INSTRUCTION MANUAL FOR BASi EPSILON FOR ELECTROCHEMISTRY

Version 2.10.73

EC FAQs: Electrodes

Most electrochemical cells I've seen have only 2o electrodes. Why do I need 3 electrodes for cyclic voltammetry and related techniques?

All electrochemical cells require at least two electrodes, since the potential of a given electrode can only be measured relative to another electrode, the potential of which must be constant (a reference electrode). In potentiometric measurements (such as measurement of pH), there is no current through the cell, and these two electrodes are sufficient (it should be noted that many pH and ion-selective electrodes used in potentiometric measurements are combination electrodes – both electrodes are contained within the same body). However, in a cyclic voltammetry experiment, an external potential is applied to the cell, and the current response is measured. Precise control of the external applied potential is required, but this is generally not possible with a two electrode system, due to the potential drop across the cell due to the solution resistance (potential drop (E) = current (i) x solution resistance (R)) and the

polarization of the counter electrode that is required to complete the current measuring circuit. Better potential control is achieved using a potentiostat and a three electrode system, in which the potential of one electrode (the working electrode) is controlled relative to the reference electrode, and the current passes between the working electrode and the third electrode (the auxiliary electrode).

What are the requirements for a working electrode material, and which material should I choose?

A working electrode acts as a source or sink of electrons for exchange with molecules in the interfacial region (the solution adjacent to the electrode surface), and must be an electronic conductor. It must also be electrochemically inert (i.e., does not generate a current in response to an applied potential) over a wide potential range (the potential window). Commonly used working electrode materials for cyclic voltammetry include platinum, gold, mercury, and glassy carbon. Other materials (e.g., semiconductors and other metals) are also used, for more specific applications. The choice of material depends upon the potential window required (e.g., mercury can only be used for negative potentials, due to oxidation of mercury at more positive potentials), as well as the rate of electron transfer (slow electron transfer kinetics can affect the reversibility of redox behavior of the system under study). The rate of electron transfer can vary considerably from one material to another, even for the same analyte, due to, for example, catalytic interactions between the analyte and active species on the electrode surface.

Is there a difference between glassy carbon and pyrolytic graphite?

Glassy carbon is an amorphous form of carbon, whereas pyrolytic graphite has a more ordered structure, with distinct planes - the basal plane and the edge plane. The edge plane is considerably more conducting than the basal plane. Glassy carbon is mechanically more durable than pyrolytic graphite.

Do I need to clean the surface of the working electrode between experiments, and, if so, how?

If material adsorbs to the surface of a working electrode, then the current response will degrade, and the electrode surface needs to be cleaned. Such adsorption occurs more readily for some analytes than for other, and hence the required cleaning frequency varies. In many cases, the only cleaning required is light polishing with a fine polish, such as 1 μm diamond, or 0.05 μm alumina. A few drops of polish are placed on a polishing pad (brown Texmet for alumina, and white nylon for diamond), and the electrode is held vertically and rubbed on the polish in a figure of eight pattern for 30 seconds to a few minutes (depending upon the condition of the electrode surface). After polishing, the electrode surface is rinsed thoroughly with water (for alumina) or methanol (for diamond), and allowed to air dry (electrodes polished with alumina may also need to be sonicated in distilled water for a few minutes to remove any

residual alumina particles). The choice of polish depends upon the analyte and the electrode - use the polishing method that gives the best results (i.e., reproducible current response) for a given system. More pronounced surface defects (e.g., a scratch) may need to be polished with a more coarse polish. Once the defect has been removed, the electrode must then be polished with successively finer polish to obtain a mirror-like surface.

Electrochemical cleaning (applying large anodic or cathodic potentials to the electrode) has also been shown to be effective in some instances.

What applications are mercury drop electrodes used for, and what special requirement are needed for such electrodes?

Mercury drop electrodes have 3 major advantages over solid electrode materials such as platinum and glassy carbon:

a) a more reproducible surface
b) more negative potentials can be attained in aqueous systems
c) amalgamation with heavy metals (e.g., lead and cadmium)

Therefore, mercury drop electrodes are used for determination of trace metals using stripping voltammetry (where reproducibility is critical) and measurements at negative potentials in aqueous systems. Mercury drop electrodes consist of a mercury drop at the end of the capillary. The other end of the capillary is attached to a reservoir of mercury, and control of the flow of mercury from the reservoir is controlled by a valve. The simplest mercury electrode is the Dropping Mercury Electrode (DME), for which the valve is held open throughout the experiment. The mercury drop is therefore dynamic, growing to a certain size before falling of the capillary under its own weight (the drop can also be displaced at set time intervals using a drop knocker). An alternative mercury electrode is the Static Mercury Drop Electrode (SMDE), for which the valve is held open for a set length of time. The size of the mercury drop generated is constant once the valve is closed. The drop is displaced using a drop knocker. In the Controlled Growth Mercury Electrode (CGME), which is only available from BAS, the drop is grown incrementally, using a user-defined series of valve openings. The timing of the valve openings and drop knocks for the SMDE and CGME, and their coordination with changes in the applied potential and the current measurement require microprocessor control. An electrochemical experiment can use one mercury drop (a Hanging Mercury Drop Electrode – HMDE) (e.g., stripping experiments) or a series of mercury drops coordinated with potential pulses (e.g., pulse polarographic experiments).

What are the pros and cons of mercury drop electrodes and mercury film electrodes for stripping voltammetry?

Mercury film electrodes consist of a thin "film" of mercury deposited on an electrode surface (typically glassy carbon) by reduction of a mercury(II) salt in solution. It can be difficult to obtain a reproducible film, and this can affect the reproducibility of the results, particularly when compared to the reproducibility obtained using a mercury drop electrode. However, the surface area/volume ratio is larger for the mercury film electrode, and this electrode is more stable, which allows a faster stirring rate to be used in the deposition step. Both these factors decrease the deposition time required for the mercury film electrode. In addition, the resolution for adjacent peaks is better for the mercury film electrodes, due to sharper peaks.

Does the size of my working electrode matter?

The standard BAS working electrode for voltammetry is a disk with a diameter of 1.6 - 3 mm. Decreasing the size of the electrode to micron dimensions (microelectrodes) decreases the iR drop at the electrode, decreases the electrode capacitance (which allows a faster scan rate to be used for cyclic voltammetry), and changes the diffusion to the electrode surface from linear to radial.

What properties are required for a reference electrode?

The major requirement for a reference electrode is that the potential does not change with time. Since the passage of current through an electrode can alter the potential, such effects are minimized for the reference electrode in the three electrode system by a) having a high input impedance for the reference electrode (thereby decreasing the current passing through the reference electrode to negligible levels) and b) using a non-polarizable electrode as the reference electrode (i.e., the passage of small currents does not alter the potential).

What are the differences between the silver/silver chloride reference electrode and the saturated calomel reference electrode?

These reference electrodes are similar, and consist of a redox reaction between a sparingly soluble chloride and the metallic element in an aqueous chloride solution. They can be used interchangeably, BUT it is extremely important to specify which is used, since their potentials are different (e.g., the potential of the BAS silver/silver chloride reference electrodes is -35 mV relative to the saturated calomel electrode). Since potential values are relative to the reference electrode, failure to specify the reference electrode makes any quoted potential values meaningless.

What are liquid junction potentials, and how do they affect measured potentials?

The salt solution required for a reference electrode must be separated from the analyte solution by a frit that allows ionic conduction between the two solutions, but does not allow appreciable contamination of the analyte solution by the reference electrode solution (or vice versa). In the BAS electrode, this frit is made of either a ceramic material (RE-4 and RE-6 electrodes for aqueous solutions) or of porous Vycor (RE-5 or RE-5B for either aqueous or non-aqueous solutions). Typically, the solutions separated by the frit do not contain the same ions, and the different rates of diffusion across the frit by the different ions gives rise to a potential across the frit – the junction potential. This is a further contribution to the potential between the working and reference electrodes. Since the junction potential is different for solutions of different ionic compositions, strictly speaking, redox potentials measured in different solutions (e.g., different organic solvents) cannot be compared directly, and an internal standard is required.

What factors can affect the potential of a reference electrode?

The potential of a reference electrode varies with temperature (typically 0.5 - 1.0 mV/^{o}C). Therefore, precise measurement of redox potentials requires the use of a constant temperature bath for the cell. The potentials of the silver/silver chloride and calomel reference electrode are also affected by the concentration of chloride in the electrode solution, which must therefore be maintained at a constant value by proper storage.

How do I store reference electrodes?

Since the potential of a chloride-containing reference electrode is sensitive to chloride concentration, the electrode must be stored with the frit immersed in a solution that is identical in composition and concentration to the reference electrode solution (e.g., 3 M sodium chloride for the BAS silver/silver chloride reference electrode). Since this solution can corrode the electrode connectors, the electrodes must be stored in a appropriate storage vial that protects the connectors from the solution. When BAS reference electrodes are shipped, the frit is covered with yellow plastic to maintain electrode integrity during shipping. This plastic should be carefully removed upon receipt of the electrodes, which should then be stored in the appropriate solution. During shipping, air bubbles can become lodged at the inside of the Vycor tip. These must be dislodged (by flicking the end of the electrode) before the electrode can be used, otherwise artifacts (e.g., excessive noise) may be seen in the experimental data.

Can I use aqueous reference electrodes for non-aqueous solutions?

Aqueous reference electrodes can be used in non-aqueous solutions in many instances, but problems can arise. First, junction potentials can be quite large for non-aqueous solutions, so comparison of redox potentials between aqueous and non-aqueous solutions (and between different non-aqueous solutions) requires an internal standard. Second, salts from the electrolyte solutions can precipitate in the frit, leading to increased noise in the current response. For example, if a perchlorate salt is used in the analyte solution, and a potassium solution is used in the reference electrode, potassium perchlorate can precipitate in the frit. This problem is decreased in BAS reference electrodes by using sodium chloride in silver/silver chloride reference electrode, since sodium perchlorate is more soluble than potassium perchlorate. Third, since water and chloride ions can diffuse through the frit into the analyte solution (albeit slowly), aqueous reference electrodes are not suitable for water and chloride sensitive analytes.

I need to use anhydrous electrolyte, so an aqueous reference electrode is not suitable. What are the alternatives?

If contamination by water from aqueous electrodes is a problem, there are a number of alternatives. The simplest is to use a salt bridge containing the anhydrous electrolyte to separate the aqueous reference electrode from the analyte solution. Other alternatives include using a non-aqueous reference electrode or a pseudo-reference electrode. The BAS non-aqueous reference electrode (MF-2062) requires user assembly, and consists of a silver wire immersed in a solution containing silver nitrate (0.001 - 0.01 M) dissolved in a solution of an appropriate electrolyte. Ideally, this electrolyte is the same as that used for the analyte (to eliminate junction potentials), but not all organic solvents are suitable (acetonitrile, DMSO, methanol, ethanol, and THF are suitable, whereas DMF and chlorinated solvents are not). If the analyte electrolyte is not suitable, an acetonitrile-based electrolyte can be generally be used. The potential of the non-aqueous reference electrode depends on the solvent, the electrolyte, and the concentrations of silver nitrate and the salt. Since the potential of a non-aqueous reference electrode can vary among different electrodes, redox potentials measured using such a reference electrode should be quoted relative to an internal reference compound (e.g., ferrocene). A pseudo-reference electrode is simply a platinum or silver wire immersed in the analyte solution. This has the advantage that there can be no contamination of the analyte, but the disadvantage is that the reference potential is unknown, as it is dependent on the composition of the analyte solution. Therefore, redox potentials measured using a pseudo-reference electrode should again be quoted relative to an internal reference compound such as ferrocene.

What the requirements for the auxiliary electrode?

The auxiliary electrode is typically a platinum wire that provides a surface for a redox reaction to

balance the one occurring at the surface of the working electrode, and does not need special care, such as polishing. In order to support the current generated at the working electrode, the surface area of the auxiliary electrode must be equal to or larger than that of the working electrode. Three auxiliary electrodes are available from BAS: two are straight platinum wires for use with stationary solution voltammetry experiments, and the other (MW-1033) is a longer platinum coil that is used for experiments that generate larger currents, such as rotating disk voltammetry and bulk electrolysis. One of the platinum wire electrodes (MW-4130) should be used with C1 Cell Stands, the VC-2 Cell (MF-1052), the Microcell (MF-1065), and the C2 Low Volume Cell (MF-2040), whereas the other (MW-1032) should be used with the C2 and C3 Cell Stands.

Does the auxiliary electrode need to be isolated from the working electrode?

During any electrochemical experiment, a redox reaction occurs at the surface of the auxiliary electrode (to balance the redox reaction at the surface of the working electrode), and the products of this reaction can diffuse to the working electrode and interfere with the redox reaction occurring at that site. However, in electroanalytical experiments such as cyclic voltammetry, the time scale of the experiment is too short for this diffusion to be able to cause significant interference, so there is no need to place the auxiliary electrode in a separate compartment. However, electrosynthetic (bulk electrolysis) experiments are typically much longer than electroanalytical experiments, so separation of the auxiliary electrode is required (see, e.g., the BAS bulk electrolysis cell (MF-1056)).

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EC FAQs: Electrolyte Solutions

What medium is required for electrochemical experiment?

The medium must be conducting. This can be achieved by using either a molten salt or an electrolyte solution. An electrolyte solution is made by adding an ionic salt to an appropriate solvent.

What solvents and salts are appropriate for an electrolyte solution?

The salt must become fully dissociated in the solvent in order to generate a conducting (i.e., ionic) solution. The electrolyte solution must also be able to dissolve the analyte, must be electrochemically inert over a wide potential range (i.e., no current due to electrolyte solution oxidation/reduction), and must be pure (e.g., the presence of water decreases the size of the potential range). It must also be chemically inert, so that it will not react with any reactive species generated in the experiment (e.g., acetonitrile is nucleophilic, so can react with electrogenerated cations). If the temperature is to be varied, the electrolyte solution must have an appropriate liquid range.

What are some typical electrolyte solutions?

Electrolyte solutions can be aqueous or non-aqueous. A wide range of salts can be used for aqueous electrolyte solutions. Since the redox potentials of some compounds are pH sensitive, buffered solutions should be used for these compounds. Suitable non-aqueous solvents include acetonitrile, DMF, DMSO, THF, methylene chloride, and propylene carbonate. Salts for non-aqueous electrolyte solutions typically consist of a large cation (e.g., tetraalkylammonium cations), and large anions (e.g., hexafluorophosphate,

tetrafluoroborate, and perchlorate) to ensure full dissociation. N.B. Perchlorate salts must be handled with care, since they are potentially explosive.

How does solution resistance affect my experiments?

Although the addition of fully dissociated salts improves the conductivity of the electrolyte solution, many electrolyte solutions (particularly those based on non-aqueous solvents) have a significant resistance (hundreds of ohms). This leads to a potential drop between the electrodes (termed iR drop – potential = current (i) x solution resistance (R)). Some of this iR drop can be compensated for by using a potentiostat and a three electrode system. However, some resistance (between the working and reference electrodes) remains uncompensated. This uncompensated resistance can be decreased or eliminated by careful cell design (including use of a Luggin capillary), positive feedback iR compensation, or post-run data correction.

What is a Luggin capillary?

Uncompensated resistance can be decreased by placing the reference electrode close to the surface of the working electrode. This can be achieved using a Luggin capillary, which is a hooked capillary that is attached to the end of the reference electrode (i.e., it is an extension to the reference electrode). The tip end of the capillary is placed close to the surface of the working electrode. However, it must not be placed too close, otherwise part of the surface may be blocked. In addition, exact placement of the capillary tip is required to obtain reproducible results.

What is positive feedback iR compensation?

Positive feedback iR compensation is available on the epsilon. This method feeds back a voltage into the cell electronics to compensate for the iR drop due to the solution resistance. However, care must be taken when selecting the applied feedback voltage, since too high a voltage can drive the electronics into oscillation, which can adversely affect the surface of the working electrode (since extreme potentials are applied). This is prevented in BAS instruments by first measuring the uncompensated solution resistance, and then increasing the magnitude of the feedback incrementally, testing the system for stability after each increment.

How does uncompensated resistance affect a cyclic voltammogram?

If the uncompensated resistance is significant (hundreds of ohms), then the peak potential separation increases and the peak current decreases. These effects become more pronounced with increasing scan rate. Unfortunately, these effects are also characteristic of slow electron transfer kinetics. Since slow electron transfer kinetics are not dependent on analyte concentration, and the effects of uncompensated resistance are (E = iR), the two can be differentiated by running the experiments at different analyte concentrations.

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EC FAQs: Voltammetry

What is voltammetry?

In a voltammetric experiment, a potential is applied to a system (e.g., a transition metal complex in solution) using two electrodes (a *working* electrode and a *reference* electrode), and the current response is measured using the working electrode and a third electrode, the auxiliary electrode.

Why is there a current response to the applied potential?

The current arises from transfer of electrons between the energy levels of the working electrode and the molecular energy levels of the system under study. This current is often referred to as the *faradaic* current. Transfer of electrons from filled electrode orbitals to vacant molecular orbitals is referred as reduction, whereas transfer of electrons from filled molecular orbitals to vacant electrode orbitals is referred to as oxidation. Whether oxidation or reduction can occur depends upon the relative energies of the Fermi level of the electrode (i.e., the energy of the highest occupied electrode orbital) and the frontier molecular orbitals; for example, reduction can occur if the Fermi level is higher than the lowest unoccupied molecular orbital, whereas oxidation requires that the Fermi level is lower than the highest occupied molecular orbital.

How are the energies of Fermi level and the frontier orbitals determined?

The Fermi level is determined by the potential applied to the electrode; that is, varying the applied potential changes the oxidizing/reducing ability of the electrode. For example, more negative potentials increase the reducing ability of the electrode. In contrast, the energies of the molecular frontier orbitals

are determined by the molecular structure and can be considered to be constant. Therefore, a common approach in voltammetry experiments is to vary the applied potential, and to record the potential at which a current response is detected; that is, the energy at which oxidation or reduction occurs. The *redox potential* is a measure of this energy.

Do all molecules have a measurable redox potential?

Although all molecules do have frontier orbitals, in practice these are not always accessible in a voltammetry experiment. Molecules for which a redox potential can be measured are referred to as electrochemically active. Examples of electrochemically active molecules include organic molecules with extended π-systems (e.g., aromatic molecules) and transition metal complexes. It should also be noted that some systems have the ability to undergo more than one oxidation or reduction, and hence have more than one redox potential.

What equipment is required for voltammetry experiments?

First, a *potentiostat* is required for controlling the applied potential, and a *current-to-voltage* converter is required for measuring the current. These are both contained within the epsilon. A user interface is required to define the way the potential is applied - the potential waveform. There are a number of different potential waveforms, and these are referred to by characteristic names; for example, cyclic voltammetry, and differential pulse voltammetry. These different potential waveforms (or techniques) are discussed in more detail in the appropriate section. The epsilon must be connected to the electrochemical cell. This contains the three electrodes immersed in an electrolyte solution of the molecule.

Is the solution stirred?

Stirring the solution has a significant effect on the current response, since it affects the rate at which electroactive molecules are brought from the bulk solution to the electrode surface (this process is referred to as *mass transport*). In many voltammetry experiments, there is no stirring, and the only form of mass transport is diffusion (this gives rise to the tailed peak shape observed in cyclic voltammetry). These are referred to as *stationary solution* techniques. In other experiments, the solution is stirred, either by a stir bar or a rotating electrode (the latter is preferable, due to the more precise control of the rate of rotation). These are referred to as *hydrodynamic* techniques.

Do I need to deoxygenate the solution?

Oxygen is electroactive, and can be reduced quite easily. Therefore, it must be removed from the solution if the system under study is reducible. Oxygen is typically removed by bubbling an inert gas (e. g., nitrogen or argon) through the solution for about 10 minutes. If a stationary solution experiment is to be performed, it is important that the stirring is stopped and the solution is allowed to become quiescent before the experiment is started (although a blanketing layer of inert gas over the solution can be maintained during the experiment.

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Epsilon Chemical Test Procedure

Purpose

The purpose of this test is to perform a final examination of the epsilon before going to the customer, and to provide the customer with typical output and data. From these outputs, the customer can verify that the instrument is working properly on arrival and can gain some experience in its operation.

Instrument Installation

The PC should be set up according to the instructions included with the PC. The epsilon should be plugged into the mains supply (N.B. first check that the fuse panel has been set to the correct voltage). The **COMPUTER** port of the epsilon is connected to a **COM** port of the PC. If available, a BAS cell stand should be connected to the **CELL STAND** port of the epsilon

Test Solution

2 mM potassium ferricyanide with 1 M potassium nitrate in water.

Preparation of the Test Solution

1. Weigh 16.5 mg potassium ferricyanide and place in a 25 mL volumetric flask.
2. Weigh 2.53 g potassium nitrate and add to the same volumetric flask.
3. Add about 20 mL deionized water to dissolve the potassium ferricyanide and potassium nitrate.
4. Dilute to 25 mL with deionized water.

Cell (C3 Cell Stand)

Platinum (PTE) Working Electrode (Black lead)
Platinum Wire Auxiliary Electrode (Red lead)
Silver/Silver Chloride RE-5 Reference Electrode (White lead)

Add 10-15 mL of the ferricyanide solution to the cell vial and place in the cell holder (see Cell Stand instructions). Polish the PTE with 0.05 μm alumina following the polishing instructions provided in the polishing kit.

If the RE-5 electrode is new, carefully remove the yellow plastic sheath before use. In addition, there may be air bubbles inside the electrode next to the Vycor frit; these must be displaced (by flicking the electrode). RE-5 electrodes must be stored

in 3M sodium chloride when not in use.

Procedure

1. Turn the Power switch on the epsilon to on.

2. Open the epsilon software by clicking the epsilon icon. The **CS Dialog** box will appear, and will show the progress of establishment of the communication between the epsilon and the PC. If the link is established, the **CS Dialog** box will automatically disappear. If the link is not established, click the **Retry** button. If the link is lost after being established, use **Reconnect Epsilon** in the **Experiment** menu to reestablish the link.

3. Click **New** in the **File** menu (or use the **F2** key) to set up a new experiment. The list of available techniques is displayed (**Figure 1**) (this list can also be accessed using **Select New Experiment** in the **Experiment** menu). It should be noted that there are some techniques that are labeled as DEMO. This label indicates that this technique is NOT active on this particular epsilon. However, it is possible to load a data file for that technique to examine the parameters and the typical output. If the **RUN** button is clicked when a DEMO data file is displayed in the active window, an error message will be shown. The technique list shown in **Figure 1** is the list for the basic epsilon (i.e., pulse techniques, stripping techniques, and multi-channel amperometry are NOT available).

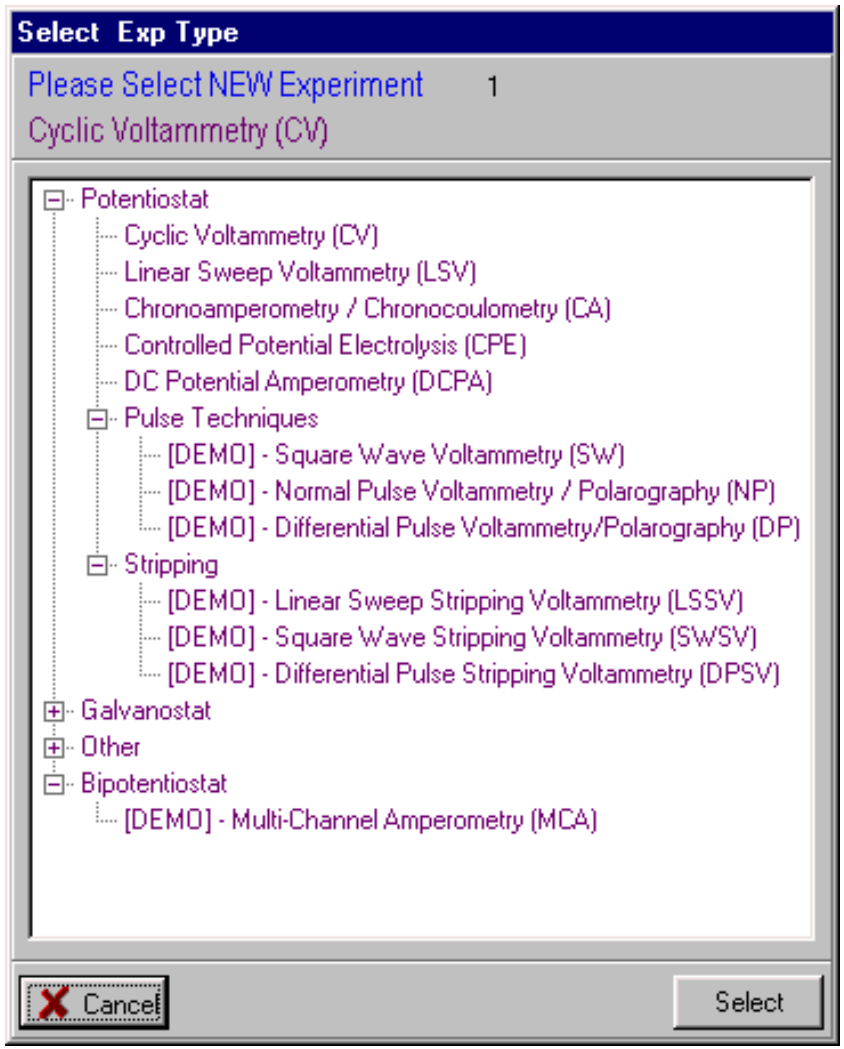

Figure 1. Technique list.

4. Select **Cyclic Voltammetry**. The **Change Parameters** dialog box will now be displayed. Enter the values shown in **Figure 2**. Note that **Switching Potential 2** is not required since there are only 2 segments (**Initial Potential** to **Switching Potential 1** to **Final Potential**). Once these changes have been entered, an experiment using these parameters can be run by clicking the **RUN** button in this dialog box. If an experiment is not to be run immediately, but these parameters are to be saved, then the **Apply** button must be clicked before exiting the dialog box. If **Exit** is clicked before **Apply**, any changes in the parameters will be lost. After exiting the dialog box, an experiment can be run using either **Run** in the **Experiment** menu, in the pop-up menu obtained by clicking the RIGHT mouse button (**Figure 3**), the **RUN** icon on the Tool Bar, or the **F5** key. This icon will change to **STOP** during the experiment, and can be used to abort the experiment.

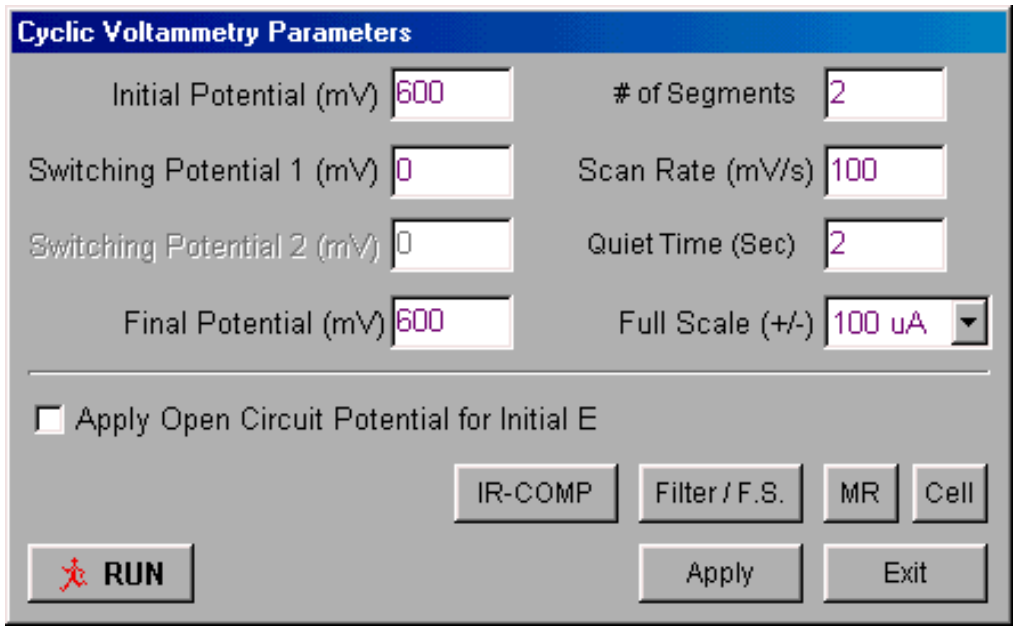

Figure 2. Change Parameters dialog box for **Cyclic Voltammetry**.

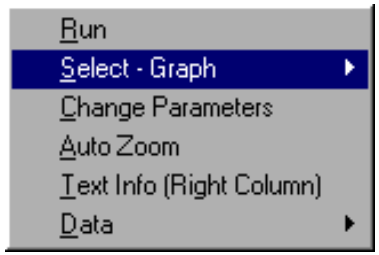

Figure 3. Right mouse button pop-up menu.

5. After the experiment has been run, the voltammogram will be displayed (**Figure 4**). Note the information about the experiment and the peak parameters on the right side of the graph (this can be removed by clicking **Text Info (Right Column)** in the **Graph-Display** menu or the pop-up menu).

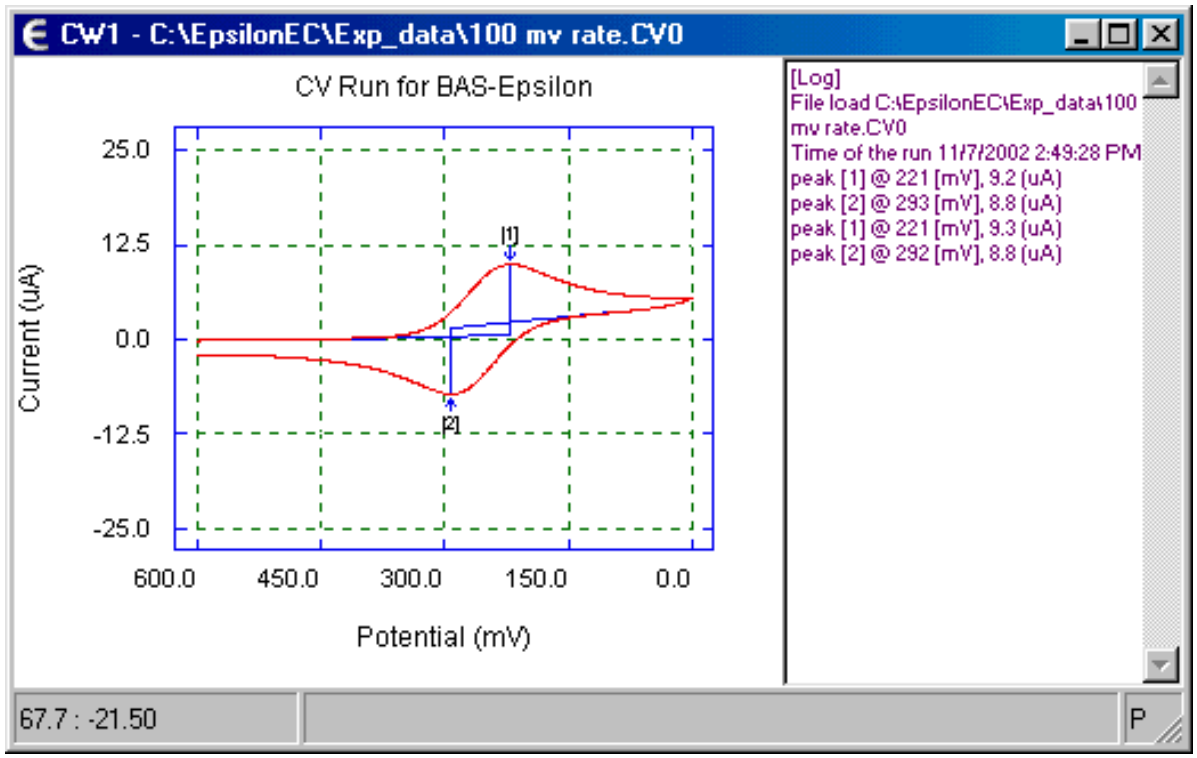

Figure 4. **Cyclic Voltammetry** graph.

6. A specific area of the graphic can be enlarged by either using the mouse cursor (and the left mouse button) to define the area (**Figure 5**) or entering the x and y values in the **Manual Zoom** dialog box (**Figure 6**). The original graph can be restored using **Auto Zoom** in the **Graph-Display** menu.

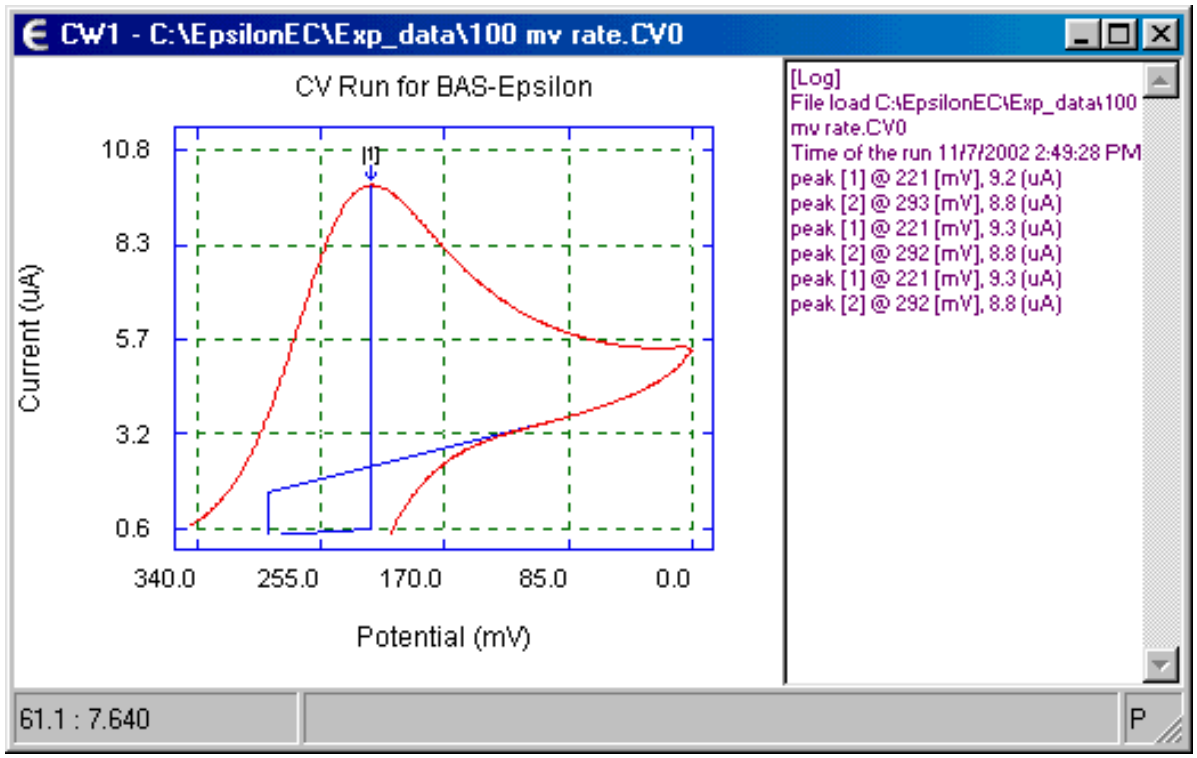

Figure 5.

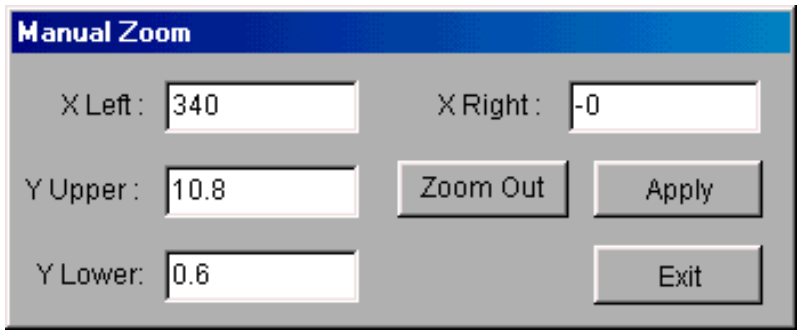

Figure 6. Manual Zoom dialog box.

7. Use **Save** in the **File** menu (or the **F4** key) to save the data in the active experiment window (it should be noted that the each technique has its own extension; for example, .cv0 for cyclic voltammetry). The data is saved in a binary format, but, once saved, it can be converted to a number of different text formats using **Convert to Text File** in the **File** menu (**Figure 7**). Select the file(s) to be converted, the format, and the delimiter, and then click **Convert** to start the conversion.

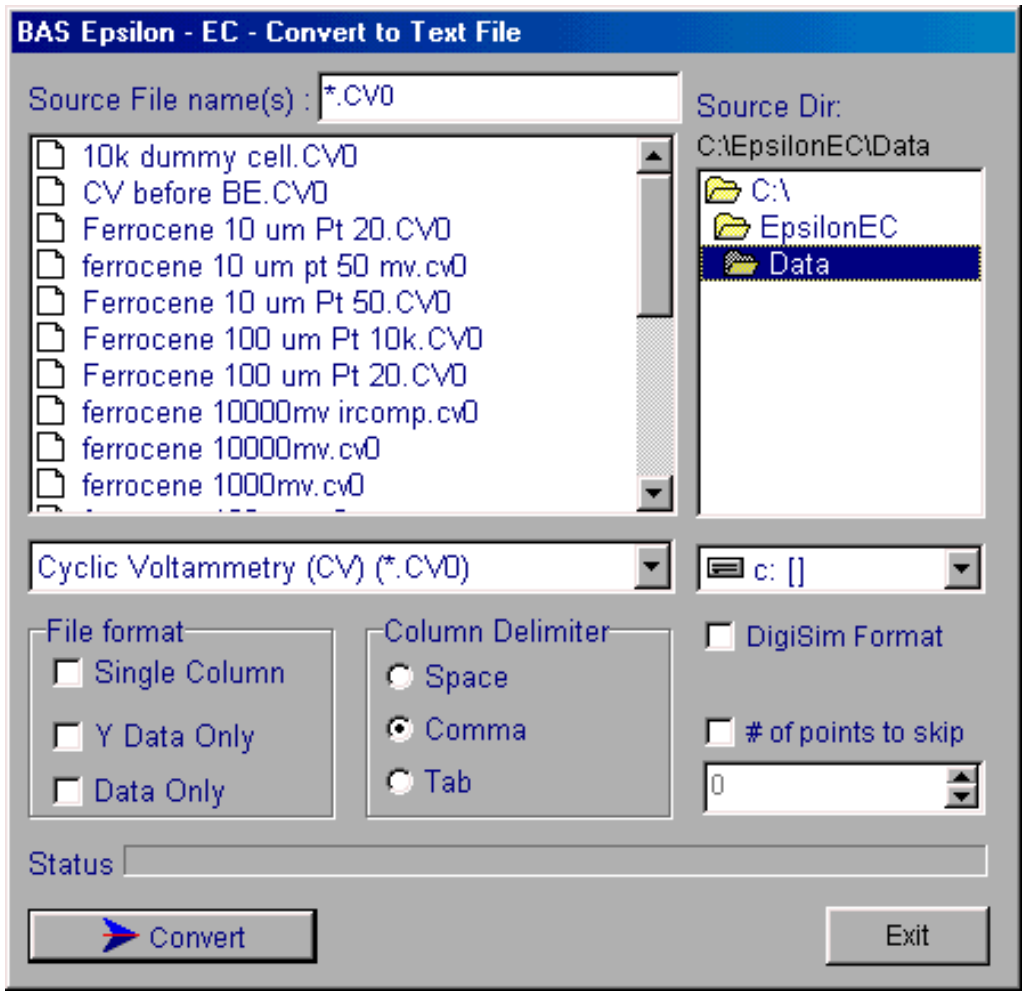

Figure 7. Convert to Text dialog box.

8. Various experimental data can be entered into the **Notes** in the **Experiment** menu (**Figure 8**). These notes will also be saved when the experimental data is saved.

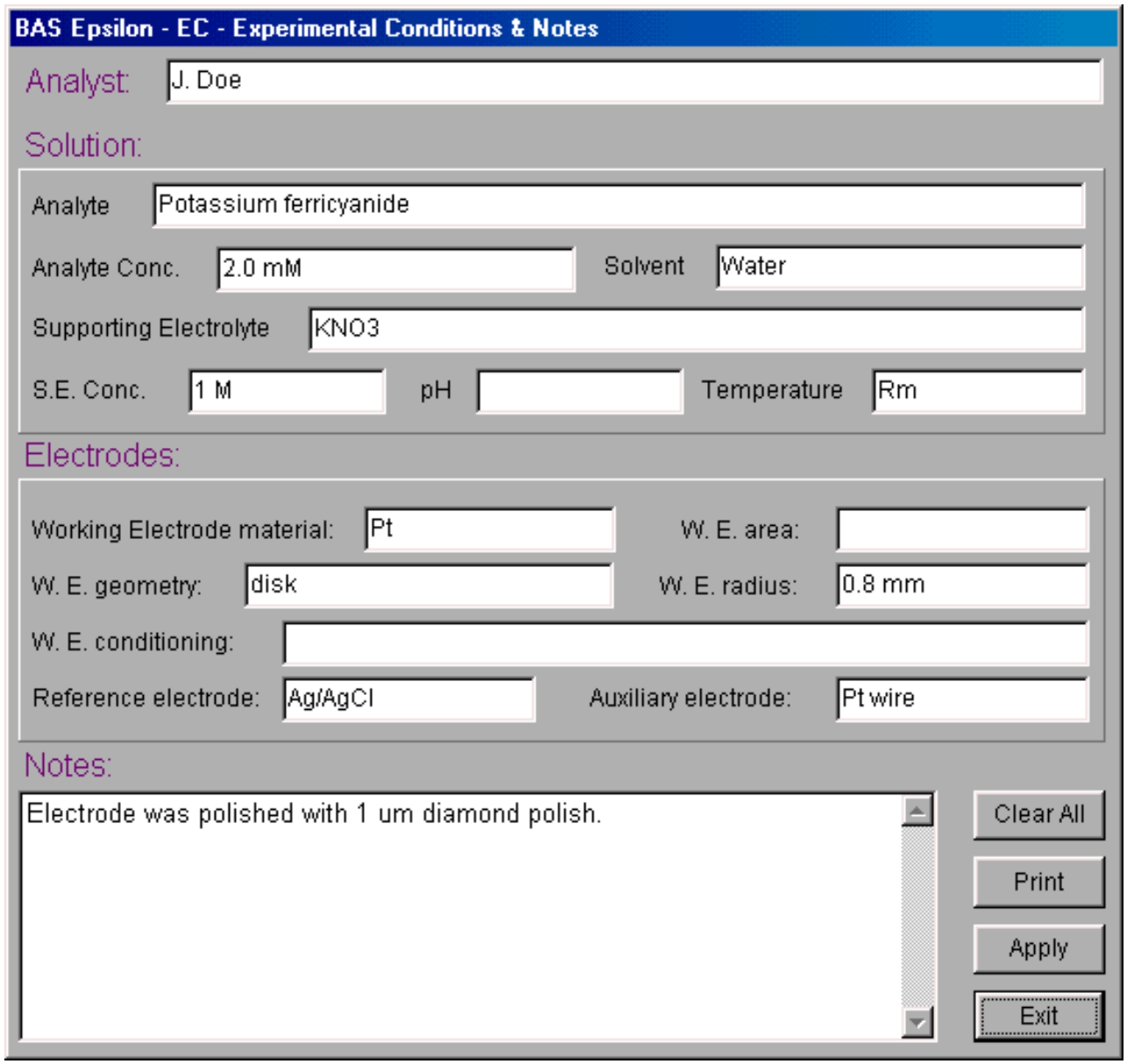

Figure 8. Notes dialog box.

9. Open the **Change Parameters** dialog box (using **Change Parameters** in either the **Experiment** menu, the pop-up menu, or the **F6** key), and change the **Scan Rate** to 200 mV/s. Run the experiment again. Note that the new data is displayed in the experiment window; that is, the new experimental data has replaced the old experimental data. Save this data. Change the scan rate to 500 mV/s, run the experiment, and save the data.

10. The three data sets run at different scan rates can be displayed on the same sets of axes using the **File Overlay** function in

the **Graph-Display** menu. The first time this function is selected after the software is started, an empty set of axes is displayed. Subsequent activations will display the previously selected data sets. Click the right mouse, and select **Setup** from the pop-up menu. The **File Overlay Setup** dialog box will be displayed (**Figure 9**).

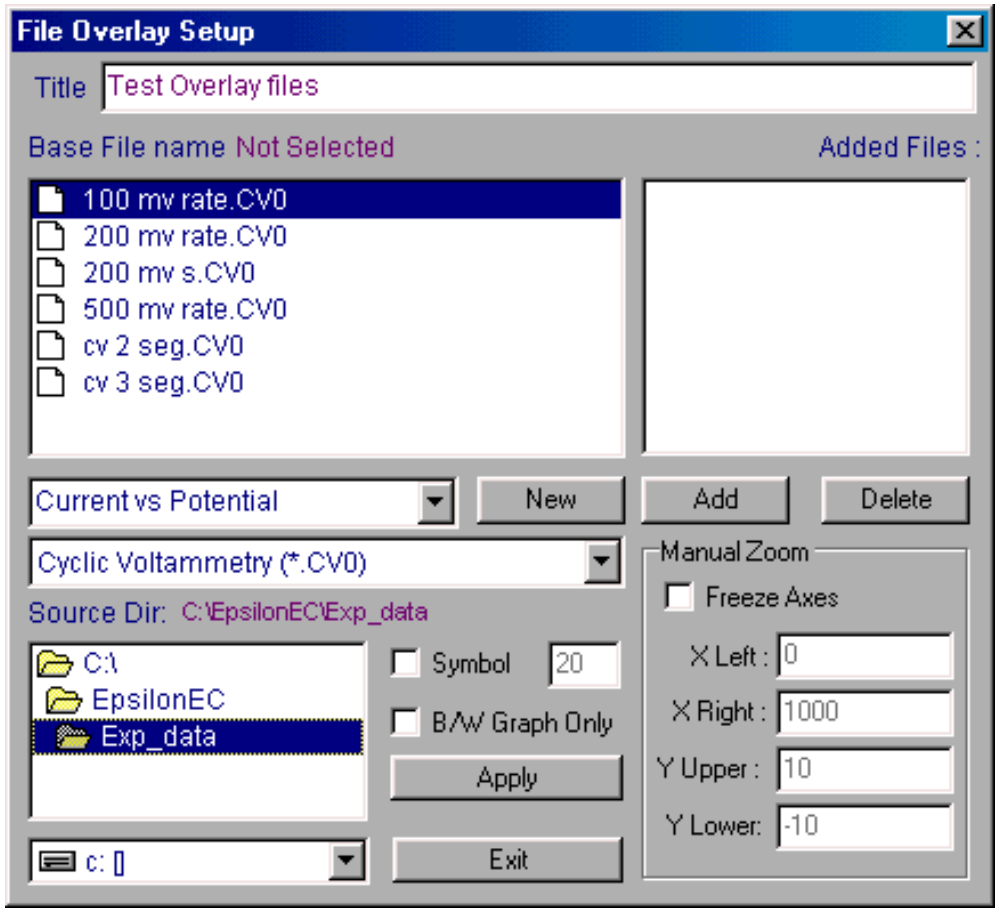

Figure 9. File Overlay Setup dialog box.

11. The scaling of the axes is determined by the **Base File**. Therefore, when comparing voltammograms with the same potential range, the voltammogram with the highest current should be selected as the **Base File**. In this example, the cyclic voltammogram run at a scan rate of 500 mV/s should be the **Base File**. Select the name of this data file, and click **New**. This data file is now displayed on the axis set (which remains in the background). The other two data files (cyclic voltammograms run at 100 and 200 mV/s) should now be selected (using standard Windows functions). Once selected, click **Add** to display these data sets on the axis set. Click **Exit** to remove the **Setup** dialog box. The overlayed data sets can now be viewed (**Figure 10**).

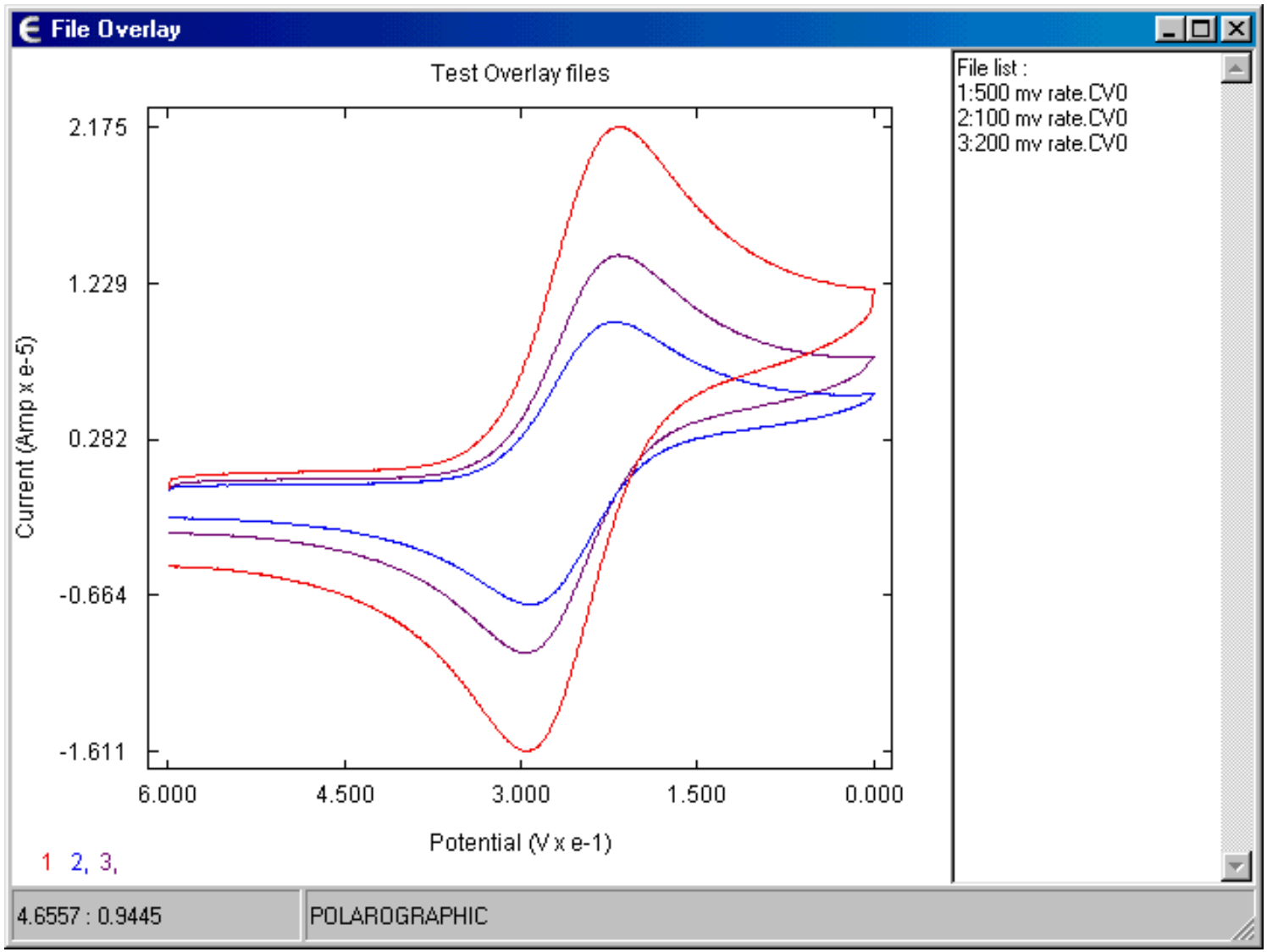

Figure 10. Overlayed cyclic voltammograms.

12. Click **New** in the **File** menu, and select **Cyclic Voltammetry** again. A new experiment window will appear, together with an associated **Change Parameters** dialog box. Enter the parameters shown in **Figure 11**, and run this experiment. Since there are 3 segments in this experiment, all 4 potential parameters must be defined (**Initial Potential** to **Switching Potential 1** to **Switching Potential 2** to **Final Potential**).

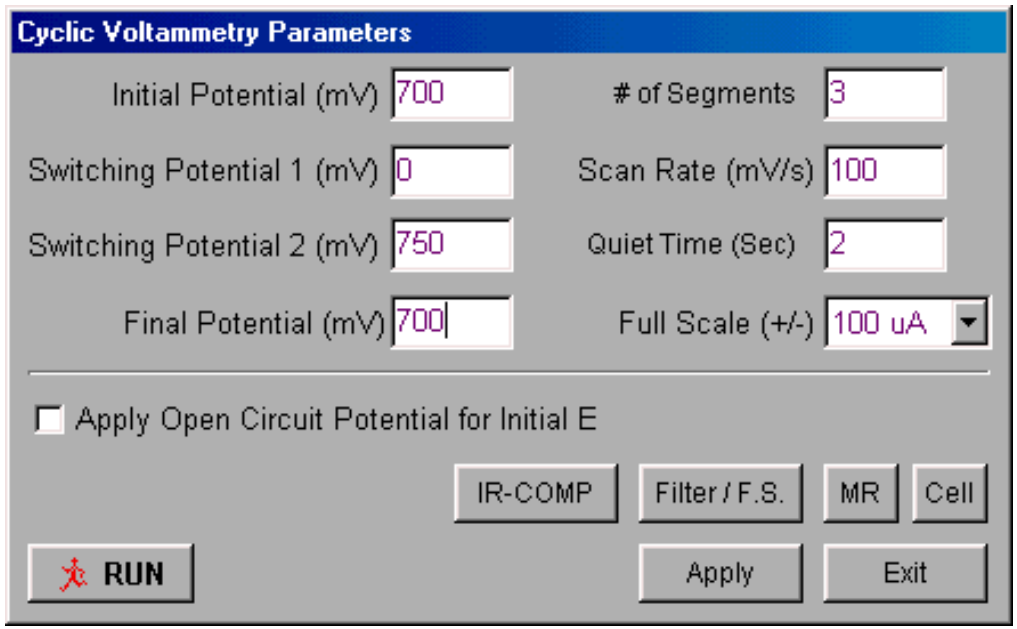

Figure 11.

13. When this experiment has finished, *both* experiment windows are displayed in the main epsilon window (**Figure 12**). Up to 6 experiment windows can be displayed. However, only one experiment window can be active at any one time, and any epsilon functions and operations are applied only to the data in the active experiment window.

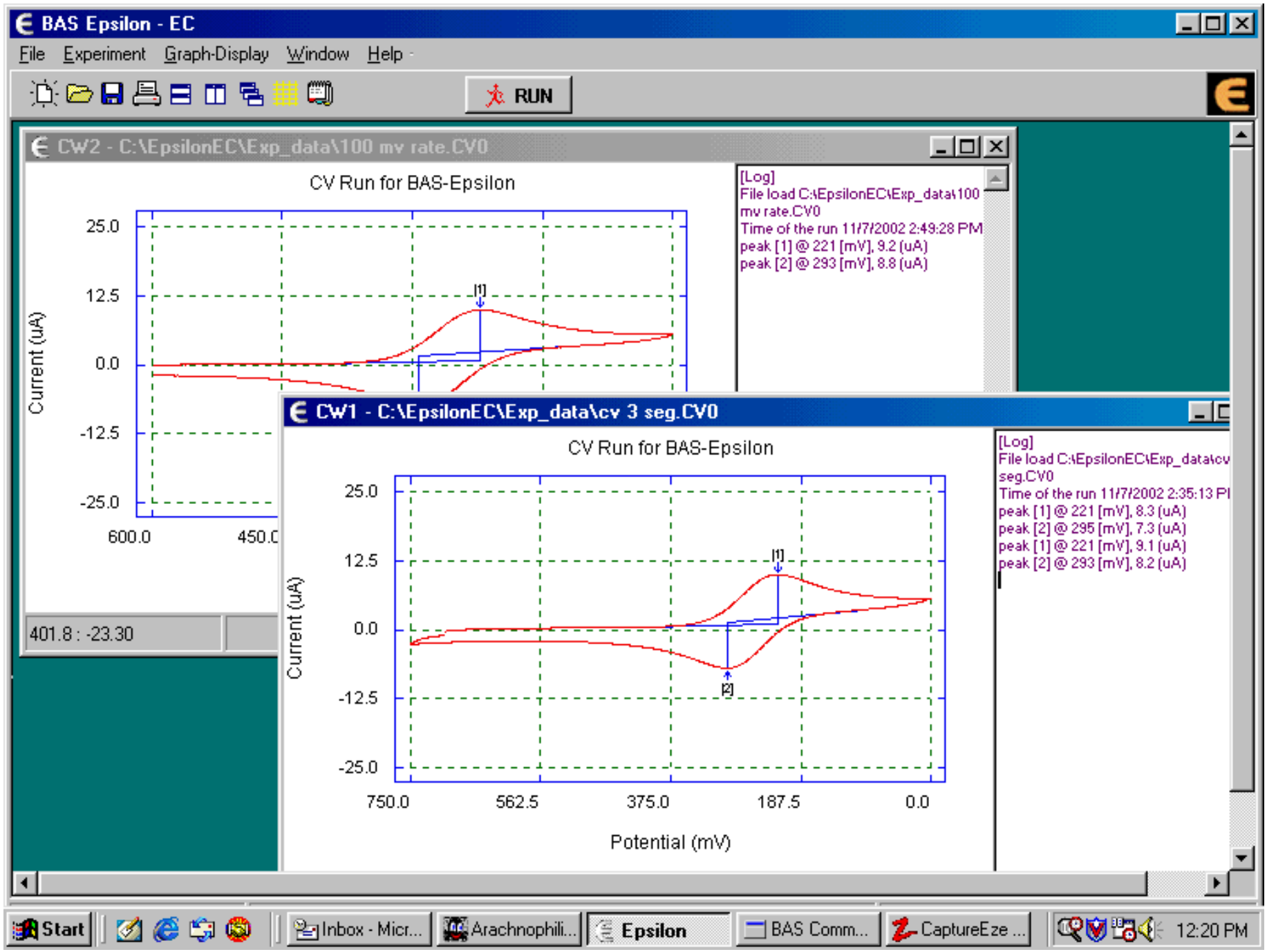

Figure 12.

14. Click **New**, and select **Chronoamperometry/Chronocoulometry** from the list of techniques. A third window will appear, together with an associated **Change Parameters** dialog box. Enter the parameters shown in **Figure 13**. Running

the experiment generates the plot shown in **Figure 14**.

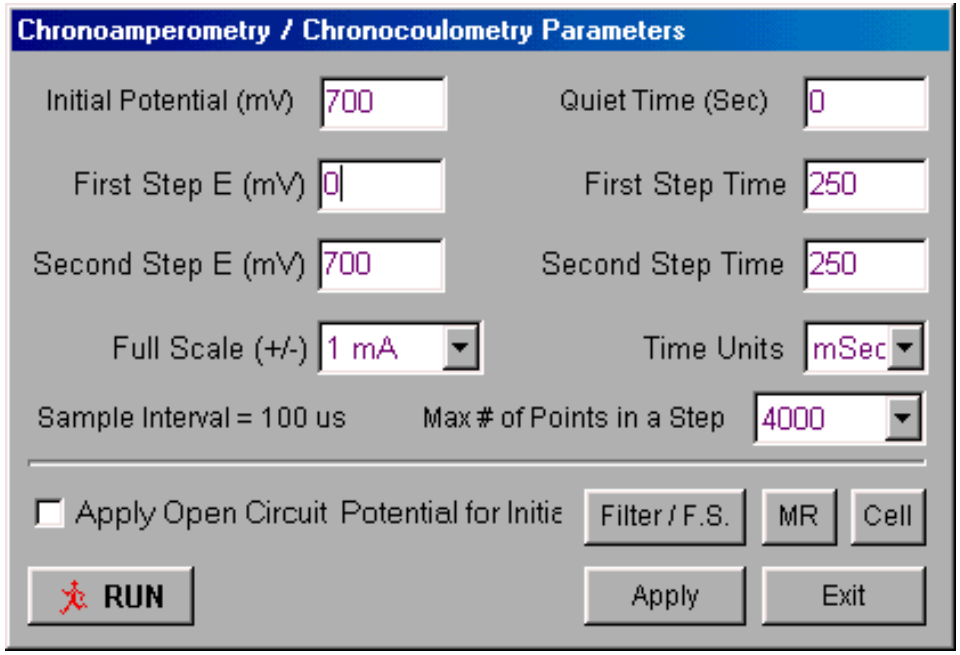

Figure 13. Change Parameters dialog box for **Chronoamperometry/Chronocoulometry**.

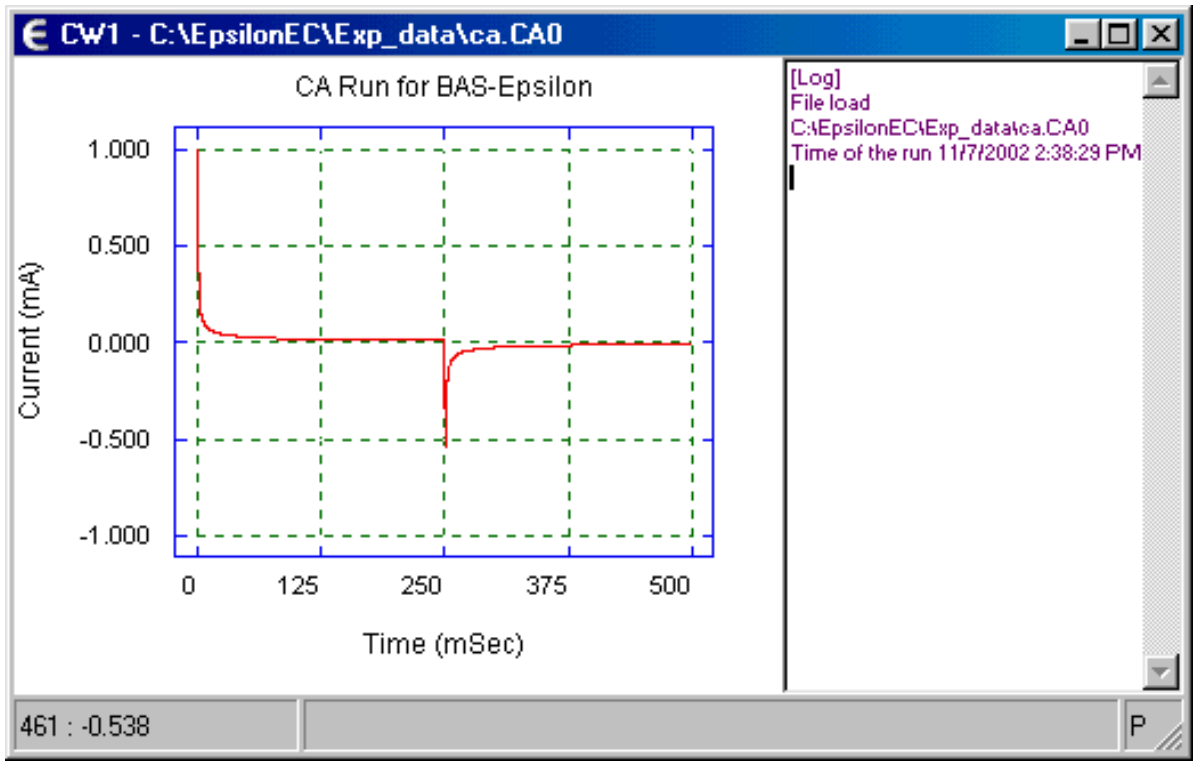

Figure 14. **Chronoamperometry/Chronocoulometry** graph.

15. The data from a **Chronoamperometry/Chronocoulometry** experiment can be plotted in a number of different formats, which can be selected using **Select Graph** in the pop-up menu in the **Chronoamperometry/Chronocoulometry** experiment window. The **Q vs. sqrt(T)** plot is shown in **Figure 15**.

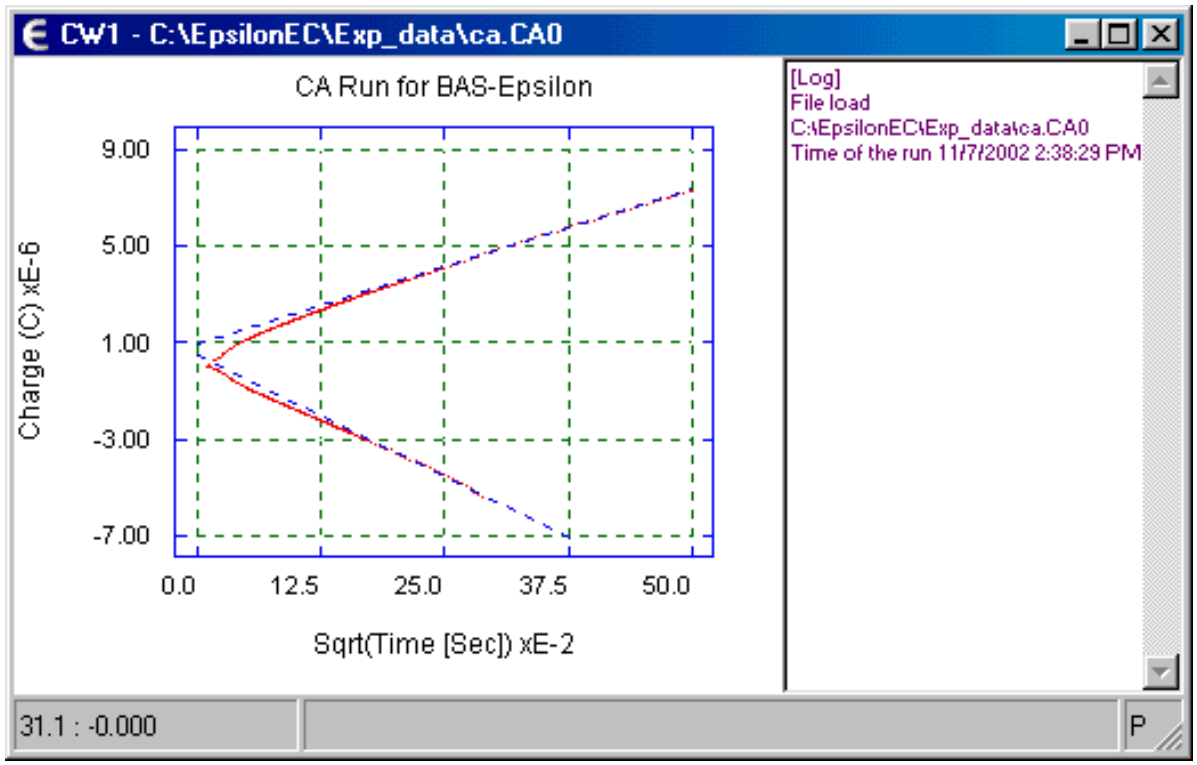

Figure 15. Q vs. sqrt(T) plot for **Chronoamperometry/Chronocoulometry**.

16. The epsilon software can calculate the slope and intercept of the linear **Q vs sqrt(T)** plot when it is displayed. Selecting **Data - Calculate CA-SIR** from the pop-up menu generates the information box shown in **Figure 16**. The lines used for the linear fitting are the dashed blue lines in **Figure 15** (note that the first 20% of the data points are not used in the calculation, due to interference from the charging current and other experimental artifacts).

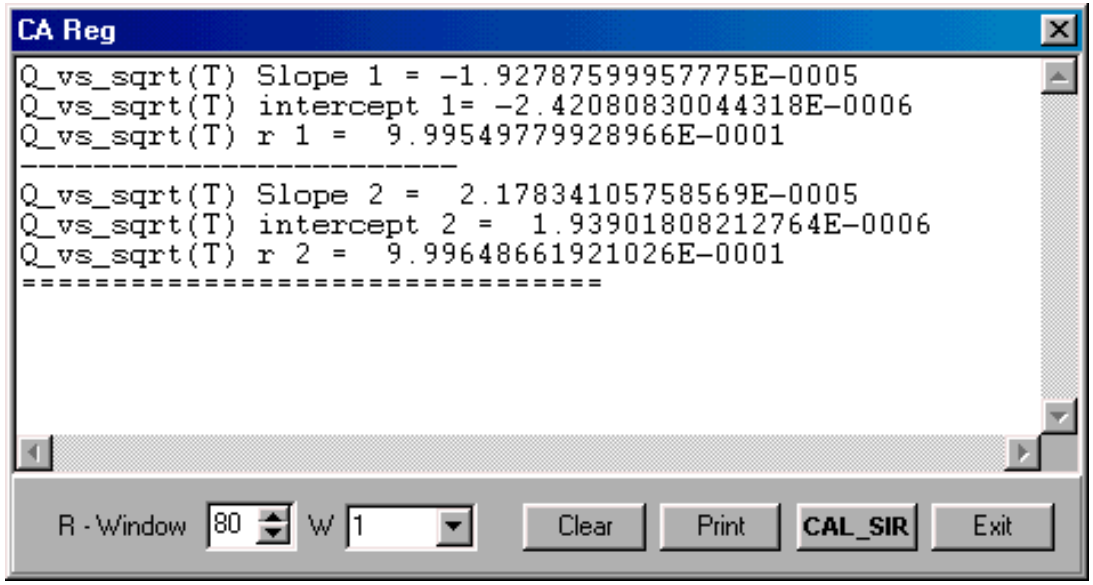

Figure 16. Calculation of slope and intercept of linear plot.

17. Click **New**, and select **Chronopotentiometry**. A fourth experiment window will be opened, together with the associated **Change Parameters** dialog box. Enter the parameters shown in **Figure 17**, then run the experiment (note the sign convention for the current - cathodic (reduction) currents are positive for **polarographic**). Typical data for a **Chronopotentiometry** experiment is shown in **Figure 18**.

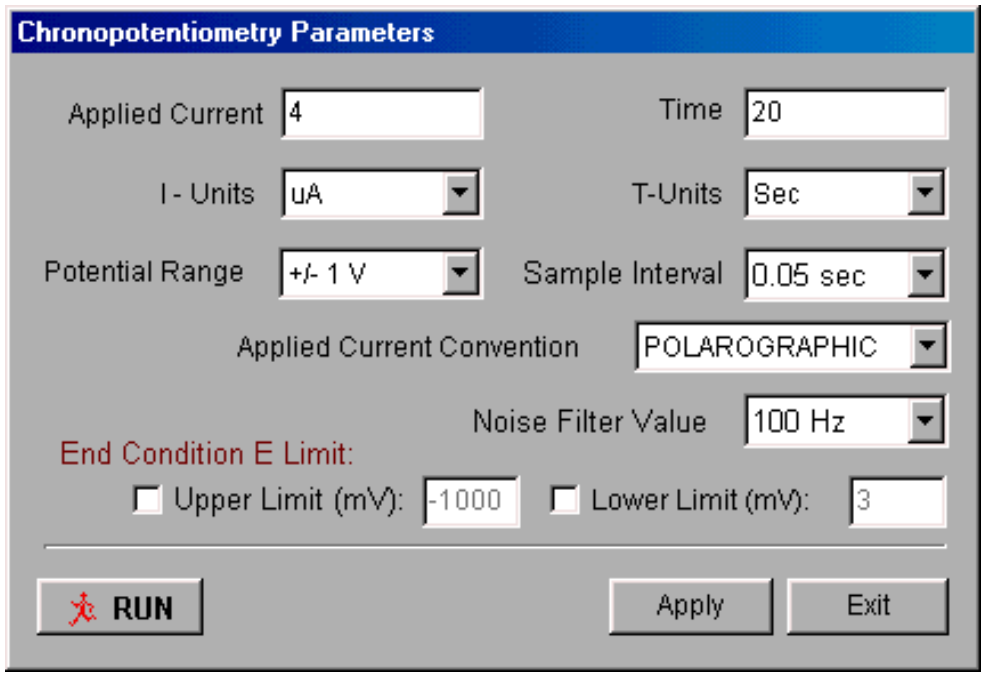

Figure 17. Change Parameters dialog box for **Chronopotentiometry**.

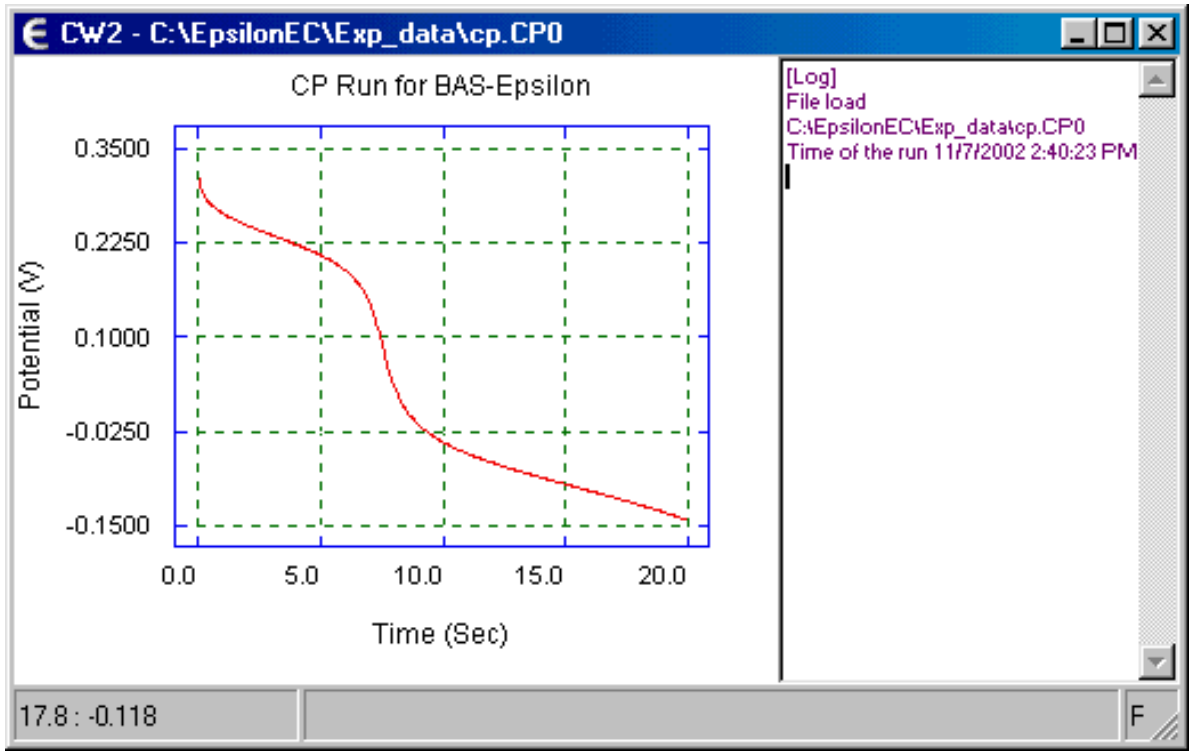

Figure 18. Chronopotentiometry graph.

18. Click **New**, and select **Square Wave Voltammetry** (note that this requires the optional Basic Plus software). A fifth experiment window will be opened, together with the associated **Change Parameters** dialog box. Enter the parameters shown in **Figure 19**, then run the experiment. Typical data for a **Square Wave Voltammetry** experiment is shown in **Figure 20**.

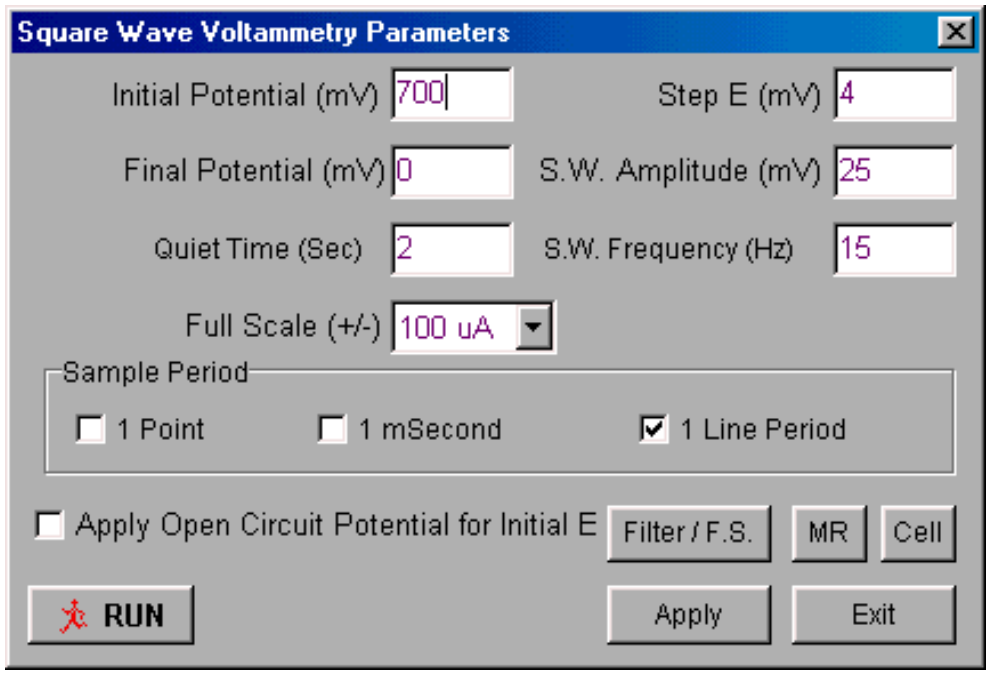

Figure 19. Change Parameters dialog box for **Square Wave Voltammetry**.

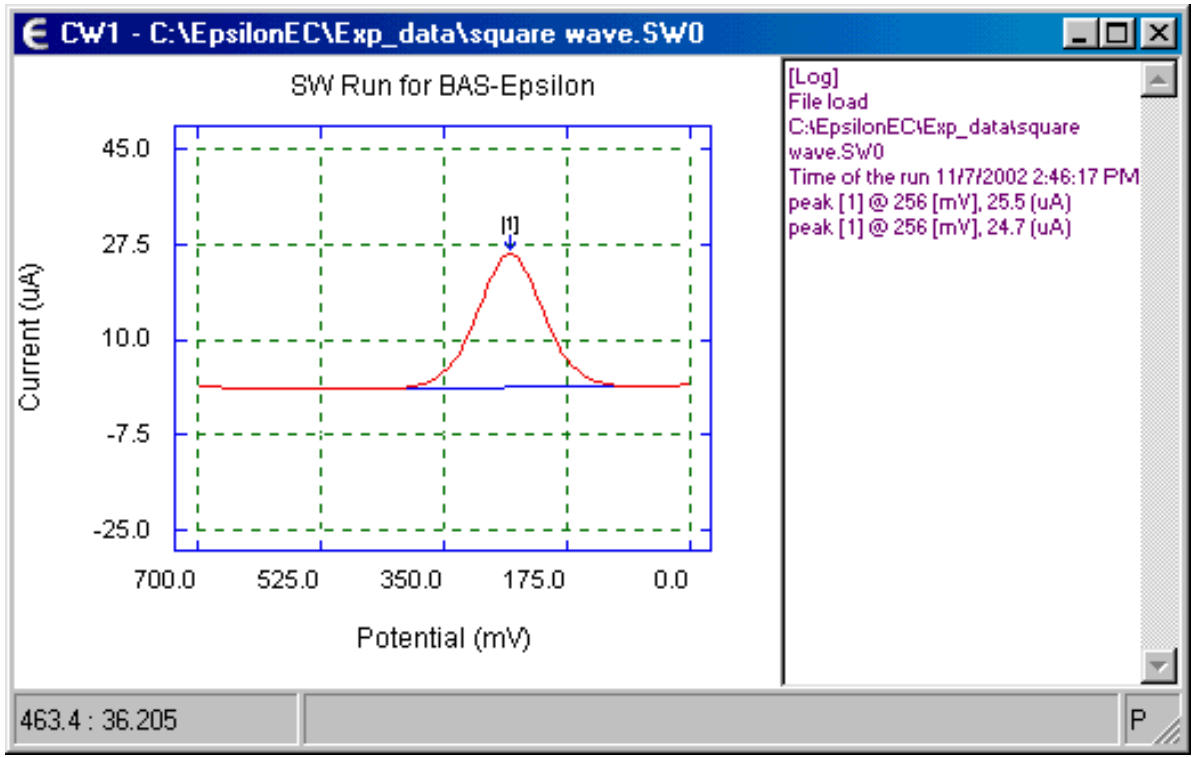

Figure 20. Default plot for **Square Wave Voltammetry**.

19. The default plot for a **Square Wave Voltammetry** experiment is the difference current; that is, the current on the forward cycle less the current on the reverse cycle. The forward and reverse currents are also available under **Select Graph** in the pop-up menu in the **Square Wave Voltammetry** experiment window. The forward current data set is shown in **Figure 21**.

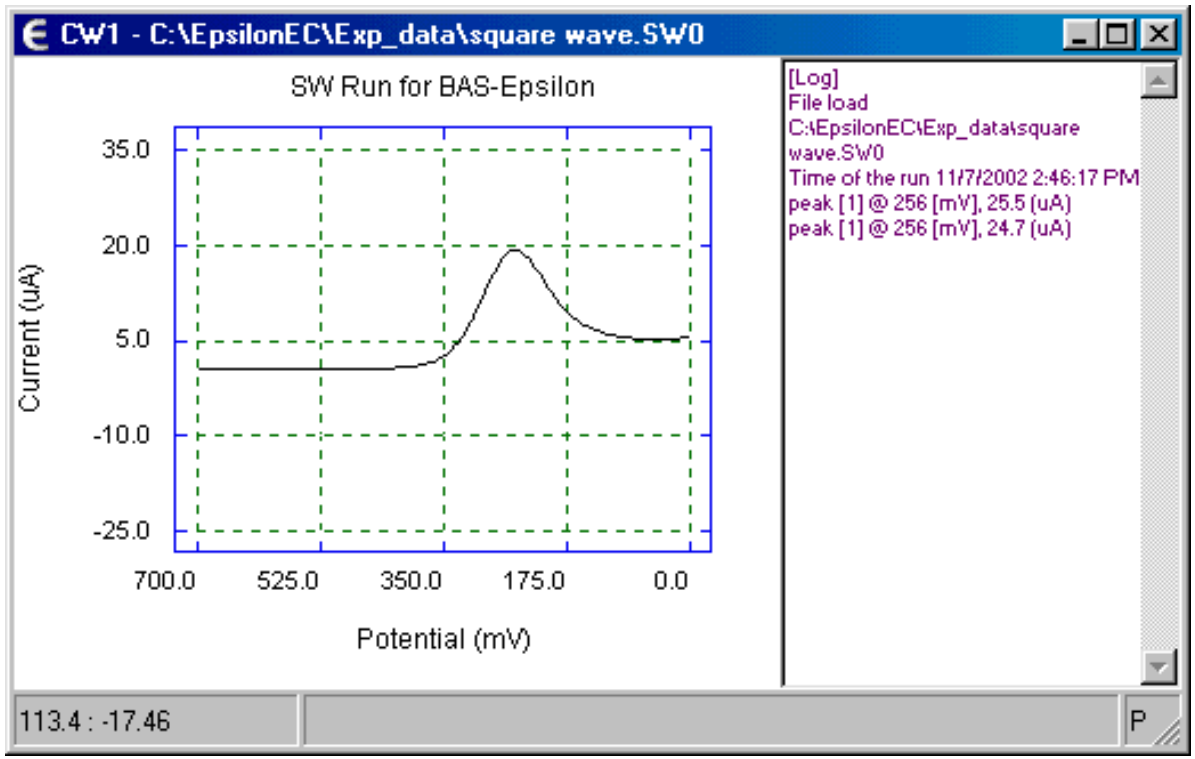

Figure 21. Forward current plot for **Square Wave Voltammetry**.

This completes the chemical test. All printed output should be shipped with the instrument. The power cord and cell lead (with alligator clips on the cell end) are shipped with the epsilon.

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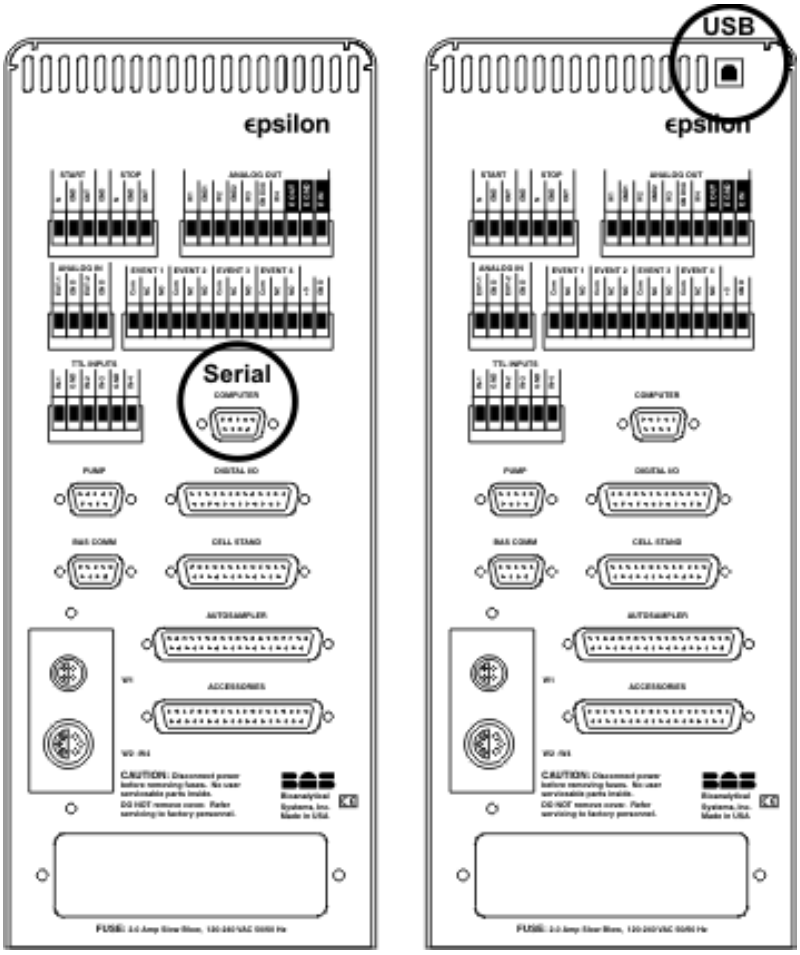
Installation

All cable connections to the epsilon system are made at the rear panel.



Power

The epsilon system requires a grounded power supply, providing either 120 or 240 V at 50/60 Hz. Before connecting the power cord, check that the indicator next to the power connection shows the correct voltage (**F1**).

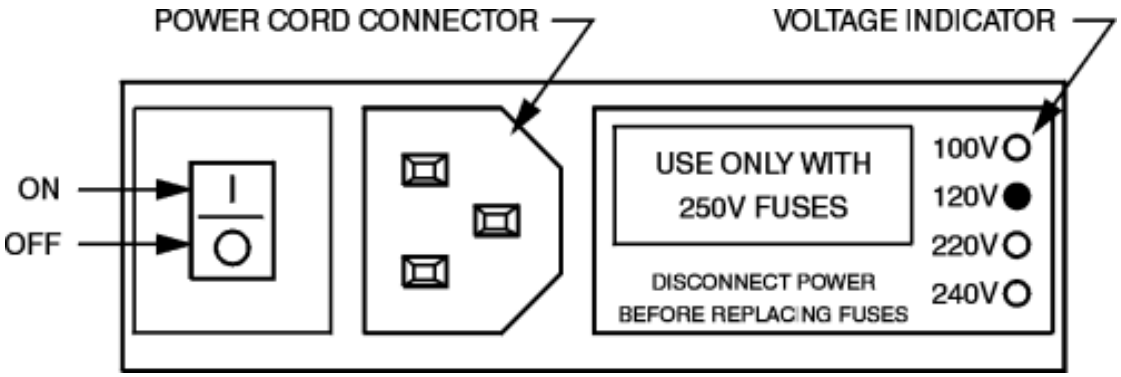


Figure 1. Power connection.

If the indicator does not show the correct voltage, pry open the cover to the right of the connector and pull out the voltage selector card (**F2**).

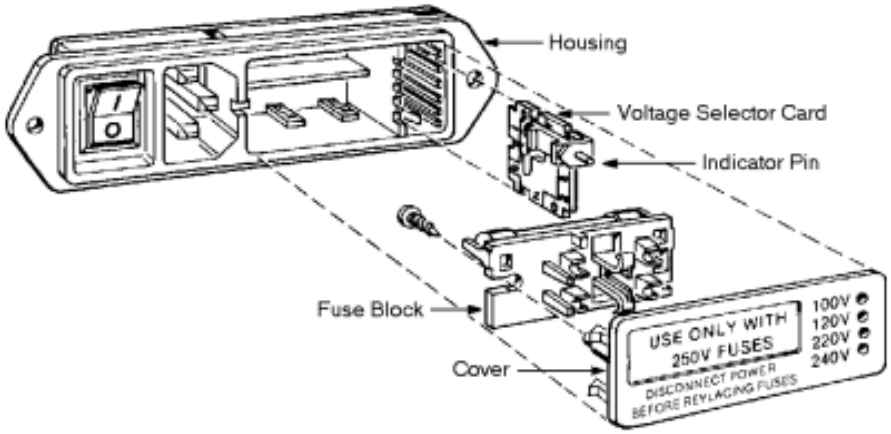


Figure 2. Accessing the voltage selector card.

Orient the card so that the label for either 120 V or 240 V (do NOT use 100 V or 230 V) gets inserted first, with the writing facing towards your left. Slide the plastic indicator around so it nestles in the correct slot opposite the indicated voltage, then reinsert the circuit board. Install the cover and make sure that the correct voltage is indicated.

Computer

Older model epsilons require serial port (COM port) computer connection and newer models use USB connection to the computer. Note the difference in the back panels at the beginning of this section. If the epsilon does not have a USB connecter in the upper right corner of the back panel, then it requires a serial port connection. The two connections are discussed below.

Serial port connection
The epsilon system requires a Pentium III or better computer, 50 MB available hard drive space running Windows 98, ME, 2000, or XP (Windows NT cannot be used to run the epsilon software after version 1.40.67). Connect a standard 9-pin, RS-232 serial cable between any COM port on the computer and the COMPUTER port on the epsilon (**F3a**).

USB connection
The epsilon system requires at least a Pentium III or better computer with 128 MB RAM, 50 MB available hard drive space running Windows 2000, or XP. Connect a standard USB cable between any USB port on the computer and the USB port on the epsilon (**F3b**).

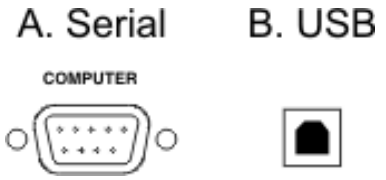


Figure 3. Computer connection: a. **COMPUTER** port for serial control and b. **USB** port.

Software Installation
The installation disk contains a **Readme.txt** file which explains the changes from the last version. It also contains three different installation programs. Selection of the proper installation program depends computer connection (Serial or USB) and on the operating systems of the computer. Examples are shown below. (Note that names may be slightly different on upgrade disk.)

- Serial-9X-ME-EpsilonEC-V160-setup.exe for Windows 98 and Me
- Serial-2K+ EpsilonEC-V160-setup.exe for Windows 2000 and XP
- USB-EpsilonEC-V161-setup.exe for Windows 2000 and XP

To install the new software, place the CD in your CD ROM drive. Open the appropriate file for your computer. Follow the instructions as they appear on the monitor. Alternatively, EC epsilon software may be downloaded from the BASi web site.

Cell Connection

The cell lead cable is the group of wires that connects the epsilon to the electrodes of the electrochemical cell. If the epsilon has only one active channel (i.e., it is a mono-potentiostat), one end of this cable plugs into **W1** on the rear panel of the epsilon (**F4**), and the other end is attached to the electrodes. If there is more than one active channel (i.e., a bipotentiostat), there is also a lead to connect the additional working electrode that plugs into **W2-W4** (note that this port is larger than the **W1** port).

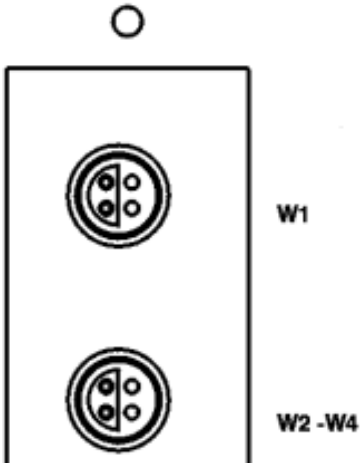


Figure 4. Cell lead connections **W1** and **W2-W4**.

WARNING: NEVER CONNECT OR ADJUST THE CELL LEADS DURING AN EXPERIMENT OR WHEN CELL=ON. DOING SO COULD DAMAGE THE SENSITIVE AMPLIFIERS AND VOID YOUR WARRANTY.

The end of the cell lead that is attached to the electrodes may be a direct connection using the general purpose cable sent with the epsilon or one for attachment to a cell stand such as the BAS C3 Cell Stand. The general purpose cable terminates with alligator clips that attach directly to the cell electrodes (**F5**).

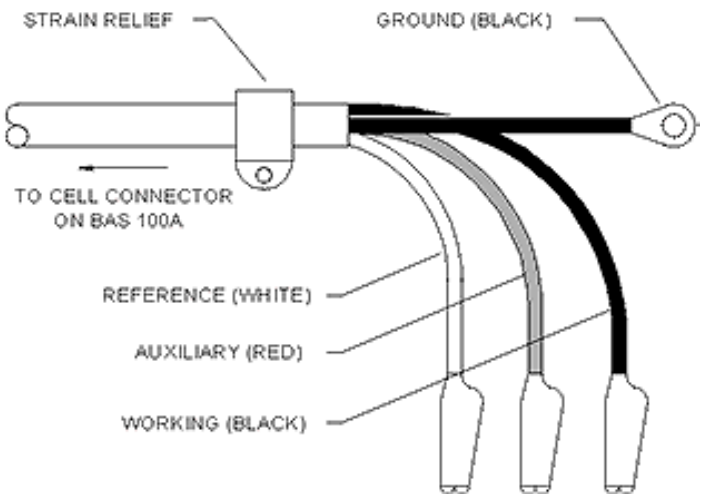


Figure 5. Cell (electrode) end of cell lead.

There are 3 electrode leads and 1 grounded (shielding) lead. The color code is:

Black covered wire:	Working electrode lead
Red covered wire:	Auxiliary electrode lead
White covered wire:	Reference electrode lead
Bare or black wire w/lug:	Earth ground connector

A plastic mounting lug near the end of the cell cable provides relief by preventing movement of the line or cell.

Analog Input/Output

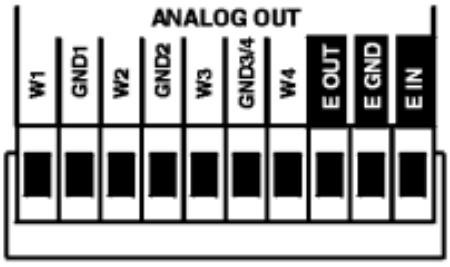


Figure 6. Analog input and output.

Analog inputs and outputs (**F6**) can only be used for potentiostatic techniques. An analog output is provided for each of the available epsilon channels (only **W1** and **W2** are currently available for the EC epsilon), and must be activated from within the software from the **Manual Settings** dialog box in the **Experiment** menu (check **External I Out**). These outputs have a full scale output of ± 10 V and are provided for connection to chart recorders and other data-acquisition devices. The **W1** or

W2 terminal should be connected to the "high" or "+" input of the peripheral device, and the **GND** terminal to the "low" or "-" input (do not use any additional grounding that may be available on the peripheral device.

An output (**E OUT**) is provided to monitor the potential applied to the cell on **W1** (or the potential of the working electrode in the **Open Circuit Potential** technique), and an input (**E IN**) is provided to apply a potential to **W1** from an external source (this external potential is summed to the potential applied by the epsilon). The **E IN** function must also be activated from the **Manual Settings** dialog box in the **Experiment** menu (check **External E In**). It should be noted that noise may be introduced into the system when **E IN** is activated.

Remote Start/Stop

Figure 7. Remote Start/Stop.

The remote start and stop connections (**F7**) provide several alternatives for sending and receiving signals to and from other instruments. These functions are fixed in time and can not be modified. For *programmable* triggers to remote instruments, see **Timed Events** below.

START IN	Allows an external device to trigger the start of an experiment. Note that this is not the start of data acqusition, and several hundred msec plus the **Quiet Time** may elapse from the trigger until data acquisition starts. A switch closure or TTL-low of at least 55 msec across the **START IN** terminal and its ground will trigger the run when the check box for **Run - External Trigger** has been selected in the **Change Parameters** dialog box.
START OUT	Used to trigger other instruments at the start of an experiment. It provides a 1 s TTL-low when the **Run** is activated.
STOP IN	Not applicable in the EC epsilon.
STOP OUT	Used to trigger other instruments at the end of an experiment. It provides a TTL-low of 1 sec duration at the end of the run. The time between the last data point acquired and the STOP OUTsignal depends upon the technique and its parameters.

Timed Events

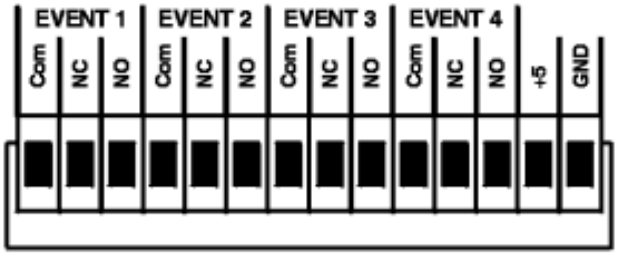


Figure 8. Timed Events.

Timed Events are programmable switch closures that provide exceptional flexibility for controlling peripheral instruments. Four switches are provided, which can be connected in a normally-open (NO) or a normally-closed (NC) configuration (**F9**). Two possible configurations to create TTL signals are shown below (**F10** & **F11**). With both configurations the trigger line will normally be at 5 V and will step to 0 V when activated. In **F11**, the resistor (e.g., 1 - 10 kohm) is required to limit the current drawn from the 5 V power supply. These switches may be manually activated from the **Manual Settings** dialog box in the **Experiment** menu or programmed in the **Sequential Techniques** dialog box.

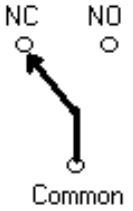


Figure 9

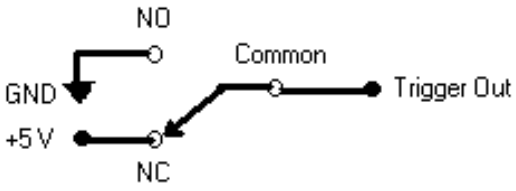


Figure 10

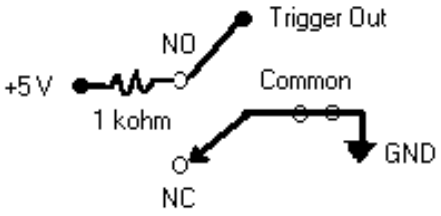


Figure 11

The maximum specifications of the relays are: 3 VA, 28 V DC or peak AC, 250 mA switching, 500 mA carry.

Starting the epsilon

The most important part of starting the epsilon is establishing the link between the epsilon and the PC. The epsilon should be switched on first, and then epsilon PC software should then be opened. The link between the PC and the epsilon will automatically be established. The status of the link will be displayed in the **CS Link Dialog** box, which will disappear once connection has been established. The **CS Link Dialog** box is slightly different, depending serial or USB connection.

Serial connection
There is a comm link indicator (**Comm1**, **Comm2**, **Comm3**, **Comm4**, or **DEMO**) in the status bar of the main window. This is used to distinguish between multiple open files when controlling more than one epsilon from a single PC.

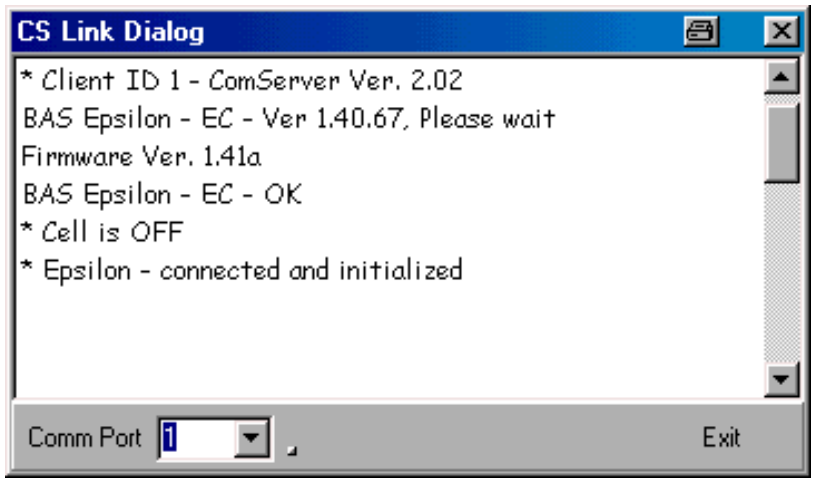


Figure 12. CS Link Dialog box.

If the link is not established (this is indicated by the message in **F13**), first check that the correct com port has been selected, then try to establish the link using the **Retry** button.

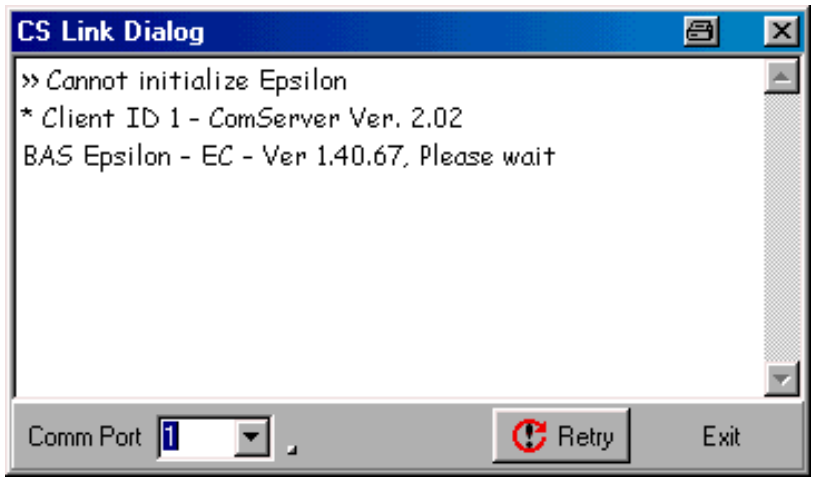


Figure 13. CS Link Dialog box with link failed message.

USB connection
A similar CS Link Dialog box is displayed with the USB connection, except it does not contain the comm. port selection. There is a link indicator (**USB** or **DEMO**) in the status bar of the main window.

If the link is broken after it has been established, the PC and epsilon can be reconnected using **Reconnect epsilon** in the **Experiment** menu.

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Interfacing BASi Accessories with the epsilon

Cell Stand (C3 and CGME)

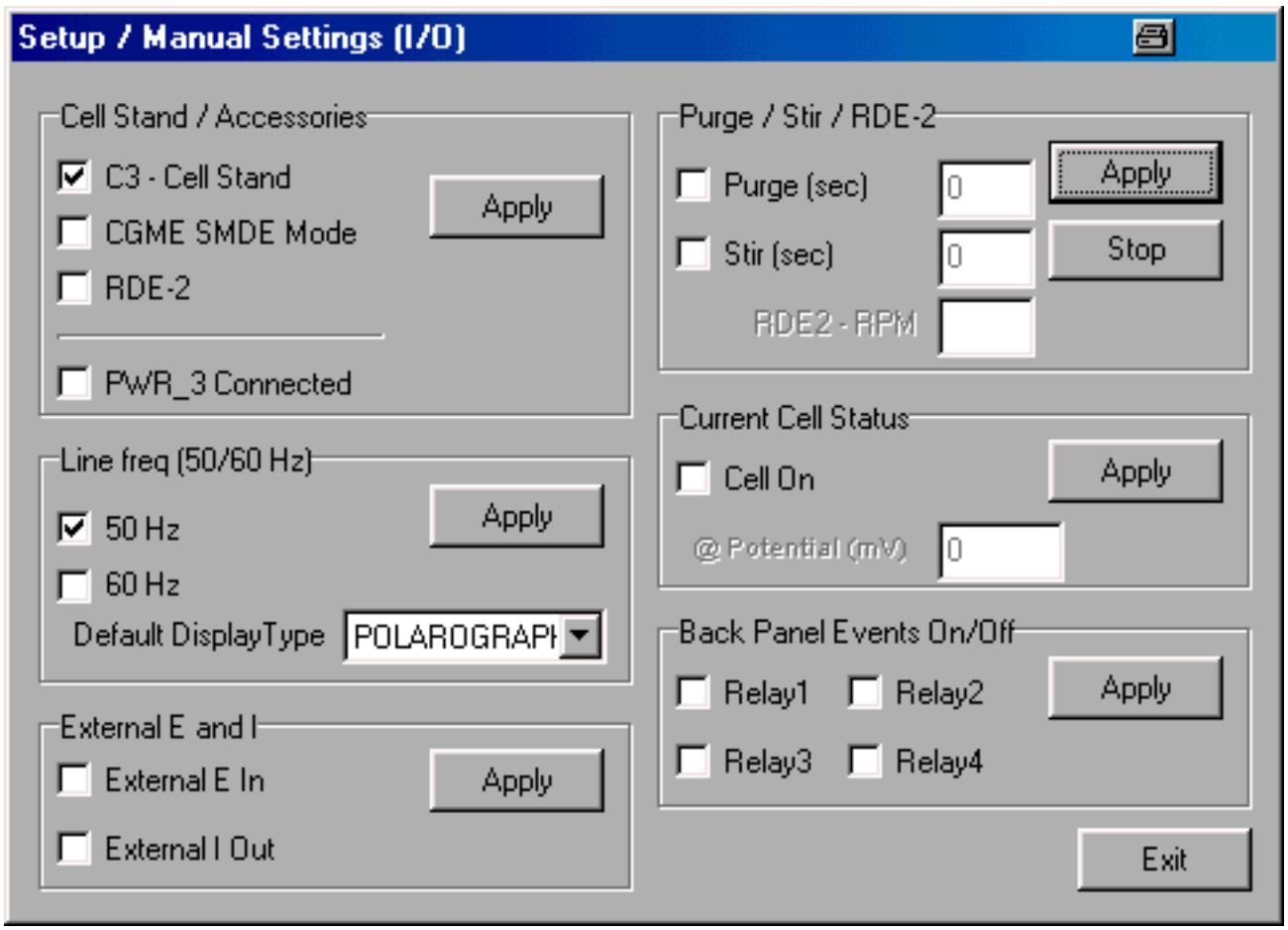


Figure 1. Manual Settings dialog box.

Various operations of BASi Cell Stands (i.e., purge and stir for the C3 Cell Stand; purge, stir, and knock/dispense for the CGME Mercury Electrode) can be controlled from the epsilon.

1. Connect the Cell Stand (C3 or CGME) to the epsilon using i) the 25-pin ribbon cable provided with the Cell Stand between the **CELL STAND** port on the rear panel of the epsilon and the **REMOTE** port of the Cell Stand and ii) the LEMO-LEMO cable provided with the Cell Stand between the **CELL** port of the Cell Stand and the **W1** port of the epsilon.
2. Select the appropriate **Cell Stand** (**C3 - Cell Stand** or **CGME SMDE Mode)** in the **Setup / Manual Settings (I/O)** dialog box (**F1**) in the **Experiment** menu.

RDE-2 Rotating Disk Electrode

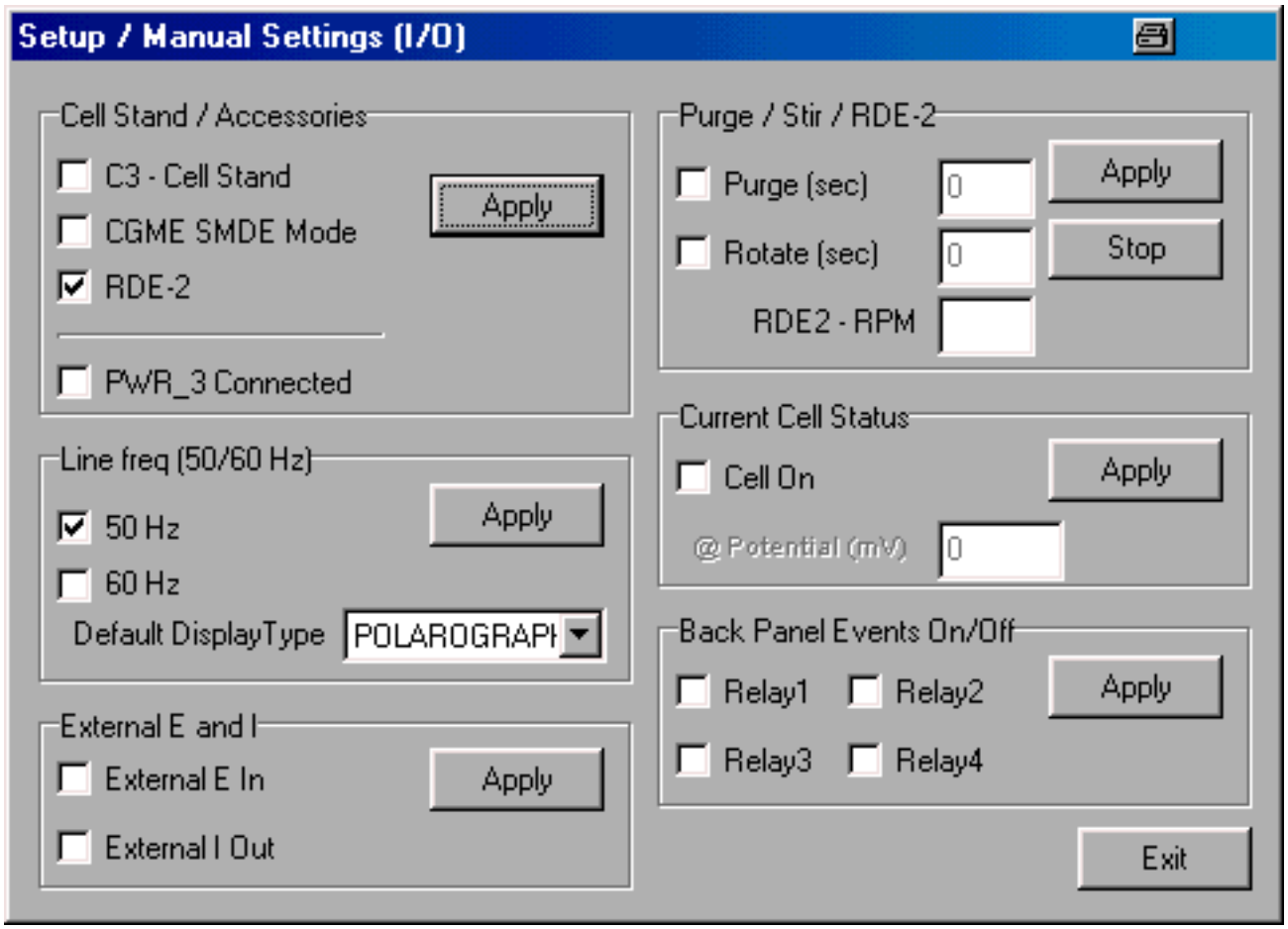


Figure 2. Manual Settings dialog box for the RDE-2.

The rotation and purging functions of RDE-2 Rotating Disk Electrode can be controlled from the epsilon.

1. Connect the RDE-2 to the epsilon using i) the 37-pin ribbon cable provided with the PWR-3 between the **ACCESSORIES** ports on the two instruments and ii) the LEMO-LEMO cable provided with the RDE-2 between the **CELL** port of the RDE-2 and the **W1** port of the epsilon.
2. Select **RDE-2** in the **Setup / Manual Settings (I/O)** dialog box (**F2**) in the **Experiment** menu. Valid rotation rates are 0, 50 - 10,000 RPM.

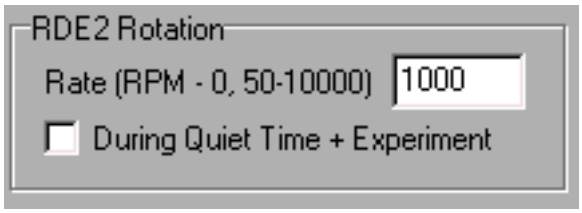
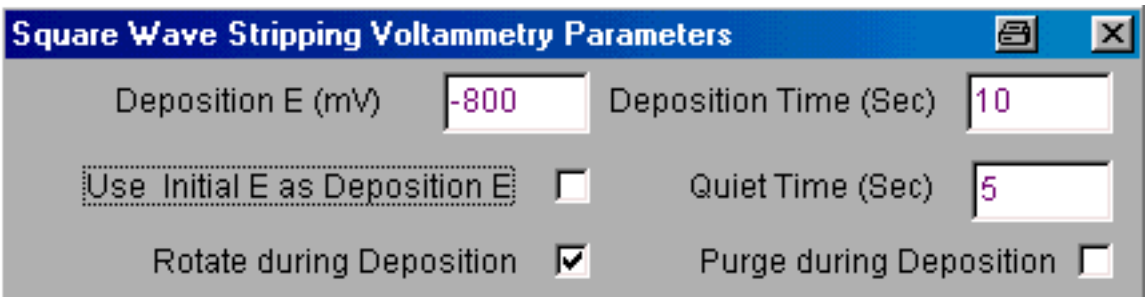


Figure 3. Control of rotation rate during an experiment

Rotation rate during an experiment is set under **Cell** in the **Parameters** dialog box (**F3**), and is available for all techniques other than Chronopotentiometry, Double Step Chronoppotentiometry, and Open Circuit Potential vs. Time.

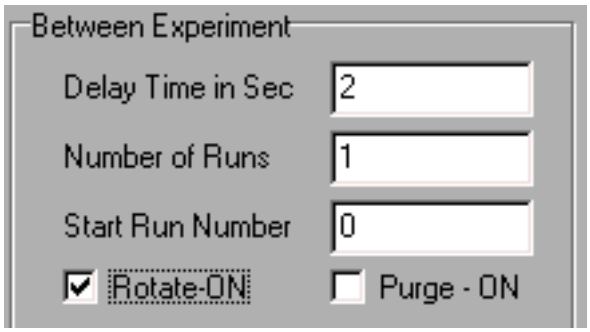
In addition to rotation during experiments, rotation can be controlled during the following periods:

1. **Deposition Time** (**Parameters** dialog box of stripping techniques)



2. **During Quiet Time + Experiment** (**Cell** in **Parameters** dialog box)

3. **Between Experiments** (**MR** in **Parameters** dialog box)



PWR-3 Power Module

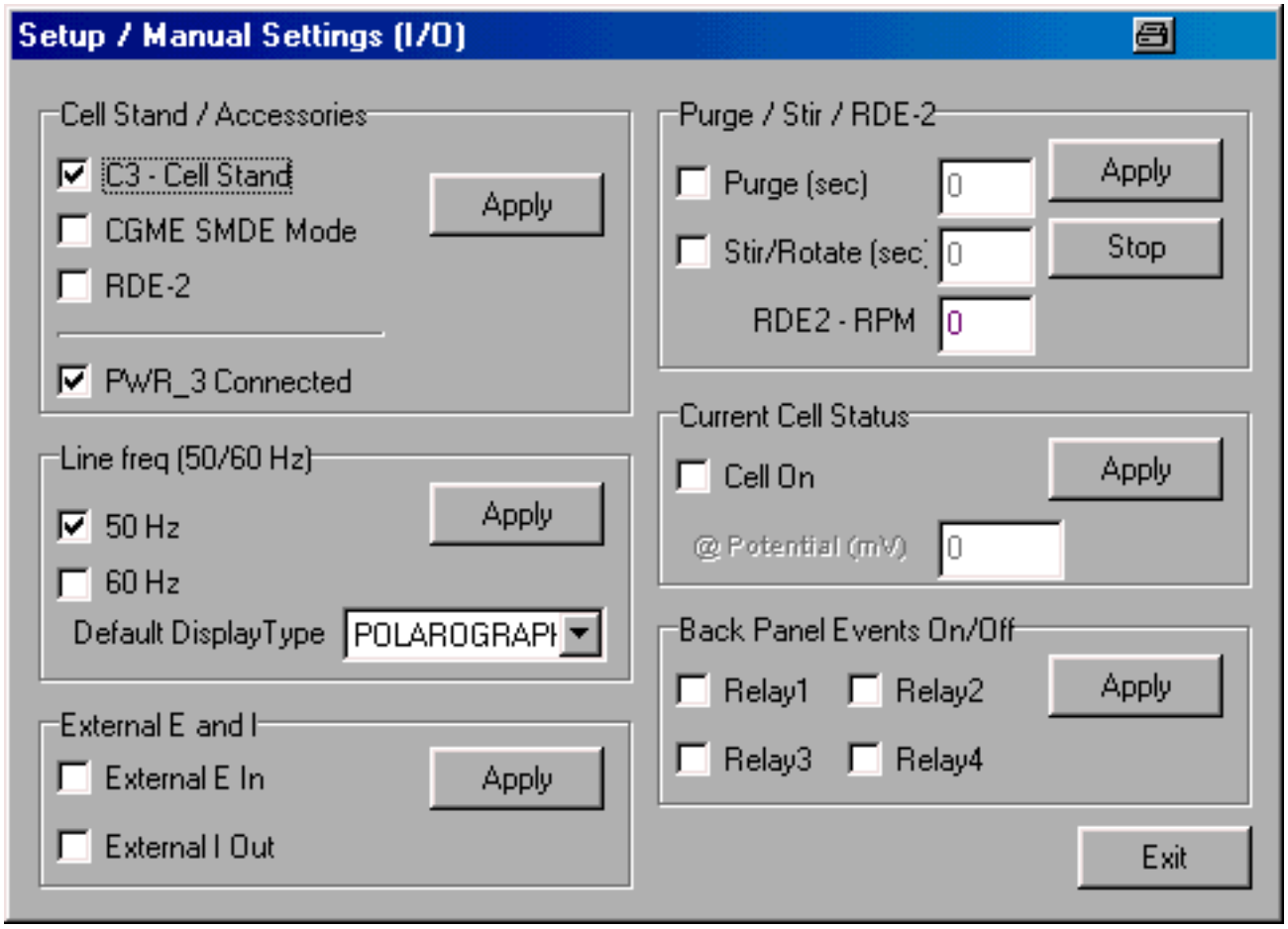


Figure 4. Manual Settings dialog box for the PWR-3.

The BASi PWR-3 Power Module can be controlled using the epsilon software.

1. Connect the PWR-3 to the epsilon using i) the 37-pin ribbon cable provided with the PWR-3 between the **ACCESSORIES** ports on the two instruments and ii) the LEMO-LEMO cable provided with the PWR-3 between the **REMOTE** port of the PWR-3 and the **W1** port of the epsilon.
2. Select **PWR-3 Connected** in the **Setup / Manual Settings (I/O)** dialog box (**F4**) in the **Experiment** menu.
3. Set the PWR-3 front panel **Function** switch to **Standby** (the epsilon will turn cell On/Off).
4. Valid **Full Scale** current ranges for the PWR-3 are 1 Amp, 100 mA, and 10 mA.

Techniques that work with PWR-3 connected are:

- Cyclic Voltammetry
- Linear Sweep Voltammetry
- Chronoamperometry/Chronocoulometry
- Controlled Potential Electrolysis
- DC Potential Amperometry

Therefore, when the PWR-3 is connected, all other techniques are labeled as DEMO under **Select NEW Experiment**. Data files for DEMO techniques can be loaded, but new experiments cannot be run (this includes files of the compatible techniques that were acquired without the PWR-3 connected).

Since the PWR-3 is a separate potentiostat, the following epsilon features will NOT work with the PWR-3 connected:

- iR compensation
- Measurement of the open-circuit (rest or equilibrium potential)
- **Apply Open Circuit Potential for Initial E**

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Epsilon EC Upgrade Guide

The epsilon platform is designed to grow with your needs. A number of upgrades are possible and the specifics of what needs to be upgraded will vary. Below are the four components that can be upgraded.

1. Computer software.
2. The firmware in the epsilon.
3. The techniques that can be performed.
4. The number of channels in the epsilon (e.g., bipotentiostat).

Computer Software Upgrade

The installation disk contains a **Readme.txt** file which explains the changes from the last version. It also contains three different installation programs. Selection of the proper installation program depends computer connection (Serial or USB) and on the operating systems of the computer. Examples are shown below. (Note that names may be slightly different on upgrade disk.)

- Serial-9X-ME-EpsilonEC-V160-setup.exe for Windows 98 and Me
- Serial-2K+ EpsilonEC-V160-setup.exe for Windows 2000 and XP
- USB-EpsilonEC-V161-setup.exe for Windows 2000 and XP

It is best to uninstall the old software and then install the new software. If uninstalling Vers 1.0 or 1.1 software, click **Start**, go to **Settings**, click on **Control Panel**, open **Add/Remove Programs**, select **EpsilonEC** and click on **Add/Remove**. Follow the instructions as they appear on the monitor.

To install the new software, place the CD in your CD ROM drive. Open the appropriate file for your computer operating system. Follow the instructions as they appear on the monitor. Alternatively, EC epsilon software may be downloaded from the BASi web site.

Note that upgrading an epsilon may require updating both the computer software as well as the firmware (internal software). Please follow the instructions in the next section for upgrading the firmware.

Firmware Upgrade

A special program is used to update the epsilon firmware (embedded software) and/or to increase the number of available techniques (see **Techniques Upgrade**). The firmware upgrade requires a file with the .sre extension. The file name will contain a larger number than predecessors. If new computer software was installed (see above), then the new .sre file will be in the same folder as the main program (e.g., C:\EpsilonEC). The following procedure must be followed for the upgrade.

NOTE: The epsilon must be switched ON in order for this program to function. THE EPILSON MUST REMAIN ON UNTIL THE UPGRADE HAS BEEN COMPLETED.

1. Open the epsilon program.
2. In the **Experiment** menu, click on **Update Hardware**. The epsilon program will close and the **Update** program will automatically open.
3. If upgrading a serial epsilon and the message appears "Can NOT find BAS - Epsilon @ Comm Port #," ensure the correct comm (serial) port has been selected in **Change Comm Port** in the **File** menu. If upgrading a USB epsilon and the message appears "Can NOT find BAS - Epsilon (USB)," then check the computer cable and restore the connection between the PC and the epsilon using **Reconnect Epsilon**, also in the **File** menu.
4. Click **Upgrade Firmware** in the **Update** menu, and select the .sre file. The upgrade process may take a few minutes. At the end of the process, the program compares the version numbers before and after the upgrade. If the upgrade has been successful (i.e., the version number has changed), the message "Firmware - Upgraded" will be displayed. If the version number remains the same, the message "Firmware - NOT upgraded" will appear.
5. Once the firmware upgrade has been completed successfully, either go to the next section to upgrade the available techniques, or close the program and re-open the epsilon software.

Techniques Upgrade

A special program is used to increase the number of available techniques or to update the epsilon firmware (embedded software) (see **Firmware Upgrade**). The techniques upgrade requires a file with the .upg extension. The new .upg file will be on a separate disk The following procedure must be followed for the upgrade.

NOTE: The epsilon must be switched ON in order for this program to function. THE EPILSON MUST REMAIN ON UNTIL THE UPGRADE HAS BEEN COMPLETED.

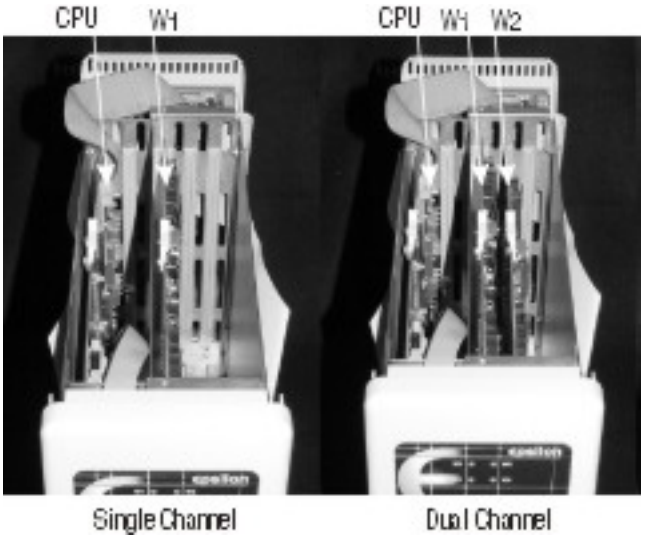
1. Once you have purchased an upgrade that contains additional techniques, you must first send BASi the serial number of your epsilon and the code that identifies the instrument before BASi can send you the file required to upgrade the number of techniques. The file for increasing the number of techniques has the .upg extension. The form shown under **Save BASi-Epsilon Information File** must be completed and sent to BAS. This form can be saved and e-mailed to

BASi at upgrade@bioanalytical.com, or it can be printed and FAXed to 765-497-1102. The identification code for your epsilon is automatically added to the form by the software.

2. Open the epsilon program.
3. In the **Experiment** menu, click on **Update Hardware**. The epsilon program will close and the **Update** program will automatically open.
4. If upgrading a serial epsilon and the message appears "Can NOT find BAS - Epsilon @ Comm Port #," ensure the correct comm (serial) port has been selected in **Change Comm Port** in the **File** menu. If upgrading a USB epsilon and the message appears "Can NOT find BAS - Epsilon (USB)," then check the computer cable and restore the connection between the PC and the epsilon using **Reconnect Epsilon**, also in the **File** menu.
5. Go to the **Update** menu. To increase the number of techniques, click **Upgrade Techniques**, and select the .upg file from the dialog box. Note that this file is unique for every epsilon and can be run only once. The upgrade process takes a few seconds. At the end of the process, the following message will appear if the upgrade is successful:
    - End: Upgrade procedure completed, you may exit now.
    - Epsilon - upgraded.
    - If it was not successful, then the following message will appear:
    - End: Upgrade procedure completed, you may exit now.
    - Epsilon - NOT upgraded.
6. Once the upgrade has been completed successfully, close the program and reopen the epsilon software.

Increase the Number of Channels

Increasing the number of channels requires that a new .upg file be loaded into the epsilon (see Techniques Upgrade) and it requires that a W2 board be inserted into the instrument. The W2 board is shipped in an anti-static envelope. Be sure to eliminate static charge on you before removing W2 board from the envelope (see below). To insert the W2 board:



1. Unplug epsilon.
2. Remove eight Phillips screws from epsilon cover, then remove cover.
3. Remove top plate from the card rack cage after removing four straight screws holding it on.
4. Hold onto epsilon chassis while removing board from bag to prevent static damage.
5. Insert analog board in appropriate slot (see above figure). Make sure it is completely inserted.
6. Replace top plate.
7. Replace cover.

The cell lead cable for the second working electrode (W2) is included with the 2nd channel upgrade. The W2 cable has a silver LEMO connector that plugs into the W2-W4 port on the rear panel. (Note that this port is larger than the W1 port.) The cable terminates with an alligator clip that attaches directly to the electrode.

WARNING: NEVER CONNECT OR ADJUST THE CELL LEADS DURING AN EXPERIMENT OR WHEN CELL=ON. DOING SO COULD DAMAGE THE SENSITIVE AMPLIFIERS AND VOID YOUR WARRANTY.

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Introduction

This manual is intended to be a detailed description of the various functions of the epsilon electrochemistry software, together with a brief description of the available electrochemical techniques and their applications (there are also a number of notes available from BAS that provide more detail about these applications). These functions can all be accessed from the drop-down menus. Some are also available as icons on the tool bar, but few have keyboard shortcuts. The available routes will be noted in the appropriate sections. If you are new to this instrument, we recommend that, once the instrument has been installed, you first try the detailed experiment listed here that provides a step by step guide to the operation of some of the more basic functions of the epsilon.

The epsilon software runs in the Windows operating system. Wherever possible, we have maintained the style of Windows in the look and feel of our software. We use similar drop-down menus, list boxes, dialog boxes, radio buttons, help screens, etc. If you are already familiar with Windows, the transition to this software will be smooth. If Windows is new to you, we urge you to learn it first, using the Windows tutorial provided with your operating system.

It is important to note there are a number of different configurations for the epsilon, which differ in their capabilities. It is clearly shown in the text of this manual whether a function or electrochemical technique is included as standard on epsilon instrument, or whether it is only available as an optional addition (at an additional cost).

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Selecting a Technique

A number of different electrochemical techniques are available in the epsilon software, depending upon the version. For example, the most basic version has cyclic voltammetry (current vs. potential for a linear potential sweep), chronoamperometry, time base, bulk electrolysis (current vs. time at a constant potential), and chronpotentiometry (potential vs. time at a fixed current). These techniques have different applications, which will be discussed in detail in other sections. Other techniques, such as normal pulse and square wave voltammetries, are only available as optional extras (at an additional cost).

There are two ways to select a technique:

Opening a stored data file
Setting up a new experiment

Open

Selecting **Open** from the **File** menu (or using the **F3** key) will generate a standard Windows file dialog box, from which a previously saved data file can be loaded (**F1**) (note that the extension for the file name is specified by the technique; e.g., a cyclic voltammetry file has the extension .cv0).

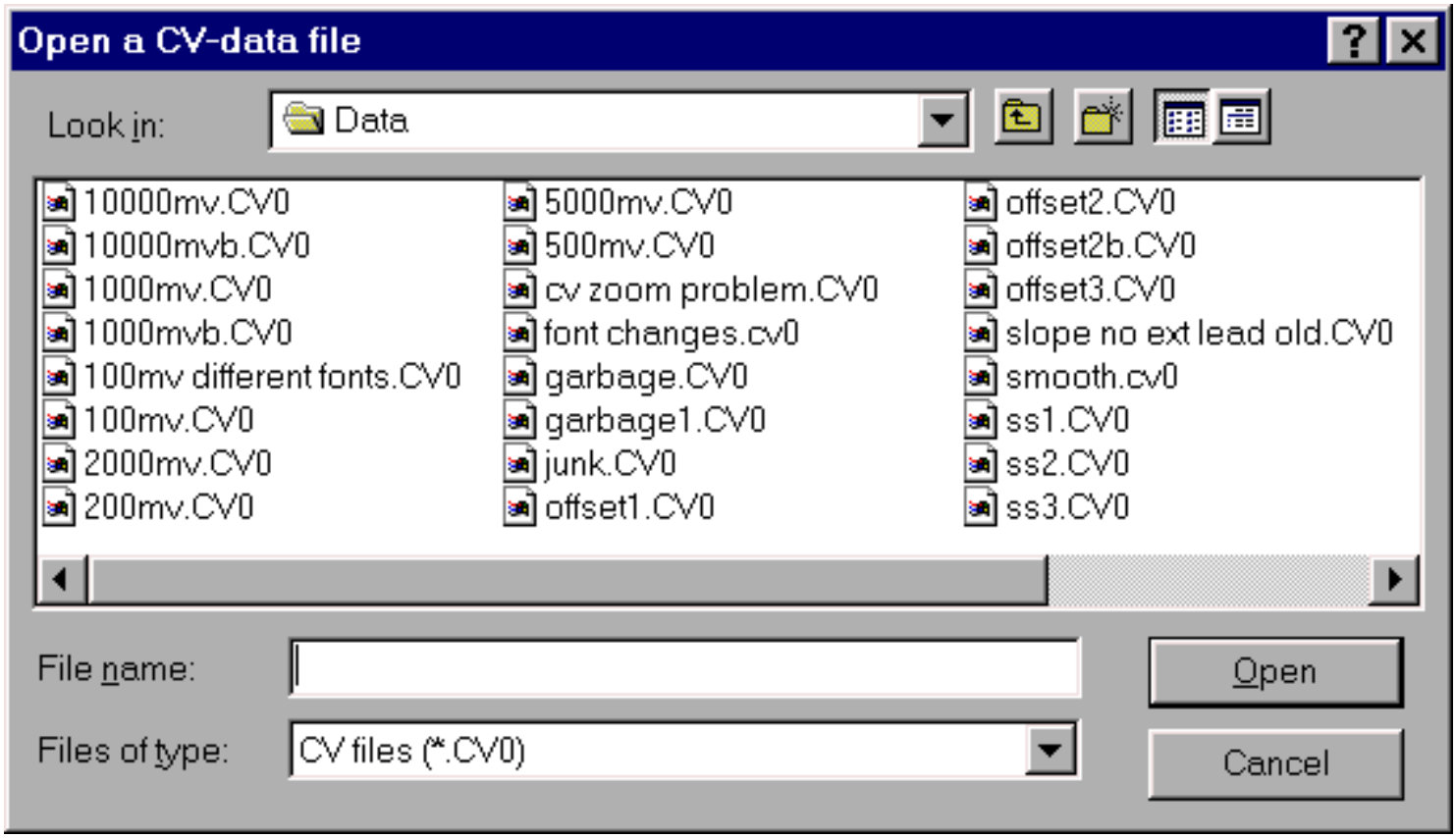

Figure 1. Open file dialog box.

Upon opening, the experimental data is displayed (**F2**), and the stored parameters are entered in the appropriate dialog boxes. The graphic options available for the experiment window are discussed in more detail in the Data Analysis and Display section.

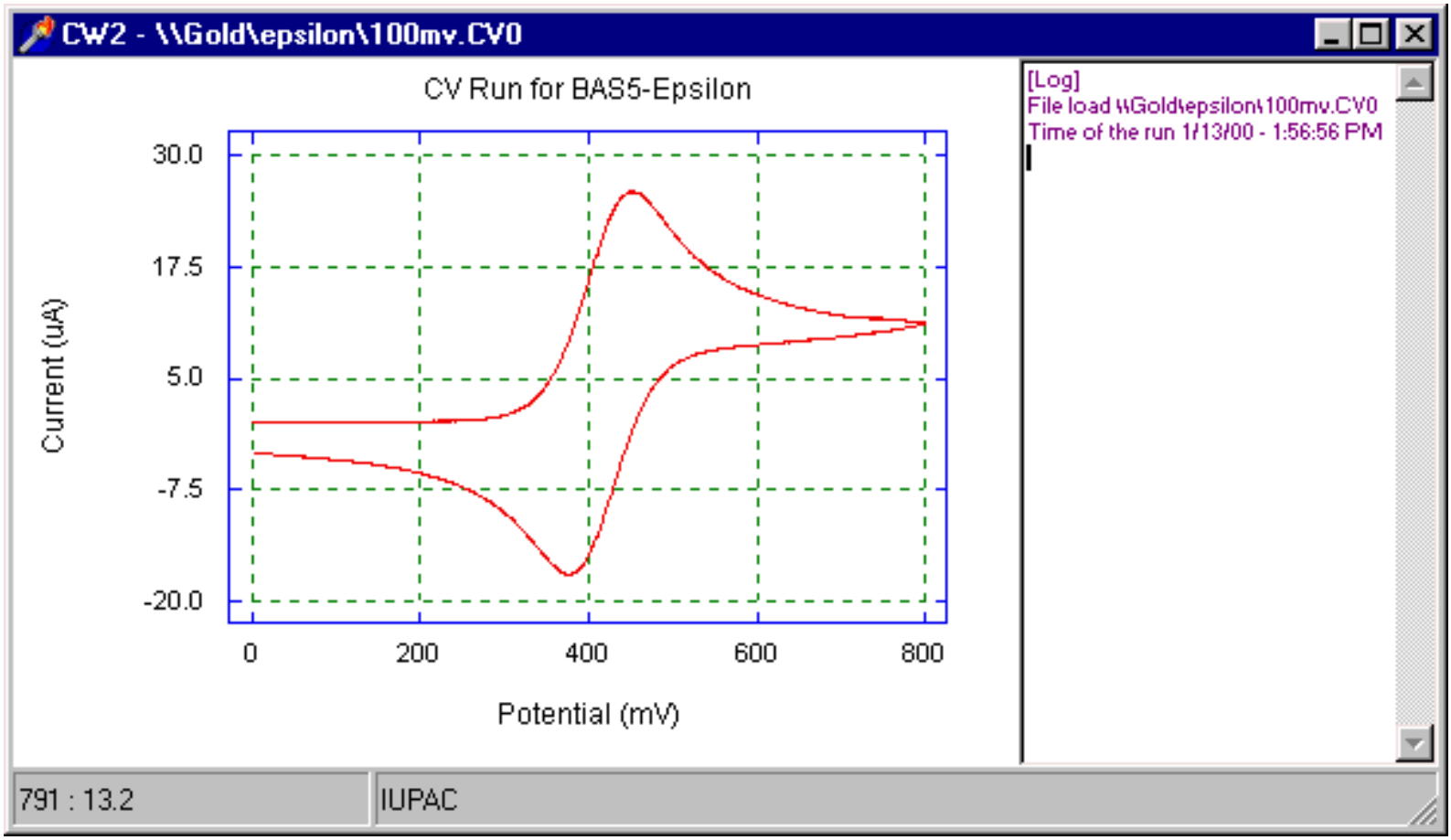

Figure 2. Opened experimental window.

If a second data file is loaded, the data for this experiment is displayed in a separate window. Although up to six data files can be opened and displayed simultaneously in separate windows, only one window can be active at any one time. The parameters entered in the various dialog boxes are associated with the active window, and experimental runs will use these parameters. The selected active window can be changed by clicking a different window.

The experimental windows can be dragged to a different position within the main window. Multiple windows can be tiled vertically, horizontally, or cascaded using the appropriate options in the **Window** menu.

Clicking the RIGHT mouse button in any experiment window will generate a pop-up menu (**F3**) with **Select Graph** and **Data** options appropriate for the technique specified for that window. The functions available in the pop-up menu are discussed in the relevant sections.

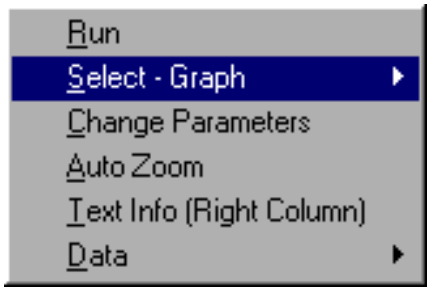

Figure 3. Right mouse button pop-up menu.

Cyclic voltammetry and linear sweep voltammetry data files from the BAS 100B/W and CV-50W can also be imported into the epsilon software for comparison and data analysis using **Read BAS 100W File** in the **File** menu. If this imported data shows oxidation currents as positive, it should be read in **as IUPAC data file**; if the oxidation currents are negative, it should be read in **as POLAROGRPAHIC data file**. It is also important to note some editing of the header may be required: if the Number of Segments = 0, this number should be reset to the appropriate number (2 or 3), and any lines related to iR compensation must be deleted. In addition, only data files for which **Sample Interval** = 1 mV can be loaded.

New

Selecting **New** from the **File** menu or the **New** icon will generate a menu that lists the available techniques (**F4**) (this list can also be generated by selecting **Select NEW Experiment** from the **Experiment** menu or by using the **F2** key).

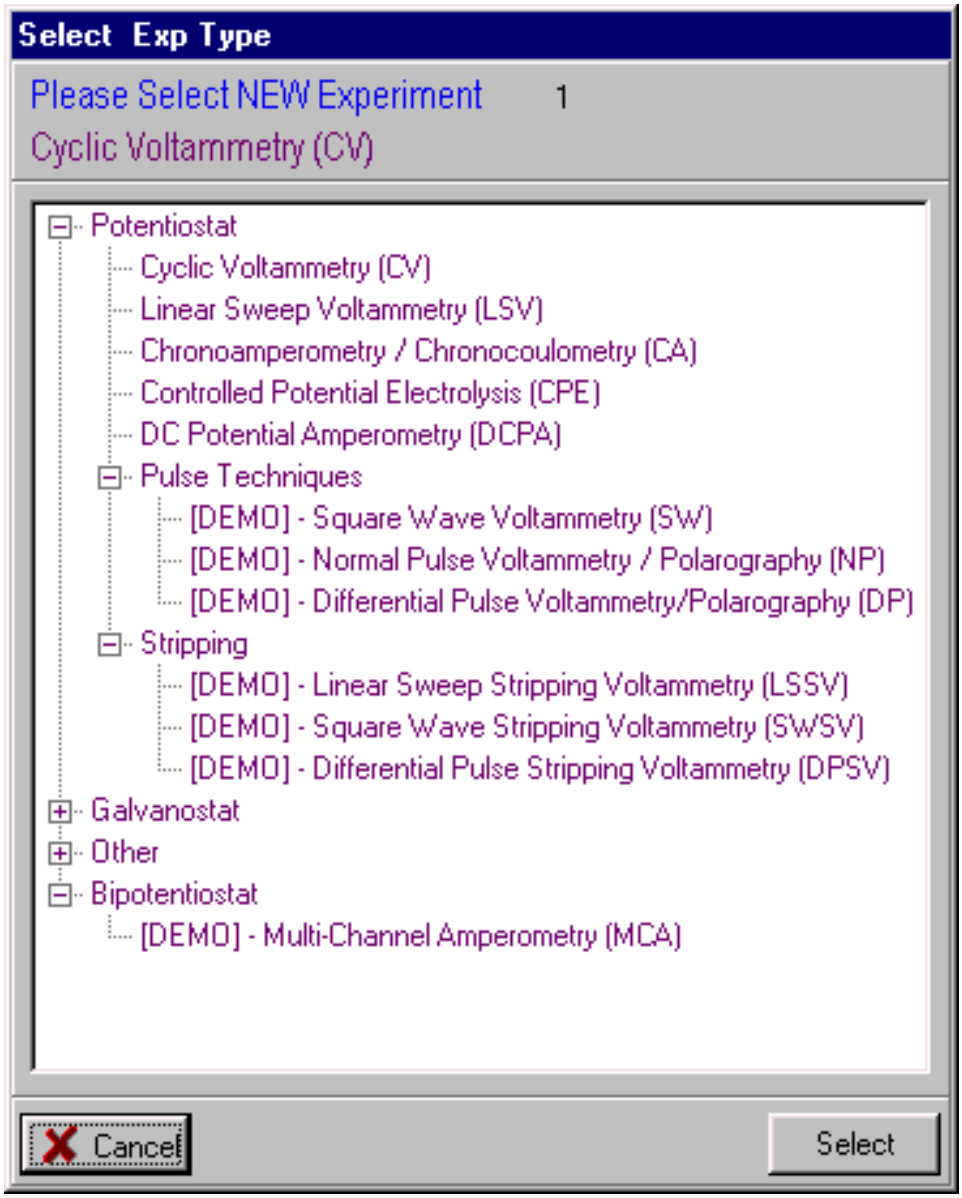

Figure 4. Technique list.

It should be noted that there are some techniques that are labeled as DEMO. This label indicates that this technique is NOT active on this particular epsilon. However, it is possible to load a data file for that technique to examine the parameters and the typical output. If the **RUN** button is clicked when a DEMO data file is displayed in the active window, an error message will be shown. The technique list shown in **F4** is the list for the basic epsilon (i.e., pulse techniques, stripping techniques, and multi-channel amperometry are NOT available).

Highlight the required technique, and click **OK** to confirm the selection. An experiment window containing an empty axis set is displayed (**F5**), and the appropriate parameters are set in the various dialog boxes. The graphic options available for the experiment window are discussed in more detail in the Data Analysis and Display section.

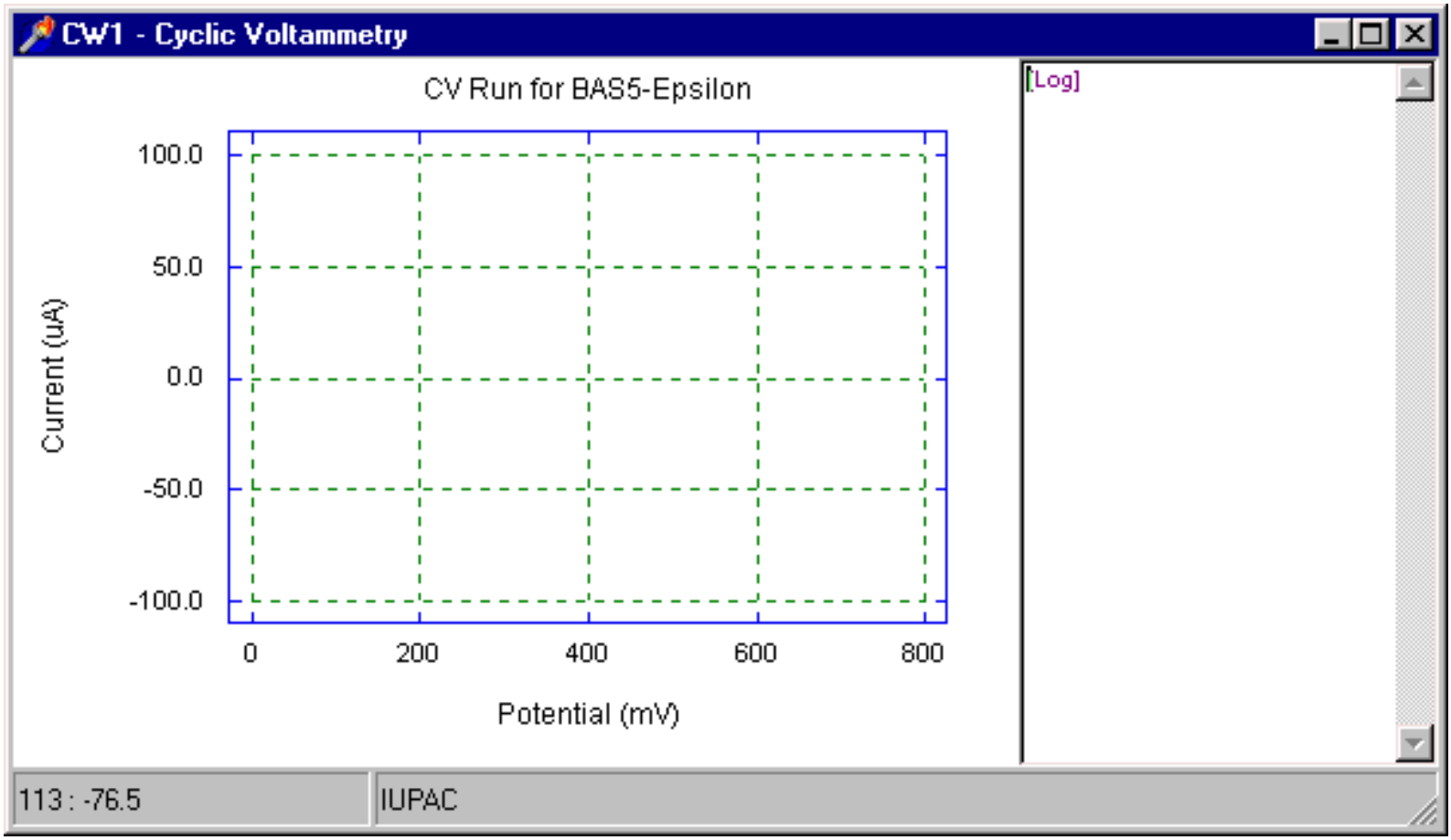

Figure 5. New experimental window.

Up to six experimental windows can be displayed simultaneously in separate windows by repeating the **Open** or **New** commands, although only one window can be active at any one time. The parameters entered in the various dialog boxes are associated with the active window, and experimental runs will use these parameters. The selected active window can be changed by clicking a different window.

The experimental windows can be dragged to a different position within the main window. Multiple windows can be tiled vertically, horizontally, or cascaded using the appropriate options in the **Window** menu.

Once the technique has been selected, the various experimental parameters (e.g., potential range, sensitivity) can then be entered using the **Change Parameters** dialog box.

Clicking the RIGHT mouse button in any experiment window will generate a pop-up menu (**F6**) with **Select Graph** and **Data** options appropriate for the technique specified for that window. The functions available in the pop-up menu are discussed in the relevant sections.

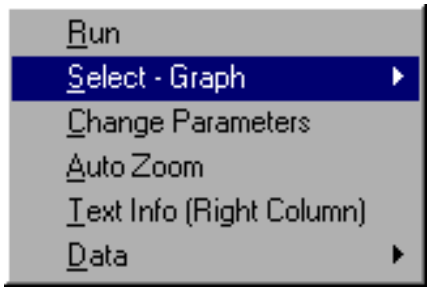

Figure 6. Right mouse button pop-up menu.

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Linear Sweep Voltammetry/Cyclic Voltammetry

Introduction

Cyclic voltammetry (**CV**) is one of the most commonly used electrochemical techniques, and is based on a linear potential waveform; that is, the potential is changed as a linear function of time. The rate of change of potential with time is referred to as the *scan rate*.

The simplest technique that uses this waveform is Linear Sweep Voltammetry (**LSV**). The potential range is scanned starting at the **Initial potential** and ending at the **Final potential**. **CV** is an extension of **LSV** in that the direction of the potential scan is reversed at the end of the first scan (the first **Switching Potential**), and the potential range is scanned again in the reverse direction. The experiment can be stopped at the **Final Potential**, or the potential can be scanned past this potential to the second **Switching Potential**, where the direction of the potential scan is again reversed (**F1**). The potential can be cycled between the two **Switching Potentials** for several cycles before the experiment is ended at the **Final Potential**. Both **LSV** and **CV** are standard techniques on the epsilon. Multichannel **CV** experiments are also available through the addition of the optional bipotentiostat board.

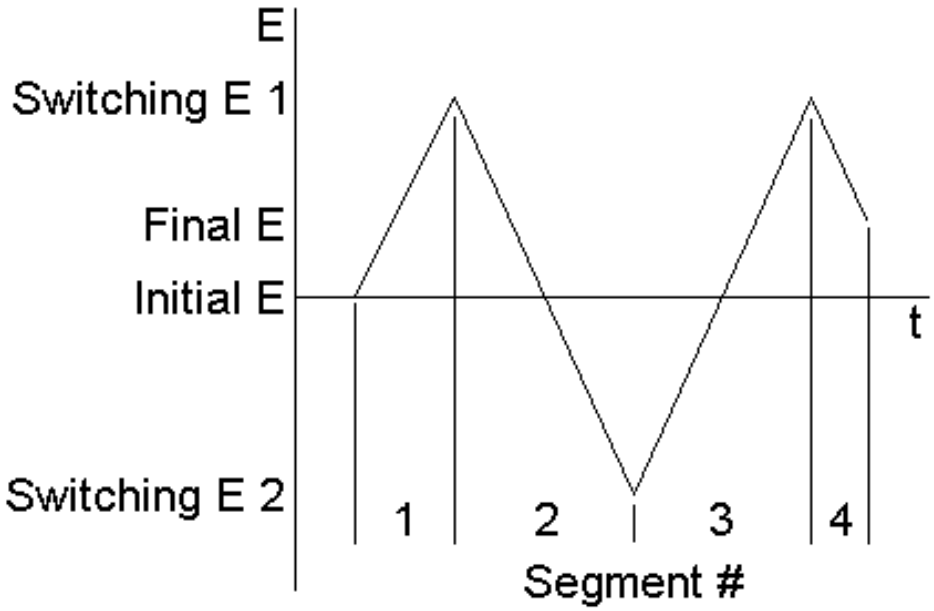


Figure 1. Potential wave form for cyclic voltammetry.

Setting Up a Linear Sweep/Cyclic Voltammetry Experiment

The potential limits and the scan rate for **LSV** are set using the **Change Parameters** dialog box (**F2**) in either the **Experiment** menu or the pop-up menu.

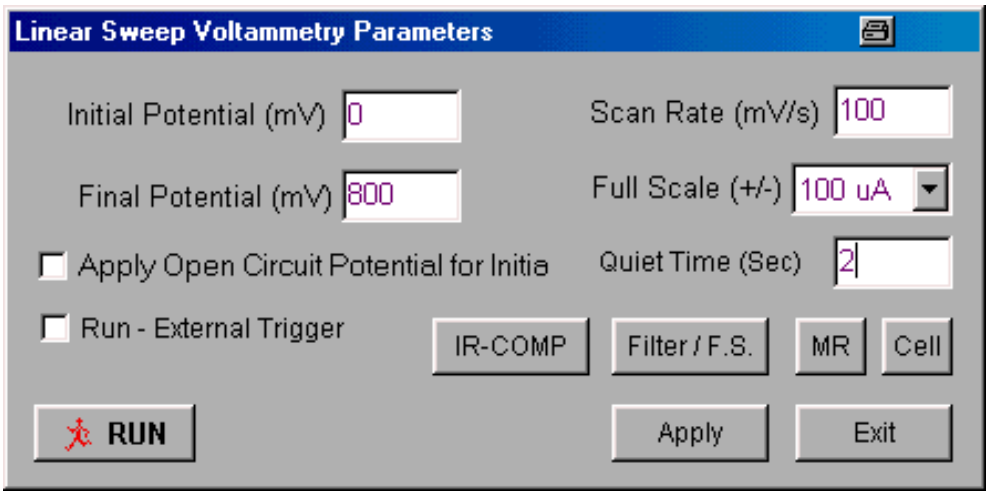


Figure 2. Change Parameters dialog box for linear sweep voltammetry.

1. Potential values are entered in mV, and the **Scan Rate** in mV/s.
2. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
3. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start In** back-panel connection.
4. When the experiment is started, the cell is held at the **Initial Potential** for the number of seconds defined by the **Quiet Time**.
5. The experiment can be run on a hanging mercury drop electrode (i.e., a single drop is used for the entire experiment) using a BASi CGME by selecting **CGME SMDE Mode** from **Cell Stand / Accessories** in the **Setup / Manual Settings (I/O)** dialog box.
6. A rotating disk experiment can be run using a BASi RDE-2 by selecting **RDE-2** from **Cell Stand / Accessories** in the **Setup / Manual Settings (I/O)** dialog box and entering the required **Rotation Rate** under **RDE2 Rotation** in the **Cell** dialog box.
7. There are two gain stages for the current-to-voltage converter. The default values of these stages that are used for a given current **Full Scale** value are determined by the software. However, they can be adjusted manually using the **Filter / F.S.** dialog box. This dialog box is also used to change the analog **Noise Filter Value** settings from the default values set by the software.
8. The default condition of the cell is that the cell is **On** (i.e., the electronics are connected to the electrodes) *during* the experiment, and is **Off** *between* experiments. However, the potential can be switched **On** *between* experiments using the **Cell** dialog box. **HOWEVER, THIS OPTION SHOULD BE USED WITH CAUTION SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**
9. A series of identical experiments on the same cell can be programmed using the **MR (Multi-Run)** option.
10. Clicking the **IR-COMP** button activates the **iR compensation** option.
11. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
12. Range of allowed parameter values:
    - **Potential** = -3275 - +3275 mV
    - **Scan Rate** = 1 - 25,000 mV/s (also see below for further discussion)
    - **Quiet Time** = 0 - 100 s
13. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

Up to four parameters are used in the epsilon software to define the potential wave form for **CV**.

1. Initial Potential
2. Switching Potential 1
3. Switching Potential 2
4. Final Potential

The defined waveform will also depend upon the number of segments.

- 1 segment - Initial Potential - Final Potential (this is equivalent to an **LSV** experiment)
- 2 segments - Initial Potential - Switching Potential 1 - Final Potential
- 3 segments - Initial Potential - Switching Potential 1 - Switching Potential 2 - Final Potential (setting Final Potential equal to Initial Potential will generate a complete potential cycle)
- 4 segments - Initial Potential - Switching Potential 1 - Switching Potential 2 - Switching Potential - Final Potential

The potential limits and the scan rate for **CV** are set using the **Change Parameters** dialog box (**F3**) in either the **Experiment** menu or the pop-up menu.

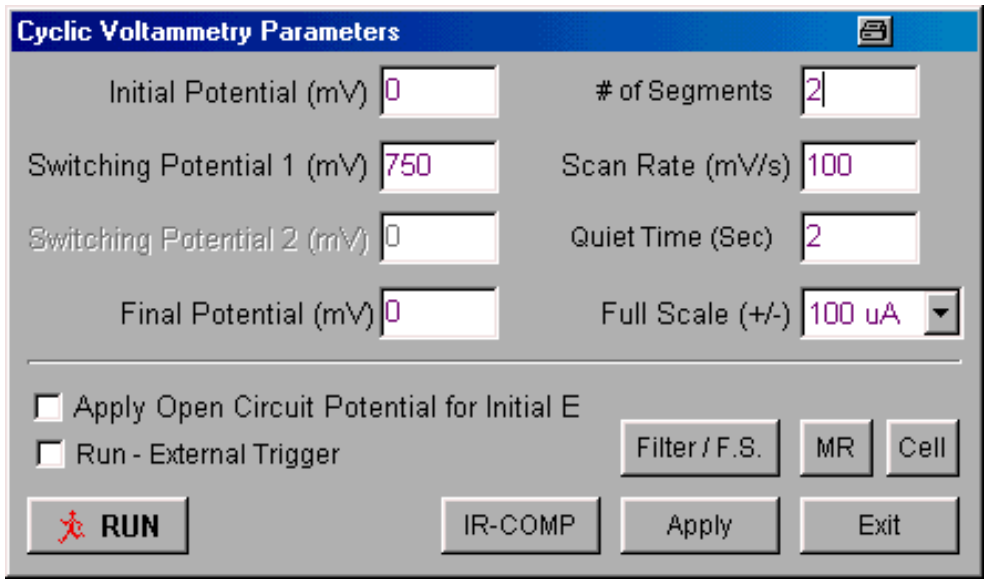


Figure 3. Change Parameters dialog box for cyclic voltammetry.

1. Potential values are entered in mV, and the **Scan Rate** in mV/s.
2. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
3. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start In** back-panel connection.
4. When the experiment is started, the cell is held at the **Initial Potential** for the number of seconds defined by the **Quiet Time**.
5. The experiment can be run on a hanging mercury drop electrode (i.e., a single drop is used for the entire experiment) using a BASi CGME by selecting **CGME SMDE Mode** from **Cell Stand / Accessories** in the **Setup / Manual Settings (I/O)** dialog box.
6. A rotating disk experiment can be run using a BASi RDE-2 by selecting **RDE-2** from **Cell Stand / Accessories** in the **Setup / Manual Settings (I/O)** dialog box and entering the required **Rotation Rate** under **RDE2 Rotation** in the **Cell** dialog box.
7. There are two gain stages for the current-to-voltage converter. The default values of these stages that are used for a given current **Full Scale** value are determined by the software. However, they can be adjusted manually using the **Filter / F.S.** dialog box. This dialog box is also used to change the analog **Noise Filter Value** settings from the default values set by the software.

8. The default condition of the cell is that the cell is **On** (i.e., the electronics are connected to the electrodes) *during* the experiment, and is **Off** *between* experiments. However, the potential can be switched **On** *between* experiments using the **Cell** dialog box. **HOWEVER, THIS OPTION SHOULD BE USED WITH CAUTION SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**
9. A series of identical experiments on the same cell can be programmed using the **MR (Multi-Run)** option.
10. Clicking the **IR-COMP** button activates the **iR compensation** option.
11. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
12. Range of allowed parameter values:
    - **Potential** = -3275 - +3275 mV
    - **Scan Rate** = 1 - 25,000 mV/s (also see below)
    - **Quiet Time** = 0 - 100 s
    - The **# of Segments** is limited by the total number of data points that can be stored (64,000) (note that in this initial version, the potential resolution of the current measurement is fixed at 1 mV).
13. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

Scan Rates

The digital waveform generator approximates a linear waveform with a staircase waveform with 100 µV steps. Since the waveform is generated digitally (the digital-to-analog converter clock speed is 1 MHz), only discrete scan rates are allowed because the step time is obtained by dividing the clock speed by integer values. The allowable scan rates (shown **T1**) are given by the equation:

Scan Rate (mV/s) = 100,000/n, where n is an integer

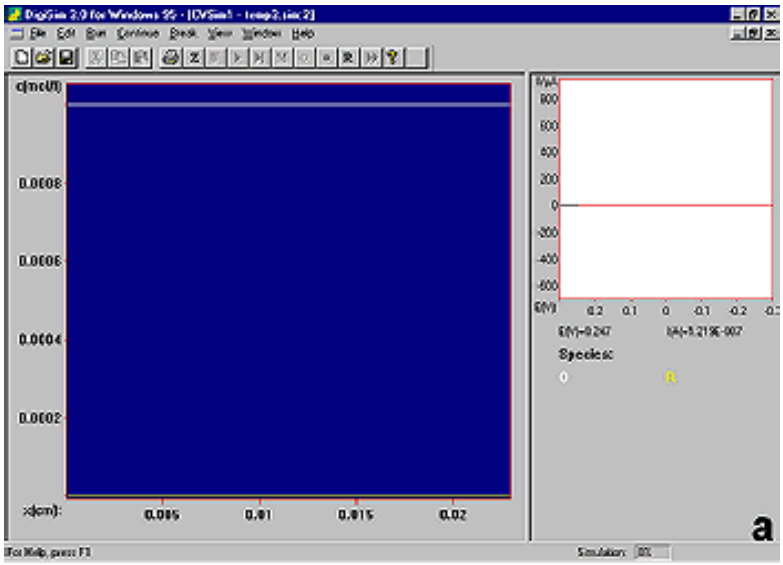
Thus, if a scan rate is entered that does not match the allowed values, the software will automatically change it to the nearest allowed value. The maximum scan rate allowed is 10,000 mV/s due to hardware limitations.

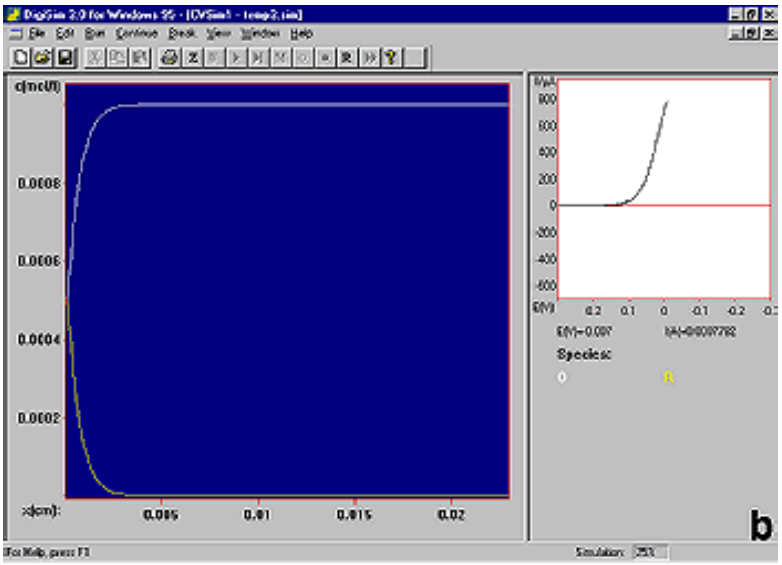
n	Scan Rate/mV s^{-1}	Approx. resolution/mV s^{-1}
4	25,000	
5	20,000	
6	16,667	
7	14,286	
8	12,500	
9	11,111	
10	10,000	
11	9,091	
12	8,330	
13	7,692	
14	7,143	

15	6,667	
16	6,250	
17	5,882	
18	5,556	
19	5,263	
20	5,000	
21-50	5,000-2,000	240
50-100	2,000-1,000	40
100-200	1,000-500	10
200-500	500-200	3
500-100,000	200-1	1

Analysis of the Current Response

The asymmetric shape of the current-voltage plot of a **CV** or an **LSV** experiment (a cyclic or linear sweep voltammogram, respectively) can be rationalized by considering the concentration profiles at different time points for O and R for the reduction reaction $O + e^- = R$ (**F3**).





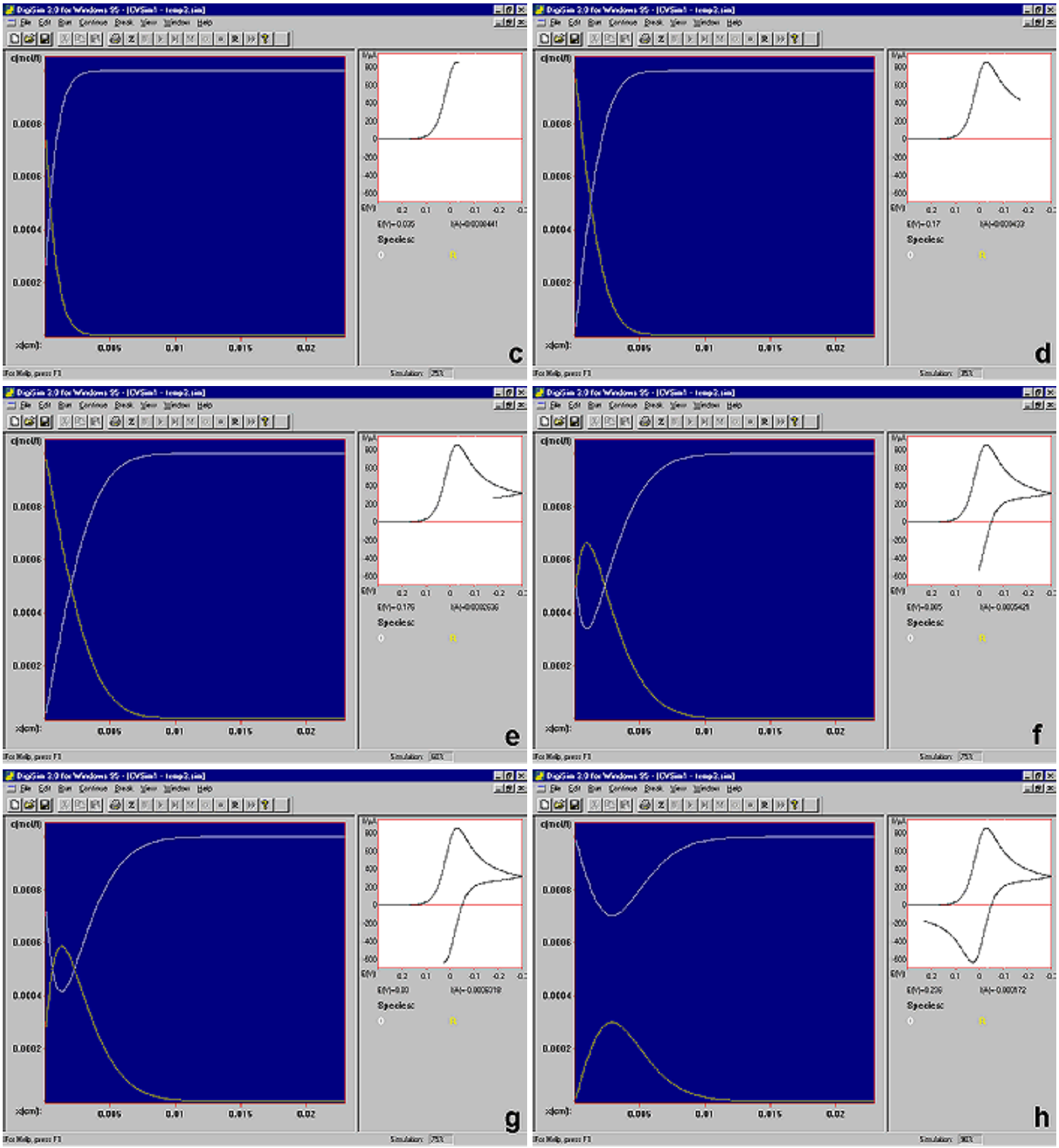


Figure 3. Concentration profiles for cyclic voltammetry for a simple reduction reaction. Simulation by DigiSim ®.

At the start of the experiment, the bulk solution contains only O, so at potentials well positive of the redox potentials, there is no net conversion of O to R (**a**). As the redox potential is approached, there is a net cathodic current which increases exponentially with potential due to the exponential potential dependence of the rate of heterogeneous electron transfer. As O is converted to R, concentration gradients are set up for both O and R, and diffusion occurs down these gradients (O diffuses

towards the electrode, and R diffuses in the opposite direction). The redox potential is at **b**, and the surface concentrations of O and R are equal at this potential. After the (cathodic) peak potential (**c**), the current decays as a result of the depletion of O in the interfacial region. The rate of electrolysis (and hence the current) now depends on the rate of mass transport of O from the bulk solution to the electrode surface; that is, it is dependent on the rate of diffusion of O, so the time dependence is $t^{-½}$. The peak is therefore asymmetric. Upon reversal of the direction of the potential scan (in a **CV** experiment), the current continues to decay with $t^{-½}$ until the potential nears the redox potential, at which point there begins a net reoxidation of R to O which causes an anodic current. However, some R molecules have diffused away from the electrode surface, and so have to diffuse back to the electrode before they can be reoxidized. Therefore, the current does not decay to zero following the reoxidation (anodic) peak on the reverse scan (**h**). The important parameters for a linear sweep (**F4**) or cyclic voltammogram (**F5**) are the peak potential(s) E_p and the peak current(s) i_p (note that there can be more than one peak in a cyclic voltammogram; hence an additional subscript (a = anodic, c = cathodic) is often used). The measurement of these parameters, and their significance, is discussed in more detail in a later section.

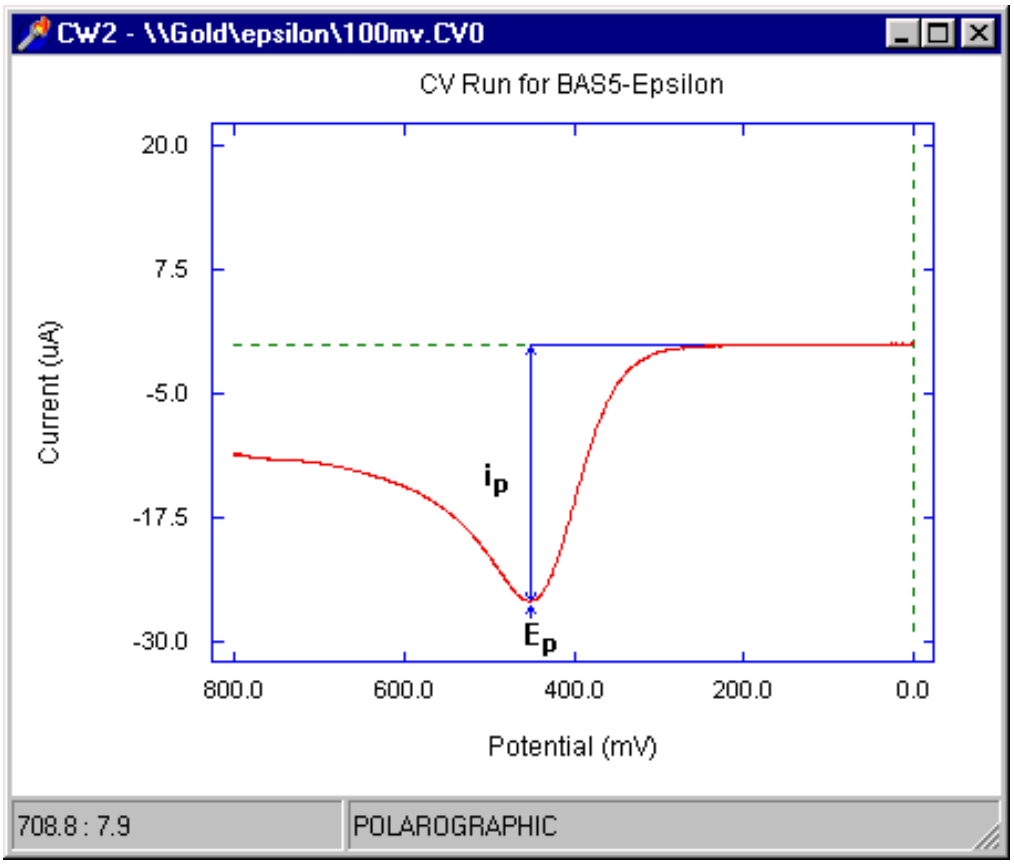


Figure 4. A typical linear sweep voltammogram showing the important parameters.

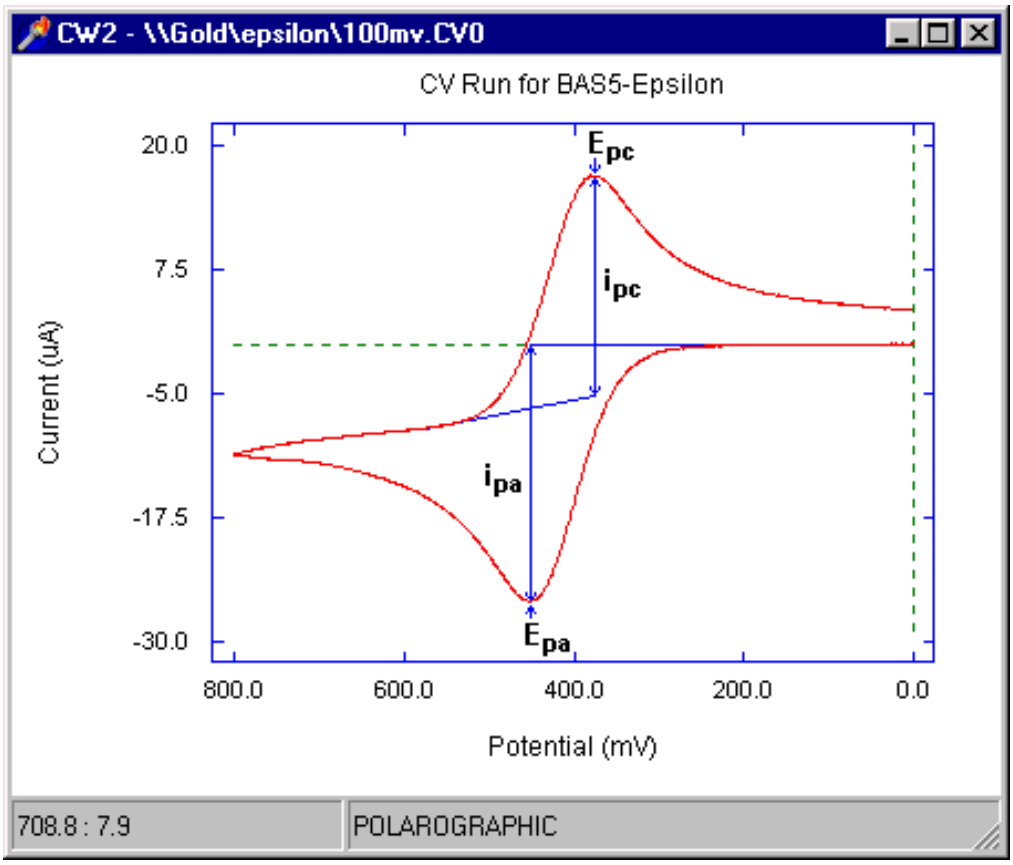


Figure 5. A typical cyclic voltammogram showing the important parameters.

Semidifferentation and Semiintegration

The default plot for **LSV** and **CV** is the current vs. potential plot. However, two other plots are available using **Select - Graph** in the pop-up menu - **SemiInt**egration (**F6**)and **SemiDiff**erentiation (**F7**). These are mathematical transforms of the basic current vs. potential plot.

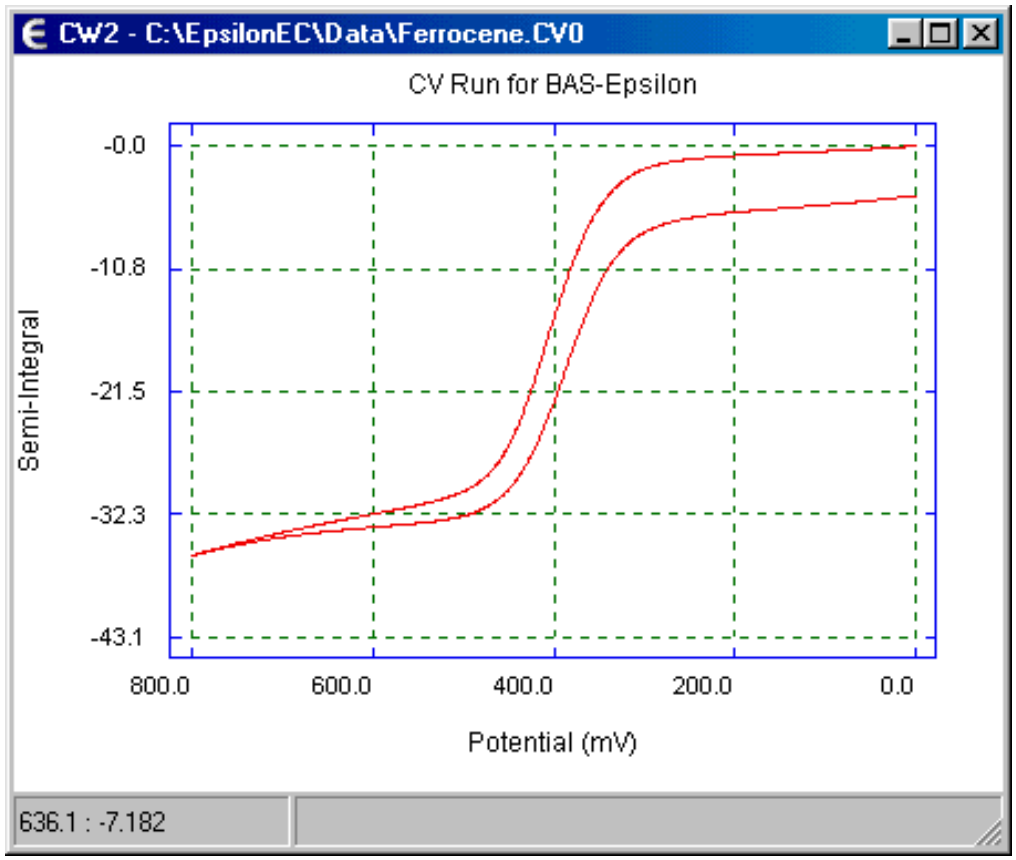


Figure 6. A typical cyclic voltammogram following semiintegration.

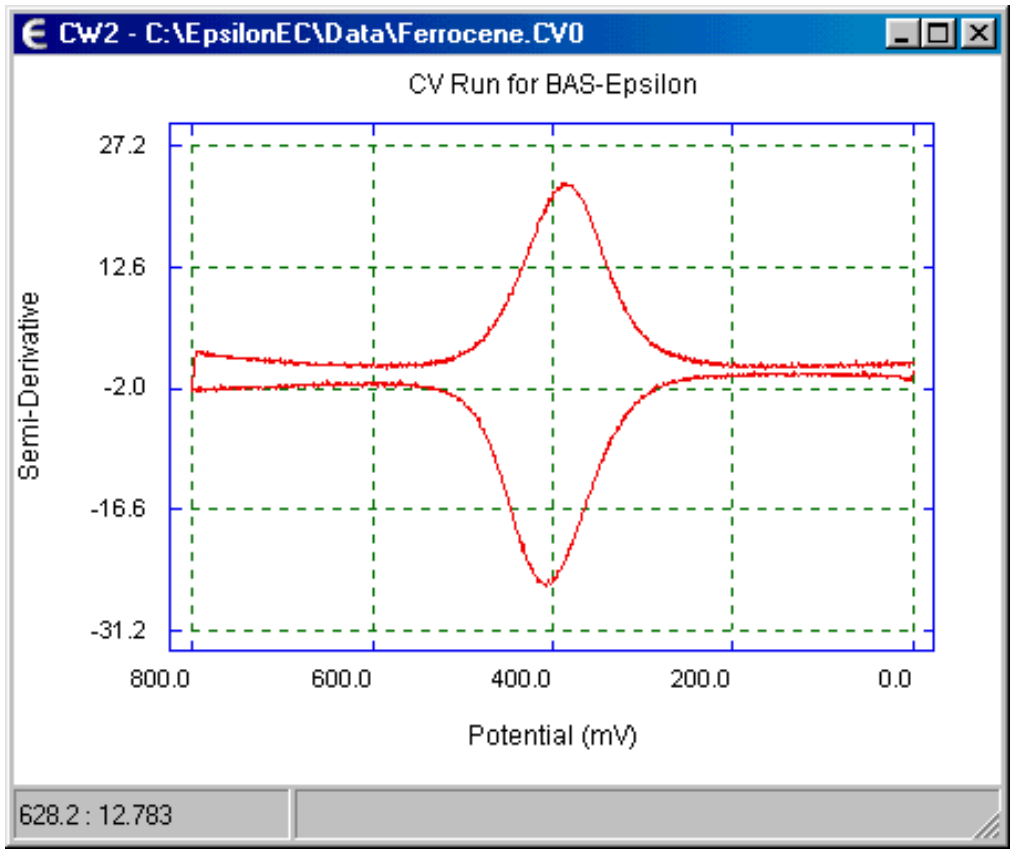


Figure 7. A typical cyclic voltammogram following semidifferentiation.

Display Selected Segments

Choosing Selected Segments in the Select Graph options allow one to view and print selected segments of the CV experiments. The dialog box (**F8**) will initially show all segments in the display list. One can move all segments out of Display list with the << button and move all into the Display list with the >> button. Highlighted individual and multiple segments can be to move out of the display list < or into the display list >. Once the desired segments are listed, then clicking the Redraw button will redraw the graph with only the selected segments shown. Two other options with the display are whether to Show Peaks (show the baseline and peak lines) and whether to Paint Peaks (show shading for area of peak).

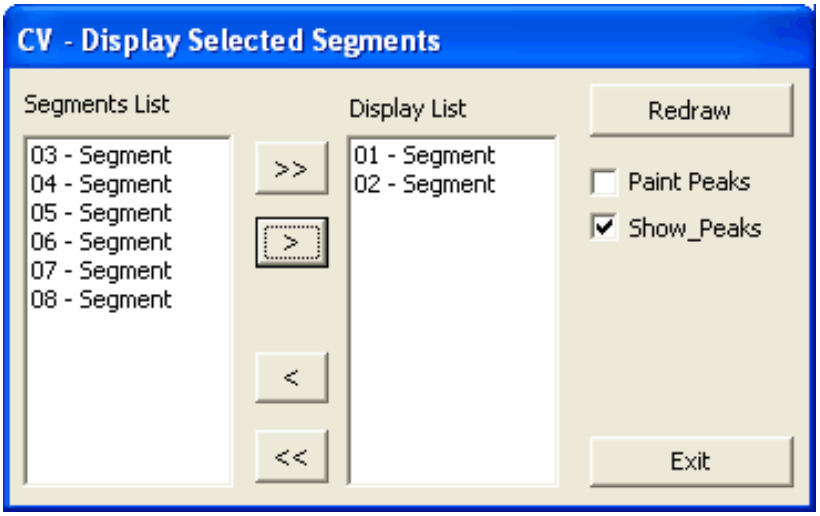


Figure 8.

With the selected Segments Display, one can perform the following operations and the selected peaks will remain displayed.

- Smooth Data
- Change Display Type
- Grid
- Show Data Points
- Copy to Clip-Board
- Text Info
- Select Colors and Fonts
- Manual Zoom
- Zoom with mouse

Performing the following commands will reset the display to all segments.

- Raw Data
- Processed data
- Auto zoom (Processed Data)
- Zoom out (Processed Data)
- Peak finding (Processed Data)

If one goes from SemiDiff or SemiInt to Display Segment, the display resets to the normal Processed Data Display.

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Chronoamperometry/Chronocoulometry

Introduction

Chronoamperometry (**CA**) and chronocoulometry (**CC**) have the same potential wave form - the potential step - which is one of the simplest potential wave forms. As shown below (**F1**), the potential is changed instantaneously from the **Initial Potential** to the **First Step Potential**, and it is held at this value for the **First Step Time**. This is a single potential step experiment. In a double potential step experiment, the potential is changed to the **Second Step Potential** after the **First Step Time**, and it is then held at this value for the **Second Step Time**. In **CA**, the current is monitored as a function of time, whereas in **CC**, the charge is monitored as a function of time. It is important to note that the basic potential step experiment on the epsilon is **CA**; that is, *during* the experiment, the *current* is recorded as a function of time. However, *after* the experiment, the data can also be displayed as *charge* as a function of time (the charge is calculated by integrating the current). Hence, chronocoulometry data can be obtained. **CA** is a standard technique on the epsilon.

CA is different from other constant potential techniques (constant potential electrolysis (**CPE**) and DC potential amperometry (**DCA**)) in that the time scale of **CA** is shorter (milliseconds and seconds) than those of **BE** and **DCA** (seconds and minutes).

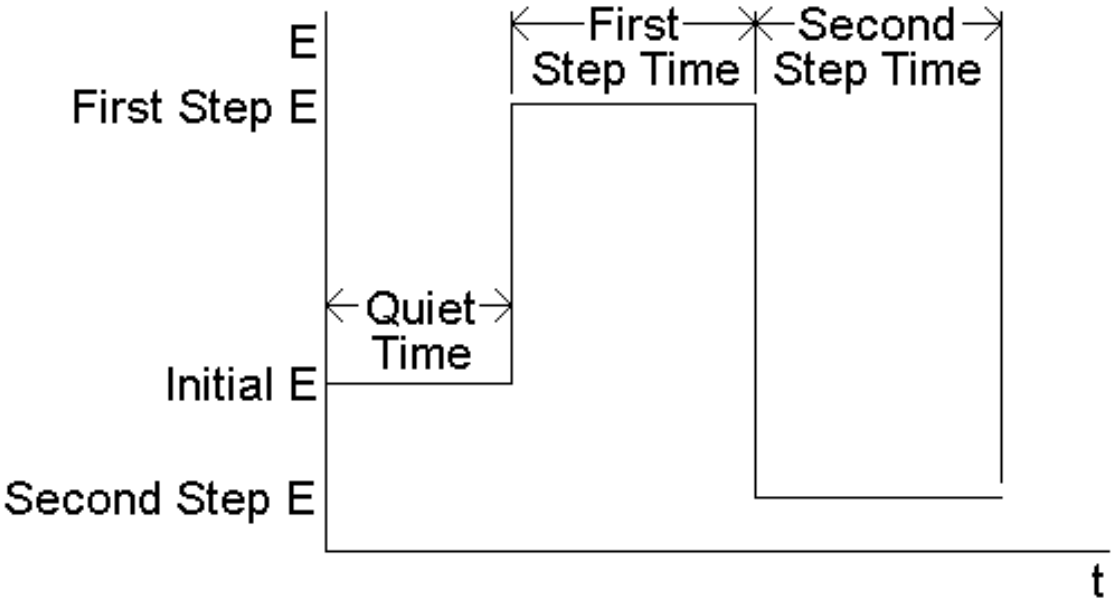

Figure 1. Potential wave form for chronoamperometry and chronocoulometry.

Setting Up a Chronoamperometry/Chronocoulometry Experiment

As shown above, five parameters are used in the epsilon software to define the potential wave form for **CA**.

1. Initial Potential
2. First Step Potential (E)
3. Second Step Potential (E)
4. First Step Time
5. Second Step Time

The values of these parameters are set using the **Change Parameter** dialog box (**F2**) in either the **Experiment** menu or the

pop-up menu.

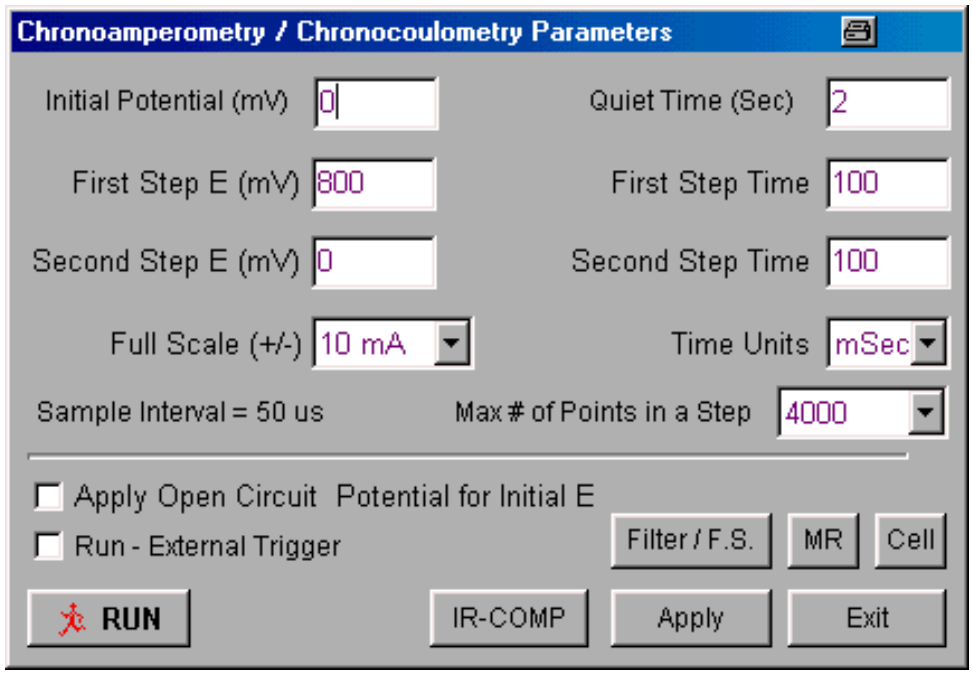

Figure 2. Change Parameters dialog box for chronoamperometry/chronocoulometry.

1. Potential values are entered in mV, and time values in ms or s (select using **Time Units**).
2. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
3. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start In** back-panel connection.
4. When the experiment is started, the cell is held at the **Initial Potential** for the number of seconds defined by the **Quiet Time**.
5. The experiment can be run on a hanging mercury drop electrode (i.e., a single drop is used for the entire experiment) using a BASi CGME by selecting **CGME SMDE Mode** from **Cell Stand / Accessories** in the **Setup / Manual Settings (I/O)** dialog box.
6. A rotating disk experiment can be run using a BASi RDE-2 by selecting **RDE-2** from **Cell Stand / Accessories** in the **Setup / Manual Settings (I/O)** dialog box and entering the required **Rotation Rate** under **RDE2 Rotation** in the **Cell** dialog box.
7. There are two gain stages for the current-to-voltage converter. The default values of these stages that are used for a given current **Full Scale** value are determined by the software. However, they can be adjusted manually using the **Filter / F.S.** dialog box. This dialog box is also used to change the analog **Noise Filter Value** settings from the default values set by the software.
8. The default condition of the cell is that the cell is **On** (i.e., the electronics are connected to the electrodes) *during* the experiment, and is **Off** *between* experiments. However, the potential can be switched **On** *between* experiments using the **Cell** dialog box. **HOWEVER, THIS OPTION SHOULD BE USED WITH CAUTION SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**
9. A series of identical experiments on the same cell can be programmed using the **MR (Multi-Run)** option.
10. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
11. Range of allowed parameter values:
    - **Potential** = -3275 mV - +3275 mV
    - **Quiet Time** = 0 - 100 s

- **Step Time** = 1 - 65 s **OR** 1 - 16000 ms
- **Maximum # of points in a step** = 1000, 2000, 4000, 8000, 16000
- The **Sample Interval** is determined by the **Step Time** and the **Maximum # of points in a step**, and can only be adjusted by the user indirectly through these latter two parameters. The relationship between these parameters is shown by the equation

  Sample Interval = **Step Time**/**Maximum # of points**

  However, it should be noted that only certain values are allowed for each of these parameters, as is shown in the table below:

Max. # of points	1000	2000	4000	8000	16000
Sample Interval	**Maximum Step Time (/ms)**				
20 µs	20	40	80	160	320
50 µs	40	81	162	325	650
100 µs	100	200	400	800	1600
200 µs	200	400	800	1600	3200
500 µs	406	812	1625	3250	6500
1 ms	1000	2000	4000	8000	16000
2 ms	2000	4000	8000	16000	
5 ms	4062	8125			
10 ms	10000				

12. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

Analysis of the Current Response

Let us consider the effect of a single potential step on the reaction $R = O + e^-$. At potentials well negative of the redox potential (E_{nr}), there is no net conversion of R to O, whereas at potentials well positive of the redox potential (E_d), the rate of the reaction is diffusion-controlled (i.e., molecules of R are electrolyzed as soon as they arrive at the electrode surface). In most potential step experiments, E_{nr} is the **Initial Potential**, and E_d is the **First Step Potential**. The advantage of using these two potentials is that any effects of slow heterogeneous electron transfer kinetics are eliminated. In double potential step experiments, (E_{nr}) is often used as the **Second Step Potential**.

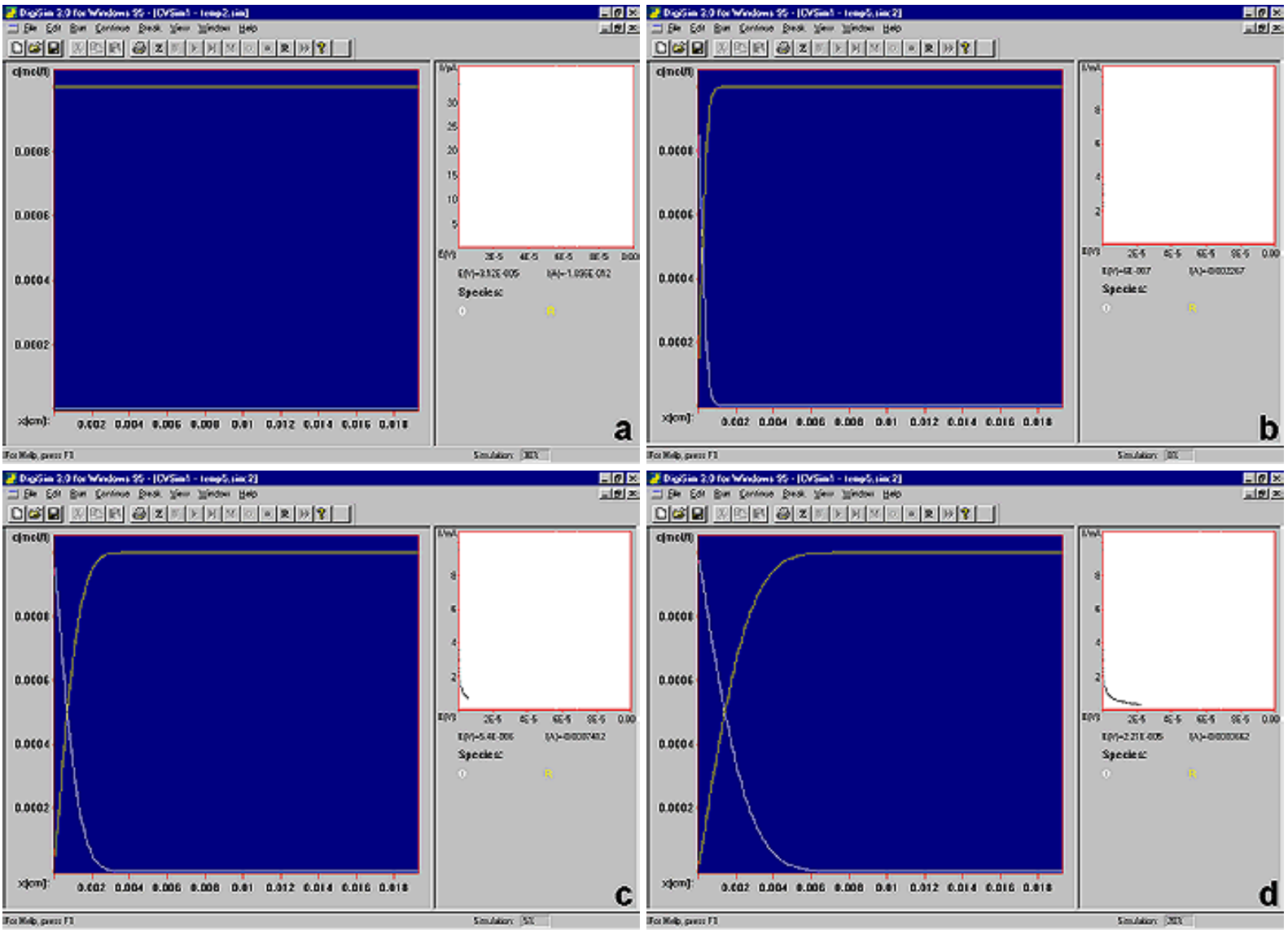

Figure 3. Concentration profiles for a single potential step experiment.

It is instructive to consider the concentration profiles of O and R following the potential step (**F3**). Initially, only R is present in solution (**a**). After the potential step, the concentration of R at the electrode surface decreases to zero, and hence a concentration gradient is set up between the interfacial region and the bulk solution (**b**). As molecules of R diffuse down this concentration gradient to the electrode surface (and are converted to O), a *diffusion layer* (i.e., a region of the solution in which the concentration of R has been depleted) is formed. The width of this layer increases with increasing time (**b-d**). There is also a net diffusion of O molecules away from the electrode surface.

Since the current is directly proportional to the rate of electrolysis, the current response to a potential step is a current 'spike' (due to initial electrolysis of species at the electrode surface) followed by time-dependent decay (**F4**) (due to diffusion of molecules to the electrode surface).

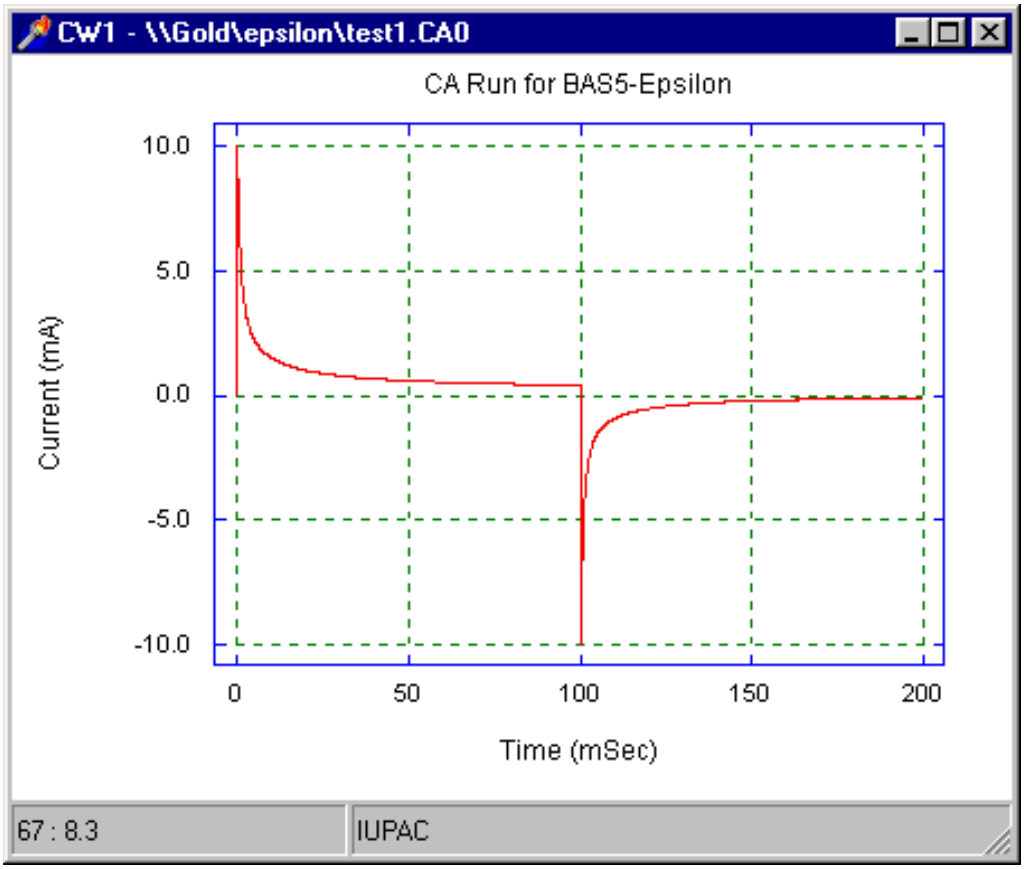

Figure 4. Current-time response for a double-potential step chronoamperometry experiment.

For a diffusion-controlled current, the current-time (i-t) curve is described by the Cottrell equation:

$i = nFACD^{½}\pi^{-½}t^{-½}$

where: n = number of electrons transferred/molecule
F = Faraday's constant (96,500 C mol^{-1})
A = electrode area (cm^2)
D = diffusion coefficient (cm^2 s^{-1})
C = concentration (mol cm^{-3})

The charge-time (Q-t) (the Anson equation) is obtained by integrating the Cottrell equation, and can be displayed in the epsilon software by selecting **Q vs T** from **Select Graph** in the pop-up menu (the original i vs. t plot can be recovered by selecting **Original** from **Select Graph** in the pop-up menu). A typical charge-time plot is shown in **F5**:

$Q = 2nFACD^{½}\pi^{-½}t^{½}$

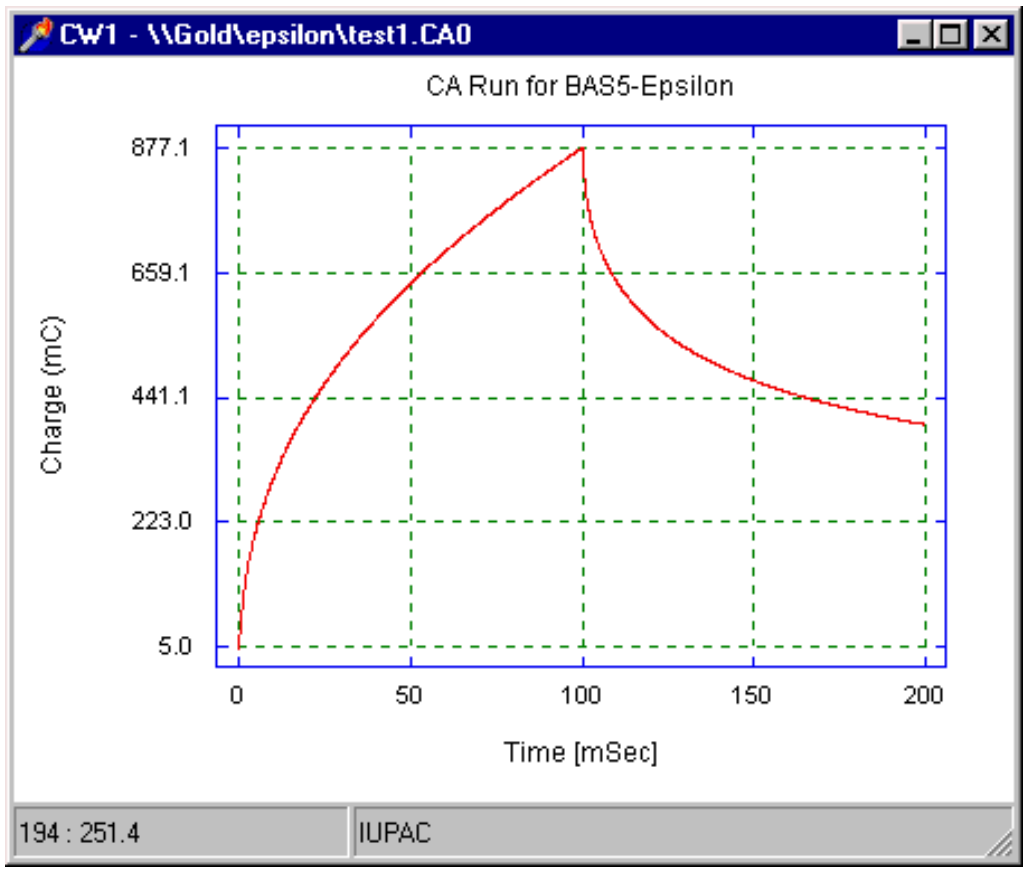

Figure 5. Charge-time response for a double-potential step chronocoulometry/chronoamperometry experiment.

Charge is the integral of current, so the response for **CC** increases with time, whereas that for **CA** decreases. Since the latter parts of the signal response must be used for data analysis (the finite rise time of the potentiostat invalidates the early time points), the larger signal response at the latter parts for **CC** makes this the more favorable potential step technique for many applications (in addition, integration decreases the noise level).

The analysis of **CA** and **CC** data is discussed elsewhere.

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Pulse Voltammetric Techniques

Introduction

The basis of all pulse techniques is the difference in the rate of the decay of the charging and the faradaic currents following a potential step (or "pulse"). The charging current decays exponentially, whereas the faradaic current (for a diffusion-controlled current) decays as a function of $1/(\text{time})^{½}$; that is, the rate of decay of the charging current is considerably faster than the decay of the faradaic current. The charging current is negligible at a time of $5R_uC_{dl}$ after the potential step (R_uC_{dl} is the *time constant* for the electrochemical cell, and ranges from µs to ms). Therefore, after this time, the measured current consists solely of the faradaic current; that is, measuring the current at the end of a potential pulse allows discrimination between the faradaic and charging currents.

The important parameters for pulse techniques are as follows:

1. **Pulse amplitude** is the height of the potential pulse. This may or may not be constant depending upon the technique.
2. **Pulse width** is the duration of the potential pulse.
3. **Sample period** is the time at the end of the pulse during which the current is measured.
4. For some pulse techniques, the **pulse period** or **drop time** must also be specified. This parameter defines the time required for one potential cycle, and is particularly significant for polarography (i.e., pulse experiments using a mercury drop electrode), where this time corresponds to the lifetime of each drop (i.e., a new drop is dispensed at the start of the drop time, and is knocked off once the current has been measured at the end of the drop time - note that the end of the drop time coincides with the end of the pulse width).

A number of different pulse techniques are available on the epsilon, which differ in their potential pulse wave forms, the number of sampling points, and whether a solid electrode (voltammetry) or a mercury drop electrode (polarography) is used. These are listed below. The discrimination against the charging current that is inherent in these techniques leads to lower detection limits (when compared to linear sweep techniques), which makes these techniques suitable for quantitative analysis.

Sampled Current Polarography

Sampled current polarograph (**SCP**) is a modification of the classical DC polarography experiment, and was designed to reduce the effect of the changing surface area of the mercury drop electrode. The potential wave form is shown in **F1** and the **Change Parameters** dialog box is shown in **F2**. The potential is varied in a series of steps, with the current sampled at the end of each step.

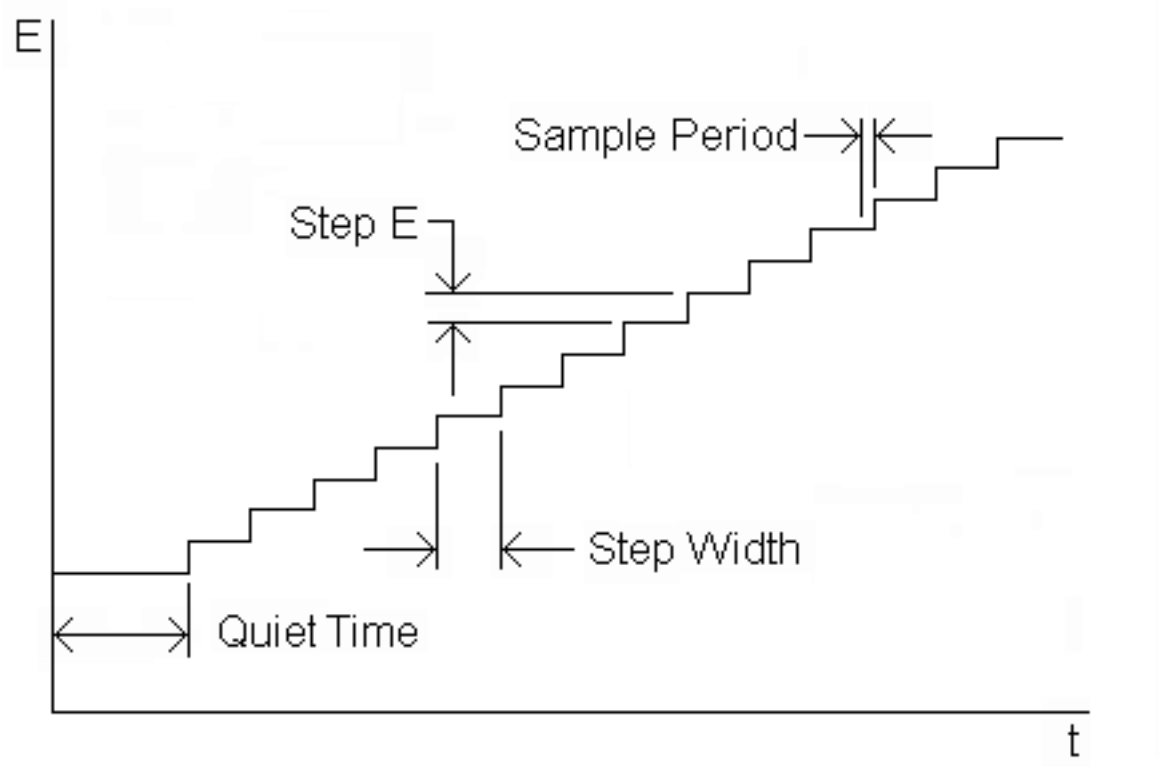

Figure 1. Potential wave form for sampled current polarography.

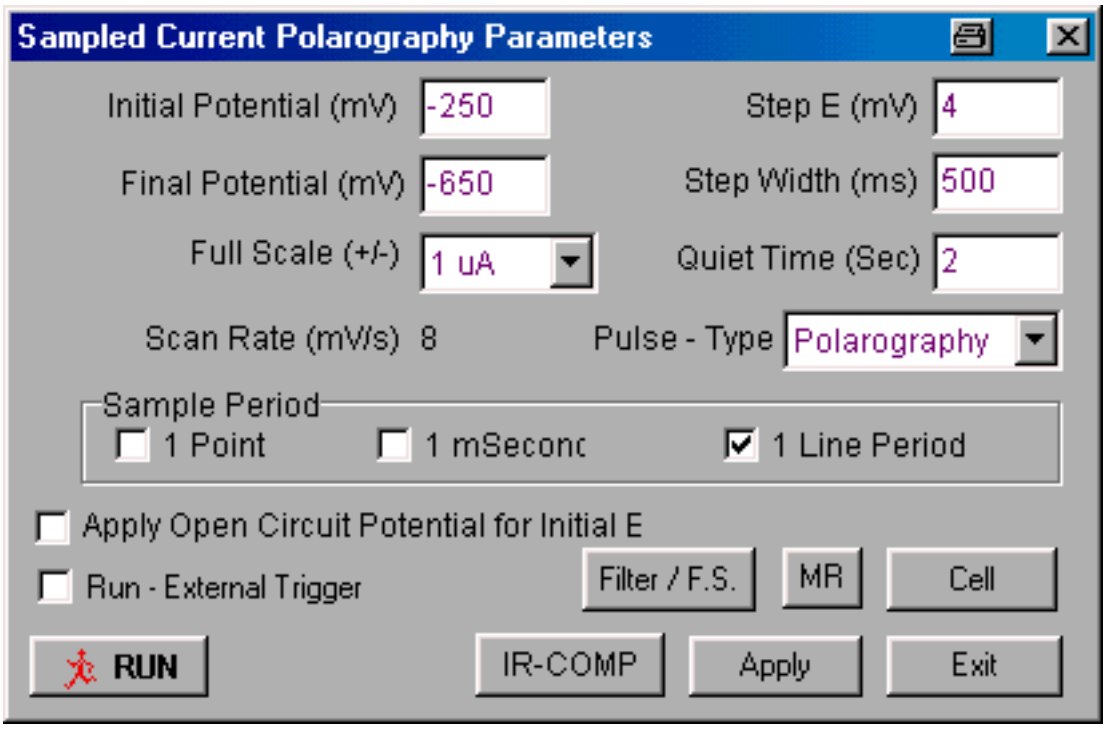

Figure 2. Change Parameters dialog box for sampled current polarography.

1. All potential values are entered in mV, and the **Step Width** is entered in ms.
2. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
3. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start In** back-panel connection.
4. The **Pulse Type** must be specified when using a mercury electrode (**CGME SMDE Mode** selected in the **Cell Stand** dialog box). If **Voltammetry** is selected, the whole experiment is performed on a single mercury drop (after the **Pre Run Drops**); if **Polarography** is selected, a new drop is used for each data point.
5. The change in the applied potential for each step is defined by **Step E**.
6. The **Scan Rate** cannot be directly changed by the user, and is determined by **Step E** x 1/**Sample Width**.
7. Three options are available for the **Sample Period**:
    - The current is measured once at the end of the **Step Width** (**1 Point**)
    - The current is measured multiple times in 1 ms at the end of the **Step Width**, and averaged (**1 mSecond**)
    - The current is measured multiple times over 1 line cycle at the end of the **Step Width**, and averaged (**1 Line Period**). The time required for 1 line cycle is the reciprocal of the line frequency (16.7 ms for 60 Hz, and 20 ms for 50 Hz). The line frequency is selected in the **Setup / Manual Settings (I/O)** dialog box.

   Generally speaking, increasing the **Sample Period** increases the signal-to-noise ratio. However, the **1 Line Period** option may not be possible for short **Step Width** values.
8. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
9. When the experiment is started, the cell is held at the **Initial Potential** for the number of seconds defined by the **Quiet Time**.
10. There are two gain stages for the current-to-voltage converter. The default values of these stages that are used for a given current **Full Scale** value are determined by the software. However, they can be adjusted manually using the **Filter / F.S.** dialog box. This dialog box is also used to change the analog **Noise Filter Value** settings from the default values set by the software.
11. The default condition of the cell is that the cell is **On** (i.e., the electronics are connected to the electrodes) *during* the experiment, and is **Off** *between* experiments. However, the potential can be switched **On** *between* experiments using the **Cell** dialog box. **HOWEVER, THIS OPTION SHOULD BE USED WITH CAUTION SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**
12. A series of identical experiments on the same cell can be programmed using the MR (Multi-Run) option.
13. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
14. Range of allowed parameter values:
    - **Potential** = -3275 - +3275 mV

- **Step E** = 1 - 40 mV
- **Step Width** = 100 - 6550 ms (**Polarography**); 4 - 6550 ms (**Voltammetry**)
- **Quiet Time** = 0 - 100 s

15. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

The current response for **SCP** is shown in **F3**. The limiting current (i_d) is given by the Ilkovic equation:

$$i_d = 708nCD^{1/2}m^{2/3}\tau^{1/6}$$

where: n = number of electrons transferred/molecule
C = concentration (mol cm^{-3})
D = diffusion coefficient (cm^2 s^{-1})
m = mercury flow rate (mg s^{-1})
τ = sampling interval (s)

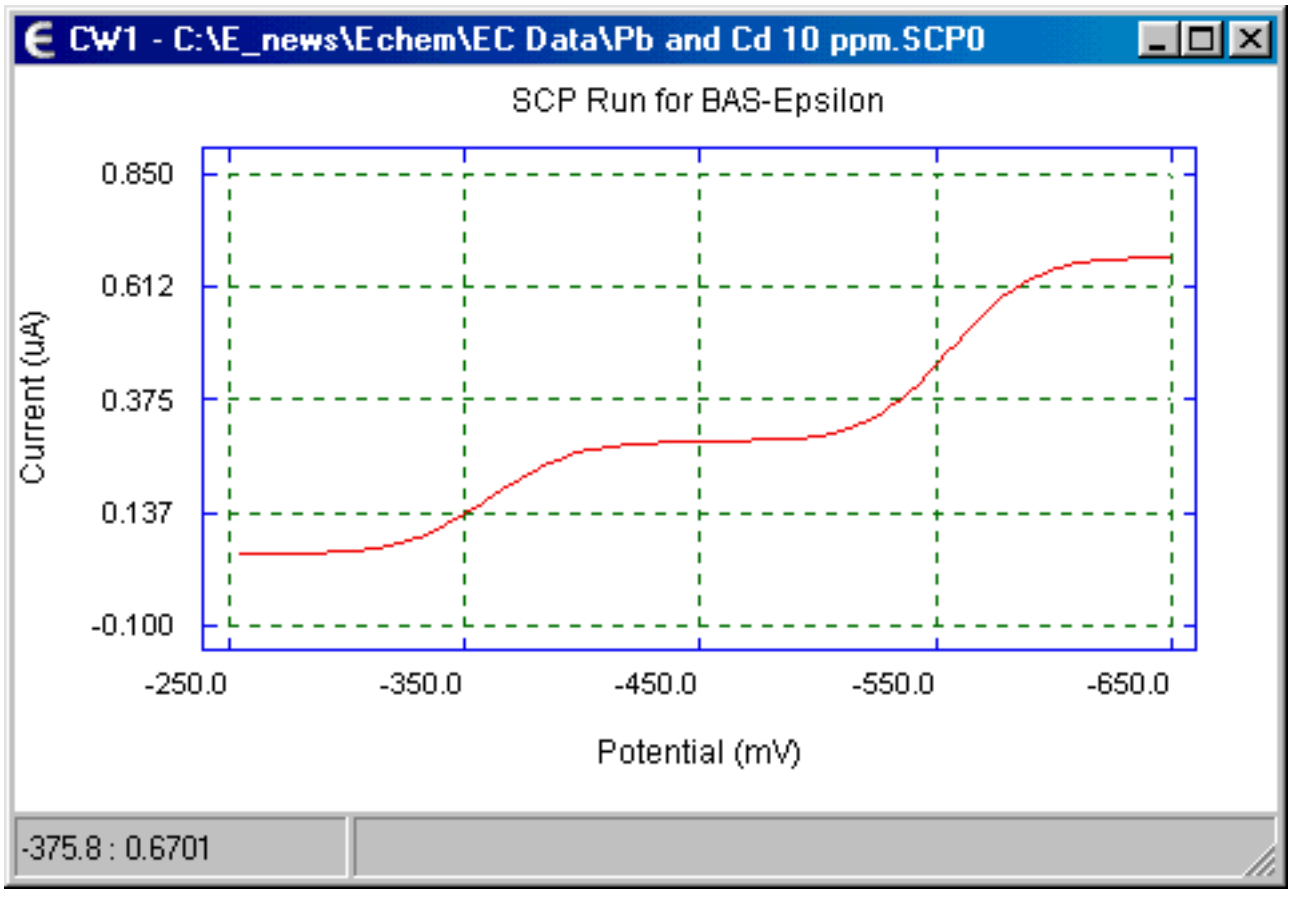

Figure 3. A typical sampled current polarogram.

Normal Pulse Voltammetry/Polarography

The potential wave form for normal pulse voltammetry/polarography (**NPV/P**) is shown in **F4** and the **Change Parameters** dialog box is shown in **F5**. The potential wave form consists of a series of pulses of increasing amplitude, with the potential returning to the initial value after each pulse.

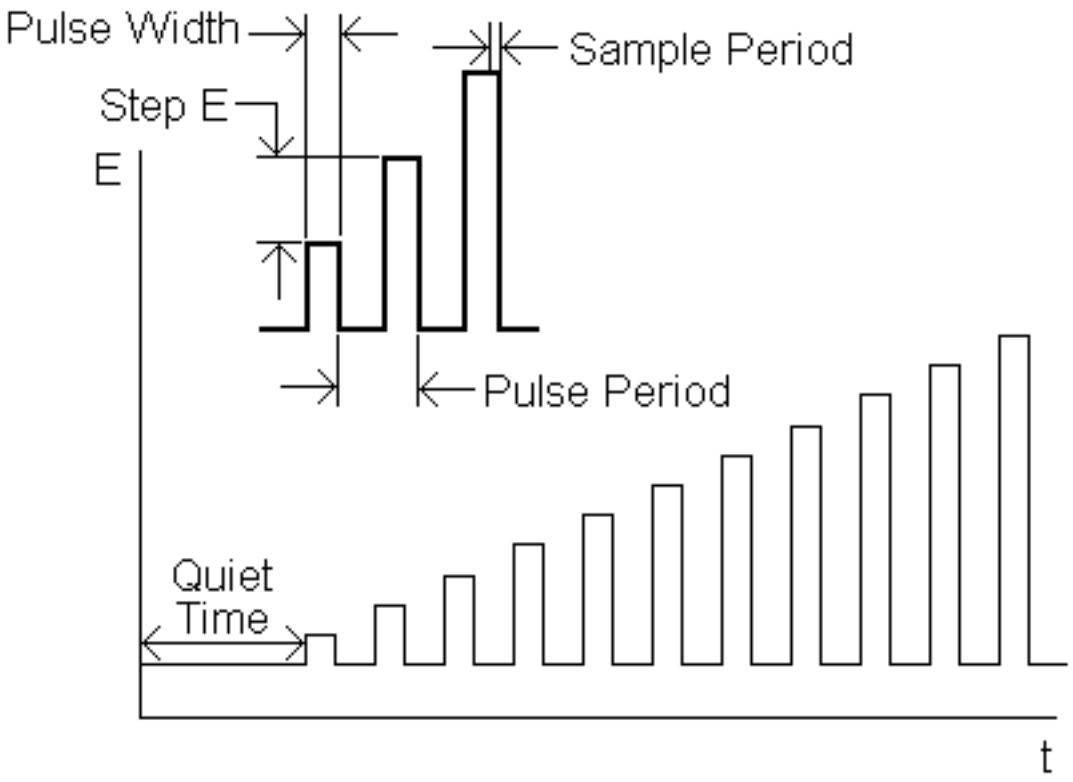

Figure 4. Potential wave form for normal pulse voltammetry.

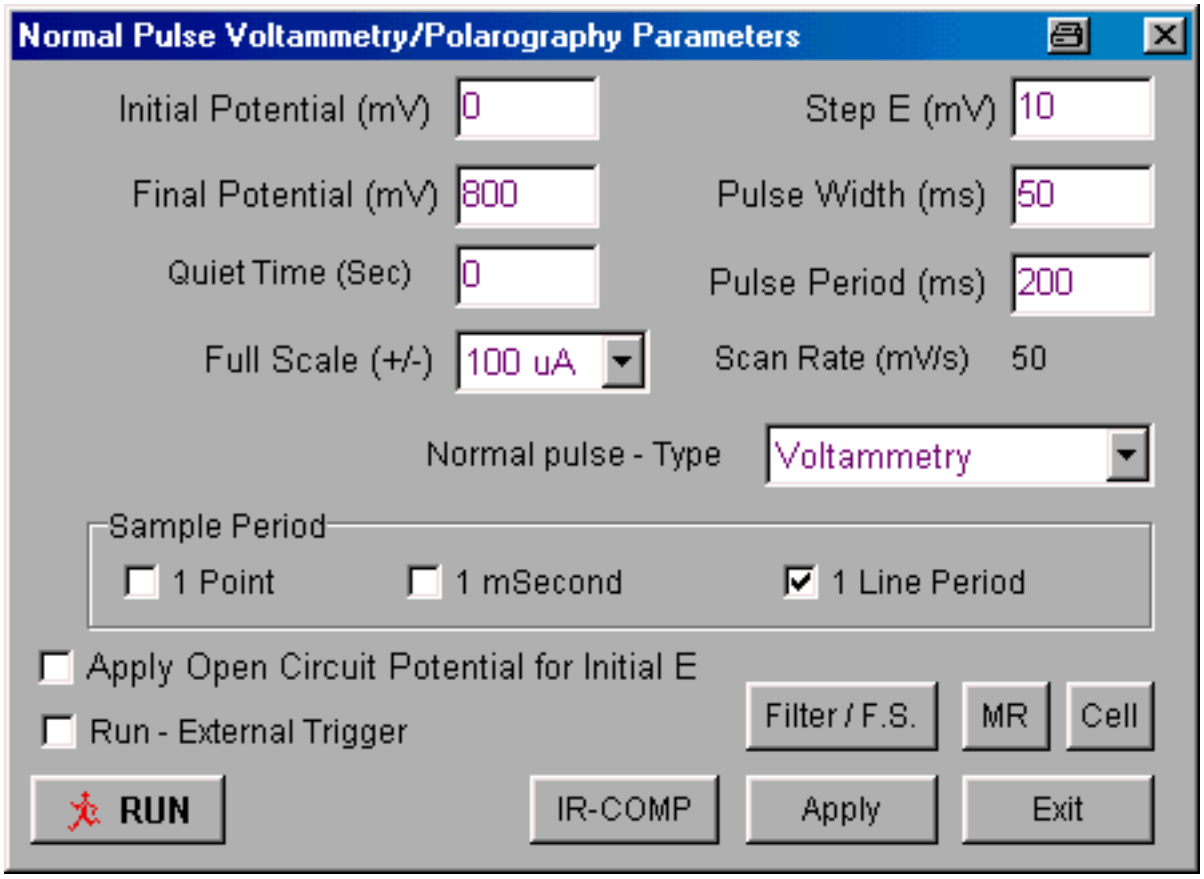

Figure 5. Change Parameters dialog box for normal pulse voltammetry.

1. All potential values are entered in mV, and the **Pulse Width** and **Pulse Period** are entered in ms.
2. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
3. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start In** back-panel connection.
4. The **Pulse Type** must be specified when using a mercury electrode (**CGME SMDE Mode** selected in the **Cell Stand** dialog box). If **Voltammetry** is selected, the whole experiment is performed on a single mercury drop (after the **Pre Run Drops**); if **Polarography** is selected, a new drop is used for each data point.
5. The amplitude of the initial potential pulse, and the incremental increases in amplitude for subsequent pulses is defined by **Step E**.
6. The **Scan Rate** cannot be directly changed by the user, and is determined by **Step E** x 1/**Pulse Period**.
7. The **Pulse Period** must be at least twice the **Pulse Width**.
8. Three options are available for the **Sample Period**:
    - The current is measured once at the end of the **Pulse Width** (**1 Point**)
    - The current is measured multiple times in 1 ms at the end of the **Pulse Width**, and averaged (**1 mSecond**)
    - The current is measured multiple times over 1 line cycle at the end of the **Pulse Width**, and averaged (**1 Line Period**). The time required for 1 line cycle is the reciprocal of the

line frequency (16.7 ms for 60 Hz, and 20 ms for 50 Hz). The line frequency is selected in the **Setup / Manual Settings (I/O)** dialog box.

Generally speaking, increasing the **Sample Period** increases the signal-to-noise ratio. However, the **1 Line Period** option may not be possible for short **Pulse Width** values.

9. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
10. When the experiment is started, the cell is held at the **Initial Potential** for the number of seconds defined by the **Quiet Time**.
11. There are two gain stages for the current-to-voltage converter. The default values of these stages that are used for a given current **Full Scale** value are determined by the software. However, they can be adjusted manually using the **Filter / F.S.** dialog box. This dialog box is also used to change the analog **Noise Filter Value** settings from the default values set by the software.
12. The default condition of the cell is that the cell is **On** (i.e., the electronics are connected to the electrodes) *during* the experiment, and is **Off** *between* experiments. However, the potential can be switched **On** *between* experiments using the **Cell** dialog box. **HOWEVER, THIS OPTION SHOULD BE USED WITH CAUTION SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**
13. A series of identical experiments on the same cell can be programmed using the **MR (Multi-Run)** option.
14. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
15. Range of allowed parameter values:
    - **Potential** = -3000 - +3000 mV
    - **Step E** = 1 - 40 mV
    - **Pulse Width** = 3 - 2000 ms
    - **Step Width** = 100 - 6550 ms (**Polarography**); 4 - 6550 ms (**Voltammetry**)
    - **Quiet Time** = 0 - 100 s
16. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

Consider a reduction. If the **Initial Potential** is well positive of the redox potential, the application of small amplitude pulses does not cause any faradaic reactions, hence there is no current response. When the pulse amplitude is sufficiently large that the pulse potential is close to the redox potential, there is a faradaic reaction is response to the potential pulse (assuming moderately fast electron transfer kinetics), and the magnitude of this current may depend on both the rate of diffusion and the rate of electron transfer. When the pulsed potentials are sufficiently negative of the redox potential that the electron transfer reaction occurs rapidly, the faradaic current depends only on the rate of diffusion; that is, a limiting current has been attained. The sigmoidal shape typically observed for **NPV/P** (**F6**) is similar to the shape of the current-potential curve obtained in the classical polarography experiment, which gives rise to the name of "normal" for this technique.

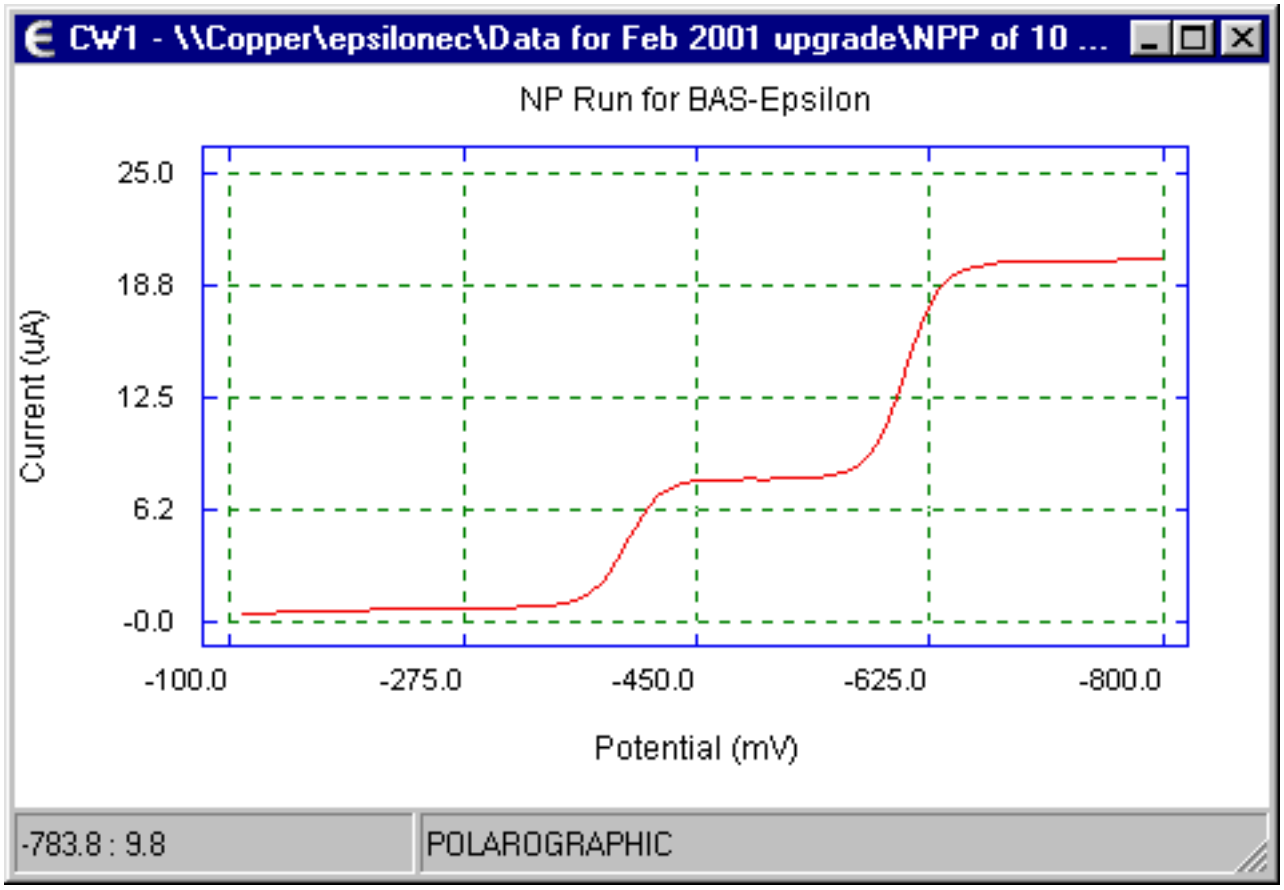

Figure 6. A typical normal pulse voltammogram.

Differential Pulse Voltammetry/Polarography

The potential wave form for differential pulse voltammetry/polarography (**DPV/P**) is shown in **F7** and the **Change Parameters** dialog box is shown in **F7**. The potential wave form consists of small pulses (of constant amplitude) superimposed upon a staircase wave form. Unlike **NPV**, the current is sampled twice in each **Pulse Period** (once before the pulse, and at the end of the pulse), and the difference between these two current values is recorded and displayed.

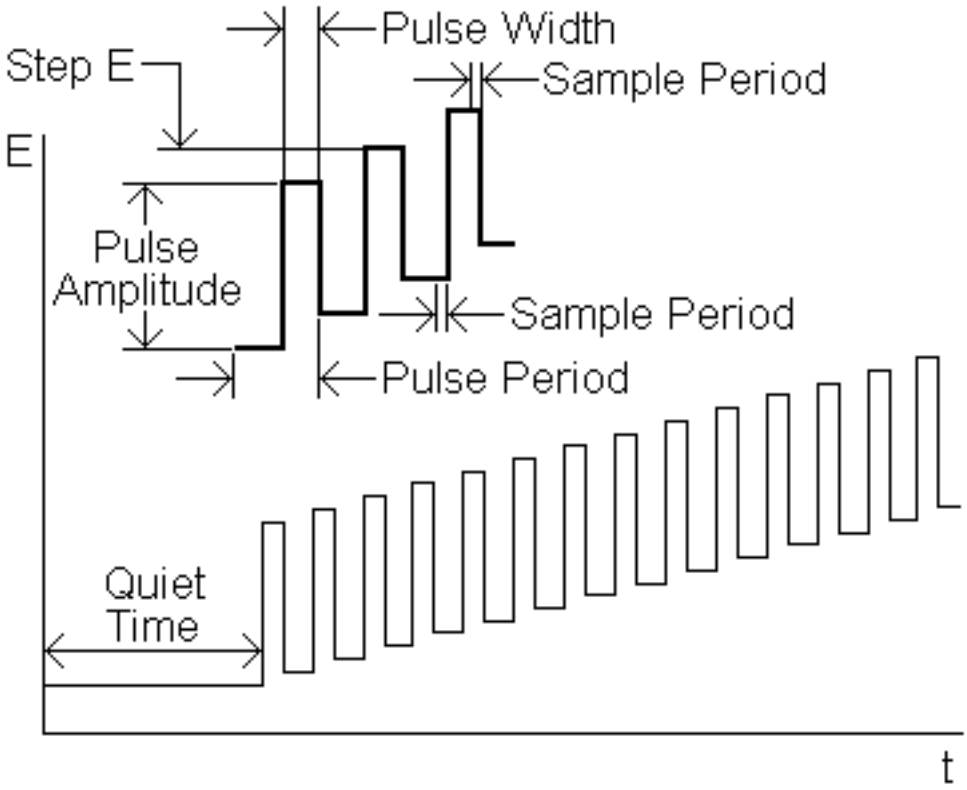

Figure 7. Potential wave form for differential pulse voltammetry.

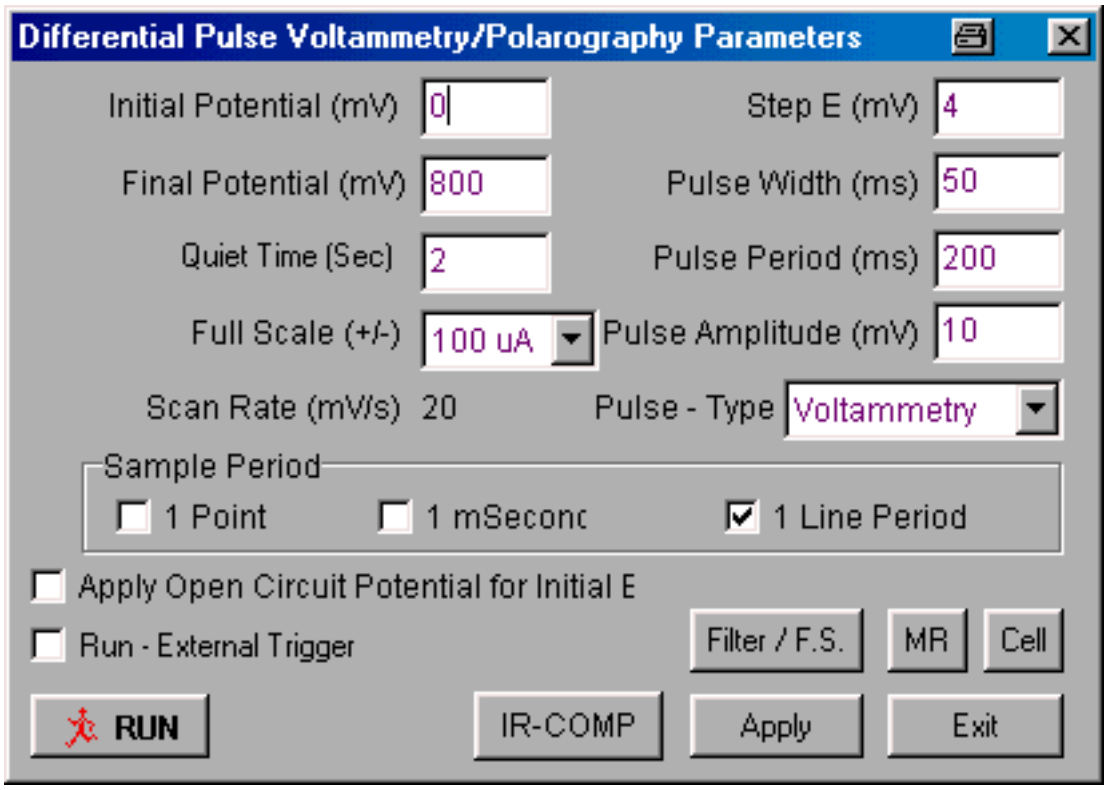

Figure 8. Change Parameters dialog box for differential pulse voltammetry.

1. All potential values are entered in mV, and the **Pulse Width** and **Pulse Period** are entered in ms.
2. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential

will automatically be measured and used as the **Initial Potential**.

3. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start In** back-panel connection.
4. The **Pulse Type** must be specified when using a mercury electrode (**CGME SMDE Mode** selected in the **Cell Stand** dialog box). If **Voltammetry** is selected, the whole experiment is performed on a single mercury drop (after the **Pre Run Drops**); if **Polarography** is selected, a new drop is used for each data point.
5. The amplitude of the potential pulse is defined by **Pulse Amplitude**, and the height of the staircase wave form is defined by **Step E**.
6. The **Scan Rate** cannot be directly changed by the user, and is determined by **Step E** x 1/**Pulse Period**.
7. The **Pulse Period** must be at least twice the **Pulse Width**.
8. Three options are available for the **Sample Period**:
    - The current is measured once at the end of the **Pulse Width** (**1 Point**)
    - The current is measured multiple times in 1 ms at the end of the **Pulse Width**, and averaged (**1 mSecond**)
    - The current is measured multiple times over 1 line cycle at the end of the **Pulse Width**, and averaged (**1 Line Period**). The time required for 1 line cycle is the reciprocal of the line frequency (16.7 ms for 60 Hz, and 20 ms for 50 Hz). The line frequency is selected in the **Setup / Manual Settings (I/O)** dialog box.

   Generally speaking, increasing the **Sample Period** increases the signal-to-noise ratio. However, the **1 Line Period** option may not be possible for short **Pulse Width** values.
9. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
10. When the experiment is started, the cell is held at the **Initial Potential** for the number of seconds defined by the **Quiet Time**.
11. There are two gain stages for the current-to-voltage converter. The default values of these stages that are used for a given current **Full Scale** value are determined by the software. However, they can be adjusted manually using the **Filter / F.S.** dialog box. This dialog box is also used to change the analog **Noise Filter Value** settings from the default values set by the software.
12. The default condition of the cell is that the cell is **On** (i.e., the electronics are connected to the electrodes) *during* the experiment, and is **Off** *between* experiments. However, the potential can be switched **On** *between* experiments using the **Cell** dialog box. **HOWEVER, THIS OPTION SHOULD BE USED WITH CAUTION SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**
13. A series of identical experiments on the same cell can be programmed using the **MR (Multi-Run)** option.
14. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
15. Range of allowed parameter values:
    - **Potential** = -3000 - +3000 mV

- **Step E** = 1 - 40 mV
- **Pulse Amplitude** = 5 - 250 mV.
- **Pulse Width** = 3 - 1000 ms
- **Step Width** = 100 - 6550 ms (**Polarography**); 4 - 6550 ms (**Voltammetry**)
- **Quiet Time** = 0 - 100 s

16. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

Consider a reduction. At potentials well positive of the redox potential, there is no faradaic reaction in repsonse to the pulse, so the difference current is zero. At potential around the redox potential, the difference current reaches a maximum, and decreases to zero as the current becomes diffusion-controlled. The current response is therefore a symmetric peak (**F9**).

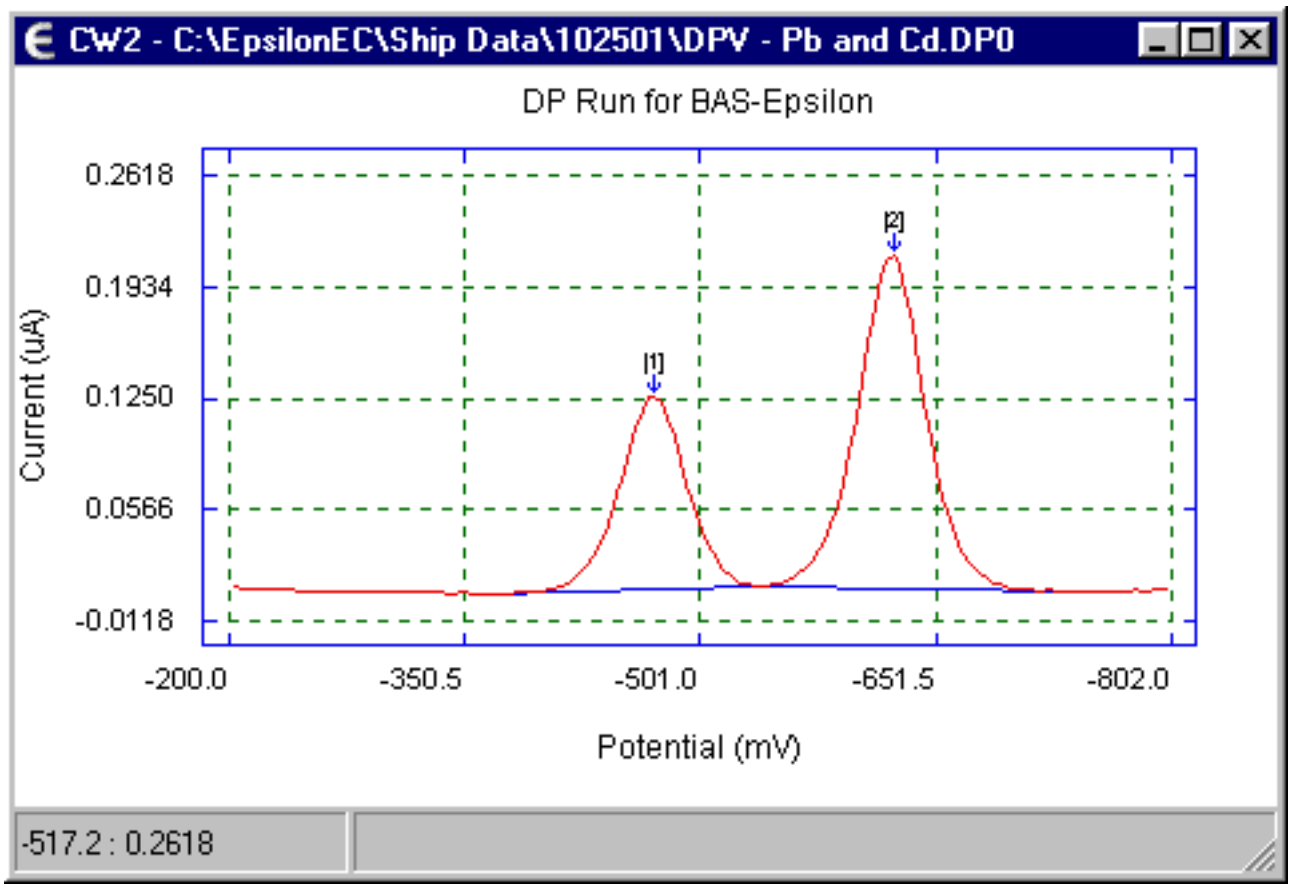

Figure 9. A typical differential pulse voltammogram.

Square Wave Voltammetry

The potential wave form for square wave voltammetry (**SWV**) is shown in **F10** and the **Change Parameters** dialog box is shown in **F11**. The potential wave form consists of a square wave of constant amplitude superimposed on a staircase wave form. The current is measured at the end of each half-cycle, and the current measured on the reverse half-cycle (i_r) is subtracted from the current measured on the

forward half-cycle (i_f). This difference current (i_f - i_r) is displayed as a function of the applied potential.

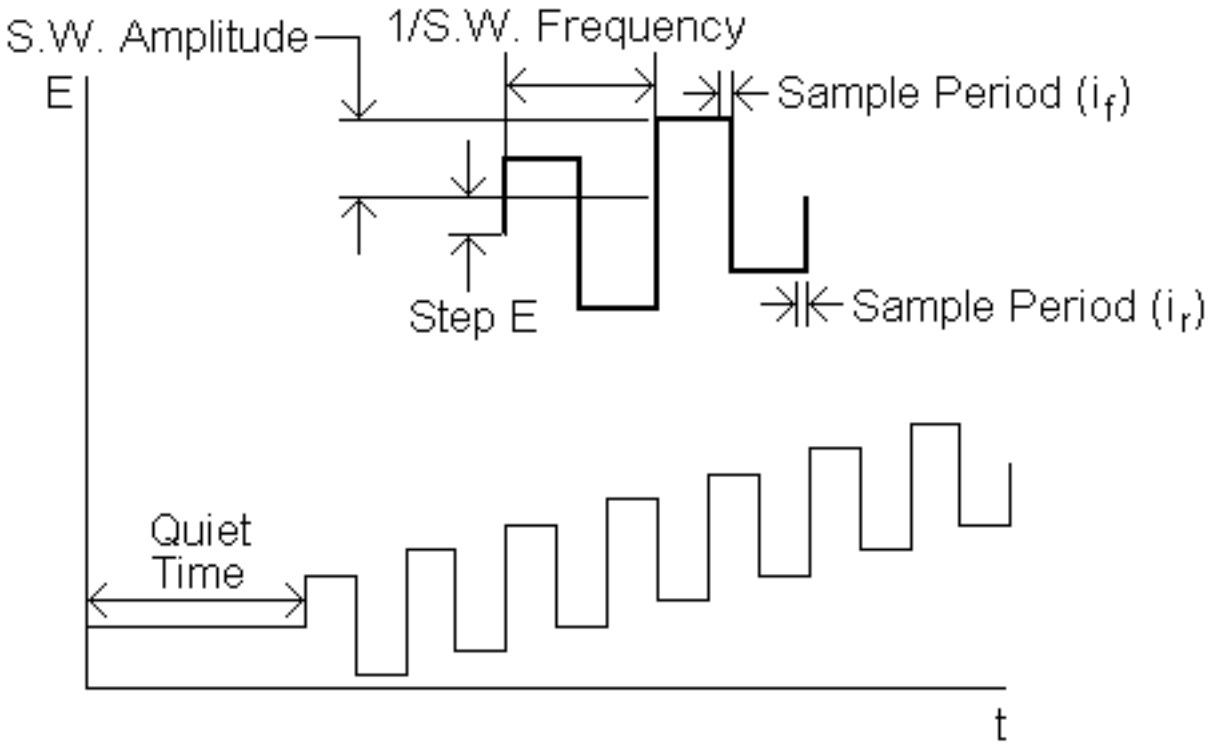

Figure 10. Potential wave form for square wave voltammetry.

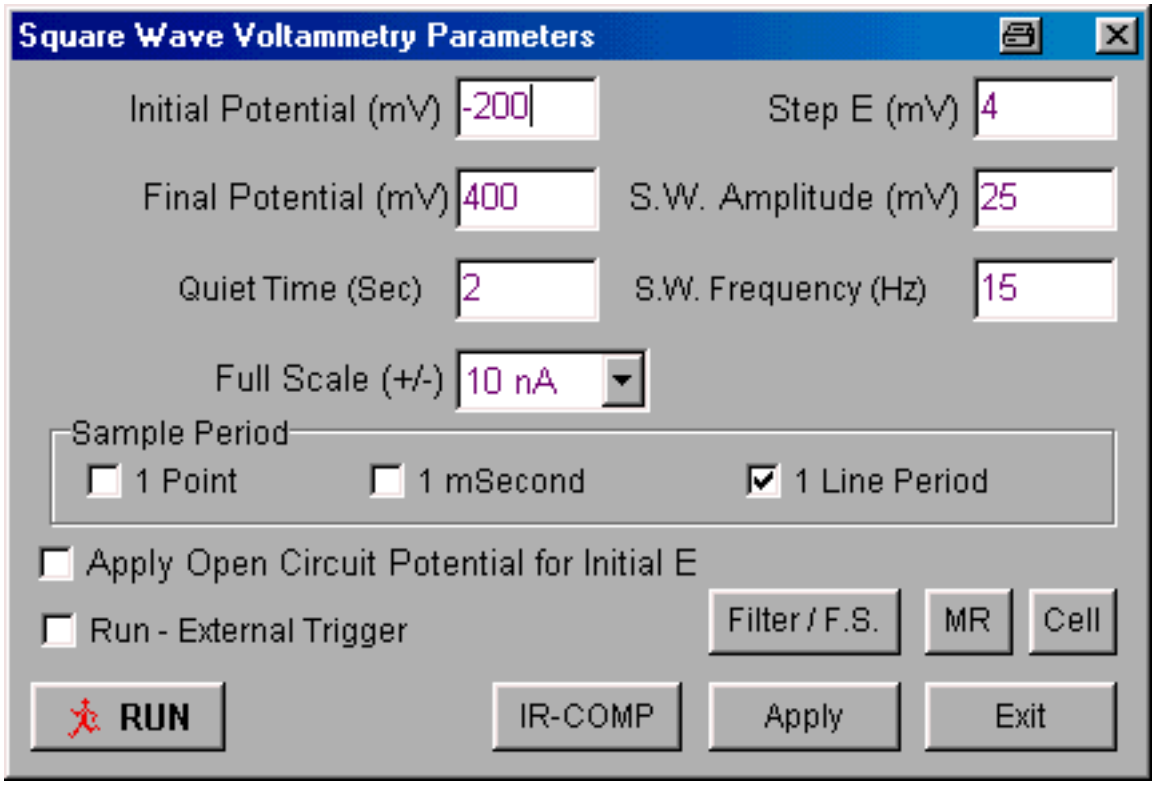

Figure 11. Change Parameters dialog box for square wave voltammetry.

1. All potential values are entered in mV.
2. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
3. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start In** back-panel connection.
4. The step height of the staircase wave form and the potential resolution is defined by **Step E**.
5. The pulse width is the length of each half-cycle, which is determined by the 1/**S.W. Frequency**.
6. The **Scan Rate** cannot be directly changed by the user, and is determined by **Step E** x **S.W. Frequency.**.
7. Three options are available for the **Sample Period** (note the options requiring longer measurement times are not available at higher frequencies):
    - The current is measured once at the end of each half-cycle (**1 Point** - maximum **S.W. Frequency** = 2000 Hz)
    - The current is measured multiple times in 1 ms at the end of each half-cycle, and averaged (**1 mSecond** - maximum **S.W. Frequency** = 125 Hz)
    - The current is measured multiple times over 1 line cycle at the end of the **Pulse Width**, and averaged (**1 Line Period**). The time required for 1 line cycle is the reciprocal of the line frequency (16.7 ms for 60 Hz, and 20 ms for 50 Hz). The line frequency is selected in the **Setup / Manual Settings (I/O)** dialog box.

   Generally speaking, increasing the **Sample Period** increases the signal-to-noise ratio.
8. If the **Apply Open Circuit Potential for Initial E** box is checked, then the open circuit potential will automatically be measured and used as the **Initial Potential**.
9. When the experiment is started, the cell is held at the **Initial Potential** for the number of seconds defined by the **Quiet Time**.
10. The experiment can be run on a hanging mercury drop electrode (i.e., a single drop is used for the entire experiment) using a BASi CGME by selecting **CGME SMDE Mode** from **Cell Stand / Accessories** in the **Setup / Manual Settings (I/O)** dialog box.
11. There are two gain stages for the current-to-voltage converter. The default values of these stages that are used for a given current **Full Scale** value are determined by the software. However, they can be adjusted manually using the **Filter / F.S.** dialog box. This dialog box is also used to change the analog **Noise Filter Value** settings from the default values set by the software.
12. The default condition of the cell is that the cell is **On** (i.e., the electronics are connected to the electrodes) *during* the experiment, and is **Off** *between* experiments. However, the potential can be switched **On** *between* experiments using the **Cell** dialog box. **HOWEVER, THIS OPTION SHOULD BE USED WITH CAUTION SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**
13. A series of identical experiments on the same cell can be programmed using the **MR (Multi-Run)** option.
14. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
15. Range of allowed parameter values:

- **Potential** = -3000 - +3000 mV
- **Step E** = 1 - 40 mV
- **S.W. Amplitude** = 1 - 250 mV
- **S.W. Frequency** = 1 - 2000 Hz
- **Quiet Time** = 0 - 100 s

16. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

There are two advantages to measuring the difference current. First, it increases the discrimination against the charging current, since any residual charging current is subtracted out. Second, the shape of the current response is a symmetric peak (**F12**), rather than the sigmoidal curve typically found for normal pulse voltammetry. If we consider a reduction, then at potential well positive of the redox potential, both the forward and reverse currents are zero, so the difference current is also zero. At potentials well negative of the redox potential, the current is diffusion-controlled, and the potential pulse has no effect; hence, the forward and reverse currents are equal, and the difference current is again zero. The largest difference between the forward and reverse currents (and hence the largest current response) is at the redox potential.

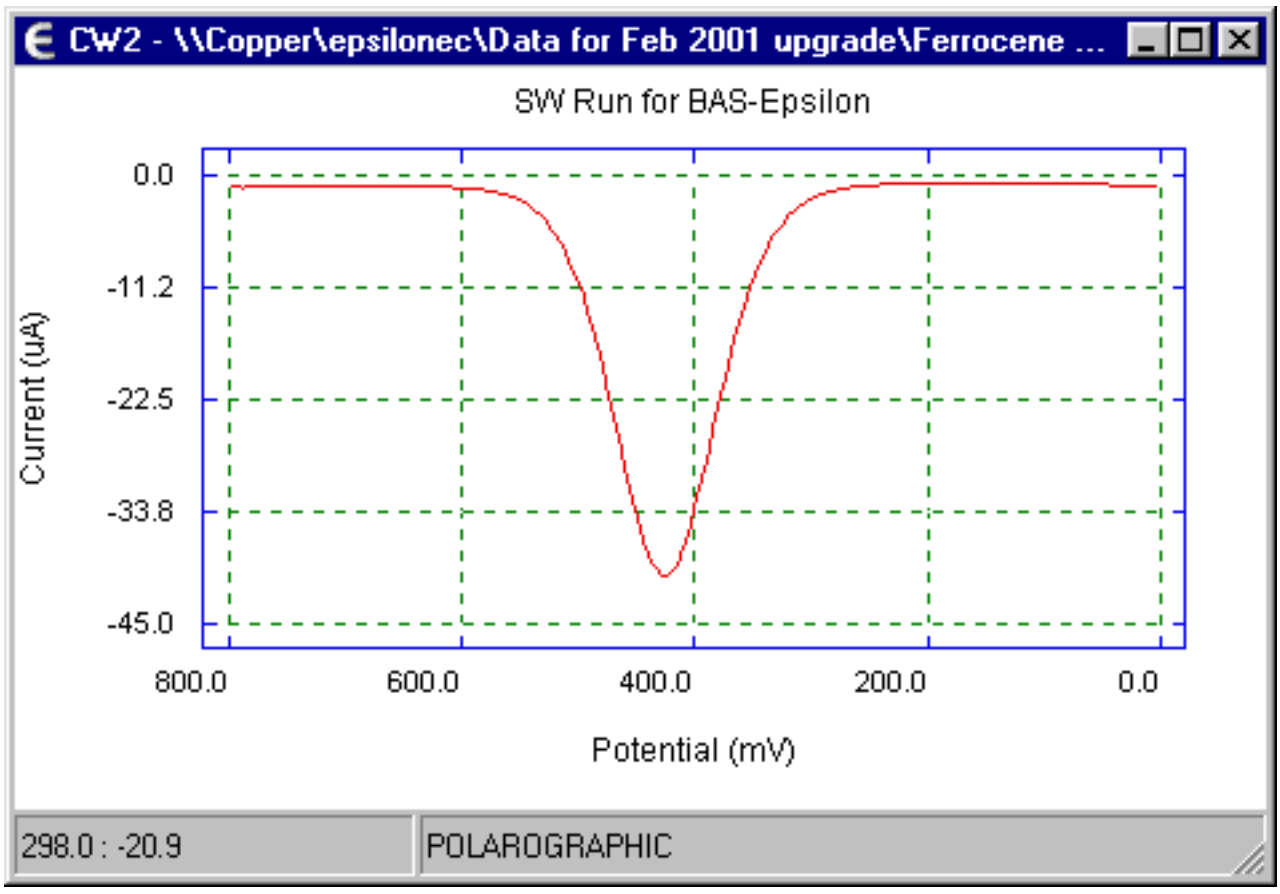

Figure 12. A typical square wave voltammogram.

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Stripping Voltammetry

Stripping voltammetry is a very sensitive method for the analysis of trace concentrations of electroactive species in solution. Detection limits for metal ions at sub-ppb concentrations have been reported.

There are 3 important parts in a stripping experiment:

- Deposition
- Quiet time
- Stripping

These components can best be explained by discussing the stripping experiment for detection of lead. In this experiment, a mercury working electrode is used - either the Hanging Mercury Drop Electrode (HMDE) (using the BASi CGME) or the Thin Mercury Film Electrode (TMFE) (using the BASi RDE-2). The TMFE is made by a depositing a mercury film on the surface of a glassy carbon electrode, typically during the deposition step.

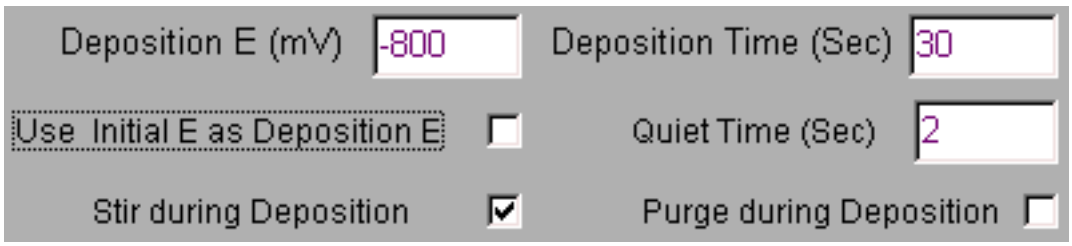

Figure 1. Parameters for deposition step when using the CGME.

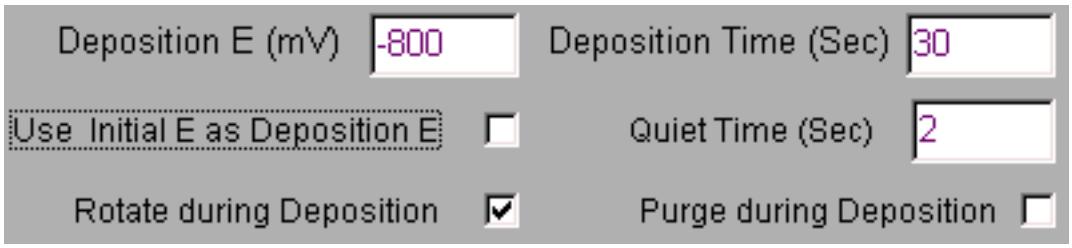

Figure 2. Parameters for deposition stepwhen using the RDE-2.

The parameters for the deposition step are shown in **F1** and **F2**. During the deposition step, the potential applied to the mercury electrode is held at a value (**Deposition E**) at which the lead ions are reduced to lead metal for a pre-determined time period (**Deposition Time**). If the **Use Initial E as Deposition E** is checked, the **Initial E** of the stripping step is used as the **Deposition Potential**. The metallic lead then amalgamates with the mercury electrode (when the TMFE is used, mercuric ions are generally added to the solution, and mercury metal is codeposited with the lead during the deposition step). The effect of this amalgamation is to concentrate the lead in the mercury electrode, and hence the concentration of

lead in the electrode is much greater (typically 2 or 3 orders of magnitude) than the concentration of lead in the solution (consequently, the deposition step is often called the preconcentration or accumulation step). The efficiency of the deposition can be increased by stirring either the solution (when using the CGME) or rotating the electrode (when using the RDE-2). Stirring (for the CGME), rotating (for the RDE-2), and purging during this step can be controlled remotely from the software by checking the **Stir/ Rotate during Deposition** and **Purge during Deposition** boxes, respectively. **Cell Stand** in **Setup / Manual Settings (I/O)** in the **Experiment** menu must be set to **CGME SMDE Mode** when using the CGME and to **RDE-2** when using the RDE-2.

After the deposition step, the stirring is stopped, and the system is allowed to reach equilibrium. This is the **Quiet Time**, which is typically 10 - 15 s.

During the stripping step, the applied potential is scanned in a positive direction, and the lead in the mercury electrode is oxidized back to lead ions in solution; that is, the lead is "stripped" from the electrode. The potential at which the stripping occurs is related to the redox potential of the analyte, and hence the potential of the current peak on the stripping step can be used to identify the analyte. The magnitude of the current of the stripping peak is proportional to the concentration of the analyte in the mercury electrode. Since the concentration of the analyte in the electrode is related to its concentration in solution, the stripping peak current is therefore proportional to the solution concentration.

A number of different wave forms have been used for the stripping step, including linear sweep voltammetry (**LSSV**), differential pulse voltammetry (**DPSV**), and square wave voltammetry (**SWSV**). **SWSV** and **DPSV** are more commonly used, due to their lower detection limits. The parameters required for each of these wave forms are described in detail elsewhere (click the appropriate link in the previous sentence).

As noted above, it is the concentration of lead in the mercury electrode that is directly measured in the stripping step rather than the concentration of lead in solution. The electrode concentration can be increased by increasing the **Deposition Time** and/or the rate of stirring. The values required for these two parameters depends on the sensitivity of the mercury electrode, which is determined by the surface area to volume ratio (i.e., how many of the deposited lead atoms are on the mercury surface and hence are detectable in the stripping step). This ratio is considerably higher for the TMFE, so a shorter **Deposition Time** is required. In addition, faster stirring can be used with the TMFE due to the relative mechanical instability of the HMDE (i.e., the mercury drop can fall off if the stirring is too fast). The signal resolution is also better with the TMFE, which can be important if there is more than one metal ion present.

However, the greater sensitivity of the TMFE can also be a disadvantage, since the solubility limit of the metal in the mercury can be exceeded more readily. This can lead to the formation of intermetallic compounds, which can affect the accuracy of the experimental results (due to e.g., shifts in the stripping potentials and depression of the stripping currents). One pair of metals that readily combine is zinc and copper.

In order to be of use as a quantitative analytical technique, the results of a stripping experiments must be reproducible. Therefore, the experimental conditions must be reproducible. A second disadvantage of the TMFE is the relatively poor reproducibility of the film. Since the film is deposited on the surface of a glassy carbon electrode, it is sensitive to the microstructure of the glassy carbon surface, which can be affected by the method used to prepare the surface. In contrast, an HMDE is highly reproducible. Whatever the chosen mercury electrode, great care must be taken in sample preparation, cleaning of glassware, etc. The rate of stirring during the deposition step must also remain constant.

The above method is called anodic stripping voltammetry (ASV), since the stripping current is anodic. This method can be used for metal ions that can be readily reduced to the metallic state and reoxidized - about 20 metal ions, including lead, copper, cadmium, and zinc. This is not as many as can be detected using atomic absorption spectroscopy (AAS), although the sensitivity of ASV is comparable with, and sometimes better than AAS. The advantage of ASV over AAS is its ability to detect several metal ions simultaneously. In addition, different oxidation states of a given metal can be detected (e.g., arsenic and antimony).

Other stripping voltammetric techniques include cathodic stripping voltammetry (CSV) and adsorptive stripping voltammetry (AdSV). The basis for CSV is the oxidation of mercury followed by the formation of an insoluble film of HgL (L is the analyte) on the surface of the mercury electrode during the deposition step. CSV is most commonly used for detection of sulfur-containing molecules (e.g., thiols, thioureas, and thioamides), but it has also been used for molecules such as riboflavin and nucleic acid bases (e.g., adenine and cytosine).

AdSV is different from ASV and CSV in that the deposition step is non-electrolytic, and occurs via the adsorption of molecules on the surface of the working electrode (the HMDE is most commonly used). The stripping step can be either anodic or cathodic. AdSV has been used for organic molecules (e.g., dopamine, chlorpromazine, erythromycin, dibutone, and ametryne) and for metal complexes of metals not amenable to detection by ASV (e.g., cobalt and nickel).

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Controlled Potential Electrolysis

Introduction

The principle behind the Controlled Potential Electrolysis (**CPE**) experiment is very simple. If only the oxidized species is initially present, then the potential is set at a constant value sufficiently negative to cause rapid reduction and is maintained at this value until only the reduced species is present in solution. The total charge passed during the **CPE** experiment (Q) is calculated by integrating the current and is related to the number of electrons transferred per molecule (n) and the number of moles of the oxidized species initially present (N) through Faraday's law:

$Q = nFN$

where F is Faraday's constant (96500 C mol^{-1}). Therefore, if one of n or N is known, the other can be calculated. Hence, **CPE** has both analytical and synthetic applications, and is a standard technique on the epsilon.

Setting Up a Constant Potential Electrolysis Experiment

The parameter values for **CPE** are set using the **Change Parameters** dialog box (**F1**) in either the **Experiment** menu or the pop-up menu.

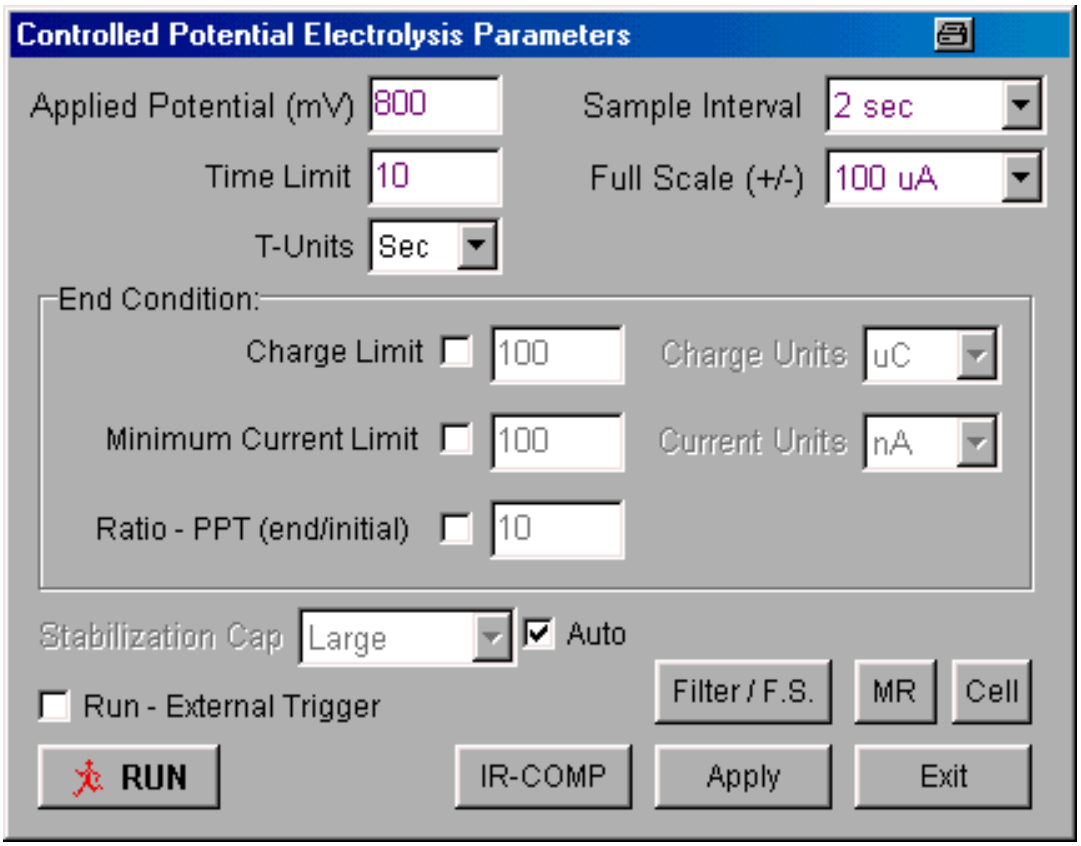

Figure 1. **Change Parameters** dialog box for controlled potential eletrolysis.

1. Potential values are entered in mV, and time values are entered in minutes or seconds (selected using **T-Units**)
2. The time resolution of the data is specified by the **Sample Interval** (e.g., the default condition is that a data point is recorded every second).
3. There are two gain stages for the current-to-voltage converter. The default values of these stages that are used for a given current **Full Scale** value are determined by the software. However, they can be adjusted manually using the **Filter / F.S.** dialog box. This dialog box is also used to change the analog **Noise Filter Value** settings from the default values set by the software.
4. A stabilizing capacitor (**Stabilization Cap**) between the auxiliary and reference electrodes is switched in during the **CPE** experiment. The **Auto** default capacitor (**Large** - 0.1 uF) can be manually changed to **Small** (0.01 uF) or **No Cap** (no capacitor).
5. The default condition of the cell is that the cell is **On** (i.e., the electronics are connected to the electrodes) *during* the experiment, and is **Off** *between* experiments. However, the potential can be switched **On** *between* experiments using the **Cell** dialog box. **HOWEVER, THIS OPTION SHOULD BE USED WITH CAUTION SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**
6. A series of identical experiments on the same cell can be programmed using the **MR (Multi-Run)** option. However, if any of the optional **End Conditions** are checked, any MR settings are ignored.
7. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
8. The end of the **CPE** experiment can be set by the user in a number of ways. The most basic criterion is the **Time Limit**, which must be set by the user; that is, the experiment will end after a user-defined time period. However, there are three optional criteria that can also be set:
    - **Charge Limit** - The absolute value of the charge limit should be specified
    - **Minimum Current Limit** - the absolute minimum current value should be specified
    - **Ratio - PPT (end/initial)** - the criterion is the ratio of the final current to the initial current in parts per thousand

    Any one of these three optional criteria can be used in addition to the **Time Limit**. However, it is important to note that the **Time Limit** always takes precedence; that is, if the **Time Limit** is attained before e.g., the charge exceeds the **Charge Limit**, the experiment will end. It should also be noted that there will typically be a delay of 1 or 2 seconds between the time the selected criterion is exceeded and the termination of the experiment, due to the time required for data processing. If any of these optional criteria are used, the multi-run capability is disabled.
9. Range of allowed parameter values:
    - **Potential** = -3275 - +3275 mV
    - **Sample Interval** = 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 30 and 60 sec
    - **Time Limit** = 0 - 32000 in sec or min (the maximum value allowed for the **Time Limit** is also determined by the **Sample Interval**, since a maximum of 64000 data points can be recorded in one experiment (e.g, the shorter the **Sample Interval**, the shorter the experiment)).
10. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).
11. Neither the **Pre Run Drops** function nor the internal dummy cell are available for CPE.

The potential required for a **CPE** experiment is determined by the redox potential of the analyte (measured by e.

g., cyclic voltammetry). For a reduction, the ideal potential is ca. 200 mV more negative than the redox potential so that the rate of electrolysis is controlled by the rate of mass transport to the working electrode. However, it is not always possible to use a potential too far removed from the redox potential due to electrolysis of other electroactive materials (e.g., electrolyte, solvent ,or other components of the solution mixture).

The cell required for **CPE** is significantly different to that required for voltammetry experiments (in which only a very small fraction of the electroactive molecule of interest is electrolyzed). The rate of electrolysis is enhanced by using a working electrode with a large surface area (e.g., platinum gauze, reticulated vitreous carbon or a mercury pool) and an auxiliary electrode with a large surface area (e.g., platinum coil or gauze); in addition, the solution is stirred to increase the rate of mass transport to and from the working electrode. The auxiliary electrode must be isolated from the working electrode to prevent species that are electrogenerated at the auxiliary electrode from interfering with electrolysis at the working electrode. However, care must be taken when choosing the material used to isolate the auxiliary electrode from the working electrode, since high resistance material may affect the efficiency of the electrolysis.

The output from a **CPE** experiment is a current vs. time plot (a typical example is shown in **F2**).

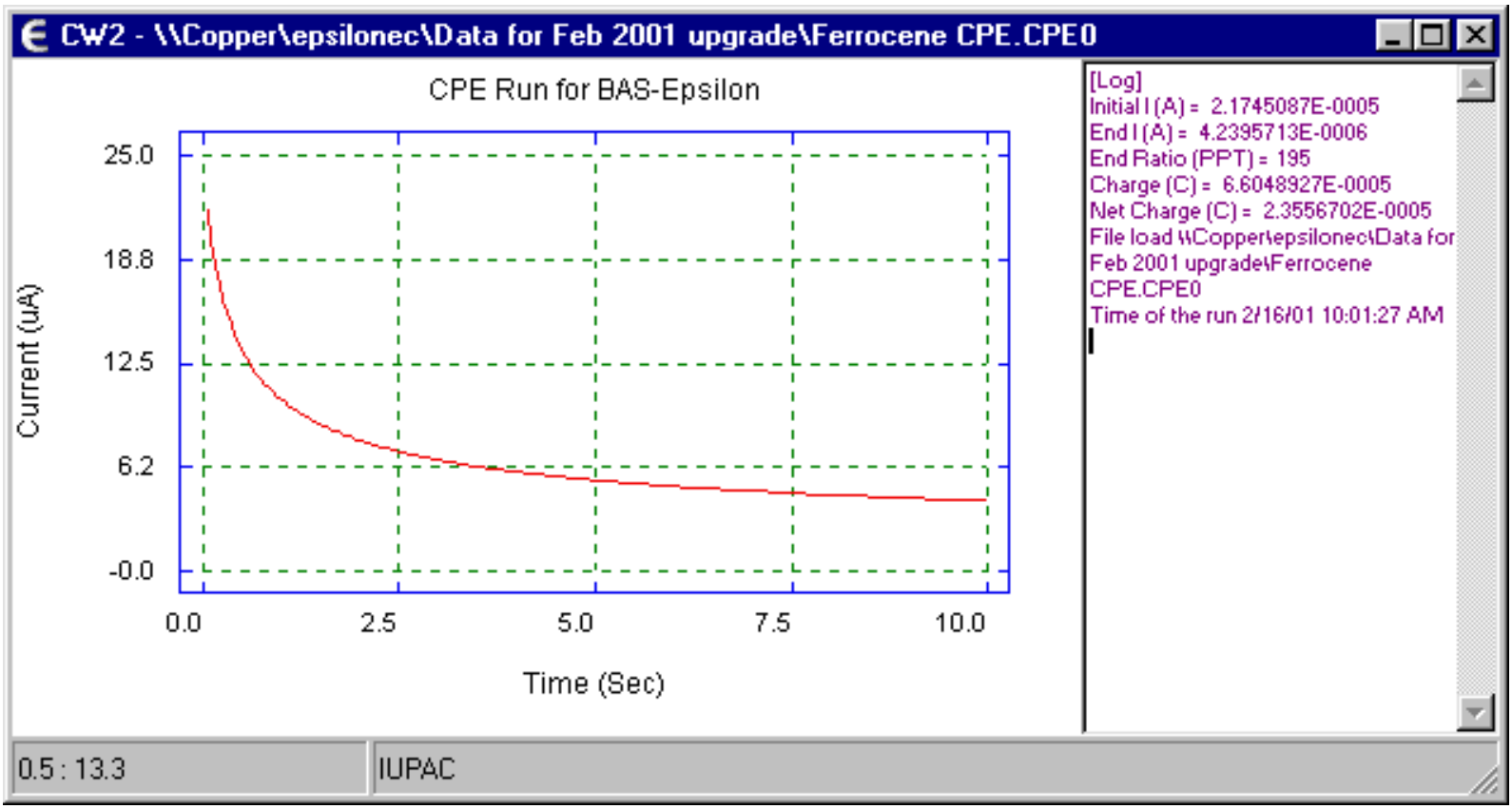

Figure 2. Current vs. time plot for constant potential electrolysis.

The following parameters are displayed in a separate window during the experiment, and are updated every second:

- **Elapsed Time**
- **Initial Current** (the current at the start of the experiment)
- **Current** (the most recent current value)

- **Current Ratio** (ratio of the most recent current value to the initial current value in part per thousand)
- **Charge** (the accumulated charge)

At the end of the experiment, the following parameters are displayed in the **Text Info** box to the right of the display (**F2**):

- **Initial Current I**
- **End Current I** (the current value at the end of the experiment, calculated as the average of the last 5 current values)
- **End Current Ratio**
- **Charge**
- **Net Charge**

Net Charge is calculated by subtracting the background charge from the total charge passed during the experiment (**Charge**). The background current is assumed to be constant during the experiment, and equal to **End I**. Therefore, the background charge is equal to the product of the background current and the experimental time. Once the **Net Charge** has been calculated, it can be used to calculate the number of electrons transferred or the amount of material electrolyzed (in moles) through Faraday's Law:

$Q = nFN$

where: n = number of electrons transferred/molecule
F = Faraday's constant (96,485 C mol^{-1})
N = amount of material electrolyzed (mol)

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DC Potential Amperometry

DC Potential Amperometry (**DCA**) is the simplest technique on the epsilon. A constant potential is applied to the electrochemical cell, and the current response is monitored. Typical applications of this technique include amperometric titrations, amperometric sensors, flow cells (including liquid chromatography with electrochemical detection), etc. **DCA** is a standard technique on the epsilon. Multichannel amperometry experiments are also available through the addition of the optional bipotentiostat board.

Setting Up a DC Amperometry Experiment

The parameter values for **DCA** are set using the **Change Parameters** dialog box (**F1**) in either the **Experiment** menu or the pop-up menu.

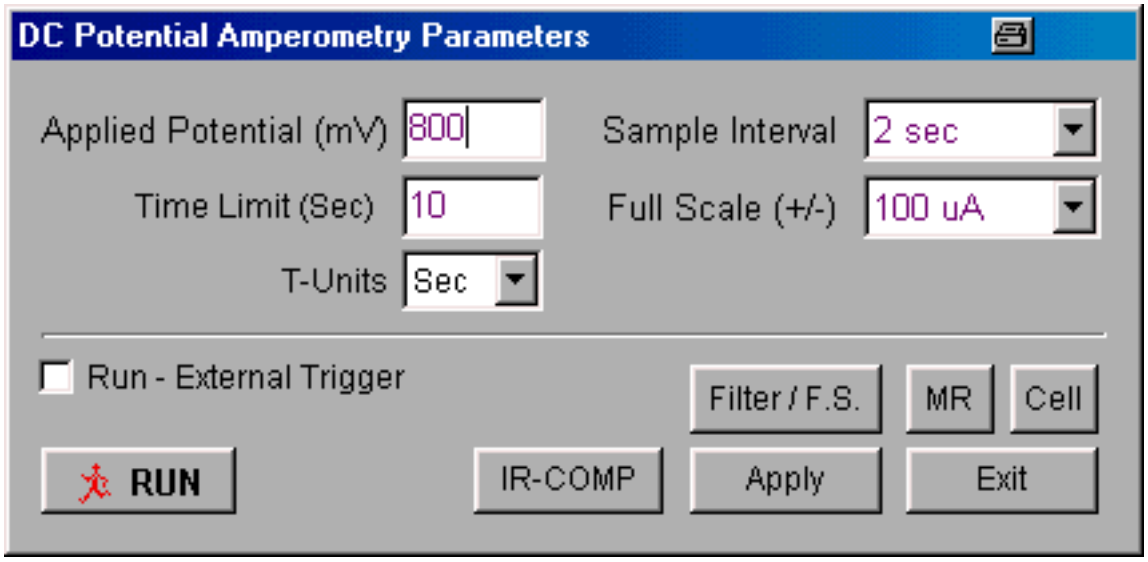

Figure 1. **Change Parameters** dialog box for DC amperometry.

1. Potential values are entered in mV, and time values are entered in minutes or seconds (selected using **T-Units**)
2. The time resolution of the data is specified by the **Sample Interval** (e.g., the default condition is that a data point is recorded every second).
3. The experiment can be run on a hanging mercury drop electrode (i.e., a single drop is used for the entire experiment) using a BASi CGME by selecting **CGME SMDE Mode** from **Cell Stand / Accessories** in the **Setup / Manual Settings (I/O)** dialog box.
4. A rotating disk experiment can be run using a BASi RDE-2 by selecting **RDE-2** from **Cell Stand / Accessories** in the **Setup / Manual Settings (I/O)** dialog box and entering the required **Rotation Rate** under **RDE2 Rotation** in the **Cell** dialog box.
5. There are two gain stages for the current-to-voltage converter. The default values of these stages

that are used for a given current **Full Scale** value are determined by the software. However, they can be adjusted manually using the **Filter / F.S.** dialog box. This dialog box is also used to change the analog **Noise Filter Value** settings from the default values set by the software.

6. The default condition of the cell is that the cell is **On** (i.e., the electronics are connected to the electrodes) *during* the experiment, and is **Off** *between* experiments. However, the potential can be switched **On** *between* experiments using the **Cell** dialog box. **HOWEVER, THIS OPTION SHOULD BE USED WITH CAUTION SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**
7. A series of identical experiments on the same cell can be programmed using the **MR (Multi-Run)** option.
8. The end of the experiment is determined by the **Time Limit** (although the experiment can be ended by the user before that time).
9. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
10. Range of allowed parameter values:
    - **Potential** = -3275 - +3275 mV
    - **Sample Interval** = 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 30 and 60 sec
    - **Time Limit** = 0 - 32000 (the maximum value allowed for the **Time Limit** is also determined by the **Sample Interval**, since a maximum of 64000 data points can be recorded in one experiment (e.g, the shorter the **Sample Interval**, the shorter the experiment)).
11. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

The **Applied Potential** is determined by the redox potential of the analyte. For example, if **DCA** is used for EC detection for HPLC, the potential should be such that the analyte is electrolyzed at the mass-transport limited rate (as determined by hydrodynamic voltammetry). However, the increase in noise and the decrease in selectivity with increasing positive or negative potentials may also need to be considered when selecting the potential value.

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Chronopotentiometry

Introduction

Epsilon instruments contain both a potentiostat and a galvanostat, and hence can perform both controlled potential (potentiostatic) and controlled current (galvanostatic) experiments. Although potentiostatic experiments are much more common, there are some applications for which a galvanostat is advantageous.

The galvanostat uses a three electrode configuration, in which a current is applied between the auxiliary and working electrodes, and the potential of the working electrode (measured with respect to the reference electrode) is monitored. The basis of controlled current experiments is that a redox (electron transfer) reaction must occur at the surface of the working electrode in order to support the applied current. For example, if ferricyanide is present in the solution, then a reducing current will lead to the reduction of ferricyanide to ferrocyanide at the working electrode (note that a balancing oxidation must also occur at the auxiliary electrode). Common applications of the galvanostat include constant current stripping potentiometry and constant current electrolysis (including applications where a constant rate of electrolysis in important, such as electrodeposition and battery studies). One advantage of all constant current techniques is that the ohmic drop due to solution resistance is also constant, as it is equal to the product of the current and the solution resistance. The ohmic distortion can therefore be simply corrected by a constant potential offset. In contrast, in potentiostatic experiments (e.g., cyclic voltammetry), the current, and hence the ohmic drop, varies with potential, and correction is more complicated.

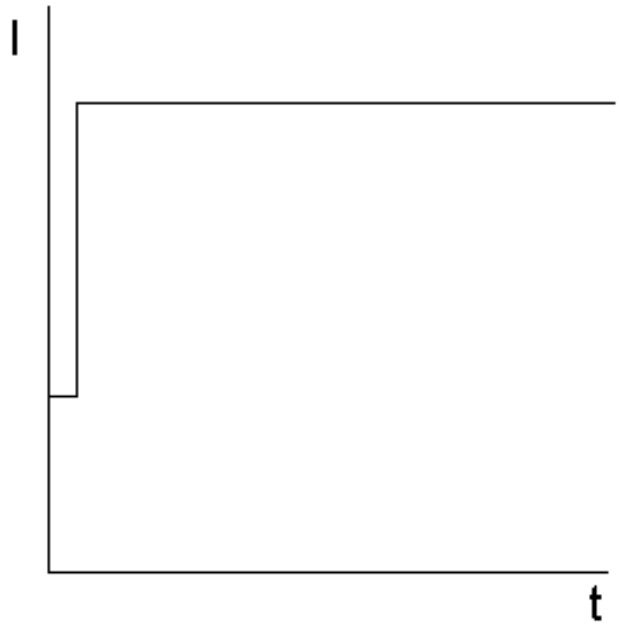

Figure 1. Current excitation signal for a chronopotentiometry experiment.

Chronopotentiometry (**CP**) is the most basic constant current experiment and is a standard technique for the epsilon. In **CP**, a current step is applied (**F1**) across an electrochemical cell (without stirring). In double step chronopotentiometry (**DSCP**), a second current step is applied (**F2**). It should be noted that the time scale of a **DSCP** experiment is typically shorter (seconds or milliseconds) than that of **CP** experiment (minutes or seconds). The protocol for defining the sampling rate is therefore different for the two techniques. **CP** is a standard technique, whereas **DSCP** is only available as an optional addition.

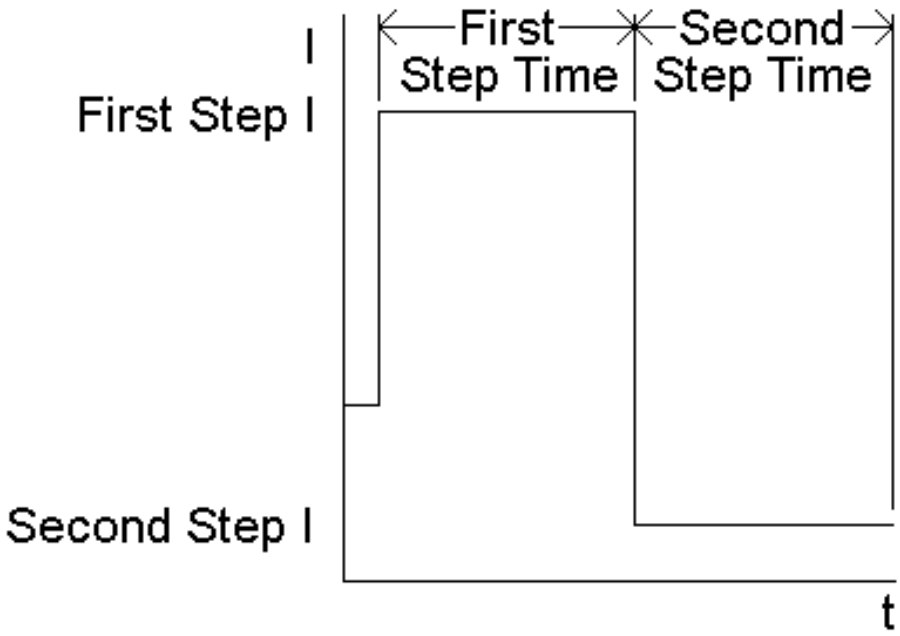

Figure 2. Current excitation signal for a double step chronopotentiometry experiment.

Setting Up a Chronopotentiometry Experiment

The parameters required for a **CP** experiment are the current value and the length of the current step. The values of these parameters are entered using the **Change Parameters** dialog box (**F2**) in either the **Experiment** menu or the pop-up menu.

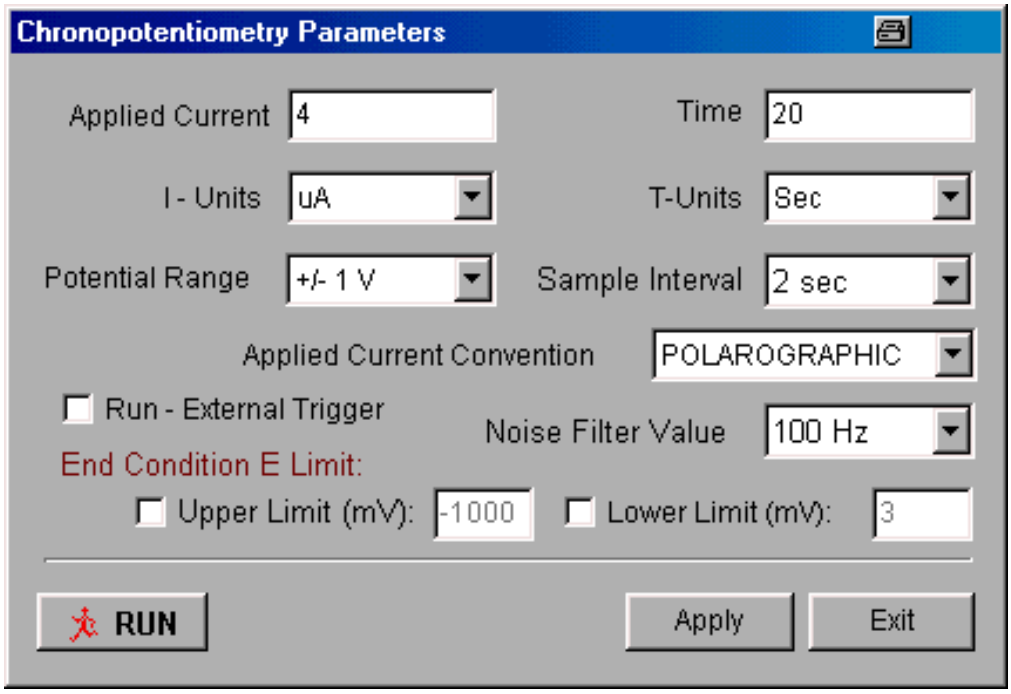

Figure 3. Change Parameters dialog box for chronopotentiometry.

1. Current values are entered in mA, µA, nA, or pA (selected using **I - Units**), and time values are entered in minutes or seconds (selected using **T-Units**).
2. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start**

In back-panel connection.

3. The rate of data acquisition is determined by the **Sample Interval** (e.g., the default rate is one point every second).
4. The current polarity is determined by the **Applied Current Convention - IUPAC** = positive oxidation current, **Polarographic** = positive reduction current
5. The **Noise Filter Value** determines the amount of analog filtering.
6. The end of the experiment can determined by the **Time** or by the **End Condition E Limit** in mV (if the appropriate check box is checked). The experiment can also be ended manually.
7. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
8. The **Multi-Run** option is not available for this technique.
9. Range of allowed parameter values:
    - **Current** = 50 pA - 50 mA (but note that there are accuracy limitations when applying sub-nA currents)
    - **End Condition E Limit** = -999 - +999 mV (for **Potential Range** = +/- 1V), or -9999 - +9999 mV (for **Potential Range** = +/- 10V)
    - **Sample Interval** = 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 30, 60 sec
    - The largest number that can be entered for **Time** is 32,000. However, the maximum number of data points that can be collected in one experiment is 64,000, so the maximum value for the **Time** of a given experiment is also determined by the **Sample Interval**.
10. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

Setting Up a Double Step Chronopotentiometry Experiment

As shown in **F2**, four parameters are used in the epsilon software to define the current wave form for **DSCP**.

1. First Step Current
2. Second Step Current
3. First Step Time
4. Second Step Time

The values of these parameters are entered using the **Change Parameters** dialog box (**F2**) in either the **Experiment** menu or the pop-up menu.

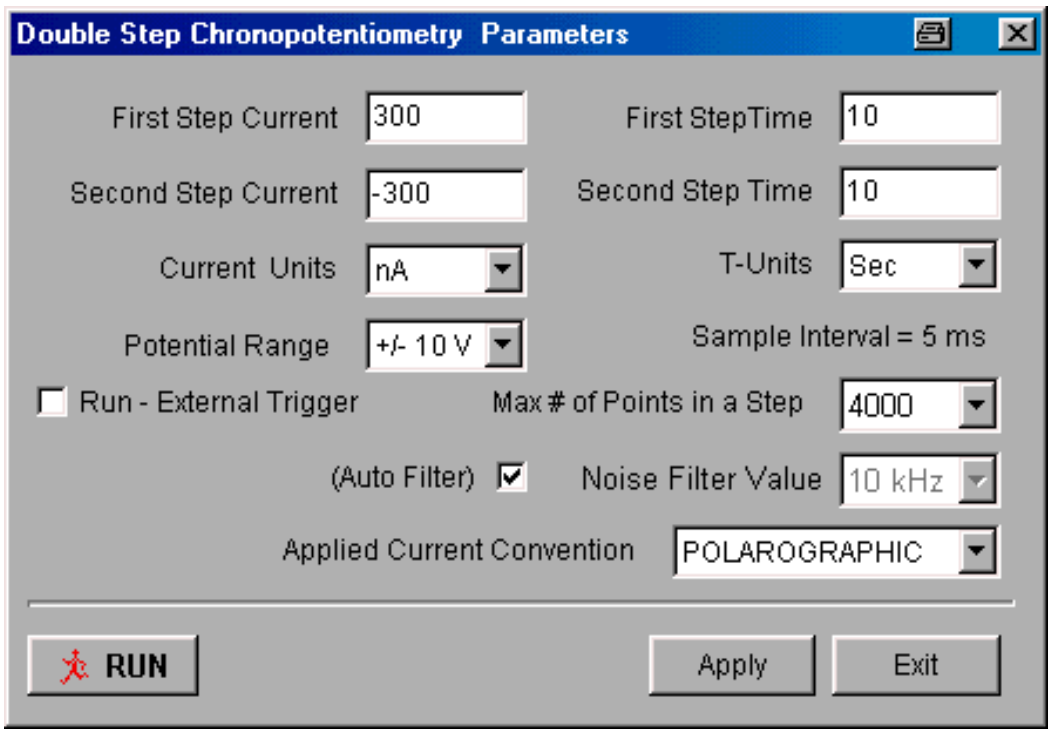

Figure 4. Change Parameters dialog box for double step chronopotentiometry.

1. Current values are entered in mA, µA, nA, or pA (selected using **Current Units**), and time values are entered in seconds or milliseconds (selected using **T-Units**).
2. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start In** back-panel connection.
3. The rate of data acquisition is determined by the **Sample Interval** (e.g., the default rate is one point every second).
4. The current polarity is determined by the **Applied Current Convention - IUPAC** = positive oxidation current, **Polarographic** = positive reduction current
5. The **Noise Filter Value** determines the amount of analog filtering. The correct filter will be set automatically if **Auto Filter** is checked.
6. Clicking **Exit** will exit the dialog box *without* saving any changes made to the parameter values. Any changes can be saved by clicking **Apply** before exiting.
7. The **Multi-Run** option is not available for this technique.
8. Range of allowed parameter values:
    - **Step Current** = 50 pA - 32 mA (but note that there are accuracy limitations when applying sub-nA currents)
    - **Step Time** = 1 - 65 seconds **OR** 1 - 16000 milliseconds
    - **Maximum # of points in a step** = 1000, 2000, 4000, 8000, 16000
    - The **Sample Interval** is determined by the **Step Time** and the **Maximum # of points in a step**, and can only be adjusted by the user indirectly through these latter two parameters. The relationship between these parameters is shown by the equation

      Sample Interval = Step Time/Maximum # of points

      However, it should be noted that only certain values are allowed for each of these parameters, as is shown in the table below:

Max. # of points	1000	2000	4000	8000	16000
Sample Interval	**Maximum Step Time (/ms)**				
20 µs	20	40	80	160	320
50 µs	40	81	162	325	650
100 µs	100	200	400	800	1600
200 µs	200	400	800	1600	3200
500 µs	406	812	1625	3250	6500
1 ms	1000	2000	4000	8000	
2 ms	2000	4000	8000		
5 ms	4062	8125			
10 ms	10000				

9. Once the parameters have been set, the experiment can be started by clicking **Run** (either in this dialog box, in the **Experiment** menu, in the pop-up menu, on the Tool Bar, or using the **F5** key).

Analysis of the Potential vs. Time Curve

The shape of the potential response can be rationalized by considering the concentration profiles of the redox species as a function of time (**F5**).

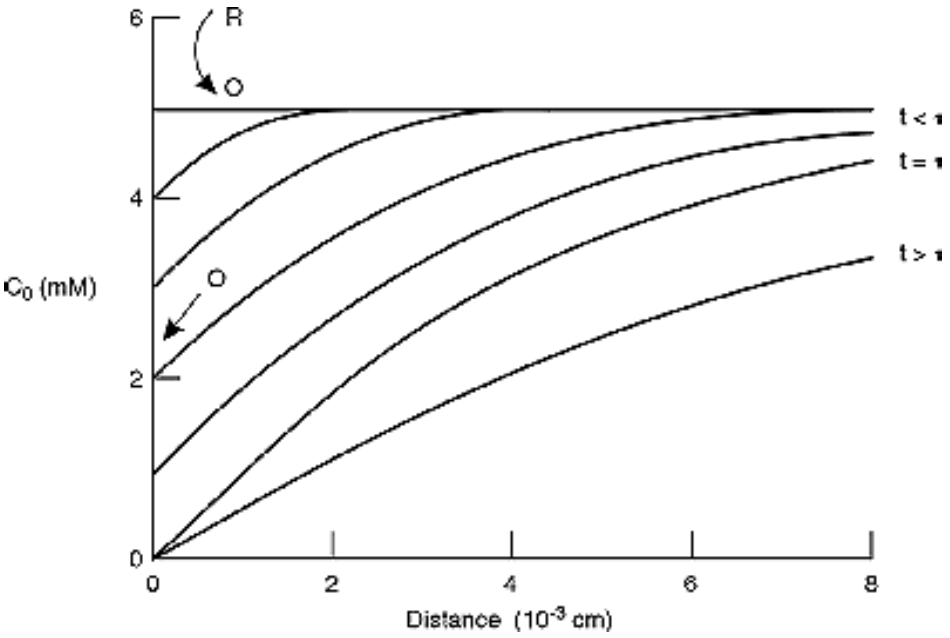

Figure 5. Concentration profiles for chronopotentiometry.

Let us consider the electron transfer reaction $O + e^- = R$. Before the current step, the concentration of O at the electrode surface is the same as in the bulk solution (i.e., 5 mM). The initial potential is the rest potential or the open circuit potential ($E_{o.c.}$). Once the (reducing) current step has been applied, O is reduced to R at the electrode surface in order to support the applied current, and the concentration of O at the electrode surface therefore decreases. This sets up a concentration gradient for O between the bulk solution and the electrode surface, and molecules of O diffuse down this concentration gradient to the electrode surface. The potential is close to the redox potential for $O + e^- = R$, and its

precise value depends upon the Nernst equation:

$$E = E^{o'} + \frac{0.059}{n} \log \frac{C_O^s}{C_R^s}$$

where C^s_O and C^s_R are the surface concentrations of O and R, respectively. These concentrations vary with time, so the potential also varies with time, which is reflected in the finite slope of the potential vs. time plot at this stage. Once the concentration of O at the electrode surface is zero, the applied current can no longer be supported by this electron transfer reaction, so the potential changes to the redox potential of another electron transfer reaction. If no other analyte has been added to the solution, the second electron transfer reaction will involved reduction of the electrolyte; that is, there is a large change in the potential (**F6**).

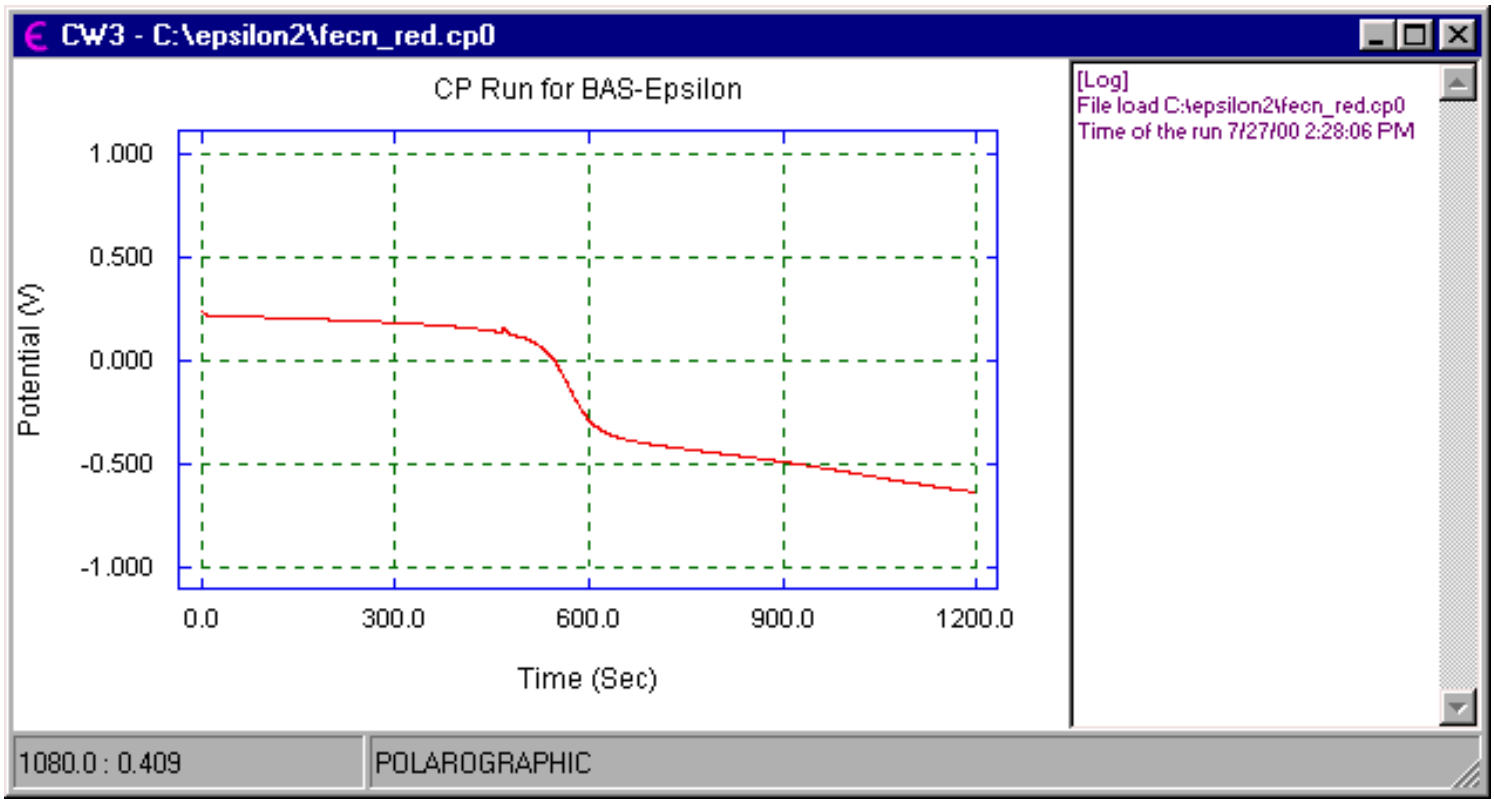

Figure 6. Typical potential response for a chronopotentiometry experiment.

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Open Circuit Potential vs. Time

Introduction

The open circuit potential (also referred to as the equilibrium potential, the rest potential, or the corrosion potential) is the potential at which there is no current; that is, experiments based on the measurement of the open circuit potential are *potentiometric* experiments. Although such measurements are very simple, they have many important applications, which are briefly discussed below. The open circuit measurement technique is standard on the epsilon.

Setting Up an Open Circuit Measurement

Setting up an open circuit potential vs. time experiment is very simple. The important parameters that need to be entered by the user (in the appropriate **Change Parameters** dialog box (**F1**) from either the **Experiment** menu or the pop-up menu) are the length of the experiment (defined by **Time** in units of seconds or minutes (as specified by **T-Units**)) and the **Sample Interval**, which determines how often a data point is acquired. The largest number that can be entered for **Time** is 32,000. However, the maximum number of data points that can be collected in one experiment is 32000, so the maximum value for the **Time** of a given experiment is also determined by the **Sample Interval**. For example, if **T-Units** = sec, and **Sample Interval** = 0.5 sec, then the maximum value for **Time** = 64,000. Note that the **Multi-Run** option is not available for this technique. If the **Run - External Trigger** box is checked, the experiment is started from an external device using the **Start In** back-panel connection.

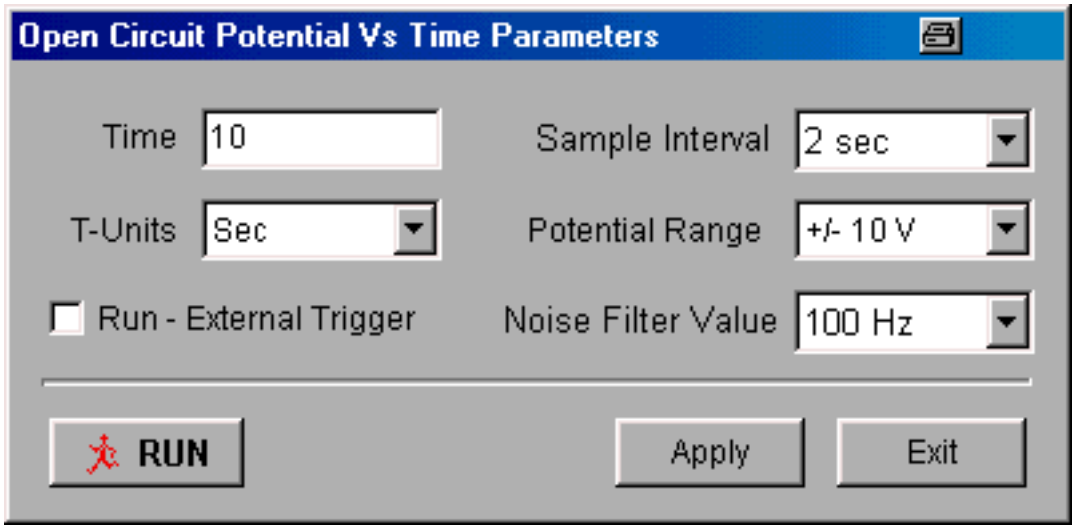

Figure 1. Change Parameters dialog box for open circuit potential measurements.

In addition to this measurement, the open circuit potential can be monitored using **Measure Open Circuit Potential** in the **Experiment** menu. Furthermore, this potential can be measured before another

experiment (e.g., cyclic voltammetry) and can be automatically used as the initial potential.

Applications

The basis of potentiometric concentration measurements (e.g., for potentiometric titrations) is the Nernst equation, which relates the concentration of electroactive species at the electrode surface (C^s) to the potential at that electrode (E); that is, for the reaction $O + e^- = R$

$$E = E^{o'} + \frac{0.059}{n} \log \frac{C_O^s}{C_R^s}$$

where $E^{o'}$ is the formal redox potential of the electron transfer reaction. The potential E is measured between two electrodes: the *indicator* electrode and the *reference* electrode (the auxiliary electrode is disconnected for potentiometric measurements on the epsilon). The indicator electrode is selected such that its potential is sensitive to the concentration of the analyte in solution (e.g., a glass membrane electrode for the measurement of pH), and the reference electrode (e.g., the saturated calomel or the silver/silver chloride electrode) provides a stable reference potential for the measurement of the potential of the indicator electrode.

Other important open circuit potential measurements are the open circuit potential of a battery, and the equilibrium (corrosion) potential of a corroding system

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Multichannel Techniques

Multichannel techniques are available on the epsilon by the addition of the optional bipotentiostat board. Bipotentiostat experiments can be run for cyclic voltammetry, chronoamperometry and DC amperometry.

The **Change Parameters** dialog box for multichannel cyclic voltammetry (**MCCV**) is shown in **F1**. Setting the parameters for Channel 1 is described in detail in the section on cyclic voltammetry.

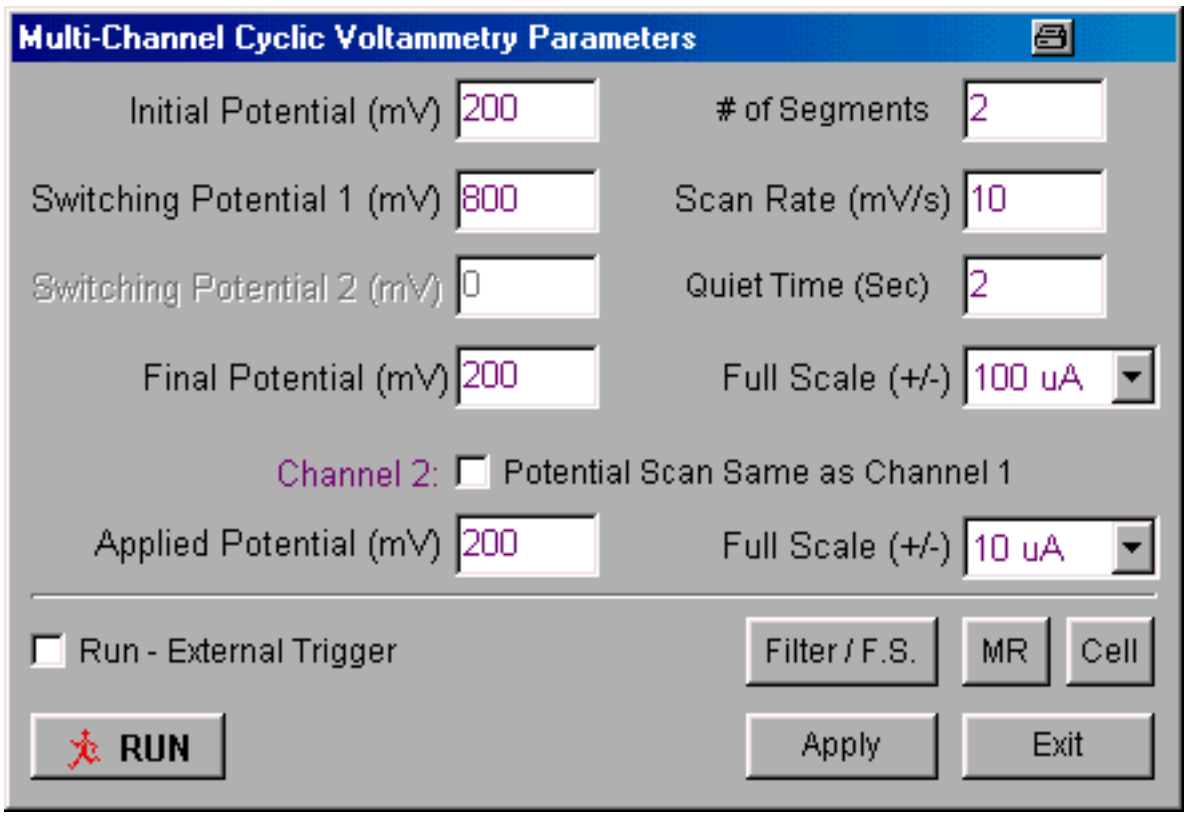

Figure 1. **Change Parameters** dialog box for multichannel cyclic voltammetry.

There are two options available for Channel 2:

a) Fixed potential. Channel 2 is held at a set potential value, as defined by the **Applied Potential**. The **Potential Scan** box should not be checked. Note that the current sensitivity (**Full Scale**) for Channel 2 must also be specified. Typical output from a "scan-hold" experiment is shown in **F2**.

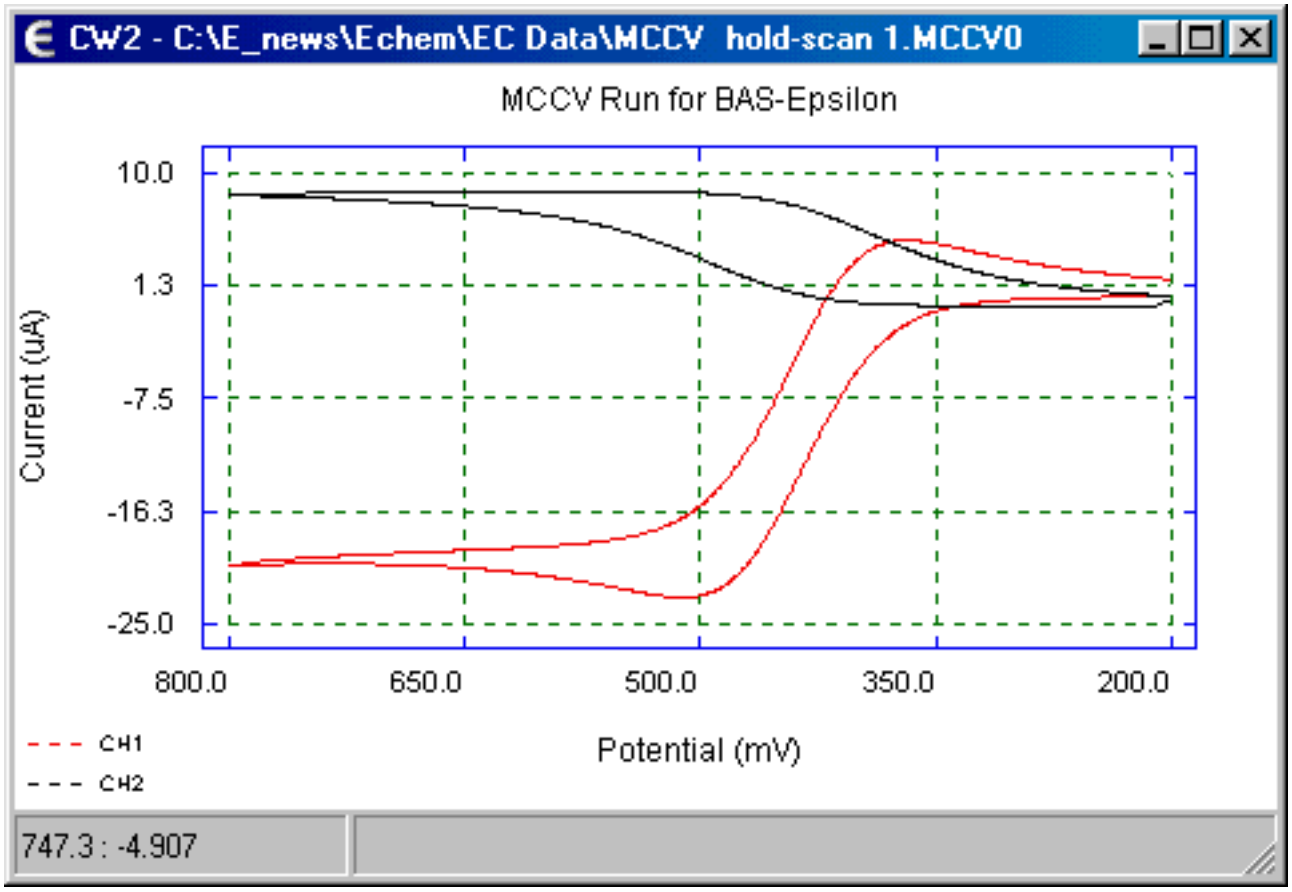

Figure 2. Typical data for a scan-hold multichannel cyclic voltammetry experiment.

b) Potential scan. Channel 2 is scanned over the same potential range and at the same scan rate as Channel 1. The **Potential Scan** box must be checked. Note that the current sensitivity (**Full Scale**) for Channel 2 must also be specified. Typical output from a "scan-scan" experiment is shown in **F3**.

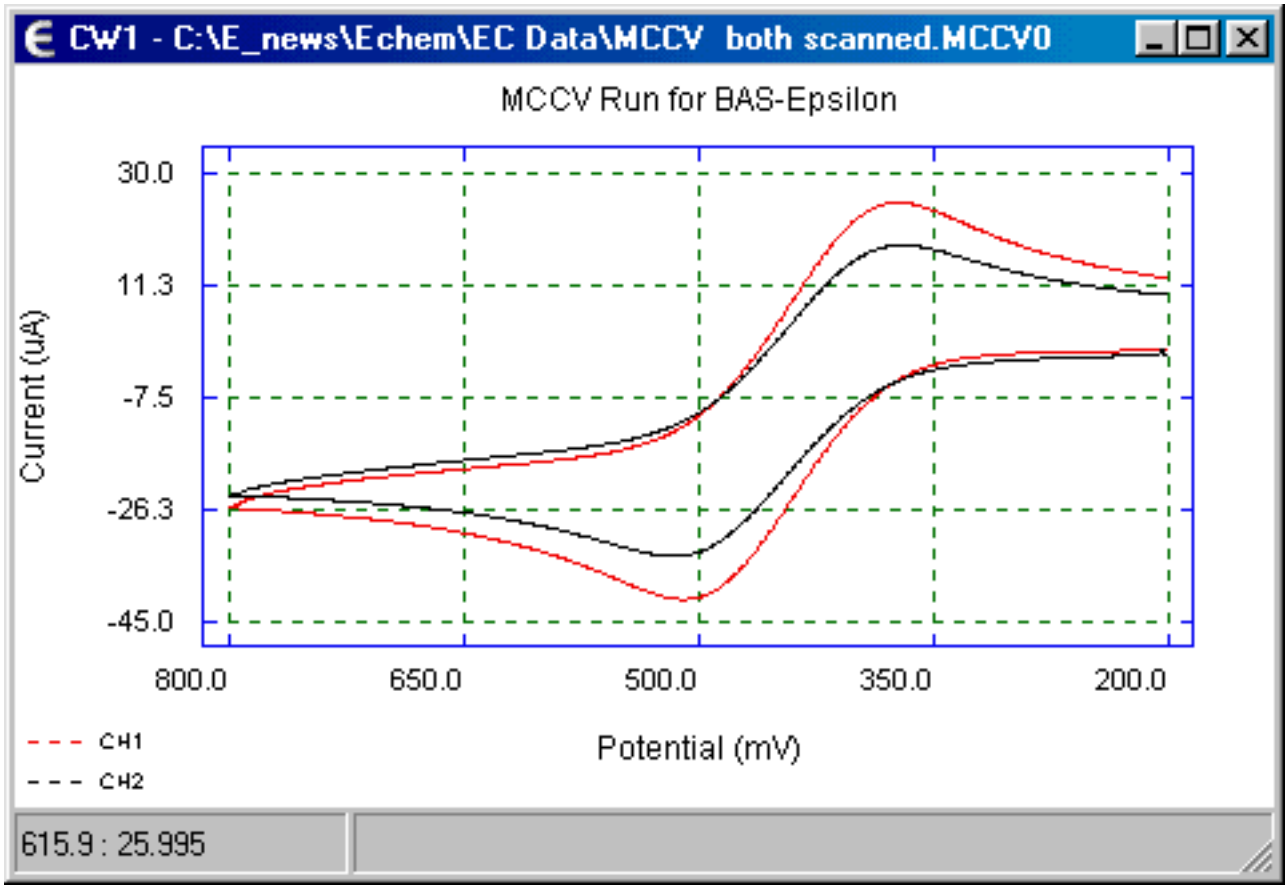

Figure 3. Typical data for a scan-scan multichannel cyclic voltammetry experiment.

The **Change Parameters** dialog box for multichannel chronoamperometry (**MCCA**) is shown in **F4**. Setting the parameters for Channel 1 is described in detail in the section on chronoamperometry.

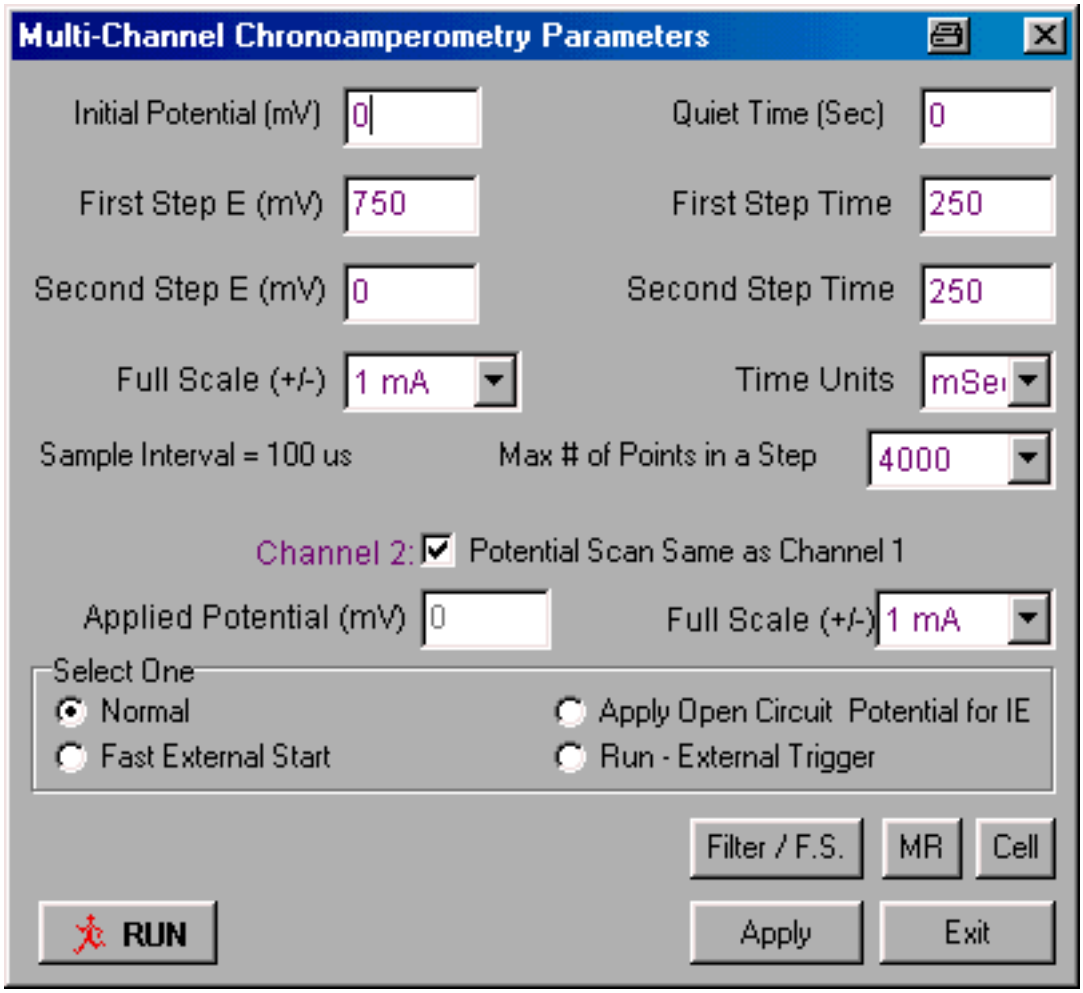

Figure 4. **Change Parameters** dialog box for multichannel chronoamperometry.

There are two options available for Channel 2:

a) Fixed potential. Channel 2 is held at a set potential value, as defined by the **Applied Potential**. The **Potential Scan** box should not be checked. Note that the current sensitivity (**Full Scale**) for Channel 2 must also be specified.

b) Potential step. The step potentials and times for Channel 2 are the same as those used for Channel 1. The **Potential Scan** box must be checked. Note that the current sensitivity (**Full Scale**) for Channel 2 must also be specified. Typical output from a "step-step" experiment is shown in **F5**.

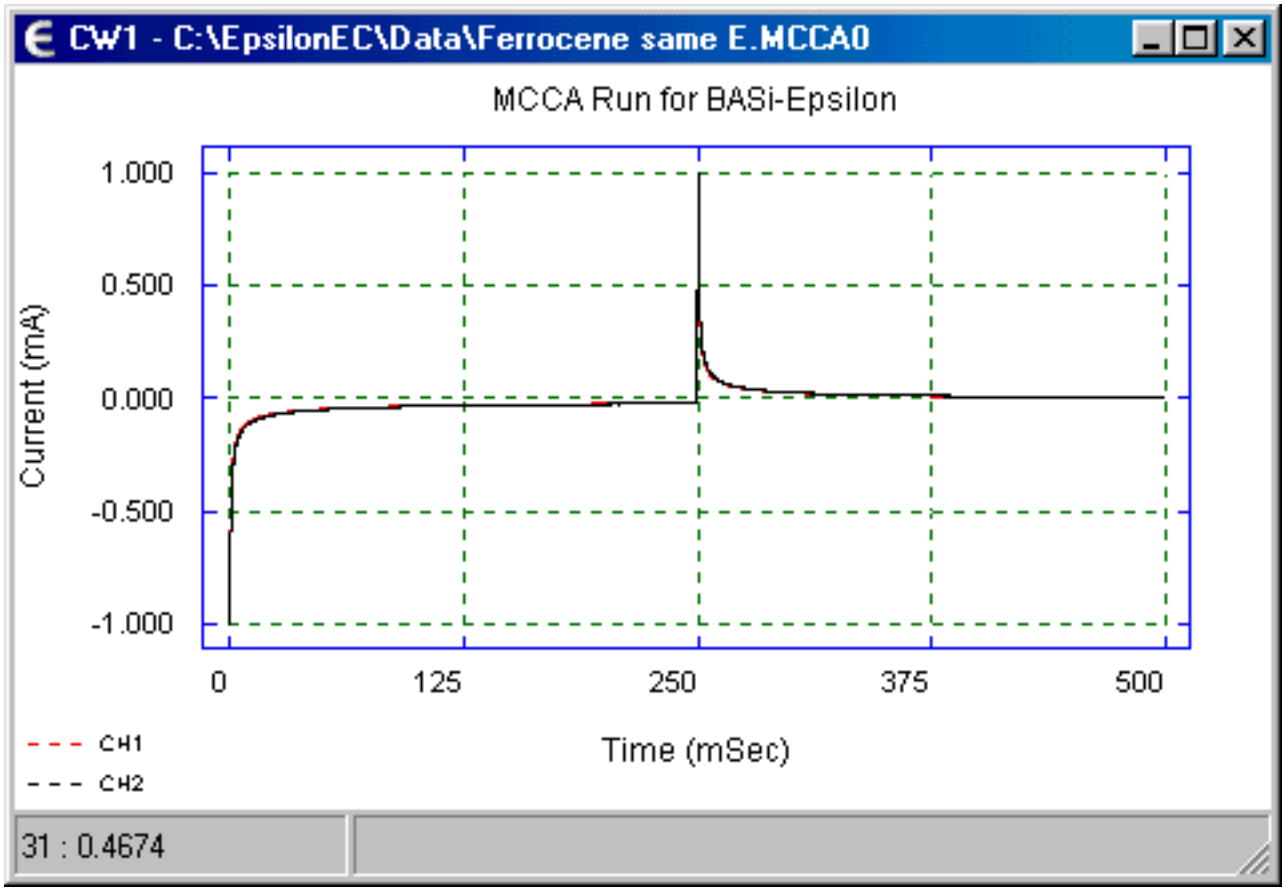

Figure 5. Typical data for a step-step multichannel chronoamperometry experiment.

The **Fast External Start** option is unique to multichannel chronoamperometry. In this option, an external trigger-in is required to start the countdown of the **Quiet Time** and the cell is at open circuit potential during the **Quiet Time** rather than at **Initial Potential**. This allows the effect of the homogeneous reaction time (i.e., the **Quiet Time**) on the electrochemical response to be determined.

The **Change Parameters** dialog box for multichannel DC amperometry (**MCA**) is shown in **F6**. Setting the parameters for Channel 1 is described in detail in the section on DC amperometry. The fixed potential for the second channel can be automatically set to the same value as the first channel (if **E Same as Channel 1** is checked), or a different value can be entered.

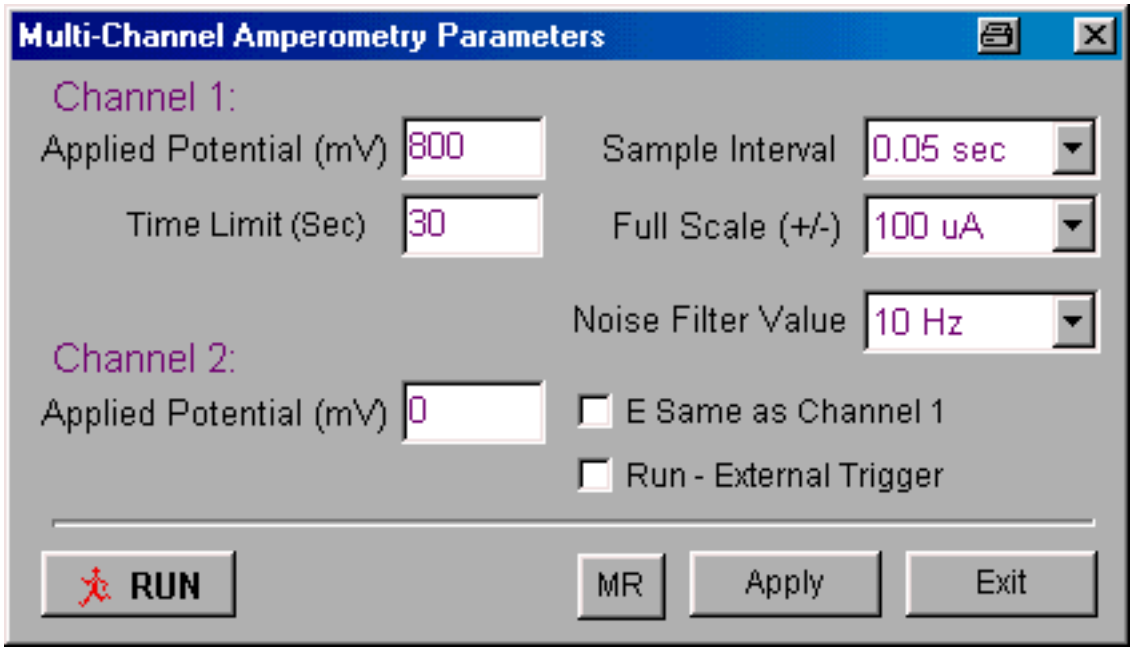

Figure 6. **Change Parameters** dialog box for multi-channel amperometry.

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Sequential Techniques

The **Sequential Techniques** function allows the user to set up a batch experiment with up to six individual experiments. The defined sequence of experiments can also be cycled, thereby allowing automated scan rate dependence and potential dependence studies. The **Sequential Techniques** is included as part of the Methods software package.

Techniques for the **Sequential Techniques** function can be defined in 2 ways. The individual experiments can be set up before opening the **Sequential Techniques** dialog box, or the experiments can be defined from within this dialog box. It should be noted that iR compensation cannot be set up from within the **Sequential Techniques** dialog box, and must be set up in the individual experiments, if required.

The **Sequential Techniques** dialog box is accessed using **New** in the **Experiment** menu. An example is shown in **F1**, with two experiments previously defined.

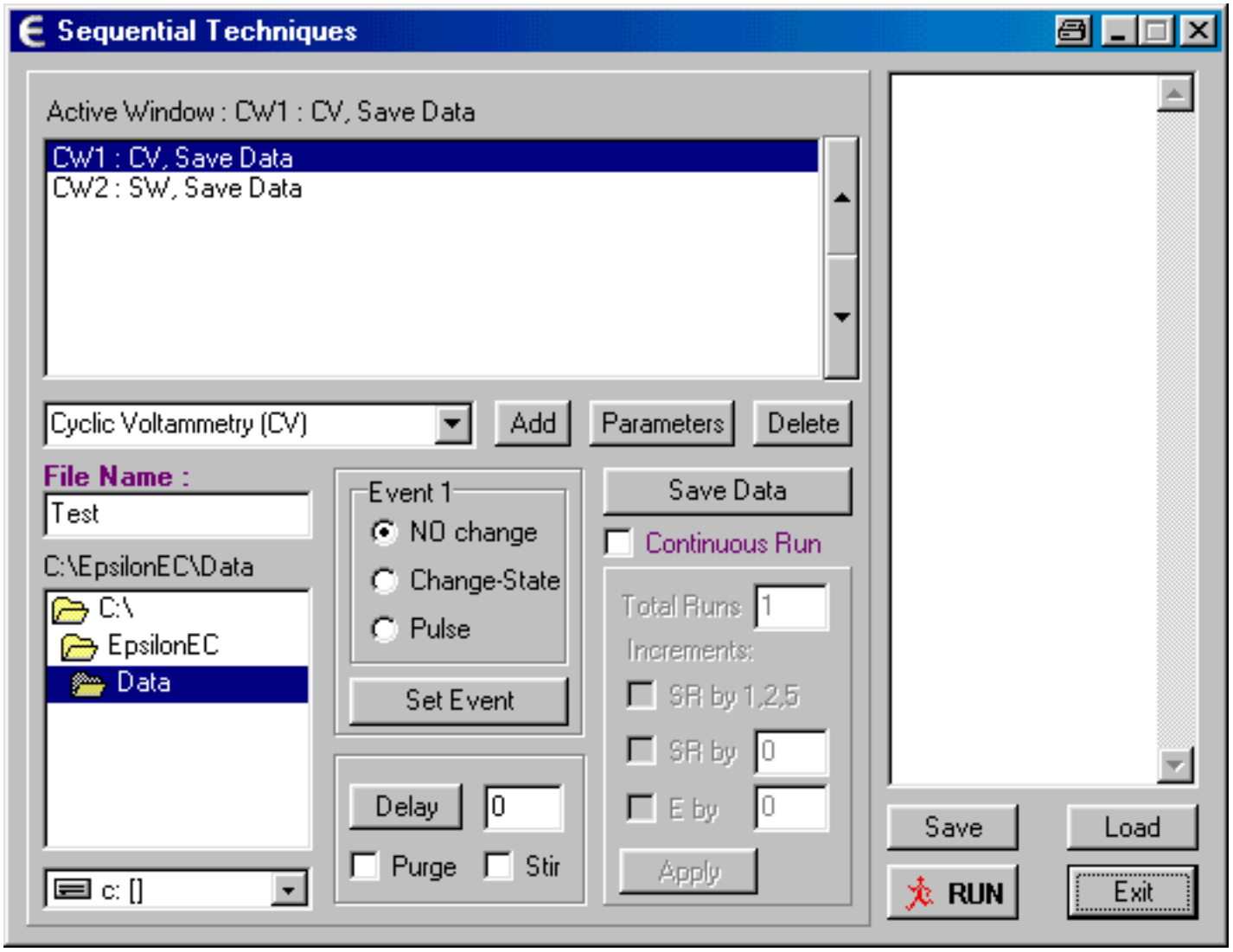

Figure 1. Sequential Techniques dialog box.

1. To define a new experiment, select the technique from the drop-down list, then click **Add**. The new experiment will be highlighted, and placed at the bottom of the list.
2. To delete an experiment, highlight the approriate experiment, then click Delete.
3. To change parameters for any of the experiments, highlight the approriate experiment, then click **Parameters**. Fill in the **Change Parameters** dialog box using the standard protocol.
4. To change the order of the experiments, highlight the experiment to be moved, and use the up or down arrows on the right side of the list box as required.
5. The default condition is that the data from each experiment is saved at the end of each experiment. Automatic data saving for the highlighted experiment can be switched on and off using the **Save Data** button.
6. The following can be programmed to occur at the end of any experiment - (Timed) **Event 1**, **Delay** (up to 3600s), **Purge** on and **Stir** on (during the **Delay** time). Highlight the required experiment, and click the required functions (**F2**). For experiments with **Sample Intervals** greater than 1 sec (e.g., **DC Potential Amperometry**, **Controlled Potential Electrolysis**), the **Delay** after the experiment MUST be at least as long as the **Sample Interval** in order for **Sequential Techniques** to run.

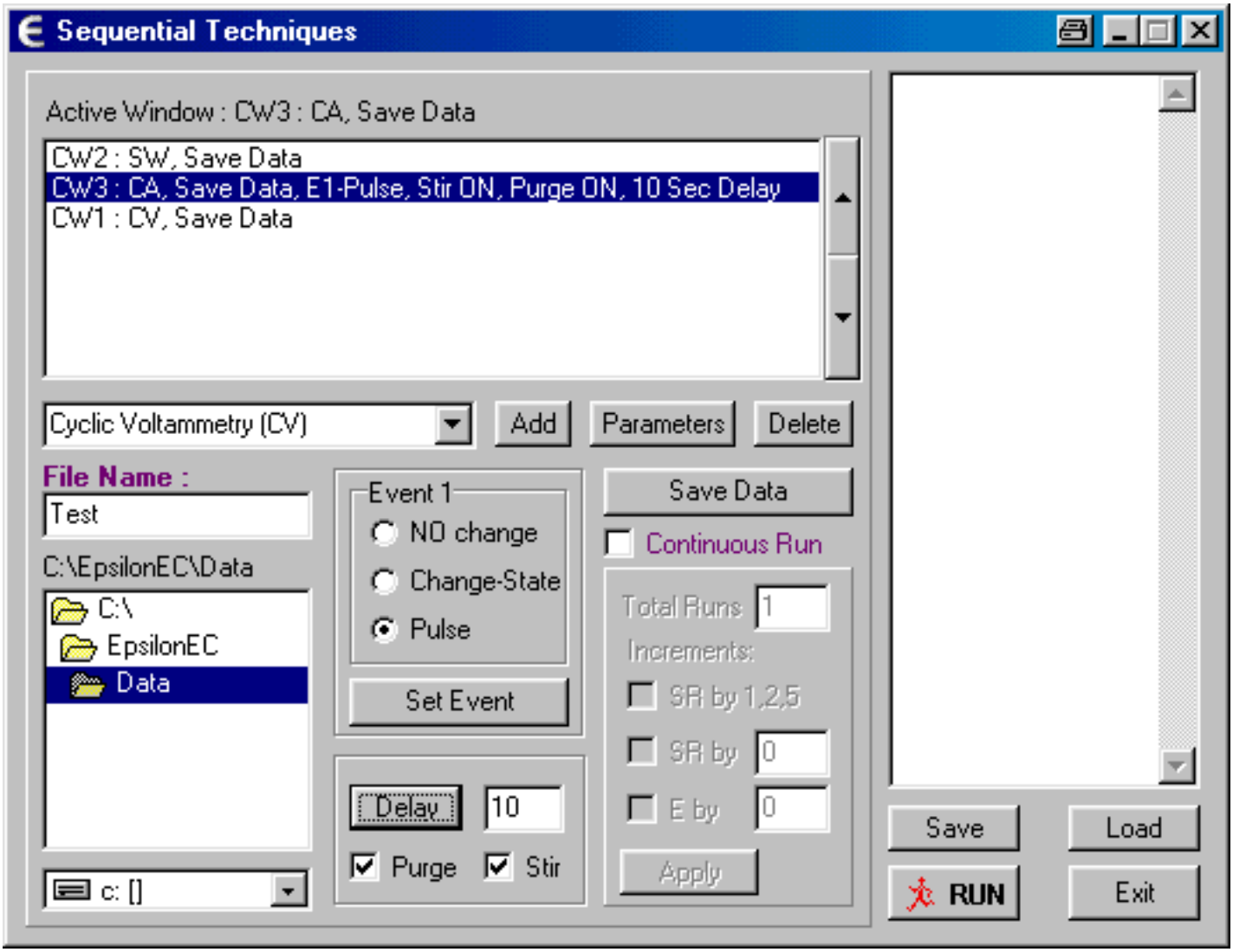

Figure 2. Post-experiment operations

7. Multiple cycles of the defined sequence of experiments can be programmed by checking **Continuous Run**. The number of **Total Runs** (up to 9999) must then be defined. In addition, the **Scan Rate** (for **CV** and **LSV** experiments) and the applied potential (for constant potential experiments **CPE** and **DCPA**) can be incremented from one cycle to the next, allowing for scan rate dependence and potential dependence studies. **Scan Rate** can be varied in a 1, 2, 5 ratio (e.g., 10, 20, 50, 100, 200, 500, etc.) or as a user-defined increment (e.g., 50 mV/sec). The applied potential is varied using a user-defined increment (e.g., 50 mV).
8. Once the sequence has been programmed, click **Run** to start the sequence. **Sequential Techniques** can be **Saved** and **Loaded** (however, **Sequential Techniques Method** files created with version 1.40 software cannot be loaded using later software versions, although the individual data files can still be loaded).

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iR Compensation

In any potentiostatic experiment, it is assumed that the potential drop across the interfacial region at the working electrode is the same as the potential applied between the reference and working electrode. However, this is not true, since there is some iR drop between these two electrodes due to solution resistance. This resistance can be lowered by addition of supporting electrolyte, and in many cases does not need to be considered. However, there are instances where it is detrimental to the experiment; in these cases, it can be compensated for electronically. This is achieved on the epsilon using positive feedback iR compensation, which is set up using the **iR Compensation Test** dialog box, which is accessed using the **IR-COMP** button in **Change Parameters** dialog boxes.

One problem with positive feedback iR compensation is determining the amount of compensation to use, since too much feedback can drive the electronics into oscillation, which can have a deleterious effect on both the electronics and the electrodes. The automatic iR compensation option on the epsilon prevents this by first measuring the uncompensated solution resistance, followed by incremental compensation and circuit stability testing. These features are described below, together with a procedure for setting up iR compensation.

Measurement of Uncompensated Resistance

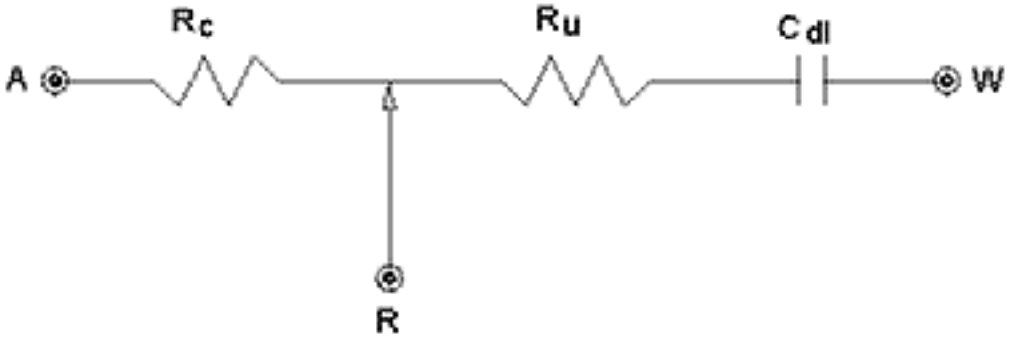

Figure 1. Model of the electrochemical cell used for iR compensation.

In this measurement, the electrochemical cell is considered to be electronically equivalent to an RC circuit (**F1**); that is, the uncompensated resistance (R_u) is in series with the double-layer capacitance (C_{dl}). Since a faradaic impedance is not considered as part of this model, the **Test potential** must be at a value at which no faradaic process occurs. A potential step is applied at this potential and the current is sampled at set points after the step is applied. The current decays exponentially (**F2**), and the initial current (I_o) is calculated by extrapolating back to zero time. Since $E = I_o R_u$, R_u can be calculated from

this measurement. To reduce any error, this measurement is performed multiple times, and the results averaged.

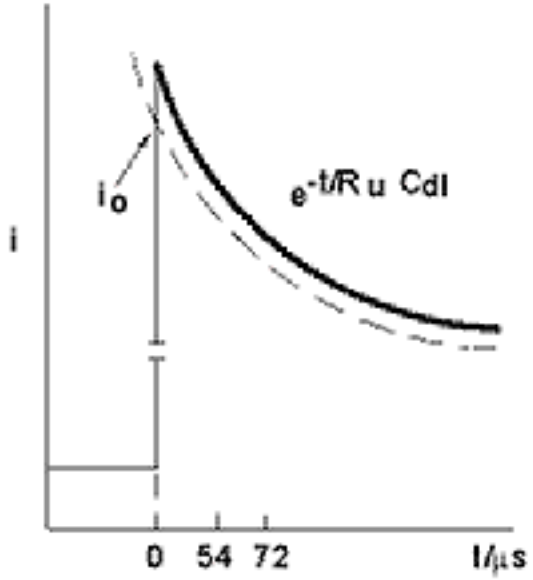

Figure 2. Exponential decay of the current response of the above RC series circuit following the applied potential step.

Compensation and Circuit Stability Testing

Compensation is achieved by positive feedback into the potentiostat. However, problems due to circuit instability can arise, even when the degree of compensation is significantly less than 100%. Therefore, the amount of positive feedback is increased incrementally, and the stability of the circuit is tested after each increment. The amount of positive feedback is increased until the (user-specified) % value is obtained (default = 100%), or the system does not pass the stability test.

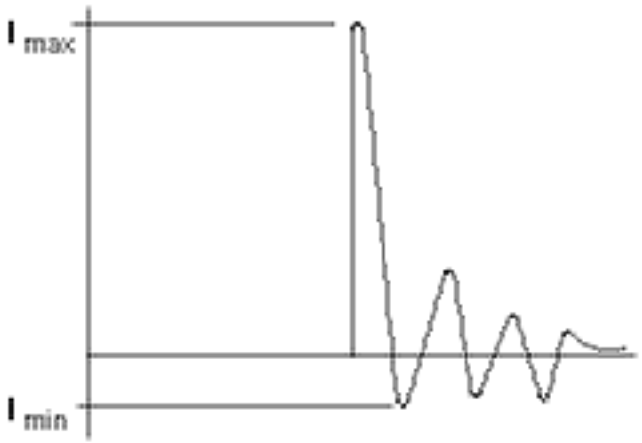

Figure 3. Current response for the stability test showing the "ringing" effect.

In the stability test, the current following a potential step at the **Test potential** is again measured. As the percent compensation increases, the current response at first exhibits a "ringing effect" following exponential decay, which is a precursor to oscillation (**F3**). The degree of pre-oscillation ringing can quantitated by a term defined as **overshoot**, which the ratio of a minimum (net negative) current value (I_{min}) to a maximum current value (I_{max}) expressed as a percentage: that is, **overshoot** = (I_{min}/I_{max}) x 100. The maximum allowable **Percentage overshoot** is defined by the user (default = 20%). If the **Percentage overshoot** value measured by the stability test is less than the maximum allowable value, then compensation is increased. If it is greater, and the desired level of compensation has not yet been achieved, a capacitor is inserted between the reference and auxiliary electrodes to stabilize the circuit, and the testing is continued until the desired level of compensation is achieved or the **Percentage overshoot** value is exceeded (if this occurs, the amount of compensation to be used in the experiment is slightly decreased from this value). One way to increase the level of compensation is to increase the **Percentage overshoot** percentage. It is usually safe to go up to 40%.

If the desired compensation cannot be obtained using automatic iR Compensation, then a user-specified compensation resistance can be applied. If this option is used, then a stabilizing capacitor may also need to be selected manually.

Setting up iR Compensation

iR compensation is set up using the **IR Compensation Test** dialog box which is accessed using the **IR-COMP** button in the **Change Parameters** dialog boxes.

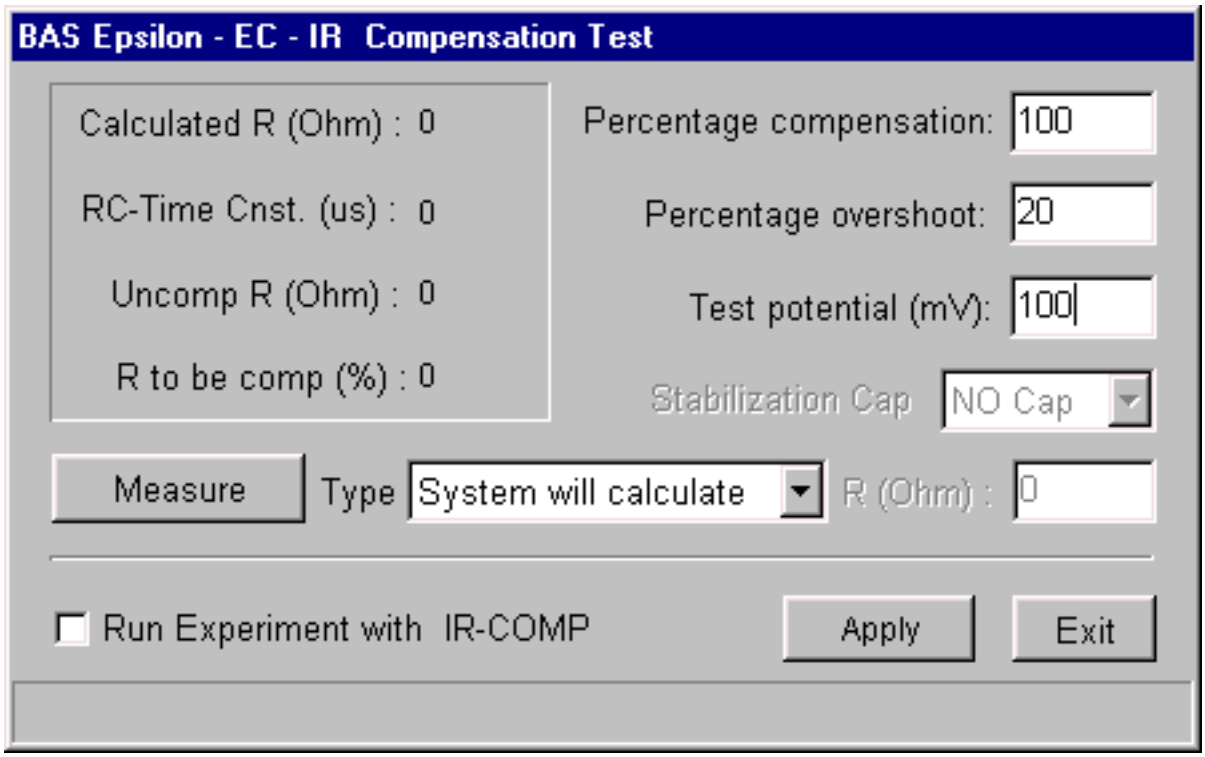

Figure 4. IR Compensation Test dialog box.

1. The simplest method for using iR compensation is to use the manual option (**Type** = **User assign value**). Enter the required resistance for the **R (ohm)**, and make sure that the **Run Experiment with IR-COMP** check box is checked. A **Stabilization Cap**acitor may be required for electronic stability (two are available - **Large Cap** and **Small Cap**). However, it is generally better to use the automatic option (**Type** = **System will calculate**), since using too high a resistance can have a deleterious effect on the electrode, the electronics, and the experimental data.
2. If the **System will calculate** (recommended) option is to be used, enter a value for the **Test potential (mV)** (note that this should be at a value at which there is no faradaic reaction). The size of the **Stabilization Cap**acitor is selected by the software.
3. Click the **Measure** button to start the test. The following results are listed:
    - The uncompensated resistance (**Calculated R**)
    - The RC- time constant of the cell (**RC-Time Cnst.**)
    - Uncompensated resistance remaining after compensation (**Uncomp R**)
    - Percentage of the uncompensated resistance to be used in positive feedback (**R to be comp.**)
4. Once the **iR Compensation Test** has been completed, make sure that **Run Experiment with IR-COMP** box is checked, and then click **Apply** before exiting the dialog box.

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Multi-Run

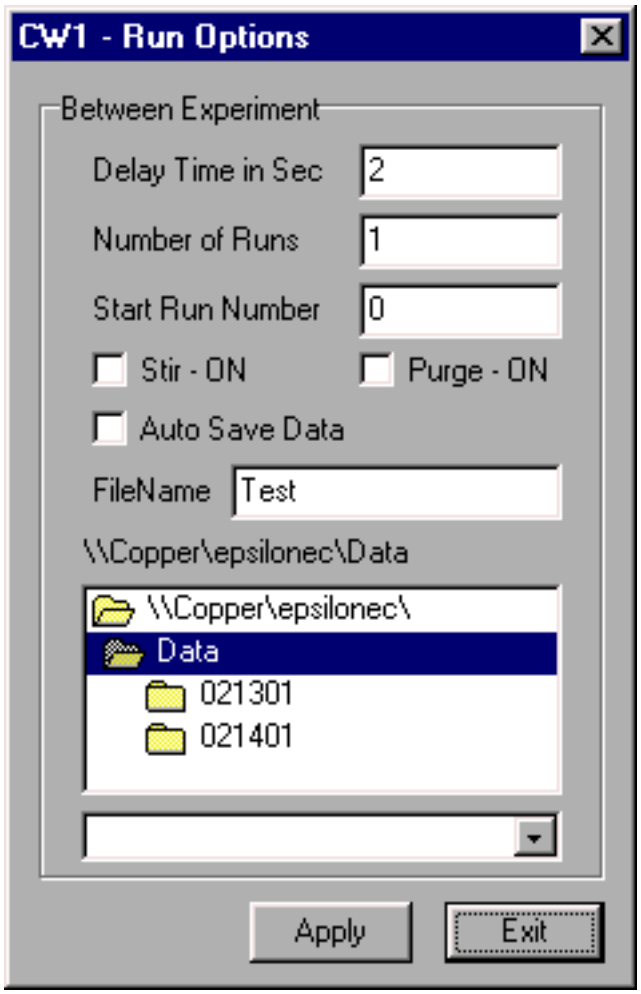

Figure 1. Multi-Run dialog box.

The **Multi-Run** option is available for all experiments other than galvanostatic and Open Circuit Potential vs. Time, and allows the user to program a series of identical experiments on the same cell to be run without user intervention. The important points are as follows:

1. **Auto Save Data** must be checked.
2. Up to 9999 sequential experiments can be run, as specified in **Number of Runs**. The experimental data are saved automatically using the filenames ABCDExxx.bin, where ABCDE is the user-defined **File Name**, and xxx is a number starting at the value defined in **Start Run Number**, and can take any value up to 9999.
3. The time between experiments is defined by the user through **Delay Time in Sec** (2-3600 s). Purging and/or stirring will be activated between the experiments if the **Purge - ON** and/or **Stir - ON** boxes are checked.

If **Auto Save Data** is checked, data from single runs started manually will also be automatically saved.

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Other Experimental Parameters

There are a number of experimental parameters required for epsilon which are designed to optimize instrument control and experimental data acquisition. However, in most instances, the default values set by the software for these parameters are the optimum values, and typically no user input is required. Indeed, if you are not sure what effect varying a given parameter will have on the experiment, it is best not to change it from the default value!

These parameters are as follows:

In all the dialog boxes described below, the **Apply** button must be clicked to activate any of the changes entered by the user. If the dialog box is exited without clicking **Apply**, the changes will not be applied.

Setup / Manual Settings (I/O)

The **Setup / Manual Settings (I/O)** dialog box is accessed from the **Experiment** menu (**F1**).

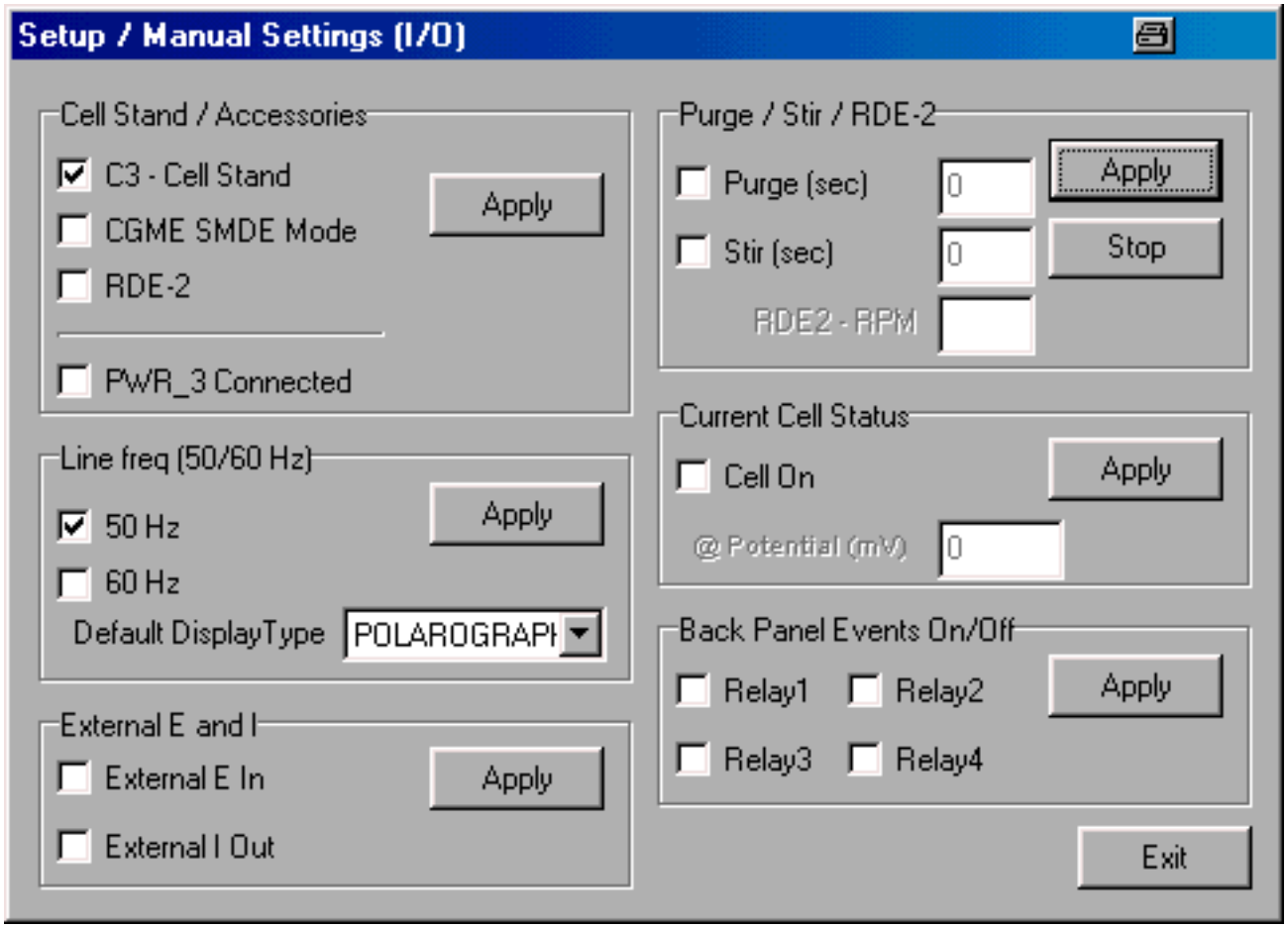


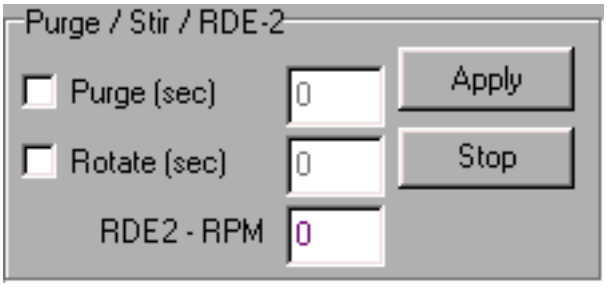
Figure 1. Manual Settings dialog box.

Cell Stand / Accessories

The correct option must be selected to control the various Cell Stand operations from the software (i.e., purge and stir for the C3; purge, stir, and knock/dispense for the CGME; and purge and rotate for the RDE-2). Before the Cell Stand can be selected, the Cell Stand must be switched on and connected to the epsilon as described under Interfacing BASi Accessories with the epsilon. Similarly, the PWR-3 must be connected to the **ACCESSORIES** port of the epsilon before it can be selected.

Purge / Stir

The purging and stirring/rotation functions of BASi Cell Stands can be switched on and off from this dialog box. If one of these functions is enabled, the time for which this function is active must also be entered. The **Stop** button is used to stop this function before the specified time. The appropriate Cell Stand from **Cell Stand / Accessories** must be selected in order to ensure proper activation of these functions. Note that selection of **RDE-2 Cell Stand / Accessories** changes **Stir** to **Rotate** and activates the **RDE2 - RPM** option.



Line freq (50/60 Hz)

This selects the frequency of the line supply, which is used to calculate the time required for one of the current sampling options (**1 Line Period**) in pulse and square wave experiments. The selected value is stored in the .ini file. Measuring the current over one line cycle is important for noise minimization.

Default Display Type

This selects the default Display Type - Polarographic or IUPAC.

Current Cell Status

This option specifies whether the electrochemical cell is actively connected (**Cell On** is checked) to the instrument at that moment. The default condition is that it is disconnected (**Cell On** is *not* checked). This is the safest option, since manipulation of the cell lead connections while the cell is connected can cause harm to the user and severe damage to the instrument. If **Cell On** is checked, the potential applied to the cell must also be specified (**@ Potential (mV)**). The **Current Cell Status** will be maintained until an experiment is run. During an experiment, the cell is obviously connected; the cell connection at the end of the experiment is defined by the **End Of Experiment Cell Condition**.

External E and I

These activate the back-panel analog inputs and outputs.

Back Panel Events On/Off

These activate the back-panel Timed Event relays.

Cell

The **Cell** dialog box is accessed using the **Cell** button in the **Change Parameters** dialog box (**F2**).

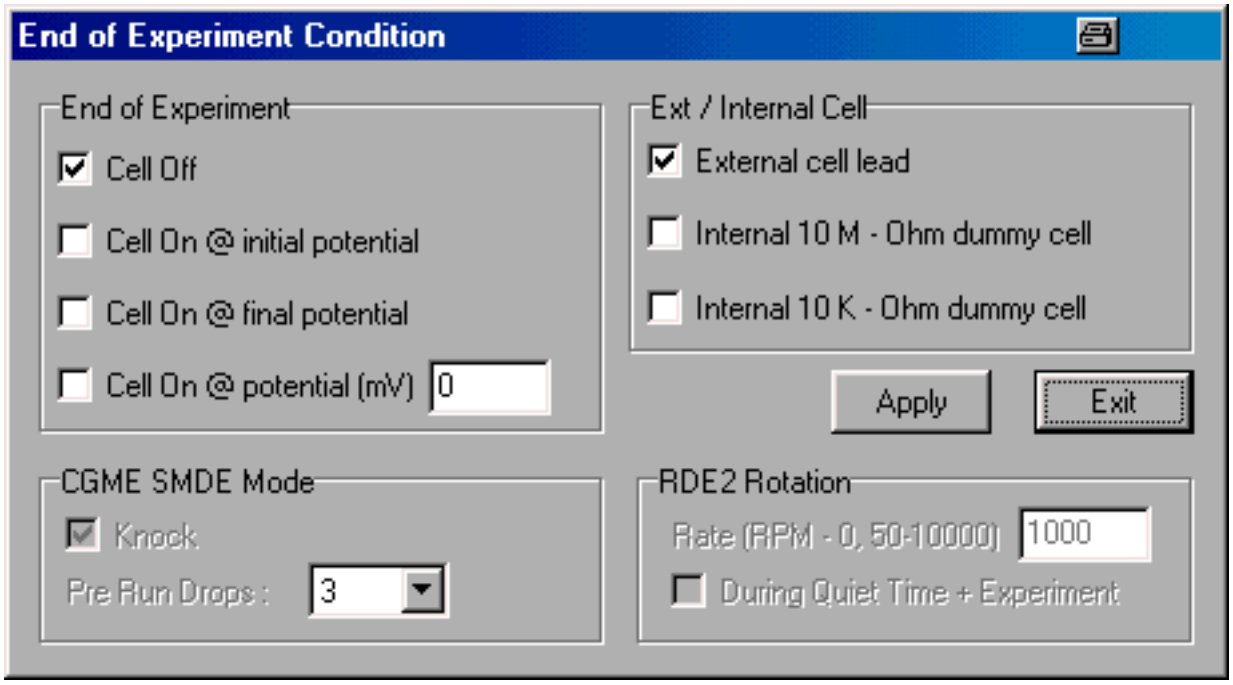


Figure 2. Cell dialog box.

End of Experiment

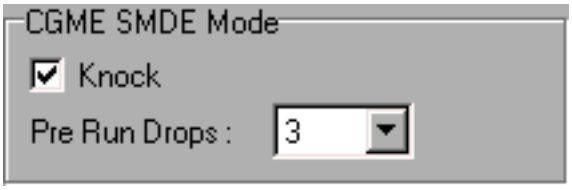
This option specifies whether the electrochemical cell remains actively connected at the end of an experiment, and, if so, at what potential. The default condition is **Cell Off** (i.e., the electrochemical is not actively connected). If the cell is to remain actively connected, the applied potential can be the initial potential (**Cell ON @ initial potential**) or the final potential (**Cell ON @ final potential**) of the experiment specified in the associated **Change Parameters** dialog box, or at a user-specified potential (**Cell On @ Potential (mV)**). **HOWEVER, CAUTION SHOULD BE USED IF ANY OF THE CELL ON OPTIONS ARE USED, SINCE CONNECTING OR DISCONNECTING THE ELECTRODES WHEN THE CELL IS ON CAN RESULT IN DAMAGE TO THE POTENTIOSTAT, THE CELL, AND/OR THE USER!**

Ext / Internal Cell

This function allows the user to select between an external cell connection (required for running an experiment on an electrochemical cell) or an internal dummy cell (for troubleshooting). Two choices are available for the internal dummy cell - a 10 KOhm or a 10 MOhm resistor. Note that the internal dummy cell is NOT available for Controlled Potential Electrolysis (CPE).

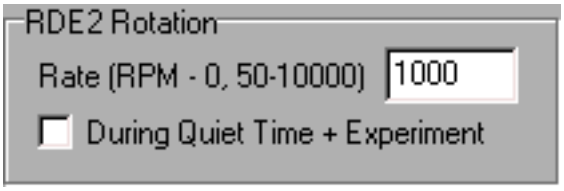
CGME SMDE Mode

This option is activated only when **CGME SMDE Mode** has been activated in the **Setup / Manual Settings (I/O)** dialog box, and is required when using the SMDE mode of the BASi Controlled Growth Mercury Electrode (CGME) for polarography and stripping experiments. It can also be used with voltammetry experiments using a single mercury drop for the entire experiment. Both the number of mercury drops before the experiment (**Pre Run Drops**) and the drop knock operation (**Knock**) can be specified in this dialog box. For most potentiostatic experiments, the **Pre Run Drops** are formed with the cell on at the **Initial Potential** (for stripping experiment, they are formed at the **Deposition Potential**). Note that the **Pre Run Drops** option is NOT available for Controlled Potential Electrolysis (CPE).



RDE2 Rotation

This option is activated only when **RDE-2** has been activated in the **Setup / Manual Settings (I/O)** dialog box. It is used to specify the **Rotation Rate** used during the experiment, and also allows the option of rotating the electrode during the **Quiet Time**.



Filter

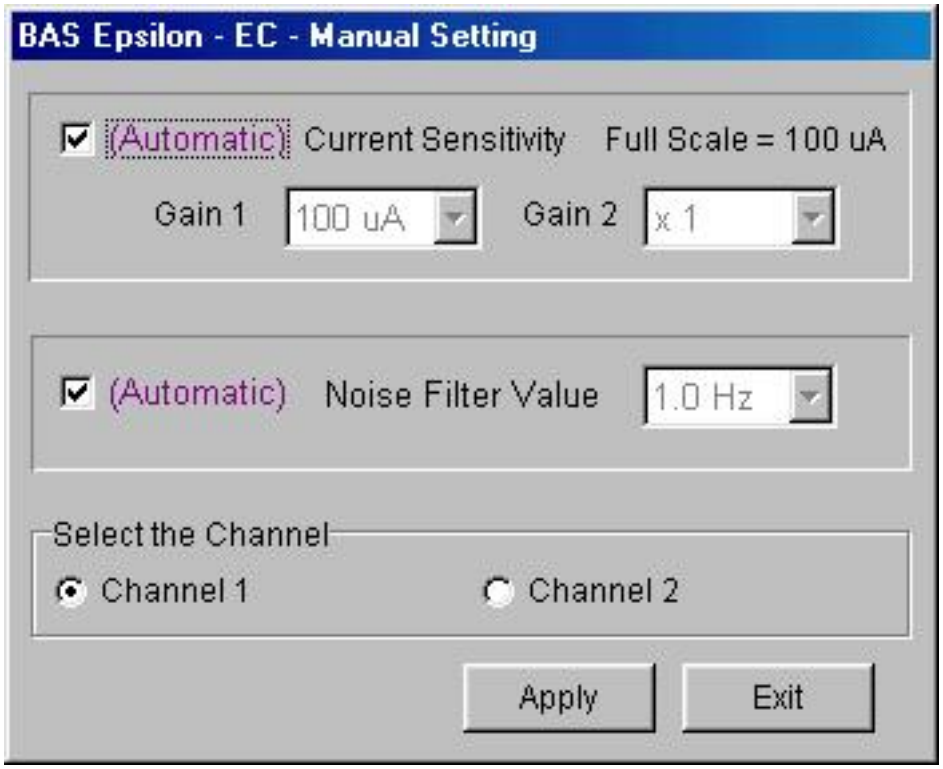


Figure 3. Filter / F.S. dialog box.

The **Filter/Full Scale** dialog box is accessed through the **Change Parameters** dialog boxes. Note that the channel selection function is enabled only for techniques that require the optional bipotentiostat board (i.e., **MCCV** and **MCA**).

Current Sensitivity

There are two gain stages for the current-to-voltage converter which control the current **Full Scale**. The first stage has values in decades from 100 nA to 10 mA, whereas the second stage is a multiplier with values of 1, 0.1, and 0.01; that is, the lowest **Full Scale** is 1 nA. There is more than one combination for intermediate values of the **Full Scale**, and the default values selected by the software are suitable for most applications. Note that the **Automatic** box must be unchecked before a different value can be selected.

Noise Filter Value	Analog filtering is used to remove noise from the experimental data. The filtering in the epsilon consists of a two-pole Bessel filter. The amount of filtering (the cut-off frequency of the filter) must be selected with care, since overfiltering can distort the experimental data. The correct filter frequency depends on the time scale of the experiment, and is selected by the software to be at least 10 time larger than the time scale of the electrochemical experiment. Although an alternative filter can be selected manually, it is generally best to use the default filter. Note that the **Automatic** box must be unchecked before a different value can be selected.

Stabilizing Capacitor

There are some operations of the epsilon that can cause some electronic instability, particularly controlled potential electrolysis experiments and iR compensation. A stabilizing capacitor is therefore used during these operations in order to provide stability. The default selections are generally optimum for virtually all conditions, although the selection can be changed.

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Notes

When an epsilon data file is saved, parameters such as the potential range, the scan rate, the current sensitivity, etc. are automatically saved along with the experimental data couples. A number of other parameters that describe the electrochemical cell (e.g., solvent, electrodes, etc.) can also be specified by the user using the **Notes** function (in both the **Experiment** menu and the pop-up menu), and saved along with the data and other experimental parameters.

The **Notes** dialog box is shown in **F1**, along with typical entries.

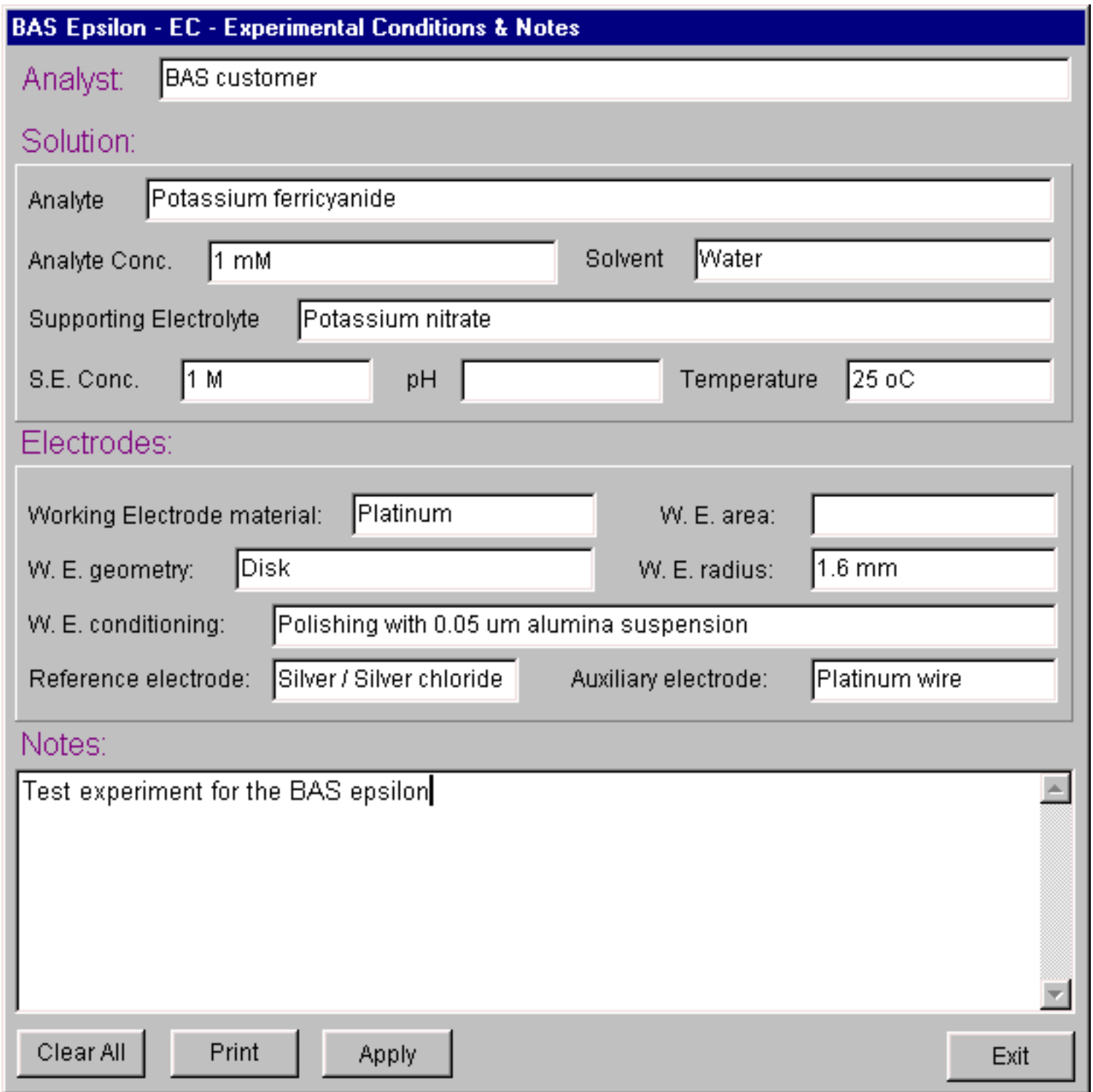

Figure 1. Notes dialog box.

The **Notes** can also be printed, either with the experimental data (**Print - Both (Graph and Notes)**) or on their own (**Print - Notes Only**).

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Storing Data in a Binary Format

Figure 1. Save file dialog box.

Once an experiment has been run, the data can be saved in a proprietary binary format. Clicking **Save** in the **File** menu or in the pop-up menu (or using the **F4** key) will generate a standard Windows file dialog box. Note that the extension depends upon the experimental technique (e.g., CV filenames have a .cv0 extension).

In addition to the data points, the parameters and **Notes** are also saved, as well as other relevant settings (e.g., filter values).

The **Auto Save Data** option in the **Multi-Run (MR)** dialog box can also be used to automatically save data from single runs started manually.

If the current active data file has not been saved (or has been modified) when the user exits the program, a "Save Data?" message will appear to prevent accidental loss of data.

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Converting Data Files to a Text Format

It is sometimes more convenient to save data in a text format (e.g., for exporting to other programs such as DigiSim® and Excel). The **Convert to Text File** function (**F1**) converts saved binary files to various different text formats.

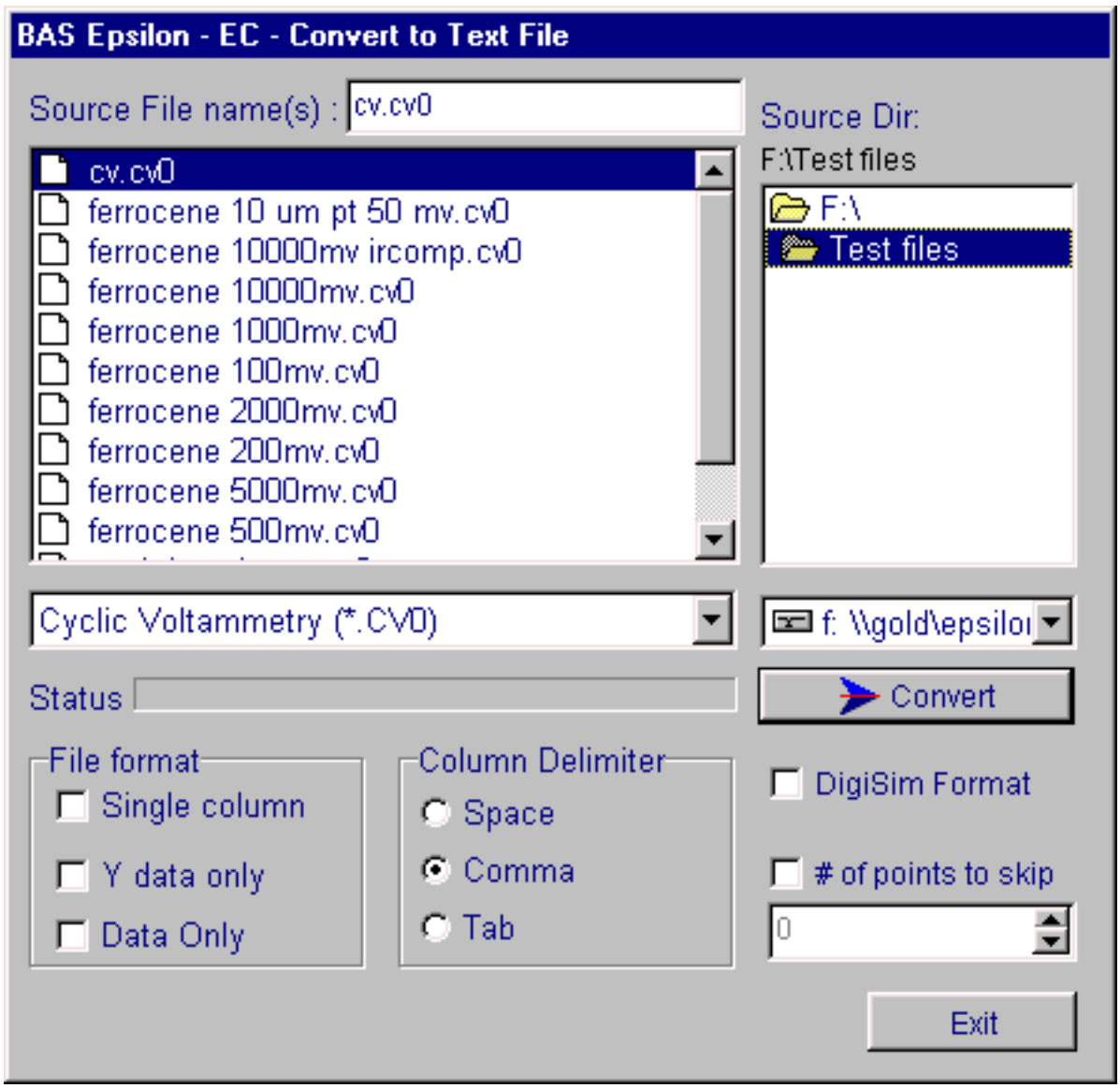

Figure 1. Convert to Text File dialog box.

1. **File format**
    a. If **Single column** is specified, the x and y data points (e.g., potential and current) will be separated by a carriage return.
    b. If **Y data only** is specified, then only y data points (e.g., current) will be contained in the text file.
    c. If **Data Only** is selected, the header containing the experimental parameters and **Notes**

will be omitted.

2. **Column Delimiter** - if both x and y data are contained in the text file, they can be separated by a **Space**, a **Comma**, or a **Tab**.
3. **DigiSim Format** - the format of the text file will be identical to that of the DigiSim .use format. Note that the extension must be changed from .dig to .use before the file can be imported into DigiSim. It should also be noted that conversion to the .use format is only allowed for cyclic voltammetry experiment files with an integral number of potential cycles (i.e., there are an even number of segments and the **Final Potential** is equal to **Switching Potential 2**). This is to ensure that the potential sweep for that experiment is consistent with the sweeps allowed by DigiSim. If a selected file does not obey this criterion, an error message will be displayed.
4. Data points can be omitted from the text file by specifying **# of points to skip** (0 = no points skipped, 1 = every other data point skipped, etc.).
5. The file(s) to be converted are identified using the **Source Dir**ectory, the **Source File name(s)**, and the technique/suffix. Click the file name(s), and then click the **Convert** button.
6. Square Wave text files have 4 columns: Potential, Difference Current, Forward Current, Reverse Current.

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Print

There are 3 options for printing experimental data.

1. **Both (Graph and Notes) -** The graph (as displayed in the active experiment window) is printed, along with any of the user's **Notes** associated with this data
2. **Graph only** - Only the graph is printed
3. **Save to PDF – Note! Acrobat Read must be installed on the computer in order for this feature to work.** Selection of this option will open Acrobat Reader, create a pdf of the display and save the file in the same folder as the data file. The name of the newly created pdf file is "file name"_extension.pdf. For example, the pdf file of ferrocene.CV0 will be ferrocene_CV0.pdf.

Note that drivers for network printers must be installed locally otherwise a system error may occur.

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Data Display Options

The options available for the graphical display of the experimental data are listed below. These are contained in the **Graph-Display** menu, and some are also available in the pop-up menu.

Zoom

When data is displayed in an experimental window (either at the end of an experiment or after loading), the axis limits are defined by the data points, as shown in **F1**.

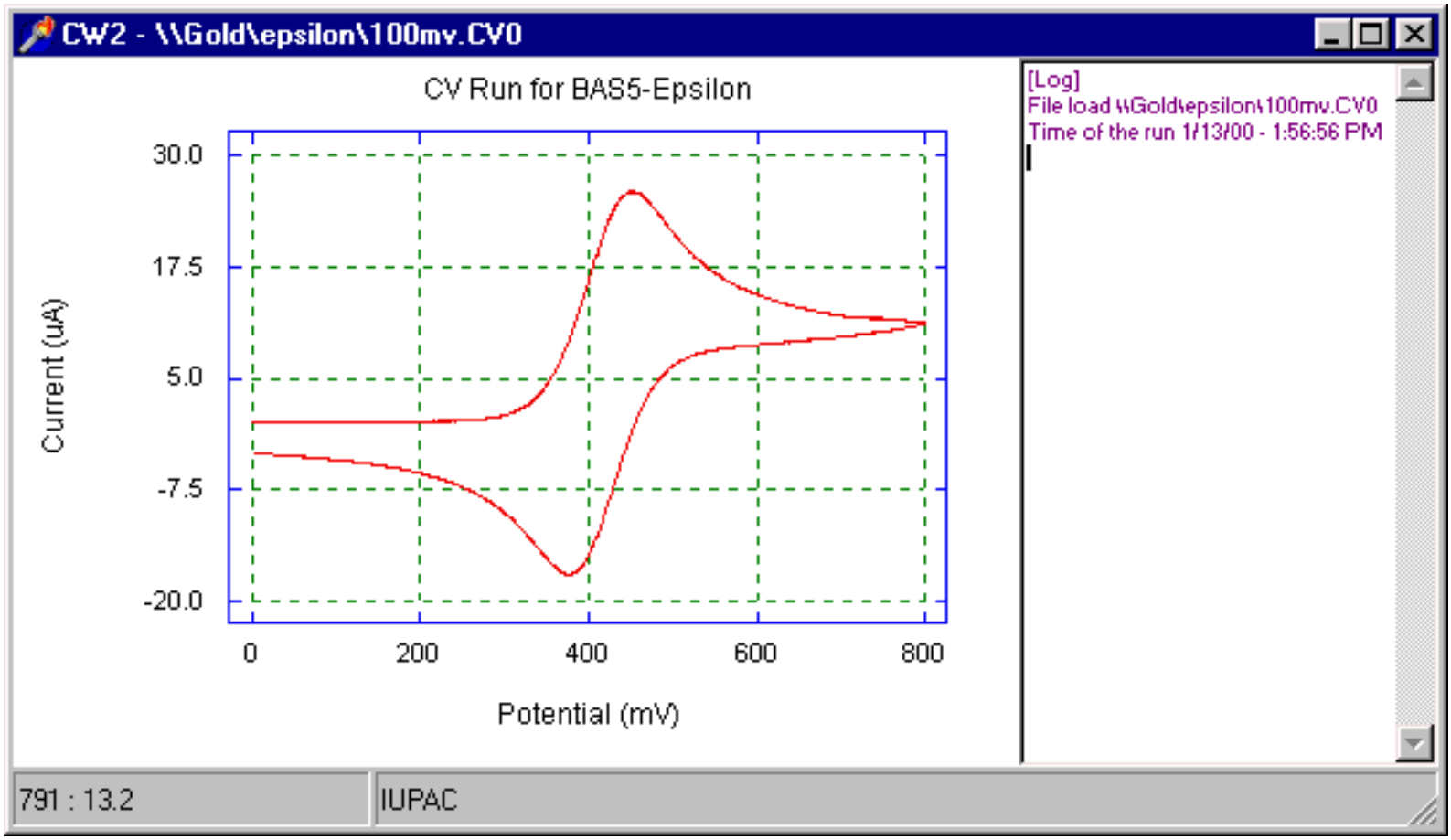

Figure 1. Default experimental window.

Three zoom options are available - **Zoom Out**, **Manual Zoom**, and mouse zoom. **Zoom Out** will increase the y axis to the values defined by **Full Scale** in the **Change Parameters** dialog box (**F2**).

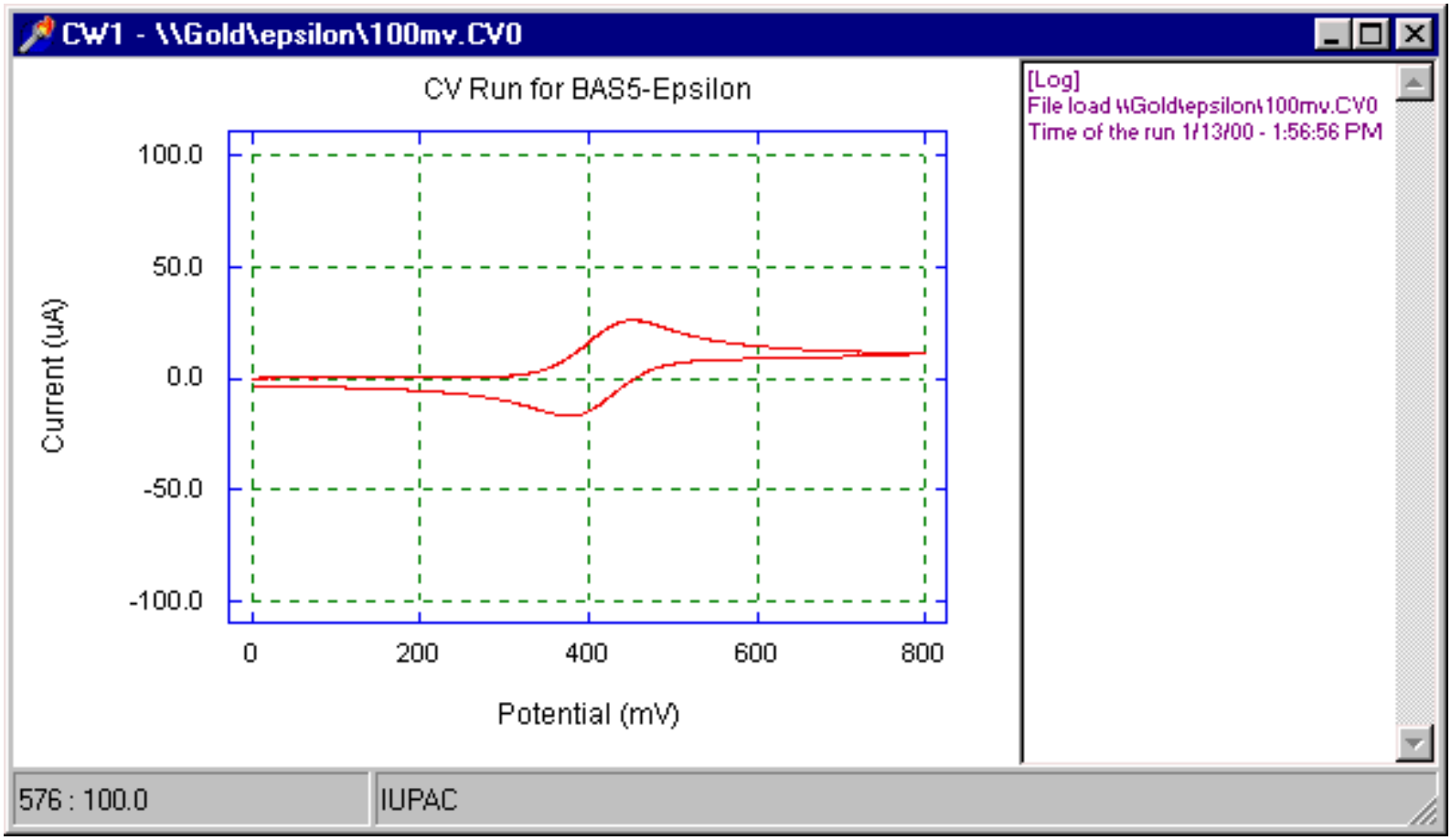

Figure 2. Zoom Out.

Mouse zoom allows the user to define an area of the window using the mouse - click the mouse with the cursor at one corner and drag the cursor to the opposite corner while holding down the mouse button (**F3**).

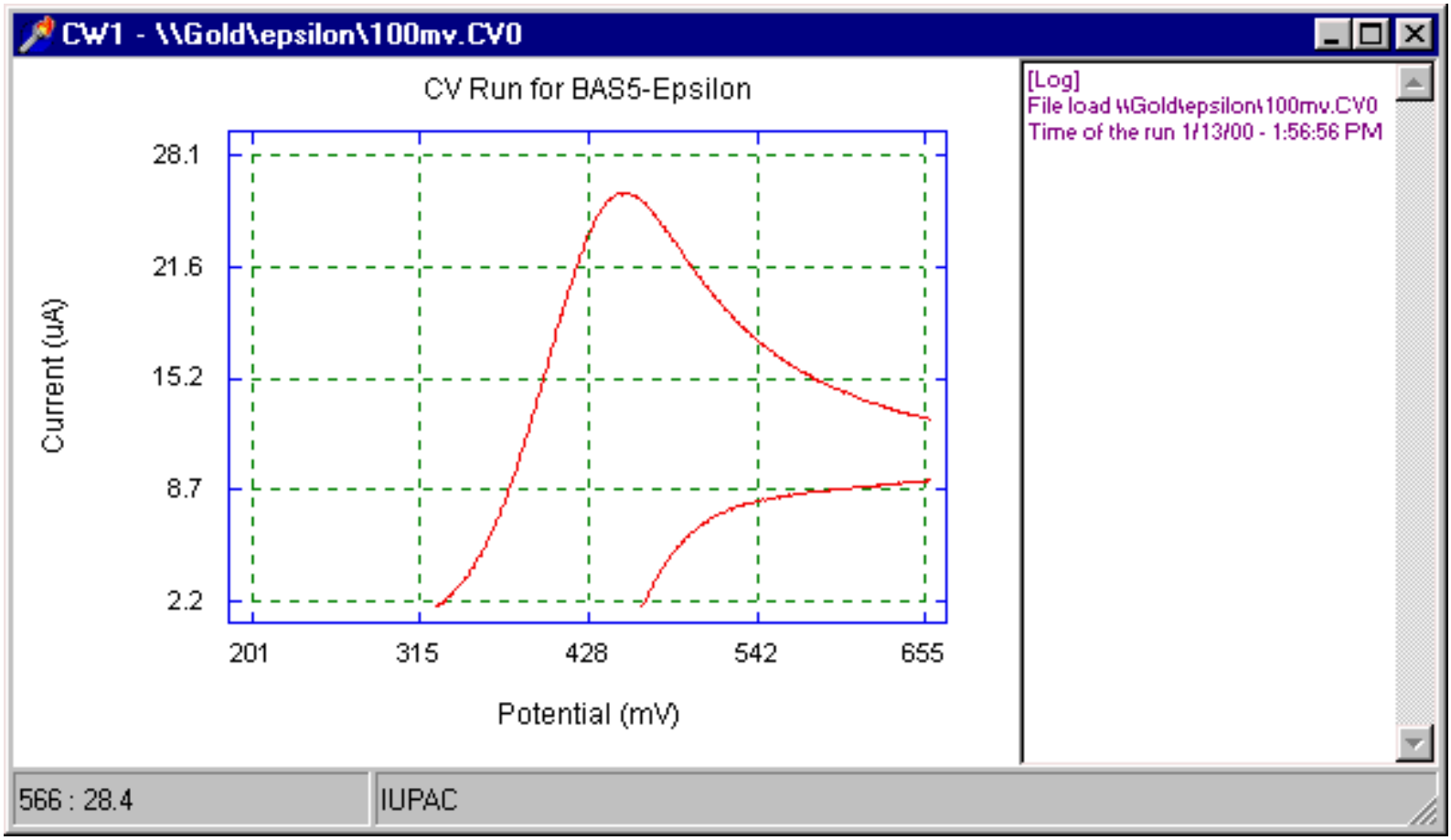

Figure 3. Mouse zoom.

Manual Zoom allows the user to specify the minimum and maximum x and y values of the section of the plot of interest (**F4**).

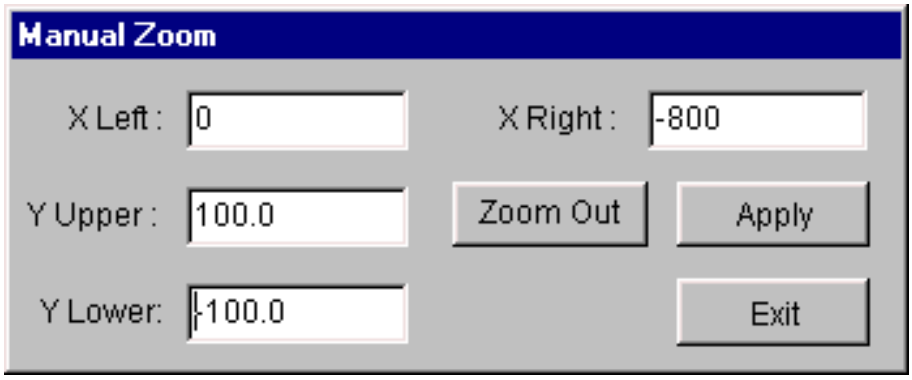

Figure 4. Manual Zoom dialog box.

The default axis settings can be restored by **Auto Zoom** (this function is also available in the pop-up menu).

Smooth Data

Digital smoothing routines are used to remove unwanted noise from the electrochemical signal after the experimental run, thereby improving the signal-to-noise ratio. However, as with analog filtering, care must be taken to avoid biasing the electrochemical signal.

The default smoothing routine on the epsilon is the moving average smooth. In this routine, data are examined in 5 point blocks (**5 pts. MPA**). Within each block, the first, second, fourth, and fifth points are summed and divided by 4. This number (i.e., an averaged current value) replaces the third point in the block. The routine moves up one point, and repeats the averaging sequence, until it has been repeated for all data points, other than the first two and last two, which are set equal to the third point, and the third from last point, respectively. A 9 point moving point average (**9 pts. MPA**) is also available.

The default condition is that the experimental data is smoothed automatically at the end of the experiment.

Change Display Type

Two axes conventions are available:

- **IUPAC** - Positive x = positive potentials; positive y = oxidative currents (**F1**).
- **POLAROGRAPHIC** - Positive x = negative potentials; positive y = reduction currents (**F5**).

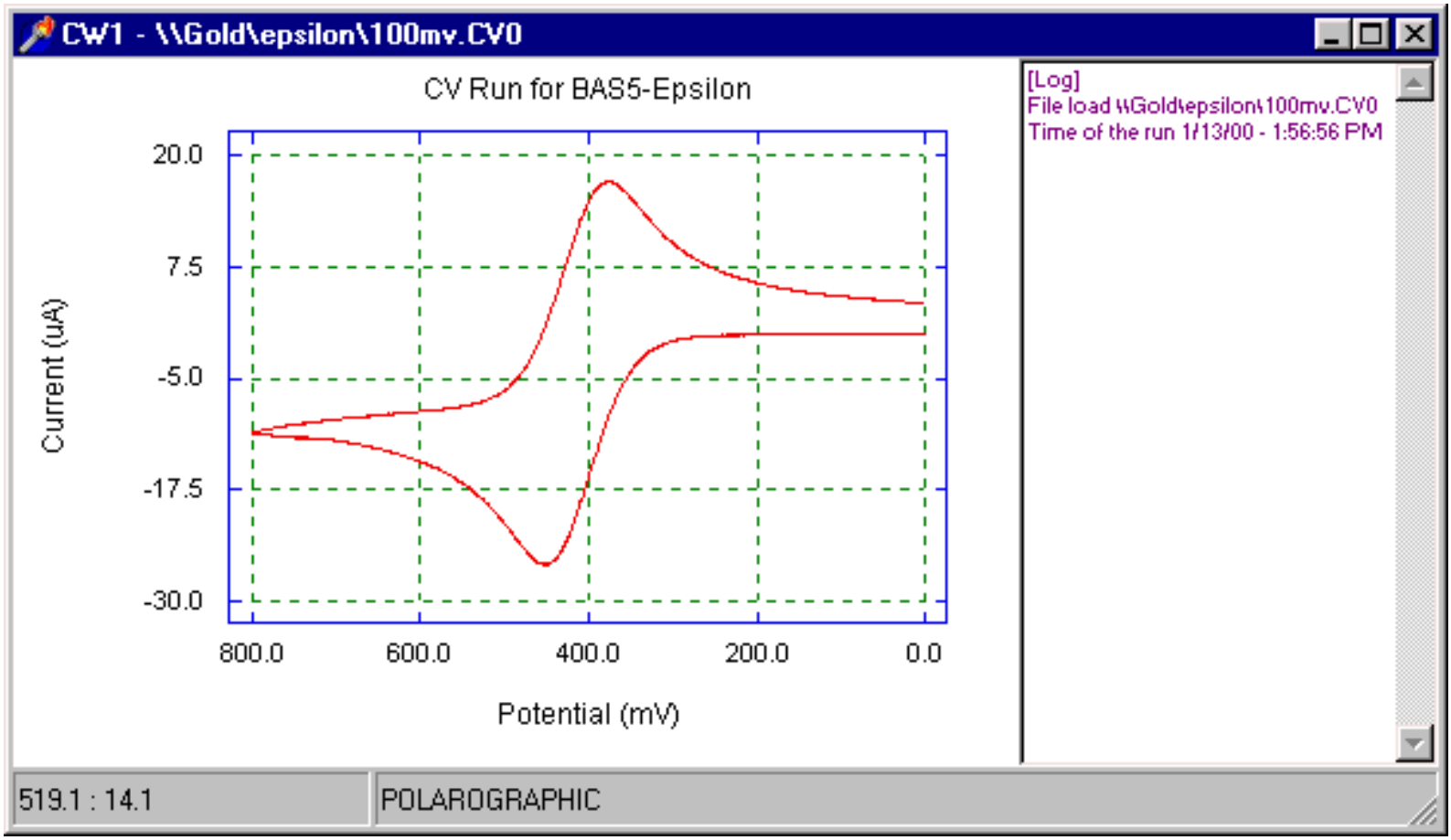

Figure 5. POLAROGRAPHIC axis convention.

Grid

The grid can be removed (**No Grid**), or a partial grid showing only the zero axes can be displayed (**Zero Line**) (**F6**). The full grid can be restored using **Full Grid**. All new and loaded data files will be displayed with the same grid selection as the last active data displayed. This selection is saved when the epsilon program is closed.

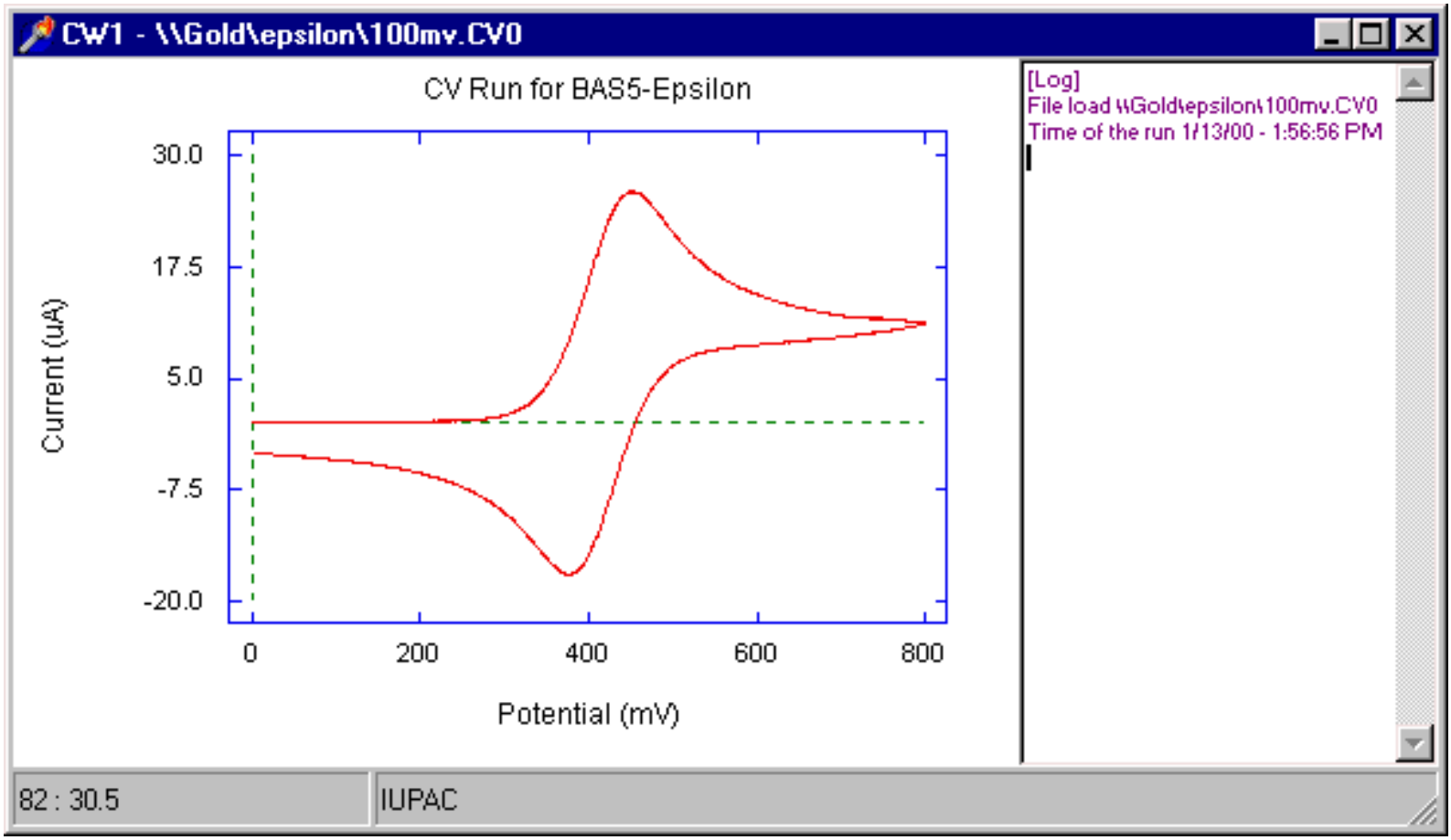

Figure 6. Grid - Zero Line

Show Data Points

This option will generate a graphic in which all the experimental data points are displayed (**F7**).

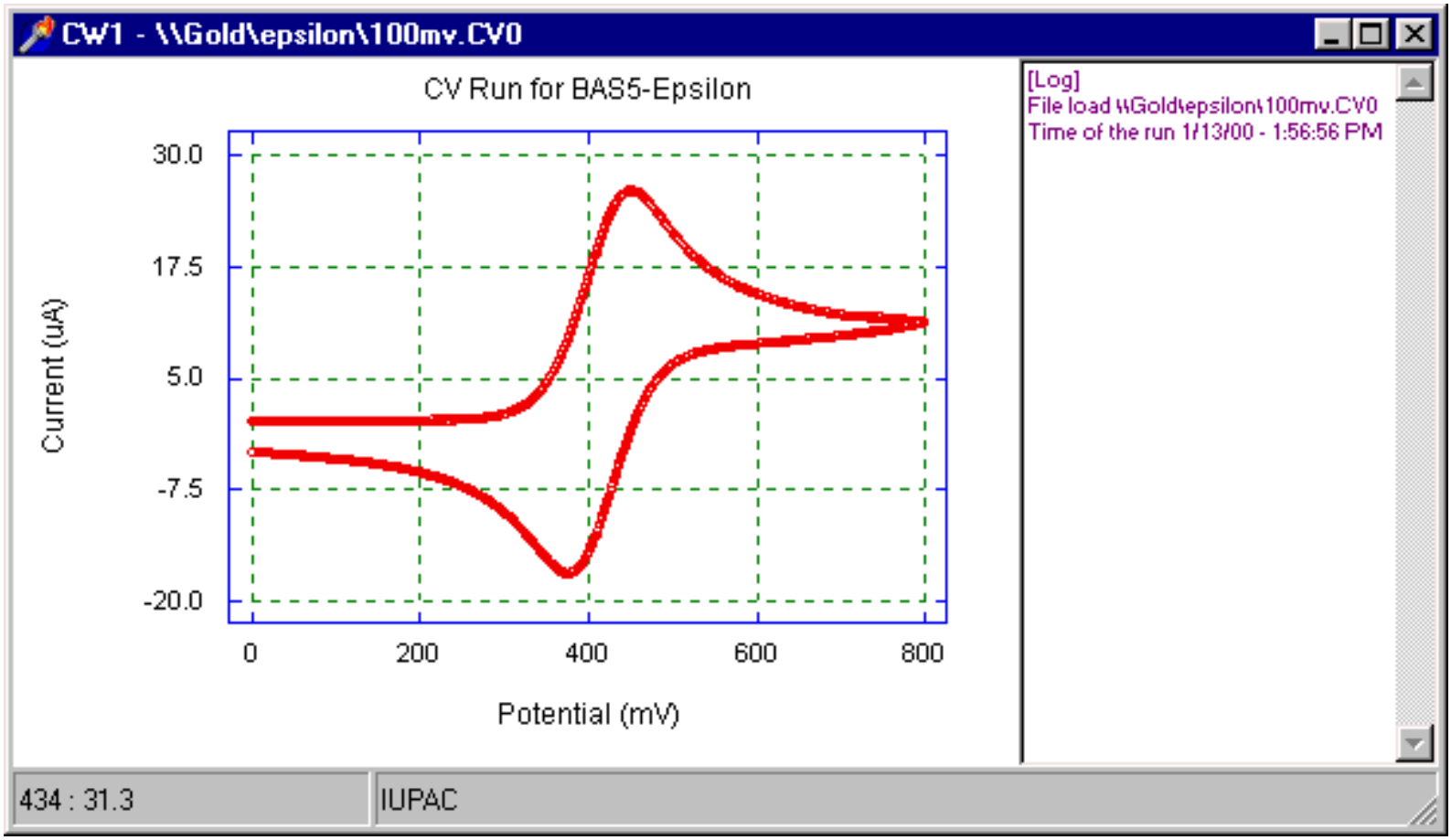

Figure 7. Graphic showing all experimental data points.

Copy to Clipboard

This command transfers the data from the active experiment window (without the frame) to the clipboard, from which it can be transferred to other Windows programs.

Text Info (Right Column)

Selected experimental information is listed in the column to the right of the plotted data (as shown in all the above figures). Clicking **Text Info (Right Column)** will remove this column (**F8**) (this option is also available in the pop-up menu).

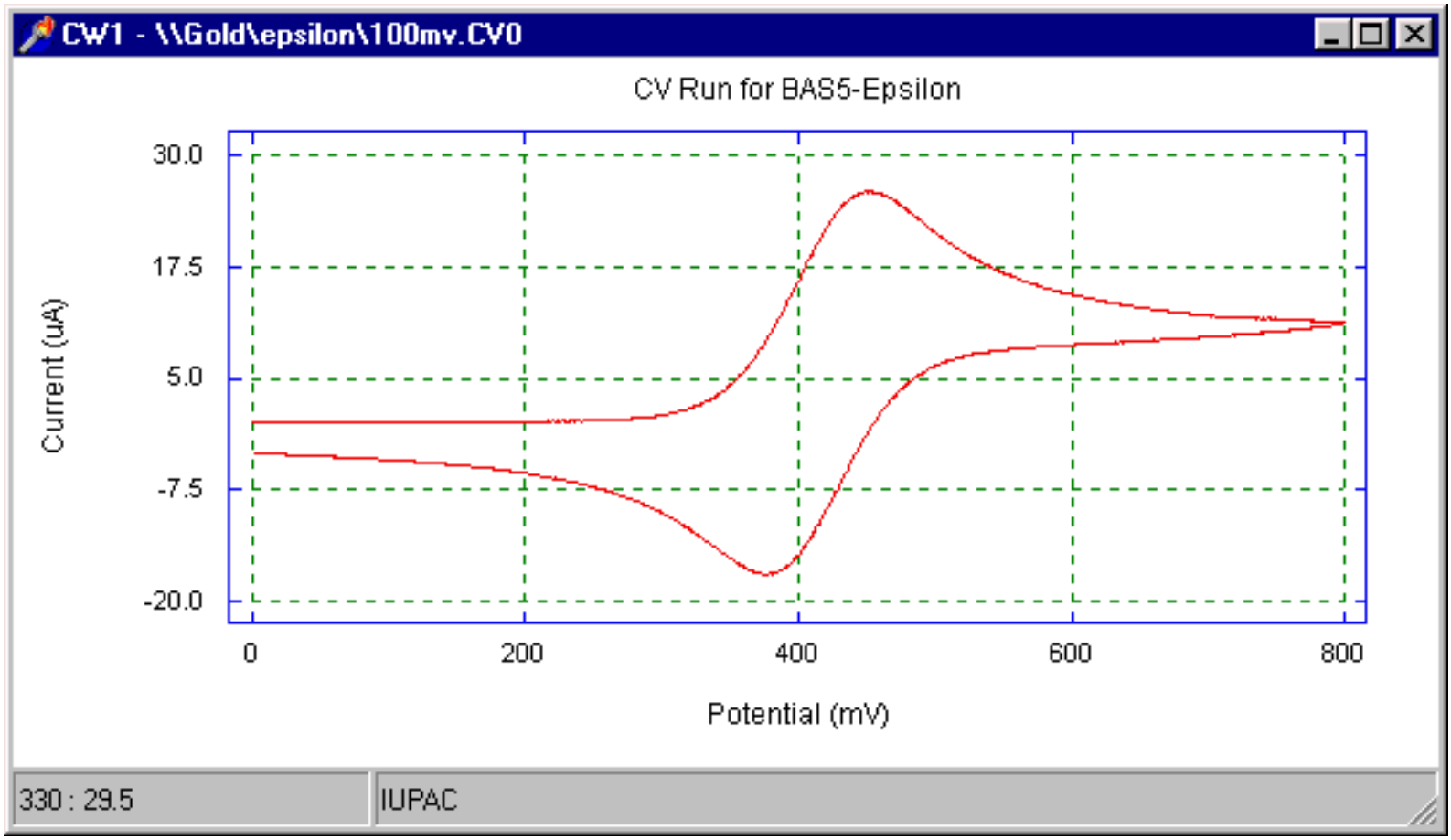

Figure 8. Experimental window without the text column.

Select Colors and Fonts

The dialog box for this option (**F9**) allows the user to define the colors and fonts for the components of the experimental window. The selections available for the fonts and the colors can be accessed by clicking the **Change Font** or **Change Colors** button, respectively. Once the desired changes have been entered, these must be registered by clicking the **Apply** button before exiting the dialog box. Note that the colors available may be limited by the PC. If printing to a black and white printer, **All Black** will give the best prints.

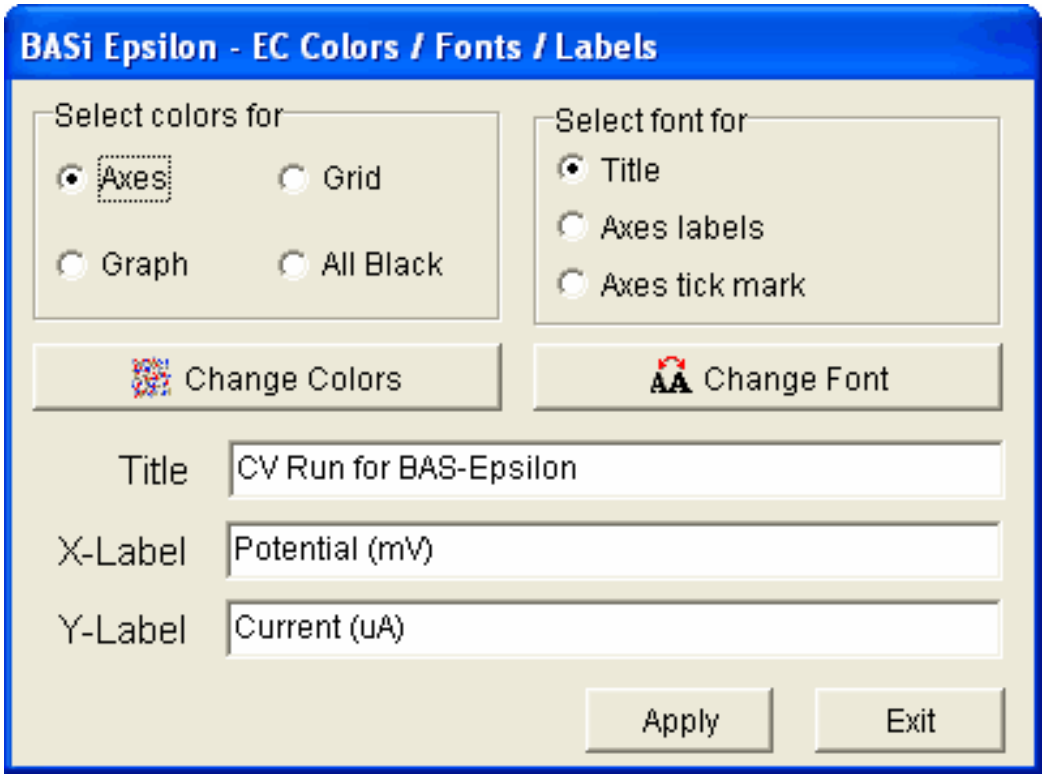

Figure 9. Select Colors and Fonts dialog box.

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File Overlay

Up to ten data files can be superimposed on a single set of axes using the **File Overlay** function in the **Graph-Display** menu. Data files can be selected from different directories. Once the files have been loaded, the overlay file can be saved. However, in order to recall overlays, the original files must still be present in the same location. Files to be overlayed must also be stored on the hard drive, NOT on a floppy disk or CD.

The default axis scale is determined by the first file to be loaded (the base file). However, the axes scales can be manually frozen and a mouse-controlled zoom is also available. The base file also limits the types of data files that can be overlayed. The available graph types are current vs. potential, current vs. time, and potential vs. time. Any given overlay can only display data of one type; that is, current vs. time plots (from, e.g., chronoamperometry) cannot be overlaid with current vs. potential plots, but pulse voltammograms can be overlaid with cyclic voltammograms. Selecting a new graph type will clear all data files from the overlay.

The procedure for overlaying data files is as follows:

1. Select **File Overlay** in the **Graph-Display** menu. The overlay window then appears (note that no non-overlay functions cannot be used while the overlay window is active). This window will display the previous overlay; if no overlay has been peformed since the program was started, the window will be empty.

2. Right-click to access the pop-up menu, and click **Setup**. The **File Overlay Setup** dialog box will appear (**F1**).

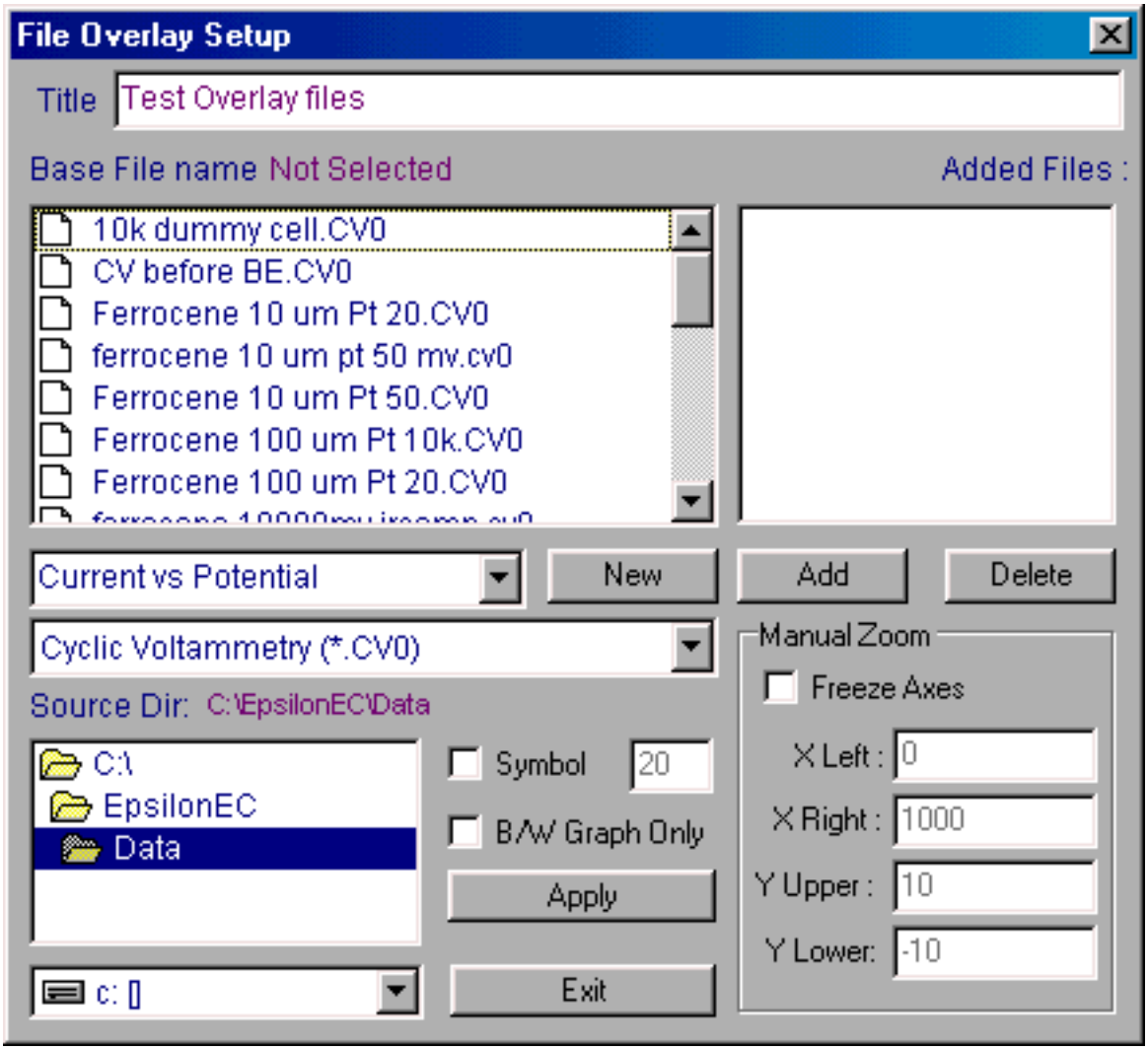

Figure 1. **File Overlay Setup** dialog box.

3. The files listed are determined by the graph type (**Current vs. Potential**, **Current vs. Time**, or **Potential vs. Time**) and the specified technique. Note that the techniques listed depend on the selection of the graph type). Select the **Base File name** and click **New** to display this file (**F2**).

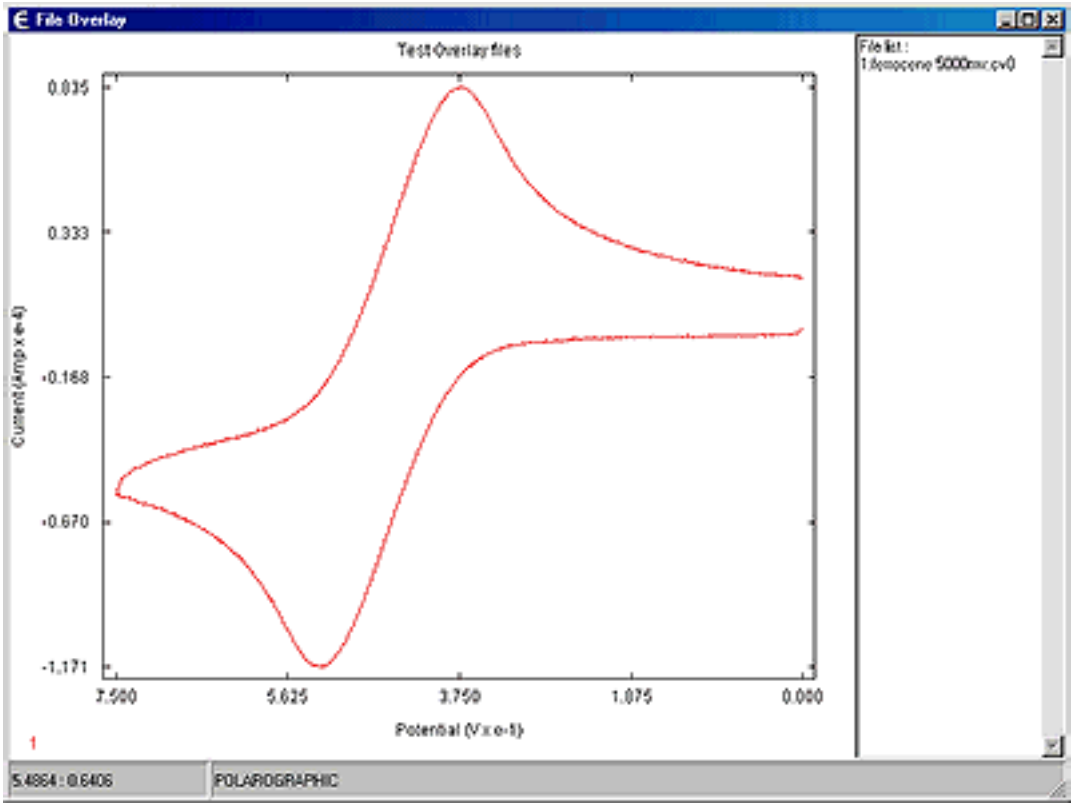

Figure 2. Base file loaded.

4. Select the files to be overlaid (up to 9 may be selected), then click **Add**. The file names will be listed on the **Added Files** list (**F3**), and the graph will be redrawn with the base file and added files (**F4**). Click **Exit** to remove the dialog box.

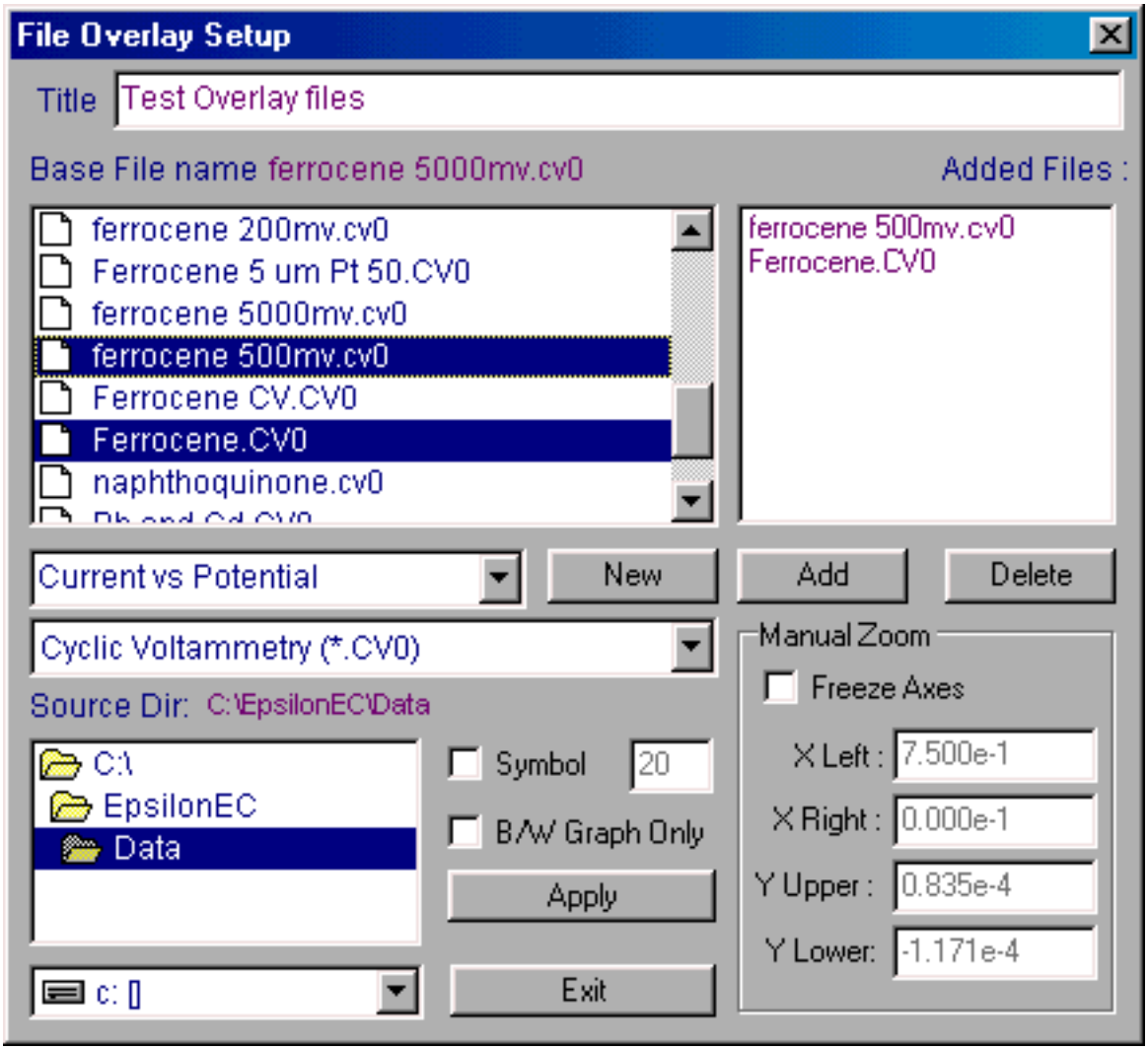

Figure 3. Selection of added files.

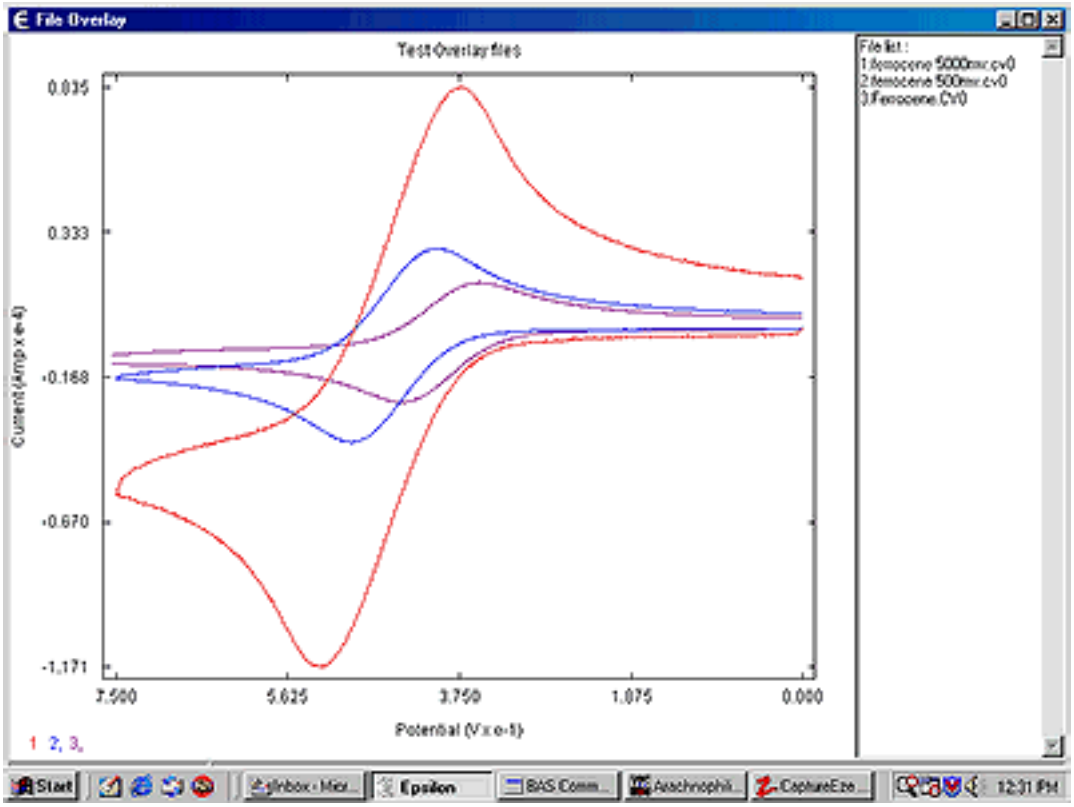

Figure 4. Overlaid graph.

5. To remove a file from the overlaid graph, select the relevant file name from the **Added** Files list, and click **Delete**.

6. Other options in the **File Overlay Setup** dialog box are as follows (note that **Apply** must be clicked in order to activate any changes in these functions):

    a. **Title**. A title can be entered for the overlaid graph.
    b. **Symbol**. If selected, a symbol will be used for the graphs instead of a line. The symbol will appear at every nth point, where n is the number entered in the adjacent box (default value = 20).
    c. **B/W Graph Only**. This will remove all colors for the graph (for printing and copying to the clipboard).
    d. **Freeze**. This function allows the user to set the maximum and minimum for each axis. If selected, the axes will remain frozen at the specified values even if a new base file is selected. When unchecked, the axes will revert to the values determined by the current base file. It should also be noted that the cursor zoom is disabled if **Freeze** is selected.

7. The other functions in the pop-up menu are as follows:

    a. **Save/Load**. An overlaid graph can be saved. However, in order to recall (**Load**) overlays, the original files must still be present and in the same location.
    b. **Grid**. The graph can be plotted with a full grid (note that the zero-line axis option is not

available for overlay graphs).

c. **Copy to Clipboard**. This command transfers the data from the active experiment window (without the frame) to the clipboard, from which it can be transferred to other Windows programs.
d. **Zoom Out**. This reverses the effects of any mouse zoom operations, and restores the default axis limits (note that this is disabled when the **Freeze** function is used).
e. **Text Info (Right Column)**. The text column to the right of the overlay graph can be removed.

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Data Analysis - General

The parameters that can be extracted from experimental data depend upon the electrochemical technique (e.g., peak potential, peak current and peak area for cyclic voltammetry, and slope and intercept for chronoamperometry/ chronocoulometry). Therefore, different measurement methods are required for different techniques. The methods available on the epsilon are as follows:

Peak parameter measurement

This function will measure and report the peak potential, current, and area under the peak for symmetric and tailing peaks, and the half-wave potential and limiting current for sigmoidal curves. The baselines for these measurements can either be determined automatically by the software or manually by the user. The operation of this function is best illustrated by an example (**F1**).

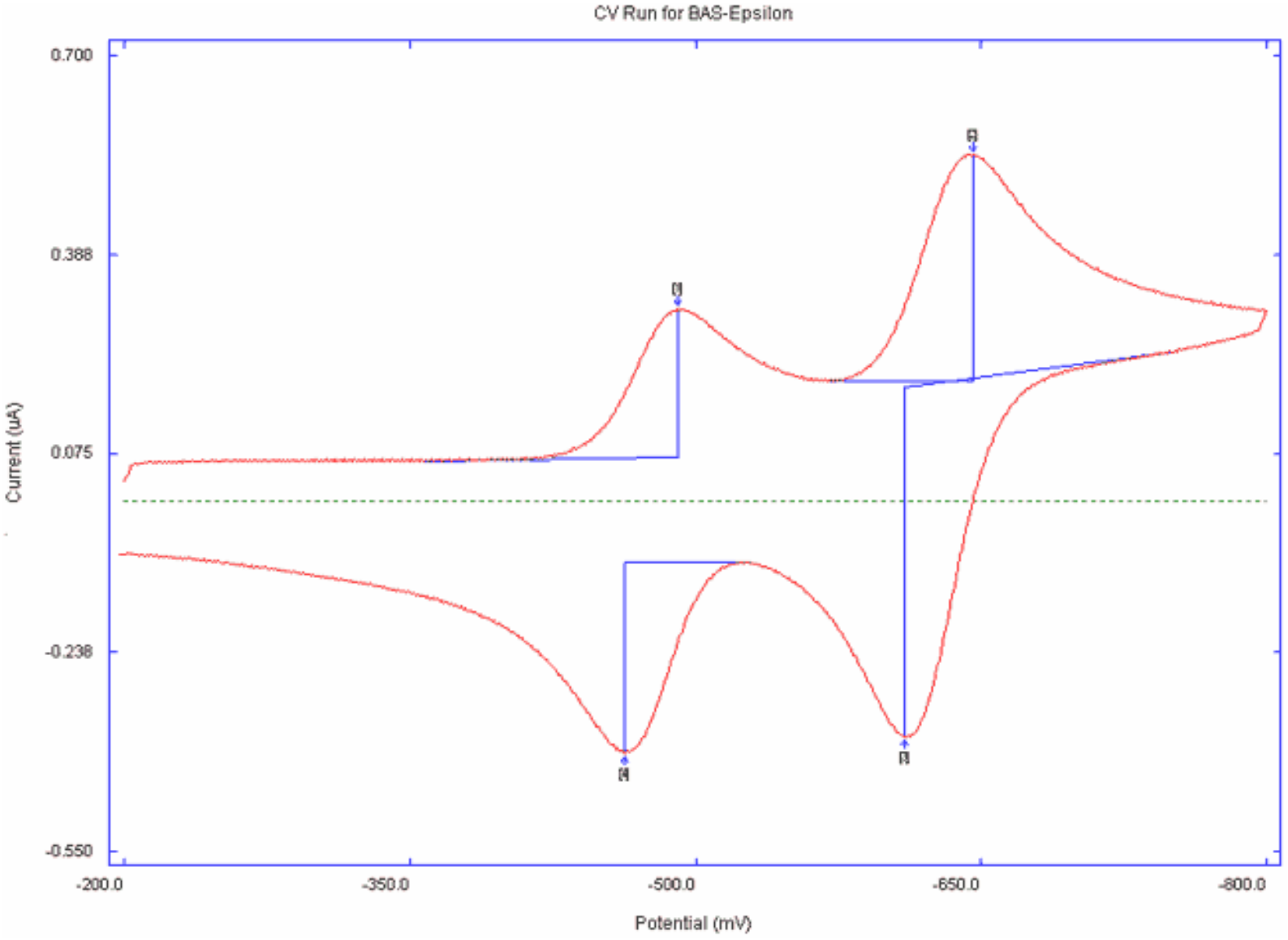

Figure 1

The cyclic voltammogram to be analyzed is shown above. The peak parameter values are calculated using the default values for the peak finding function. These paramneters can be changed using **Data - Change Peak Parameters** from the pop-up menu. The **Peak Parameters** dialog box is shown in **F2**.

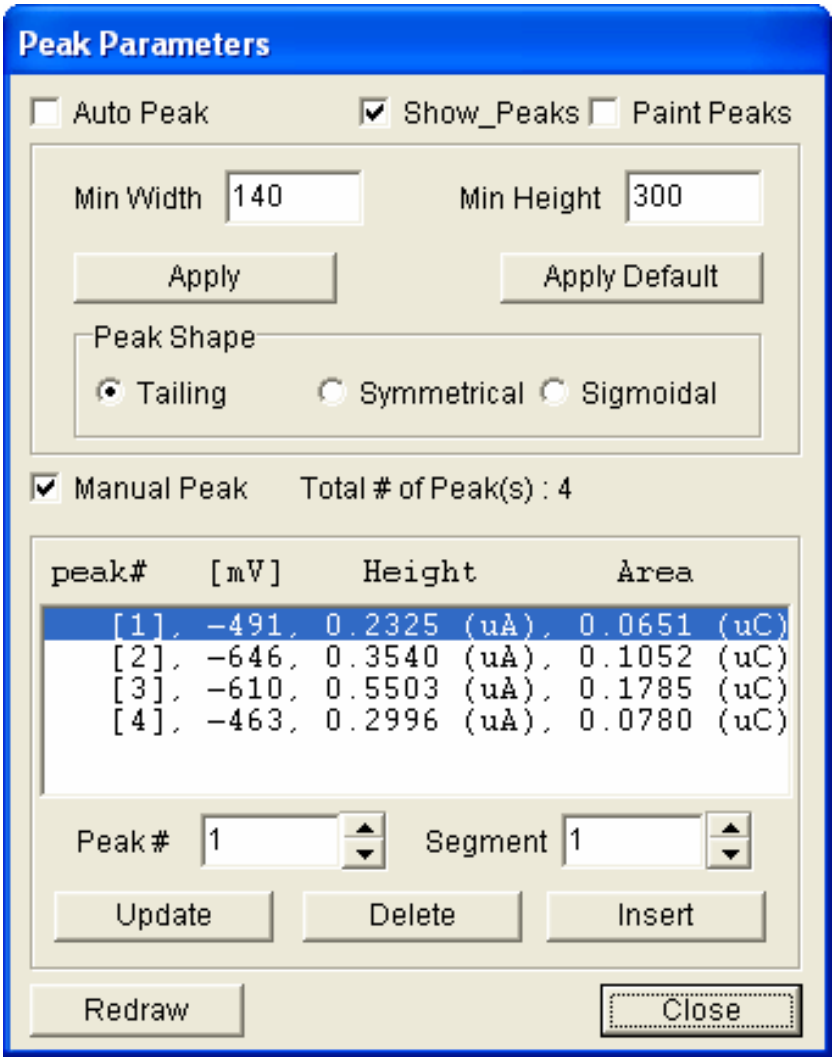

Figure 2

Note that there are two measurement options available (**Auto Peak** and **Manual Peak**), which are selected using check boxes. Let us first examine the **Auto** option. Clicking the **Apply** button will find peaks based on the **Min Width** and **Min Height** parameters, and will generate the graph shown in **F1**. The peak potentials, currents and areas are also listed.

The **Manual** option can be used if the user is not satisfied with the output from the **Auto Peak** measurement (e.g., if inappropriate baselines are used, or if there is an extraneous peak). To use the **Manual** option, first click the **Manual Peak** check box. Since the peaks must be analyzed individually when using this option, the first peak to be examined must be selected. This is done either by clicking the appropriate **peak [#]** in the listing or by selecting the appropriate # in the **Number** box (**F3**). Note that, once a peak has been selected, that segment is highlighted (**F4**).

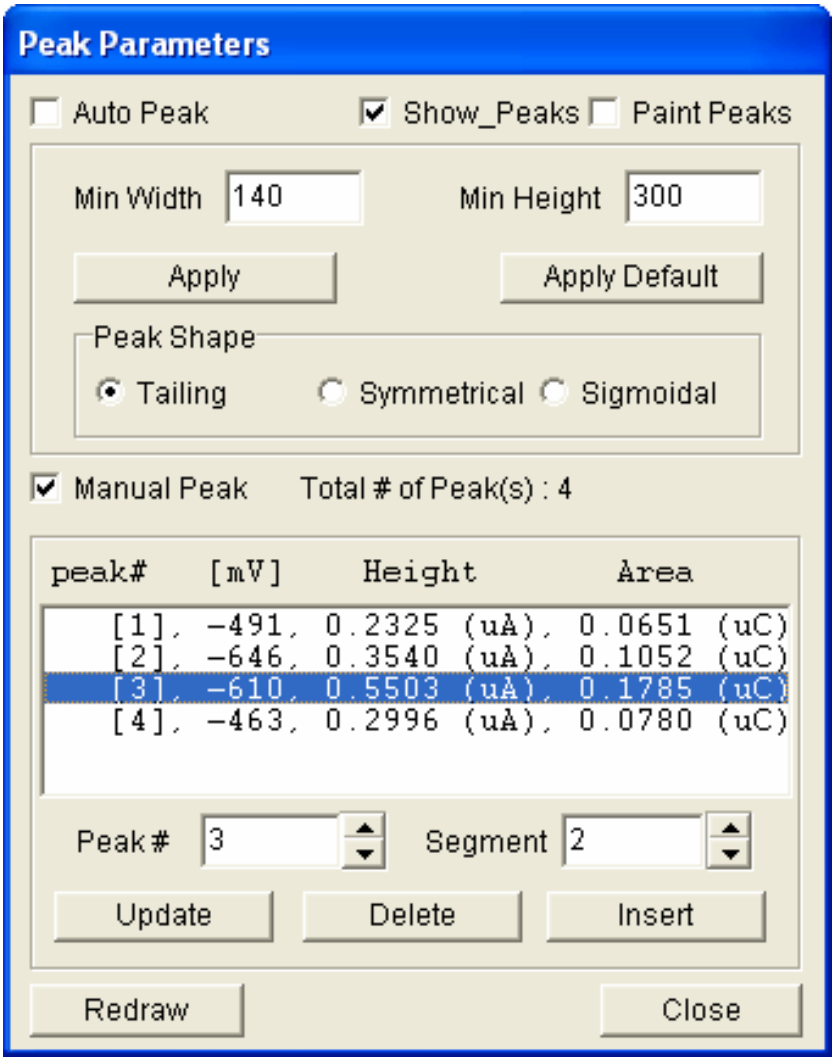
Peak Parameters
Auto Peak
Show_Peaks
Paint Peaks
Min Width
140
Min Height
300
Apply
Apply Default
Peak Shape
Tailing
Symmetrical
Sigmoidal
Manual Peak
Total # of Peak(s) : 4
peak# [mV] Height Area
[1], -491, 0.2325 (uA), 0.0651 (uC)
[2], -646, 0.3540 (uA), 0.1052 (uC)
[3], -610, 0.5503 (uA), 0.1785 (uC)
[4], -463, 0.2996 (uA), 0.0780 (uC)
Peak #
3
Segment
2
Update
Delete
Insert
Redraw
Close

Figure 3

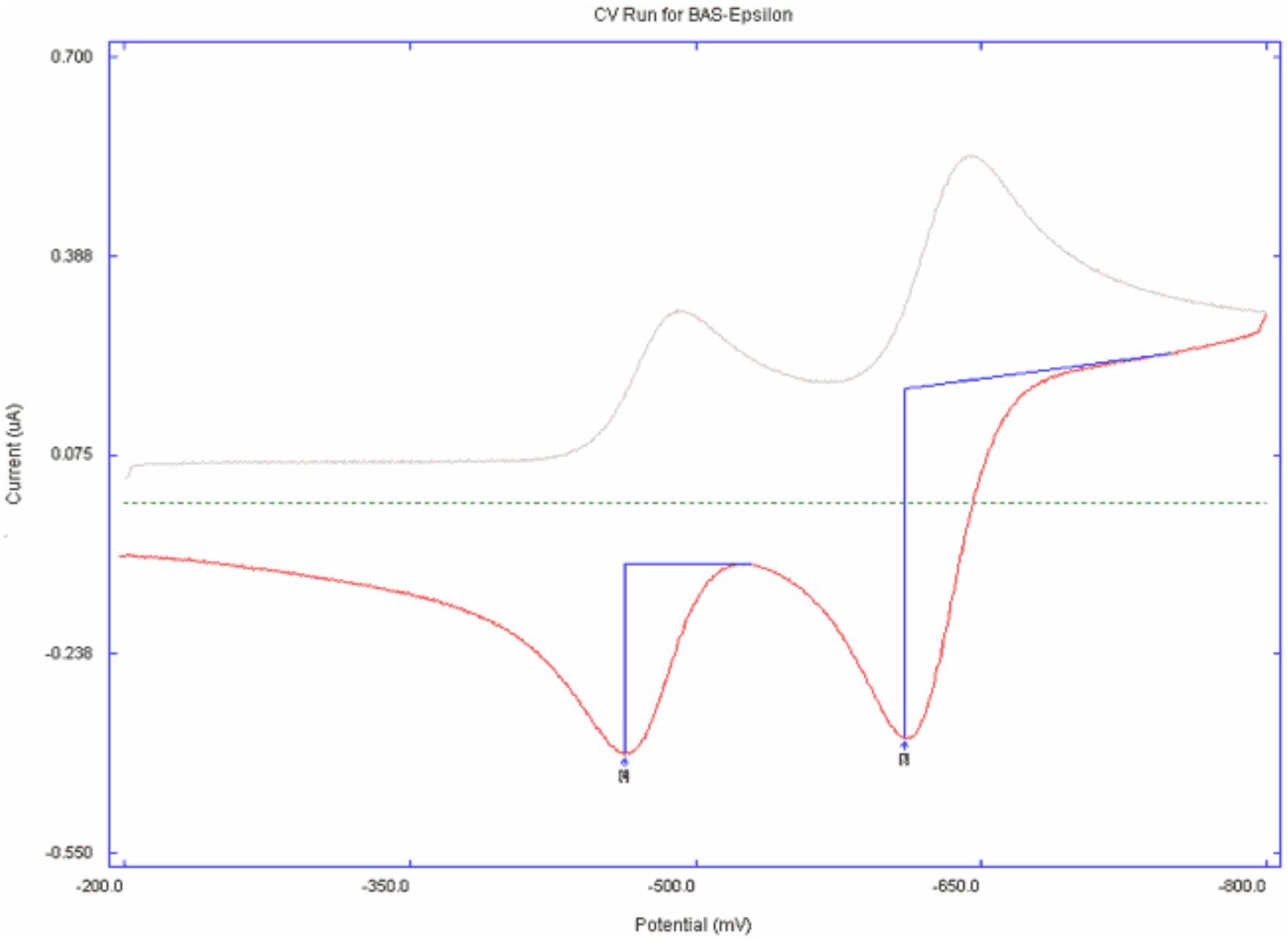

Figure 4

If this peak is not required, it can be removed by clicking **Delete**. Note that the listing changes automatically upon deletion.

The baseline for measurements of a *selected* peak can be redefined by first clicking **Update**, and then redrawing the line using the left mouse button. The peak measurement values based on this new baseline will replace the old values. A *new* peak can be measured on the specified segment by clicking **Insert**, and then defining the baseline. Once all the peaks have been detected, and their baselines defined, clicking **Redraw** will show the baselines for all the peaks in the voltammogram. **F5** shows the effect of checking the **Paint Peaks** box; that is, the calculated peak area is shown for each peak. The **Peak Parameters** dialog box can then be closed (by clicking the **Close** button).

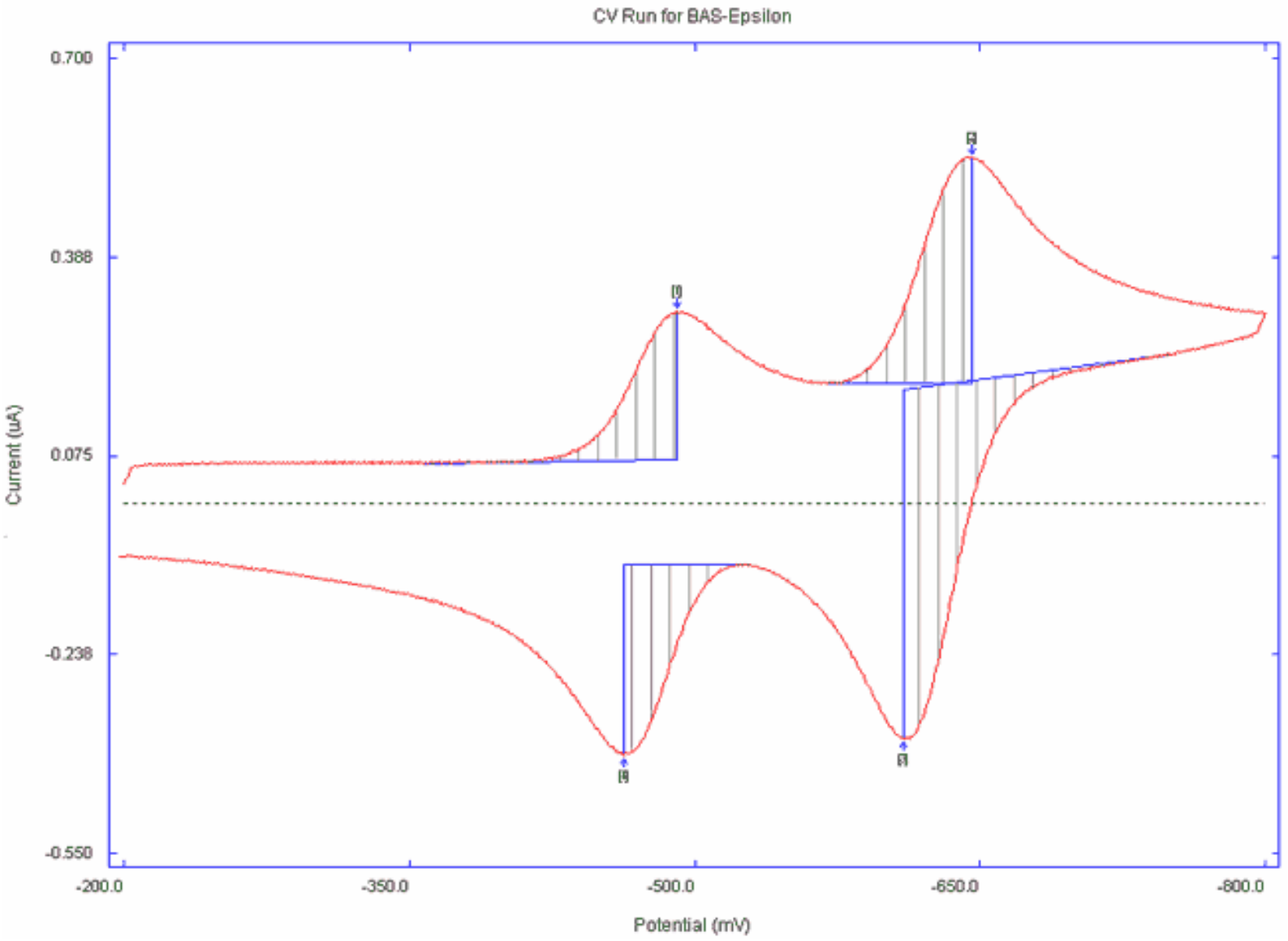

Figure 5

The above description used a cyclic voltammogram as an example, but it also applies for data from other techniques that generate a peak-shaped or sigmoidal response (however, note that the baseline used for the **Manual** option for a **Symmetrical** peak is based on the x values of the line defined by the user). It is important to ensure that the correct **Peak Shape** is selected (e.g., **Symmetrical** for differential pulse voltammetry, **Tailing** for cyclic voltammetry with linear diffusion (planar disk electrodes on millimeter dimensions), and **Sigmoidal** for normal pulse voltammetry or cyclic voltammetry with radial diffusion (e.g., microelectrodes at slow scan rates)).

Note that all Peak baselines and peak lines are saved with the data file. If one reanalyzes saved data and manually redraws baselines, then be sure to resave the file.

Linear fit measurement

Data from potential step experiments can be analyzed using the linear relationship between the response and some

function of time. Clicking the **Select Graph** item in the pop-up menu produces a sub-menu of the available graph options, and the appropriate option is selected (e.g., **Q vs sqrt(T)**).

Once the correct graph has been selected, the dialog box required for the calculation is opened by selecting **Data - Calculate CA-SIR** from the pop-up menu (**F6**).

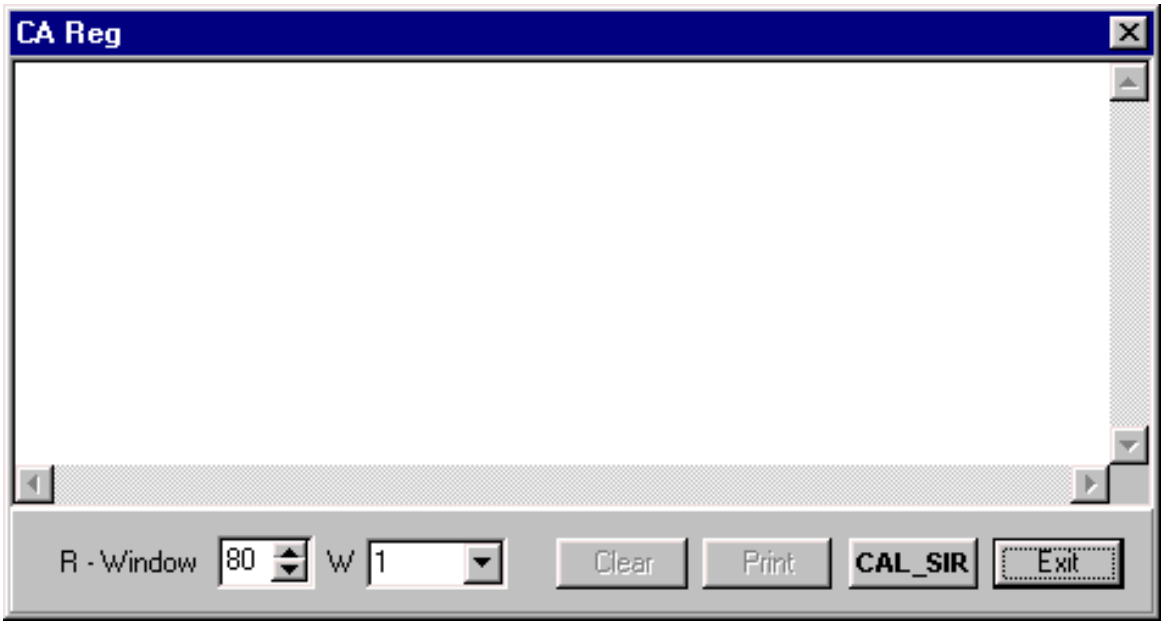

Figure 6

There are two parameters to be specified for the linear fit. **R - Window** specifies the percentage of data points to be used in the fit. This parameter is required since the finite time required to change the potential from the initial value to the step value means that the first few data points are not valid. The default condition is that the final 80 % of the data points are used for the calculation (i.e., the first 20 % are discarded). **W** is the weighting factor used in the calculation (x, 1/x, or $1/x^2$). On clicking **CAL_SIR**, the parameter values are calculated and displayed in the window (**F7**) (this window must be displayed if the results are to be printed with the graph). The graph now displays the lines used for the calculations (**F8**).

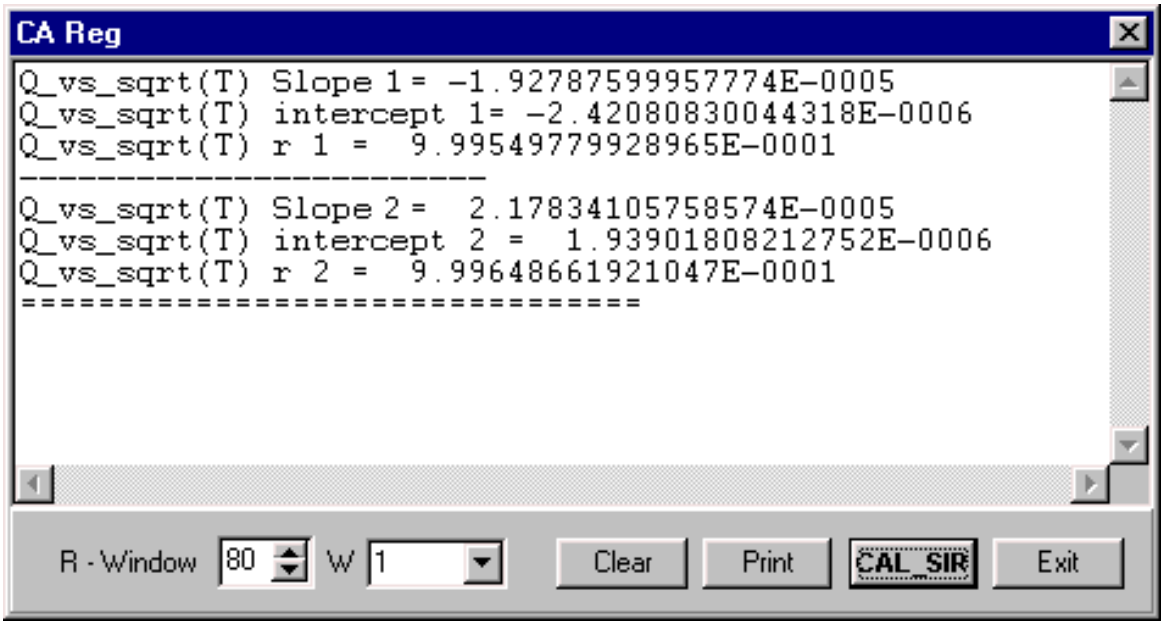

Figure 7

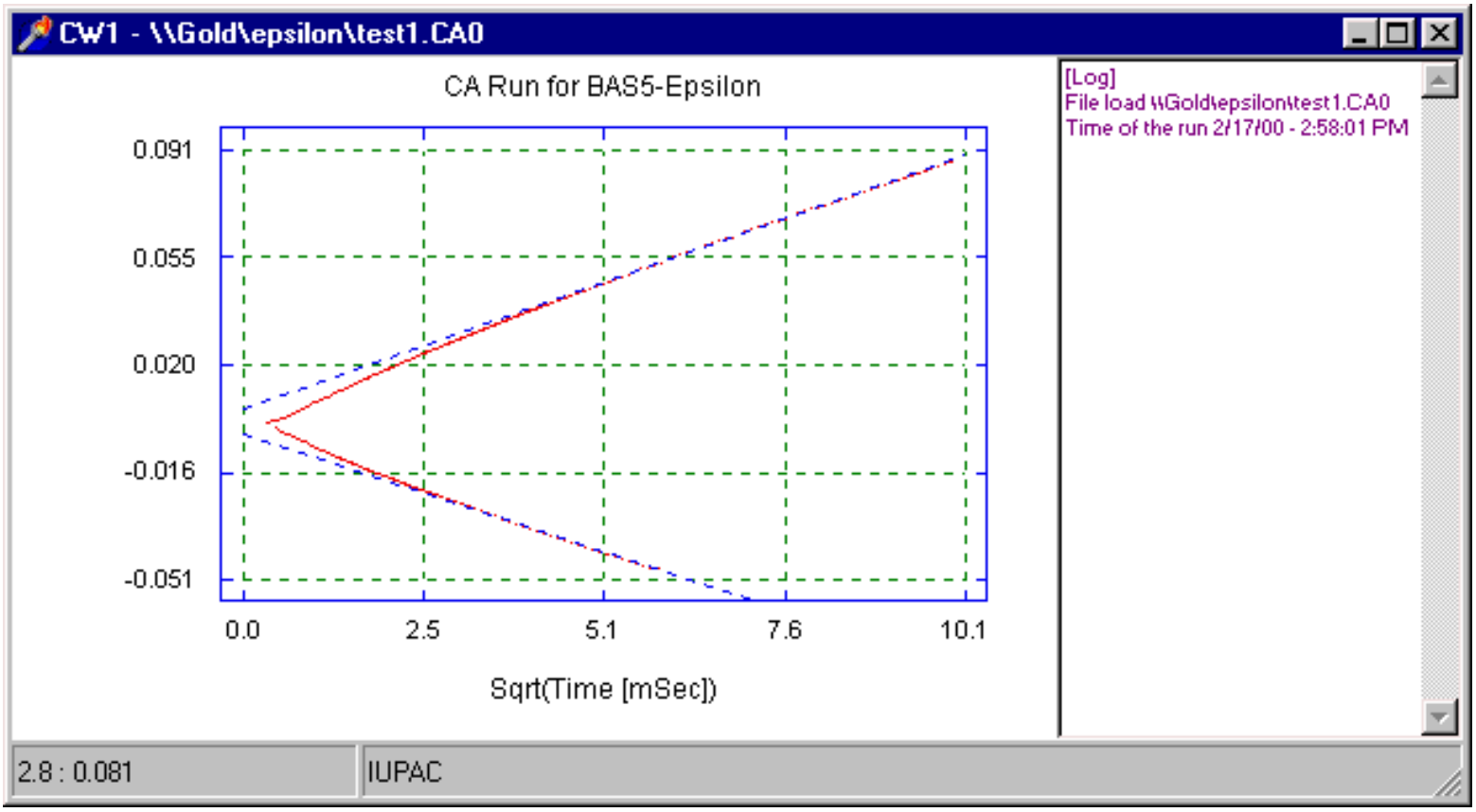

Figure 8

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Cyclic Voltammetry - Data Analysis

The important parameters for a cyclic voltammogram are the peak potentials E_p and peak currents i_p (**F1**), which are measured using the Peak Parameters operation.

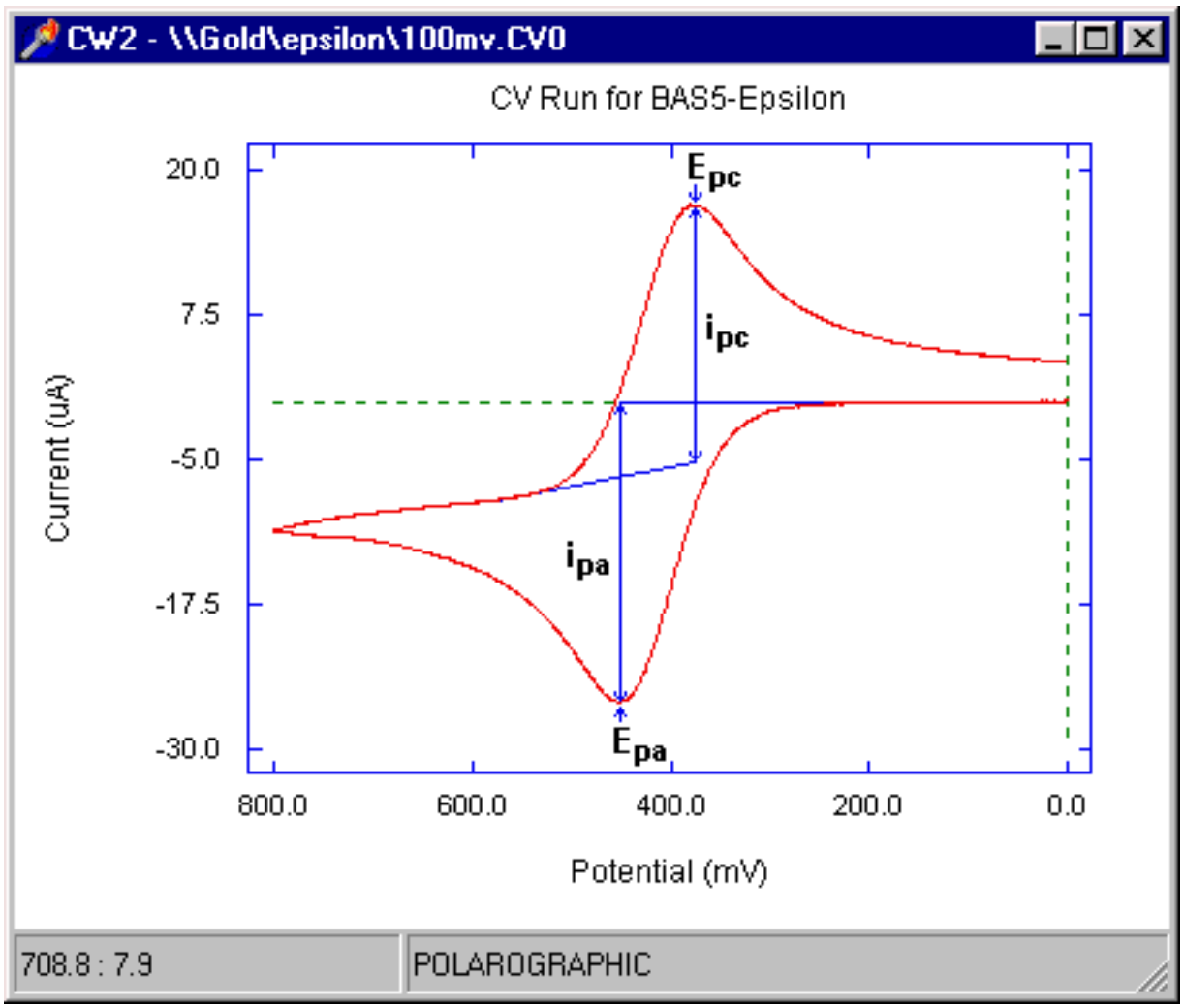

Figure 1. A typical cyclic voltammogram showing the important peak parameters.

If a redox system remains in equilibrium throughout the potential scan, the redox process is said to be *reversible* (equilibrium requires that the surface concentrations of O and R are maintained at the values required by the Nernst equation). The following parameter values are used to characterize the cyclic voltammogram of a reversible process:

a. the peak potential separation ΔE_p (= E_{pc} - E_{pa}) = 58/n mV at all scan rates at 25 °C.
b. the peak current ratio = i_{pa}/i_{pc} = 1 at all scan rates
c. the peak current function $i_p/\nu^{1/2}$ (ν = scan rate) is independent of ν (see equation for peak

current)

The peak current is given by the equation:

$i_p = 2.69x10^5 n^{3/2} A C D^{1/2} \nu^{1/2}$

where: n = number of electrons transferred/molecule
A = electrode surface area (cm^2)
C = concentration (mol cm^{-3})
D = diffusion coefficient (cm^2 s^{-1})

For a reversible process, $E^{o'}$ is given by the mean of the peak potentials.

Departures from reversible behavior for a redox process are shown by variations of the above parameters from the values observed for reversible processes. There are two major causes for irreversible behavior and these are discussed below.

1) Slow Electron Transfer Kinetics

Reversibility requires that the electron transfer kinetics are fast enough to maintain the surface concentrations of O and R at the values required by the Nernst equation. Hence, reversibility depends on the relative values of the standard heterogeneous electron transfer rate constant (k_s) and the rate of change of potential - the scan rate ν. If the ratio of k_s/ν is sufficiently small that Nernstian concentrations cannot be maintained, then the process is said to be *quasi-reversible*. A quasi-reversible process is characterized by $\Delta E_p > 58/n$ mV, with the value increasing with increasing ν.

Since reversibility depends on the value of k_s/ν, it may be possible to change a process from quasi-reversible to reversible by decreasing ν (which allows more time for the surface concentrations to adjust to the new values required by the changing potential). In addition, ΔE_p depends on the value of k_s/ν, and k_s can therefore be calculated from the variation of ΔE_p with ν.

Unfortunately, increases in ΔE_p with increasing ν can also be due to uncompensated solution resistance R_u. The effect of R_u can be minimized by careful experimental design, electronic positive feedback compensation and post-run data manipulation. The two effects can be distinguished by varying the analyte concentration (the potential drop due to uncompensated solution resistance, and hence the resulting ΔE_p, increase with increasing current, whereas k_s is independent of analyte concentration).

2) Chemical Reactions of O and R

Equilibrium values of O and R can only be maintained during a cyclic voltammetry experiment if both O and R are stable on the experimental time scale. For example, if the reduction of O to R is followed by the conversion of R to P, then more R must be generated to compensate for the loss of R. Therefore, the rate of reduction increases and E_{pc} moves to a more positive value. In addition, i_{pa}/i_{pc} is less than unity (since only a fraction of the molecules that were reduced on the forward scan are available for reoxidation on the reverse scan). The value of the current function can also be affected by chemical reactions following electron transfer.

The effect of a chemical reaction depends on the value of the ratio k/ν (where k is the rate of the chemical reaction). If this value is large, then the chemical reaction has a significant effect, whereas any effect is much less if this ratio is small. Therefore, it may be possible to eliminate the effect of the chemical reaction (thereby restoring reversiblity) by increasing ν. k can be calculated either by simulation studies or by investigating the effect of ν on i_{pa}/i_{pc}.

Although cyclic voltammetry is very widely used for the initial redox characterization of a molecule (i. e., the redox potentials, and the stability of the different oxidations states) and for qualitative investigation of chemical reactions that accompany electron transfer, there are a number of disadvantages inherent in this technique:

a. The effects of slow heterogeneous electron transfer and chemical reactions cannot be separated. If both of these effects are present, then the rate constants for these processes can only be calculated using simulation methods.
b. There is a background charging current throughout the experiment of magnitude νC_{dl} (where C_{dl} is the capacitance of the interface at the working electrode). This restricts the detection limit to about 10^{-5} M. In addition, the ratio of the peak faradaic current to the charging current decreases with increasing ν (since i_p is proportional to $\nu^{1/2}$), and this places an upper limit on the value of ν that can be used

In spite of these limitations, cyclic voltammetry is very well suited for a wide range of applications. Indeed, in some areas of research, cyclic voltammetry is one of the standard techniques used for characterization.

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Chronoamperometry/Chronocoulometry - Data Analysis

The analysis of chronoamperometry (**CA**) data is based on the Cottrell equation, which defines the current-time dependence for linear diffusion control:

$$i = nFACD^{1/2}\pi^{-1/2}t^{-1/2}$$

where: n = number of electrons transferred/molecule
F = Faraday's constant (96,500 C mol^{-1})
A = electrode area (cm^2)
D = diffusion coefficient (cm^2 s^{-1})
C = concentration (mol cm^{-3})

This indicates that, under these conditions, there is a linear relationship between the current and the 1/ square root of time. A plot of i vs. $t^{-1/2}$ is often referred to as the Cottrell plot. This plot is available in the epsilon software by selecting **I vs 1/sqrt(T)** from **Select Graph** in the pop-menu.

The analysis of chronocoulometry (**CC**) data is based on the Anson equation, which defines the charge-time dependence for linear diffusion control:

$$Q = 2nFACD^{1/2}\pi^{-1/2}t^{1/2}$$

Therefore, under these conditions, there is a linear relationship between the charge and the square root time. A plot of Q vs. $t^{1/2}$ is often referred as the Anson plot. This plot is available in the epsilon software by selecting **Q vs sqrt(T)** from **Select Graph** in the pop-menu.

The slope and intercept of the Cottrell and Anson plots can be measured by the epsilon software (click here for details). Since the slope of the Cottrell and Anson plots are determined by n, A, D, and C, one of these parameters can be calculated from the slope, provided the other three are known. One application of **CA** and **CC** is the determination of either D or A.

It is important to note that in any potential step experiment, there is a delay in attaining the step potential due to the finite rise time of the potentiostat. This non-ideal behavior affects the validity of the data points measured during this delay time, and hence these data are discarded when calculating the slope and intercept (the default condition for the epsilon software is that the final 80 % of data points are used). The non-linearity of the early data points is most clearly shown in the Cottrell plot (**F1**), due to the reciprocal time function (i.e., early data points = large x). In contrast, the non-linearity is much less

pronounced in the Anson plot (**F2**).

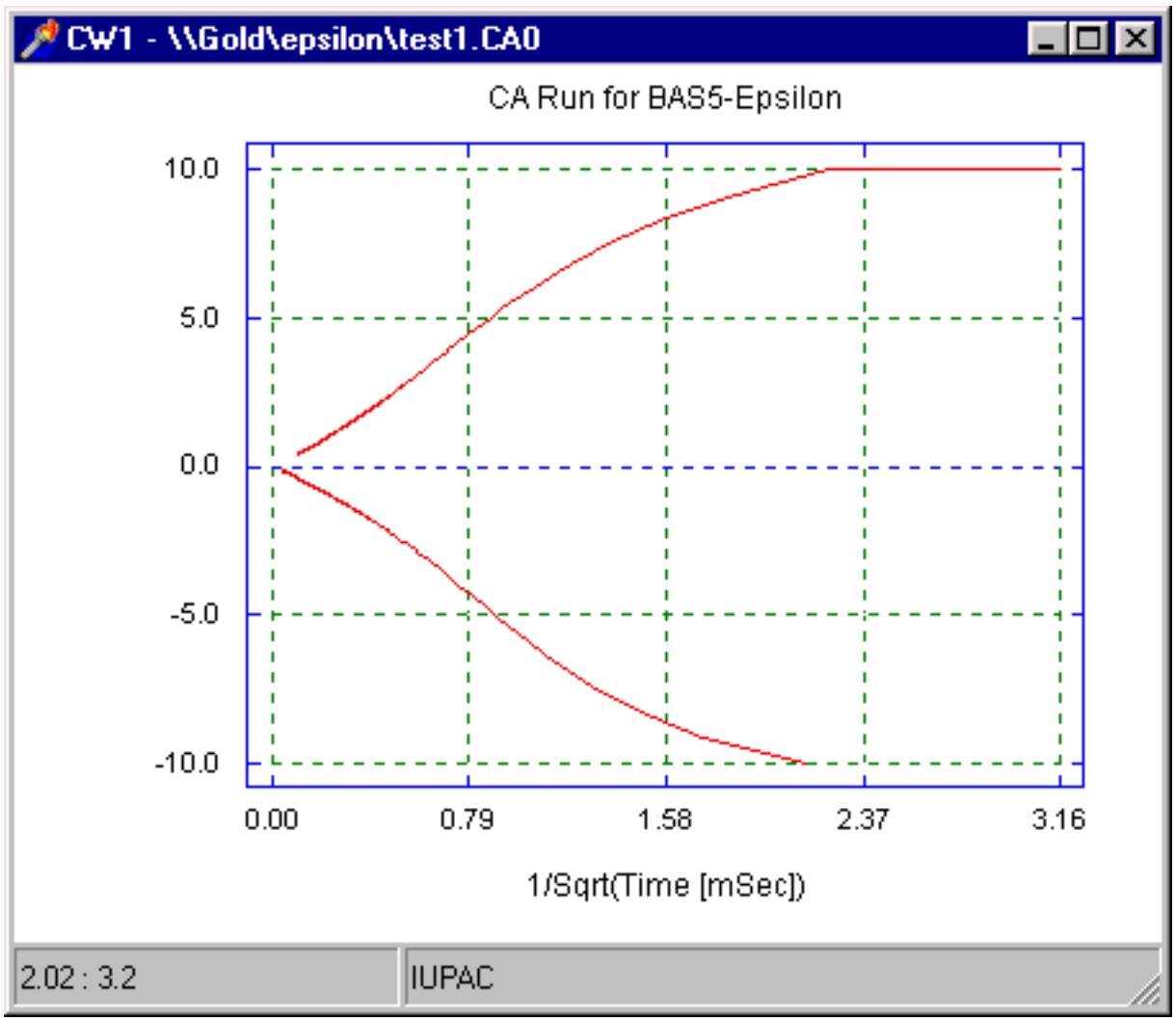

Figure 1. Cottrell plot for a chronoamperometry experiment.

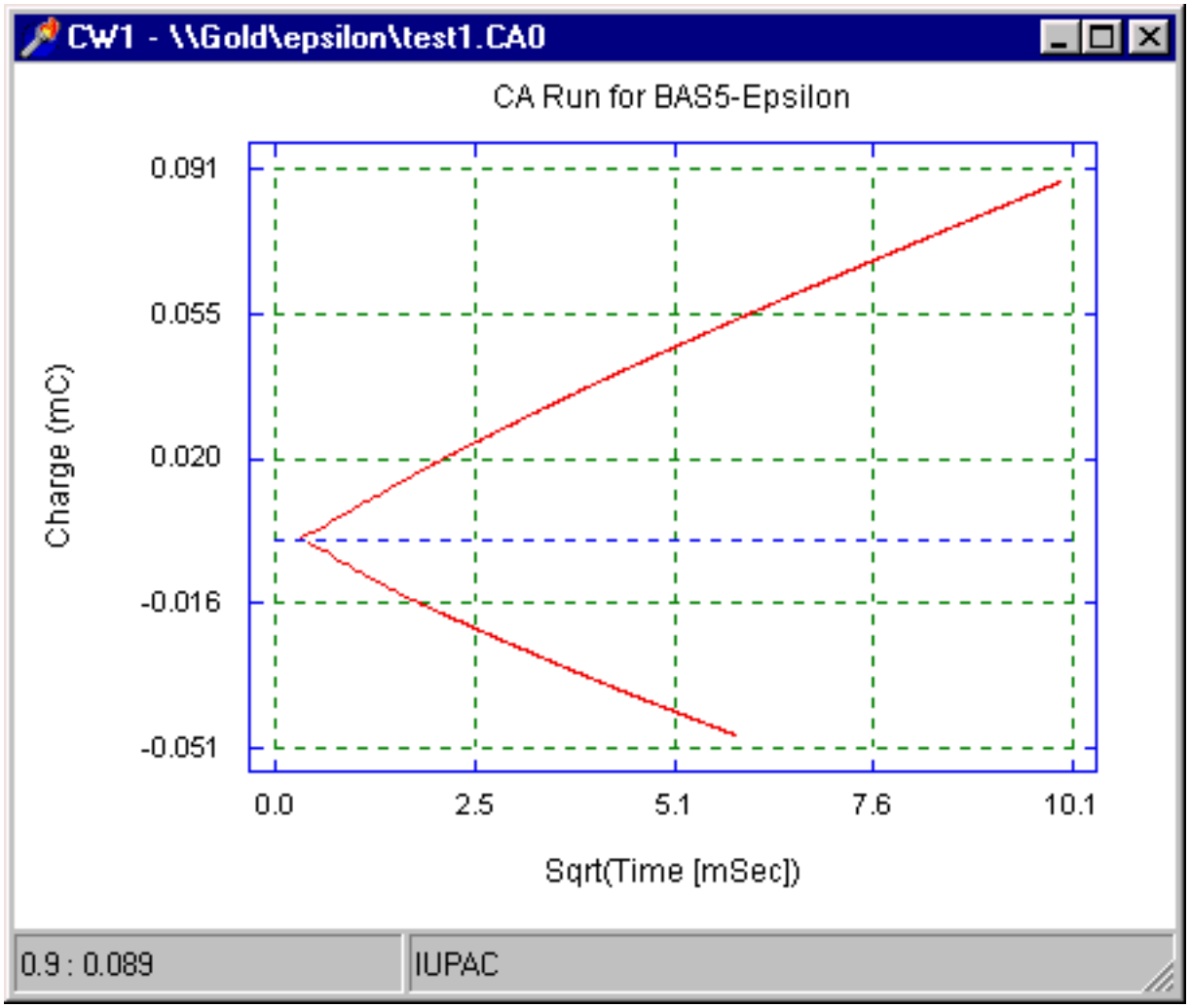

Figure 2. Anson plot for a chronocoulometry experiment.

Double potential step techniques can be used to investigate the kinetics of chemical reactions following electron transfer. As discussed elsewhere, only a fraction of the molecules of O that are formed as a result of the first potential step are reduced again during the second step. Therefore, the current or charge due to the second step (i_r or Q_r) is less than that due to the first step (i_f or Q_f). If O undergoes a chemical reaction to a molecule that is not reduced after the second step, then even fewer molecules of O are available for reduction, and i_r and Q_r show a corresponding decrease. The rate of the chemical reaction (k) can be calculated by investigating the effect of changing the **Step Time** on the i_r/i_f (or Q_r/Q_f) ratio and comparing these values to published working curves. Although working curves are available for both i_r/i_f and Q_r/Q_f, **CC** is generally more favored due to the better signal to noise ratio.

One of the major applications of **CC** is the study of species adsorbed to the surface of the working electrode (indeed, it was originally devised for such studies). The advantage of using **CC** rather than **CA** is that it is possible to separate the charge due to the electrolysis of the adsorbed molecules from the charge due to the electrolysis of molecules in solution and the double layer charge (the analogous separation of currents is generally not possible). This is achieved using the Anson plot.

As discussed above, the electrolysis of solution species is diffusion-controlled, and depends on $t^{1/2}$. In contrast, the electrolysis of adsorbed species is essentially instantaneously, as is the double layer charging. The equation for the total charge Q is:

$$Q = Q_{diff} + Q_{ads} + Q_{dl}$$

or

$$Q = 2nFACD^{1/2}\pi^{-1/2}t^{1/2} + nFA\Gamma_0 + Q_{dl}$$

where: Q_{diff} = charge due to electrolysis of solution species

Q_{ads} = charge due to electrolysis of adsorbed species

Q_{dl} = double-layer charging

Γ_0 = surface concentration of adsorbed species (mol cm^{-2})

Therefore, the intercept of the Anson plot is the sum of Q_{dl} and Q_{ads}. One method for eliminating Q_{dl} from the equation is to run the identical experiment on the electrolyte alone. However, this approach assumes that Q_{dl} is the same both in the presence and in the absence of the adsorbed analyte, which is generally not a valid assumption. The alternative method is to use the double potential step experiment. If only one of O and R adsorbs, then Q_{ads} is the difference of the intercepts of the Anson plots for the two steps.

It is important to note that data from the later time domains of the experiment are being used to investigate behavior that occurred at early time points. This shows that integration retains information about electrolysis that occurs essentially simultaneously with the potential step. This is a major advantage of **CC**, since direct measurement of such behavior is generally very difficult.

In all the above applications, the initial potential is at a value at which electrolysis does not occur, and the step potential is at a value at which electrolysis occurs at a diffusion-controlled rate (the second step is generally from the step potential back to the initial potential). Therefore, before these potentials can be determined, the redox potential must first be known. In general, the simplest way to find these potentials is to record the cyclic voltammogram of the analyte.

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File Subtraction

This command is listed in the **Experiment** menu and is used to subtract a voltammogram stored on the hard disk from the active voltammogram (e.g., for background subtraction). The voltammogram to be subtracted is selected from a standard Windows dialog box. The x axis should be the same for both files. For time base experiments such as CPE, files of different length can be subtracted. The data in common will be subtracted and the extra points in the longer file will be truncated.

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Working Electrodes

Electrode Polishing

The fundamental process in electrochemical reactions is the transfer of electrons between the working electrode surface and molecules in the interfacial region (either in solution or immobilized at the electrode surface). The kinetics of this heterogeneous process can be significantly affected by the microstructure and roughness of the electrode surface, the blocking of active sites on the electrode surface by adsorbed materials, and the nature of the functional groups (e.g., oxides) present on the surface. Therefore, there has been considerable effort devoted to finding methods that remove adsorbed species from the electrode and produce an electrode surface that generates reproducible results.

The most common method for surface preparation is mechanical polishing. The protocol used for polishing depends on the application for which the electrode is being used, and the state of the electrode surface. There are a variety of different materials available (e.g., diamond, alumina, silicon carbide), with different particle sizes suspended in solution (BAS supplies 0.05 μm alumina polish, and 1, 3, 6, and 15 μm diamond polishes; these should be shaken well before use to ensure that the particles are suspended). The pad used for polishing also depends on the material being used for polishing - Texmet pads are used with alumina polish, and nylon pads should be used with diamond polish. Working electrodes supplied by BAS have first been lapped to produce a flat surface, and have then been extensively polished to a smooth, mirror-like finish at the factory. Therefore, they typically only require repolishing with 0.05 μm or 1 μm diamond polish by the user in between experiments. The electrode should be moved in a figure-of-eight motion when polishing to ensure uniform polishing. Materials that have a rougher surface (e.g., commercial electrodes that have been scratched) must first be polished using a larger particle polish, in order to remove the surface defects. After the defects have been removed, the polishing should continue with successively smaller particle size polish (e.g., 15 μm, then 6 μm, then 3 μm, and then 1 μm).

Once polishing has been completed (this can require from 30 s to several minutes, depending upon the state of the electrode), the electrode surface must be rinsed thoroughly with an appropriate solvent to remove all traces of the polishing material (since its presence can affect the electron transfer kinetics). Alumina polishes should be rinsed with distilled water, and diamond polishes with methanol or ethanol. The rinsing solution should be sprayed directly onto the electrode surface. After the surface has been rinsed, electrodes polished with alumina should also be sonicated in distilled water for a few minutes to ensure complete removal of the alumina particles. If more than one type of polish is used, then the

electrode surface should be thoroughly rinsed between the different polishes.

As discussed above, the effect of any surface pretreatment can be determined by its effect on the rate of electron transfer. This can be judged qualitatively by examining the separation of the peak potentials in a cyclic voltammogram of a molecule whose electron transfer kinetics are known to be sensitive to the state of the surface (a more quantitative determination can be made by calculating the value of the standard heterogeneous rate constant k_s from this peak potential separation). For example, k_s for potassium ferricyanide at a glassy carbon surface following a simple polishing protocol is typically in the range 0.01 - 0.001 cm s^{-1} (this should be compared with the values measured for k_s for a platinum electrode, which are at least one order of magnitude larger). The strong dependence of the electron transfer kinetics of ferricyanide on the state of the electrode surface means that there can be significant variations in the peak potential separation after each polishing, since polishing alters the microstructure, roughness, and functional groups of the electrode surface in addition to removing adsorbed species. The materials used for the polishing can also affect the value of k_s. For example, the electrode surface can be contaminated by the agglomerating agents required to keep the alumina particles suspended in solution and by the components of the polishing pad. The presence of these species can have a deleterious effect on the electron transfer kinetics by blocking the active sites for the electron transfer reaction. However, it should be noted that such pronounced dependence on the state of the electrode surface is only observed for certain systems (the most well characterized examples are the reduction of ferricyanide, the oxidation of ascorbate, and the adsorption of dopamine). For such systems, polishing is often used in combination with another pretreatment (e.g., heat or electrochemical). However, for many other systems, the simple polishing described above is adequate (for example, when using non-aqueous electrolytes, since blocking of active sites by adsorbed species is less common in such electrolytes than it is in aqueous electrolytes).

Electrochemical Pretreatment

Another method for preparation of the electrode surface that is becoming more widely used is electrochemical pretreatment (ECP), particularly for electrodes which cannot readily be polished (e.g., carbon fiber cylinder electrodes). ECP consists of applying conditioning potentials to the electrode surface before the experiment. As with polishing, this has the effect of removing adsorbed species and altering the microstructure, roughness and functional groups of the electrode surface. The precise ECP protocol depends upon the application, and varies considerably. The potential waveforms typically are either held at, or cycle to, a large positive or negative potential, either using steps or sweeps (constant potential, potential scan, triangular wave, and square wave). Although the development of the preconditioning protocols has been largely empirical, there has been some characterization of the pretreated electrode surface in order to elucidate the reasons for the activation of the electrode surface. For glassy carbon electrode, in addition to the removal of adsorbed species, the preconditioning potential leads to the formation of an oxygen-rich layer on the carbon surface. This layer contains oxides as well

as other oxygen-containing functional groups which may catalyze electron transfer reactions (the composition of the functional groups in this layer is sensitive to the pretreatment conditions, and depends on the solution pH as well as the potentials used for the pretreatment). The oxide layer can also adsorb and/or exchange ions from the solution, which leads to improved detection limits. However, electrochemical pretreatment of electrodes can increase the background current of the electrode relative to that of a polished electrode, which may be disadvantageous for some applications.

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Reference Electrodes

Introduction

In all electrochemical experiments, the reactions of interest occur at the surface of the working electrode. Therefore, we are interested in controlling the potential drop across the interface between the surface of the working electrode and the solution (i.e., the interfacial potential). However, it is impossible to control or measure this interfacial potential without placing another electrode in the solution. Thus, two interfacial potentials must be considered, neither of which can be measured independently. Hence, one requirement for this counter electrode is that its interfacial potential remains constant, so that any changes in the cell potential produce identical changes in the working electrode interfacial potential.

An electrode whose potential does not vary with current is referred to an ideal non-polarizable electrode, and is characterized by a vertical region on a current vs. potential plot. However, there is no electrode that behaves in this way (although some approach ideal non-polarizable behavior at low currents). Consequently, the interfacial potential of the counter electrode in the two-electrode system discussed above varies as current is passed through the cell. This problem is overcome by using a three-electrode system, in which the functions of the counter electrode are divided between the reference and auxiliary electrodes; that is, the potential between the working and reference electrodes is controlled and the current passes between the working and auxiliary electrodes. The current passing through the reference electrode is further diminished by using a high-input-impedance operational amplifier for the reference electrode input.

The requirements for the counter electrode of the two-electrode system include a high exchange current (fast electron transfer kinetics), very large surface area (to lower the current density) and a high concentration of the species involved in the redox reaction, such that the concentrations are not significantly changed by the passage of a current. One previously widely used reference electrode that fulfills these criteria is the saturated calomel electrode (with a large surface area mercury pool). However, since the current passing through the reference electrode in the three-electrode system is many

orders of magnitude lower than the current that passes through the two-electrode system, the requirements for the reference electrode are less demanding; hence, smaller, more polarizable electrodes can be used.

One aspect that is often overlooked is the variation of the reference electrode potential with temperature. Ideally, the potential should be temperature independent; however, it typically changes by 0.5 - 1 mV per degree Celsius. Consequently, precise potential measurements require the use of a constant temperature apparatus. In addition, the temperature at which the measurements were carried should always be reported. The absence of any temperature control limits the accuracy of the measurements to about 5 - 10 mV (although this level of precision may be acceptable for some experiments).

Two widely used aqueous reference electrodes are the silver/silver chloride electrode and the saturated calomel electrode. These are now discussed in more detail.

Silver/Silver Chloride Reference Electrode

The redox process for this electrode is

$AgCl + e^- <=> Ag + Cl^-$

This electrode consists of a silver wire, coated with silver chloride, which is immersed in a solution containing chloride ions. The BAS RE-5B electrode uses an aqueous solution containing 3M sodium chloride (the use of sodium as the cation rather than potassium is discussed below); a porous Vycor® frit is used for the junction between the reference electrode solution and the sample solution.

The potential E for any electrode is determined by the Nernst equation, which relates E to the *standard* potential E^0 and the activities of the redox components (the standard potential is the potential of the electrode at unit activity under standard conditions). The Nernst equation for the silver/silver chloride electrode is

$$E = E^0 + \frac{RT}{nF} \ln \frac{1}{a_{Cl^-}}$$

(the activities of the solid silver and silver chloride under standard conditions are unity).

It is generally more convenient to consider concentrations rather than activities. These parameters are related by the activity coefficient γ:

$$a_{Cl^-} = \gamma_{Cl^-}[Cl^-]$$

The Nernst equation can therefore be rewritten as follows:

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{1}{[Cl^-]}$$

where $E^{0'}$ is the formal potential and is related to the standard potential by the equation:

$$E^{0'} = E^0 + \frac{RT}{nF} \ln \frac{1}{\gamma_{Cl^-}}$$

When quoting a redox potential, it is important to be specific. For example, the standard redox potential (E^0) for the silver/silver chloride redox reaction at 25 °C is +0.222 V (vs. NHE), whereas the redox potential (E) for the BAS silver/silver chloride reference electrode at this temperature is +0.196 V (vs. NHE).

The above equations show that variations in the chloride ion concentration in the electrode change the redox potential. Since there is generally a large chloride concentration gradient across the reference electrode frit, there is slow diffusion of chloride ions from the reference electrode solution into the sample solution; that is, the reference potential will gradually change when used. There are some precautions that can be taken to minimize this potential drift. When the electrodes are made, the Vycor frit is covered in plastic to prevent leakage. This plastic should be carefully removed immediately upon receipt, and the Vycor frit should be immersed in a 3M aqueous sodium chloride solution. The reference electrode should also be removed from the electrochemical cell and stored in this solution between experiments (this is particularly important when using non-aqueous solvent systems, for reasons discussed below). Occasionally, air bubbles will form in the solution next to the Vycor frit; these should be removed by gently flicking the end of the electrode.

Saturated Calomel Reference Electrode

The redox process for this electrode is

$Hg_2Cl_2 + 2e^- <=> 2Hg + 2Cl^-$

The BAS RE-2 saturated calomel electrode (SCE) is an H-cell. One arm contains mercury covered by a layer of mercury(II) chloride (calomel). This is in contact with a saturated solution of potassium

chloride; a porous Vycor frit is again used for the junction between the reference electrode solution and the sample solution at the end of the other arm.

The RE-2 electrode is provided as a kit requiring user assembly (N.B. the kit does NOT include any mercury). Once assembled, the electrode should be stored with the Vycor frit immersed in a saturated solution of potassium chloride to maintain the chloride concentration in the reference electrode.

Liquid Junctions Potentials

As noted above, the composition of the reference electrode solution (i.e., high chloride ion concentration) is generally different from the composition of the sample solution. This leads to a potential difference across the interface of the two solutions (i.e., the Vycor frit), due to unequal rates of diffusion of the constituent ions through the frit. This liquid junction potential cannot be measured (although it can be estimated), and can cause problems with voltammetric measurements. For example, the redox potentials of a given analyte measured in different solvent systems cannot be directly compared, since the liquid junction potential will be different for each solvent system. However, the junction potential can generally be ignored for a given solvent system provided it is constant and reproducible. If there is any doubt that this is so, an internal reference (e.g., ferrocene) can be used; that is, the reference compound is added to the sample solution at the end of the experiment, and its redox potential is recorded. This approach can also be used to compare redox potentials measured in different solvent systems.

Using Aqueous Reference Electrodes in Non-Aqueous Solvents

There has been much debate over the use of aqueous reference electrodes such as the silver/silver chloride electrode and saturated calomel electrode with non-aqueous solvent systems. One area of concern is the junction potentials across the salt bridge, which can range from tens to hundreds of millivolts; however, as discussed above, such problems can be compensated for by the use of an internal reference. There are two more serious problems; the precipitation of electrolyte and the contamination of the sample solution.

The electrolytes commonly used in reference electrodes (sodium and potassium chloride) are not very soluble in organic solvents, and prolonged immersion of aqueous reference electrodes in organic solvents can lead to precipitation of these electrolytes in the Vycor frit. Salts that are combinations of the ions of the two electrolytes can also be precipitated; for example, potassium perchlorate is insoluble in acetonitrile, and can be deposited in the frit of an aqueous potassium chloride reference electrode in an acetonitrile solution of tetraethyl ammonium perchlorate. Such precipitation can be avoided by judicious choice of electrolytes. For example, sodium perchlorate is much more soluble that potassium

perchlorate, so sodium chloride is used in BAS silver/silver chloride reference electrodes rather than potassium chloride. Tetraethylammonium chloride has also been used as the reference electrode electrolyte, since it is soluble in both aqueous and non-aqueous media (such reference electrodes are not available commercially). The precipitation of electrolyte salts increases the reference electrode impedance and changes the liquid junction potential, which causes the reference potential to change with time. Therefore, prolonged exposure to organic solvents should typically be avoided, and the stability of the reference potential should be regularly checked (by using an internal reference or by comparing with another reference electrode). However, aqueous reference electrodes can be used for bulk electrolysis experiments in non-aqueous solvents, since a large overpotential is typically used and the small potential drift that occurs during the experiment should therefore have little effect (although the magnitude of the potential change should be checked after the experiment).

Another potentially serious problem that can occur is contamination of the sample solution by components of the reference electrode solution (e.g., water and chloride ions). For example, many organometallic compounds are highly reactive to water, and hence cannot be exposed to the small amounts of water that diffuse from the reference electrode during the experiment. One approach that has been used to overcome this has been the use of 'double-junction' reference electrodes, in which the aqueous reference electrode is isolated from the sample solution using a salt bridge containing a non-aqueous solvent/electrolyte system. However, this approach does not rigorously exclude water, so it is not appropriate for highly-water sensitive systems. In addition, there are disadvantages to this approach, as the introduction of the second junction not only alters the reference potential by the addition of another junction potential, it also increases the impedance of the reference electrode.

Another reference electrode modification that can be particularly appropriate for non-aqueous systems is the use of a Luggin capillary. This allows the tip of the reference electrode to be placed very close to the working electrode surface, thereby decreasing the uncompensated solution resistance (R_u) between the reference and working electrodes. However, exact placement of the Luggin probe is required in order to obtain reproducible resistance compensation; in addition, if the tip is too close, part of the electrode surface is blocked, which leads to non-uniform current distribution. The Luggin capillary also increases the reference electrode impedance.

There are two reference electrode systems that do not require water, and hence are suitable for non-aqueous electrochemistry of water-sensitive systems. These are the pseudo-reference electrode and the silver/silver ion electrode.

Pseudo-Reference Electrodes

Pseudo-reference electrodes are simply metal wires (e.g., platinum or silver) immersed in the sample solution. Although such electrodes do provide a constant potential, the reference potential is unknown,

and is dependent on the composition of the sample solution. Consequently, redox potentials measured using a pseudo-reference electrode should be quoted relative to redox potential of the internal reference compound. One advantage of pseudo-reference electrodes is their low impedance.

Silver/Silver Ion Electrode

The redox process for this electrode is

$Ag^+ + e^- <=> Ag$

This electrode is less stable than the aqueous electrodes discussed above (due to diffusion of silver ions out of the electrode and the photoreactivity of these ions), and must be prepared frequently. BAS provides a non-aqueous reference electrode kit, which requires assembly by the user. The BAS non-aqueous reference electrode consists of a silver wire immersed in a solution of silver nitrate or perchlorate (0.001M to 0.01M) and electrolyte (e.g., 0.1M TBAP) in the desired organic solvent. Suitable organic solvents include acetonitrile, dimethylsulfoxide, methanol, ethanol and tetrahydrofuran. Silver ions are reduced by dimethylformamide and are insoluble in methylene chloride; these solvents are therefore not suitable for this reference electrode (acetonitrile can be used as the reference electrode solvent when one of these other two solvents is used for the sample solution).

The potential for the silver/silver ion reference electrode depends on the solvent, the silver ion concentration as well as the nature and concentration of the electrolyte. It is also changed by the introduction of salt bridges, which are used to decrease contamination of the sample solution by silver ions.

Reference Electrode Impedance

The impedance of the reference can have a significant effect on the current response of the cell. A high impedance reference electrode can not only slow the response of the potentiostat (slow rise time), it also increases the susceptibility of the system to environmental noise (particularly power line noise). There are a number of factors that can increase the impedance (see above), and the construction of the reference electrode can require careful consideration.

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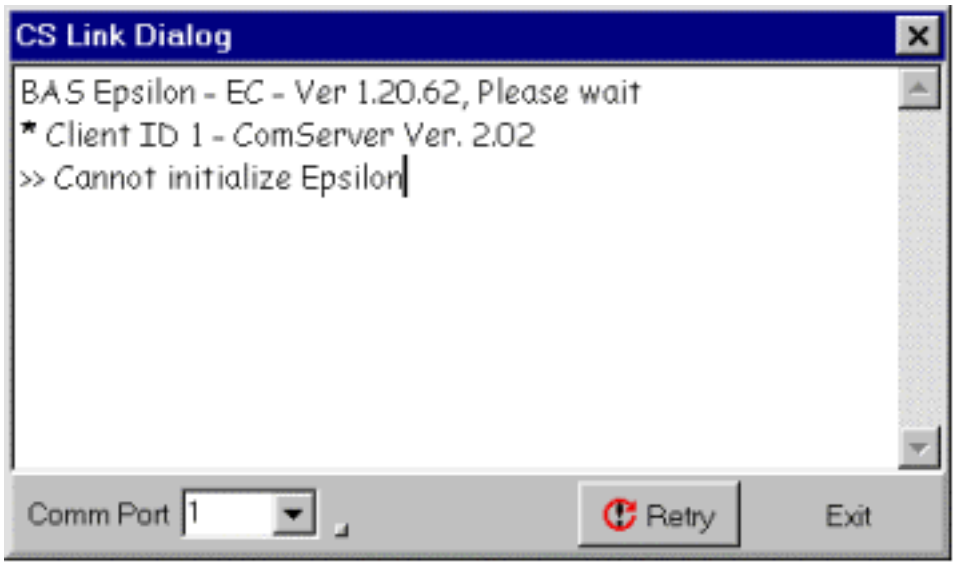
Troubleshooting

Epsilon will not link with computer and following dialog box appears:



1. Click the **Retry** button.
2. Check that the epsilon is turned on.
3. Check the cable between computer and epsilon. Verify the computer comm port number matches the number in the dialog box.
4. Make sure that there are no other programs running that require the comm port specified for the epsilon.

The epsilon links with computer, but it does not take data (e.g., runs freeze at end of Quiet Time).

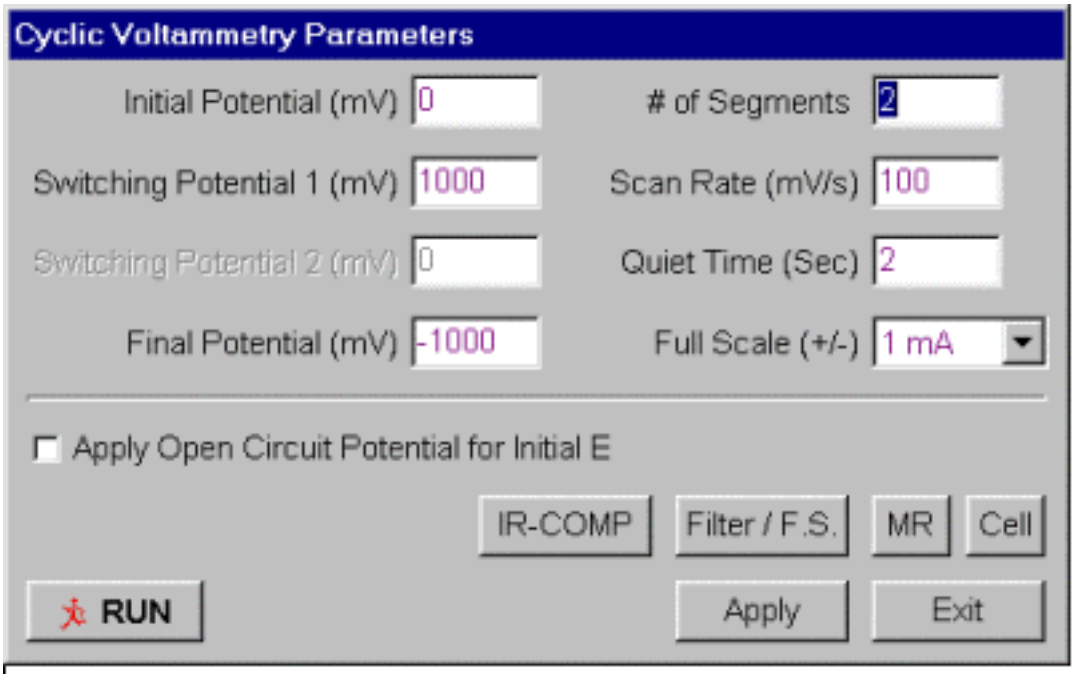
1. Go to the **Experiment** menu and click on **Update Hardware**. The epsilon program will close and the **Update** program will open.

2. Click on **Send BAS-Epsilon Information File**.
3. Contact BAS about the problem and send BAS the file, either by e-mail or fax.

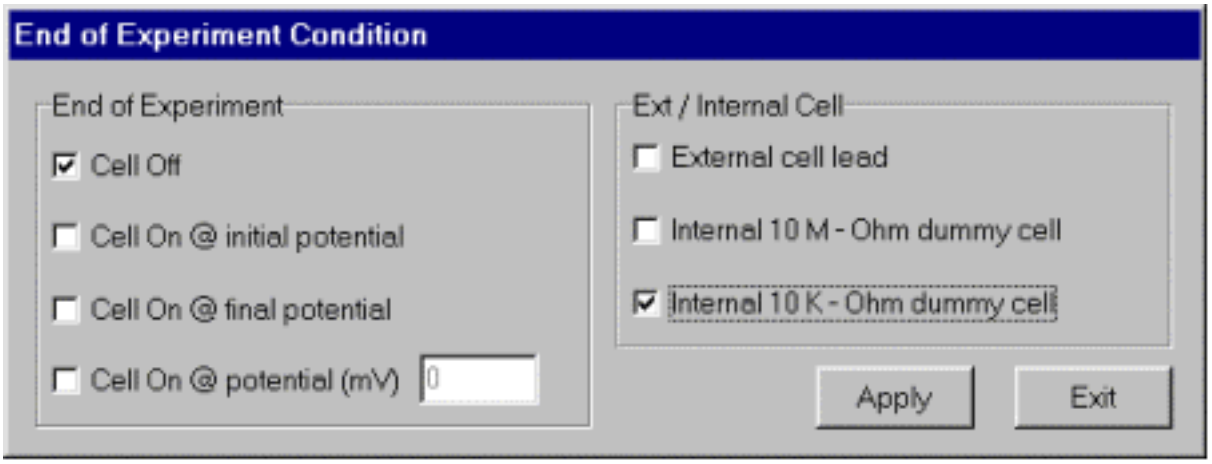
The epsilon appears to have an electronics problem.

Perform the following analog electronics test.

1. Open a **New Cyclic Voltammetry** experiment, set the parameters as shown and then click **Apply** button.

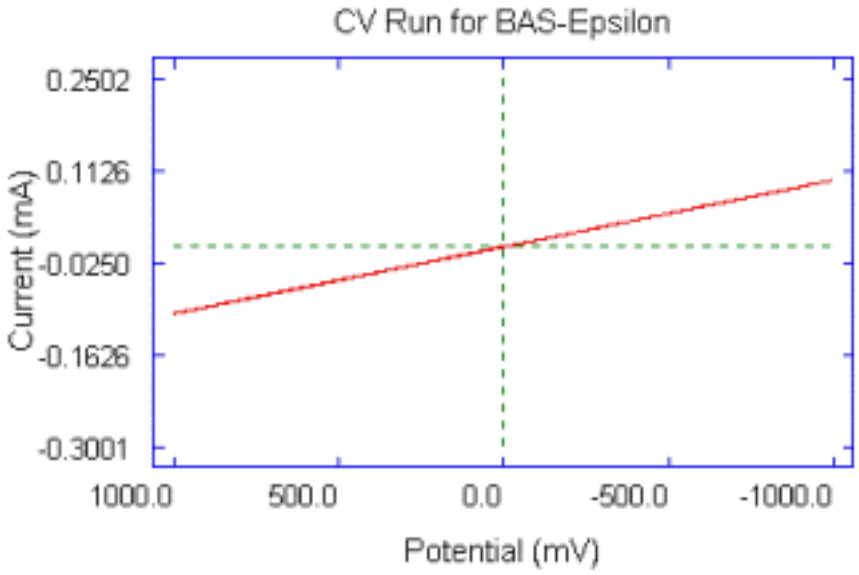


2. Click the **Cell** button.



3. Check the **Internal 10K-Ohm dummy cell** box.

4. Click **Apply**, followed by **Exit**.
5. Run the experiment. The plot should be a sloping line going through 0 from -0.1 mA to 0.1 mA (as shown below).



If the epsilon passes this test, then the problem could be in the cell lead, but is more likely to be with the cell.

All l.e.d.s on front panel stay lit after power up.

Call BAS service.

Some techniques are marked demo.

If some techniques are marked demo, then they have not been enabled in that particular epsilon instrument. Contact BAS for price quote to add the additional techniques to the instrument.

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Fan Filter

The epsilon and other BAS instruments use cooling fans to prevent overheating. These fans have filters which prevent dust from entering the instrument. As dust accumulates the volume of airflow decreases, reducing the cooling efficiency.

CLEAN THE FAN FILTER EVERY THREE MONTHS, OR MORE OFTEN IF VISIBLY DIRTY.

Clean the filter as follows:



1. Remove the front panel of the epsilon to access the filter.
2. Grab the filter retaining grid by pinching one of the slots and pull it off. (Do not undo any screws -- these hold the entire fan in place!)
3. You may vacuum the filter or wash it in warm sudsy water. Be careful not to tear it.
4. If you've washed the filter, blot it well between sheets of paper towels, then allow it to dry.
5. Reinstall the filter by holding it in place over the fan opening, then snapping the retaining grid in place.
6. Replace the front cover

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HOW TO CONTACT BAS

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WARRANTY AND SERVICE INFORMATION

Product Warranty Damaged Shipments Service Information

Product Warranty

Bioanalytical Systems, Inc. products are fully warranted against defects in material and workmanship. Epsilon hardware is unconditionally warranted for one year from date of shipment, except when failure is due to obvious abuse or neglect, unauthorized tampering, procedures not described in manuals, or improper connection of electronic units to other components. Electrochemical cells are warranted for 60 days from date of shipment under the same exclusions. Chromatographic columns and injection valves are warranted for 30 days. The following items are not covered under any warranty: carbon paste, activated aluminum oxide, lamps, panel lights, fuses, pump seals, valve seals, reference electrodes.

For any product expressly covered under this warranty, Bioanalytical Systems is liable only to the extent of replacement of defective items. Bioanalytical Systems, Inc. shall not be liable for any personal injury, property damage, or consequential damages of any kind whatsoever. The foregoing warranty is in lieu of all other warranties of merchantability and fitness for a particular purpose.

To activate your warranty, and receive product update information news and valuable information related to this and other BAS products, fill out and return the Warranty Enrollment Card which was shipped with the instrument.

Damaged Shipments

Breakage of any part of this instrument during shipping should be reported immediately to the BAS Service Coordinator. It will be necessary to retain the original packing box and contents for inspection by the freight handler. BAS will replace any new instrument damaged in shipping with an identical product as soon as possible after the claim filing date. Claims not filed within 30 days after shipping date will be invalid.

Do not return damaged goods to Bioanalytical Systems without first contacting the BAS Service Coordinator for a Return Authorization Number (RA#). When a defective part is returned to BAS, the RA# immediately identifies you as the sender and describes the item being returned. Bioanalytical Systems refuses all unauthorized return shipments.

Service Information

Bioanalytical Systems provides a skilled service staff available to solve your equipment-oriented problems. For further details call the BAS Service Coordinator, who may choose to route your problem to the correct individual.

Following discussion of your specific difficulties, an appropriate course of action will be described and the problem resolved accordingly. Do not return any products for service until a RETURN AUTHORIZATION NUMBER (RA#) has been obtained. The RA# identifies you as the sender and describes to us the problem you are having in full detail.

Turnaround time on service can be quoted to you at the time your RA# is issued, although we can not determine the actual amount of service required until we have received your unit and diagnosed the problem. All correspondence and shipments should be sent to:

RA #, Service Department
Bioanalytical Systems, Inc.
2701 Kent Avenue
West Lafayette, IN 47906

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Accuracy Limitations for Sub-nA Galvanostatic Experiments

The epsilon typically has a background current of about 30 pA, and a drift of about 5 pA over an 8 hour period. However, it may be possible to determine the average background current for a given instrument, and hence "correct" the applied current to compensate for the background and drift.

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Peak Area

The measurement of peak area was introduced in version 1.4. Data files saved from previous versions of the software will display peak areas of zero when loaded into version 1.4. The correct peak areas can be calculated by reanalyzing the data. The data files should then be resaved in order to save these peak area values.

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