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CV-50W Version 2.3

January 2001

MF-9093 INSTRUCTION MANUAL

Voltammetric Analyzer

Bioanalytical Systems, Inc

2701 Kent Avenue
West Lafayette
Indiana 47906

www.bioanalytical.com

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1. Introduction

Sweep Techniques
Linear Sweep Voltammetry
Cyclic Voltammetry

Step Techniques
Chronoamperometry
Chronocoulometry

Pulse Techniques
Differential Pulse Voltammetry and Polarography
Normal Pulse Voltammetry and Polarography
Sampled Current Polarography

Square Wave Techniques
Osteryoung Square Wave Voltammetry

Stripping Techniques
Differential Pulse Stripping Voltammetry
Linear Sweep Stripping Voltammetry
Osteryoung Square Wave Stripping Voltammetry

Time Base
Amperometric

Miscellaneous
Bulk Electrolysis with Coulometry

Table 1-1. Electrochemical repertoire of the CV-50W.

Features

- Fifteen techniques
- PC control through Windows interface
- Interaction with other Windows applications
- Point & click user interaction
- High resolution graphics
- 100 µV potentiostat resolution
- True charge to voltage converter for chronocoulometry
- Hardware interfaces with Voltammetric Cell Stand, and Controlled Growth Mercury Electrode,

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- Control of stirring, inert gas purging and mercury drop knock & dispense
- Multiple experimental runs and averaging
- Automatic and manual peak finding routines
- Anson and Cottrell plots
- Laser printer and digital plotter output
- Multiple data set display and printing
- Digital smoothing by Moving Average and Least Squares
- Integration, differentiation, semi-integration and semi-differentiation
- Background subtraction
- Standard math operations
- Data storage (binary and text formats)
- Macro capability

Specifications

I/O

Cell stand port	Custom port for control of BAS Cell Stands and Controlled Growth Mercury Electrode
Data link port	RS-232C serial port for communication between CV-50W and remote PC

Potentiostat

Output compliance voltage	±10 volts minimum
Applied voltage range	-3.276 volts to +3.276 volts
Minimum potential step size	100 microvolts
Absolute accuracy	±2.5 millivolts
Reference input impedance	$>10^{11}$ ohms
Maximum output current	190 milliamperes
Risetime	<2 microseconds
Slew rate	10 Volts/microsecond minimum
Stability	500 microvolts/day
Effects of ±10% input power line variation	100 microvolts maximum
Noise and ripple	100 microvolts RMS maximum

Current to Voltage Converter

Maximum current	190 milliamperes
Ranges	100 milliamperes/volt
	10 milliamperes/volt
	1 milliamperes/volt
	100 microamperes/volt
	10 microamperes/volt
	1 microampere/volt
	100 nanoamperes/volt
Fullscale output	±10 volts

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Input voltage drift	500 microseconds/day maximum
Input current drift	25 picoamperes/day maximum
Conversion rate	20,000 conversions/sec or
	50 microseconds/conversion
Absolute accuracy	1% fullscale
Resolution	0.05% fullscale

Charge to Voltage Converter

Maximum charge	3.2 millicoulombs
Range	10 microcoulombs/volt (auto range)
	1 microcoulombs/volt
	100 nanocoulombs/volt

General

Input voltage	110 volts, 120 volts, 220 volts, 240 volts
Alternating Current	50 or 60 Hertz
Input power	720 watts maximum

Minimum Personal Computer Requirements

Processors	80386, 16 MHz
	80387, 16 MHz
Memory	2 MB RAM
Hard drive	80 MB
Floppy drives	1.2 MB 5.25”
	1.44 MB 3.5”
Ports	2 serial
	1 parallel
Mouse	PS/2
Monitor	14” color VGA

Unpacking and Inspection

Carefully unpack the CV-50W from the shipping containers. Examine all packing materials before discarding it. Inspect all parts for obvious damage. Compare items received with the packing documents.

Damaged Shipments

If any damage has occurred whether obvious or concealed, all claims must be made to the carrier, usually within 15 days of your receiving the shipment; otherwise, the carrier may not honor the claim. Once the item has been assigned to a carrier for shipment, the carrier is responsible for its safe delivery. The following are some guidelines to follow when damage is discovered. You should contact the carrier directly for specific claim procedures.

United Parcel Service (UPS), Parcel Post, Air Parcel Post

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1. Retain container, packing material, and broken item for inspection by the carrier.

2. Write or phone BAS with our order number, the data received and a description of the damage. BAS will do everything possible to expedite repair or replacement of the items damaged.

Air Freight, Express or Truck

1. Contact the local agent of the transportation company immediately and request an inspection.

2. Retain the container, packing material and damaged goods until the examining agent has made an inspection report.

In all of the above cases, do not return damaged goods to BAS without first contacting our customer service personnel for a Return Authorization Number (RA#). When a defective part is returned to BAS, the RA number immediately identifies you as the sender and describes the item being returned. To avoid confusion, BAS refuses all unauthorized return shipments.

Product Warranty

Bioanalytical Systems, Inc. (BAS) warrants equipment by the company to be free from defects in material and workmanship for a period of 1 year from the date of shipment, except as provided hereinafter. This assumes normal usage under commonly accepted operating parameters. BAS agrees to either repair or replace, at its sole option and free of part charges to the buyer, any parts of such instrumentation which, under proper and normal conditions of use, prove to be defective within 1 year from the date of shipment. Electrochemical cells and working electrodes are warranted for 60 days. This warranty and remedy are given expressly and in lieu of all other warranties, expressed or implied, of merchantibility or fitness for particular purpose and constitutes the only warranty made by BAS.

BAS neither assumes or authorizes any person to assume for it any other liability in connection with the sale, installation, service or use of its instrumentation. BAS shall have no liability whatsoever for special, consequential or punitive damages of any kind from any cause arising out of the sale, installation, service or use of its instrumentation.

All products manufactured by BAS are tested and inspected prior to shipment. Upon prompt notification by the Buyer, BAS will correct any defects in warranteed equipment of its manufacture either (by our option) by return of the item to our factory, or shipment of a repaired or replacement part. BAS will not

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be obliged, however, to replace or repair any piece of equipment that has been abused, improperly installed, altered, damaged or repaired by others. Defects in equipment do not include decomposition, wear or damage by chemical action or corrosion.

Limited obligations covered by this warranty include:

a. In the case of instruments not of BAS manufacture, the original manufacturer's warranty applies.

b. Shipping charges under warranty are covered only in one direction. The Buyer is responsible for shipping charges to the factory, if return of the part is required.

c. Expendable items including (but not limited to) carbon paste, reference electrodes, source lights, panel lights and fuses are excluded from this warranty.

Warranty Card

Each BAS analyzer system is shipped with a warranty card which should be completed and returned by the end user. This card will enable us to identify and contact the individual responsible for the operation of the instrument. Please return the card as soon as possible so that we may inform you of product updates and other pertinent technical information.

Extended Warranty Agreement

BAS offers an extended warranty "Full Protection Service Agreement" to customers purchasing this system. Please contact you Sales Representative or the Service Department at BAS for further details.

Service Information

Bioanalytical Systems provides a skilled staff available to solve you technical and equipment-oriented problems. For service, call (800) 845-4246 during normal working hours (Eastern Standard Time the year round) and ask for Customer Service. The operator will route your problem to the correct individual. Following discussion of your specific difficulties, an appropriate course of action will be described and the problem will be 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 the problem you are having in full detail. All correspondence and shipments should be sent to:

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

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2. Installation

The installation of the CV-50W Voltammetric Analyzer can be divided into 2 parts: installation of the potentiostat and installation of the Personal Computer (PC). These will be considered in turn.

2.1 Installation of the CV-50W Potentiostat

Placement

As the potentiostat stands in a vertical position, it requires little bench space. However, adequate space should be left near the Analyzer for the PC and any other accessories (e.g., Cell Stands, Low Current Module, Rotating Disk Electrode). In addition, the area in front of the Analyzer should not be obstructed, as an airflow through the Analyzer is required for cooling.

Power Requirements

The potentiostat can be powered by any of the following A.C. voltages: 100V, 120V, 220V, 240V. The A.C. frequency may be either 50 or 60 Hz. The main power source in the location must be the same as the voltage selected in the power cord connector on the rear panel of the potentiostat (Figure 2-1). For best results, an isolated power line is recommended.

All potentiostats are configured for the correct voltage and frequency for the "SHIPPED TO" destination. If the instrument is going to be operated at a voltage other than the standard voltage for the "SHIPPED TO" area, then a change must be made to the input power connector. The instructions for changing the voltage requirements are discussed below.

110/120 Volts and 60 Hz Operation

110/120V and 60 Hz are the standard power requirements for the Analyzer and its peripheral devices. All of these can be plugged into the usual mounted, main power outlets.

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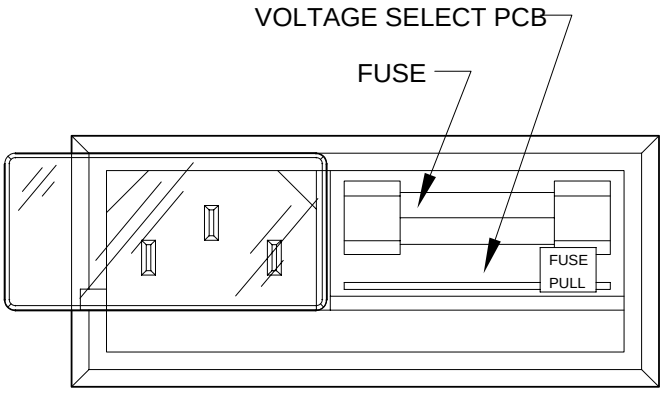


Figure 2-1. Power connector and voltage select.

Before plugging the Analyzer power cord into a power socket, confirm that the correct voltage has been selected in the power cord connector. This is done as follows:

a. Remove the power cord from the power cord connector.

b. Slide the plastic window to the left to expose the voltage select printed circuit card (this card is shown in Figure 2-1). The orientation of this card in the connector determines the voltage option.

c. If the number printed on the outer edge of the board does not correspond to the available voltage, pull out the card (the fuse must be removed first), and turn it (either by rotation or inversion) such that the desired voltage is exposed on the outside edge of the top board. Reinsert the board and replace the fuse.

If the potentiostat is operated from a power outlet without a safety ground connection, an appropriate adapter must be used. The ground connection of this adapter must be securely fastened to an external earth ground for safety and proper operation. A proper ground connection cannot be overemphasized.

The power cord is shipped as a separate item and must be plugged into the connector on the rear panel. To insert the power cord into the power socket, push up the plastic window and plug in the female end of the power cord. The plug type on the male end of the power cord may vary depending on the country of destination.

The A.C. frequency is checked for 50 or 60 Hz operation during the Self-Test sequence of the potentiostat that occurs on power up (see Section 5.11 for more details on this Self-Test).

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220/240V and 50 Hz Operation

220/240V and 50 Hz are the standard power conditions available in many countries. The potentiostat can operate using such power sources.

To check or change the power requirements of the potentiostat:

a. Remove the power cord from the power cord connector.

b. Slide the plastic window to the left to expose the voltage select printed circuit card (this card is shown in Figure 2-1). The orientation of this card in the connector determines the voltage option.

c. If the number printed on the outer edge of the board does not correspond to the available voltage, pull out the card (the fuse must be removed first), and turn it (either by rotation or inversion) such that the desired voltage is exposed on the outside edge of the top board. Reinsert the board and replace the fuse.

If the potentiostat is operated from a power outlet without a safety ground connection, an appropriate adapter must be used. The ground connection of this adapter must be securely fastened to an external earth ground for safety and proper operation. A proper ground connection cannot be overemphasized.

The power cord is shipped as a separate item and must be plugged into the connector on the rear panel. To insert the power cord into the power socket, push up the plastic window and plug in the female end of the power cord. The plug type on the male end of the power cord may vary depending on the country of destination.

The A.C. frequency is checked for 50 or 60 Hz operation during the Self-Test sequence of the potentiostat that occurs on power up (see Section 5.11 for more details on this Self-Test).

Cell Connection

The cell lead cable is the group of wires that connects the Analyzer electronics to the electrodes of the electrochemical cell. One end of this cable plugs into CELL on the rear panel of the potentiostat and the other end is attached to the electrodes. This may be a direct connection using the general purpose cable sent with the Analyzer or one for attachment to a cell stand such as the BAS C3 Cell Stand.

The general purpose cell cable terminates with alligator clips that attach directly to the cell electrodes (Figure 2-2). There are 3 electrode leads and 1 grounded (shielding) lead.

The color code is:

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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

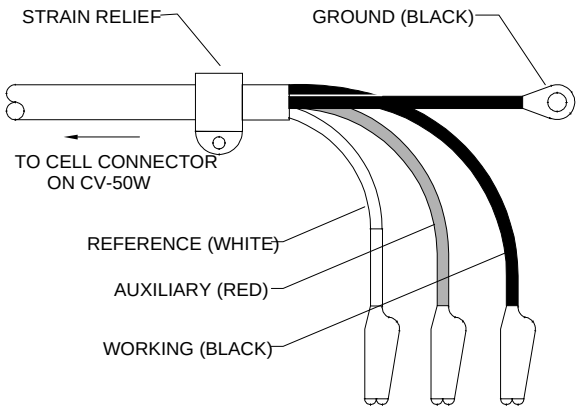


Figure 2-2. Cell (electrode) end of cell cable.

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

Cell Stand Connector

This connector is used to control cell stand functions (i.e., stirring, gas purging and drop knocking), and is plugged into the CELL STAND port on the rear panel of the potentiostat.

There are 3 cell stand configurations available for the CV-50W Analyzer (through **Setup** in the **File** menu). One configuration (**C2**) is for the BAS C2 and C3 Cell Stands, and the other two are for the BAS Controlled Growth Mercury Electrode (CGME) - one for the SMDE mode (**SMDE**) and one for the CGME mode (**CGME**).

BAS C2/C3 Cell Stands

The purging and stirring functions on the BAS C2 and C3 Cell Stands can be controlled manually or through the CV-50W. The REMOTE port on the rear of the Cell Stand is connected via a 25 pin ribbon cable to the CELL STAND port on the rear panel of the potentiostat.

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CGME

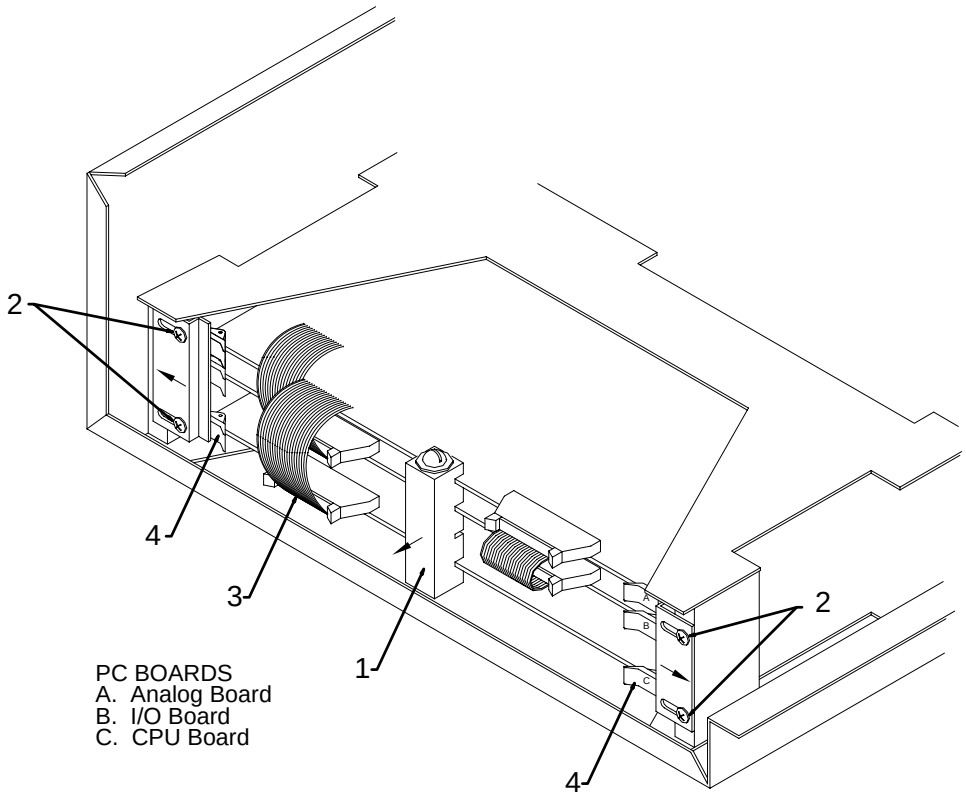
The purge and stir functions on the BAS Controlled Growth Mercury Electrode (CGME) can be controlled manually or through the CV-50W. In addition, the knock and dispense routines required for the SMDE and CGME modes are controlled by the CV-50W, and the **Cell Stand** option in the **Setup** dialog box must be set appropriately.

Data Link

This port is used to communicate with the external PC via the cable and one of the serial communication ports (COM ports) on the PC via a standard RS-232C cable.

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2.2 Installation of Replacement ROMs in the CV-50W



a) Remove white plastic board support (Item 1).

b) Loosen four designated screws (Item 2) on card rack and slide card retainer plates outward.

c) Remove necessary ribbon cables (Item 3) by pressing ejectors outward from connectors and remove.

d) Remove the old CPU board (bottom board) by pressing ejectors (Item 4) outward and pulling boards straight out. NOTE: Many of the large scale integrated circuits are static sensitive. DO NOT place on plastic (e.g., bubble pack), carpeting or other surface which may have static build-up.

e) Lay CPU board (Figure 2-3) on a flat surface. Components of the CPU board are sensitive to static. Do not lay the board on carpeting, plastic (e.g., bubble wrap), or other surfaces that build up static charge.

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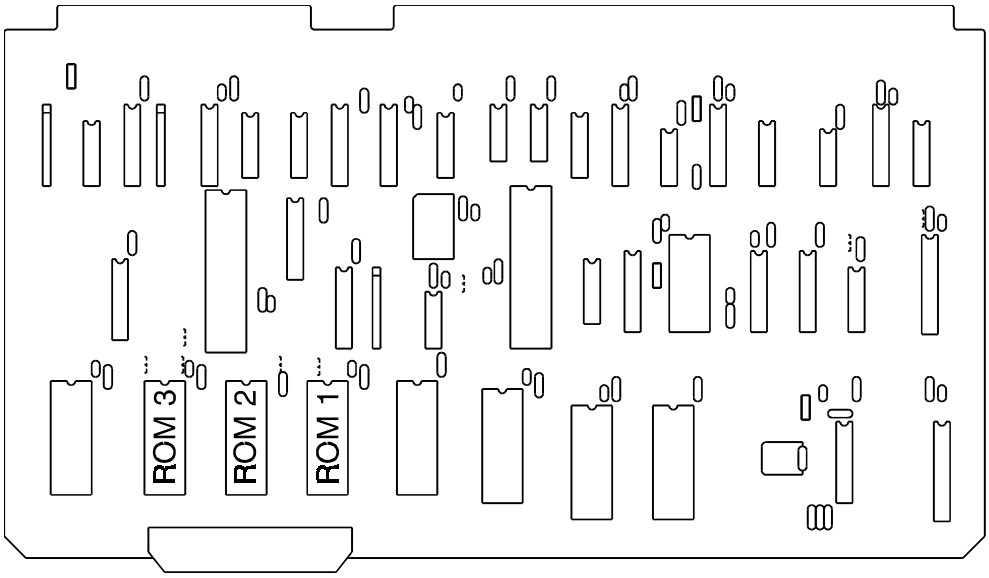


Figure 2-3. CPU Board

f) Carefully pry ROM 1 out of its socket - be careful not to bend the legs of the chips.

g) Properly align new ROM1 on the socket and press in. It is imperative that the chip oriented as shown in Figure 2-3 (notched end away from the board edge with the ribbon cable connector). Be careful not to bend the legs and ensure that all the legs are inserted into the socket.

h) Replace ROMs 2 and 3 in the same way, and reinstall board.

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2.3 Personal Computer (PC) Installation

Machine Requirements

The BAS Windows software was written for use on BAS PCs. Other IBM compatible PCs may be able to run this software, but there are no guarantees.

The MINIMUM requirements for the BAS Windows software are:

a) 80386 processor running at 16 MHz, together with a math co-processor.

b) Hard disk drive.

c) MS-DOS version 5.0 or greater.

d) MS-Windows 3.1 or greater.

e) VGA monitor.

f) 2 serial interface connectors (one for communication with the Electrochemical Analyzer and one for plotting using a serial port plotter)

g) 1 parallel interface connector for a parallel port printer (e.g., laser printer).

h) PS/2 mouse (do NOT use a serial mouse).

PC Connections

The important connections are:

a) VGA video display connector.

b) Keyboard connector

c) PS/2 mouse connector

d) Power cable connectors for the system unit and the monitor. The female ends the two power cables should be connected to these. The male end of the monitor power cable should be plugged into the power socket on the rear of the system unit. The male end of the system unit power cable should be connected to a grounded power strip or outlet. It is VERY important to check that the correct voltage has been chosen using the line voltage connector (110/220 V). It is also advisable to install a line noise/surge protector between the power source and the PC.

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e) Serial interface connectors (COM1 and COM2). These can be used for any serial RS232C device; for the CV-50W, they are used for communication with the potentiostat and for plotting. COM1 is connected with the DATA LINK port on the rear panel of the potentiostat, and COM2 is connected with the chosen plotter.

f) Parallel interface connector. There is one parallel interface connector (LPT1), which is used to connect a parallel printer via a parallel printer cable.

Setting up the BAS PC is described in more detail in the enclosed User's Guide.

Once the above connections have been made, the system unit and monitor can be powered up.

Software

All BAS PCs are shipped with MS-DOS, MS-Windows and CV-50W Windows software already loaded on the hard disk drive, which is labeled as the C: drive. If a non-BAS PC is being used, the CV-50W Windows software is loaded according to the following instructions (which assume that MS-DOS and MS-Windows have already been loaded).

1. Enter by Windows by typing win at the DOS prompt.

2. Insert the CV-50W software disk into the appropriate floppy disk drive.

3. Select **Run** from the **File** menu in the **Program Manager**, enter **a:install** (or **b:install**) in the **Command Line** (Figure 2-4), then click **OK**.

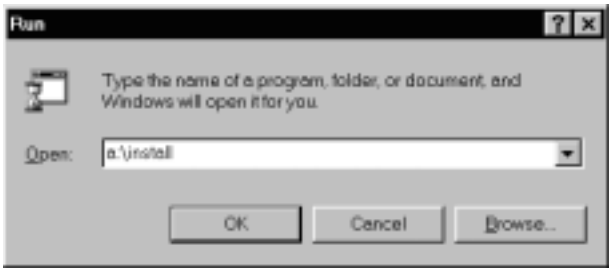


Figure 2-4. Run dialog box.

4. The **Install** dialog box will appear (Figure 2-5). Unless specified otherwise, the CV-50W software will be installed in the \CV50W directory created by the installation routine. The CV-50W icon will be installed in the BAS Programs group. Click **Install CV50W** to start the installation.

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Figure 2-5. Install dialog box.

5. The CV-50W software is opened by double-clicking the CV-50W icon. Before any operation, it is advisable to check that the communication parameters are correct. These are contained in the **Setup** dialog box in the **File** menu (Figure 2-6).

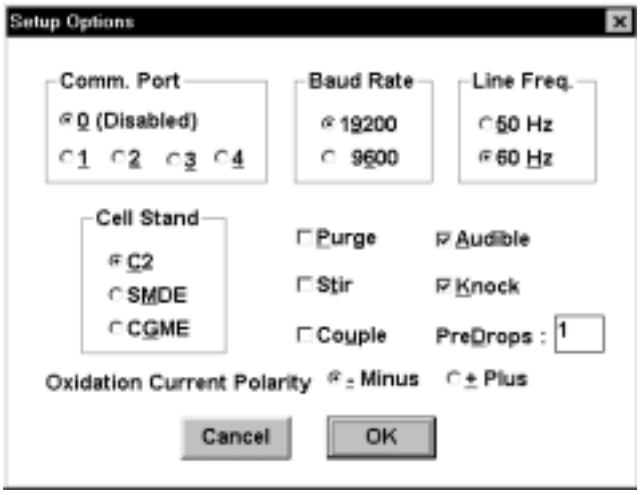


Figure 2-6. Setup dialog box.

The **Setup** communications options are as follows:

Com Port — This specifies which PC communications port is connected to the potentiostat. A value of 0 disables the communication.

Baud Rate — This specifies the rate at which information is transferred between the PC and the potentiostat.

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Line Freq. This specifies the line frequency of the local A.C. voltage. The selected frequency determines the default **Sample Width** for pulse experiments.

Cell Stand The CV-50W can control the purging and stirring for BAS Cell Stands and the BAS Controlled Growth Mercury Electrode (CGME). The knock/dispense routines for the **SMDE** and **CGME** modes of the Mercury Electrode are also controlled by the CV-50W, so the **Cell Stand** option must be set accordingly.

The other parameters in the **Setup** dialog box are discussed in Section 3 (see page 3-4).

Once the **Setup** communication parameters have been checked, the potentiostat can be powered up. The system is now ready for use.

Printer/Plotter Configuration

Although a printer/plotter can be selected using the **Print** Options dialog box (see Section 9.2), the appropriate driver must first be installed. The drivers for older models of printers/plotters are contained on the Windows 3.x disks, and are installed using the Printer dialog box in the Control Panel. However, the drivers for more recent models have to be provided by the printer manufacturer, and require a different method of installation; however, explicit instructions are typically provided with the printer, so installation should cause no problems.

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3. File Menu

3.1 File Dialog Box

The CV-50W software uses standard Windows file dialog boxes for transfer of data files between disk drives and the main memory and for other file manipulation. The **Load Data File** dialog box is shown in Figure .

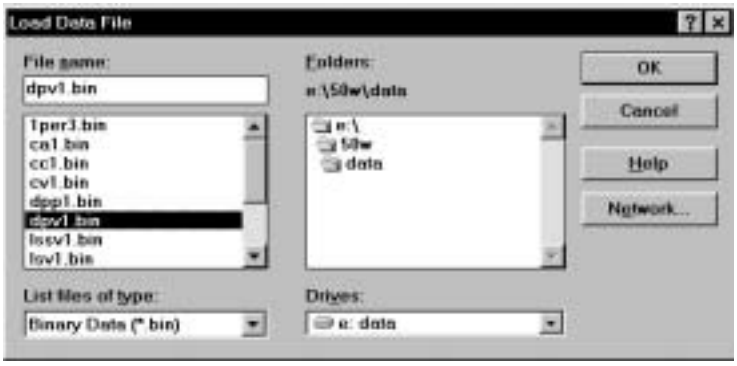


Figure 3-1. File dialog box.

File Name

This field is used to specify the name of the file, which can be either typed or selected from the **File List box** below. Once the file name is shown in the field, click **[OK]** to activate the selected operation.

File List box

This list box lists all files of the type specified in the **List Files of Type** field from the sub-directory selected in the **Directories List** field. To select a file, double-click on the file name or click on the file name and then click **[OK]**.

To select two or more data files (for commands that accept multiple files) drag the mouse over the desired file names or hold down the **<Shift>** key as you select the first and last files in the group. If the files are separated, hold down the **<Ctrl>** key while selecting. Multiple files must be in the same directory.

List Files of Type

CV-50W recognizes its own files by using specific extensions, such as .BIN, .TXT or .MOD. If only one extension type is permitted, then that type of file is selected automatically. When more than one type of file is allowed,

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the program initially selects the previous choice, but allows selection of the alternate file types.

Directories List — The current pathname is shown above this list box, and is updated when a different disk drive or directory is selected. The path is changed by selecting one of the directories shown in this list and then clicking [**OK**] or pressing <**Enter**> (alternatively, you can double-click on the desired directory). Files in the selected directory (which is now the default directory) will then be listed in the **Files List**.

Drive Select — This drop-down list box show the current disk drive. To select a different drive, click on the [**Down-Arrow**] box and select the desired drive.

3.2 Load Data

The **Load Data** command reloads a data file previously saved by the 100W software, in either binary (.BIN) or text (.TXT, .CRL, .SPC and .TAB) format. .TXT files from earlier BAS File Service programs can also be loaded.

3.3 List Data

The **List Data** command lists the data currently in main memory. This allows review of the data without having to save the data as a text file. During listing, you can press <**Enter**> to Pause the listing or press <**Esc**> to Cancel further lines or click on [**Pause**] or [**Cancel**] in the CV-50W Listing box.

3.4 Save Data

Data can be saved in the CV-50W's compact binary (.BIN) format or in the text (.TXT, .CRL, .SPC and .TAB) format, which can be read by other programs.

3.5 List Text File

The **List Text File** command is used to list data files previously saved in the text (.TXT, .CRL, .SPC and .TAB) format. Any text file having the .TXT, .CRL, .SPC and .TAB extension can be listed. During listing, you can press <**Enter**> to Pause the listing or press <**Esc**> to Cancel further lines or click on [**Pause**] or [**Cancel**] in the CV-50W Listing box.

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3.6 Convert Files

Convert Files is used to convert data files between the binary (.BIN) and text (.TXT, .CRL, .SPC and .TAB) formats. Up to 100 files can be selected. After the file(s) have been selected, the program prompts you to confirm the number of files. The text format is determined by the **Text Data Format** dialog box (3.10).

As the converted files are listed on the screen, you can press <**Enter**> to Pause the listing or press <**Esc**> to Cancel further lines or click on [**Pause**] or [**Cancel**] in the CV-50W Listing box.

Note: Files cannot be directly converted from one text format to another text format.

3.7 Delete Files

Delete Files can delete up to 100 files of any type. After the file(s) have been selected, the program prompts you to confirm the number of files.

As the deleted files are listed on the screen, you can press <**Enter**> to Pause the listing or press <**Esc**> to Cancel further lines or click on [**Pause**] or [**Cancel**] in the CV-50W Listing box.

3.8 Rename Files

The **Rename Files** command allows the names of up to 100 files of any type to be changed. After the file(s) have been selected, the program prompts you to enter the new file name.

3.9 Setup

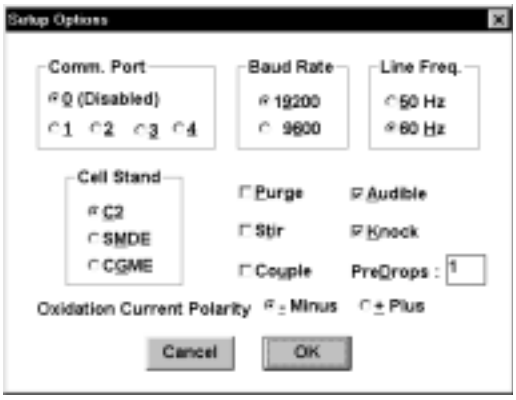


Figure 3-2. Setup dialog box.

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Com Port This specifies which PC communications port is connected to the potentiostat. A value of 0 disables the communication.

Baud Rate This specifies the rate at which information is transferred between the PC and the potentiostat.

Line Freq. This specifies the line frequency of the local A.C. voltage. The selected frequency determines the default **Sample Width** for pulse experiments - 17 ms for 60 Hz and 20 ms for 50 Hz (1 line cycle is selected in order to minimize line frequency interference).

Cell Stand The CV-50W can control the purging and stirring for the BAS Cell Stands and the BAS Controlled Growth Mercury Electrode (CGME). The knock/dispense routines for the **SMDE** and **CGME** modes of the Mercury electrode are also controlled by the CV-50W, so the **Cell Stand** option must be set accordingly.

Purge/Stir This activates purging/stirring between experiments.

Couple This couples purging and stirring during the deposition step of stripping experiments.

Audible This activates a beep before and after each run

Knock This synchronizes the drop knock/dispense of a mercury electrode with the end of the potential pulse. If **Knock** is not checked, then no knock or dispense will occur before or during the experiment when using the **SMDE** or **CGME** modes (however, if **Controlled DME** in the **Controlled Growth** dialog box is checked, then the valve is held open, but no knock occurs).

PreDrops This is the number of mercury drops dispensed from a mercury electrode before the start of an experiment (provided the **Knock** option is checked). For **SMDE** experiments using the BAS CGME, the number of **Pre Drops** depends on the selected drop size as well as the number entered. For **CGME** experiments, the number of **Pre Drops** delivered will match the number entered, regardless of the drop size, and entering 0 will allow the same drop to be used for multiple experiments (except in polarography experiments).

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Oxidation Current Polarity	This specifies the sign of an oxidation current - positive (IUPAC convention) or negative (classical convention).

3.10 Text Data Format

When data are listed on the screen, or saved in a text format, each data point includes an X value (typically potential or time), and one or more Y values (typically current or charge). The **Text Data Format** dialog box provides a selection of data column delimiters.

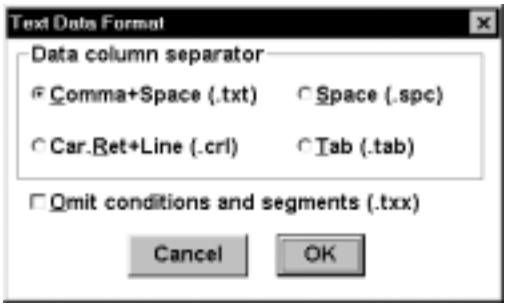


Figure 3-3. Text Data Format dialog box.

The file extension for each format option is indicated in parentheses. The default delimiter is **Comma + Space**, and the default extension is **.txt**.

Omit conditions and segments will allow conversion of **.bin** to a text format without the header and the separators between segments. These files cannot be loaded back into the 100W program.

3.11 Exit

Upon exiting the software, the method parameters for the last experiment are saved in a TEMP.MOD file, and the **Setup** options, **Graph Options** and **Colors**, window sizes and positions are saved in a 50W.INI file.

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4. Method Menu

4.1 Load/Save Method

This allows an experimental **Method** (.MOD) to be **Load**ed or **Save**d. Method files contain the parameters entered in the **Method** and **Control** menus, and the **Results Options**. These operations are performed using standard Windows file dialog boxes.

4.2 Select Mode

There are 15 **Technique**s available on the CV-50W, which are divided into 9 **Categories**. When a given **Category** is highlighted, the modes associated with that Category are displayed in the **Technique** list box (Figure 4-1). The required technique can then be selected. After selection, the **General Parameters** dialog box is automatically opened (Figure 4-2).

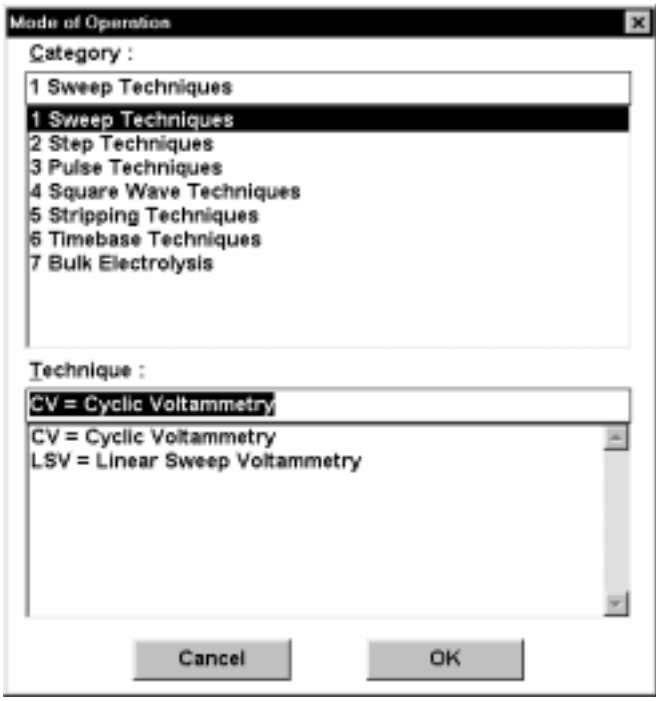


Figure 4-1. Select Mode dialog box.

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4.3 General/Specific Parameters

Some electrochemical techniques require many different parameters, and this can cause confusion. For ease of operation, the parameters are divided into two categories, **General** and **Specific**.

General Parameters must be set by the user for each experiment, as there are no standard values for these parameters. **General parameters** always include the potential range (**Initial E**, **Final E**, **High E** and **Low E**) and the **Sensitivity** (the gain of the current-to-voltage converter) (Figure 4-2).

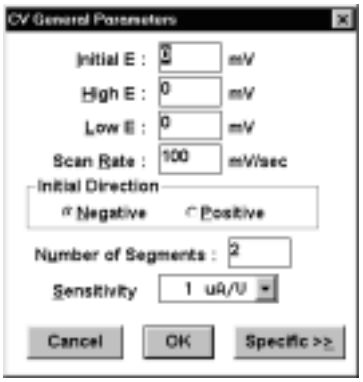


Figure 4-2. General Parameters dialog box for **CV**.

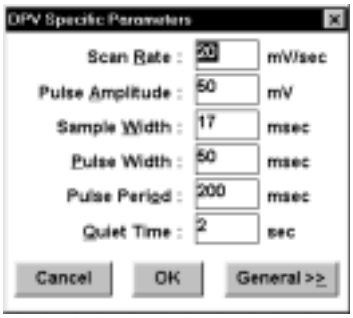


Figure 4-3. Specific Parameters dialog box for **DPV.**

Specific Parameters have default values, which have been chosen to be reasonable for most conditions. They do not have to be set by the user for each experiment, although values other than the default values can be entered. **Specific Parameters** typically include the parameters that define the potential wave form (for techniques other than linear sweep, potential step and time base); for example, the **Amplitude** and **Frequency** of the square wave potential and the **Sample Width**, **Pulse Width** and **Pulse Period/Drop Time** for pulse experiments (Figure 4-3).

4.4 List Parameters

The **List Parameter** command lists the present values of the **General** and **Specific Parameters**.

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4.5 Filter

Analog filtering is used during data acquisition to lower the output noise. The analog filtering in the CV-50W is a two stage network (Figure 4-4). The first stage is an RC filter, which is followed by a Bessel filter. The filtering characteristics of each stage can be varied, and are related to the time scale of the technique being used. The capacitor in the RC filter should be chosen to give a time constant (RC) that is at least 10 times smaller than the time scale of the experiment. Similarly, the cut-off frequency for the Bessel filter must be at least 10 times larger than the frequency of the electrochemical technique being used. If too much filtering is used, then significant distortion of the experimental data can occur.



Figure 4-4. Filter dialog box.

The amount of filtering used can be determined automatically using the **Auto** option (this is the default option). It is generally advisable to use this option. However, the filters can be changed by the user through the **Manual** option (the desired filter is selected fromdrop-down list boxes).

4.6 Deposit Options

Deposit Options is used to define the deposition potential for stripping experiments. The default for this parameter is the initial potential for the potential scan (**Initial E**). If some other potential is required, then the **Deposit E** option should be selected, and the required potential should be entered in the **Deposit E** field (Figure 4-5).

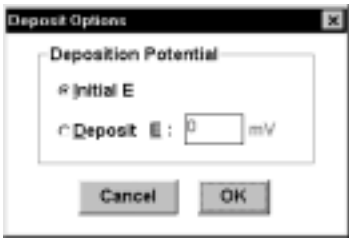


Figure 4-5. Deposit Options dialog box.

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4.7 Stabilizing Capacitor

A stabilizing capacitor is only required when using iR compensation, or for Bulk Electrolysis (**BE**) experiments. In both these cases, the **Auto** option switches a 0.1 µF or 1 µF capacitor into the circuit. The **Manual** option generally only needs to be used when using the **Manual iR** option (Figure 4-6). The **Manual** option should be used with caution, since the addition of capacitors can affect the frequency response of the system.

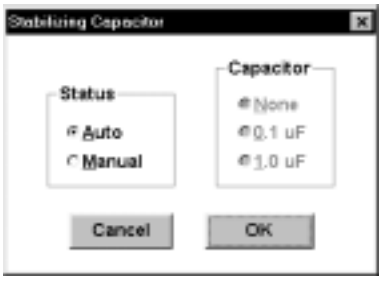


Figure 4-6. Stabilizing Capacitor dialog box.

4.8 Controlled Growth

This specifies drop growth parameters for the CGME mode of the BAS Controlled Growth Mercury Electrode for both pulse and stripping experiments (Figure 4-7). The **CGME** mode must be selected for the **Cell Stand** options in the **Setup** dialog box for this item to be activated.

In the **CGME** mode, the mercury drop is grown using a series of valve openings (pulses). There are three parameters that defined this series: **Pulse Width** (the duration of each pulse), **Number of Pulses** and **Delay Time** (the time between the pulses). These parameters are entered under **Knock and Dispense Control**.

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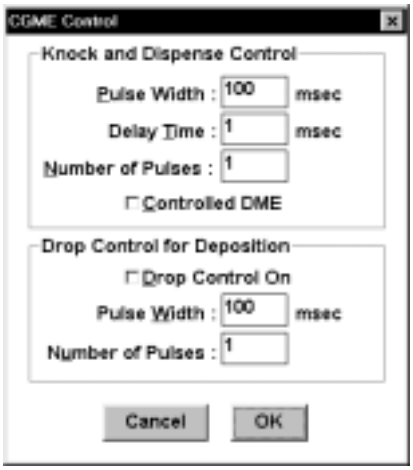


Figure 4-7. Controlled Growth dialog box.

The CGME can also be used as a DME when in the **CGME** mode by activating the **Controlled DME** check box. This will open the valve at the start of the experiment and close it at the end of the experiment. The mercury will flow freely during the course of the experiment and the **Dropping Time** (i.e., the time between activations of the drop knocker) is selected using **Specific Parameters** (the natural drop time at low potentials in aqueous solution for the standard 150 μm capillary is typically slightly less than 1 s).

The **CGME** mode can also be used for anodic stripping voltammetry (Z. Kowalski and J. Migdalski, Electroanalysis 4 (1992) 915). The mercury drop is grown incrementally during the deposition step using a series of pulses. The drop size is again determined by the **Pulse Width** and the **Number of Pulses**, which are entered under **Drop Control for Deposition**. The incremental growth in activated by clicking the **Drop Control for Deposition** check box. The Delay Time is determined by the **Deposit Time** and the **Number of Pulses**: if the **Deposit Time** is 60 s and the **Number of Pulses** is 4, then the pulses will occur at the beginning and at 15, 30 and 45 s of the **Deposit Time**.

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5. Control Menu

5.1 Start Run

This command (or **F2**) initiates the experiment. During runs, all menus are disabled except the **Control** commands: **Start Run**, **Hold/Continue Run**, **Reverse Scan** and **Stop Run**. After completion of the run, the menus are re-enabled according to the present mode and data set.

After a single run, the graph is replotted according to the present **Graph Options** if data are available. The **Filename** label that appears above the graph is cleared to indicate that the data are not yet saved. For single runs, the data are not saved automatically; the **Save Data** command in the **File** menu must be used.

5.2 Hold/Continue

Clicking this option (or **F3**) holds the experiment at a given potential. The experiment can be restarted by clicking the option again.

5.3 Reverse Scan

The command (or **F4**) reverses the direction of the potential scan for **CV** experiments. The data for experiments in which this function has been used should be saved as text files (binary files will not save the revised potential values correctly).

5.4 Stop Run

This command (or **F5**) stops the experiment.

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5.5 Run Options

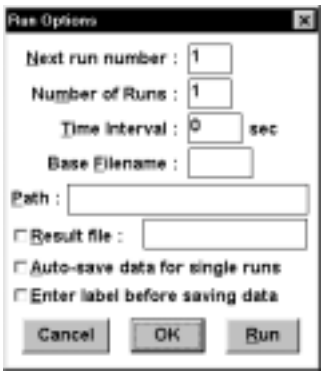


Figure 5-1. Run Options dialog box.

This command allows some automation when running experiments.

a) It allows repeated experimental runs under the same conditions. The **Number of Runs** and the **Time Interval** between the runs must be specified by the user (Note: the **Time Interval** is in addition to the time required to transfer the data to disk). The data files are stored automatically after the run in the binary (.BIN) format (the **Base Filename** and the **Path** (drive and directory) must be specified by the user). The first run starts immediately after [**OK**] is selected, unless a warning is given that existing files will be overwritten by this operation. During each run, the title of the graph shows the filename of that run. Between runs, a small dialog box shows the filenames of the previous and next runs, and the time remaining before the next run. The filenames of the completed runs are listed in the **Main** window.

   If the **Find peaks after run** box is checked (**Results Options** in the **Analysis** menu), a **Results Graph** and **Results List** is produced after each run, rather than a **Single Graph**. Note that is may require additional time to calculate the results: therefore, if the **Time Interval** between runs is critical, this option should be unchecked.

   Pressing <**Esc**> at any time during a series of **Multiple Runs** will abort the present run and any further runs.

   The number of the first run can be specified using **Next Run Number**. This allows a previous set of multiple runs to be continued.

b) If a **Result file** name is entered, the program creates a file containing one result line for each run, nicely formatted according to the **Data Column Separator** option selected in the **Text Data Format** dialog box. Both multiple and single runs append lines to the result file if it is enabled. Comma+Space format (.CSV

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extension) and Tab format files are very easy to import into Excel. For convenience of importing, all text labels are extracted from the Result file, leaving just the data values. Note: Car. Ret + Linefeed format works differently than the other formats--it saves an exact copy of all lines listed on the screen during each run.

c) The data from single experimental runs can be save automatically by clicking **Auto-save data for single runs**. The **Path** and **Base Filename** must be specified.

d) Clicking **Enter label before saving data** allows the user to specify a label for the data file of the experiment just run (a dialog box is displayed after each run). This can be used for both single and multiple runs. However, for multiple runs, the time available for entering the label is limited by the **Time Interval**. If it is less than 10 seconds, this option is not available. For longer Time Intervals, once the time has expired, the data are saved with whatever label has been entered, and the next run is then started. After a label has been entered, and [**OK**] has been clicked, the standard timer dialog box appears to count down any excess time that remains.

5.6 List Run Data

When this command is checked in the menu, the experimental data are listed on the screen during runs if the data rate is slow enough (as determined by the software) to allow time for listing.

5.7 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. On the CV-50W, this is achieved by the **iR Compensation command**.

There are two stages to **Auto iR Compensation** on the CV-50W (P. He and L.R. Faulkner, Anal. Chem. 58 (1986) 523):

a) measurement of the uncompensated resistance
b) compensation and circuit stability testing

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Measurement of Uncompensated Resistance

In this measurement, the electrochemical cell is considered to be electronically equivalent to an RC circuit; that is, the uncompensated resistance (R_u) is in series with the double-layer capacitance (C_{dl}) (Figure 5-2). Since a Faradaic impedance is not considered as part of this model, the test potential (**Test E**) must be at a value at which no Faradaic process occurs. A 50 mV potential step (ΔE) is applied around this potential (i.e., **Test E**-25 mV to **Test E**+25 mV), and the current is sampled at 54 µs and 72 µs after the step is applied. The current decays exponentially, and the initial current (I_o) is calculated by extrapolating back to zero time (Figure 5-3). Since $\Delta E = I_o R_u$, R_u can be calculated from this measurement. To reduce any error, this measurement is performed 256 times, and the results averaged.

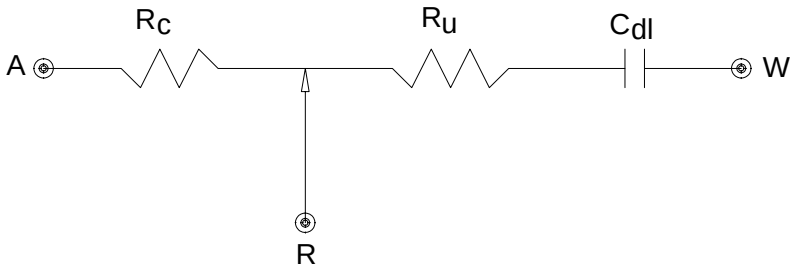


Figure 5-2. RC circuit used for calculation of the solution resistance.

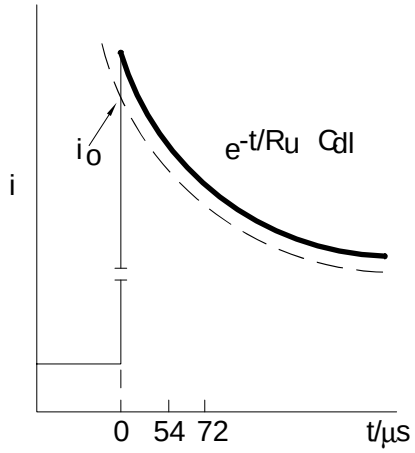


Figure 5-3. Exponential decay of current response.

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R_u/Ω	measured RC time constant/μs	measured R_u/Ω	error of R_u measurement/ %
50.3	38	29	-42
100.4	94	92	-8.4
150	146	145	-3.3
200	198	198	-1.0
250	250	249	-0.4
300	302	301	+0.3
347	350	349	+0.6
401	406	404	+0.7
452	360	449	-0.7

Table 5-1. Measured resistance and time constant via exponential extrapolation (P. He and L.R. Faulkner, Anal. Chem. 58 (1986) 523).

Table 5-1 shows the results of resistance measurements for various dummy cells using exponential extrapolation. There is very good agreement when the time constant is greater than 200 μs; however, the error in the extrapolation is large if the time constant is below 100 μs, since the current has decayed significantly by the time the response is sampled. Therefore, the **Auto iR Compensation** may not work when the uncompensated resistance is low, and/or the time constant is small.

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 positive feedback is applied in increments of the calculated uncompensated resistance: 5% increments up to 80%, 2% increments from 80% to 90%, and 1% increments thereafter. The stability of the circuit is tested after each increment. The degree of compensation is defined by the user (default = 100%).

In the stability test, a 50 mV potential step around **Test E** is again applied, and the current data are collected at a rate of 20000 points/sec for 50 ms. A baseline is measured by collecting data shortly before the potential step is applied, and these baseline values are subtracted from the potential step data to yield net current values.

As the percent compensation increases, the current response at first exhibits a "ringing effect" following exponential decay (Figure 5-4) which would eventually go into oscillation. 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 **Overshoot** value is defined by the user (Default = 10%). If the measured **Overshoot** value is less than

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the maximum allowable value, then compensation is continued. 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 **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 **Overshoot** percentage. It is usually safe to go up to 40%.

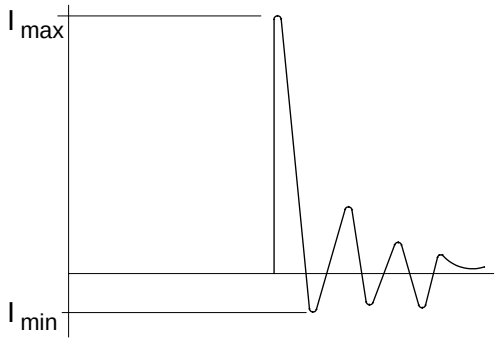


Figure 5-4. "Ringing" of the current response.

If the desired compensation cannot be obtained using **Auto iR Compensation**, then a user-specified compensation resistance can be applied using the **Manual** option. If this option is used, then a stabilizing capacitor may also need to be selected manually (see **Stabilizing Capacitor** in the **Method** menu)



Figure 5-5. iR Compensation dialog box.

1) Using **Auto iR Compensation**:

   a) Select the **Auto** option from **Status**.

   b) Select the appropriate option from **Enable**. If **Once** is chosen, then only the next experiment performed will be iR compensated. If **Always** is

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selected, then the amount of compensation determined by the **iR Test** will be used for every subsequent run (Note: if **Always** is chosen, the instrument does not redo the **iR Test** before every run).

c) Before **Auto iR Compensation** can be used the **iR Test** must first be run. This test requires three parameters values to be specified by the user:

Test E (this must be a potential at which no Faradaic process occurs)
Comp. Level (the degree of compensation: default = 100%)
Overshoot (the extent of instability allowed in the circuit: default = 10%)

d) Click **iR Test** . As the test is running, the following results are displayed in the **Main** window:

Uncompensated resistance (R_u)
Cell RC constant (the product of R_u and C_{dl}) (these are the results of the resistance measurements)
R to be compensated (percentage of R_u used in positive feedback)
Uncompensated R (uncompensated R remaining after compensation) (these are the results of the stability testing)

e) Ensure that the **iR Comp for Next Run** check box is activated.

f) Click **OK** to exit.

2) Using **Manual iR Compensation**

a) Select the **Manual** option from **Status**.

b) Select the appropriate option from **Enable**.

c) Enter the desired **Resistance**.

d) Ensure that the i**R Comp for Next Run** check box is activated.

e) Click **OK** to exit.

5.8 Measure Rest Potential

This command measures the open circuit potential. This potential is particularly important in studies on corrosion (corrosion potential) and batteries (open circuit potential), and it can be used as the initial potential in voltammetry experiments.

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5.9 Immediate Purge/Stir

The **Immediate Purge/Stir** command allows stirring and/or purging for a set length of time. Purging and stirring can be coupled by checking both boxes in the dialog box.

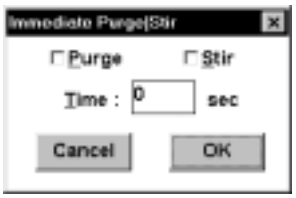


Figure 5-6. Immediate Purge/Stir dialog box.

5.10 Clean Electrode

The **Clean** command is used to hold the electrode at a fixed potential for a set length of time without accumulating any data. This can be useful for generating clean, reproducible working electrode surfaces.

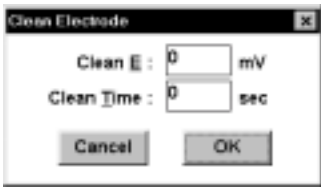


Figure 5-7. Clean Electrode dialog box.

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5.11 Self-Test Hardware

This command initiates the potentiostat electronic self-test. The results of the test are displayed in the **Main** window (Figure 5-8).

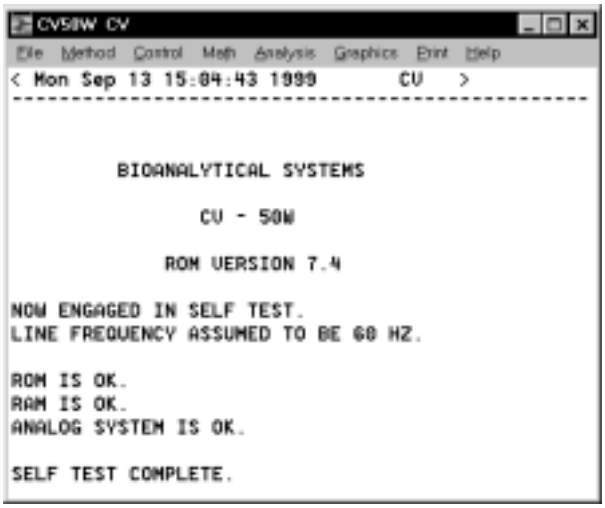


Figure 5-8. Self-Test Hardware result.

5.12 Cell On/Off

When **Cell On** is selected, the working electrode is connected at all times. When **Cell Off** is selected, the working electrode is only connected during experimental runs. For most experiments, the cell should be off between runs, since there is more chance of damaging the instrument (and of personal injury when using the PWR-3) if the cell leads are connected/disconnected when the cell is on.

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6. Math Menu

6.1 Operators

A variety of mathematical operations can be performed on either the X or Y data. These are addition, subtraction, multiplication, division, reciprocal, square, square root, exponent and logarithm (Figure 6-1). In addition, the slope of the baseline can be adjusted. Activating **Replace Current Data** will transfer the processed data to main memory. If this is not activated, the processed data can be displayed only once (after the math operation has been completed).

It should be noted that there is a difference in the way the X data is saved for binary and text files. In binary files, only the initial and final X points and the X sample interval are saved, and the remaining X data points are generated when the file is loaded. However, in text files, all the X data are saved. Therefore, processed X data can only be saved in the text format.

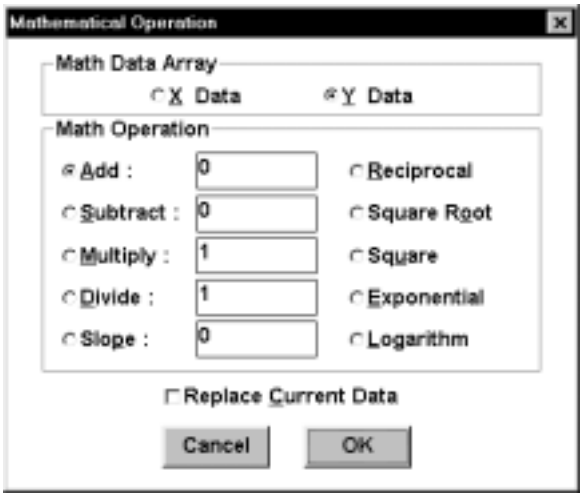


Figure 6-1. Operators dialog box.

6.2 Smooth

The digital smoothing routines are used to remove unwanted noise from the electrochemical signal thereby improving the signal-to-noise ratio and giving more reliable information. In all data manipulation programs, attempts are made not to bias the signal. The major effect of the programs in the CV-50W is the elimination of the

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higher frequency components of the signal, typically 10's of Hz and greater (the exact cutoff frequency depends on both the electrochemical and smoothing techniques). There are 2 methods for digital smoothing. These are:

a) a modified variable point linear smoothing routine (**Moving Average**)
b) a variable point least squares smoothing routine (**Least Square**)

Moving Average

In the modified 5-point linear smooth, data is examined in 5 point blocks. Within each block, the first, second, fourth and fifth points are summed and divided by 4. This number (an averaged current value) replaces the third point in the block. The averaging routine moves up 1 point, and repeats the averaging sequence. This routine is repeated for all points.

The first 2 points of the data set are set equal to point 3 and the last 2 points of the data set are set equal to the third from last point. At times, this appears as spurious data points at the ends of the plot. This is unavoidable and is normal.

The only requirement for the number of points is a block is that this number is odd. Any odd number between 5 and 25 can be chosen on the CV-50W - the larger the number of points, the greater the smoothing.

Least Squares

This digital smoothing function is based on the work of Savitzky and Golay: A. Savitzky and M. J. E. Golay, Anal. Chem. 36 (1964) 1627 - 1639. The smoothing is a quadratic least squares operation working on data blocks of n points (where n is any odd number between 5 and 25).

The dialog box for **Smooth** is shown below (Figure 6-2).

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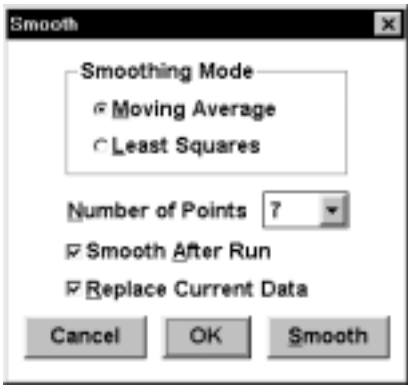


Figure 6-2. Smooth dialog box.

Smoothing Mode Default: **Moving Average**

Point This controls the degree of smoothing (higher **Point** produces greater smoothing). Default: 7 (**Point**).

Smooth After Run When activated, the experimental data is automatically smoothed at the end of the experiment.

Replace Current Data Activating this command will transfer the processed data to main memory

Smooth This command activates selected smoothing routine on the data in main memory.

OK This command exits the dialog box whilst retaining any changes.

Cancel This command exits the dialog box without saving any changes.

6.3 Derivative/Integral

These are self-explanatory mathematical operations on the current data of the I-E curves. For differentiation, the 1st, 2nd and 3rd order derivatives are available (Figure 6-3), and are selected using the **Order** option. Additional smoothing is available for the **Derivative** mode, since differentiation can lead to an increase in the noise level. Activating the **Replace Current Data** transfers the processed data to main memory.

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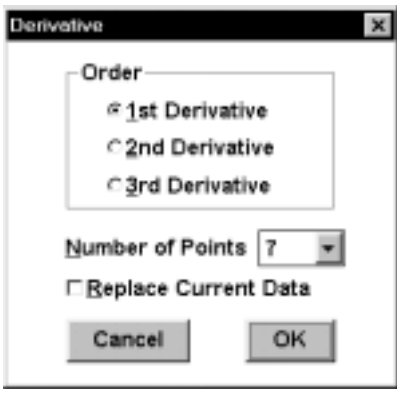


Figure 6-3. Derivative dialog box.

Differentiation of I is often used for accurate calculation of peak potentials (1st derivative) and half-wave potentials (2nd derivative).

6.4 Convolution

In addition to differentiation and integration, semi-differentiation and semi-integration are also commonly used for processing electrochemical data. Both of these processes are available on the CV-50W as **Convolution Mode** options (Figure 6-4). Additional smoothing is available for semi-differentiation, since this process can increase the noise level. The convoluted data can transferred to main memory using **Replace Current Data**. Semi-differentiation is particularly useful for cyclic voltammetry, since it can produce a considerable improvement in the resolution of closely spaced peaks. Semi-integration can be used to remove the effects of iR drop.

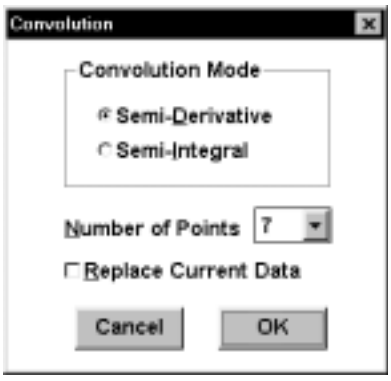


Figure 6-4. Convolution dialog box.

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6.5 Background

This command can be used to subtract a voltammogram stored on the hard disk from the voltammogram in the main memory. The data file for subtraction is selected from the **Background File** dialog box (Figure 6-5) (for a more detailed discussion of file dialog boxes, see the **File** menu section). The potential range of the two voltammograms MUST be the same. The subtracted data can be transferred to main memory using **Replace Current Data**.



Figure 6-5. Background File dialog box.

6.6 Average

This command is used to average data files. Up to 100 files can be selected (from the **Average Files** dialog box (Figure 6-6) - see **File** menu section for a more detailed description of file dialog boxes).

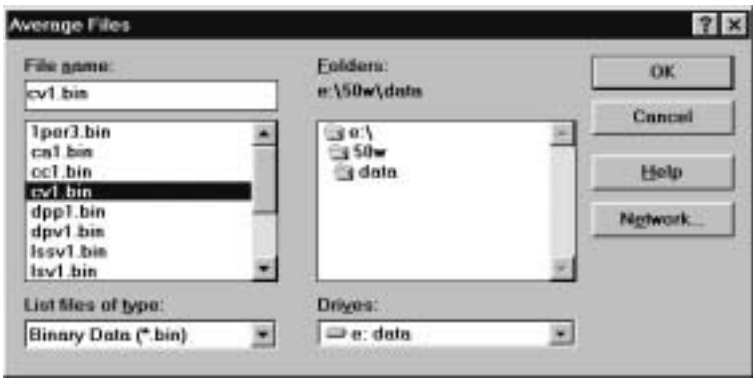


Figure 6-6. Average Files dialog box.

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7. Analysis

7.1 Results Graph

The data available from an electrochemical experiment may be peak potentials and currents, half-wave potentials and limiting currents, slopes and intercepts of straight line plots or the amount of charge passed during the experiments. These data can be obtained using the **Results Graph**.

There are two options available: **Auto** and **Manual**. These can be selected from the **Results Options** dialog box. When the **Auto** option is selected, the **Results Graph** windows displays the experimental data, the baseline for peak measurements and the best fit straight line for linear plots (the size and position of this windows can be changed by the user (by dragging the borders or the caption), and are defined initially by the CV50W.INI file). The **Auto** option also selects the appropriate **Peak Shape**. The experimental results (see below) are listed in the **Main** window.

CV, **LSV**	Selected plot - tailed curve Experimental results - peak potential, current, and area
DPV/P, **OSWV**	Selected plot - symmetric curve Experimental results - peak potential, current, and area
DPSV, **LSSV**, **OSWSV**	Selected plot - symmetric curve Experimental results - peak potential, current, and area
NPV/P, **SCP**	Selected plot - sigmoidal curve Experimental results - half-wave potential
CA, CC	Selected plot - straight line plots (i vs. $t^{-1/2}$ for CA, Q vs. $t^{1/2}$ for CC) Experimental results - slope and intercept

(N.B. Due to the finite time required for the potential step to be complete, the data in the first few milliseconds of potential step experiments is often distorted.

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The CV-50W **Auto** option therefore only uses the last 80% of the collected data when calculating slopes and intercepts).

BE	Experimental results - Initial current End current Current ratio Time Total charge Net charge

In addition to the **Results Graph**, the **Results Graph** window also displays the coordinates of the mouse cursor as it is moved within the axes. A selected area can be expanded (Zoomed) by dragging the mouse (using the left mouse button) between diagonally opposite corners of the defining rectangle. This operation can be reversed by clicking the left mouse button.

When using the **Manual** option, the baselines for calculation of results are defined by the user. Click and hold down the **right** mouse button at the starting point of the baseline and drag the mouse across the graph to the end point of the baseline. As the mouse is moved within the **Results Graph** window, the coordinates of the mouse cursor are shown in the lower left corner. The number of baselines that must be defined depends on the nature of the plot:

a) Symmetric and tail curves - define one baseline
b) Sigmoidal curves - define two baselines
c) Straight line plots - define two points on the X axis

For symmetric and tailed plots, the peak area is also listed in the Main window (the peak area is the area between the curve and the user-defined baseline (Figure 7-1)).

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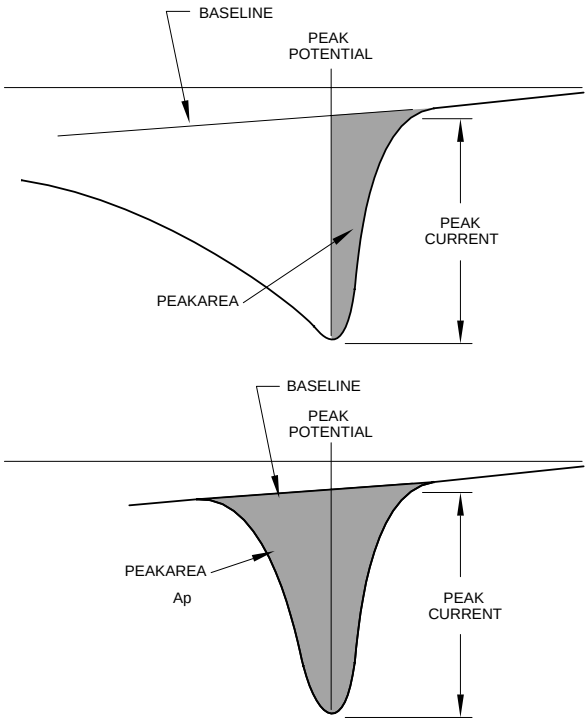


Figure 7-1. Peak area for symmetric and tailed curves.

Determination of Peak Potentials and Inflection Points

NOTE: If there are fewer than 30 points available in a data set of segment, peak finding is not possible and a warning message is shown.

The peak potentials of tailed and symmetric current-potential curves and inflection points of sigmoidal current-potential curves are determined by the manipulation of the first or second derivatives respectively. First derivatives are calculated as differentials across a potential window, ΔE, of about 25 mV; that is, ΔI is calculated as I(E-25 mV)-I(E). This order is used to produce a consistent sign convention. The 25 mV interval is not rigid. The actual value is chosen such that an odd number of data points intervene, so that the ΔI value can be assigned to the middle potential of the interval. The derivative plots are actually plots of these ΔI's vs. assigned median ΔE values, not $\Delta I/\Delta E$ vs. ΔE, so the vertical axis has dimensions of current on the same scale used for the ΔI vs. ΔE plot. The derivative values for the first 12 mV and the last 12 mV in a scan are simply equated to the values assigned to the first and last potentials at which ΔI values could be assigned. The second derivative works in the same way, but it operates on the first derivative array.

Peak potentials are determined by examining the first derivative plots. The peak potential value, E_p, is determined by first looking for a sign reversal; that is, plus to minus or minus to plus. The first ΔI sign reversal becomes the E_p window (note

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that a 25 mV potential window is being examined for each ΔI calculated). To ensure that it is a true peak (i.e., not merely noise), two criteria must be met. First, the 3 points (ΔI values) on either side of the E_p window are examined for continuity of sign; that is, there are three consecutive positive values on the plus side and three consecutive negative values on the minus side. If this test is passed, the actual E_p value is determined by choosing the largest current value, I_{max}, in a potential window that is 25 mV greater than and less than the median E of the E_p window.

The second criterion provides a measure of the rate at which the peak is being generated. A rapidly changing peak is more likely to be noise rather than a real electrochemical peak. This noise discrimination routine is implemented by examining the peak width at 50, 100 and 150 mV preceding the peak potential E_p (Figure 7-). The peak width ratio ΔE50/ΔE100, ΔE50/ΔE150 and ΔE100/ΔE150 are calculated; if these are less than the corresponding values for peak with a **Half Peak Width** of 200 mV (**Half Peak Width** is the difference between the potentials at which the current is half the peak current), then the peak is reported

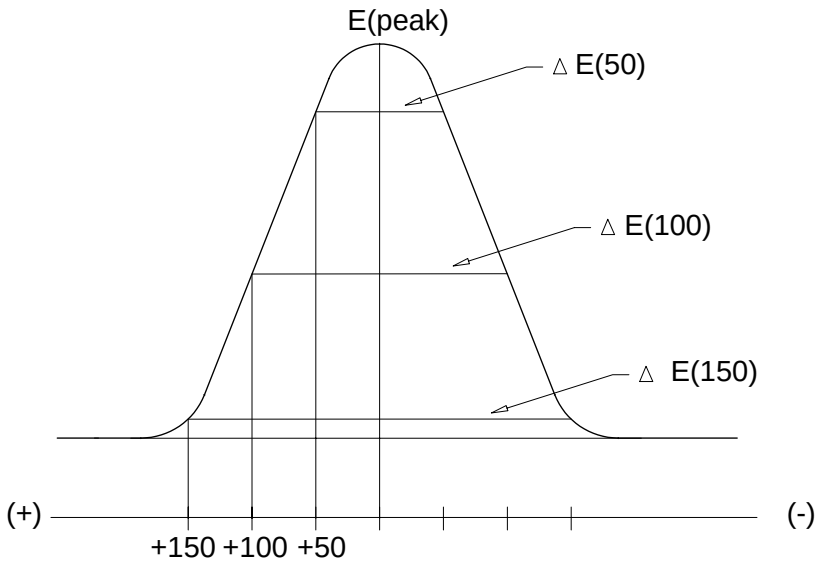


Figure 7-2. Peak finding criteria.

Determination of Peak Currents, Limiting Currents and Peak Areas

The most important part of these measurements is the determination of the current baseline. The method for this depends on the curve shape. Peak area is given in units of Amps x Volts. To convert into coulombs, for cyclic voltammetry, the area must be divided by the scan rate (Volts/Sec).

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a) **Symmetric** curves - The baseline is the line between the two current minima in the range of E_p + 250 mV (Figure 7-3).

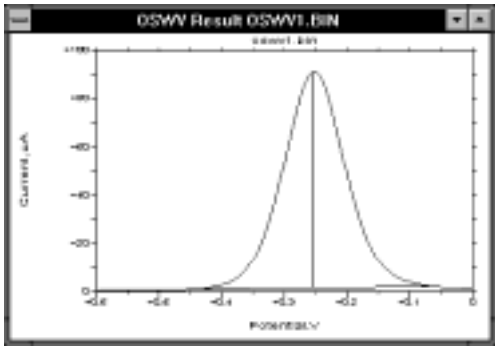


Figure 7-3. Symmetric current response.

b) **Tail** curves - The baseline is the line between two points on the I vs. E curve 50 mV apart in a range of 250 mV preceding E_p (Figure 7-4).

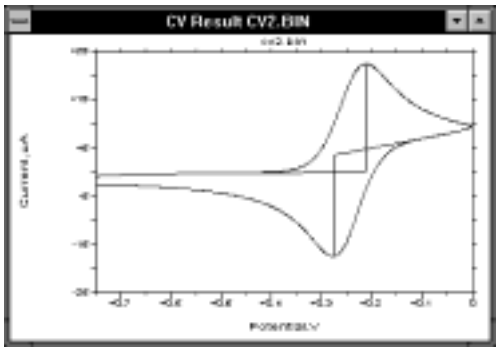


Figure 7-4. Tailed current response.

c) **Sigmoidal** curves - Two baselines are required to measure the limiting current. These are defined by two points on the I vs. E curve 50 mV apart in a range of 250 mV either side of $E_{1/2}$ (the half-wave potential) (Figure 7-5). Different values are chosen to find the lines of absolute minimum slope.

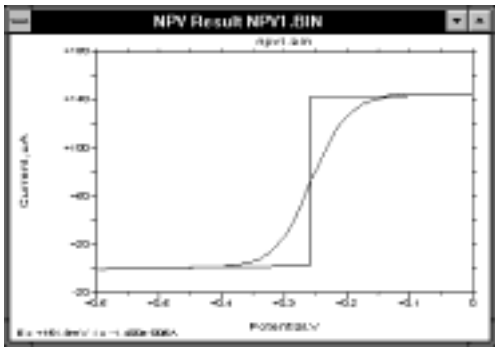


Figure 7-5. Sigmoidal current response.

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Determination of the Slope and Intercept of an Anson or Cottrell Plot

The slope and intercept of the **CA** Cottrell plot and the **CC** Anson plot are determined by an unweighted linear least squares fit routine on the last 80% of the data points following both the forward and reverse potential steps (Figure 7-6).

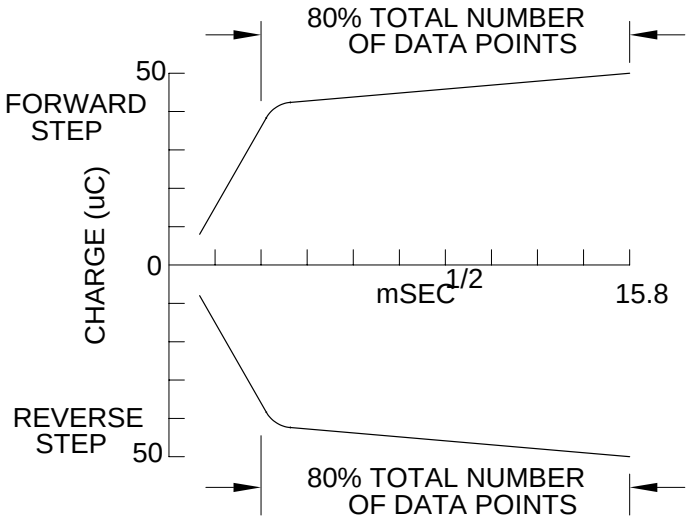


Figure 7-6. Selection of points for the Anson plot.

In all these cases, the lines selected by the **Auto** option are displayed on the screen. These can easily be changed using the **Manual** option. The units of calculated slopes are $mA \cdot ms^{1/2}$ for Cottrell plot and $C/ms^{1/2}$ for Anson plot.

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7.2 Results Options

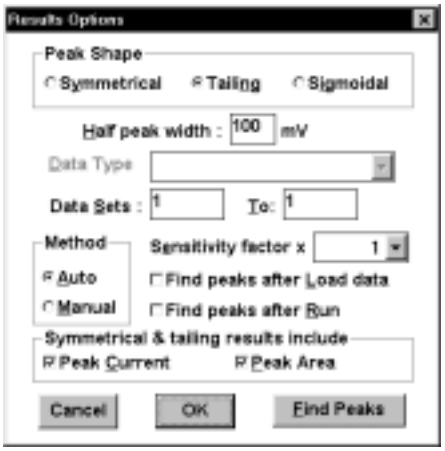


Figure 7-7. Results Options dialog box.

Peak Shape

This defines the shape of the curve. There are instances when the default peak shape selection is not appropriate: for example, when using microelectrodes at low scan rates, as this produces a sigmoidal plot for **CV**.

Half Peak Width

This defines the expected width of the peak (it may be necessary to increase this value for broader peaks).

Data Type

This defines how the experimental data is presented when there is more than one presentation format (i.e., **BE**, **CA** and **CC**). The default **Data Types** are as follows: **Current vs. Time** (for **CA**) and **Charge vs. Time** (for **BE** and **CC)**.

Data Sets

This defines which data set is displayed when there is more than one data set (i.e., **CV**, **OSWV**, **OSWSV**). For **CV**, the number of **Data Sets** is defined by the **Number of Segments** (specified in **General Parameters**). **OSWV** and **OSWSV** have **Data Sets** 1 to 3. The default **Data Sets** are as follows: all segments for **CV**, the first segment for **OSWV** and **OSWSV**

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Method	This specifies which option (**Auto** or **Manual**) is to be used.
Sensitivity Factor	This command adjusts the sensitivity of the peak search operation. The height of the smallest detectable peak decreases by a factor of 10 for each stepwise decrease in the **Sensitivity Factor**.
Find Peaks after Load Data	If this command is activated, the **Results Graph** will be displayed automatically when a data file is loaded (if it is not activated, the **Single Graph** will be displayed).
Find Peaks after Run	If this command is activated, the **Results Graph** will be displayed when the experiment has ended (if it is not activated, the **Single Graph** will be displayed).
Symmetrical and Tailing Results Included	Select whether Peak Current and /or Peak Area are reported in the results.

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7.3 Calibration

This command is used to set up a calibration curve for quantitative analysis. First, the **Mode** must be selected, and the **General** and **Specific Parameters** entered.

The **Analysis Calibration** dialog box appears when **Calibration** is clicked (Figure 7-8).

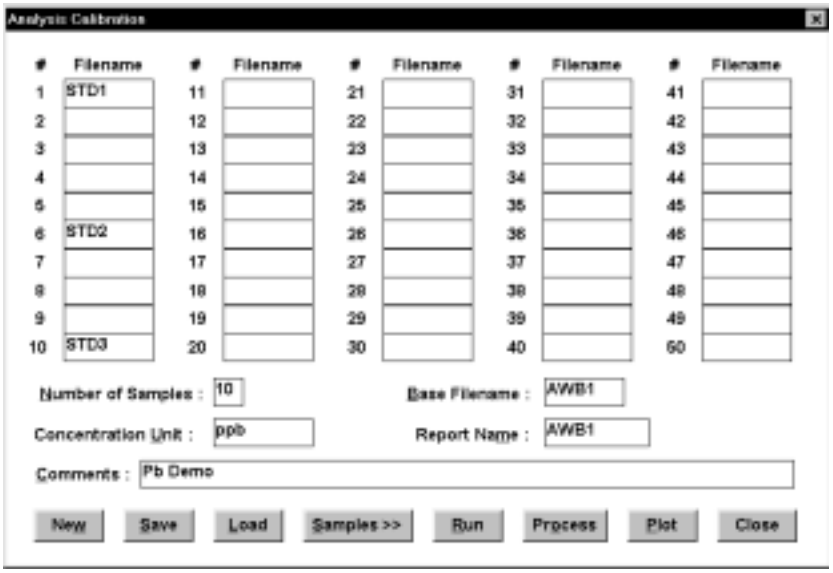


Figure 7-8. Analysis Calibration dialog box.

The maximum **Number of Samples** is 50. A **Filename** can be specified for each sample; if no **Filename** is specified, the **Base Filename** + the sample # will be used (e.g., awb11 for sample 1). The **Report Name** and **Concentration Unit** must be specified. In the above example, a total of 10 samples were run, 3 of which were standards - #1, #5 and #10. The **Analysis** parameters and results can be saved (and reloaded) using the **Analysis File** dialog box.

Clicking **Samples** produces a dialog box which is used to specify each **Sample** as either an **Unknown** or a **Standard** (Figure 7-). For each **Standard**, the **Conc**entration and peak potential (**Ep**) must been entered for each analyte, together with a **Tol**erance for **Ep**. The **Number of Peaks** (i.e., the number of analytes being determined) must also be specified. No information is required for **Unknown**s. Use **Prev** and **Next** to move between sample numbers and click **Escape** to return to the **Analysis Calibration** dialog box.

Click **Run** to start the analysis. At the end of each sample run, the software will request the next sample. When all the samples have been run, the calibration curve

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for a specified peak can be examined by clicking **Plot**. A report that lists the unknown concentration is saved as a .REP file; the results are also listed in the Main window.

Process is used for reprocessing of existing files (e.g., if incorrect concentrations or peak potentials were used initially). Since 3-digit run numbers are used in the data file names, it may be necessary to rename data files before reprocessing. It should also be noted that the first run number is now 001, not 0 as in previous versions of the CV-50W software.

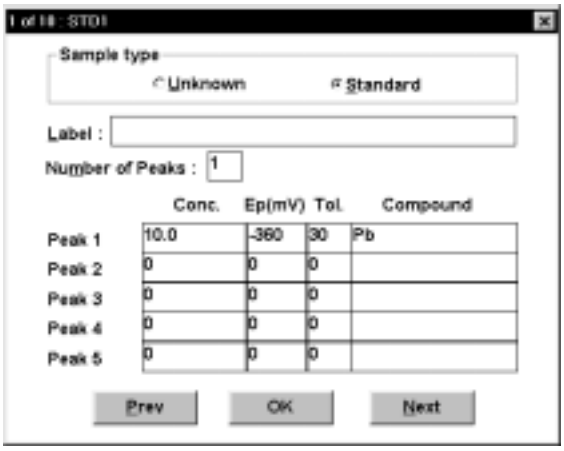


Figure 7-9. Samples dialog box.

7.4 Standard Addition

This command is used to construct a standard addition curve for quantitative analysis. First, the **Mode** must be selected, and the **General** and **Specific Parameters** entered.

The **Standard Addition** dialog box appears when **Std. Addition** is clicked (Figure 7-10).

The **Number of Peaks**, **Number of Additions**, **Concentration Unit** and **Base Filename** must all be specified. In addition, the peak potentials (**Ep**) (and **Tol**erances) and the total standard concentration after each addition must be entered; in the above example, there are three standard additions of 10 ppb. The **Standard Addition** parameters and results can be saved using the **Standard Addition File** dialog box.

Click **Run** to start the experiment. After each measurement, the software will request the next standard addition. When all the standard additions have been made, the standard addition curve can be examined by clicking **Plot**. A report that lists the unknown concentration is saved as a .REP file; the results are also listed in the Main window.

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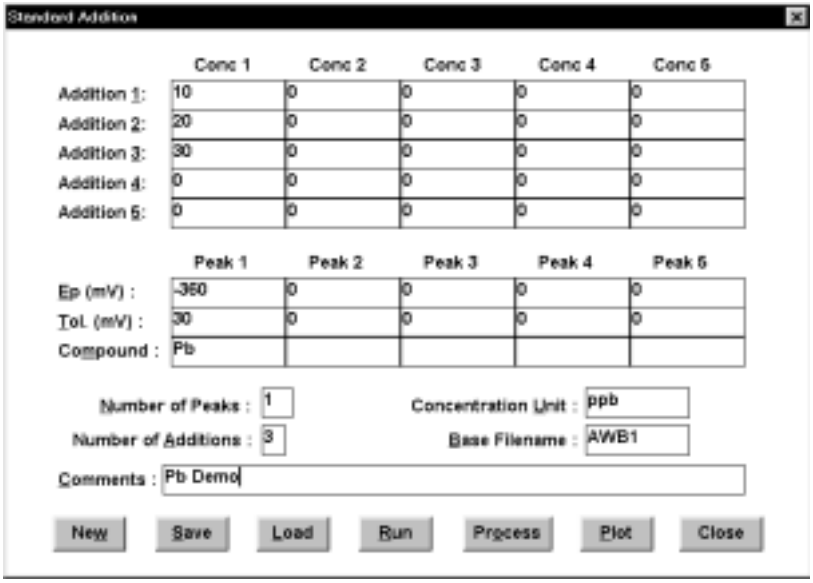


Figure 7-10. Standard Addition dialog box.

Process is used for reprocessing of existing files (e.g., if incorrect standard additions or peak potentials were used initially). Since 3-digit run numbers are used in the data filenames, it may be necessary to rename data files before reprocessing. It should also be noted that the first run number is now 001, not 0 as in previous versions of the CV-50W software.

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8. Graphics Menu

This Menu is used to display the experimental data after the experimental run and after any post-run data processing.

8.1 Single Graph

The **Single Graph** window displays the experimental data (Figure 8-1). The size and position of this windows can be changed by the user (by dragging the caption or the borders), and are defined initially by the CV50W.INI file.

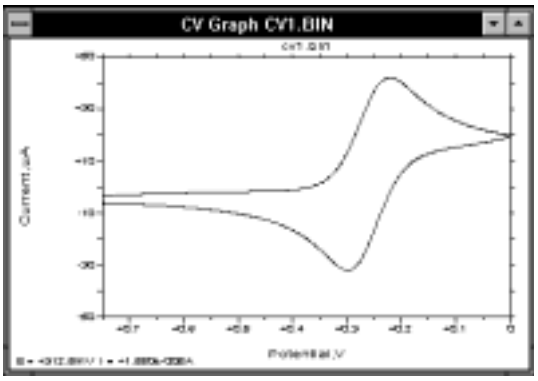


Figure 8-1. Single Graph window.

The **Single Graph** windows can be displayed automatically at the end of an experiment and after a data file has been loaded (the **Find peaks**.. check boxes in the **Results Options** dialog box need to be unchecked). The data are graphed according to the **Data Type** specified in **Graph Options**, or according to the default **Data Sets**.

In addition to the **Single Graph**, the **Single Graph** window also displays the coordinates of the mouse cursor as it is moved within the axes. Pressing the right mouse button leaves a plus mark on the graph, the coordinates of which are also displayed. A selected area can be expanded (Zoomed) by dragging the mouse between diagonally opposite corners of the defining rectangle. This operation can be reversed by clicking the left mouse button.

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8.2 Graph Options

This dialog box controls the appearance of the graph on the PC screen and on the hard copy (Figure 8-2). All **Graph Options** are saved in the CV50W.INI file (except **X/Y Freeze** and the **Min.** and **Max**. values, which typically only apply to a particular data file).

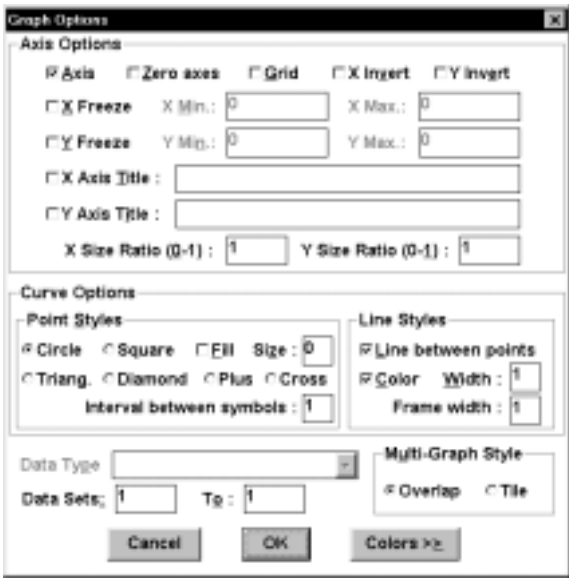


Figure 8-2. Graph Options dialog box.

Axis Options

All the axis options can be enabled or disabled by checking the appropriate box.

Axis — When activated, both axes are drawn.

Zero Axes — When activated, dashed lines are drawn on the graph at X=0 and Y=0, if they are within the range of the graph.

X/Y Grid — When activated, an X/Y grid is displayed.

X/Y Invert — When activated, the polarity of the X/Y axis is inverted.

X/Y Freeze — When activated, the range of axes is frozen at the selected **Min**. and **Max.** values; otherwise, the range is adjusted automatically to encompass the

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range of the data set. **Y Freeze** (but not **X Freeze**) also applies to graphs displayed during experimental runs. It is a good idea to run the first experiment with **Y Freeze** disabled. After the data for the first run are regraphed with auto-scaling, the **Min**. and **Max.** values are correct for the present graph.

X/Y Titles — When activated, the specified text replaces the default labels on the axes.

X/Y Size Ratio — This defines the fraction of the total windows area that is occupied by the graph

Curve Options

These control the way the curves are drawn.

Point Styles — Six **Style**s are available in **Size**s from 0 to 7. The interior of the **Circle**, **Square**, **Diamond** and **Triangle** symbols can be colored by checking **Fill**. **Interval between symbols** specifies the interval where dots are replaced by symbols for the data points.

Line Styles — Select **Line between points** to connect the points with a line of the given **Width**, and select **Color** to draw the points and lines colored pen.

Data Type — This defines how the experimental data is presented when there is more than one presentation format (i.e., **BE**, **CA** and **CC**). The default **Data Types** are as follows: **Current vs. Time** (for **CA**), **Charge vs. Time** (for **BE**).

Data Sets — This defines which data set is displayed when there is more than one data set (i.e., **CV**, **OSWV** and **OSWSV.** For **CV**, the number of **Data Sets** is defined by the **Number of Segments** (specified in **General Parameters**). **OSWV** and **OSWSV.** The default **Data Sets** are as follows: all segments for **CV**, the first segment for **OSWV** and **OSWSV.**

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Multi-Graph Style The **Overlap** option draws all curves on the same set of axes and the range of the axes is determined by the data in main memory. The **Tile** option displays each data file on its own set of axes.

8.3 Graph Colors

The colors of each feature on the graph can be selected (for both the PC screen and the hard copy). These **Graph Colors** are saved in the CV50W.INI file. To change a color, first click the colored check box beside the selected feature; a cross will replace the color and the sample color patch will change to the present color of that feature. Any color can then be mixed by using the Red, Green and Blue scroll bars or by typing a number between 0 and 255 in the edit box. To apply the present color mix to the selected feature, click the checkmarked box once more. Note that the accuracy of the colors depends the number of colors the display adapter can depict.

For **Multi-Graphs** using the **Overlap** option, the **Curve 1** through **Curve 8** colors are used for the first 8 curves, and this sequence repeats for curves 9 through 16, etc.

Default Colors changes all of the colors back to the original colors.

8.4 Multi-Graph

This plots multiple data files, including the data in main memory. The **Overlap** option draws all curves on the same set of axes and the range of the axes is determined by the data in main memory. The **Tile** option displays each data file on its own set of axes. Up to 41 files can be displayed, and are selected using the **Multi-Graph Files** dialog box (Figure 8-3). If all the data files are for the same **Mode of Operation**, the **Data Sets** and **Data Type** specified in **Graph Options** are used to graph the data. If the data files use different **Modes of Operation**, then the default **Data Sets** and **Data Type** are used.

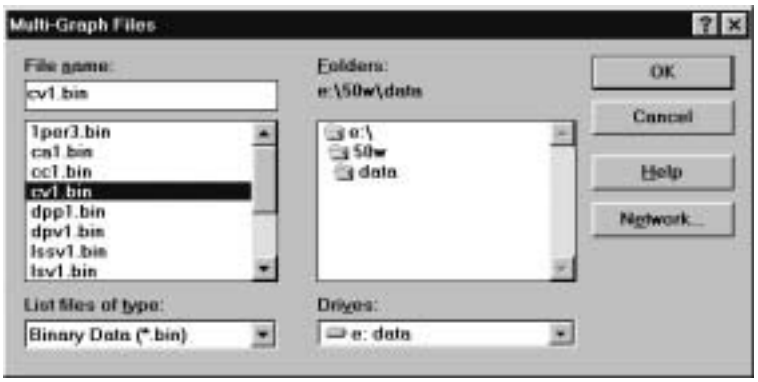


Figure 8-3. Multi-Graph Files dialog box.

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9. Print Menu

9.1 Print Graph

This command transfers the present graph (**Single Graph** or **Multi-Graph**) to the default printer (an alternative printer can be selected using **Printer Setup**) using the options specified in **Print Options**.

9.2 Print Options

This dialog box contains graph options that pertain only to printed graphs (Figure 9-1).

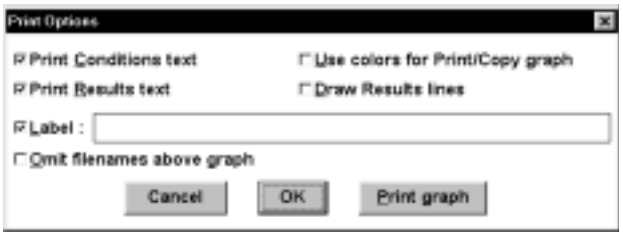


Figure 9-1. Print Options dialog box.

Print Conditions text — This option lists the experimental conditions.

Print Results text — This lists the results from the data analysis.

Label — This is an optional description of the experiment (69 characters maximum).

Use colors when printing — This option tells the program that the printer in use knows how to translate colors into ink. If it is not checked, everything is printed in black or white. On black-and-white printers, some colors cannot be printed and hence are invisible. In such cases, uncheck this option or try different colors.

Draw Results lines — This option specifies whether the Results lines (e.g., baselines for peak measurement) are to be drawn on the printed graph (this option also requires the **Print Results text** to be active).

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Omit file names above graph	This option specifies whether the file name is above the graph, both on the monitor and on printed/ copied to clipboard graphs.

9.3 Multi-Print Files

This command sets up a print queue for data files. Up to 100 files can be selected from the **Multi-Print Files** dialog box. Each data file is printed on a separate page (use the **Multi-Graph** option in the **Graphics** menu followed by **Print Graph** for multiple graphs on the same page). If all the data files are for the same **Mode of Operation**, the **Data Sets** and **Data Type** specified in **Graph Options** are printed. If the data files use different **Modes of Operation**, then the default **Data Sets** and **Data Type** are used.

9.4 Print Text

Print Text prints any text selected (highlighted) by dragging the mouse over the desired lines in the **Main** window.

9.5 Copy Text

This command copies to the **Clipboard** any text selected (highlighted) by dragging the mouse over the desired lines in the **Main** window. From the **Clipboard**, it can be transferred to other Windows programs.

9.6 Copy Graph

Copy Graph transfer the present graph window (without its frame) to the **Clipboard**. From the **Clipboard** it can be transferred to other Windows programs.

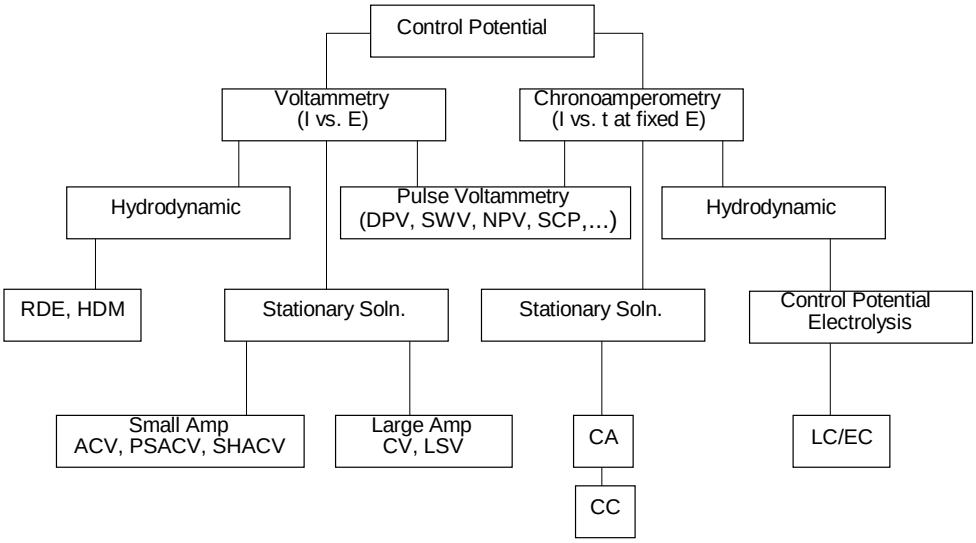
9.7 Print Setup

This command allows the default printer and other printer options to be changed without using the **Control Panel**. The options available depend on the type of printer and the printer driver installed in Windows.

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10. Operation Modes

There are 15 techniques available on the CV-50W. This may appear to be a bewildering number, but many of these techniques are related, or are variations of other techniques. There are a number of broad divisions that can be made.



a) Voltammetry vs. chronoamperometry (potential step). In voltammetry, the potential is varied in a defined manner, and the current response is monitored. In chronoamperometry, the potential is held at a fixed value (or is stepped between two values) and the current response is monitored as a function of time.

b) Stationary solution vs. Hydrodynamic. This determines the rate at which electroactive molecules are brought to the surface of the working electrode (i.e., the rate of mass transport). In stationary solutions, the only mode of mass transport is diffusion, whereas in hydrodynamic techniques, there is a combination of convection (e.g., stirring) and diffusion. Therefore, in these latter techniques, the rate of mass transport can be controlled.

There is another set of techniques (pulse techniques) in which the applied potential is a combination of voltammetry and potential step. This are discussed in more detail below.

Sweep Techniques (Stationary Solution)
Cyclic Voltammetry (**CV**)
Linear Sweep Voltammetry (**LSV**)

Step Techniques (Stationary Solution)

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Chronocoulometry (**CC**)
Chronoamperometry (**CA**)

Pulse Techniques (Stationary Solution)
Differential Pulse Voltammetry/Polarography (**DPV/P**)
Normal Pulse Voltammetry/Polarography (**NPV/P**)
Sampled Current Polarography (**SCP**)

Square Wave Techniques (Stationary Solution)
Osteryoung Square Wave Voltammetry (**OSWV**)

Stripping Techniques
Differential Pulse Stripping Voltammetry (**DPSV**)
Linear Sweep Stripping Voltammetry (**LSSV**)
Osteryoung Square Wave Stripping Voltammetry (**OSWSV**)

Time Base
Time Base (**TB**)

Miscellaneous
Bulk Electrolysis with Coulometry (**BE**)

There are a number of parameters that are common to all techniques.

a) Potential range. When only a single potential is required, this is defined by **Initial E**. If a potential range is required, this is defined by **Initial E** and **Final E** (for single sweep/scan/step experiments), or **Initial E**, **High E** and **Low E** (for two or more sweep/ scans/steps in the experiment). The range for any potential is -3276 to +3276 mV.

b) **Sensitivity**. This is the gain of the current-to-voltage converter output. For all techniques (except **CC**,), the range of sensitivities is 100 mA/V to 100 nA/V.

c) **Quiet Time**. This is the time between the initiation of the **Run** and the start of the potential scan/step. The working electrode is connected at **Initial E** during this time, so that equilibration can occur before the start of the experiment. The allowed range for the **Quiet Time** is 0 to 65535 seconds.

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10.1 Linear Sweep Techniques (LSV, CV)

In **LSV**, the potential is varied linearly from an initial potential (**Initial E**) to a final potential (**Final E**) at a constant rate (**Scan Rate**), and the current is monitored as a function of the applied potential. The potential wave form for **LSV** is shown in Figure 10-1

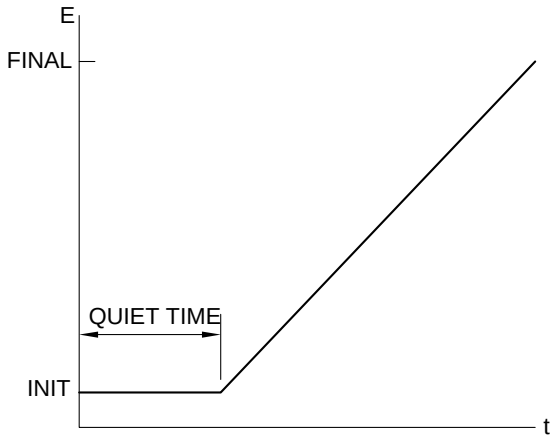


Figure 10-1. **Potential wave form for** LSV**.**

A more commonly used variation of **LSV** is **CV**. In this technique, when the final potential is reached, the scan direction is reversed and the same potential range is swept again in the opposite direction. Therefore, the product of the electrochemical reaction on the forward scan can be examined on the reverse scan. This feature is one of the main reasons for the widespread use of this technique.

In **CV**, the potential can be cycled over the same range many times. Three potential parameters are required; the initial potential (**Initial E**), and the two switching potentials (i.e., the potential at which the direction of the scan is reversed), **High E** and **Low E**. The potential wave form for **CV** is shown in Figure 10-2.

The simplest I-E curve for **CV** is shown in Figure 10-3. The asymmetry of the curve is due to the diffusional mass transport. However, there are many other parameters that can affect the shape of this curve; for example, slow heterogeneous transfer kinetics, instability of the oxidized or reduced species, and adsorption. If the heterogeneous electron transfer is rapid (relative to the timescale of the experiment) and both the oxidized and reduced species are stable (again, on the timescale of the experiment),then the redox process is said to be electrochemically reversible. The standard redox potential is the mean of the two peak potentials (E_{pa} and E_{pc}), and the separation of the peak potentials is 57/n mV (n = number of electrons transferred per molecule).

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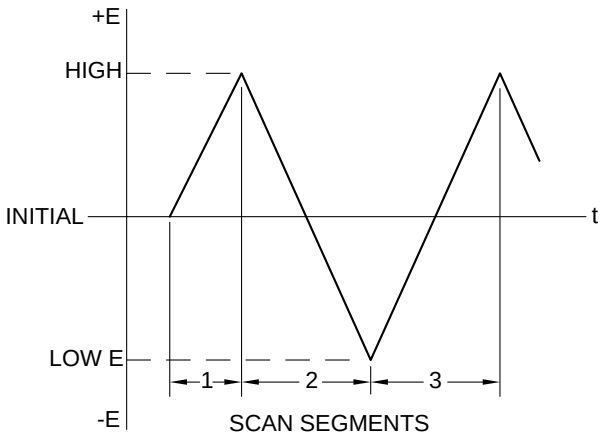


Figure 10-2. Potential wave form for **CV.**

The peak current for a reversible process is given by the Randles-Sevcik equation:

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

where: i_p = peak current (A)
n = number of electrons transferred per molecule
A = electrode surface area (cm^2)
D = diffusion coefficient (cm^2/s)
C = concentration (mol/cm^3)
υ = scan rate (V/s)

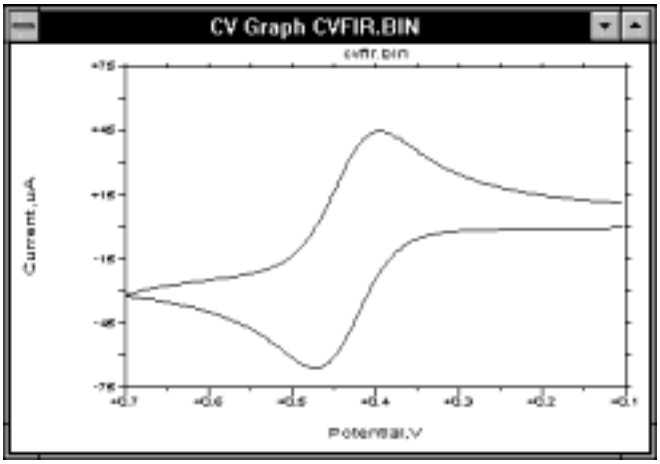


Figure 10-3. Typical current response for **CV**.

Therefore, for a reversible process, i_p is proportional to the concentration, C, and the square root of the scan rate, $\upsilon^{1/2}$.

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As discussed above, there are many parameters that can affect the shape of the **CV** curve. Slow electron transfer kinetics can increase the separation of the peak potentials (ΔE_p), and the rate constant for electron transfer can be calculated by examining the variation of ΔE_p with scan rate. However, uncompensated resistance between the working and reference electrodes can also increase ΔE_p. The effect of uncompensated resistance can be lowered or eliminated using electronic iR compensation (see **iR Compensation** under the **Control** menu).

Another application for **CV** is the study of the reactions of electrolyzed species. These are generated on the forward scan, and their reactivity can be examined on the reverse and subsequent scans. Qualitative estimates of reaction rates can be obtained by varying the scan rates.

The simplicity and speed of **CV** means that it is often used as the first technique to characterize a redox system, and it is a very powerful technique for qualitative analysis of kinetics and mechanism. However, quantitative kinetic measurements using **CV** generally require digital simulation, since there is no other way to separate the effects of slow electron transfer and chemical reactivity.

The charging current that is present in **CV** and **LSV** limit their usefulness as techniques for quantitative analysis. However, **LSV** is used as one of the techniques for the detection of trace metals using stripping voltammetry. This is discussed in more detail in section 10.5.

It is important to note that the potential wave form used for **CV** and **LSV** on the CV-50W (and other digital instruments) is a staircase wave form, since it is impossible to generate digitally a true linear wave form. There has been much discussion on the equivalence of "digital staircase" **CV** and **LSV** and "analog" **CV** and **LSV**, and it has been shown that variation of the parameters used for the "staircase" techniques can lead to significant differences. Theoretical studies have shown that equivalence can only be guaranteed if the potential step height of the staircase wave form is less than 0.3/n mV (where n = number of electrons transferred). Therefore, the potential wave form used on the CV-50W for **CV** and **LSV** is identical to a true analog linear wave form, since the step height is 0.1 mV.

BAS has a considerable number CV Notes, together with articles and Capsules that describe the applications of CV (the articles and capsules are listed below). These can be obtained at no charge from BAS.

BAS Capsules

132	Adsorption of Reduced Glutathione on a Mercury Surface
141	Determination of Heterogeneous Electron Transfer Rate Constant
264	Electrochemical Conversion of $[FeIr_5(CO)_{16}]^-$ to $[FeIr_5(CO)_{15}]^{3-}$

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265 Identification of the Products of Oxidation of $[CpFe(CO)_2]_2$ Using Infrared Spectroelectrochemistry

266 Potentiostatic Measurements of a Tc(III)/Tc(II) Couple Using an OTTLE Cell

267 Cis-Trans Isomerization of $Ru(MeOCS_2)_2(PPh_3)_2$

271 Two Electron Reduction of $[CpCo(NO)]_2$

272 Reductive Dimerization of $CpW(NO)I_2$

273 Investigation of Electron Transfer Chain Catalysis Using Cyclic Voltammetry

274 Calculation of the Standard Heterogeneous Charge Transfer Rate Constant (k_s) for Dimeric Iron Fulvalene Complexes Using Cyclic Voltammetry

275 Investigation of E-Z Isomerization of Iron Alkenyl Complexes Using Semi-Derivative Voltammetry

276 Investigation of the Metal-Initiated Oligomerization of Alkynes

Current Separation Articles

1 Voltammetry Primer: Basic CV, R.E. Shoup, 4 (1982) 31.

2 Cyclic Voltammetry as a Tool for Assessing Dual Electrode Detector Feasibility, R.E. Shoup, 4 (1982) 48.

3 Electrochemistry for the Nonelectrochemist, P.T. Kissinger, 6 (1985) 62.

4 Voltammetric Microelectrodes, J.O. Howell, 8 (1987) 2.

5 Cyclic Voltammetry: The Electrochemical Equivalent of Spectroscopy, W.R. Heineman and P.T. Kissinger, 9 (1989)15.

6 Doing Things by Halves: Semidifferentiation in Voltammetry, K. Oldham and R. Philp, 10 (1990) 3.

7 The Electrochemical Behavior of Nifedipine and Related Compounds and Quantitation of Nifedipine in Plasma by LCEC, K. Bratin and P.T. Kissinger, 4 (1982) 4.

8 Reduction of Anthracyclines at a Glassy Carbon Electrode, J. Pursley, 4 (1982) 11.

9 Electrochemical Characterization of $Ni/Ni^{2+}Fe(CN)_6^{4-}$, K. Kuo, 5 (1983) 30.

10 Electrochemical Characterization of Battery Electrodes, K. Kuo, 5 (1983) 45.

11 Chromatographic and Electrochemical Investigation of Codeine, D.A. Meinsma and P.T. Kissinger, 6 (1985) 42.

12 Electrochemical Oxidation of Caffeic Acid: Formation of 6,7-Dihydroxycoumarin, T.M. Kenyhercz and P.T. Kissinger, 6 (1985) 48.

13 Cyclic Voltammetric Studies of Transition Metal Complexes, K.A. Connor and R.A. Walton, 6 (1985) 67.

14 Transient Electrochemical Response of Thermal Ruthenium Oxide Thin Films in Aqueous Electrolytes, E.W. Tsai, P. Abraham and K. Rajeshwar, 9 (1990) 130.

15 Electrochemistry of C60 and C70 Fullerenes, A.W. Bott, 10 (1991) 137.

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16 Cyclic Voltammetry in Organometallic Chemistry, A.W. Bott, 10 (1991) 139.
17 Analysis of the Isomerization of $Cr(CO)_3(\eta^3\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2)$ Using Cyclic Voltammetry Simulation, A.W. Bott, 13 (1994) 45.
18 Electron-Transfer-Induced Isomerization of (Cyclooctatetraenecyclo pentadienyl-cobalt, A.W. Bott, 13 (1994) 49.
19 Electrochemical Deligation of Bis(arene)iron(II) Dications, A.W. Bott, 13 (1994) 70.

Mode = LSV

General Parameters

Initial E (mV) = 0	-3276 to 3276
Final E (mV) = 0	-3276 to 3276
Scan rate = 100 mV/s	1 to 51200
Sensitivity = 1 µA/V	100 mA/V to 100 nA/V

Specific Parameters

Sample Interval (mV) = 1	1 to 20
Quiet Time (sec) = 2	0 to 65535

Mode = CV

General Parameters

Initial E (mV) = 0	-3276 to 3276
High E (mV) = 0	-3276 to 3276
Low E (mV) = 0	-3276 to 3276
Scan Rate = 100 mV/s	1 to 51200 (mV/s)
Initial Direction = Negative	Negative or Positive
Number of Segments = 2	0 to 65535
Sensitivity = 1 µA/V	100 mA/V to 100 nA/V

Specific Parameters

Sample Interval (mV) = 1	1 to 20
Quiet Time (sec) = 2	0 to 65535

Comments (LSV/CV)

a) The wave form generator that drives the potentiostat is a Digital-to-Analog Converter (DAC) with 2^{16} (65,636) resolution elements. The resolution of the staircase potential wave form is 0.1 mV, which generates a potential range of ±3276 mV. The rate at which the potential can change (the **Scan Rate**) is dependent on the rate at which each digital element can be changed. This rate is determined by the speed of the clock pulses, which is set at 2.048×10^6

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pulses/s in the CV-50W. The rate of change from the DAC is controlled by allowing only a fraction of the clock pulses to reach the DAC. The allowed **Scan Rates** are calculated from the equation shown below and some values are listed in Table 10-1. If the entered scan rate is between two values, the higher scan rate will be used.

$$\frac{2.048 \times 10^6 \text{ pulses/s}}{\text{Frequency divisor}} \times 0.1 \text{ mV/pulse} = \textbf{Scan Rate} \text{ (mV/s)}$$

Frequency divider	Scan Rate (mV/s)	Frequency divider	Scan Rate (mV/s)
4	51200	200	1024
5	40960	201	1019
6	34166	202	1014
7	29257	203	1009
8	25600	204	1004
9	22755	205	999
10	20480	206	994
11	18618	207	989
12	17066	208	984
13	15753	209	980
14	14628	210	975
15	13653	..	..
16	12800	..	..
17	12047	500	410
18	11378	501	409
19	10799	502	408
20	10240	503	407
21	9752	..	..
22	9309	(1 mV/s resolution)	

Table 10-1. Some allowed **Scan Rates** for mV/s.

b) The **Sample Interval** (potential resolution) is dependent on the **Scan Rate**. The best potential resolution for the **Scan Rates** are shown below.

Scan Rate (ν)/mV/s	Resolution/mV
$\nu \leq 15753$	1
$17066 \leq \nu \leq 29257$	2
$34166 \leq \nu \leq 40960$	3
$\nu = 51200$	4

CV

c) The maximum number of data points that can be collected in one experiment is 8000. Therefore, a **Sample Interval** of greater than 1 mV may be required for multisegment experiments. Any such changes are made automatically by the software.

d) When the **Number of Segments** is 0, one complete potential cycle is performed. If **Initial E** is between **High E** and **Low E**, start at **Initial E**,

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sweep to one switching potential, reverse and sweep to the other switching potential, reverse and return to the **Initial E**. If **Initial E** is the same as either **High E** or **Low E**, then **Number of Segments** = 0 is the same as **Number of Segments** = 2.

e) The maximum **Number of Segments** is determined by the data storage capacity, and hence depends on the potential range, **Sample Interval**, etc.

Graphics Menu (**LSV** and **CV**)

Single Graph displays the current vs. potential plot.

Analysis Menu (**LSV** and **CV**)

The **Auto** option for **Results Graph** displays the current vs. potential plot, and the peak potentials and peak currents are listed in the **Main** window for all the segments scanned. Alternative baselines can be set by the user through the **Manual** option.

Math Menu (**LSV** and **CV**)

The derivative voltammogram is sometimes used to measure the peak potential more accurately, since the sign of the first derivative change at the peak potential. The convoluted voltammograms (both semi-derivative and semi-integral) are sometimes reported. The semi-differential voltammogram has symmetric peaks and better resolution than the standard voltammogram (see BAS Capsule 275 and Current Separation article 6. The semi-integral is used to correct for iR drop.

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10.2 Potential Step Techniques (CA, CC)

In these techniques, the potential is stepped from one value to another, and the current (**CA**) (or charge (**CC**)) response is monitored as a function of time (it should be remembered that charge is simply the integral of current). After the potential has been held at this value for a time τ, the potential can be stepped to another value (often the original potential). Therefore, potential step experiments can be single step, or double step.

The **General Parameters** are slightly different for **CA** and **CC**. For **CA**, an initial potential (**Initial E**), and high and low potentials (**High E** and **Low E**) are required. The potential can be stepped from **Initial E** to either **Low E** or **High E** (this is determined by the **Initial Direction** - **Positive** or **Negative** respectively). After time τ (the **Pulse Width**), the potential can be stepped in the opposite direction (from **Low E** to **High E** or **High E** to **Low E**), and is held at this value for time τ (Figure 10-4). For **CC**, the only potentials are the initial potential (**Initial E**) and the final potential (**Final E**) (Figure 10-5).

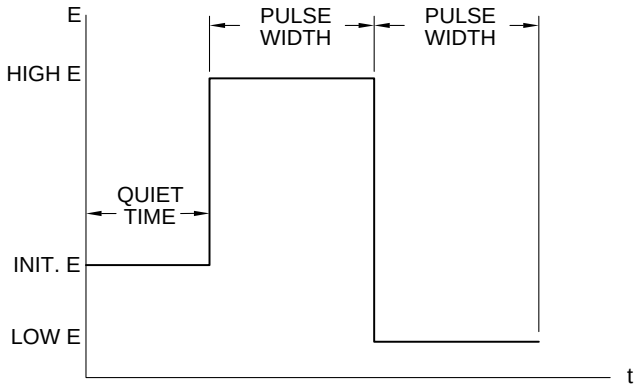


Figure 10-4. Potential wave form for **CA**.

The current/charge response depends on the values of the initial and final potentials. If no faradaic reaction occurs at either potential (a faradaic reaction is the electrolysis of any molecules in solution), then the response is due to charging of the electrode (the charging or background current). The response is a current 'spike', which decays exponentially.

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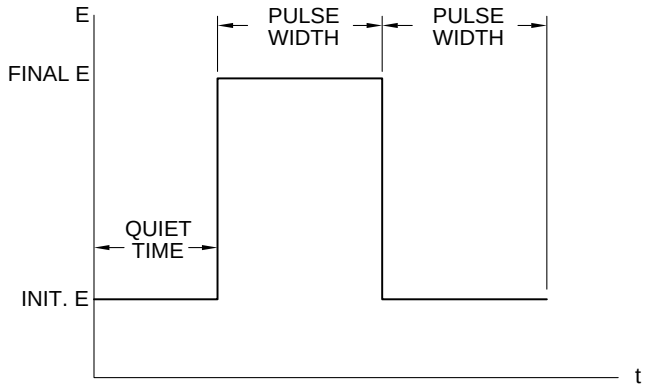


Figure 10-5. Potential wave form for **CC**.

Often, the initial potential is a potential at which no faradaic reaction occurs, and the final potential is a potential at which the Faradaic reaction occurs very rapidly; that is, the electroactive molecules are electrolyzed as soon as they arrive at the surface of the working electrode. The current is therefore determined by the rate of mass transport
from the bulk solution to the surface of the working electrode; that is, the rate of diffusion. The diffusion controlled current is given by the Cottrell equation.

$$i = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}}$$

where: i = current (A)
n = number of electrons transferred per molecule
F = Faraday`s constant (96,485 C/eq)
A = electrode area (cm^2)
D = diffusion coefficient (cm^2/s)
C = concentration (mol/cm^3)
t = time (s)

The diffusion controlled faradaic current therefore decays with $t^{-1/2}$ (a typical chronoamperogram is shown in Figure 10-6). The analogous expression for the diffusion controlled charge (Q_{diff}) is the integral of the above expression (i.e., Q_{diff} is proportional to $t^{1/2}$), and a typical chronocoulogram is shown in Figure 10-7.

Although i (or Q) vs. t plot is displayed during the experimental run, it is also useful to plot i vs. $t^{-1/2}$ (for **CA**) and Q vs. $t^{1/2}$ (for **CC**). For diffusion controlled systems, these are straight line plots, and are often referred to as the Cottrell plot (for **CA**) and the Anson plot (for **CC**). These plots are available as standard plots on the CV-50W.

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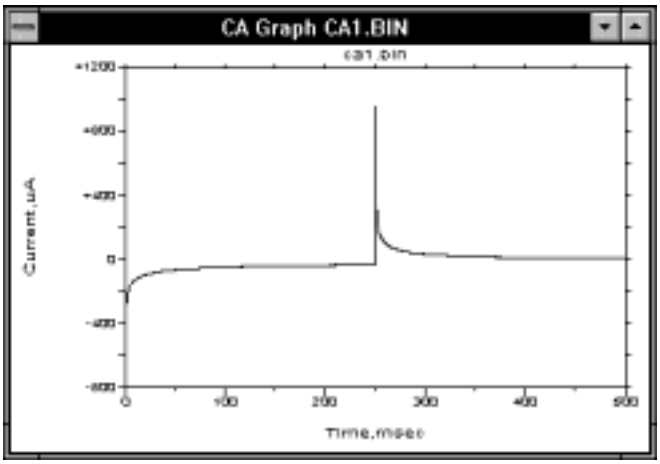


Figure 10-6. Chronoamperogram (current-time) response for double-potential-step **CA**.

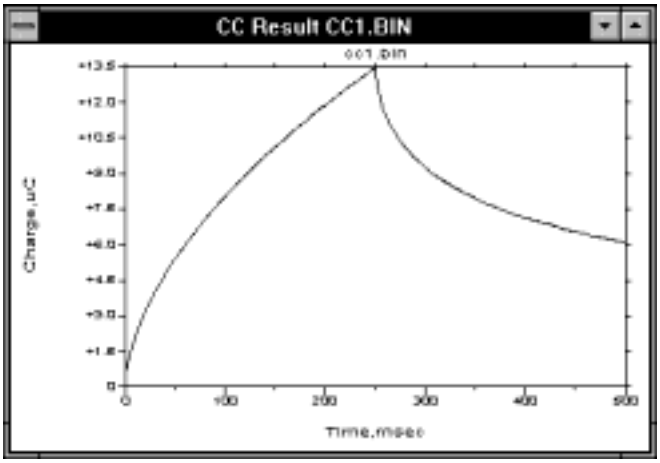


Figure 10-7. Chronocoulogram (charge-time) response for double-potential-step **CC**.

Therefore, both **CA** and **CC** can be used to measure one of n, C, A and D using the gradients of these straight line plots, provided the other three constants are known. However, other techniques (e.g., pulse techniques) have lower detection limits, so **CA** and **CC** are generally not used for concentration measurements. However, A and D are frequently measured using these techniques (1-3).

The relationship between i and $t^{-1/2}$ (or Q and $t^{1/2}$) can be used to investigate the period of time for which the current (or charge) is strictly controlled by diffusion. Figure 10-8 shows a plot of $i/t^{-1/2}$ vs. time. The deviation from ideality at short times is due to the finite length of time required to charge the working electrode to the step potential. The deviations at long times are due to natural convection.

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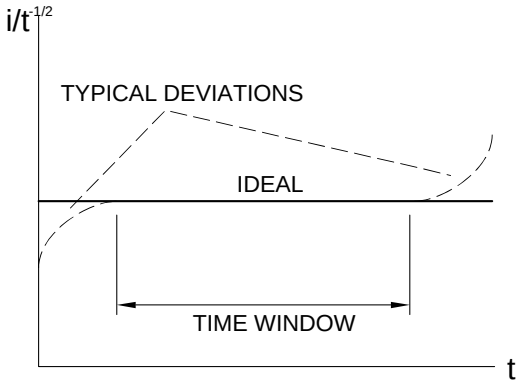


Figure 10-8. Plot of $i/t^{-1/2}$ vs. t for **CA** showing "time window" for condition of planar diffusion.

Although **CA** and **CC** are not used to measure absolute concentrations, they can be used to measure changes in concentrations due to homogeneous chemical reactions of the electrolyzed molecules (3,4). This uses the double step technique, and measures the ratio of the forward and backward currents (or charges). If the molecules undergo a chemical reaction after electrolysis in the forward step, then these molecules are not available for electrolysis in the reverse step. Hence, the faster the chemical reaction, the smaller the current/charge on the reverse step. The rate of the chemical reaction can be calculated by measuring the current (or charge) ratio at different pulse widths.

If the final potential is at a value at which the electron transfer does not occur rapidly, then the current (or charge) response may be influenced by the rate of heterogeneous electron transfer as well as the rate of diffusion. The rate of electron transfer can therefore be measured by **CA** and **CC** (5).

CC has several advantages over **CA**. The signal increases with time, so the latter parts of the response, which are least distorted by the finite charging time of the electrode, offer better signal-to-noise ratios (in addition, any white noise tends to averaged by integration) . In addition, since charge is a summation over the time frame of the experiment, the information from the early response is retained. However, in some instruments, this is not strictly the case, since the charge is obtained by integrating the discrete current values, and some charge is invariably lost. In contrast, in the CV-50W, there is a 'true' charge-to-voltage converter, which means that none of the early information is lost.

Another application of **CC** which takes advantage of it's ability to retain early information is the detection of species adsorbed to the surface of the working electrode (3). Such species are electrolyzed very rapidly when the potential is stepped. The total charge measured during the **CC** experiment is

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

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Q_{dl} is the charge due to charging of the working electrode, and Q_{ads} is the charge due to electrolysis of the adsorbed species, and is directly proportional to the surface concentration of the adsorbate. Of the three components, only Q_{diff} is time dependent. Therefore, the intercept of the Anson plot is $Q_{dl} + Q_{ads}$. One way of calculating Q_{ads} is to measure Q_{dl} by performing the **CC** experiment on the background solution. However, this assumes that Q_{dl} is the same in the presence and absence of the electroactive species; this is not necessarily true. A more accurate method is to use double step **CC**, since Q_{dl} can be eliminated by calculating the difference between the intercepts of the forward and reverse Anson plots (Figure 10-9).

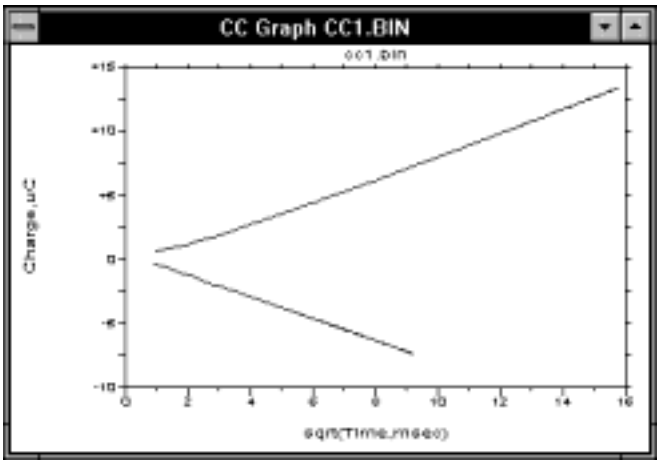


Figure 10-9. Forward and reverse Anson plots.

References

1) BAS Capsule, No. 133 Determination of Electrode Area with Chronocoulometry
2) BAS Capsule, No. 143 Determination of Diffusion Coefficients Using Chrono coulometry
3) W.R. Heineman, Curr. Seps 7 (1986) 58-67.
4) BAS Capsule, No. 268 Measurement of Reaction Kinetics Using Chronocoulometry.
5) A. J. Bard and L. R. Faulkner "Electrochemical Methods" Wiley, New York, 1980; p. 204-206

Mode = CA

General Parameters

Initial E (mV) = 0	-3276 to 3276
High E (mV) = 0	-3276 to 3276
Low E (mV) = 0	-3276 to 3276
Initial Direction = Negative	Negative or Positive
Pulse width (msec) = 250	1 to 32000
Sensitivity = 1 μA/V	100 mA/V to 100 nA/V

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Specific parameters

Number of Steps = 2	1 or 2
Quiet Time (sec) = 2	0 to 65535

Graphics Menu

Single Graph displays the **Current vs. Time** plot as the default plot. The Cottrell plot (**Current vs. 1/sqrt (Time)**) can be selected using the **Data Type** drop-down list box in the **Graphics Options** dialog box.

Analysis Menu

The **Auto** option for **Results Graph** displays the plot selected in **Data Type**, and the slope, intercept and correlation coefficient are listed in the **Main** window. Since data at early time points can be distorted due to the finite time required for the potential step, the **Auto** option uses only the last 80% of the data. An alternative line can be defined by the user through the **Manual** option (the line is specified by the X values of 2 points on the plot). The units for the slope are $mA \bullet ms^{1/2}$.

Comment: The maximum data file length is 1000 pts/step.

Mode = CC

General Parameters

Initial E (mV) = 0	-3276 to 3276
Final E (mV) = 0	-3276 to 3276
Pulse Width (msec) = 250	3 to 32000
Sensitivity = 1 μC/V	100 nC/V to 10 μC/V

Specific Parameters

Number of Steps = 2	1 or 2
Quiet Time (sec) = 2	0 to 65535

Comments

The maximum file length is 1000 points/step. The circuitry for CC is a direct charge-to-voltage converter. The integrating capacitor that is used to accumulate the charge in the 10 μC/V **Sensitivity** range is automatically discharged and reset to zero when it nears the voltage saturation level. This operation allows a much greater charge to be measured during the experiment. Discharging the capacitor requires 0.5 msec during which time no charge is measured. We have never had a situation where this has caused a noticeable error in the output, since discharge typically occursafter the initial large current transients have decayed and the current isrelatively small (so the charge lost over 0.5 msec is less than the

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resolution of the instrument and the expected precision of the experiment). However, errors can occur if the initial current are very large, since this may cause discharging at short times. Such errors are shown by discontinuities in the **Charge vs. Time** plot. If this occurs, the initial current must be decreased by, for example, decreasing the concentration and/or the electrode surface area.

The automatic discharge is not allowed for the 100 nC/V and 1 μC/V ranges, since the charge lost during the 0.5 msec may be significant.

Too much current may also cause the digital accumulators to overload. This occurs after 32 discharge-charge cycles, and is shown by sharp discontinuities in the **Charge vs. Time** plot as the charge drops to zero.

Graphics Menu

Single Graph displays the **Charge vs. Time** plot as the default plot. The Anson plot (**Charge vs. sqrt (Time)**)can be selected using the **Data Type** drop-down list box in the **Graph Options** dialog box.

Analysis Menu

The **Auto** option for **Results Graph** displays the plot selected in **Data Type**, and the slope, intercept and correlation coefficient are listed in the **Main** window. Since data at early time points can be distorted due to the finite time required for the potential step, the **Auto** option uses only the last 80% of the data. An alternative line can be defined by the user through the Manual option (the line is specified by the X values of 2 points on the plot). The slope is reported in units of $C/ms^{1/2}$.

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10.3 Pulse Techniques (SCP, NPV/P, DPV/P)

The basis of all pulse techniques is the difference in the rate of decay of background and faradaic currents following a potential step. The background current decays exponentially, whereas the faradaic current decays as a function of $1/(\text{time})^{1/2}$; that is, the rate of decay of the background current is considerably faster than the decay of the faradaic current. The background current is negligible at a time of $5R_uC_{dl}$ after the potential step (R_uC_{dl} is the time constant for a given 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 the potential pulse allows discrimination between the faradaic and charging current.

The important parameters for Pulse techniques are as follow:

a) **Pulse Amplitude** is the height of the potential pulse in mV.

b) **Pulse Width** is the duration of the potential pulse in msec.

c) **Sample Width** is the time (in msec) at the end of the pulse during which the current is measured. It must be at least 2 msec shorter than the **Pulse Width**. The current is sampled and averaged 16 times per msec. The default **Sample Width** is the time required for 1 line cycle.

d) **Pulse Period**/**Dropping Time** - This is the time required for one potential cycle (in msec) and must be at least twice the **Pulse Width**. **Pulse Period** is used for voltammetry experiments, whereas **Dropping Time** applies to polarography experiments, in which the potential pulse, current sampling and renewal of the mercury drop are coordinated (this is controlled by the CV-50W). As discussed above, the current is sampled at the end of the pulse, and the mercury drop is knocked off at the end of the **Sample Width** (which coincides with the end of the pulse). For polarography experiments using a dropping mercury electrode (DME), the advantage of sampling the current at the end of the drop lifetime is that the rate of change of the surface area (which contributes to the charging current) is at a minimum at this point.

Three different pulse techniques are available on the CV-50W Voltammetric Analyzer. These differ in the potential pulse waveforms and the number of sampling times. The discrimination against the charging current that is inherent in these techniques leads to lower detection limits (compared to linear sweep techniques), which make these techniques suitable for quantitative analysis.

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Sampled Current Polarography (**SCP**) or Tast polarography is a modification of the classical D.C. polarography experiment, and was designed to reduce the effect the changing surface area of the mercury drop. The potential wave form is shown in Figure 10-10. The potential is varied in a series of steps (it is held at each step for the **Drop Time**), and the current is sampled at the end of each drop. The **Drop Time** and the size of the potential step can be varied (through variation of the **Scan Rate**). This potential waveform is often referred as a staircase waveform.

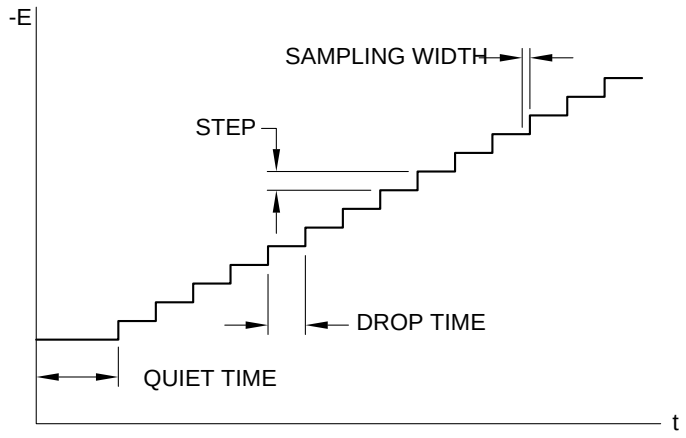


Figure 10-10. Potential wave form for **SCP**.

The current response is shown in Figure 10-11. The limiting current (i_d) is given by the Ilkovic equation:

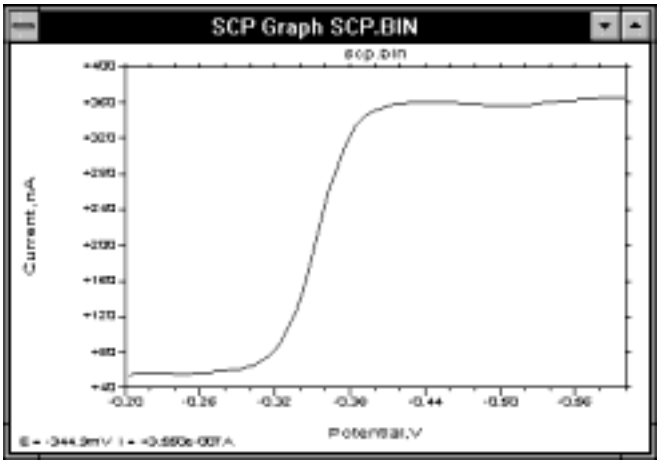


Figure 10-11. Typical current response for **SCP**.

$$i_d = 708nD^{1/2}Cm^{2/3}\tau^{1/6}$$

where: n = number of electrons transferred/molecule
D = diffusion coefficient (cm^2/s)
m = mercury flow rate (mg/s)
τ = sampling interval (s)

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The sensitivity and detection limit of **SCP** are similar to those of DC polarography (5 μA/mM and 10^{-5} M). The major advantage of **SCP** over D.C. polarography is the smoothed current output, which facilitates measurement of the half-wave potentials and limiting currents.

Although this is a essentially a polarographic technique, it can be used as a slow scan rate voltammetry technique. This modification is often called "staircase" voltammetry.

The potential wave form for Normal Pulse Voltammetry/Polarography **(NPV/P)** is shown in Figure 10-12, and consists of a series of pulses of increasing amplitude, with the potential returning to the initial value in between the pulses.

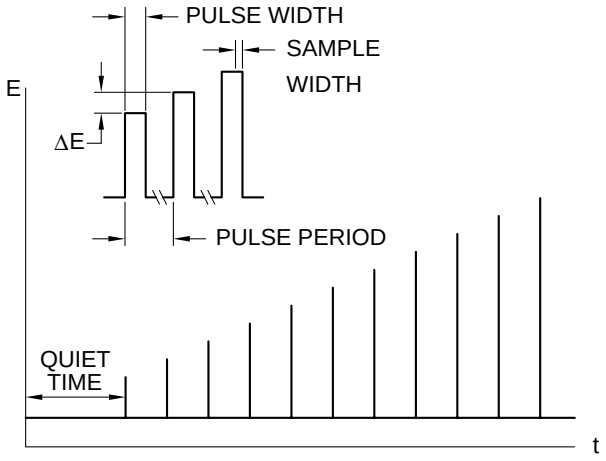


Figure 10-12. Potential wave form for **NPV/P**.

Consider a reduction. If **Initial E** is well positive of the redox potential, the application of small amplitude pulses does not cause any faradaic reaction, so there is no faradaic current response. When the pulse amplitude is sufficiently large that the pulsed potential is around the redox potential, there is a faradaic reaction in response to the pulse (assuming moderately rapid electron transfer kinetics), and the magnitude of this faradaic 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 occurs rapidly, the faradaic current depends only of the rate of diffusion; that is, a limiting current has been reached. This current response is shown in Figure 10-13. The sigmoidal shape is similar to the shape of the curve obtained in the classical polarography experiment, which gives rise to the name of normal for this pulse technique. The limiting current for **NPV/P** is greater than that for **SCP**, and is therefore a more sensitive technique (30 μA/mM) and has a lower detection limit (10^{-6} M).

There is a variation of this technique called Reverse Pulse Voltammetry/Polarography (RPV/P). In **NPV/P**, the initial potential is at a value at which no faradaic reaction occurs, whereas in RPV/P, the initial potential is at a value at which the faradaic

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reaction of interest occurs at the diffusion limited rate. This technique is useful for discriminating between a reversible redox process (rapid electron transfer) and an irreversible redox process (slow electron transfer on the reverse step), since both can be detected by NPV/P, whereas only the reversible process can be detected by RPV/P. One example of this is the detection of metal ions (reversible) in the presence of oxygen (irreversible).

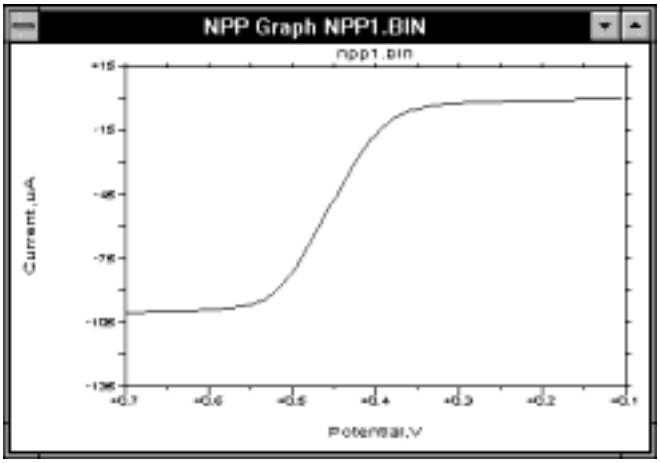


Figure 10-13. Typical current response for **NPV/P**.

Differential Pulse Voltammetry/Polarography (**DPV/P**) is different from the previous two techniques in that the current is sampled twice in each **Pulse Period**. The potential wave form is shown in Figure 10-14. The **Pulse Amplitude** is constant with respect to the base potential, and the base potential increases in small steps; that is, the potential wave form consists of small amplitude pulses superimposed upon a staircase waveform.

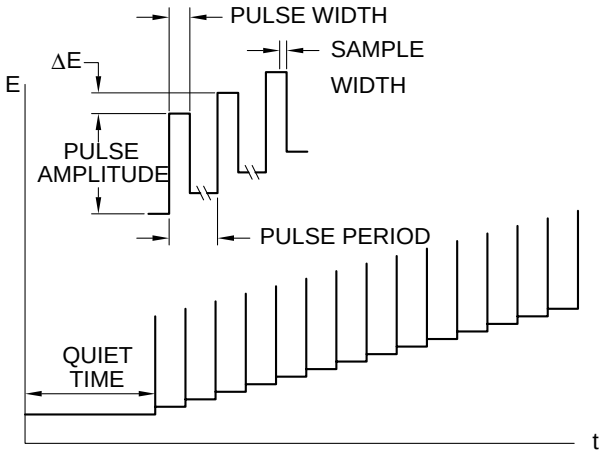


Figure 10-14. Potential wave form for **DPV/P**.

The current is sampled just before the pulse (i_1) and at the end of the pulse (i_2), and the difference (i_2 - i_1) is recorded as a function of the base potential. Consider a

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reduction. At potentials well positive of the redox potential, there is no faradaic reaction is response to the pulse, so the differential current is zero. At potentials around the redox potential, the differential current reaches a maximum and decreases to zero as the current becomes diffusion-controlled. The current response is therefore a symmetric peak (Figure 10-15).

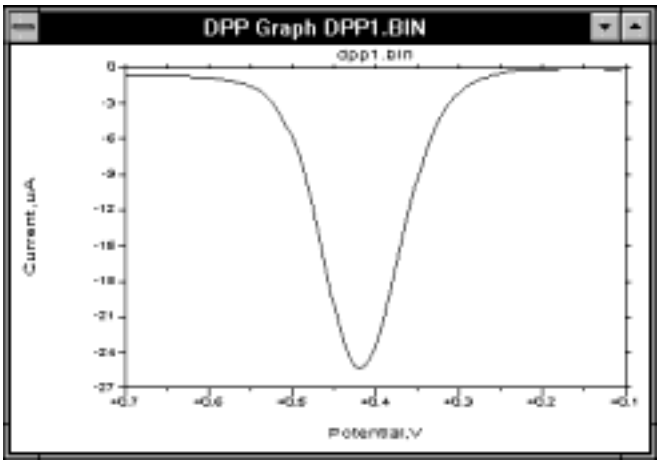


Figure 10-15. Typical current response for **DPV/P**.

The sensitivity of **DPV/P** is intermediate between **NPV/P** and **SCP** (20 µA/mM), but the detection limit of **DPV/P** is significantly lower (10^{-7} M) due to more effective discrimination against the charging current.

Mode = SCP

General Parameters

Initial E (mV) = 0	-3276 to 3276
Final E (mV) = 0	-3276 to 3276
Sensitivity = 1µA/V	100 mA/V to 100 nA/V

Specific Parameters

Scan Rate (mV/s) = 4	1 to 200
Sample Width (msec) = 17	1 to 250
Drop Time (msec) = 1000	100 to 8000
Quiet Time (sec) = 2	0 to 65535

Comments

a) Increasing the **Sample Width** can reduce noise.

b) The step height (or sampling interval) is the product of the **Scan Rate** and the **Dropping Time** (e.g. the default values is 4 mV).

Graphics Menu

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Single Graph displays the current vs. potential plot.

Analysis Menu

The **Auto** option for **Results Graph** displays the current vs. potential plot, and the half-wave potential and limiting current are listed in the **Main** window. Alternative baselines can be set by the user through the **Manual** option.

Mode = NPV/P

General Parameters

Initial E (mV) = 0	-3276 to 3276
Final E (mV) = 0	-3276 to 3276
Sensitivity = 1μA/V	100 mA/V to 100 nA/V

Specific Parameters

Scan Rate (mV/sec) = 20 (4)	1 to 200
Sample Width (msec) = 17	1 to 250
Pulse Width (msec) = 50	3 to 2000
Pulse Period (msec) = 200	40 to 8000
Drop Time (msec) = 1000	100 to 8000
Quiet Time (sec) = 2 (0)	0 to 65535

Comments

a) The **Pulse Period** is used in **NPV**, the **Drop Time** in **NPP**. When thedefault parameter value for **NPP** is different from that for **NPV**, it is shown in parentheses

b) Increasing the **Sample Width** can reduce the response noise.

c) The sample interval is equal to the product of the **Scan Rate** and the **Pulse Period** (or **Drop Time**) (e.g., the default value is 4 mV).

Graphics Menu

Single Graph displays the current vs. potential plot.

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Analysis Menu

The **Auto** option for **Results Graph** displays the current vs. potential plot, and the half-wave potential and limiting current are listed in the **Main** window. Alternative baselines can be set by the user through the **Manual** option.

Mode = DPV/P

General Parameters

Initial E (mV) = 0	-3276 to 3276
Final E (mV) = 0	-3276 to 3276
Sensitivity = 1μA/V	100 mA/V to 100 nA/V

Specific Parameters

Scan Rate (mV/sec) = 20 (4)	1 to 200
Pulse Amplitude (mV) = 50	-250 to 250
Sample Width (msec) = 17	1 to 250
Pulse Width (msec) = 50	3 to 2000
Pulse Period (msec) = 200	40 to 8000
Drop Time (msec) = 1000	100 to 8000
Quiet Time (sec) = 2 (0)	0 to 65535

Comments

a) **Pulse Period** is used for **DPV**, and **Drop Time** is used for **DPP**. When the default parameter value for **DPP** is different from that for **DPV**, it is shown in parentheses.

b) The product of the **Pulse Period** (or **Drop Time**) and **Scan Rate** must be less than the **Pulse Amplitude**, and greater than 1 mV.

c) When the **Pulse Amplitude** is negative, the direction of the **Pulse** is opposite to that of the scan.

d) Increasing the **Sample Width** can reduce the noise.

e) The sample interval is equal to the product of the **Scan Rate** and the **Pulse Period** (or **Drop Time)** (e.g., the default value is 4 mV).

Graphics Menu

Single Graph displays the current vs. potential plot.

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The **Auto** option for **Results Graph** displays the current vs. potential plot, and the peak potential and peak current are listed in the **Main** window. Alternative baselines can be set by the user through the **Manual** option.

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10.4 Square Wave Techniques (OSWV)

Osteryoung Square Wave Voltammetry (OSWV) is related to both pulse techniques and A.C. voltammetric techniques. It is similar to **DPV/P** in that the current response is a symmetric peak and that there is effective discrimination against background charging currents. Its chief advantages are greater sensitivity and faster speed.

The potential wave for (**OSWV**) is shown in Figure 10-16.

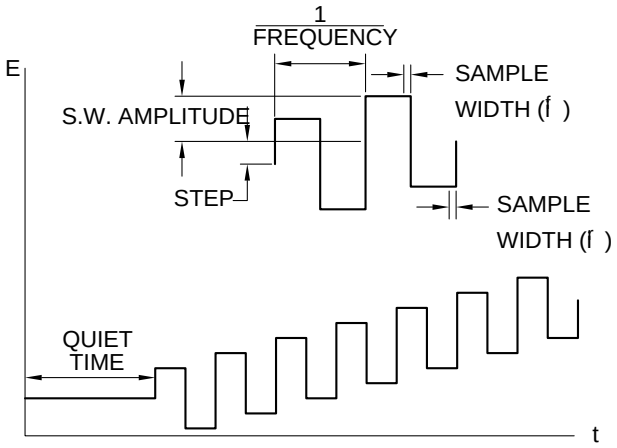


Figure 10-16. Potential wave form for **OSWV**.

The potential wave form for **OSWV** consists of a square wave superimposed on a staircase wave form. It can also be viewed as a series of pulses alternating in direction (hence, the relation to both pulse and A.C. techniques). The current is sampled at the end of each of the pulses (or half-cycles). The default current output is the difference current (Figure 10-17), but the forward current (i_f) and reverse current (i_r) can also be examined (Figure 10-18). For a reversible system, the reverse current is significant, so the difference current is greater than either the forward or reverse currents. This is one reason for the greater sensitivity of **OSWV** compared with **DPV/P**. The magnitude of the reverse current can also be used to investigate the reversibility of the electron transfer.

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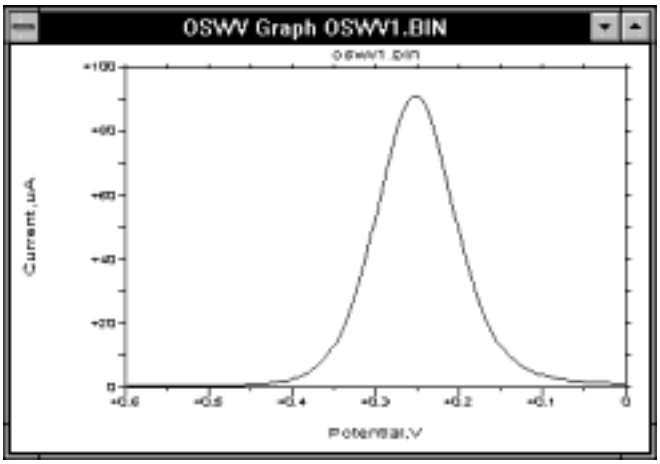


Figure 10-17. Difference current response for **OSWV**.

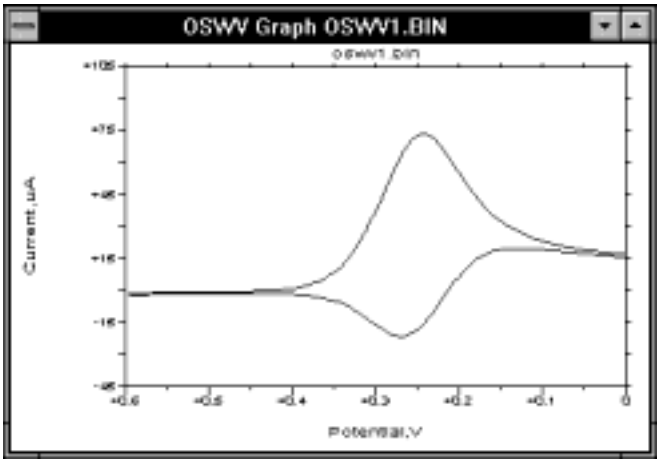


Figure 10-18. Forward and reverse current responses for **OSWV**.

The other advantage of **OSWV** compared to **DPV/P** is its speed. Scan rates of up to 8 V/s are available on the CV-50W, although scan rates of 100s mV/s to a few V/s are typically used (note that the scan rate for **OSWV** depends on the square wave frequency). This is significantly faster than the scan rate for **DPV/P** (ca. 10 -20 mV/s). In addition, the sensitivity of **OSWV** (compared with **DPP/V**) increases with increasing scan rate, even for irreversible processes. The greater sensitivity and faster speed of **OSWV** has increased the popularity of this technique for quantitative determination of electroactive species in solution. The detection limit can be further lowered by using stripping methods, which are discussed in section 10.5.

Mode = OSWV

General Parameters

Initial E (mV) = 0	-3276 to 3276
Final E (mV) = 0	-3276 to 3276
Sensitivity = 1µA/V	100 mA/V to 100 nA/V

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Specific Parameters

Step E (mV) = 4	1 to 40
S.W. Amplitude (mV) = 25	1 to 250
S.W. Frequency (Hz) = 15	1 to 200
Sampling Points = 256	1, 16, 256
Quiet Time (sec) = 2	0 to 65535

Comments

a) The **S.W. Amplitude** must be greater than **Step E** (which is the potential step height for the staircase potential wave form).

b) **Sampling Points** is the number of current samples taken and averaged at the end of each half-cycle. The 2 current sampling options are:

   i) 256 samples taken and averaged over 1 line cycle (maximum **S.W. Frequency** = 15 Hz).
   ii) 16 samples taken and averaged over 1 msec (maximum **S.W. Frequency** = 200 Hz)

   The maximum frequency for each option is such that the sampling time is no longer than 1/2 of each half-cycle. The option is selected by the software.

c) The scan rate (mV/s) is the product of the **S.W. Frequency** and **Step E**.

d) The sample interval is equal to **Step E**.

e) Maximum data file length is 1279 points.

Graphics Menu

Single Graph displays the current vs. potential plot(s) of the **Data Sets** specified in the **Graph** and **Results Options** dialog boxes.

Analysis Menu

The **Auto** option for **Results Graph** displays the current vs. potential plot(s) of the **Data Sets** specified in the **Graph** and **Results Options** dialog boxes, and the peak potential and peak current are listed in the **Main** window. Alternative baselines can be set by the user through the **Manual** option.

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10.5 Stripping Techniques (DPSV, LSSV, OSWSV)

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

There are 3 important parts in a stripping experiment. These are:

a) Deposition
b) Quiet Time
c) Stripping

These can best be explained by discussing the stripping experiment for detection of lead. In this experiment, a mercury electrode is used; this is either the Hanging Mercury Drop Electrode (HMDE) or the Thin Mercury Film Electrode (TMFE). The latter electrode is made by depositing a mercury film on the surface of a glassy carbon electrode. This deposition can be done either prior to the stripping experiment or during the deposition step.

During the deposition step, the potential is held at a value (**Deposition Potential**) at which the lead ions are reduced to lead metal for a pre-determined time period (**Deposit Time**). The metallic lead then amalgamates with the mercury electrode (when the TMFE is being used, mercuric ions are added to the solution, and mercury metal is co-deposited with the lead during the deposition step). The effect of the deposition step is to concentrate the lead in the mercury electrode; that is, the concentration of lead in the mercury electrode is significantly greater than the concentration of lead in solution (this step is often called the preconcentration step). The efficiency of the deposition step is increased by stirring the solution or using a Rotating Disk Electrode. The time elapsed during the deposition step is shown on the PC screen by a software generated clock.

During the **Quiet Time**, the stirring is stopped and lead distributes within the mercury electrode to produce a uniform concentration. Typically, 5 to 10 sec are required for this step.

During the stripping step, the potential is scanned in a positive direction, and the lead in the mercury electrode is oxidized back to lead ions in solution at a specific potential; that is, the lead is 'stripped' from the electrode. The stripping potential can be used for qualitative identification of the metal, and the stripping current can be used for quantitation of the concentration of metal ions in solution. There are a number of different waveforms available for this potential scan: Differential Pulse (**DPSV**), Linear Sweep (**LSSV**), and Osteryoung Square Wave (**OSWSV**). Of these

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options, **DPSV** and **OSWSV** are most often used, due to their good sensitivity and low detection limits, together with their speed of operation. A typical current response for the stripping step for **OSWSV** is shown in Figure 10-19.

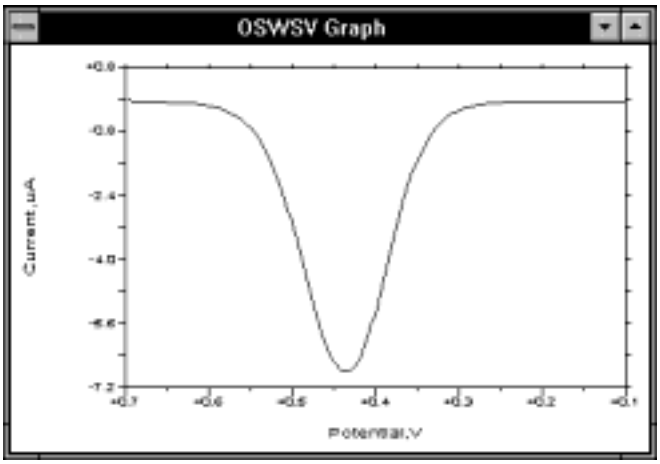


Figure 10-19. Typical current response for **OSWSV**.

It is important to note that it is the concentration of lead in the mercury electrode that is important rather than the concentration of lead in solution. The concentration of lead in the mercury electrode can be increased (and hence the detection limit of the experiment lowered) by increasing the **Deposit Time** and/or the stirring rate. The magnitude of these two parameters depends on the sensitivity of the mercury electrode, which depends on the surface area to volume ratio (i.e., how many of the lead atoms deposited are on the surface and detectable in the stripping step). This ratio is considerably higher for the TMFE, so a shorter deposition time is required (ca. 1-2 minutes vs. 5 minutes). In addition, faster stirring can be used with the TMFE due to the relative mechanical instability of the HMDE. The signal resolution is also better with the TMFE, which can be important when there is more than one metal ion present.

However, the greater sensitivity of the TMFE can also be a disadvantage, since the solubility 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 (e.g., shifts in the stripping potential and depression of the stripping current). 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 stripping experiments must be reproducible. Therefore, experimental conditions must be reproducible. Great care must be taken in the sample preparation, cleaning of glassware, etc. The rate of stirring during the deposition step and the condition of the mercury electrode must also remain constant. The advantage of using the Rotating Disk Electrode with a TFME is the precise control of the rotation rate; however, it is easier to obtain a reproducible electrode surface with the HMDE than with the TMFE

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(for which careful cleaning and polishing of the glassy carbon electrode surface is required between experiments).

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, which includes about 20 metal ions (e.g., Pb, Cu, Zn, Cd). 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 (up to 6, depending on the stripping potentials of the metals present). In addition, different oxidation states of one particular metal can be detected.

Other stripping 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. This film is then removed in the stripping step using a cathodic scan. CSV is most commonly used for the detection of sulfur-containing molecules (e.g., thiols, thioureas and thioamides), but it has also been used for molecule such as riboflavin and nucleic acid bases (e.g., adenine and cytosine).

AdSV is different from ASV and CSV in that the preconcentration step is non-electrolytic, and occurs via the adsorption of molecules on the surface of the working electrode (the mercury drop is most commonly used). The stripping step can be either cathodic or anodic. AdSV has been used for organic molecule (e.g., dopamine, chlorpromazine, erythromycin, dibutone, ametryne) and for metal complexes (e.g., dimethylglyoxime complexes of cobalt and nickel); hence, AdSV can be used for detection of metal ions that are not suitable for ASV.

References

1 Stripping Voltammetry, A.W. Bott, Curr. Seps. 12 (1993) 141.

2 BAS Capsule No. 150 Anodic Stripping Voltammetry of Lead and Cadmium

3 An Inexpensive Approach to Inorganic Gunshot Residue Analysis using Anodic Stripping Voltammetry. S. Chouchoiy and R.C. Briner, Current Separations 4 (1982) 20

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Deposit Options for **DPSV**, **LSSV** and **OSWSV**

The **Deposit Options** dialog box in the **Method Menu** is used to control the **Deposition Potential**. The default for this parameter is the initial potential for the potential scan (**Initial E**). However, if some other potential is required for the **Deposition Potential**, then the **Deposit E** option should be selected. The desired **Deposit E** can then be entered. The electrode potential is always held at **Initial E** during the **Quiet Time**.

Mode = DPSV

General Parameters

Initial E (mV) = 0	-3276 to 3276
Final E (mV) = 0	-3276 to 3276
Sensitivity = 1μA/V	100 mA/V to 100 nA/V
Deposit Time (sec) = 15	1 to 65535

Specific Parameters

Scan Rate (mV/sec) = 20 (4)	1 to 200
Pulse Amplitude (mV) = 50	-250 to 250
Sample Width (msec) = 17	1 to 250
Pulse Width (msec) = 50	3 to 2000
Pulse Period (msec) = 200	40 to 8000
Quiet Time (sec) = 10	0 to 65535

Comments

a) **Sample Width** is the time at the end of the pulse during which the current is measured. The default value is the time required for 1 cycle. Increasing the **Sample Width** can decrease the noise level.

b) **Pulse Width** is the duration of the pulse, and must be at least 2 msec longer than the **Sample Width**.

c) **Pulse Period** is the time required for 1 potential cycle, and must be at least twice the **Pulse Width**.

d) The product of the **Pulse Period** and **Scan Rate** must be less than the **Pulse Amplitude**, and greater than 1 mV.

e) When the **Pulse Amplitude** is negative, the direction of the **Pulse** is opposite to that of the scan.

f) The sample interval is equal to the product of the **Scan Rate** and the **Pulse Period** (e.g., the default value is 4 mV).

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Mode = LSSV

General Parameters

Initial E (mV) = 0	-3276 to 3276
Final E (mV) = 0	-3276 to 3276
Scan rate = 100 mV/s	1 to 51200
Sensitivity = 1 µA/V	100 mA/V to 100 nA/V
Deposit Time (sec) = 15	1 to 65535

Specific Parameters

Sample Interval (mV) = 1	1 to 20
Quiet Time (sec) = 10	0 to 65535

Mode = OSWSV

General Parameters

Initial E (mV) = 0	-3276 to 3276
Final E (mV) = 0	-3276 to 3276
Sensitivity = 1µA/V	100 mA/V to 100 nA/V
Deposit Time (sec) = 15	1 to 65535

Specific Parameters

Step E (mV) = 4	1 to 40
S.W. Amplitude (mV) = 25	1 to 250
S.W. Frequency (Hz) = 15	1 to 200
Sampling Points = 256	1, 16, 256
Quiet Time (sec) = 10	0 to 65535

Comments

a) The **S.W. Amplitude** must be greater than **Step E** (which is the potential step height for the staircase potential wave form).

b) **Sampling Points** is the number of current samples taken and averaged at the end of each half-cycle. The 2 current sampling options are:

   i) 256 samples taken and averaged over 1 line cycle (maximum **S.W. Frequency** = 15 Hz).
   ii) 16 samples taken and averaged over 1 msec (maximum **S.W. Frequency** = 200 Hz)

   The maximum frequency for each option is such that the sampling time is no longer than 1/2 of each half-cycle. The option is selected by the software.

c) The scan rate (mV/s) is the product of the **S.W. Frequency** and **Step E**.

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d) The sample interval is equal to **Step E**.

Graphics Menu

Single Graph displays the current vs. potential plot for the stripping step.

Analysis Menu

The **Auto** option for **Results Graph** displays the current vs. potential plot for the stripping step, and the peak potential and peak current are listed in the **Main** window (it should be noted that the default **Peak Shape** for all the stripping techniques is **Symmetric**). Alternative baselines can be set by the user through the **Manual** option.

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10.6 Time Base (TB)

This is a chronoamperometric technique; that is, the current is measured as a function of time. Generally, such techniques are used for amperometric titrations, amperometric sensors, flow cells, etc.

The simplest potential waveform is obviously a fixed potential, and this is the waveform for **TB**. The wave form for TB and a typical current response are shown in Figure 10-20 and Figure 10-21 respectively.

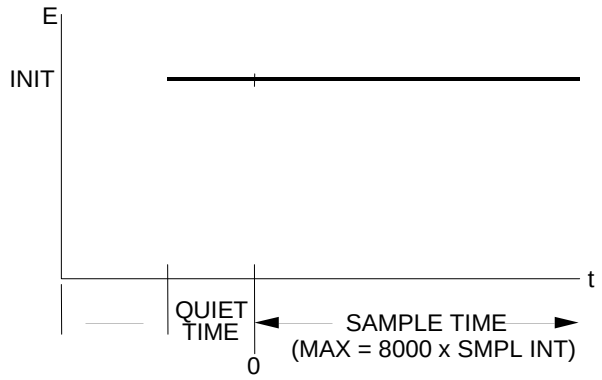


Figure 10-20. Potential wave form for **TB**.

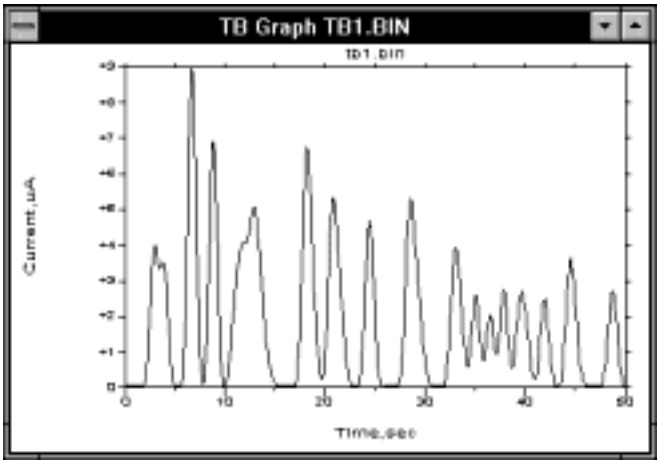


Figure 10-21. Typical current response for **TB**.

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Mode = TB

General Parameters

Initial E (mV) = 0	-3276 to 3276
Sample Interval (msec) = 500	50 to 20000
Run Time (sec) = 4000	1 to 65535
Sensitivity = 1 μA/V	100 mA/V to 100 nA/V

Specific Parameters

Real Time Integrator = Off	Off/On
Quiet Time (sec) = 2	0 to 65535

Comments

a) The **Sample Interval** is the time resolution of the experiment.

b) The number of data points recorded in an experiment must be less than or equal to 8000, which is the data storage limit. If the product exceeds 8000, then the **Run Time** is automatically adjusted to an acceptable value.

c) A **Precondition** potential can be applied for the **Precondition Time** before the start of the experiment.

d) When enabled, the **Real Time Integrator** adds all the current values to give the charge accumulated.

Graphics Menu

Single Graph displays the current vs. time plot.

Analysis Menu

Results Graph is disabled for **TB**.

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10.7 Bulk Electrolysis with Coulometry (BE)

The principle behind the Bulk Electrolysis (**BE**) experiment is very simple. If only the oxidized species is initially present, then the potential is set at a 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 **BE** experiment (Q) 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/mole). Therefore, if one of n or N is known, the other can be calculated. Hence, **BE** has both analytical and synthetic applications.

The cell required for **BE** 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.

Before a **BE** experiment can be run, the potential must be chosen. For a reduction, the ideal potential is ca. 200 mV more negative than the redox potential (measured by e.g.,
Cyclic Voltammetry) 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).

When the **BE** experiment is running, a software generated clock on the PC screen indicates the experiment run time. At each **Sample Interval**, the current passed during that interval and the total charge passed to that time are displayed on the screen. The ratio of the average current during the time interval just passed to that of the first time interval is also shown. This ratio is an important criterion for

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determining the extent of the electrolysis; that is, electrolysis is generally complete when this ratio reaches 1% (any residual current being background current). This **End Current Ratio** can be set by the user (1% is the default value). In addition to numerical results (see below), the experimental data can be presented by a charge vs. time plot (Figure 10-22) or a current vs. time plot (Figure 10-23).

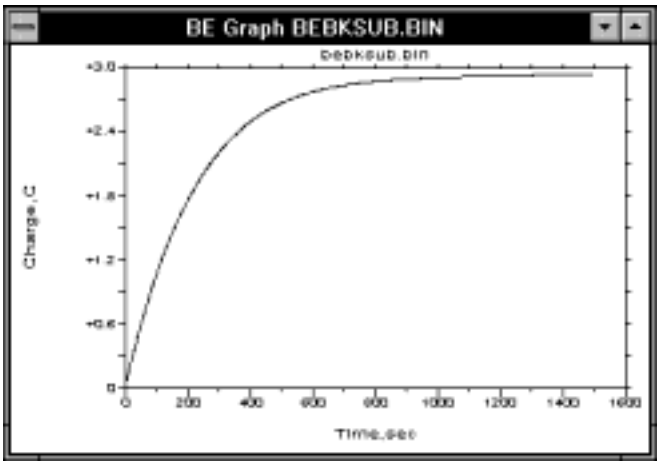


Figure 10-22. Typical charge vs. time plot for **BE**.

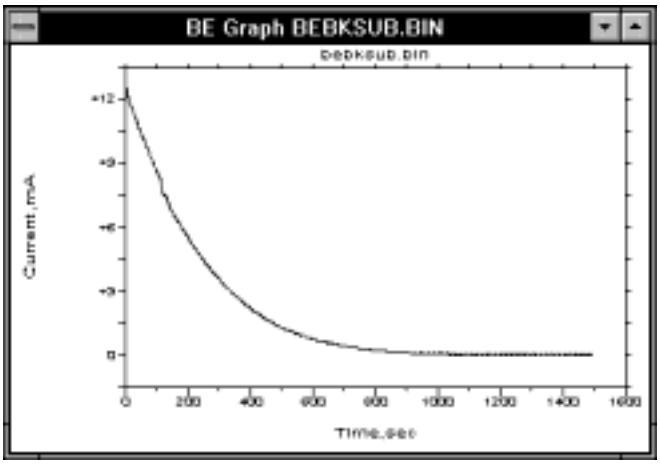


Figure 10-23. Typical current vs. time plot for **BE**.

The total charge is measured by taking successive readings from the I-E converter and adding these values together. Although this simplifies the measurement, some charge is invariably lost. The error depends on the timescale of the **BE** experiment. At very short time (less than 0.1 sec), the error is typically 1-5%; however, at 10 seconds, the error is only about 0.03 to 0.05%. As the timescale of **BE** experiments is typically of the order of minutes, the charge loss due to the simplified measurement technique is generally negligible.

Another potential source for error in the charge measurement is the use of automatic **Sensitivity** control, since about 3 msec is required for this measurement, during

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which time no measurement can be taken. This error is only significant if the time constant of the cell is short. In these cases, it is better to use manual **Sensitivity**. However, for most BE experiments, the automatic Sensitivity control gives the most accurate results. If the manual **Sensitivity** selection is too low, then accuracy is lost, but if it is too high, overload will occur and the experiment has to be repeated.

Using a working electrode with a large surface area can lead to oscillation in the electronic circuits. To stabilize the system, a 0.1 μF capacitor is automatically connected between the reference and auxiliary electrodes. The stabilizing capacitance can be increased or removed using the **Manual** option for **Stabilizing Capacitor** in the **Method Menu**. However, there is generally no need to use the **Manual** option.

Mode = BE

General Parameters

Initial E (mV) = 0	-3276 to 3276
Sample Interval (msec) = 1000	100 to 65535
End Current Ratio (per thousand) = 10	1 to 1000
Sensitivity = Auto	Auto, 100 mA/V to 100 nA/V

There are no **Specific Parameters**.

NOTE: Once the End Current Ratio has been reached, the experiment should be ended by clicking Stop in the Control Menu (or F5).

Comment: The maximum file length is 4096 data points.

Graphics Menu

Single Graph displays the **Charge vs. Time** plot. The **Current vs. Time** plot can be displayed using **Data Type** in **Graphics** or **Results Options**. The shape of these plots can indicate chemical reactivity of the electrolyzed species.

Analysis Menu

The **Auto** option for **Results Graph** displays the same plot as **Single Graph**, and Init i, End i, i ratio, Time, Total Q and Net Q are listed in the **Main** window (Net Q is the Total Q minus the background Q, where the background i is assumed to be End i).

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11. Service and Troubleshooting

11.1 Preventative Maintenance

Routine maintenance for the CV-50W consists of making certain that the forced air cooling systems are cleaned and checked regularly. Forced air is employed for both the power supply and circuit board enclosure. The cooling air inlet and air filter are located on the front panel. A routine inspection (perhaps weekly in a dusty area) is required for the filter. Cleaning is required if the filter has trapped dust and lint on its surface, or is turning white in color. The filter is not removable for cleaning, but can be easily cleaned with a vacuum cleaner equipped with a brush accessory. Be sure that the CV-50W power switch is off before cleaning so that the internal fans do not pull in dust that is dislodged during filter cleaning.

If a fan operates in a “sluggish”, “noisy” or abnormal way, then replacement is recommended.

Periodically examine both internal and external cables and wires for damage to the insulation or connectors and replace as needed. Periodically check the system for loose screws, brackets, fans, etc.; tighten as necessary.

11.2 Troubleshooting

When intermittent or unusual problems arise, often they are induced into the CV-50W through the environment or power source. Ungrounded or fluctuating electrical power sources many also cause abnormal operation. Operate your CV-50W from a power source that is free from heavy loads or cycling devices such as; refrigerators and ovens.

A major culprit causing CV-50W malfunction can be the discharge of static into the unit. Symptoms include aborting of an experiment in mid-run, resetting periodically with no operator intervention, or an inoperable keyboard. Anytime the unit is doing unusual starting, stopping, drifting into uncalled responses or commands, static discharge is most often the problem. The solution is to eliminate it or provide a means to dissipate the charge. For example, placing the unit on a good static mat should reduce this problem. This problem is also more prevalent in the winter months when the humidity is low.

Analog electronic devices tend to drift over time (months, years), and so periodically require recalibration. This typically required that the circuit board(s) be returned to BAS. In contrast, any problems in the digital circuitry generally leads to catastrophic failure, so should be obvious.

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11.3 Reference Electrodes

A poor reference electrode can cause considerable problems, so these should be carefully maintained. BAS Ag/AgCl electrodes are shipped with the Vycor frit covered by yellow plastic. This should be removed upon receipt, and the electrode should be stored with the Vycor frit immersed in a solution of 3M NaCl, where it should remain when not in use. Other reference electrodes should also be stored in the appropriate solution (e.g., saturated KCl for the saturated calomel electrode).

Failure to store reference electrodes properly can lead not only to a drift in the electrode potential but it can also causes precipitation of salts in the frit. This can in turn result in very noisy data. Similar effects can also be caused by presence of air bubbles next to the Vycor frit. These can be removed by gently flicking the end of the electrode.

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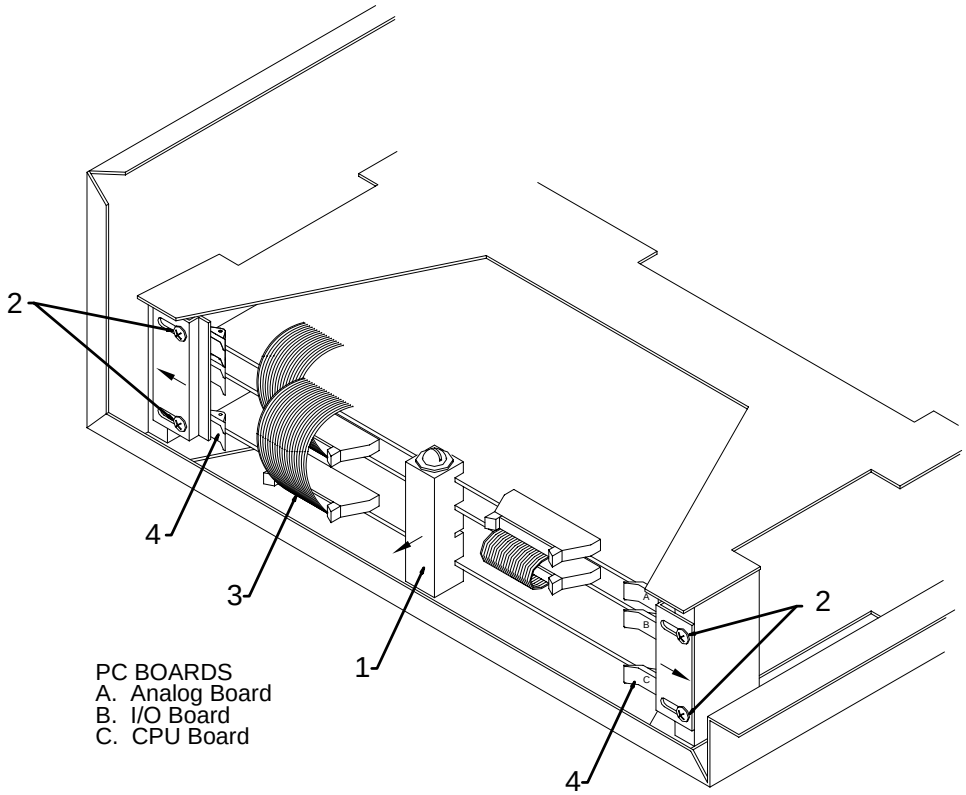
Symptom	Possible Cause	Corrective Action
When CV-50W is turned-on, fans do not run	Not plugged in Blown fuse Defective power cord Defective power switch Defective fans	Plug in! Replace fuse Replace cord Replace switch Replace fans
	Defective power supply	Check power supply Call BAS customer service
Self-Test Diagnostic Failures:		
Any ROM error, error in RAM 1,3,4,6 or BANK SWITCH ERROR	Defective CPU board	Replace CPU board. Call BAS Customer Service
Error in RAM 5	Defective I/O board	Replace I/O board. Call BAS Customer Service
Self-Test reads “RAM OK, ROM OK” and doesn’t continue on to analog test	40 pin jumper between analog and I/O boards not making contact	Check connection, plug in
Error in 1 or 2 analog tests	Small offset is present in analog system. This may be caused by temperature changes or long term calibration drift.	No cause for undue concern. Call BAS Customer Service for advice/repair.
Error in several analog ranges	Power supply voltages out of tolerances Defective analog board	Test power supply DC. Make sure all output cables are disconnected before testing. Replace analog board Call BAS Customer Service.
Operation appears to be normal but no data is acquired	Poor connections at either end of cell cable Cell lead defective	Check cell cable connections Replace cell lead Call BAS Customer Service
Random malfunctions	Static discharges Power line disturbances Overheating Poor connections at either end of cell lead Defective cell leads	Install anti-static mat. Connect to a “clean” power line. Clean filters and check fans (don’t block cabinet vents!) Check lead connections Replace cell lead Call BAS Customer Service.
The following Analog errors simultaneously Error in ranges 5,4,3	CC discharge relay sticking	Replace relay Call BAS Customer Service

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Bipolarity	
General Protection Fault	Restart CV-50W software
CV-50W doesn’t respond to PC commands	Run Self-Test Hardware
“Linked Failed” error message	Reset potentiostat or restart CV-50W software

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11.4 Removal of Circuit Boards



a) Remove white plastic board support (item 1).

b) Loosen four designated screws (Item 2) on card rack and slide card retainer plates outward.

c) Remove necessary ribbon cables (Item 3) by pressing ejectors outward from connectors and remove.

d) Remove circuit board by pressing ejectors (Item 4) outward and pulling boards straight out. NOTE: Many of the large scale integrated circuits are static sensitive. DO NOT place on plastic (e.g., bubble pack), carpeting or other surface which may have static build-up.

e) To reinstall boards, reverse the above procedure.

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