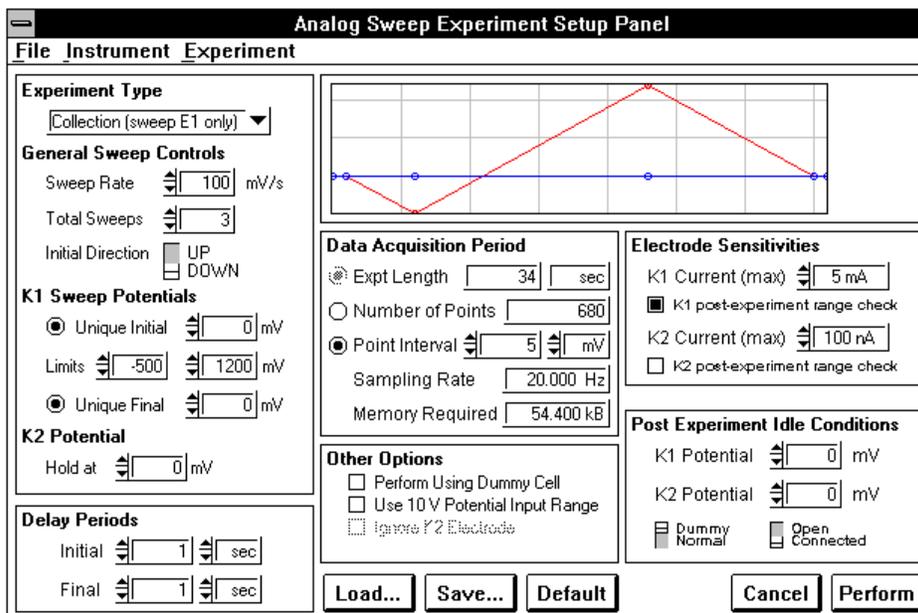**FIGURE 1.4: SETUP FOR AN EXPANDED BACKGROUND SCAN**

9) After acquiring a satisfactory background voltammogram, save it on the disk and/or print it out on the printer.

10) *Pushing the envelope.* If the sweep limits are extended to more extreme potentials, relatively large background currents are observed. At extreme positive potentials, the solvent (water) begins to be oxidized at the working

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electrode.   At negative potentials, the hydronium ion is reduced to hydrogen gas.   The large currents observed at either extreme limit the range of potentials in which meaningful voltammetry can be carried out. To observe these so called "background limits", return to the **Analog Sweep Voltammetry** setup panel, and change the K1 SWEEP POTENTIALS to those shown in Figure 1.4. Note that you may also have to adjust the ELECTRODE SENSITIVITY for the K1 CURRENT to a much higher setting in order to observe these larger currents.

11)   After acquiring another satisfactory voltammogram, save it on the disk and/or print it out on the printer.

C.   THE EFFECT OF CONCENTRATION

In this part of the experiment, several cyclic voltammograms are obtained with solutions of varying concentration. At least five standard solutions, with iron(III) concentrations ranging from 5 to 70 mM, should be used. The standards should be prepared using 1.0M *hydrochloric acid solution* as the solvent.

12)   Equip a clean electrochemical cell with an SCE reference electrode and a platinum auxiliary electrode.   Carefully mount the platinum working electrode in the cell as well.

13)   Fill the electrochemical cell with the standard solution that has the lowest iron concentration. Make sure that all three electrodes are immersed in the solution. If desired, the oxygen in the cell may be purged by bubbling nitrogen through the solution for one or two minutes.

14)   Before making electrical connections between the cell and the potentiostat, it is a good idea to place the AFCBP1 Bipotentiostat in DUMMY mode.   This can be done using the controls on the INSTRUMENT STATUS panel.
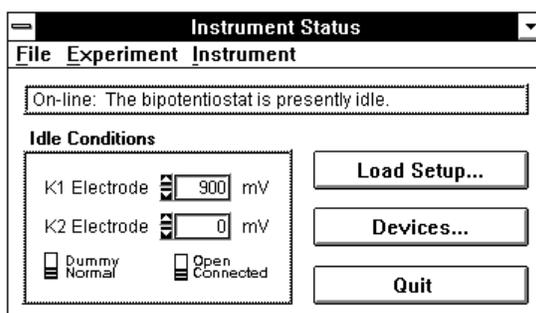
FIGURE 1.5: IDLE CONDITIONS FOR A CELL FILLED WITH AN IRON SOLUTION

15)   After the cell has been properly configured, use the INSTRUMENT STATUS panel of the **PineChem** software package to adjust the IDLE CONDITIONS as shown in Figure 1.5. Note that the K1 electrode potential should idle at about +900 mV, a potential which is *more positive* than the formal potential for the iron redox couple.   Use the front panel voltmeter to

confirm the K1 electrode potential (E1). Note also that the AFCBP1 should be placed in NORMAL mode rather than DUMMY mode.

16) Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and then enter the experimental parameters shown in Figure 1.6 below. The ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered. (The largest current that should be observed during the experiment can be roughly estimated by multiplying the electrode area by the solution concentration and by the quantity 450 mA $\underline{M}^{-1}$ cm^{-2}.)

FIGURE 1.6: EXPERIMENTAL SETUP FOR CONCENTRATION STUDY

17) Once the experiment settings have been adjusted to match those in Figure 1.6, click on the PERFORM button to initiate the experiment. A fairly prominent cathodic wave should appear during the sweep from +900 mV to zero millivolts. On the return sweep, an anodic wave of equal size should appear.

18) After acquiring a satisfactory voltammogram, save it on the disk and/or print it out on the printer.

19) Plot the voltammogram as a current versus time graph by choosing the **I1 vs. t** option from the **Plot** menu. Then, use the **Peak Height Tool** found in the **Toolbox** menu to measure the height of the cathodic peak as shown in Figure 1.7. Note that the cathodic peak is the first peak and that it points downward on the **I1 vs. t** plot. The software presents the peak height result as a negative number, but you should record it as a positive number in your lab notebook.

20) Acquire similar voltammograms for the remaining standard solutions in order of increasing iron(III) concentration. Use the same sweep rate (100 mV/s) for all solutions. Clean the cell between solutions.

21) After the last standard solution has been studied, *leave it in the cell* and use it for the next part of the experiment.
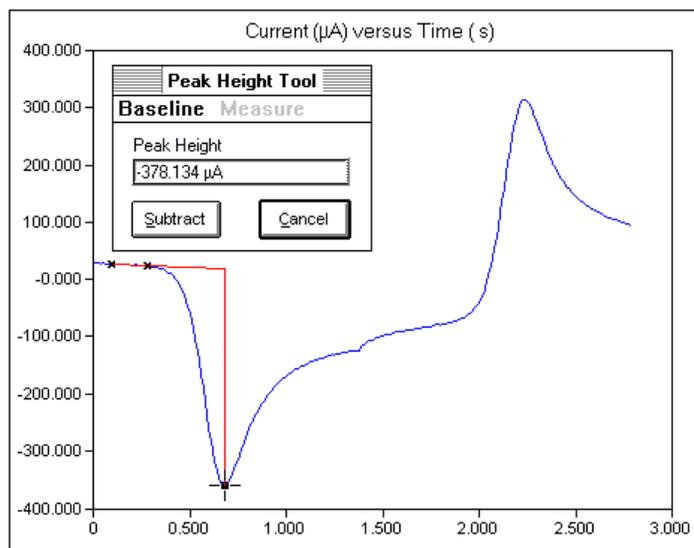

FIGURE 1.7: MEASURING THE PEAK HEIGHT

D. THE EFFECT OF SWEEP RATE

Using the standard iron solution with the highest iron(III) concentration, a series of cyclic voltammograms should be acquired at various sweep rates. The peak current observed in these voltammograms should exhibit a noticeable dependence on the sweep rate.

22) Using sweep parameters similar to those in Figure 1.6, acquire voltammograms at the following sweep rates: 225, 170, 120, 80, and 50 mV/s. Be sure to save each voltammogram on a disk and/or print it out on the printer. In addition, use the **Peak Height Tool** to measure the height of the cathodic peak from each voltammogram. Note that the ELECTRODE SENSITIVITY should be adjusted from time to time as progressively lower sweep rates are used.

E. THE UNKNOWN SOLUTION

The instructor may provide a solution which has an unknown iron(III) concentration. This solution should be examined using the same sweep rate as that used to examine the series of standard iron(III) solutions (100 mV/s). If the unknown solution has a concentration on the same order as your standards, then it may be examined directly as supplied by the instructor. If the unknown iron(III) concentration is much greater than those of your standards, then the unknown solution must first be diluted to a lower concentration.

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23)   Using sweep parameters similar to those in Figure 1.6, acquire a voltammogram of the unknown iron solution using a 100 mV/s sweep rate. Be sure to save the voltammogram on a disk and/or print it out on the printer. In addition, use the **Peak Height Tool** to measure the height of the cathodic peak in the voltammogram. Note that the ELECTRODE SENSITIVITY may need to be adjusted to a value different than that shown in Figure 1.6.

Data Analysis

Concentration Study

a)   Using the cathodic peak currents for the series of standard solutions, prepare a plot of peak current versus concentration. (Make sure that each of the voltammograms was acquired using the same sweep rate.)

b)   Perform a linear least squares analysis on the data to find the equation of the best straight line which fits the data.

c)   Use the slope of the line to calculate the diffusion coefficient for the iron(III) cation in 1.0M hydrochloric acid.

Unknown Solution

d)   Using the equation from (b), above, compute the concentration of iron(III) in the unknown solution. Report your result in moles per liter using three significant figures.

Sweep Rate Study

e)   Using the cathodic peak currents measured from the series of voltammograms acquired at different sweep rates, prepare a plot of peak current versus the square root of the sweep rate. (Make sure that each of the voltammograms was acquired using the same standard solution.)

f)   Perform a linear least squares analysis on the data to find the equation of the best straight line which fits the data.

g)   Use the slope of the line to calculate the diffusion coefficient for the iron(III) cation in 1.0M hydrochloric acid.

h)   Using the voltammogram obtained using the slowest sweep rate, determine the formal potential, E^o, for the iron(III/II) redox couple. Express the result in volts versus the standard hydrogen electrode (SHE), and compare it to an accepted value from a reference textbook.

Report Questions

1)   Explain, in terms of what happens in the diffusion layer immediately adjacent to the electrode surface, why faster sweep rates give higher peak currents.

2) Examine the observed currents (at E^o) for each of the standard solutions and for the background scan. Then give a rough estimate of the following concentrations:
   (a) At what concentration does the cathodic current equal ten times the charging current? This concentration is defined as the Limit of Quantitation (LOQ).
   (b) At what concentration does the cathodic current equal three times the charging current? This concentration is defined as the Limit of Detection (LOD).

3) When a group of molecules or ions are randomly diffusing through a solution, the average distance, x, that they move in a period of time, t, can be estimated using $x = (2\,D\,t)^{1/2}$, where D is the diffusion coefficient. Using your experimental result for the diffusion coefficient of iron(III), show that it takes more than a day for a group of iron(III) cations to diffuse just one centimeter.

Prelab Questions

Answer the following questions before beginning the lab experiment.

1)   In the "pushing the envelope" portion of section B in the lab procedure, the electrode is intentionally swept to extreme positive and negative potentials. Large currents flow due to the reduction of hydronium ion or oxidation of water. Write the half-reaction for each of these two processes and estimate the working electrode potential required to initiate each process.

2)   In section C of the lab procedure above, you are encouraged to examine the standard solutions in order of increasing concentration. Why is it a good idea to do this?

3)   A 4.500 m$\underline{M}$ standard solution of an analyte is prepared and studied using cyclic voltammetry at 25.0°C. A platinum disk electrode with diameter 5.0 mm is used. The analyte exhibits a simple one electron redox couple (n = 1) and has a diffusion coefficient, D, equal to 7.56×10^{-5} cm^2/s. The sweep rate is 200.0 mV/s. Using the Randles-Sevcik equation (Eqn. 1.4), calculate the peak current that should be observed.

Instructor's Notes

The iron(III/II) redox couple (in acidic solution) is one of the most well behaved, reversible redox couples available for instructional purposes. The electrochemistry of most other metal cations is complicated by oxide formation reactions, plating on to the electrode surface, or formal potentials too extreme to be observed in aqueous solution. Iron(III) chloride was chosen as the analyte because it is widely available and inexpensive. Other well behaved, reversible systems that can be investigated are listed below:

Analyte	Formula	Concentrations	Electrolyte Solution
potassium ferricyanide	$K_3Fe(CN)_6$	1 to 10 mM	$1\underline{M}$ KNO_3 in H_2O
ferrocene & derivatives	$Fe(C_5H_5)_2$	0.2 to 2 mM	$0.1\underline{M}$ $(C_4H_9)_4NPF_6$ in CH_3CN
paraquat dichloride	$(C_6H_7N)_2$ Cl_2	0.2 to 2 mM	$0.1\underline{M}$ $(C_4H_9)_4NPF_6$ in CH_3CN

Preparing a standardized, stock solution of iron(III) chloride is complicated by the fact that the salt is quite hygroscopic. The salt must be weighed quickly to avoid errors caused by the absorption of water from the air. It also leaves undesirable brown stains on just about every surface it contacts. For this reason, it is a good idea to purchase the stock solution from a chemical manufacturer. Solutions containing iron(III) are sold as atomic absorption standards and for other wet chemical analyses.

A "concentrated" solution of iron(III) chloride from a chemical manufacturer is usually 40% (w/v) iron(III) chloride. If this solution is diluted by a factor of ten (using $1.0\underline{M}$ hydrochloric acid, of course) it will have an iron(III) concentration near $0.25\underline{M}$, which is that required for the stock solution in this experiment. For exact results, such a solution must then be standardized. However, if all students use the same stock solution, and the unknown is prepared from it as well, then the standardization can be skipped as long as students are given a reasonable value for the stock solution's concentration. This may cause an error in diffusion coefficient calculations, but the unknown determinations can still be graded strictly because everyone (including the instructor) used the same stock solution.

The diffusion coefficient for the iron(III) cation is reported as 4.7×10^{-6} cm^2/sec in $1\underline{M}$ hydrochloric acid in reference 1. The instructor should note that cyclic voltammetry is the least reliable electrochemical method for determination of a diffusion coefficient, and grading policies should allow for deviation from the

accepted value. In 1$\underline{M}$ perchloric acid and 1$\underline{M}$ sulfuric acid, the values are 4.7×10^{-6} cm^2/sec and 3.0×10^{-6} cm^2/sec, respectively. The lower value in sulfuric acid is attributed to complexation with the sulfate anion. Students should calculate their value using the peak currents for the reduction of iron(III) to iron(II). Students tend to make a lot of calculation errors when determining the diffusion coefficient. Unit analysis is particularly difficult for them.

Students are asked to measure the formal potential, E^o, for the iron(III/II) redox couple, which has an accepted value of +0.700 V versus SHE. Formal potentials determined using cyclic voltammetry are good to within about 50 millivolts. Excessive solution resistance or a clogged glass frit at the end of a reference electrode can cause significant measurement errors. (The SCE reference is at +0.2444 volts versus SHE.)

An interesting extension to this experiment is to also use spectroscopy to determine the unknown concentration. This allows students to make a direct comparison between two widely different analytical techniques. To perform this additional procedure, the standard (and unknown) solutions used in this experiment, which have concentrations in the range from 5 to 70 m$\underline{M}$, must be diluted by at least a factor of 100. After this dilution, the solutions should give absorbance readings in the range from 0.2 to 2.0 using 1.0-cm cuvets. Dilutions can be performed using either water or 1.0$\underline{M}$ hydrochloric acid as the solvent.
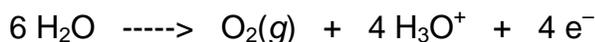
Answers to Prelab Questions

Question 1
At the negative (cathodic) potential limit, hydronium ions are reduced to hydrogen gas according to the following half-reaction:

$$2\,H_3O^+ \;+\; 2\,e^- \;\text{-----}>\; H_2(g) \;+\; 2\,H_2O$$
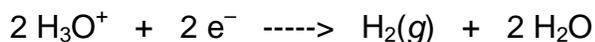
At the positive (anodic) potential limit, water is oxidized to oxygen gas as follows:

$$6\,H_2O \;\text{-----}>\; O_2(g) \;+\; 4\,H_3O^+ \;+\; 4\,e^-$$

Note that either of the above reactions can be written using H$^+$ to denote the hydronium ion as long as the appropriate number of water molecules are removed from both the left and right sides of the balanced equations.

Question 2
The reason for examining standard solutions in order of increasing concentration (in any analytical method) is to minimize the contamination of one standard solution by another. If a new solution is being added to an electrochemical cell that inadvertently contains some of the previous solution, then the amount of contamination is less significant if the previous solution had a lower iron(III) concentration.

Question 3
The main point here is careful attention to unit analysis. The general form of the Randles-Sevcik equation is given below:

$$i_{\text{p}} \; = \; 0.4463 \; n \, F \, A \, C \, (n \, F \, v \, D \, / \, R \, T)^{1/2}$$

Given: $n = 1$
$F = 96485$ C/mol
$A = \pi \, r^2 = 0.19635$ cm^2
$C = 4.5$ m$\underline{M} = 4.5 \times 10^{-6}$ mol/cm^3
$v = 200$ mV/s $= 0.200$ V/s
$D = 7.56 \times 10^{-5}$ cm^2/s
$R = 8.314$ J / mol K $= 8.314$ C V / mol K
$T = 25.0°$C $= 273.15$ K

Result: $i_{\text{p}} = 923.0$ μA

Answers to Report Questions

Question 1
Faster sweep rates generate steeper concentration gradients at the electrode surface, causing larger peak currents. Another way to look at this is that faster scan rates cause the same amount of charge to passed in a shorter period of time. Because current is the ratio of charge to time, a faster sweep rate gives a larger current.

Question 2
The lowest detectable iron(III) concentration (using 100 mV/sec sweep rate) is about 0.4 m$\underline{M}$ and depends on solvent purity.

Question 3
Using the accepted value for the iron(III) cation's diffusion coefficient, a group of such cations would diffuse just 9.0 mm in a single day. Student's results will vary, of course.

References
1)   R.N. Adams, *Electrochemistry at Solid Electrodes* (Marcel Dekker: New York, **1969**) ch. 8.
2)   A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications* (John Wiley & Sons: New York, **1980**) ch. 6.

Experiment 2
DETERMINATION OF ACETAMINOPHEN IN A CHILDREN'S PAIN RELIEF ELIXIR

Description

Acetaminophen (*4-acetamidophenol*) is the active ingredient in several over-the-counter pain relief medications. Several liquid formulations of this medication have been developed for easy administration to children. This experiment uses cyclic voltammetry to determine the concentration of acetaminophen in one of these elixirs. The result is then compared with that stated by the manufacturer on the package label. Note that this experiment is a simplified version of a much more extensive mechanistic experiment described elsewhere[1].

Experimental Apparatus

- Pine Instrument Company AFCBP1 Bipotentiostat
- Pine Instrument Company ASWCV2 **PineChem**™ software package
- Three electrode cell (provision for nitrogen deaeration is optional)
- Glassy carbon electrode
- Platinum auxiliary electrode
- SCE reference electrode
- Alumina polishing solution

Reagents and Chemicals

Description	per expt	per 20 expts*
concentrated perchloric acid ($HClO_4$, 70%)		8 mL
4-acetamidophenol ($C_8H_9NO_2$, 151.2 g/mol)		11 g
potassium chloride (KCl, 74.55 g/mol)	40 g	800 g
sodium hydrogen phosphate heptahydrate ($Na_2HPO_4 \bullet 7H_2O$, 268.1 g/mol)	2 g	40 g
citric acid monohydrate ($C_6H_8O_7 \bullet H_2O$, 210.1 g/mol)	25 g	500 g
acetaminophen elixir (100 g/L)	1 mL	25 mL
ultrapure water		22 L

* includes amounts needed by instructor to prepare stock solution for entire group.

Discussion

Acetaminophen enjoys tremendous popularity as a general pain relief medication. It has largely replaced aspirin as the medication of choice for children and infants. (Aspirin has been linked to the development of Reye's Syndrome in some cases.) Because children typically have a difficult time swallowing pills or capsules, acetaminophen is delivered to them in the form of a liquid solution or *elixir*. The elixir is an aqueous solution containing various

colorings and flavorings and an acetaminophen concentration between 30 and 100 grams per liter. (The recommended dosage for a child is around 80 mg.)

Acetaminophen exhibits what is known as *irreversible* electrochemical behavior. If an analyte can be easily and repeatedly oxidized and reduced at an electrode surface, it is said to exhibit *reversible* electrochemical behavior. An example of such an analyte is the iron(II) cation. It can be oxidized to iron(III) and then reduced back to iron(II) over and over again in a cyclic voltammetry experiment.

The behavior of acetaminophen at an electrode is not so simple. It can be easily oxidized at a working electrode just like the iron(II) cation, but the similarity ends there. Along with losing two electrons, the acetaminophen is rapidly converted to the hydrate of *N-acetyl-4-quinoneimine* as shown in the half-reaction below.

acetaminophen   N-acetyl-4-quinoneimine hydrate
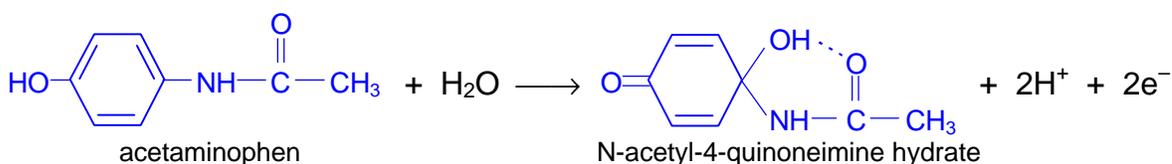
The conversion to hydrated N-acetyl-4-quinoneimine consists of several chemical steps (*i.e.*, the loss of two hydrogens and the addition of water), and once these steps have occurred they cannot easily be reversed. Thus, the electrochemical behavior of acetaminophen is said to be *irreversible*.

The irreversible electrochemical behavior of acetaminophen shows up in a dramatic way when it is studied using cyclic voltammetry (*see* Figure 2.3). When the working electrode potential is swept in a positive direction (towards more oxidizing potentials), an anodic current flows as electrons are removed from the acetaminophen molecules near the electrode surface. The shape of the peak traced out during this forward sweep has the same familiar appearance as any other voltammogram.

However, when the direction of the potential sweep is reversed, no cathodic current is observed during the reverse sweep. Even though the voltammogram exhibited a peak during the forward sweep, there is not a corresponding peak in the reverse sweep. The reason is that the oxidized analyte is no longer present. It has long since been converted to hydrated N-acetyl-4-quinoneimine (which is electrochemically inactive), so that there is now nothing present which can be reduced during the reverse sweep. Thus, no cathodic current flows during the reverse sweep.

While such irreversible behavior on the part of acetaminophen yields an unusual looking voltammogram, the anodic peak observed during the forward sweep is still useful for analytical work. Because the anodic peak current is directly proportional to the acetaminophen concentration, a series of standard solutions of acetaminophen can be studied using cyclic voltammetry, and a calibration curve can be constructed for an analytical determination. Then, an unknown

solution of acetaminophen, such as a commercial elixir, can be examined, and the amount of acetaminophen in the elixir can be determined.

Procedure

All glassware used for electrochemistry should be as clean as possible. The solvents and reagents used to make solutions should be as pure as possible. A supply of ultrapure water is required for proper solution preparation. The ultrapure water can be either deionized, ultrafiltered (DIUF) water or "conductivity water" or "HPLC grade" water.

A. SOLUTION PREPARATION

1) The following stock solution should be prepared by the instructor for use by a group of 20 students. When not in use, this solution should be stored in a refrigerator.

    Acetaminophen Stock Solution (2 liters)

    WARNING: Concentrated perchloric acid poses a very real threat of fire and/or explosion! Take extreme care to prevent the concentrated acid from spilling and/or coming into contact with organic substances. Once diluted, perchloric acid poses much less of a threat. Take the time to read all warning labels associated with this acid.

    Prepare a very clean 2000 mL volumetric flask being sure that the last rinsing of this flask is done with ultrapure water. Fill the flask with about 1500 mL of ultrapure water. Then, using extreme caution, transfer about 8 mL of concentrated (70%) perchloric acid into the flask and mix well. Take the time to rinse all of the acid down the inside walls of the flask and into the solution using ultrapure water. Mix the acid into the water by swirling. Put away the perchloric acid reagent bottle before proceeding.

    Precisely weigh 10.60 grams of acetaminophen into the flask and allow it to dissolve. Once the solid has dissolved completely, fill the flask "to the line" using ultrapure water. The resulting solution has an acetaminophen concentration near 35 m$\underline{M}$. Calculate the exact concentration to four significant digits and provide it to the students.

2) Each individual student should prepare a one liter supply of a special acid buffer that will be used to prepare subsequent solutions of acetaminophen. This special buffer solution will not only maintain the pH at 2.2, but it will also maintain the ionic strength of the solution at 0.5$\underline{M}$. The peak current observed in a cyclic voltammogram is somewhat affected by the ionic strength of the solution, so it is a good idea to have all solutions at the same ionic strength.

    Acid Buffer (1 liter)
    Use ultrapure water to make this solution. Rigorously clean a 1000 mL volumetric flask and make sure that the last rinsing of the flask is done

with ultrapure water. Add the following three solids to the flask using the exact amounts as listed below:

- potassium chloride   KCl   37.20 grams
- sodium hydrogen phosphate heptahydrate $Na_2HPO_4 \bullet 7H_2O$ 1.070 grams
- citric acid monohydrate $C_6H_8O_7 \bullet H_2O$ 20.60 grams

Add about 600 mL of ultrapure water to the flask to dissolve the solids. After dissolution is complete, fill the flask "to the line" using ultrapure water and mix well. Use the *Acid Buffer* solution for all subsequent solution preparation. Return any extra *Acid Buffer* solution to your instructor at the end of the lab period.

Acetaminophen Standard Solutions (100 mL each)

pipette volume (mL)	flask volume (mL)	standard concentration (m$\underline{M}$)
5	100	1.75
7	100	2.45
10	100	3.50
15	100	5.25
20	100	7.00

Using the table above as a guide, prepare five standard solutions by pipetting various volumes of *Acetaminophen Stock Solution* directly into a series of clean 100 mL volumetric flasks. Fill the flasks "to the line" using the *Acid Buffer* solution prepared earlier. The resulting standard solutions will have concentrations near the values listed in the table; however, the student must calculate the actual concentration values taking into account the concentration of the *Acetaminophen Stock Solution* prepared by their instructor.

Elixir Test Solution (100 mL)
Most commercially available elixirs have an acetaminophen concentration around 660 m$\underline{M}$ (100 g/L). The manufacturer's label on the elixir should list the actual concentration, and you should write this information down in your lab notebook for later reference. Note that the elixir label is likely to list the concentration in an unusual way, such as 80 mg per 0.8 mL or perhaps 80 mg per 2.5 mL. Be sure to convert the concentration to units of *molarity* and also *grams per liter* before proceeding.

To prepare the elixir for electrochemical study, it must be diluted down to a concentration on the same order as the standard solutions. If the elixir has the typical concentration of 660 m$\underline{M}$, then a suitable solution can be prepared as follows: Pipet exactly 1.0 mL of elixir directly into a very clean 100 mL volumetric flask. Dilute the flask "to the line" using the *Acid Buffer* solution.

B. BACKGROUND SCAN

A simple *background* voltammogram of the pure *Acid Buffer* is a good way to confirm the purity of the solution, the cleanliness of the glassware, and the preparation of the polished working electrode all in a single step. Any electroactive impurities from the solvent or dirty glassware will show up as unexplained peaks in the background scan. In addition, a fouled or improperly polished electrode surface usually causes a larger background current.

3) Obtain a glassy carbon disk working electrode. Be sure to note the surface area of the disk in square centimeters in your lab notebook. Polish the electrode as needed using an alumina slurry on a polishing cloth. After polishing, wash the electrode with ultrapure water and wipe clean. The electrode surface should be mirror bright and free of defects.

4) Equip a clean electrochemical cell with an SCE reference electrode and a platinum auxiliary electrode. Carefully mount the glassy carbon working electrode in the cell as well.

5) Fill the electrochemical cell with pure *Acid Buffer* solution. If desired, the oxygen in the cell may be purged by first bubbling nitrogen through the solution and then continuously blanketing the solution with a steady flow of nitrogen for the duration of the experiment. Oxygen is unlikely to interfere with this experiment, however.

6) From the INSTRUMENT STATUS panel of the **PineChem** software package, adjust the IDLE CONDITIONS as shown in Figure 2.1. Confirm that the AFCBP1 Bipotentiostat is in DUMMY mode, and then make all necessary electrical connections between the electrodes and the potentiostat. Also, adjust the front panel voltmeter of the AFCBP1 so that it is displaying the working electrode potential (E1). It should confirm that the K1 electrode is idling near zero volts.
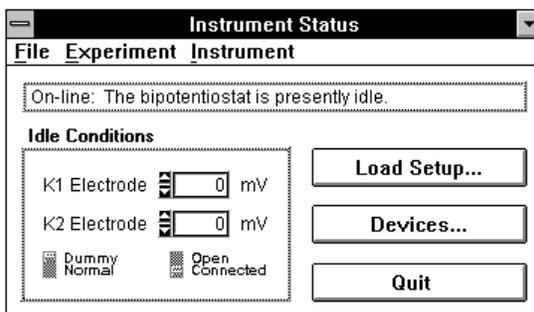

FIGURE 2.1: INITIAL INSTRUMENT STATUS PANEL SETTINGS

7) Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and then enter the experimental parameters shown in Figure 2.2 below. Note that these settings are only suggested starting points for performing a background scan. It may be necessary to make some

adjustments in order to obtain a satisfactory voltammogram. In particular, the ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.

FIGURE 2.2: EXPERIMENTAL SETUP FOR ACETAMINOPHEN VOLTAMMETRY

8)   Once the experiment settings have been adjusted to match those in Figure 2.2, click on the PERFORM button to initiate the experiment. The resulting cyclic voltammogram should be relatively featureless and exhibit no significant peaks. If significant peaks are apparent, then the glassware, electrode surface and/or solvent are contaminated.   If the background current is excessive, the electrode should be polished.

9)   After acquiring a satisfactory background voltammogram, save it on the disk and/or print it out on the printer.

C.   VOLTAMMOGRAMS OF STANDARDS AND ELIXIR

In this part of the experiment, several cyclic voltammograms are obtained with solutions of varying concentration.   At least five standard solutions, with acetaminophen concentrations ranging from 1.0 to 7.0 m$\underline{M}$, should be used. The standards should be prepared using the *Acid Buffer* as the solvent.

10)   Equip a clean electrochemical cell with an SCE reference electrode and a platinum auxiliary electrode. Carefully mount the glassy carbon working electrode in the cell as well.

11)   Fill the electrochemical cell with the standard solution that has the lowest acetaminophen concentration.   Make sure that all three electrodes are immersed in the solution. If desired, the oxygen in the cell may be purged using nitrogen.

12) Before making electrical connections between the cell and the potentiostat, it is a good idea to place the AFCBP1 Bipotentiostat in DUMMY mode. This can be accomplished by adjusting the controls on the INSTRUMENT STATUS panel so that they match the settings in Figure 2.1.

13) Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and adjust the experiment settings so that they match Figure 2.2. The ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.

14) Once the experiment settings have been adjusted to match those in Figure 2.2, click on the PERFORM button to initiate the experiment. A fairly prominent anodic wave should appear during the sweep from zero mV to +1000 millivolts. On the return sweep, no cathodic wave should be apparent. Figure 2.3 shows a typical voltammogram for acetaminophen. Note that as displayed by the software, positive potentials are plotted to the right and anodic currents are plotted toward to the top of the graph.

15) After acquiring a satisfactory voltammogram, save it on the disk and/or print it out on the printer.

16)
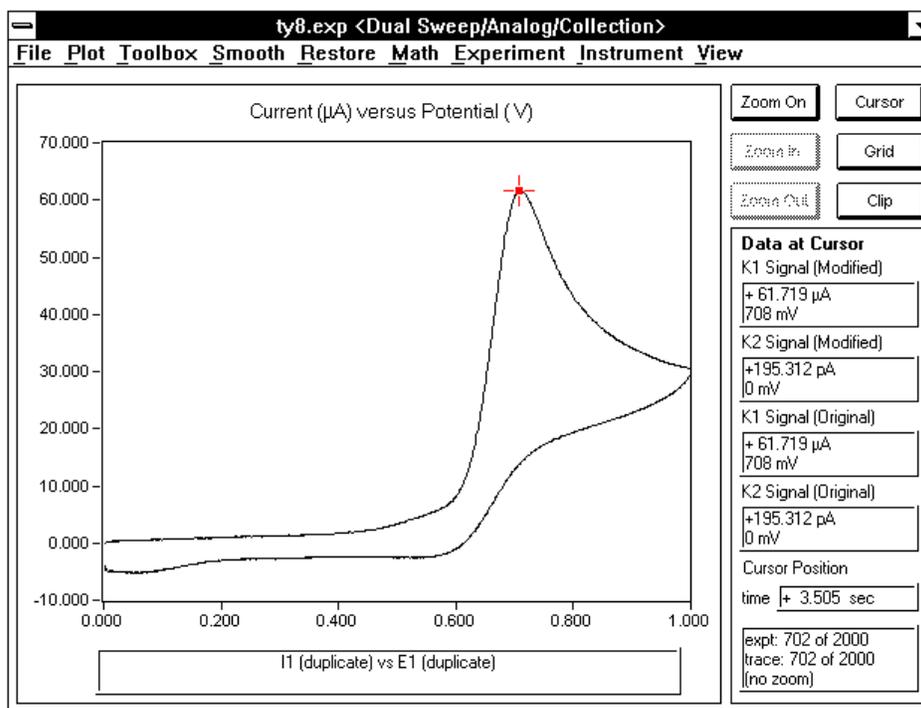
FIGURE 2.3: TYPICAL ACETAMINOPHEN VOLTAMMOGRAM

16) Plot the voltammogram as a current versus time graph by choosing the **I1 vs. t** option from the **Plot** menu. Then, use the **Peak Height Tool** found in the **Toolbox** menu to measure the height of the anodic peak as shown in Figure 2.4.
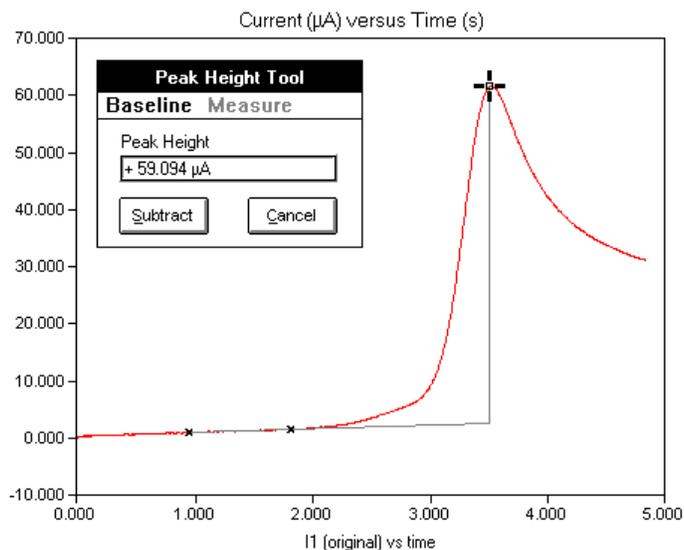
FIGURE 2.4: MEASURING THE PEAK HEIGHT

17) Acquire similar voltammograms for the remaining standard solutions in order of increasing acetaminophen concentration. Use the same sweep rate (200 mV/s) for all solutions. Clean the cell between solutions.

18) Acquire a voltammogram of the *Elixir Test Solution* using the same experimental parameters as for the standard solutions. Clean the cell and electrodes well before filling the cell with the test solution.

Data Analysis

Calibration Curve

a) Using the anodic peak currents for the series of standard solutions, prepare a plot of peak current versus concentration. (Make sure that each of the voltammograms was acquired using the same sweep rate.)

b) Perform a linear least squares analysis on the data to find the equation of the best straight line which fits the data.

Elixir Concentration

d) Using the equation from (b), above, compute the concentration of acetaminophen in the elixir. Remember to take into account any dilution of the original elixir during the solution preparation process. Report the acetaminophen concentration in *grams per liter* using three significant figures.

e) Convert the acetaminophen concentration listed on the manufacturer's label to units of *grams per liter* using three significant figures.

f) Assuming the manufacturer's label gives the "correct" concentration, what was the percent error in your result?

Report Questions

1) List at least two reasons that are outside of your control that could explain why your result differs from that listed on the manufacturer's label.

2) How would your results have been affected if you had failed to measure the anodic peak current against the proper background baseline?

3) Examine the peak height shown in Figure 2.4. Given that the oxidation of acetaminophen involves the removal of two electrons from the molecule, how many molecules per second must be oxidized in order to produce the peak current observed in Figure 2.4?

4) Examine the observed currents (at E^o) for each of the standard solutions and for the background scan. Then give a rough estimate of the following concentrations:
   (a) At what concentration does the anodic current equal ten times the charging current? This concentration is defined as the Limit of Quantitation (LOQ).
   (b) At what concentration does the anodic current equal three times the charging current? This concentration is defined as the Limit of Detection (LOD).

Instructor's Notes

The pH-dependent electrochemical behavior of acetaminophen has been examined and a more extensive lab experiment has been reported in Ref. 1. This reference suggests using a solid acetaminophen tablet as the commercial unknown, but it is usually difficult to get a tablet to dissolve completely (due to insoluble binding agents in the tablet). Using a liquid form of acetaminophen is much easier.

The buffer used in this experiment buffers both the pH and the ionic strength of the solution. Directions for the preparation of a series of these buffers covering a range of pH (2 to 8) are given in Ref. 2.

Glassy carbon electrodes need frequent repolishing. If you notice any unusual electrochemical behavior from the acetaminophen solutions, try repolishing the electrode before assuming the solution is bad.

Target solution volumes for this experiment are 100 mL. If you have a small volume electrochemical cell available, you may wish to cut the amounts of reagents in half to conserve ultrapure water.

A titrimetric assay for acetaminophen with a colorimetric endpoint exists. The analyte is converted to 3-nitroacetaminophen using nitrous acid. Then, standard sodium hydroxide solution is used to titrate to the endpoint. The endpoint is signaled by the appearance of the yellow 3-nitroacetaminophen anion (λ = 430 nm). It may be of interest to have students use this method to confirm their electrochemical results.

Answers to Report Questions

Question 1
While there are any number of reasons for discrepancy between student results and the actual concentration, several are listed below for reference.

- The formulation of any one particular batch of the elixir is likely to have an acetaminophen concentration different than that on the label. Presumably, drug manufacturing companies have good quality control, so the concentration is not likely to vary much from batch to batch.
- Similarly, the students rely on the acetaminophen standard prepared by the instructor.
- Using a fouled or dirty electrode.
- Dilution errors
- The acetaminophen might bind to some other component of the elixir, thus the concentration of the "free" acetaminophen might be lower than the total.
- Other components of the elixir may cause the viscosity or solution resistance of the test solution to be significantly different than the standard solutions. This can cause distortion of the peak current observed for the test solution.

Question 2

Failure to remove background current from the *Elixir Test Solution* signal causes the reported concentration to be too high. Failure to remove background current from standard solution signals skews the calibration curve. The skewing is more pronounced at lower concentrations.

Question 3

The observed peak current is 59.094 μA. Using 96485 C/mol as the value for Faraday's constant, this current corresponds to a flow of 3.688×10^{14} electrons per second. This is chemically equivalent to oxidizing 1.84×10^{14} molecules per second.

References

1) J.J. Van Benschoten, J.Y. Lewis, W.R. Heineman, D.A. Roston, P.T. Kissinger, *J. Chem. Ed. 60* (**1983**) 772.
2) P.J. Elving, J.M. Markowitz, I. Rosenthal, *Analytical Chemistry 28* (**1956**) 1179.

<div style="border: 1px solid black;">

Experiment 3
SURVEY OF THREE VOLTAMMETRIC METHODS

</div>

Description

The purpose of this experiment is to compare and contrast three different voltammetric methods by using each method, in turn, to examine the very same analyte solution. The methods studied are *cyclic voltammetry*, *rotated disk voltammetry*, and *chronoamperometry*. Each method is used to determine the diffusion coefficient of the analyte.

Experimental Apparatus

- Pine Instrument Company AFCBP1 Bipotentiostat
- Pine Instrument Company ASWCV2 **PineChem**™ software package
- Pine Instrument Company AFMSRX Analytical Rotator
- Platinum rotated disk electrode (mounted on arbor)
- Three electrode cell (with large opening for rotated disk electrode)
- Platinum auxiliary electrode
- SCE reference electrode
- Alumina polishing solution

Reagents and Chemicals

Description	per expt	per 20 expts
potassium ferricyanide, $K_3Fe(CN)_6$ (329.26 g/mol)	250 mg	5 g
potassium nitrate, KNO_3 (101.11 g/mol)	30 g	600 g
ultrapure water	300 mL	6 L

Discussion

A general definition for the term *voltammetry* is any electrochemical technique that involves controlling the potential of an electrode while simultaneously measuring the current flowing at that electrode. The electrode in question is usually referred to as the *working electrode* in order to distinguish it from other electrodes that are present in the electrochemical cell.

Voltammetry is usually performed by connecting an electrochemical potentiostat to an electrochemical cell. The cell contains a test solution and three electrodes: *working*, *reference*, and *auxiliary*. Special electronic circuitry within the potentiostat permits the working electrode potential to be controlled with respect to the reference electrode *without any appreciable current flowing at the reference electrode*. Rather, the current is forced to flow between the working electrode and the auxiliary electrode. This unusual arrangement has two principle benefits. First, the reference electrode is protected from internal

electrochemical changes caused by current flow. Second, measurement errors related to the resistance of the test solution are kept to a minimum.

There are quite a number of voltammetric techniques. Each differs in the precise manner that the working electrode potential is changed during the experiment. In some techniques, a potential sweep is applied to the working electrode, in others, a sudden potential step or complex pulse sequence is used. Another distinguishing feature is whether or not the solution is moving with respect to the surface of the working electrode. In most cases, the solution is motionless, but there exist many *hydrodynamic* methods in which solution moves toward the electrode along a well-defined flow pattern.

This experiment compares two very common voltammetric techniques, *cyclic voltammetry* and *chronoamperometry*, with a hydrodynamic technique called *rotated disk voltammetry*. The three techniques share a lot in common, but each gives its own unique experimental response. In order to provide a very direct comparison, the same analyte solution is analyzed using all three techniques.

The analyte used in this experiment is the ferricyanide anion, $Fe(CN)_6^{3-}$, which contains an iron atom in the +3 oxidation state. At the surface of a working electrode, a single electron can be added to the ferricyanide anion. This causes it to be reduced to the *ferro*cyanide anion, $Fe(CN)_6^{4-}$, which contains an iron atom in the +2 oxidation state. This simple one electron exchange between the analyte and the electrode is very well behaved, and it is *reversible*. This means that the analyte can be easily reduced to $Fe(CN)_6^{4-}$ and then easily oxidized back to $Fe(CN)_6^{3-}$ again.

A pair of analytes differing only in oxidation state is known as a *redox couple*. The electrochemical half-reaction for the $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$ redox couple can be written as follows:

$$Fe(CN)_6^{3-} \;+\; e^- \;\Longleftrightarrow\; Fe(CN)_6^{4-} \tag{3.1}$$

The formal potential associated with this half-reaction is near +400 mV vs. the normal hydrogen electrode (NHE). If the working electrode is held at a potential more positive than +400 mV, then the analyte tends to be oxidized to the $Fe(CN)_6^{3-}$ form. This oxidation at the working electrode causes an *anodic* current to flow (*i.e.*, electrons go into the electrode from the solution). At potentials more negative than +400 mV, the analyte tends to be reduced to $Fe(CN)_6^{4-}$. This reduction at the working electrode causes a *cathodic* current to flow (*i.e.*, electrons flow out of the electrode into the solution).

Cyclic Voltammetry

In *cyclic voltammetry*, the working electrode potential is swept back and forth across the formal potential of the analyte. Repeated reduction and oxidation of the analyte causes alternating cathodic and anodic currents flow at the electrode. The solution is not stirred. Experimental results are usually plotted as a graph of current versus potential, and a voltammogram like that shown in Figure 3.3 is

recorded. The voltammogram exhibits two asymmetric peaks, one cathodic and the other anodic.

The signal of primary interest to the analytical chemist is the height of the peak. The peak height, i_p, is directly proportional to the analyte concentration, C, as described by the *Randles-Sevcik* equation:

$$i_p = 0.4463\, n\, F\, A\, C\, (n\, F\, v\, D\, /\, R\, T)^{1/2} \tag{3.2}$$

In this equation, n is the number of electrons appearing in half-reaction for the redox couple, v is the rate at which the potential is swept (V / sec), F is Faraday's constant (96485 C / mol), A is the electrode area (cm^2), R is the universal gas constant (8.314 J / mol K), T is the absolute temperature (K), and D is the analyte's diffusion coefficient (cm^2/sec). Note that if the temperature is assumed to be 25°C (298.15K), the Randles-Sevcik can be written in a more concise form,

$$i_p = (2.687\text{x}10^5)\, n^{3/2}\, v^{1/2}\, D^{1/2}\, A\, C \tag{3.3}$$

where the constant is understood to have units (*i.e.*, $2.687\text{x}10^5$ C mol^{-1} V $^{-1/2}$).

Chronoamperometry

In *chronoamperometry*, the working electrode potential is suddenly stepped from an initial potential to a final potential, and the step usually crosses the formal potential of the analyte. The solution is not stirred. The initial potential is chosen so that no current flows (*i.e.*, the electrode is held at a potential that neither oxidizes or reduces the predominant form of the analyte). Then, the potential is stepped to a potential that either oxidizes or reduces the analyte, and a current begins to flow at the electrode. This current is quite large at first, but it rapidly decays as the analyte near the electrode is consumed (*see* Figure 3.9).

The signal in chronoamperometry is transient. If the point in time when the potential is stepped is taken as time zero, then the *Cottrell* equation describes the how the current, $i(t)$, decays as a function of time, t

$$i(t) = n\, F\, A\, C\, (D\, /\, p)^{1/2}\, t^{-1/2} \tag{3.4}$$

Although the current decay may appear to be exponential, it actually decays as the reciprocal of the square root of time. This dependence on the square root of time reflects the fact that physical diffusion is responsible for transport of the analyte to the electrode surface.

Rotated Disk Voltammetry

Rotated disk voltammetry is similar to cyclic voltammetry in that the working electrode potential is (slowly) swept back and forth across the formal potential of analyte. It differs significantly in that the working electrode itself is rotated at a very high speed. This rotational motion sets up a well defined flow of solution towards the surface of the rotating disk electrode. The flow pattern is akin to a vortex that literally sucks the solution (and the analyte) towards the electrode.

Experimental results are generally plotted as a graph of current versus potential, and a typical rotated disk voltammogram is shown in Figure 3.6. The

voltammogram exhibits a sigmoidal shaped wave, and the height of this wave provides the analytical signal.

It is important to note that the layer of solution immediately adjacent to the surface of the electrode behaves as if it were stuck to the electrode. While the bulk of the solution is being stirred vigorously by the rotating electrode, this thin layer of solution manages to cling to the surface of the electrode and appears (from the perspective of the rotating electrode) to be motionless. This layer is called the *stagnant layer* in order to distinguish it from the remaining bulk of the solution.

Analyte is conveyed to the electrode surface by a combination of two types of transport. First, the vortex flow in the bulk solution continuously brings fresh analyte to the outer edge of the stagnant layer. Then, the analyte moves across the stagnant layer via simple molecular diffusion. The thinner the stagnant layer, the faster the analyte can diffuse across it and reach the electrode surface. Faster electrode rotation makes the stagnant layer thinner. Thus, faster rotation rates allow the analyte to reach the electrode faster, resulting in a higher current being measured at the electrode.

The *Levich* equation predicts the current observed at a rotating disk electrode. This equation takes into account both the rate of diffusion across the stagnant layer and the complex solution flow pattern. In particular, the Levich equation gives the height of the sigmoidal wave observed in rotated disk voltammetry. The sigmoid wave height is often called the Levich current, i_L, and it is directly proportional to the analyte concentration, C. The Levich equation is written as

$$i_L = (0.620)\ n\ F\ A\ D^{2/3}\ \omega^{1/2}\ \nu^{-1/6}\ C \tag{3.5}$$

where ω is the angular rotation rate of the electrode (radians/sec) and ν is the kinematic viscosity of the solution (cm^2/sec). The kinematic viscosity is the ratio of the solution viscosity to its density. For pure water, $\nu = 0.0100\ cm^2$/sec, and for the solvent used in this experiment (1.0$\underline{M}$ KNO_3), $\nu = 0.00916\ cm^2$/sec.

Procedure

All glassware used for electrochemistry should be as clean as possible. The solvents and reagents used to make solutions should be as pure as possible. A supply of ultrapure water is required for proper solution preparation. The ultrapure water can be either deionized, ultrafiltered (DIUF) water or "conductivity water" or "HPLC grade" water.

A.   SOLUTION PREPARATION

The two solutions required for this experiment should be prepared by the student. The *Electrolyte Solution* is 1.0 $\underline{M}$ potassium nitrate (KNO_3) in water. This solution provides an electrically conductive solvent suitable for use with voltammetry. The *Analyte Solution* is an 6.4 m$\underline{M}$ solution of potassium ferricyanide made using the *Electrolyte Solution* as the solvent.

1) **Electrolyte Solution (250 mL)**
   Prepare a very clean 250 mL volumetric flask being sure that the last rinsing of this flask is done with ultrapure water. Transfer about 25.30 grams of potassium nitrate (KNO_3) to the flask. Fill the flask with about 200 mL of ultrapure water and allow the potassium nitrate to dissolve. Once dissolution is complete, fill the flask "to the line" using ultrapure water and mix well. The resulting solution is about 1.0$\underline{M}$ KNO_3.

2) **Analyte Solution (100 mL)**
   Prepare a very clean 100 mL volumetric flask being sure that the last rinsing of this flask is done with ultrapure water. Using a sensitive microbalance, transfer exactly 210.7 milligrams of potassium ferricyanide, $K_3Fe(CN)_6$, into the flask. Fill the flask with about 75 mL of *Electrolyte Solution* and allow the $K_3Fe(CN)_6$ to dissolve. Once dissolution is complete, fill the flask "to the line" using *Electrolyte Solution* and mix well. The resulting solution should have an analyte concentration of 6.4 m$\underline{M}$, but the student should compute a more accurate concentration based on the actual mass of $K_3Fe(CN)_6$ that was used to prepare the solution.

B. BACKGROUND SCAN

A simple *background* voltammogram of the pure *Electrolyte Solution* is a good way to confirm the purity of the solution, the cleanliness of the glassware, and the preparation of the polished working electrode all in a single step. Any electroactive impurities from the solvent or dirty glassware will show up as unexplained peaks in the background scan. In addition, a fouled or improperly polished electrode surface usually causes a larger background current.

3) Obtain a platinum disk working electrode suitable for mounting in the electrode rotator apparatus. Be sure to note the surface area of the disk in square centimeters in your lab notebook. Polish the electrode as needed using an alumina slurry on a polishing cloth. After polishing, wash the electrode with ultrapure water and wipe clean. The electrode surface should be mirror bright and free of defects.

4) Equip a clean electrochemical cell with an SCE reference electrode and a platinum auxiliary electrode. Carefully mount the platinum disk working electrode in the rotator and then lower it into the cell. Note that the electrode should not be rotating during the background scan.

5) Fill the electrochemical cell with pure *Electrolyte Solution*. If desired, the oxygen in the cell may be purged by first bubbling nitrogen through the solution and then continuously blanketing the solution with a steady flow of nitrogen for the duration of the experiment. Oxygen is unlikely to interfere with this experiment, however.

6) Use the INSTRUMENT STATUS panel of the **PineChem** software package to place the AFCBP1 Bipotentiostat in DUMMY mode. Then, make all

necessary electrical connections between the potentiostat and the electrochemical cell.

7) Next, adjust the IDLE CONDITIONS on the INSTRUMENT STATUS panel to match those shown in Figure 3.1. Look at the front panel on the AFCBP1 Bipotentiostat and confirm that it is in NORMAL mode. Also, adjust the front panel voltmeter so that it is displaying the working electrode potential (E1). It should confirm that the K1 electrode is idling near +800 mV.
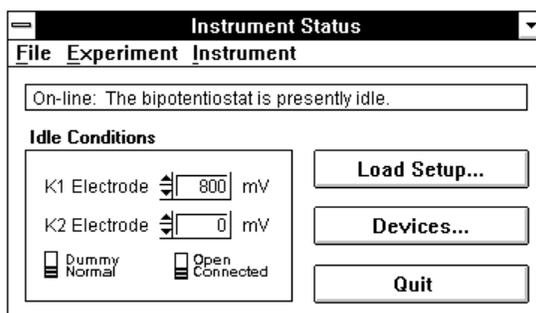

FIGURE 3.1: INITIAL INSTRUMENT STATUS PANEL SETTINGS

8) Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and then enter the experimental parameters shown in Figure 3.2. Note that these settings are only suggested starting points for performing a background scan. It may be necessary to make some adjustments in order to obtain a satisfactory voltammogram. In particular, the ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.

9) Once the experiment settings have been adjusted to match those in Figure 3.2, click on the PERFORM button to initiate the experiment. The resulting cyclic voltammogram should be relatively featureless and exhibit no significant peaks. At negative potentials, the voltammogram should exhibit some cathodic current due to the reduction of hydronium ion. If the background current is excessive, the electrode should be polished and/or the *Electrolyte Solution* is contaminated.

10) After acquiring a satisfactory background voltammogram, save it on the disk and/or print it out on the printer.
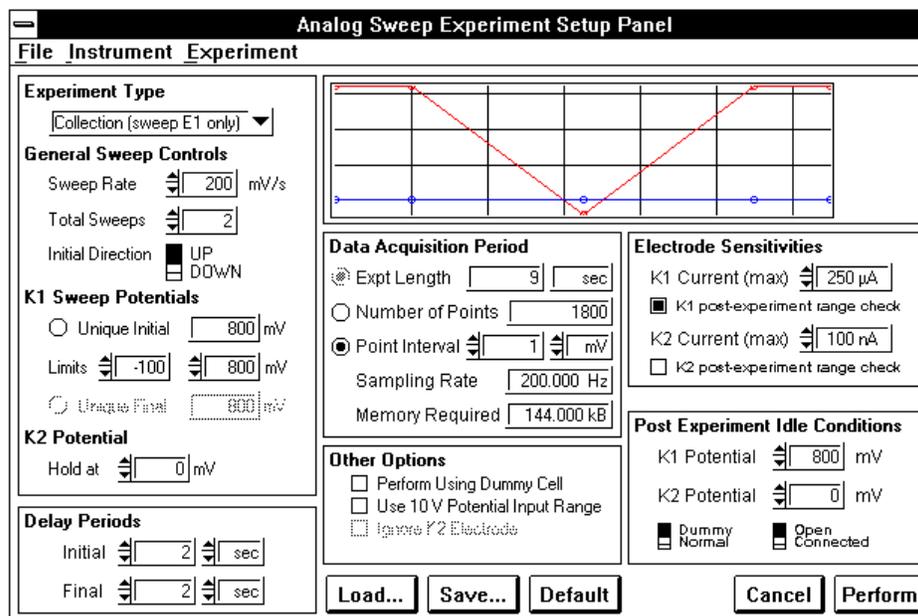
FIGURE 3.2: EXPERIMENTAL SETUP FOR CYCLIC VOLTAMMETRY

C. CYCLIC VOLTAMMETRY

In this part of the experiment, several cyclic voltammograms are obtained using various sweep rates. The same *Analyte Solution* should be used for all voltammograms, and the electrode should not be rotating.

11) Equip a clean electrochemical cell with an SCE reference electrode and a platinum auxiliary electrode. Carefully mount the platinum disk working electrode in the rotator and then lower it into the cell. (Note that the electrode is not to be rotated during this part of the experiment, the rotator simply serves as a convenient way to mount the electrode.)

12) Fill the electrochemical cell with the *Analyte Solution*. If desired, the oxygen in the cell may be purged by first bubbling nitrogen through the solution and then continuously blanketing the solution with a steady flow of nitrogen for the duration of the experiment. Oxygen is unlikely to interfere with this experiment, however.

13) Place the AFCBP1 Bipotentiostat in dummy mode using the controls found on the INSTRUMENT STATUS panel of the **PineChem** software. Then, make all necessary electrical connections between the electrodes and the potentiostat. Also, adjust the front panel voltmeter of the AFCBP1 so that it is displaying the working electrode potential (E1).

14) From the INSTRUMENT STATUS panel of the **PineChem** software package, adjust the IDLE CONDITIONS as shown in Figure 3.1. Confirm that the AFCBP1 Bipotentiostat is now in NORMAL mode, and that the K1 electrode is idling near +800 millivolts.

15) Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and adjust the experiment settings so that they match Figure 3.2. Note that these settings are for a cyclic voltammetry experiment in which the potential is swept from +800 mV down to –100 mV and back using a sweep rate of 200 mV/sec. Note also that the ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.

16) Once the experiment settings have been adjusted to match those in Figure 3.2, click on the PERFORM button to initiate the experiment. A fairly prominent cathodic wave should appear during the sweep from +800 mV to –100 mV. On the return sweep, an anodic wave of equal size should be apparent. Figure 3.3 shows a typical voltammogram of potassium ferricyanide. Note that as displayed by the **PineChem**™ software, positive potentials are plotted to the right and anodic currents are plotted toward to the top of the graph.
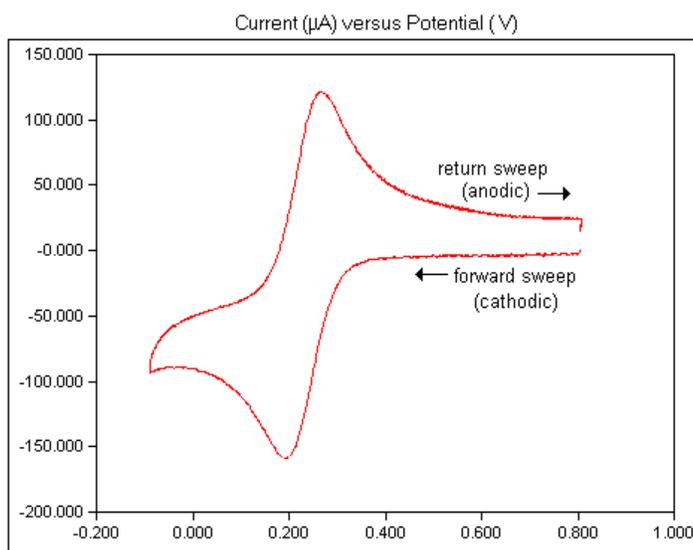
FIGURE 3.3: A CYCLIC VOLTAMMOGRAM FOR POTASSIUM FERRICYANIDE

17) After acquiring a satisfactory voltammogram, save it on the disk and/or print it out on the printer.

18) Next, plot the voltammogram as a current versus time graph by choosing the **I1 vs. t** option from the **Plot** menu. Then, use the **Peak Height Tool** found in the **Toolbox** menu to measure the height of the anodic peak as shown in Figure 3.4. Note that the cathodic peak is the first peak and that it points downward on the **I1 vs. t** plot. The software presents the peak height result as a negative number, but you should record it as a positive number. Write down both the peak height and the sweep rate in your lab notebook.
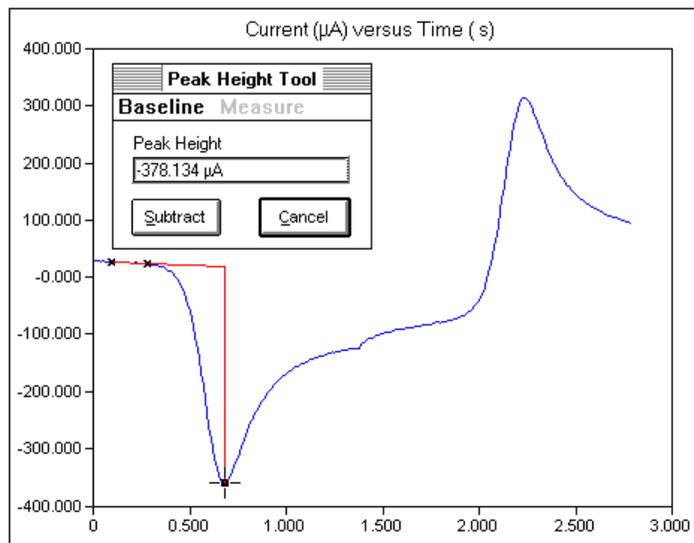
FIGURE 3.4: MEASURING THE PEAK HEIGHT

19) In addition to the voltammogram just acquired at 200 mV/sec, repeat steps 15 through 18 as needed to acquire voltammograms at these four other sweep rates: 150, 100, 75, and 50 mV/sec. In each case, be sure to note the sweep rate and the peak height in your lab notebook.

20) Leave the *Analyte Solution* in the electrochemical cell for use with the next part of the experiment.

D. ROTATED DISK VOLTAMMETRY

In this part of the experiment, several rotated disk voltammograms are obtained using various rotation rates. The same *Analyte Solution* is used for all voltammograms.

21) Turn on the electrode rotator and adjust the rotational speed of the electrode to 4000 RPM. Make certain that the flow of solution in the cell is non-chaotic and that the surface of the rotating electrode remains immersed in the solution.

22) Select the **Analog Sweep Voltammetry** option from the **Experiment** menu and adjust the experiment settings so that they match Figure 3.5. These settings correspond to a slow (10 mV/s) sweep of the potential from +500 mV down to –100 mV and then back again. Note that the ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.
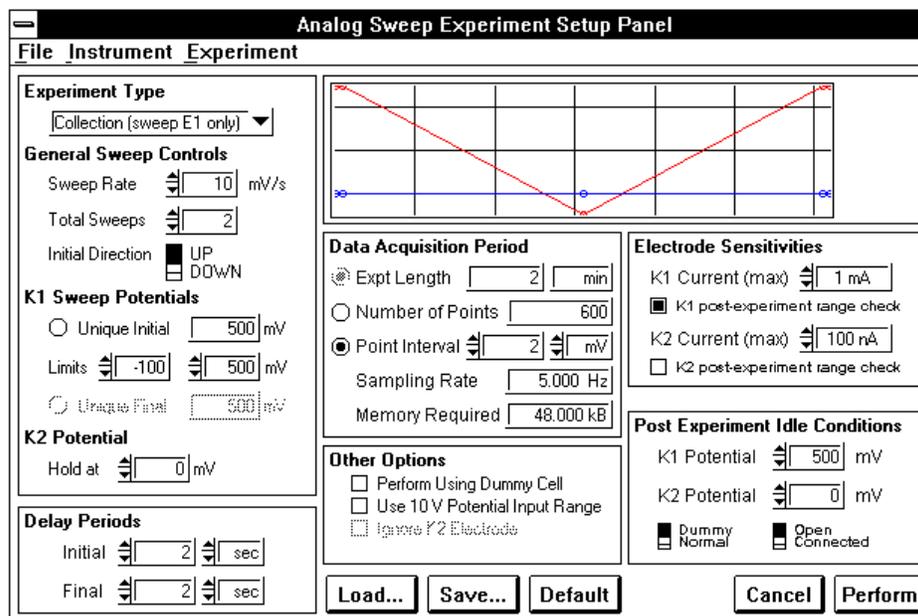
57

FIGURE 3.5: EXPERIMENTAL SETUP FOR ROTATED DISK VOLTAMMETRY

23) Once the experiment settings have been adjusted to match those in Figure 3.5, click on the PERFORM button to initiate the experiment. A fairly prominent cathodic wave should appear during the sweep from +500 mV to –100 mV. The wave should have a sigmoidal appearance rather than the asymmetric peak shape observed during cyclic voltammetry. On the return sweep, the current signal should retrace the path followed during forward sweep. Figure 3.6 shows a typical rotated disk voltammogram for potassium ferricyanide. Note that as displayed by the software, positive potentials are plotted to the right and cathodic currents are plotted toward to the bottom of the graph.
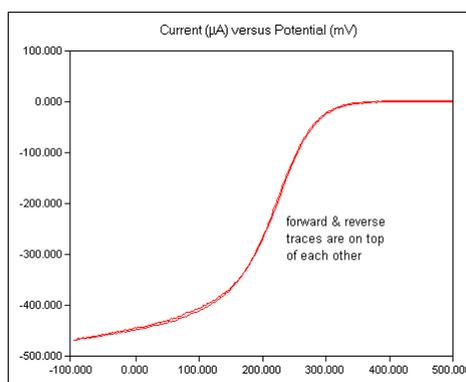
FIGURE 3.6: A ROTATED DISK VOLTAMMOGRAM FOR FERRICYANIDE

24) After acquiring a satisfactory voltammogram, save it on the disk and/or print it out on the printer.

25) Plot the voltammogram as a current versus time graph by choosing the **I1 vs. t** option from the **Plot** menu. The voltammogram has an unusual appearance when plotted in this fashion. Then, use the **Sigmoid Height Tool** found in the **Toolbox** menu to measure the height of the sigmoid as shown in Figure 3.7. Write down the sigmoid height and the rotation rate in your lab notebook. Note that the sigmoid height is the Levich current.
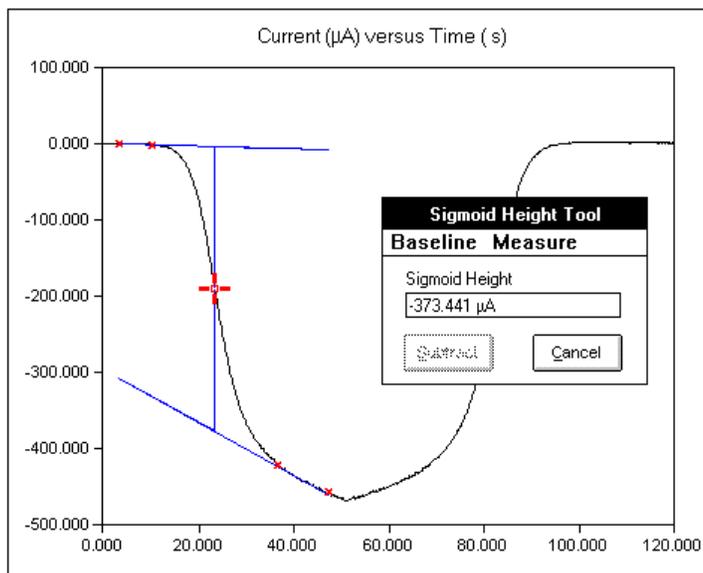

FIGURE 3.7: MEASURING THE HEIGHT OF A SIGMOIDAL FEATURE

26) In addition to the voltammogram just acquired at 4000 RPM, repeat steps 23 through 25 and acquire voltammograms at these other four rotation rates: 3200, 2500, 1600, and 900 RPM. In each case, be sure to note the rotation rate and the Levich current in your lab notebook.

27) Leave the *Analyte Solution* in the electrochemical cell for use with the next part of the experiment.

E. CHRONOAMPEROMETRY

In this part of the experiment, a simple potential step is applied to the working electrode, and a chronoamperometry result is recorded.

28) Turn off the electrode rotator and wait for the solution to stop moving.

29) Select the **Electrolysis** option from the **Experiment** menu and adjust the experiment settings so that they match Figure 3.8. These settings are for a chronoamperometry experiment where the working electrode potential is stepped from +500 mV to zero mV. Note that the ELECTRODE SENSITIVITY for the K1 CURRENT may need to be altered.
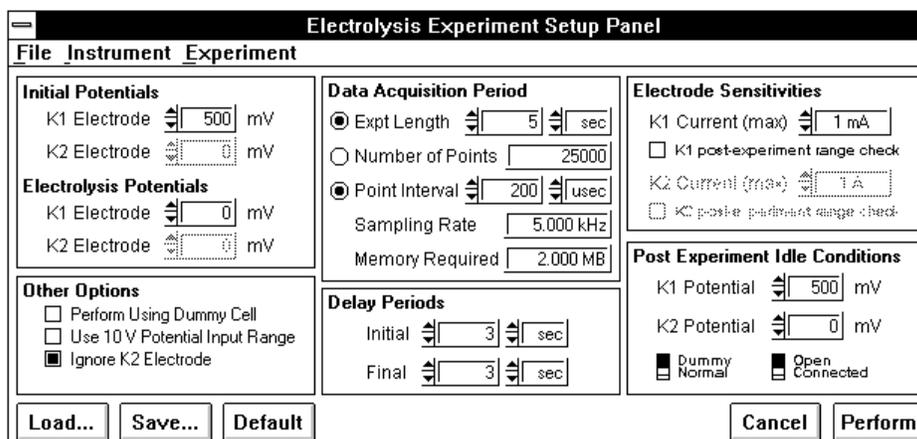
FIGURE 3.8: EXPERIMENTAL SETUP FOR CHRONOAMPEROMETRY

30) Once the experiment settings have been adjusted to match those in Figure 3.8, click on the PERFORM button to initiate the experiment. A current transient that decays away rather rapidly should be observed. Figure 3.9 shows a chronoamperometry result for a solution of potassium ferricyanide. Note that as displayed by the **PineChem**™ software, cathodic currents are plotted in the downward direction.
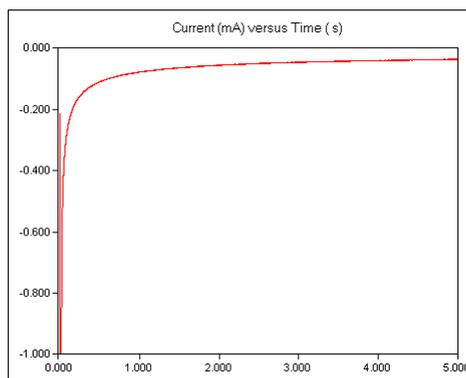

FIGURE 3.9: TYPICAL CHRONOAMPEROMETRY RESPONSE

31) After acquiring a satisfactory chronoamperometry result, save it on the disk and/or print it out on the printer.

32) Using the DATA AT CURSOR display provided by the **PineChem**™ software, pick ten data points from your results and write down the time and current for each of the ten points. Be sure the ten data points you choose span the entire range of useful data from 100 msec to 5 sec. This data is used later to produce a Cottrell plot.

Data Analysis

Cyclic Voltammetry

a) Using the cathodic peak currents from the series of cyclic voltammograms acquired at various sweep rates, prepare a plot of peak current versus the square root of sweep rate.

b) Perform a linear least squares analysis on the data to find the equation of the best straight line which fits the data.

c) Use the slope of the line together with the Randles-Sevcik equation to estimate the diffusion coefficient for the ferricyanide anion. Pay close attention to proper units and report your answer in cm^2/sec.

Rotated Disk Voltammetry

d) Using the Levich currents (sigmoid heights) from the series of rotated disk voltammograms acquired at various rotation rates, prepare a plot of the Levich current versus the square root of the angular rotation rate. Note that the rotation rates may have to be converted from units of RPM to radians per second using the relationship $\omega = 2 \pi f / 60$.

e) Perform a linear least squares analysis on the data to find the equation of the best straight line which fits the data.

f) Use the slope of the line together with the Levich equation to estimate the diffusion coefficient for the ferricyanide anion. Pay close attention to proper units and report your answer in cm^2/sec. Note that the kinematic viscosity for 1.0$\underline{M}$ KNO$_3$ is 0.00916 cm^2/sec.

Chronoamperometry

g) Using the ten data points extracted from your chronoamperometry result, prepare a plot of the current versus the reciprocal of the square root of time (*current vs.* $1/\sqrt{time}$). Such a plot is called a Cottrell plot.

h) Perform a linear least squares analysis on the data to find the equation of the best straight line which fits the data.

i) Use the slope of the line together with the Cottrell equation to estimate the diffusion coefficient for the ferricyanide anion. Pay close attention to proper units and report your answer in cm^2/sec.

Report Questions

1) List the three diffusion coefficient results that you obtained and compute the average result. Which of the three techniques do you believe yielded the most reliable result?

2)   For all three techniques, the method by which the analyte arrives at the electrode surface is diffusion. The distance that a molecule diffuses in a given amount of time is always related to the square root of the time. Show how this dependence on the square root of time manifests itself in each of the three voltammetric techniques studied. (*Hint*: examine the units on each of the variables appearing in the Randles-Sevcik, Levich, and Cottrell equations.)

Instructor's Notes

This experiment is a good introductory procedure for getting students acquainted with modern voltammetry. If you only enough time in your lab schedule for one voltammetry experiment, then this one is good for giving students a broad exposure to the topic.

A major advantage to this experiment is that once the students fill the cell with the *Analyte Solution*, the solution remains in the cell until the end of the experiment. This experiment goes much faster compared to other procedures which involve extensive solution transfers.

If your students do not have access to a microbalance or if you wish to further simplify the solution preparation step, you may wish to purchase a commercially available *Stock Solution* of potassium ferricyanide. For example, Fisher Scientific sells a 10% (w/v) potassium ferricyanide solution (cat # LC19050-1). While this is not a standardized solution, it is still reasonable to assume that the potassium ferricyanide concentration is 105.3 g/L or 320 m$\underline{M}$. Using this *Stock Solution*, the directions for step (2) in the procedure can be replaced as follows:

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2) **Analyte Solution (100 mL)**
Prepare a very clean 100 mL volumetric flask being sure that the last rinsing of this flask is done with ultrapure water. Using a pipette, transfer exactly 2.000 mL of the $K_3Fe(CN)_6$ *Stock Solution* into the flask. Fill the flask "to the line" using *Electrolyte Solution* and mix well. Given that the *Stock Solution* is 320 m$\underline{M}$ $K_3Fe(CN)_6$, the resulting *Analyte Solution* should be 6.4 m$\underline{M}$ $K_3Fe(CN)_6$. The student should confirm these concentrations as needed.

Once the students have finished acquiring all of the data, they have to do quite a bit of data manipulation to extract the diffusion coefficients. It is a good idea to provide students with a scientific graphing software package capable of performing a linear least squares analysis rather than requiring them to do the analysis manually.

The experimental data used to prepare the figures for this document has been analyzed for your reference. All of this data was obtained using a platinum rotating disk electrode (diameter 5.0 mm, area 0.1963 cm^2) to study a 2.55 m$\underline{M}$ potassium ferricyanide solution. Note that this is a smaller analyte concentration than that called for in the procedure.

Sample Cyclic Voltammetry Results

Figure 3.10 below shows the cathodic wave from each of five voltammograms taken at 200, 150, 100, 75, and 50 mV/sec. As expected, the peak current increases with larger sweep rates. The Randles-Sevcik equation predicts that the peak current should be proportional to the square root of the sweep rate. For the particular experiment depicted in Figure 3.10, the electrode area, *A*, was 0.1963 cm^2 and the concentration, *C*, was 2.55 m$\underline{M}$.
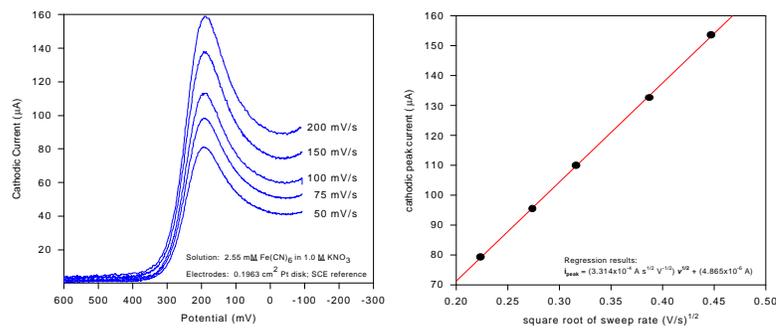

FIGURE 3.10: RESULTS FROM SWEEP RATE STUDY

As expected, the plot of peak current versus the square root of sweep rate yields a straight line. The Randles-Sevcik equation can be modified to give an expression for the slope of this straight line as follows,

$$(slope) \ = \ (2.687 \times 10^5) \ n^{3/2} \ A \ D^{1/2} \ C \qquad (3.6)$$

where the constant is understood to have units (*i.e.*, 2.687×10^5 C mol^{-1} V$^{-1/2}$).

For the results in Figure 3.10, the slope is 3.314×10^{-4} A s$^{1/2}$ V$^{-1/2}$. After careful substitution and unit analysis, you can solve for the diffusion coefficient, *D*, and obtain a value equal to 6.057×10^{-6} cm^2/s.

Sample Rotated Disk Voltammetry Results

Here are the results for a series of rotated disk voltammograms taken at different scan rates. Such a study is referred to as a Levich study. The limiting current (or Levich current) is measured and plotted against the square root of the rotation rate, producing a Levich plot. Note that the experimental rotation rate, *f*, is measured in RPM and must be converted to the angular rotation rate, ω, using the equation, $f = 2 \pi \omega / 60$, so that it has units of radians per second.

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Levich Plot

2.55m$\underline{M}$ Fe(CN)$_6$ in 1.0$\underline{M}$ KNO$_3$

Least Squares Regression:
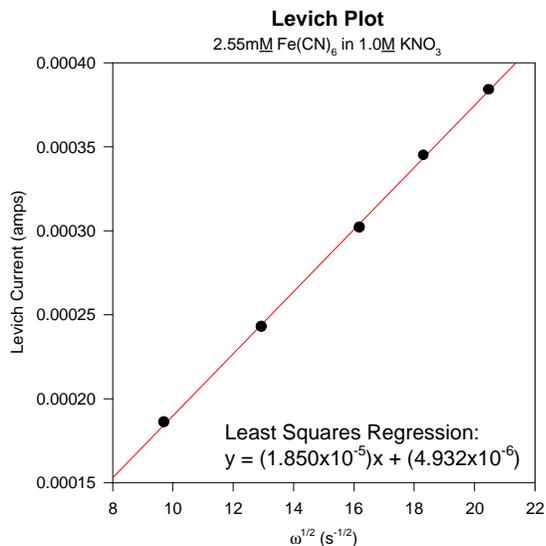$y = (1.850\text{x}10^{-5})x + (4.932\text{x}10^{-6})$

FIGURE 3.11: RESULTS FROM A LEVICH STUDY

The linear relationship between Levich current and the square root of the rotation rate is obvious from the Levich plot. A linear least squares fit of the data produces an equation for the best straight line passing through the data. From the Levich equation, an equation for the slope can be written:

$$(slope) = (0.620)\ n\ F\ A\ D^{2/3}\ \nu^{-1/6}\ C \qquad (3.7)$$

The electrode area, *A*, was 0.1963 cm^2, the analyte concentration, *C*, was $2.55\text{x}10^{-6}$ mol/cm^3, and the solution had a kinematic viscosity, ν, equal to 0.00916 cm^2/sec. After careful substitution and unit analysis, you can solve for the diffusion coefficient, *D*, and obtain a value equal to $4.75\text{x}10^{-6}$ cm^2/s. This result is a little low, probably due to the poor shape of the sigmoidal signal observed in this particular experiment.

The kinematic viscosity is the ratio of the absolute viscosity of a solution to its density. Absolute viscosity is measured in poises (1 poise = gram cm^{-1} sec^{-1}). Kinematic viscosity is measured in stokes (1 stoke = cm^2 sec^{-1}). Extensive tables of solution viscosity and more information about viscosity units can be found in the *CRC Handbook of Chemistry and Physics*.

Sample Chronoamperometry Results
Here are the results for a typical chronoamperometry experiment. Nine data points are chosen from the experimental data depicted in Figure 3.9. These nine points are plotted as current versus the reciprocal of the square root of time. On this type of plot, called a Cottrell plot, the data points are expected to fall along a straight line as shown in Figure 3.12.
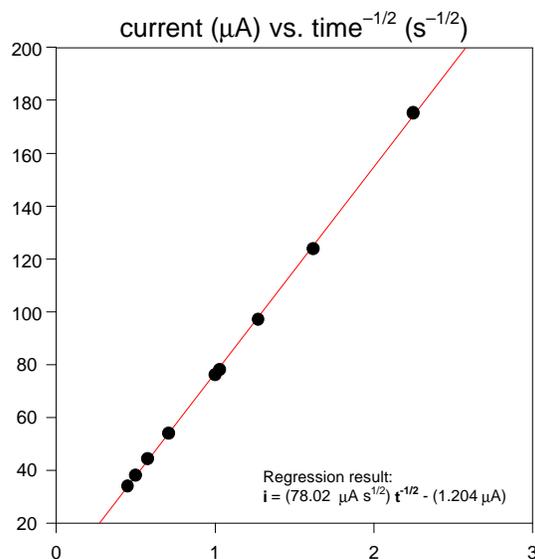
current (μA) vs. time$^{-1/2}$ (s$^{-1/2}$)

Regression result:
i = (78.02 μA s$^{1/2}$) **t$^{-1/2}$** - (1.204 μA)

FIGURE 3.12: A TYPICAL COTTRELL PLOT

A linear least squares regression is performed on the data used to make the Cottrell plot in order to extract a value for the slope of the line. By rearranging the Cottrell equation, an expression for the slope of the Cottrell plot can be written as follows:

$$(slope) \ = \ n \, F \, A \, C \, (D / \pi)^{1/2} \qquad (3.8)$$

For the particular experiment depicted in Figures 3.9 and 3.12, the electrode area, A, is 0.1963 cm^2, and the analyte concentration, C, is 2.55 mM. Substituting this information and the slope into Eqn. 3.8 yields a value for the diffusion coefficient equal to 8.19x10^{-6} cm^2/sec.

Answers to Report Questions

Question 1

Typical student results will vary from 6.0x10^{-6} to 8.0x10^{-6} cm^2/sec. Chrono-amperometry provides the most direct measure of diffusion coefficients, with the electrode area and concentration being the only sources of uncertainty. Cyclic voltammetry results rely on proper subtraction of background current and precise knowledge of the sweep rate. Rotated disk voltammetry results rely on precise knowledge of the rotation rate and the kinematic viscosity, but are less prone to error from non-Faradaic currents.

Question 2

The $t^{-1/2}$ time dependence for chronoamperometry is rather obvious from the Cottrell equation. For cyclic voltammetry, the Randles-Sevcik equation includes the square root of the sweep rate, reflecting a $t^{-1/2}$ time dependence. In rotated disk voltammetry, the Levich equation includes the square root of the rotation rate, again reflecting a $t^{-1/2}$ time dependence.