VERSION 1.5
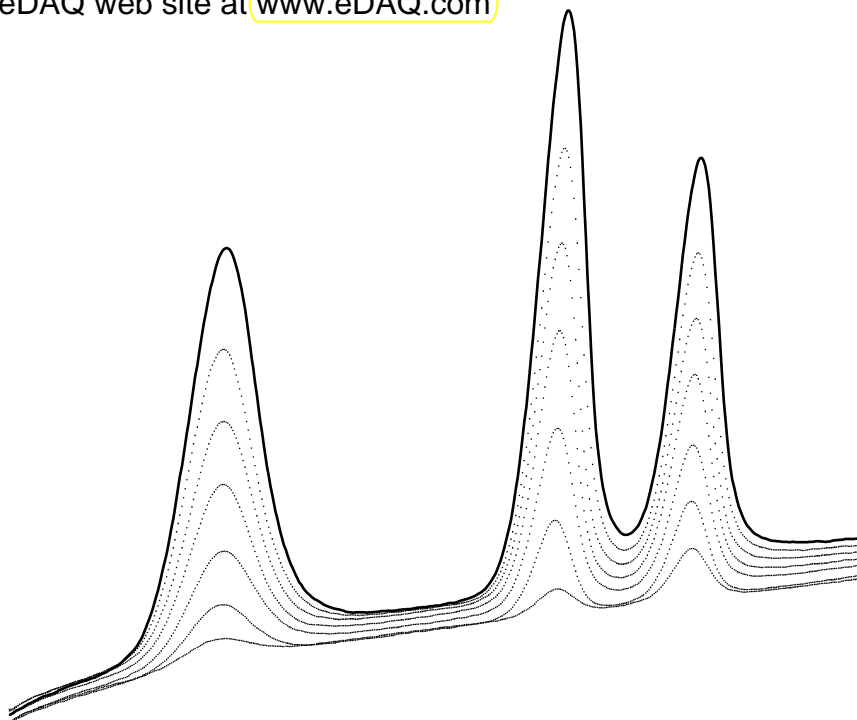
EChem
User's Guide

& using Chart & Scope software for Electrochemistry

Please check for the release of the EChem v2 manual on the eDAQ web site at www.eDAQ.com

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1 Getting Started

Welcome to the ADInstruments PowerLab/EChem electrochemistry system. EChem software lets you use your computer[*] and PowerLab analog-to-digital interface unit as an electrochemistry workstation suitable compatible with a wide variety of potentiostats and patch and voltage clamps. EChem causes the PowerLab unit to generate the potential waveform for most staircase ramp and pulse voltammetric techniques, as well as pulsed amperometric experiments, samples and signal averages the current signal at appropriate times, and displays the results in real time. Chapter 7 has a full description of the techniques available. In addition, when used with the ADInstruments Potentiostat, full software control of gain ranges, filter settings and polarity convention is available.

Many other types of electrochemistry experiment can be performed with the Chart and Scope software included with your PowerLab system. Consult Chapter 8 for further details of these experiments.

This chapter contains instructions on the installation of EChem software, and its hardware requirements.

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*. EChem software, version 1.5, is suitable for use with Macintosh, Windows 95, 98, NT, 2000 or Me computers.

Learning to Use EChem

Where to Start

To install and use EChem you should be familiar with the operating system of your computer.

You will find that EChem works similarly to other programs that you use on your computer. If you have used earlier versions of EChem software, you should find that although this version has much in common, it also has many new features.

Start by reading the introductory chapters in your *Getting Started with PowerLab* booklet which describes how to connect the PowerLab unit to your computer. If you are not using an ADInstruments Potentiostat then you should also read Chapter 9 before using the system. If you are new to electrochemical techniques, then first familiarise yourself with the various terms defined in the Glossary at the end of this guide.

How to Use this Guide

If you are in a hurry at least read the rest of this chapter, and the Overview of EChem in the next chapter, to familiarise yourself with some of the key features of EChem before you begin your experiments.

We recommend, however, that you work through this guide in front of your computer. The information in the following chapters is set out in the order you will probably require it. If you are unfamiliar with electrochemical methods then read Chapters 7 and 8. The appendices also have much useful information including electrolyte syntheses, solvent purification methods, and sources of general information.

The rest of this chapter, covers system configurations and installing and personalising your copy of EChem.

If you are using a third party potentiostat with EChem then please read the potentiostat operator's manual carefully to determine its limitations safe operating procedure. In particular be aware of the

maximum potential and current that your potentiostat can generate. Never touch the electrodes while the potentiostat is in operation as this is extremely dangerous with high powered models.

Computer Requirements

Your particular needs will determine the computing requirements and hence which model of computer you use. Your ADInstruments representative will be happy to discuss your requirements and suggest suitable configurations.

Apple Macintosh

Minimum: The minimum requirement is a Macintosh computer with a 68020 microprocessor and a hard disk, System 7, 8MB RAM, and a 13 inch monitor. If you own an early model Apple Macintosh then we can supply EChem version 1.3 on request. Although EChem 1.3 has fewer features than EChem 1.5, it will run even on early model 68000 Apple Macintosh computers with System 6 or System 7, and on computers with 9 or 12 inch black and white or color monitors (for example a Mac SE with system 6 will happily run EChem version 1.3). Data files collected with EChem 1.3 can also be opened with EChem 1.5.

Chart and Scope software, versions 3.3.8, are also available for use with PowerLab units used with early model Apple Macintosh computers.

Recommended: a Power Macintosh G3, with a hard disk, System 8, 32 MB RAM, and a 14-inch or larger color monitor.

Printers: there are numerous printers available that can be used to produce reports from EChem. Some recommended printers are: the Apple Color StyleWriter 2500, a color inkjet printer producing high quality color printouts at near laser printer quality; and the Apple LaserWriter series. If you buy a laser printer ensure that it has true PostScript® capability — which will ensure that you get the highest quality graphic output for plotting your results.

Microsoft Windows

Minimum: An IBM compatible computer with Pentium microprocessor with Windows 95, Windows 98, or Windows NT (v4.0) operating system, and 16 MB RAM (32 MB for NT), and a 14 inch or larger monitor, a color VGA card and a CD ROM or floppy disk drive. A suitable SCSI card will need to be installed (contact ADInstruments for names of suitable brands).

Recommended: An IBM compatible computer with Pentium-level or faster CPU and a fast hard disk, Windows 98 or Windows NT (v4.0) operating system, at least 32 MB RAM (48 for NT), an accelerated color Super VGA card (or equivalent), and a 16-inch or larger monitor, and a CD ROM. A suitable SCSI card will need to be installed (contact ADInstruments for names of suitable brands).

Printers: there are numerous printers available that can be used to produce reports from EChem, most Windows compatible printers will be suitable — but dot matrix and other low resolution printers may not give you the graphic resolution you require for publication quality diagrams. If you buy a laser printer ensure that it has true PostScript® capability — which will ensure that you get the highest quality output when plotting your results.

The EChem System

The EChem/PowerLab system is an integrated hardware and software system designed to record, display, and analyse experimental data. The PowerLab hardware interface is connected between the potentiostat and the computer. EChem software runs on the computer to which the PowerLab is connected. You must have installed software on the computer and connected the PowerLab hardware to the computer to collect experimental data. However, pre-existing data files can be opened with, analysed by, and printed from the software, whether or not the PowerLab unit is connected.

Data collected with EChem software on a Windows computer can be read by the Macintosh version of EChem and vice versa. You can

transfer data between computers on Windows formatted floppy disks (Macintosh computers read Windows formatted disks).

Other ADinstruments software that runs with PowerLab units, includes Chart and Scope software (supplied with the PowerLab unit). Other software that can be used with your PowerLab hardware is available separately and includes PowerChrom software (for chromatographic data collection), and DoseResponse software (for pharmacological studies).

Compatible MacLab or PowerLab Units

EChem 1.5 software can be used with the following new and older models of PowerLab and MacLab.

PowerLab e systems:

- •PowerLab/200, MacLab/200, MacLab/2e
- •PowerLab/400, MacLab/400, MacLab/4e, MacLab/4
- •PowerLab/800, MacLab/8e, MacLab/8

PowerLab S systems:

- •PowerLab/4SP, PowerLab/4s, MacLab/4s
- •PowerLab/8SP, PowerLab/8s, MacLab/8s
- •PowerLab/16SP, PowerLab/16s, MacLab/16s
- •PowerLab/4ST

The PowerLab/410 is unsuitable for use with EChem software. Consult your ADInstruments representative for the latest information on our range of products. Please note that MacLab units have now been superseded by the PowerLab range.

Optional Analysis

For general purpose data analysis and the production of specialist plots for theses, reports, slides, and publications we recommend IGOR Pro™ software (WaveMetrics). Other suitable graphing software includes Origin™ (Microcal) and Kaleidagraph™ (Synergy).

Installation Instructions

You will have been provided with a CD ROM which contains the EChem installer software. If your computer does not have CD ROM capability then contact your ADInstruments representative who can arrange installation from a set of floppy disks. You will need at least 3 MB of free space on your hard disk for the installation. It is recommended that you first install the Chart and Scope software that also came with your PowerLab system. To install EChem:

1. Insert the EChem PowerLab CD ROM into the appropriate drive.

2. Double click the installer icon.

The installation creates an EChem folder (directory) in which you will find the EChem program and sample data files. On Macintosh systems the 'Potentiostat' driver software is also placed in the 'ADInstruments' folder in the System Folder. On a Windows system the Potentiostat driver is part of the EChem software. This driver is only required if you are using the ADInstruments Potentiostat.

If you have used an earlier version of EChem it is strongly recommended that you remove these versions from your Macintosh hard disk before you install EChem 1.5. On Windows systems older versions of software will be automatically uninstalled. Data files from earlier versions of EChem will open with EChem version 1.5. If there are multiple versions of a program present on your hard disk then you may accidentally use the older version for your experiments.

Keep your installer CD ROM in a safe place after the installation. Please remember that each purchased copy only licenses you to use the software on one computer at any one time. Please enquire about a cost–saving departmental license if you want to run multiple copies in your workplace.

Opening EChem for the first time

Figure 1–1
The EChem program icon

EChem v1.3

Ensure that the PowerLab unit is connected properly to your computer (this is covered in the *Owner's Guide* that came with your PowerLab unit), and that it is turned on. Click the EChem icon and select Open from the File menu (or double-click the icon). There may be a short delay while the program initialises the PowerLab unit.

Figure 1–2 Enter your name and that of your organization when you first use EChem.
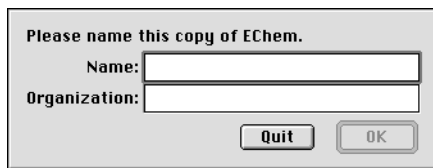
When you start EChem for the first time, a dialog box will appear (Figure 1–2), asking you to name the copy of the application. If the computer has an owner's name already assigned (for file sharing), then the name will be put into the Name box. Just start typing if you want to overwrite it.

If the PowerLab unit is not connected, then the dialog box in Figure 1–3 will appear. If this dialog box appears when the PowerLab unit is properly connected and turned on, see the *Owner's Guide* that came with your PowerLab for help. Some of the information about start-up problems from the *Owner's Guide* is also repeated in Appendix B at the back of this manual.

Figure 1–3 Dialog boxes that appear (Macintosh upper, Windows lower) if the PowerLab is not present or not connected.
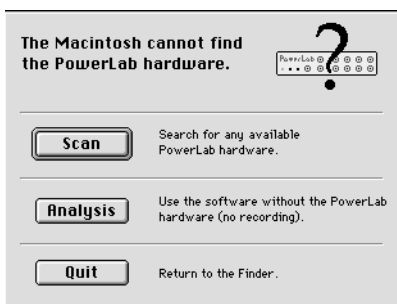
The PowerLab is not connected or not turned on. Click on the Analysis button to open a data file for further analysis or for printing.
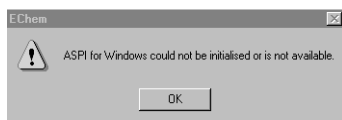
The SCSI card has not been installed correctly or the computer was turned on before the PowerLab unit.
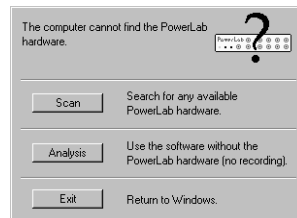
The the PowerLab unit is not turned on or not connected. Click on the Analysis button to open a data file for further analysis or for printing.

Quitting EChem

If you want to exit EChem after naming your copy of the software, choose Quit from the File menu. If you want to proceed, working through this guide, you can leave the file open.

2
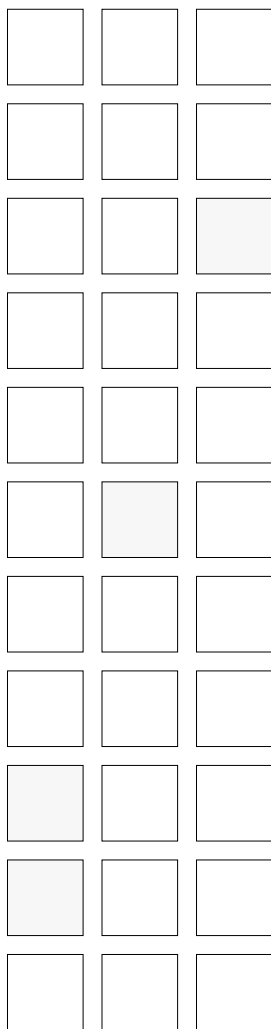
EChem Basics

EChem is a sophisticated program for performing voltammetric and amperometric electrochemical experiments. This chapter provides a general overview of EChem, looks at the main graphic window, and deals with the basics of recording data.

An Overview of EChem

EChem, together with the PowerLab hardware and computer, gives you the display capabilities of a two-channel storage oscilloscope, as well as the features of a versatile waveform generator. You can perform a variety of electrochemical techniques with any potentiostat that has an external input and analog (XY, or chart recorder) outputs.

Display Controls—Chapter 4

Your results are displayed in the main EChem window which can be resized, and the control panels moved to where you want them. The data display can be set to show I (current), E (potential) and t (time) in different formats:

- I vs E, with I on the Y and E on the X axis.

- E vs I, with E on the Y axis and I on the X axis.

- I and E on separate graphs versus time.

- I versus time (for amperometric experiments).

The current and potential axes can be dragged, stretched, or set to exact values for optimum data display. The current range can be adjusted. If an ADInstruments Potentiostat is connected then its controls can also be accessed through the software. Display colors, patterns, and grids can be altered.

Display and Analysis—Chapter 4

EChem records data in sweeps, like a normal oscilloscope, however each new sweep is recorded to a different 'page', creating a set of recorded scans numbered for easy reference, or for overlaying. Thus a new file does not have to be created for each experiment. You can add your own written comments to each 'page' of data to emphasize features of interest, or to log standard concentrations. There is also a Notebook feature for making general observations about a data file.

When you have finished recording, you can move through your data using the page controls and make measurements directly from the recording — you are given a direct read-out, with no chance of

measurement errors. You can measure from a selected reference point, using the Marker, or a baseline (which you can also set). EChem allows you to overlay data from any selection of pages, for direct comparison. The Data Pad feature enables you to make and store parameters such as peak height, potential at peak height, etc. EChem has a Zoom window for examining a section of the recording in more detail. Refer to Chapter 5 for more details.

Working with Files—Chapter 5

EChem results can be printed, edited, and saved to a disk for later review. You can also save 'settings files' — empty data files that are preconfigured for particular experiments — so that any experiment can be repeated quickly and easily, without having to go through the process of entering all the sweep parameters again. Pages of data can be printed in a variety of formats, or cut, copied, and pasted between EChem files, and whole files can be appended to the end of an open file, allowing you to produce summaries in a single file. Data can be transferred as text to spreadsheets or word processors and, conversely, correctly formatted text can even be pasted into an EChem file.

Techniques— Chapters 7 and 8

EChem provides a range of electrochemical methods from simple staircase linear sweep voltammetry through to complicated pulse sequences. You can define the sampling periods for each step or pulse.

Customising and Automating— Chapter 6

EChem can be extensively customised for your purposes. Controls, and menus and their commands (and Command-key / Control-key equivalents) can be locked, hidden, or altered, and the appearance of EChem simplified, say, for student or technician use. Macros can also be created to automate complex, or repetitive tasks.

Figure 2–1
EChem desktop icons:
double-click one to open
EChem

EChem v1.3

Echem Data File

EChem Macro

EChem Settings

Opening an EChem File

To open an EChem file,:

1. click on one of the EChem icons in the Finder to select it, and choose Open from the File menu; or

2. double-click the icon (see Figure 2–1).

There will be a short delay while EChem initialises the PowerLab. The top icon in Figure 2–1 shows the EChem application, which will open a new untitled file if double-clicked. The second icon shows a file of prerecorded data. The last two icons show a settings file and macro file — these are like the 'template' or 'stationery' files used in some spreadsheet or word processor documents. If you open ether of these then an empty, but preconfigured, document will be opened ready to begin a new experiment.

It is best to have the sample EChem data file open while working through this section, so that you can try the commands, controls, and settings as they are discussed in the text. First, make sure that the PowerLab unit is properly connected to your computer, and that it is turned on. You may also wish to learn EChem without the PowerLab — if you have taken a copy for your home computer for instance. In this case, on opening a file, a dialog box will offer the Analysis option, which allows you to use EChem to view and manipulate existing data without the PowerLab attached. Unusable controls appear dimmed.

In each case, EChem opens and the EChem window will appear. By default, a new, untitled file will fill the screen. Its size can then be readjusted if need be.

Once the EChem application has already been loaded, you can open another file or create a new one by choosing Open… or New from the File menu. The Open dialog box appears (Figure 2–2). By default only EChem files are shown in the scrolling list. You can navigate through your hard disk to find the file you want. EChem allows you to open only one file at a time.

There are two radio buttons and three checkboxes at the bottom of the Open directory dialog box. The radio buttons allow you to choose

Figure 2–2
The Open file dialog box

Radio buttons

Check boxes

Appearance may vary (as shown) depending your computer and operating system. Radio buttons are full when on and empty when off. Check boxes show a tick or cross when on, and are empty when off.
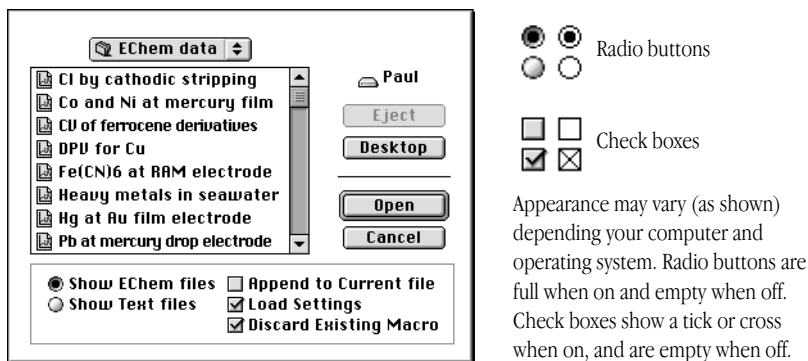
between opening EChem files, or ASCII text files which may have come from other electrochemical systems. Only the selected type of file is displayed in the scrolling list and is able to be opened. The checkboxes allow you to append a file to a currently open file, to load the settings of the new file, and whether to discard macros when the file is opened. Opening text files and appending files are discussed in Chapter 5.

The information in an EChem file is made up of data and settings. Data refers to the recorded waveforms, which are normally loaded when opening a file. Settings are of two types:

> 1. Recording settings: those that affect recording, such as the current ranges, technique settings—scan rate, pulse height etc.; and

> 2. Display settings: those that affect the way the data looks, such as the window size, display settings, and menu configuration. (Macros are also stored in a settings file.)

When you start EChem by double clicking an existing data file, or a settings file, then both types of settings are loaded. However, if EChem is already open and you use the Open... dialogue then there are several possibilities.

If the Load Settings checkbox is on (marked with a tick or cross — depending on the computer and operating system) when opening a data file, then the data and 'recording settings' are loaded. These settings will apply to a subsequent experiment. All settings are retained in memory, and used for all subsequent recording, until changed by loading new settings. Opening a settings file (which

Note
To start EChem with its factory default settings, hold down the Command key (Macintosh) or Control key (PC) immediately after you start the software by double-clicking the icon. Release the key when the alert box appears, and click the OK button.

contains no data) with the Load Settings checkbox off will load only display settings, not those affecting recording of data.

If you have a file open when opening a second file, then the first file will be closed. If there are any unsaved changes to the first file, an alert box will appear asking if you want to save them before opening the new file. If the Load Settings checkbox is on, then both the settings and the data will be loaded, otherwise the current settings from the first file are retained.

Using the sample data file as you work through this user's guide will show you some real data and perhaps give a better idea of what is going on in EChem.

Closing or Quitting an EChem File

To close an EChem file, choose Close from the File menu or click in the close box in the Main window (upper left corner, Figure 2–3). To quit EChem, choose Quit from the File menu. In either case, if you have made any changes, a dialog box will appear, asking you if you wish to save your work. Click the Save button if you wish to keep the changes you have made. Click the Don't Save button if you want to discard the changes.

The Main Window

The essential controls for recording data are provided in the Main window and its various control panels, illustrated in Figure 2–3. These controls are discussed below, and in greater detail elsewhere in this manual. The window itself consists of, the data display area, which contains recorded data; and some controls at the bottom of the window. Various movable control panels surround the window proper. The menu bar at the top of the screen contains the EChem menus (see Appendix A), allowing you to set up and modify the way EChem looks and behaves. The EChem Window command from the Windows menu returns to this window from another, or opens a new, untitled file if the window has been closed.

Basic Window Controls

The close box, title bar, zoom box, and size box all work as they do in other software.

Click the close box to close an open EChem file (this is the same as choosing Close from the File menu). The title bar shows the title of the file, and has horizontal lines across it if it is active (that is, the frontmost window). Drag the title bar to move the EChem window to another area of the screen, or to another monitor if you have one attached (you can do this while recording). Drag the size box to set the size of the window: this is useful if you want other applications on the screen, and does not affect recording fidelity — the resolution of recorded data is independent of the resolution of the display. Click

Figure 2–3
The Main window of a newly created file showing the i vs E display mode

Title bar File title Zoom box Cursor information panel

Close box

i Channel control panel

Scale pop-up menu

Range pop-up menu

Input Amplifier dialog button

The data display area is empty when opening a new file

Axis label

Technique description

'Vertical space'

Marker

Page Comment button

Page buttons

Display pop-up menu (i vs E display selected)

Scale pop-up menu

Page Corner controls

Size box

Start/Stop button

the zoom box to toggle the EChem window between a set size and the full size of the screen.

The three control panels (Cursor, i Channel, and Sample) cannot be resized, but they can be moved independently around the screen if necessary. Blank panels appear behind the control panels to reduce clutter: these, too, can be moved.

Navigating
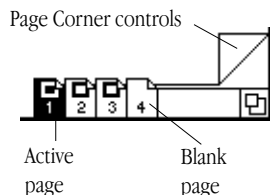
Page Corner controls

Active page

Blank page

EChem stores sweeps of data as if they were pages in a pad of paper. The numbered Page buttons along the bottom of the EChem window and the Page Corner controls (the 'dog-ears') at the bottom right of the data display area allow you to move through multiple pages of an EChem file. The highlighted Page button indicates the page of data currently viewed. EChem will always have one blank page, the last one, in a file. As pages of data are recorded, they are numbered consecutively, with the blank page remaining at the right. New data is recorded to this page.

Click the upper, folded corner of the Page Corner controls to move to the next, and the lower corner to move back to the previous page. Clicking the numbered Page buttons takes you immediately to that page, or choose Go To Page… from the Display menu, or type Command-G (or Control-G), and enter the number in the dialog box that appears. If there are too many pages to show all the buttons along the bottom of the window, then left and right arrow scrolling buttons will appear at either side: click them to move a page left or right, or press them to scroll left or right through many pages.

Scrolling buttons
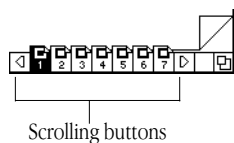
You can also move a page left or right by pressing, respectively, the left and right arrow keys on the keyboard. Hold down the Command (or Control) key while pressing the left or right arrow key to go to the beginning or the end of the file (the first or last numbered pages).

The EChem Axes

When EChem is displaying both I and E versus time, or I versus time, there will be a horizontal Time axis, above the Page buttons along the bottom of the Main window. This shows the time from the start of sampling, When the I versus E display mode is chosen, the horizontal

axis becomes the applied potential (E) and the vertical axis the recorded cell current (I). This is reversed for the E versus I mode.

Note that the graph area remains blank until some data is actually recorded. The scale for each axis is initially set by the current range control on the right side of the window and the chosen technique. Both i and E axes can be stretched or dragged using the pointer. Display options can be chosen from the Scale pop-up menu.

The i Channel (current) Control

The current scale settings are located at the right of the main window. The control panel is labelled 'i Channel', Figure 2–4.

The i Channel panel, controls the current sensitivity and setup of either the PowerLab Channel 1 input amplifier, or the ADInstruments Potentiostat, if connected.

If you are using the ADInstruments Potentiostat press the Range pop-up menu to choose the full scale current range (±20 nA to ±100 mA). Click on the Potentiostat button to bring up a dialog that allows you to adjust the Potentiostat settings — filters, polarity, dummy/real cell setting, etc.

If you are using another brand of potentiostat then click the Input Amplifier button to bring up a dialog box to adjust the Channel 1 controls of the PowerLab. The signal for the potentiostat is a voltage level that represents the current signal. You will have to adjust the input sensitivity to your potentiostat full scale output (often 1 or 10 V — read the potentiostat manual). For example if you are using a BAS CV-27 potentiostat, which you have adjusted to a setting of (say) 1 $\mu A/V$, you will still need to keep the PowerLab i Channel setting at 10 V because this is the maximum output from the plotter connections of the CV-27, that is, the CV-27 can report currents of up to 10 μA when set at 1 $\mu A/V$.

Technique Description Panel

The area under the i Channel settings displays information about to the selected sweep including the its name, start and end potential, sweep rate, etc. Once the scan has been completed the time and date are also displayed.
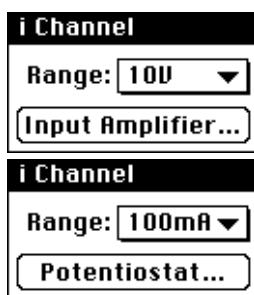
Data Display Area

Data is displayed in the Main Window in the area bounded by the i and E axes, or the i, E and time axes when in the iE vs t mode. When the iE vs time display mode is chosen, two channels are displayed. The channel separator between them can be dragged by the black handle at its right end up or down to vary the size of the channel display areas. Dragging it to the top of the display or double-clicking it will overlay channels A and B in the one display, Chapter 4.

Cursor Panel

Cursor

t = 0.0520s

I = 1.5910µA

E = 0.9840V

Cursor

t = 0.0520s Δ-0.0600

I = 1.5910µA Δ0.8130

E = 0.9840V Δ0.4800

Cursor

t = 1.48s Δ0.68

I = 1.4030mV Δ0.0720

The Cursor panel shows the value of the coordinates of the cursor position as the pointer is moved over the data display area. For voltammetric experiments it displays the current (I), potential (E), and time (t) values which are updated constantly as you move the cursor along the waveform. For amperometric experiments viewed in the I vs t mode only time and current are reported. The Cursor display will be blank if the pointer is not over the waveform display area. If the Marker (see below) is positioned on the trace then the differences, Δ, in current, potential, and time between the marker and cursor positions are also displayed.

The Marker

The 'marker' can be dragged onto the trace

The Marker can be found in the box at the bottom left of the EChem window. It can be dragged onto the data display area to a particular data point on the voltammogram which becomes the 'zero' reference point. Relative measurements can now be made. Double-clicking the Marker or clicking its box sends it back home. You can also drag the marker close to its lair and let go of the mouse button. The marker will automatically find its way back.

Page Comment Button

The 'page comments' button changes appearance when a comment is added

The Page Comment button can be found at the bottom left of the EChem window, to the right of the Marker. Click it to bring up the Page Comment window for noting down comments about particular pages of data, for example you might want to enter the concentrations of metal ions in a standard solution. When there are

comments noted down for the active page, the button icon changes from a blank note to a marked one.

Start Button

Sample
Start

To start recording, click the Start button in the Sample panel. The button then changes to Stop — click it, if required, to stop recording. The button may show a dimmed Wait… while starting or stopping. After the first sweep in a new file you will be asked to save the file. Second and subsequent sweeps will be automatically saved at the end of each sweep. This autosave feature can be turned off from the Preferences/Options command in the Edit menu.

Pointer

$+$ I $\blacktriangle$

The pointer can be a cross, I-beam, or arrow shape

The pointer will change shape as you move it about the EChem window, giving you an indication of its function in certain areas — it becomes an I-beam over a text entry area, and a cross in the graph area, for instance. It becomes dimmed when it cannot effect a function under particular conditions. Do not confuse the 'pointer' (controlled by the mouse) with the 'cursor' that follows the pointer when it is in the data display area, but which remains on the trace. It is the coordinates of the cursor that are reported in the Cursor Panel, and in the Data Pad.

Recording

Note
EChem does not record in the background: it must be the active (top) application to function.

To start recording (sampling), click the Start button in the Sample panel in the lower right hand corner of the screen. The button then changes to Stop — click it, if required, to stop recording. The button may show a dimmed Wait… while starting or stopping.

EChem emulates some of the basic functions of a standard oscilloscope, proving a visual image of an electrical signal against time. However, unlike oscilloscopes EChem lets you record a large number of sweeps as different 'pages' of data, creating a series of recorded waveforms, automatically stored and numbered for easy reference. EChem can overlay any selection of these stored sweeps. Also a single background sweep can be subtracted from sweeps that were recorded under similar conditions (same scan rate, start and finish potentials etc.).

Display While Recording

At slow sampling speeds you will see data drawn on the screen as it is recorded. A short vertical line segment, the Trace Indicator, moves left to right across the top of the data display area, tracking the front edge of the advancing waveform as it is drawn on screen.

At fast scan rates, it will appear that the whole scan of data is drawn at once, and no Trace Indicator is seen.

Interruptions While Recording

You can stop sampling mid way through a scan, by clicking the Stop button in the Sampling panel, or typing Command-period (Control-period) or Command-spacebar (Control-spacebar). EChem will stop the scan but retain the data already recorded (as long as the 'Keep Partial Data' box is checked in the Preferences/Options... command of the Edit menu).

Please note that EChem does not record in the background. It must be the active, or top, application while recording. If you switch to another application (including the Finder) by choosing it from the Application menu or clicking outside the area of the EChem window and its control panels, then EChem will stop recording. On switching back to EChem, the experiment will restart.

Length of Recording

The number of pages of data that you can record depends primarily on the memory that you have allocated to EChem. If you find that you run out of memory, you can increase EChem's memory allocation on Macintosh by quitting, selecting the application icon in the Finder, choosing Get Info from the File menu (or typing Command-I, or Control-I), and typing a larger value in the 'Preferred size' box. There is an upper limit of 1000 pages in any one file.

The amount of memory available for recording on Macintosh can be seen in the lower portion of the EChem dialog box, Figure 2–5, by selecting the About EChem… command from the Apple (⌘) menu (click the dialog box to make it go away again).

Figure 2–5
The available memory
indicator bar on a Macintosh.
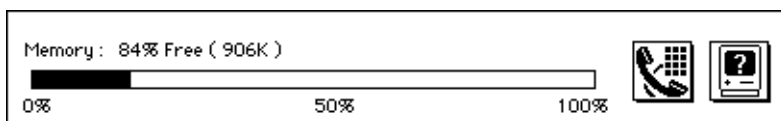
On a Windows PC the amount of memory is allocated by the
operating system and you can record data until you run out of hard
disk space (or exceed 1000 pages).

Data is compressed while it is being recorded, the efficiency of
compression depending on how the signal varies: signals that change
very slowly, such as a straight line or gradual curve, can be
compressed a great deal, while complex and rapidly changing signals
may not compress much at all. The extent of compression is usually
in the order of 25–33%.

On a Macintosh EChem uses a certain amount of memory for an off-
screen buffer to speed up data display. If the EChem window is large
and the display is grayscale or color, more memory is used, especially
if the monitor display has been set to thousands (16 bit color) or
millions (24 bit color) of colors. If the EChem window filled a 14"
monitor displaying millions of colors, the memory used by this
would be about 1.25 MB. If you find yourself running out of memory,
you can use less by shrinking the EChem window to a smaller size
and changing the display to 256 colors (or even grayscale or black
and white). Since EChem only uses eight colors there is no advantage
to be gained by running in thousands or millions of colors.

The largest EChem data file, 1000 pages at about 10 K per page, could
take, at worst, up to 10 megabytes of memory (but probably more like
7–8 Mb), plus the overhead necessary for EChem to maintain the off-
screen buffer. Of course it is much more likely that your experiment
will only have a relatively few pages of data and that it will occupy
much less space (usually much less than a megabyte).

EChem User's Guide

3

Setting Up EChem

EChem software supports the use of many third party potentiostats as well as the ADInstruments Potentiostat.

This chapter describes connection of third party potentiostats to the PowerLab, and basic settings controls such as the current range and units conversion. Also described is the use of the ADInstruments' Potentiostat with EChem software.

For more information about third party potentiostats see Chapter 12.
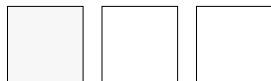
Using 3rd Party Potentiostats

EChem can be used with numerous third party potentiostats. If you are using an ADInstruments' Potentiostat you can skip this section and start reading from 'The ADInstruments Potentiostat'.

If you own an existing potentiostat then there is a good chance that it will be able to be used with an EChem system. Chapter 12 lists a wide variety of compatible third party equipment. You should refer to this chapter to determine if your potentiostat is compatible with EChem. More information can be obtained by e–mailing us at support@adinstruments.com. Please contact your ADInstruments representative if you wish to make specific enquiries regarding compatibility with your equipment.

Connecting to PowerLab

Many commercial potentiostats are suitable for connection to a PowerLab unit and can be operated with the EChem software. These instruments must have the ability to accept an external waveform. You may need to consult Chapter 12 or your potentiostat's user manual to see if an external input is available.

You will need to connect the analog output of the PowerLab to the external input of the potentiostat. This will usually be located on the potentiostat front or back panel and will be labelled 'E in', 'External Input', 'Ext. In.', or something similar. Connect the potentiostat external input to the PowerLab 'Output +' (or 'Output 1') BNC front panel connector.

Different manufacturers use opposite conventions about whether a negative potential corresponds to reduction or oxidation at the working electrode. If you find that after connecting to the PowerLab that your peak potentials are the opposite polarity to that which you expect (for example a peak is found at +0.25 V when it should be at –0.25 V) then remove the cable from the PowerLab 'Output +' (or 'Output 1') connector and attach it to the PowerLab 'Output –' (or 'Output 2') connector. This reverses the polarity of the potential waveform signal, which in turn will change a reducing potential to an oxidising potential (and vice versa) at the working electrode.

Please note that the MacLab/2e and /4e units have been superseded by the PowerLab /200 and /400 models

In order to record current and potential data you will need to locate the potential and current outputs located on your third party potentiostat. These are often labelled as 'Applied E', 'App. E', 'E out', 'E monitor', 'I monitor', 'I out', or something similar. The current (I) output of the potentiostat should be connected to the CH1+ connector of the PowerLab. If you need to sample the potential values, then the potential (E) output of the potentiostat should be connected to the CH2+ connector of the PowerLab. Potential monitoring can be done in EChem in the Multi Pulse method if potential sampling is selected.

For most methods in EChem the potential values that are used for plotting are the calculated potentials — it is assumed that the potentiostat will accurately follow these. Thus the points are always exactly evenly spaced along the potential axis. Note, however, that even if you do not connect the potentiostat to channel 2, EChem still uses this channel to store the potential values, and thus channel 2 cannot be used for connecting to other instruments.

It is possible to alter the cable that links your potentiostat to the back of the PowerLab /200 or /400 via the Multiport. Consult the *PowerLab Owner's Guide* for the functions of the different pins. However, you should exercise care when modifying such a cable to ensure that shorts do not occur between channels, or between signal lines and power rails. Construction of such a cable should only be attempted by a competent technician. If you have a special requirement then please contact your ADInstruments representative.

Adjusting the Input Range

When a third party potentiostat is used with EChem you will have to adjust the range of the 'i Channel' (channel 1 of the PowerLab) to match the output of your potentiostat. Many potentiostats have a full scale output of 1 V or 10 V representing current ranges of 1 μA, 10 μA, 100 μA, 1 mA, 10 mA, 100 mA, and 1 A.

As an example, if the potentiostat produces an I(out) output of 1 V representing the full scale setting for the 1 mA current range, then the i Channel range should be set to 1 V. If the output from the potentiostat was ±10 V representing the full scale current range of 1 mA then the i Channel range should be set to 10 V (Figure 3–1).

Figure 3–1

Adjusting the i Channel range
to match the output range of
the potentiostat
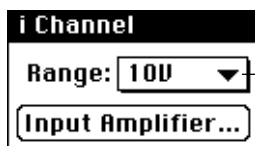
Use this pop-up menu to set
the range of the i channel to
match the output range of the
potentiostat

If you are dealing with very low currents (which do not give full scale
output on the potentiostat, even at its most sensitive settings) you can
try choosing a smaller range from the i Channel range pop-up menu.
This causes the PowerLab unit to amplify the incoming signal and
may give you a better result — but bear in mind that any incoming
noise will also be magnified.

You can also adjust the i Channel range inside the Input Amplifier
dialog box. This is discussed in the next section.

Using the Input Amplifier Dialog Box

The Input Amplifier dialog box (Figure 3–2) allows, among other
things, software control of the current recording channel in the
PowerLab. For EChem this is channel 1 of the PowerLab. The signal
present at that channel's input is displayed so that you can
immediately see the effects of any changes. This allows you to
measure the current signal from the potentiostat and use it to check or
calibrate this channel to appropriate current units. Once you have
changed the settings in the dialog box, click the OK button if you
wish to apply the changes to the channel. The Input Amplifier dialog
box appears when you click the Input Amplifier… button in the i
Channel panel. The dialog box in Figure 3–2 will appear.

Signal Display

The input current signal is displayed so that you can see the effect of
changing the settings. Data is not actually being recorded while you
do this — as it disappears from the screen it is lost. The incoming
signal value is displayed at the top left of the display area. Slowly
changing signals will be represented quite accurately, whereas very
quickly changing signals will be displayed as a solid dark area
showing only the envelope (shape) of the signal formed by the
minimum and maximum recorded values.

Figure 3–2
The Input Amplifier dialog box.

Pause/Scroll button

Input Amplifier Channel 1

0.000 V

Signal amplitude

Range pop-up menu

Range:
10U

Low pass filter

☐ 50Hz LP

☒ Positive
☐ Negative

☐ Invert

Current Amplitude axis

Units...

Cancel

OK

Applied Potential:
0.000V
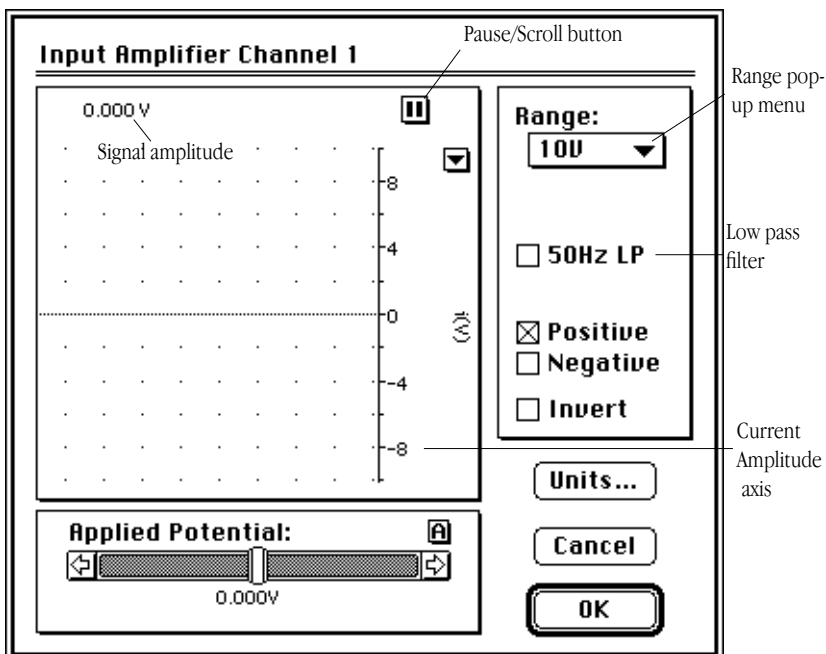
PowerLab /200 and /400 Input Amplifier Dialog. PowerLab /800 does not have the Positive and Negative boxes.

Filter:

✓	Off
	20kHz
	10
	5
	2
	1
	200Hz
	100
	50
	20
	10
	5
	2
	1

PowerLab /4SP, /8SP and /16SP models have a choice of low pass filters from 1 Hz to 20 kHz

Input Amplifier Channel 1

0.000 V

Range:
10U

Filter:
Off

☐ Invert

Units...

Cancel

OK

Applied Potential:
0.000V
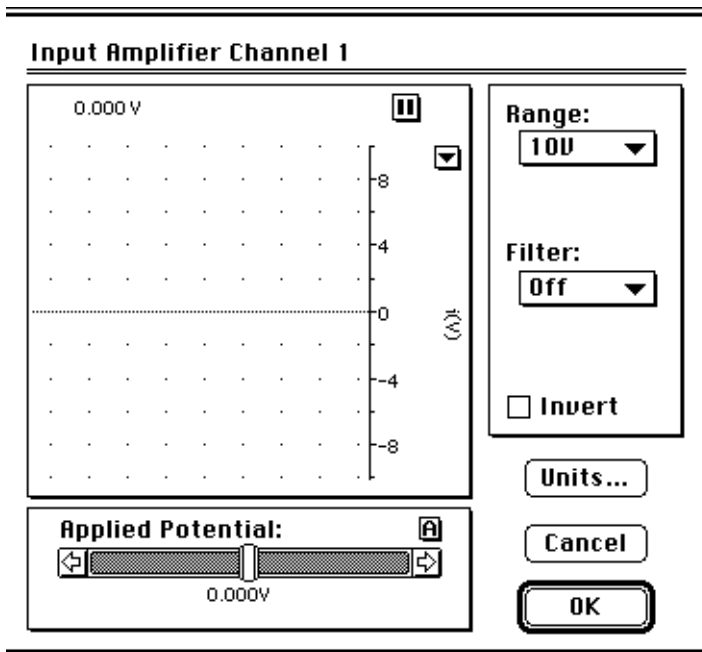
PowerLab/4SP, /8SP and /16SP Input Amplifier Dialog. PowerLab/4SP, also features Positive and Negative boxes (not shown here).

If your potentiostat has positive feedback resistance compensation (iR compensation), you can use this window to monitor the signal while you adjust the amount of compensation. After setting the gain simply increase the resistance compensation until the current signal is driven to oscillation, then decrease the amount of compensation slightly (usually by about 10%) so that potential control is re-established.

You can stop the signal scrolling by clicking the Pause button at the top right of the data display area (it looks like the pause button on a tape player). It then changes to the Scroll button (like the play button on a tape player): click it to start scrolling again. The incoming signal is shown

The scroll button changes when clicked on and off

You can shift and stretch the vertical Current Amplitude axis to make the best use of the available display area — drag a tick label on the axis to stretch or shrink, or drag the area between the labels to offset the axis. Apart from being at the right rather than the left, it is the same as the Amplitude axis in the main window, and the controls function identically. The Scale pop-up menu to the right of the axis is also the same. Changes made in the Amplitude axis here will be reflected in the main window.

Setting the Range

The Range pop-up menu lets you select the full scale input range, or sensitivity, of the i channel (normally channel 1). Changing the range in the Input Amplifier dialog box is equivalent to changing it in the main window. All dialog box changes are made in the main window on clicking the OK button.

The range menu will always display full scale volts or millivolts, irrespective of the application of units conversion. The range menu starts at +10 V full scale and can be set as low as 2 mV full scale.

Filtering

PowerLab /200, /400, /800 units can apply a 50 Hz, 2-pole Bessel, low pass filter to the incoming signal which may aid in the removal of high frequency noise. With other PowerLab models such as the /4SP, /8s, and /16s, you can select an appropriate low pass filter (1 Hz to 20 kHz) from a menu, Figure 3–2. Your Potentiostat may also have filter settings which can also be used. However, remember that for

high speed scans, or for work with short period pulses, you will need to keep filtering to a minimum.

Differential or Single-ended Inputs?

⊠ Positive
☐ Negative

Most potentiostats provide a single ended output and the current signal needs to be connected to the CH1+ of the PowerLab unit. If your potentiostat is giving an exceptionally noisy signal you may also want to try connecting it differentially as this can sometimes reduce noise levels. The PowerLab /200, /400, /4s, /4SP, /4ST, and older MacLab/2e and /4e units, can accept a differential signal. Use either the front panel BNC connectors labelled CH1+ and CH1–, or via the front panel DIN connectors — see the PowerLab *Owners Guide*. You will also need to make sure that you cross *both* the Positive and Negative checkboxes to activate the differential input.

Inverting the Signal

☐ Invert

The Invert checkbox allows you to invert the current signal from the potentiostat. It provides a simple way to change the direction of the recorded current signal without having to reconnect leads. Use this if you find that your peaks are going to negative current values when you would prefer them to go to positive current values (or vice versa).

Units

Units...

Clicking the Units… button brings up the Units Conversion dialog box, allowing you to display the signal from the potentiostat in the correct units of current. This provides an easy way to calibrate the channel to the range of the potentiostat. Using Units Conversion is discussed in the next section.

Units Conversion

To bring up the Units Conversion dialog box (Figure 3–3) click the Units… button in the Input Amplifier dialog box.

Units conversion lets you scale the i Channel Axis so that the incoming current signal from the potentiostat (which is actually a voltage signal) is displayed in appropriate current units such as mA or µA.

Figure 3–3 The Units
Conversion Dialog box.

Voltage value, use
units of mV or V   Equivalent current value

Current units
pop-up menu
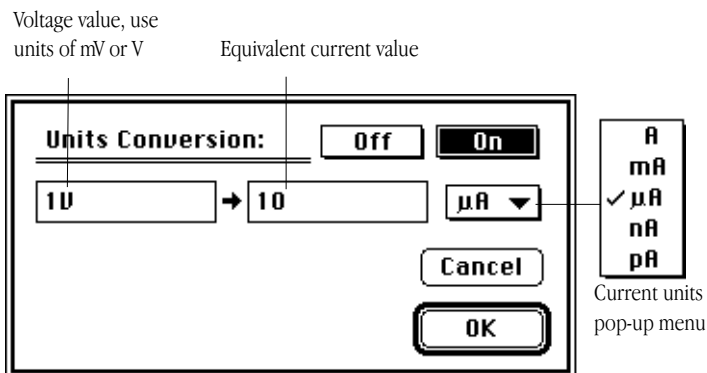
Converting Units

Note
*There must be a
proportional relationship
between the recorded
voltage and the new units
for the units conversion to
work properly. Most
potentiostats provide such
a signal.*

Before using the Units Conversion feature you must turn it on by
clicking the On button. Underneath there are two edit text boxes: the
left-hand box is used to enter the potential value, and the right-hand
box is used to enter the equivalent current value. Both of the boxes
must have values in order to calculate the relationship between
potential and current. You can press Tab to move between the fields.

If, for instance, you are using a potentiostat that produces a 10 V
signal for a full scale current of 1 mA then you would type in '10' in
the left box and '1' in the right box. Then choose 'mA' from the
Current units pop-up menu. Once you click the OK button the i
Channel axis will now display the correct units of current.

You can turn units conversion off or on without losing the values you
have entered by clicking the Off or On buttons.

Applied Potential

The applied potential slider control allows you to adjust the control
voltage sent to the external input of the potentiostat. To change the
value simply drag the control left or right to set an appropriate
potential — or click on the A-button to enter an exact value.

Applied Potential:

0.726V
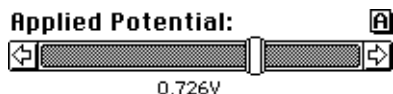
The ADInstruments Potentiostat

If you are using an ADInstruments Potentiostat the EChem interface will be slightly different as the Potentiostat is designed to be completely controlled from within EChem. First connect the Potentiostat to the PowerLab unit—you should read Chapter 9 for details.

Changing Potentiostat settings

When the Potentiostat is properly connected to the PowerLab and you run EChem you should see the i Channel control panel shown in Figure 3–4.

Current range pop-up menu

Click this button to access the Potentiostat dialog box
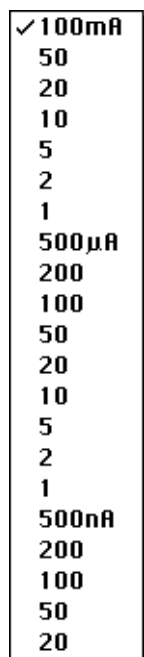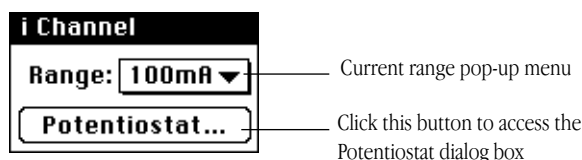
You should see the Potentiostat button at the bottom of the panel. If the button says 'Input Amplifier' then quit, turn off the PowerLab unit, recheck the Potentiostat's connections, and try again. If you are using a PowerLab/200 or /400 with Multiport connection to the Potentiostat ensure that there is nothing connected to the CH1 and CH2 front panel input connectors of the PowerLab unit.

Adjusting the Current Range

The Potentiostat range control reads directly in full scale current values. The Potentiostat supports ranges from ±100 mA down to ±20 nA. To adjust the current range choose an appropriate full scale current from the range pop-up menu in the i Channel control panel.

The Potentiostat Dialog Box

The additional controls of the ADInstruments Potentiostat can be accessed by clicking the Potentiostat button in the i Channel control panel.

The current range pop-up menu

Figure 3–5
The Potentiostat Input
Amplifier dialog box
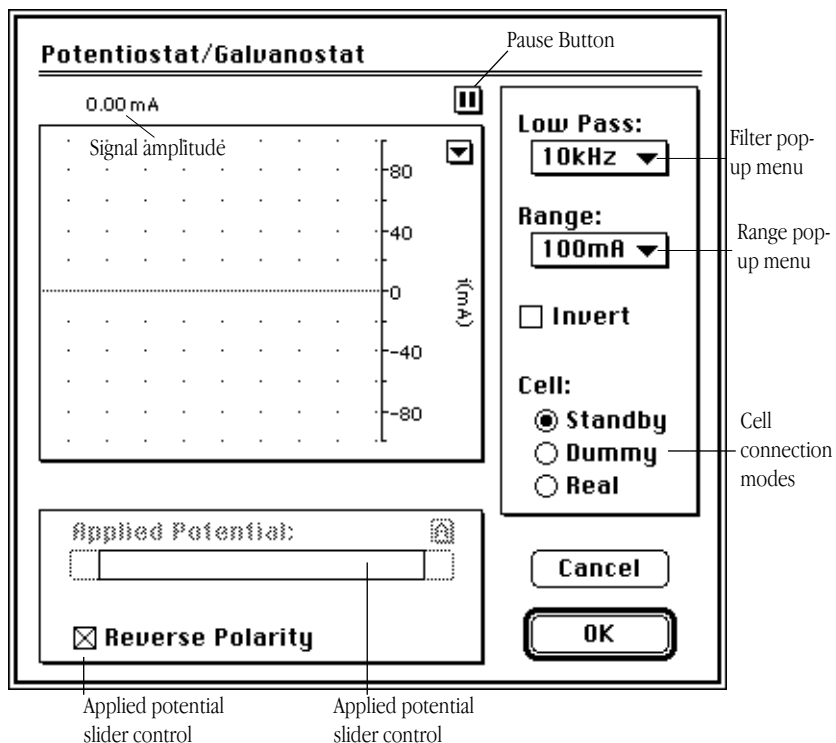
This dialog (Figure 3–5) allows you to adjust the current range, filtering and cell connection settings. Galvanostat functions are only enabled when using Chart or Scope software, see Chapter 8.

Signal Display

The current signal from the connected cell is shown in the scrolling display area. By using the Dummy or Real modes the effect of an applied potential can be seen prior to actually recording the data. No data is actually recorded when the Potentiostat dialog box is open. When the dialog is closed the signal trace is lost.

You can stop the signal scrolling by clicking the Pause button at the top right of the display area (it looks like the pause button on a tape player). It then changes to the Scroll button (like the play button on a tape player): click it to start scrolling again.

You can shift or stretch the vertical Amplitude axis to make the best use of the available display area. Apart from being at the right rather

than the left, it is the same as the amplitude axis in the main EChem
window.

Setting the Range

Range:
`100mA ▾`

The range pop-up menu lets you select the input current range or
sensitivity of the Potentiostat. Changing the range here also changes
the range in the Scope and Chart window. The default setting is
100 mA and goes to 20 nA in 1, 2, 5 steps.

Filtering

✓10kHz
1
100Hz
50
10

*The filter
pop-up
menu*

The Potentiostat has a number of low pass filter settings, for removal
of high frequency noise at 10 kHz, 1 kHz, 100 Hz, 50 Hz, and 10 Hz.
The pop-up menu can be used to select the appropriate filter. The 10
Hz setting is very effective in removing 50 or 60 Hz mains hum but be
careful that it does not distort your voltammograms. As a rough
approximation the 10 Hz filter can be used safely for linear sweep or
cyclic voltammograms up to about 100 mV/s, or for pulse techniques
where the pulses are longer than about 100 ms.

For very high speed scans or for work with millisecond pulses you
will need to use the 10 kHz filter setting.

Inverting the Current Signal

☐ Invert

The Invert checkbox allows you to invert the signal on the screen. It
provides a simple way to change the direction of the recorded current
signal. This will allow you to display your data according to whether
you prefer that a current signal greater than zero represents an
oxidation or a reduction process at the working electrode. If you find
that your voltammetry experiments have peaks that point to greater
negative currents when they should point to greater positive currents
(or vice versa) use the invert checkbox.

Cell Control

Three modes are provided to control the way in which the
Potentiostat connects to the cell. Each of these modes is analogous to
the settings found on traditional potentiostats.
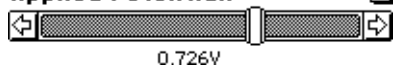
Cell:
◉ Standby
○ Dummy
○ Real

Standby – the external cell is disconnected and the internal dummy cell is connected to the Potentiostat. When the Potentiostat dialog is closed and the Chart, Scope or EChem start button is clicked the external cell will be connected to enable the experiment. This mode is used if you do not wish to connect to the external cell until the experiment is actually performed. The Applied Potential control is disabled in this mode.

Dummy – the Potentiostat is connected to the internal dummy cell (an internal 100 kΩ resistor network). You can use the Applied Potential slider control to vary the voltage applied to the dummy cell. The Potentiostat will remain connected to the dummy cell even when the Potentiostat dialog is closed and Chart, Scope or EChem is recording. This is useful for testing a method using the dummy cell.

Real – the external cell is connected to the Potentiostat while you are in the Potentiostat dialog. The Applied Potential slider control can be used to adjust the voltage applied to the external cell. When you close the Potentiostat dialog the external cell will be disconnected until the Start button is pressed and Chart, Scope or EChem begins to record an new experiment. This is similar to the Standby mode except it allows you to modify the applied potential before the method is started.

Applied Potential

Applied Potential: Ⓐ
◁ ▭▭▭▭▭▭ ▯ ▭▭▭▭▭ ▷
0.726V

The applied potential slider control is enabled in either Dummy or Real modes. It allows you to adjust the voltage applied to either the dummy cell or external cell depending on the mode selected. To change the value simply drag the control left or right to set an appropriate potential — or click on the A-button to enter an exact value.

Reverse Polarity

⊠ Reverse Polarity

Depending on your local convention you may wish to define a 'more oxidizing potential' at the working electrode as either a more positive, or as a more negative potential.

If the Reverse Polarity box is crossed then the Potentiostat will produce oxidizing potentials at the working electrode at more

positive applied potentials. If the box is unchecked then the working electrode becomes more reducing at more positive potentials.

In practice what you might find is that your voltammogram exhibits a peak at (say) 300 mV when it should be at –300 mV. The chances are that the polarity setting is the opposite of what you want. Reverse the polarity and try again.
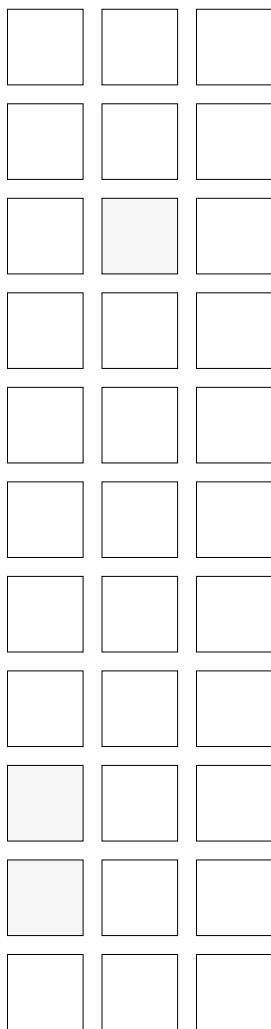
You can save your preferred polarity convention as the default Start-Up, or as a settings file.

EChem User's Guide

4

Data Display and Analysis

EChem allows you great flexibility in displaying data. You can change the lines, patterns, and colors of the display. You can resize the EChem window, change the size of the channel's display, or overlay the voltage and current channel, or invert or interchange the current and potential axes. You can zoom to see a small section of data in great detail, or overlay data from any selection of pages in a file.

The whole purpose of recording data, of course, is to find things out through analysis of the recording. Voltammograms can be measured using the Cursor, to give absolute coordinates or relative readings from marker. A background page can be set, so that the voltammogram on it is subtracted from all others in the file. The inbuilt Data Pad calculates and stores statistics about recorded data, calculates peak maxima, and areas. The current signal can also be smoothed, integrated or differentiated according to your requirements.

This chapter describes the display options available in EChem, from the basic settings through to Amplitude axis manipulation and the Zoom window, and also discusses the available analysis options.

The Main EChem Window

Recorded data is displayed in EChem's main window. By default, the current and potential data is displayed in an XY plot with current on the vertical axis and potential on the horizontal axis (I vs E). You can also change the display mode to show both potential and current against time (IE vs t), potential versus current (E vs I), or current versus time (I vs t), Figure 4–1. To change the display choose the appropriate mode from the display mode pop-up menu at the bottom left of the Main window.

Figure 4–1
There are four main display modes that can be accessed by the display mode pop-up menu.
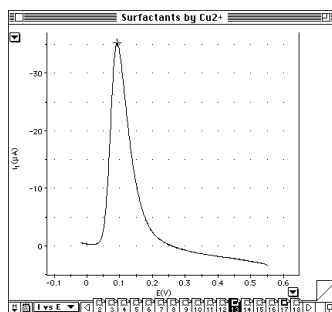
I vs E mode, current on the Y axis and potential on the X axis.
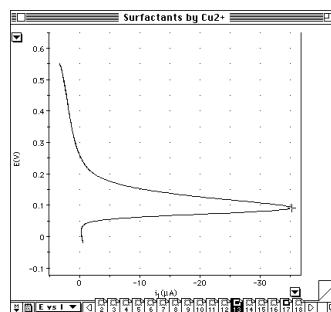
E vs I mode, current on the X axis and potential on the Y axis.
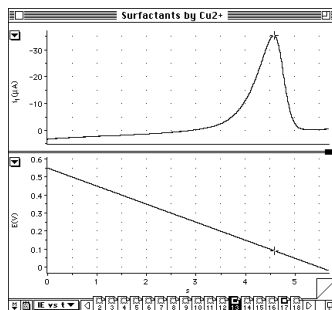
IE vs t mode, current and potential on separate Y axes and time on the X axis.
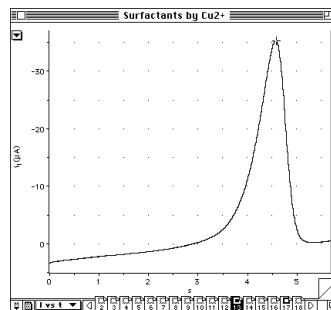
I vs t mode, time on the X axis and current on the Y axis.

IE vs t Display — Extra Features

When the display is in the IE vs t mode you can vary the relative sizes of the channel display areas Figure 4–2.

Figure 4–2 Changing relative heights of the channels and overlaying current and potential data in the IE vs t display mode.
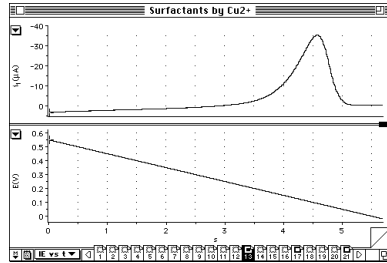
Move the pointer over the channel separator. It changes shape:

Drag the channel separator (the short black bar) up and down, to the desired position — middle picture; or double click the separator to overlay the channels — bottom picture.
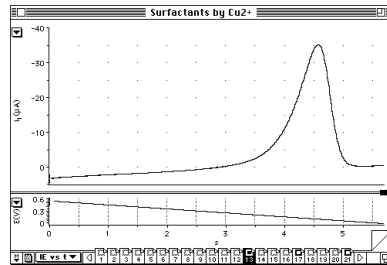
After you have resized the two channels you can double click the separator to return to equal spacing.
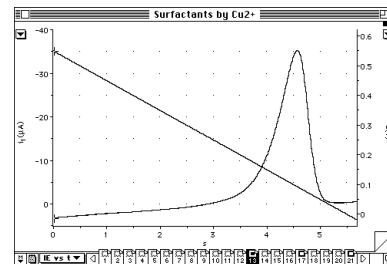
Position of channel separator in overlay mode. Double click to show separate channels.

By dragging the separator to the top of the window you can overlay the current and potential traces.

By dragging the channel separator to the top of the window you can overlay the current and voltage signals — the current axis is on the left, and the potential axis is on the right, Figure 4–2. Both Y axes can be shifted and stretched independently to adjust the graphs as required. The channel separator handle moves to the top right of the window — double-click it to toggle back to separate channel display.

The Axes

The limits and direction of the current and potential axes can be set from the Scale pop-up menu. The button for which, Figure 4–3, is located on the left-hand side of the current axis (when it is the Y axis) or the lower right hand side of the current axis (when it is the X axis, in E vs I display mode). There is a similar button on the potential axis. The Bipolar and Single Sided options are disabled if Units Conversion is already applied.

Location of the axis menu button

Scale Range i₁

Top 50.00 µA
Bottom -50.00 µA

[Cancel] [OK]

Single Sided
Bipolar
Set Scale...
Invert Axis

Units Conversion...

Computed Functions...

i₁ (µV)

40
20
0
-20

The set scale dialog allows you to enter exact limits for the axis.

The current axis pop-up menu

Units Conversion: [Off] [On]

1V → 1 [µA ▼]

Set Units for:
◉ All Pages and New Data
○ Current Page Only

[Cancel] [OK]

Units Conversion (current axis only) allows you to rescale the output of the potentiostat so it displays the correct units.

Computed Functions allow you to transform the data

Computed Functions

┌─ I Channel ──────────────────┐ ┌─ E Channel ──────────┐
Smooth: [⬍] 1   Math: [Subtract ▼]
Math: [Add ▼]   250 [⬍] mV
5 [⬍] µA
Function: [Differentiate ▼]

I Ch = Differentiate(Smooth(i,1)+5µA)
E Ch = E-250mV

[Cancel]
[OK]

Single Sided. Shifts the axis so that zero is located at the bottom (or left) of the display area. This option can be used if you wish to view only current signals larger than zero. Any readings below zero will be off the screen (to see them, select the Bipolar option). If the axis is in bipolar display (below) double clicking it will make it single sided display.

Bipolar. This is the default mode for each channel. It displays zero at the centre of the axis. Double clicking the axis will make it return to bipolar display.

Set Scale. This option allows you to adjust the axis directly to display the range of values you desire. It works whether Units Conversion is on or off. When you choose Set Scale…, the Scale Range dialog box appears (Figure 4–3), allowing you to type in directly the lower and upper limits of the axis to be displayed.

Note that Set Scale is meant for fine-tuning the scale setting rather than for use as a gross magnification tool, and will allow expansion or compression to no more than twice the original range chosen, with neither the upper or lower value being over three times the original limit. First set the range approximately from the Range pop-up menu for the channel, and then set the axis to the precise values required. If you are trying to enlarge very small features you should consider using the Zoom window, or (preferably) recording the data at a higher gain.

Invert Axis. This will reverse the direction of the axis. Useful if you want positive current values to go in the downwards direction (or towards the left when current is on the X axis). The direction of the potential axis can also be reversed so that oxidative potentials can be displayed to the left or right.

Units Conversion… Choosing the Units Conversion item brings up the Units Conversion dialog box (current axis only) which allows you to readjust the conversion factors for the current signal. You have a choice of reassigning conversion factors for all the pages in the file of just for a particular page. See Chapter 3 for more details of Units Conversion.

Computed Functions… Choosing this item is the same as selecting Computed Functions... from the Display menu, and is discussed more

fully later in this Chapter. You can smooth, and perform various mathematical transformation on the current signal. You can offset the potential signal (if you want to set a new reference potential).

Dragging and Stretching the Axes

The scale of the potential and current axes can be independently dragged (offset) or stretched for optimum data display. This allows you to enlarge the signal viewed on the screen, for instance, or move it to better fit in the display area.

The pointer changes as it is moved over the axis area as shown in Figure 4–4. In the data display area, it is a normal, leftward-pointing arrow. Over the axes, though, the pointer leans to the right, and a small marker appears beside it. Between the axis tick labels, a double-headed arrow indicates that dragging will move the axis. If the pointer is near an axis tick labels then dragging will stretch or compress the axis.

Dragging or compressing the scale allows you to set the axis to three times the range limit, and stretching allows you to expand the axis up to 20 times.

Double-clicking in the axis area returns the scale to its normal, unstretched position, with zero at the mid-point of the axis. Double-clicking again toggles between this Bipolar display and the Single Sided display, which has zero at the bottom of the display area.
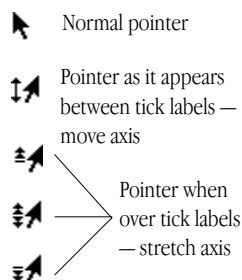
Figure 4–5
The Display Settings dialog box for changing line types and colors.

Display Settings

Graticule
Color: Gray

Background buttons

Graticule buttons

I Channel
Color: Blk

E Channel
Color: Blk

Cancel

OK

Colour pop-up menu

Line type buttons
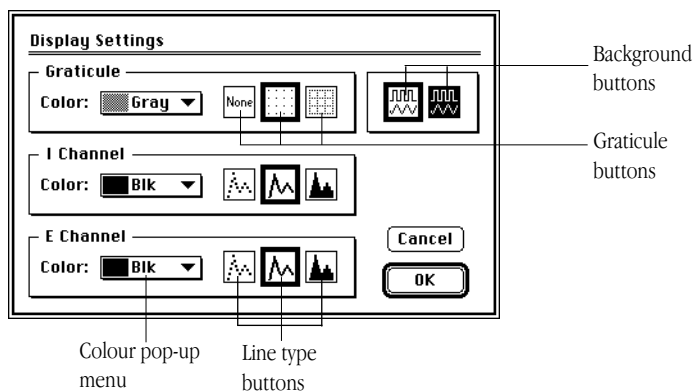
Graph Lines, Patterns & Colors

The Graph Lines, Patterns & Colors dialog box allows you to set the type, pattern, and color of the voltammogram for each channel, the pattern and color of the graticule (the display grid), and whether the background is white or black. The flexibility over the display will depend on which display mode you are using, IE vs t or I vs E. The differences in the dialog controls is shown in Figure 4–5. To bring up the dialog box, choose Graph Lines & Colors from the Display menu.

The Color Menus

The Color pop-up menus, Figure 4–6, for the graticule and channels let you choose the pattern and color of each. Press them to bring up the options. The choices are the basic system colors; black, red, blue, green, magenta, cyan, and yellow; and lighter patterns of the solid colors: gray, light red, and so on. Colors appear as greys on a gray-scale monitor. Colors and greys can be printed as well as displayed, if you have an appropriate printer.

Other Controls

The Graticule buttons let you choose the form of the display grid. Click to select a button — it is highlighted with a heavy border. You can choose to have a dot graticule (the default setting, no graticule at all, or a line graticule.

The Background buttons let you choose whether the background of the voltammogram is white or black. Click to select a button — it is highlighted with a heavy border.

The Line type buttons for each channel give you the choice of displaying the data points joined by lines, as unjoined dots (individual data points), or as a solid fill. Click to select a button — it is highlighted with a heavy border. A continuous line is the default for EChem.

Figure 4–6
The Color pop-up menu
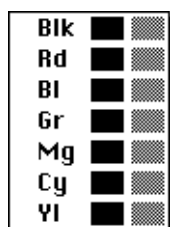
Graticule buttons

Background buttons

Line type buttons

Overlay Display Settings

By default, the voltammogram shown on the active page is colored black and those on the overlaid pages are in gray. You can change colors and patterns of the active and overlaid voltammograms by choosing Overlay Display Settings… from the Display menu. The Overlay Display Settings dialog box will be displayed. The controls in the Overlay Display Settings dialog, Figure 4–7, work in the same way as those in the ordinary Display Settings dialog, Figure 4–5, except that they define the settings for overlaid data only.
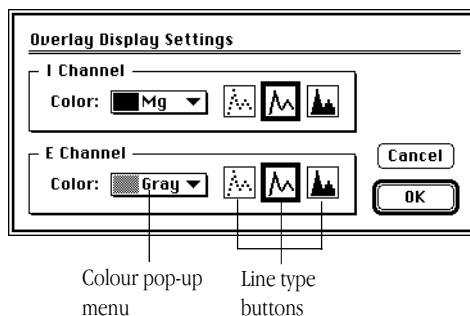
Colour pop-up menu   Line type buttons

Navigating

Active page   Blank page

EChem stores sweeps of data as if they were pages in a pad of paper. The numbered Page buttons along the bottom of the EChem window and the Page Corner controls (the 'dog-ears') at the bottom right of the data display area allow you to move through multiple pages of a EChem file. The highlighted Page button indicates the page of data being viewed, the active page.

Scrolling buttons

Click the upper folded corner of the Page Corner controls to move a page right, and the lower corner to move left. You can also move a page left or right by pressing, respectively, the left and right arrow keys on the keyboard. Hold down the Command key (Macintosh), or Control key (Windows PC), while pressing the left or right arrow key to go to the beginning or the end of the file (the first or last numbered pages).
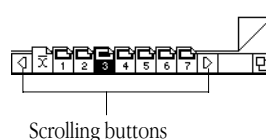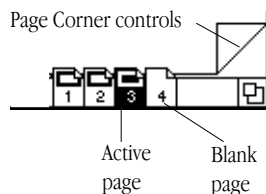
To go to a specific page, choose Go To Page… from the Display menu, or type Command-G (Macintosh) or Control-G (Windows PC). The Go To Page dialog box appears (Figure 4–8): and you type the number of the page in the text entry box (which will be selected) and click the OK button (or press Return or Enter).
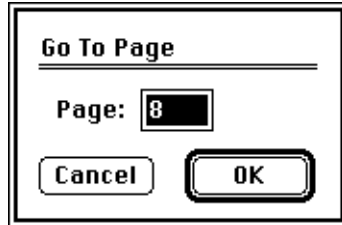
You can also click a numbered Page button to go to that page. If there are too many pages to show all the buttons along the bottom of the window, then left and right arrow buttons will appear at either side: click them to move a page left or right, or press them to scroll left or right through many pages.

Overlaying Pages

You can overlay pages of data recorded at different times or under different conditions one atop the other.

Choose the Show Overlay from the Display menu. The nominated pages selected can be seen through the active page as if each voltammogram were on a pad of transparent plastic sheets. The menu command then changes to Hide Overlay and only the active page is visible. These commands turn the page overlaying display on or off, respectively, and do not affect which particular pages have been selected for overlay.

To overlay all pages, choose Overlay All from the Display menu, or type Command-A (Macintosh), or Control-A (Windows). The data in all pages appears, drawn atop each other. By default, the data shown on the active page is black and other, overlaid, pages are in gray (these settings can be changed). To remove all pages from the overlay, choose Overlay None from the Display menu, or type Command-H (Macintosh), or Control-H (Windows PC). Only the active page remains visible, and none of the others is selected for overlaying.

Using the Page Buttons

The Page buttons along the bottom of the main window indicate the status of pages. The active page is highlighted; Pages selected for overlaying have icons containing black rectangles and those not selected have icons with gray rectangles.

Not included
in overlay

Selected
page

Blank
page

Included
in overlay
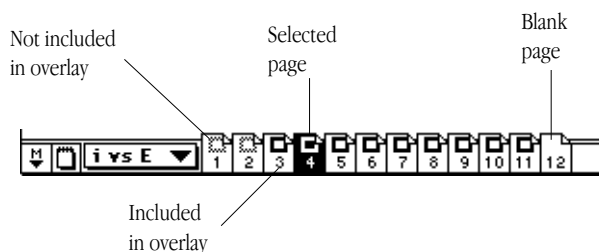
As mentioned, you can click a numbered Page button to go to that page. The active page does not need to be included in overlaying, since it will always appear (so that you can, for instance, quickly check a set of overlays against a set of reference pages which are not themselves overlaid). Command-click (Macintosh), or Control-click (Windows PC), or double-click a Page button to add the page to or remove it from the set of overlaid pages. Option-click (Alt-click) a Page button to hide all pages except the one whose icon was clicked. Press and hold a Page button to activate the pop-up menu which duplicates the various overlay and navigation functions (Figure 4–10).

Go To Page 4

✓ **Include in Overlay**
Hide from Overlay
Overlay Only 4

In case you press rather than click the Page button

Command-click (Control-click) or double-click
Command-click (Control-click) or double-click
Option-click (Alt-click)

Click and hold the mouse down
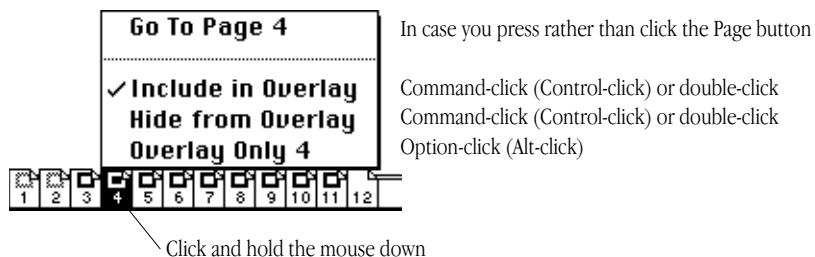
The Scale of Overlaid Pages

When you overlay pages with different vertical ranges, data on other pages is automatically shown scaled to the range of the active page. However in IE vs t, and I vs t, modes the horizontal time axis is not

scaled and the overlaid pages, which could have different time bases, may not be shown to scale.

The Zoom Window

With the Zoom window, you can look at a small section of data in great detail. To zoom in on a data selection, drag to select an area of interest in the main window, and then choose Zoom Window from the Windows menu: the Zoom window appears (Figure 4–11).
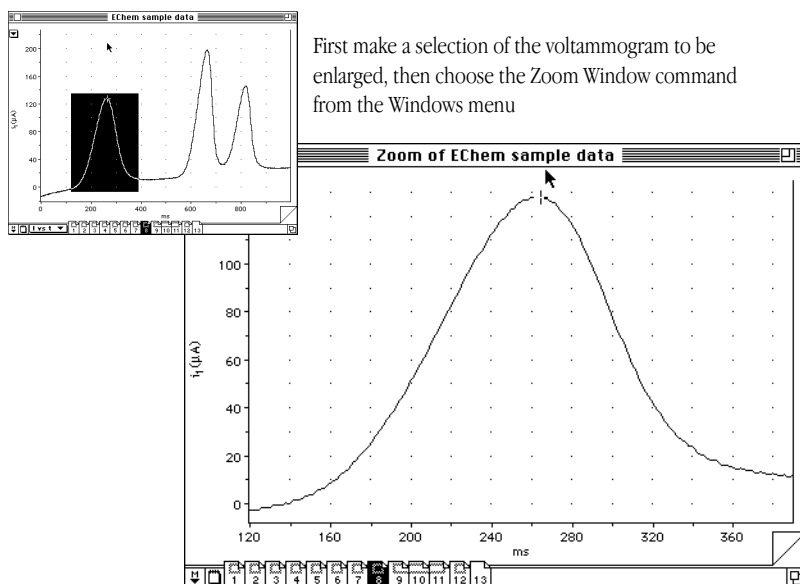
First make a selection of the voltammogram to be enlarged, then choose the Zoom Window command from the Windows menu

You can make a further selection in the data display area of the Zoom window: this automatically zooms in further on that data. If the selection contains less than four data points, the Zoom window will appear gray. If this happens, you should reselect an area in the main EChem window.

Data Display

The Zoom window does not have the Display pop-up menu to switch between I vs E, or IE vs t etc., but has the other controls (Marker and page buttons etc.) of the Main window.

In IE vs t display mode, if the selection covers only one channel, then only one channel is displayed, and the separator handle is dimmed (see Figure 4-12). If the selection covers two channels, then by default the channels are overlaid, but as in the Main window, double-clicking or dragging the channel separator handle will separate them. Channel overlaying is independent of that in the Main window: you can have the channels separate there and overlaid in the Zoom window, for instance.

Figure 4–12
The Zoom Window in IE vs t display mode
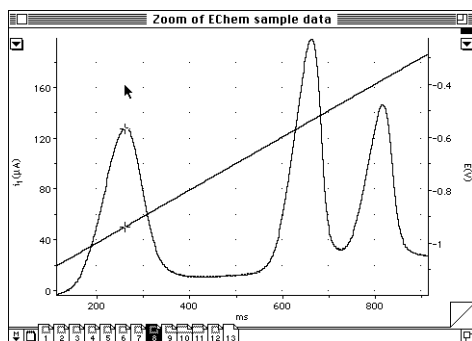
The channel separator in overlay mode. Double click to show separate channels.
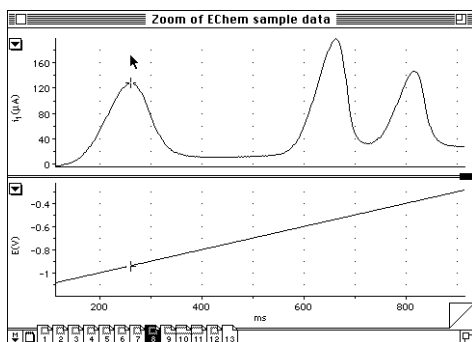
Drag the channel separator (the short black bar) up and down, to the desired position or double click the separator to overlay the channels — top picture.

The scale of the vertical axis of each channel can be independently dragged or stretched for optimum data display, just as in the main EChem window.

When moving between pages, the selection area remains the same with regard to the raw data (and will remain in the same relative position in the EChem window).

The Marker from the Main window knows about the Marker in the Zoom window — moving it onto a voltammogram in one window will do the same in the other, double-clicking it will send it to its lair

— and the Page Comment button will bring up the Page Comment window for the active page.

As you move the pointer across the data display area, the Cursor tracks the displayed data, and the current (i) and potential (E) readings at the tracking point are indicated in the Cursor panel.

Printing the Zoom Window

When the Zoom window is active, then when Print… is chosen from the File menu, the contents of the Zoom window are printed, after the appropriate dialog boxes have been dealt with. The printed page is headed with the window title and the number of the EChem page.

Display and Printer Resolution

EChem allows a flexible data display, so that the display can be rescaled and resized. The controls are not difficult to get used to, especially since the axes are always visible, but they may make the voltammogram look abnormal if you expect it to have the same size and aspect ratio of a standard chart or XY recorder.

The screen display on a monitor is generally about 72 dots per inch, so the apparent resolution is not that good if the display is kept small. The signal might appear jagged and unresolved on a small screen. However, the resolution of the recorded data is independent of the resolution of the display: sampled data is always recorded at 12 bit (0.024%) fidelity at each sensitivity setting. The one important rule is to record your data at the maximum sensitivity (gain) that will keep your voltammogram within the full scale range.

High-resolution printing will show the selected voltammogram accurately. A print-out might not appear as smooth as the pen output of a standard pen recorder if you are using a low resolution dot matrix printer. To get high quality output you should use a laser printer or inkjet printer with a resolution of 300 dpi or greater. Laser printers that use Adobe PostScript® are recommended for maximum quality output.

It is important to check display settings carefully when examining a data, to be sure that what you are looking at is what you think you

are looking at, especially if the settings on your machine might have been altered. A trace may end up looking very strange if it has been stretched vertically or had an inappropriate baseline subtracted.

Making Measurements

When you have finished recording you can make direct or relative measurements from the voltammogram (or amperomogram).

When the pointer is over the data display area, the Cursor tracks the voltammogram, Figure 4–13. In this case, The Cursor panel shows the current, potential, and time coordinates at the cursor location

The Cursor only gives discrete measurements, jumping from data point to data point (you can see this more clearly in the Zoom window). It cannot provide a reading on the line that is drawn between the individual data points.

Current, potential and time (I, E and t) cursor coordinates

The pointer is positioned with the mouse.

Figure 4–13
Use of the Pointer and Cursor.

The cursor is attached to the trace but follows the pointer.
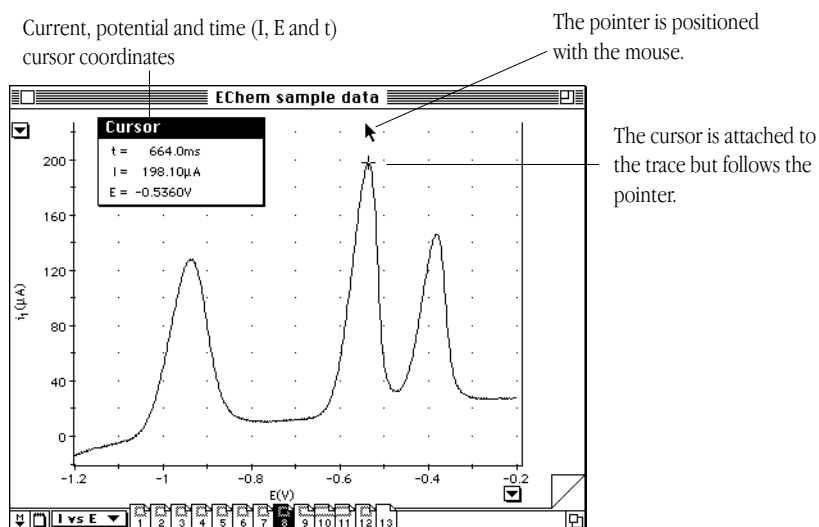
Using the Marker

The Marker can be found in its 'lair', a box at the bottom left of the EChem window. It is used to set a particular data point as a zero reference point, so that relative measurements can be made with respect to that point, Figure 4–14. To set the Marker, drag it from its

lair into the voltammogram — it will lock onto the voltammogram when you release the mouse button. Option-drag the Marker to position it the anywhere on the screen. Use the display in the Cursor panel to help to select a data point. If you need finer control of the Marker position, use the Zoom window to look at a selection in more detail: the Marker is duplicated there, and can more easily be assigned to a particular data point.

Double-clicking the Marker or clicking its box at the bottom left of the EChem (or Zoom) window sends it back to its lair.

Once the Marker is in position, measurements relative to it (preceded by Δ) are given in the display in the Cursor panel. The 'Δ' symbol before a value indicates that it is a difference, not a direct reading. If the channels are overlaid and the Marker is not on a voltammogram, the voltammogram closest to it is the one for which relative readings are made.

Figure 4–14
Using the Marker tool
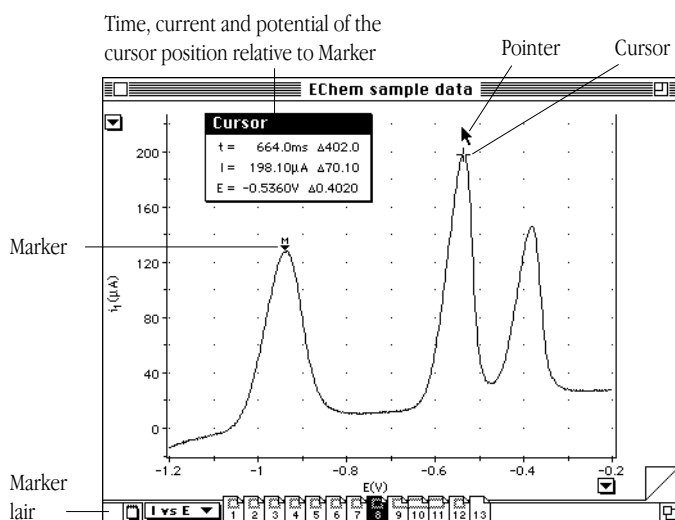
Setting and Removing Baselines

The Marker is also used for setting relative measurements where the baseline of the voltammogram (or amperomogram) is not zero. If you find that the baseline value is not zero when it should be — that is, there is some slight offset — a baseline may already be set up. Place the Marker at a point you want the baseline to intersect. Then Command-drag (Macintosh), or Control-drag (Windows PC), from

the Marker lair (or from the Marker itself) a duplicate Marker, which can be placed to set the second point defining the baseline (Command-Option-drag, or Control-Alt-drag, to place this duplicate Marker off the curve). The baseline is displayed as a dotted line passing through the two Markers, Figure 4–15. The baseline can only be positioned when you are in I vs t, or IE vs t, display modes. You cannot set a baseline when in the I vs E, or E vs I, display modes.

Figure 4–15
Using the Marker tools to create a baseline
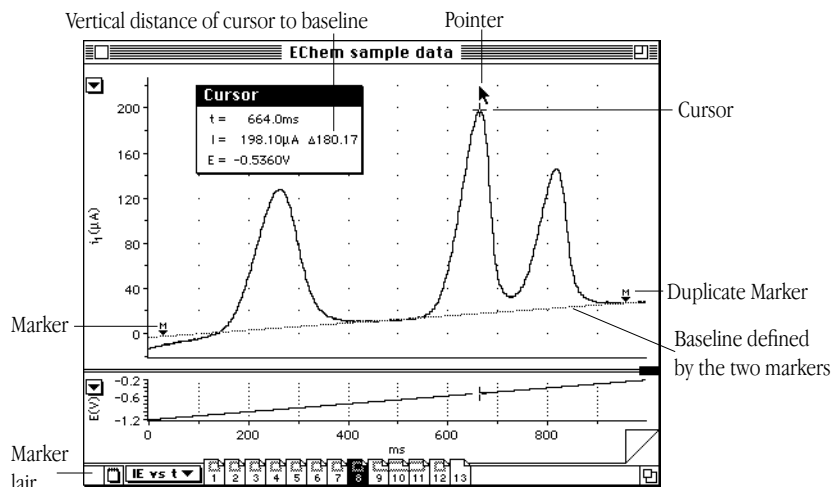
The value along the baseline is set at zero: the Cursor panel shows the absolute time and potential, but the current signal at the cursor is shown relative to the baseline.

Note that the baseline is set for a particular channel on a particular page of data. When moving between pages, the baseline may move considerably if locked to the voltammogram; if independent, it will remain static. Removing one Marker removes both Markers, and the baseline. Attempting to set a vertical or near-vertical slope will also remove the baseline and send the Marker and its duplicate home.

The Marker Miniwindow

To display the exact Marker position, or both Marker positions when a baseline is set, choose Marker from the Windows menu: the Marker miniwindow appears, Figure 4–16. The Marker miniwindow 'floats' in front of the active window, can be moved around with its title bar, and can only be dismissed by clicking its close box. It has a display area divided into three panels, showing the channel (i or E) in which

the Marker is active, and the time and signal readings at the Marker position, Figure 4–16. If the Marker is inactive, the two lower panels are blank and the top panel displays 'Off'.

Figure 4–16
The Marker miniwindow

marker not on graph

marker on I vs E graph

marker on i channel in IE vs t graph

marker on E channel in IE vs t graph
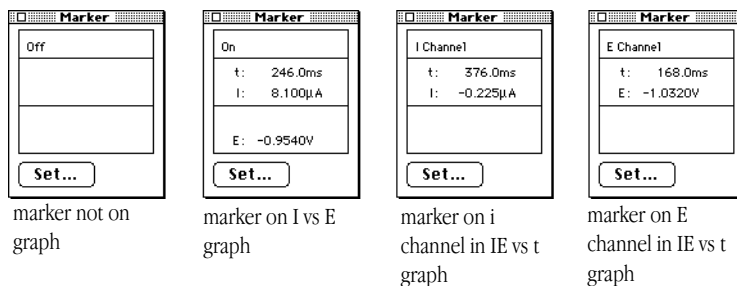
Clicking the Set… button brings up the Set Marker Position dialog box, Figure 4–17,which allows you to alter or define the Marker or baseline position by typing values into the text entry boxes, then clicking the OK button to apply them to the EChem window.

Figure 4–17
Positioning the Marker
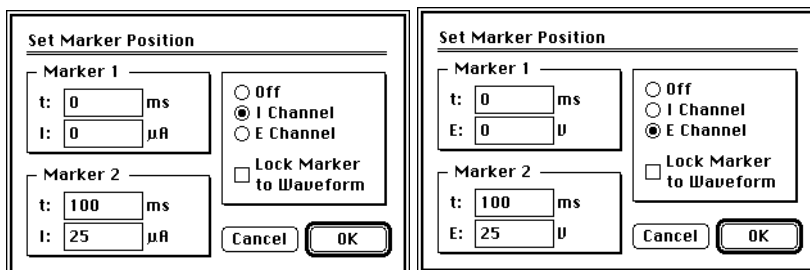
Clicking the Off radio button turns the Marker off, clicking one of the other radio buttons selects the channel in which the Marker will appear. If the Lock Marker to Waveform checkbox is on, the Marker will position itself on the signal, and the text entry box for I or E values is inactivated (appears dimmed). If the checkbox is off, the Marker is independent of the voltammogram, and you can enter the I or E and hence assign the vertical position of the marker. Entering values into the Marker 2 text entry boxes as well as those of Marker 1 will create a straight baseline joining the two markers.

In the I vs E (or E vs I) display mode, the Marker miniwindow shows 'On' in the top panel, and I and E values in the other two panels. Since there is only the one Marker and you cannot set a baseline, the

Set Marker Position dialog box is simplified for the I vs E display, Figure 4–18. The Marker is set independently of the signal trace if you use this dialog box to position it.

Figure 4–18
Positioning the Marker when in the I vs E (or E vs I) display modes
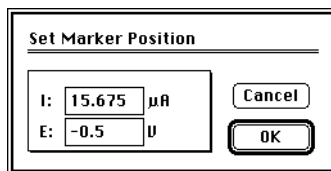
Background Subtraction

It is possible to set up a background page, the voltammogram from which is subtracted from all other pages in a file with the same settings (potential range, scan rate, and so on). This has a number of uses, for instance, non-linear baseline subtraction. A reference voltammogram can be made of a 'blank' sample, then standard additions could be made and the blank trace subtracted to give the readings for the analytes of interest. Background subtraction can also be used a to isolate a small signal from a noisy background, or from a sloping baseline.

To set up background subtraction, go to the page you want to use as a background page, and choose the Subtract Background command from the Display menu. The voltammogram on the active page is subtracted from itself (so it shows a line at zero current), and all other pages in the same file that have been recorded under the same conditions (potential range, scan rate, etc. — if these settings were different, distortion and clipping would result.). Note that scans recorded at different sensitivities (but otherwise identical settings) can be subtracted. The Page button for the background page shows the page number underlined.
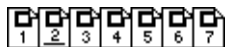
The Background page is underlined

Once a background page has been set, EChem stores it in memory, so it does not have to be in the same file as the voltammograms from which it is subtracted. This means that you can set up files of calibration pages to subtract from new data, set the appropriate background page, and then open a new file to sample with

background subtraction. It also means you will not necessarily see the background page button, but the menu commands Subtract Background and Clear Background in the Display menu will be undimmed when a background page is in memory, so this will tell you if such a page has been set.

The Subtract Background command toggles with the Don't Subtract Background command. Both leave the background page in memory, but will subtract it or not subtract it, respectively, from voltammograms in the open file, so that you can compare voltammograms before and after subtraction.

Choosing Clear Background from the Display menu clears the background page from memory, and restores the raw data.
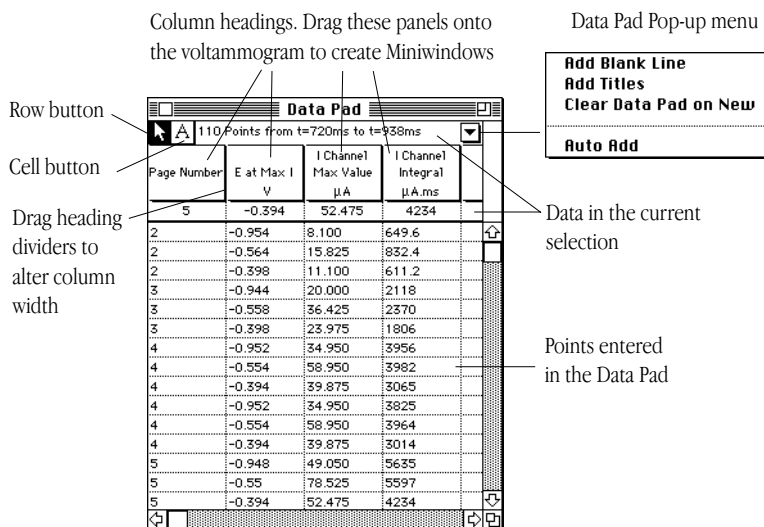
The Data Pad

The Data Pad can store large amounts of data (cursor coordinates, peak maxima and minima etc.) in spreadsheet format — up to 32 columns with 32,000 rows, with each cell having at most 255 characters to a maximum of 2000 characters per row. Its contents can be saved as a text file, or copied to the Clipboard for transfer to other software, or printed directly. To bring up the Data Pad, Figure 4–19, choose Data Pad from the Windows menu.

The Data Pad window is a normal window with a close box, size box, and title bar, and can be moved around the screen or left in the background while the EChem window is active. It can be resized using the size box at its bottom right corner. Click the zoom box to toggle the window between the set size and the full size of the screen.

Information on the current selection or active point is displayed immediately above and beneath the column headings: the readings beneath the column headings are separated from recorded data by a heavy line, and are centered rather than left-justified to help to distinguish them. In EChem, the active point is the last point clicked in the data display area.

As data is added to the Data Pad, new rows of values are created below existing rows in the data area. Use the scroll bars to move down or across through rows and columns. There are two tools that

Figure 4–19
The Data Pad window

Column headings. Drag these panels onto
the voltammogram to create Miniwindows

Data Pad Pop-up menu

Row button

Cell button

Drag heading
dividers to
alter column
width

Data in the current
selection

Points entered
in the Data Pad

can be used to deal with the data in the pad, indicated by the buttons at the top left of the window. By default the Row button is selected and the Pointer appears as a heavy cross when over the data area. Click to select a row, Shift-click or Shift-drag to select contiguous rows, or Command-click (or Control-click) to select or deselect rows individually; the data can then be cleared, or cut or copied to the Clipboard as tab-separated text, using the commands in the Edit menu. If the Cell button (with the A) is clicked, the pointer changes to an I-beam when over the data area, and text in each cell can be edited in the normal way. Clicking the Cell button deselects all selected rows.

The Data Pad pop-up menu allows you to add blank rows to the Data Pad, or to add the current column headings to it as three lines — which is useful to keep track of changed settings, or when transferring data to other software. You can also choose whether or not to save the Data Pad settings when a new file is opened: a tick appears beside this menu command when it is active. It applies only to the current file. The Auto Add command adds the defined data to the Data Pad for every sweep, whether single, multiple, superimposed, or average, and whether or not each sweep is on a new page.

The width of columns can be changed to suit the displayed data and headings. You might want to narrow columns to display more on screen, for example, or have a wide column to the right in which to add comments. Position the pointer on the heavy dividing line between column headings, so that it changes into the resizing pointer, drag until the column is the desired width — a gray line appears, to indicate position — then release the mouse button.

Adding Data to the Data Pad

To add data from a selection in the EChem window to the Data Pad, choose Add to Data Pad from the Windows menu, or type Command-D (Macintosh) or Control-D (Windows PC). If you want to add data on the whole page, the whole page must be selected. Some time-based functions (such as Integral) will only operate when you are in the IE vs t, or I vs t, display modes. If there is no selection, data at the active point is transferred. As a shortcut, you can double-click in the data display area to transfer data at a point (which becomes the active point). This can also be done from the Zoom window; the magnification it provides may prove useful in locating particular features.

The data recorded will depend on the choices made in the Data Pad Column Setup dialog box.

Setting Up the Columns

As previously noted, the data recorded will depend on the choices made in the Data Pad Column Setup dialog box. This dialog box appears on clicking a column heading panel, Figure 4–20, and will have the column number (1 – 32) in its title.

Figure 4–20
Setting up the Data Pad columns
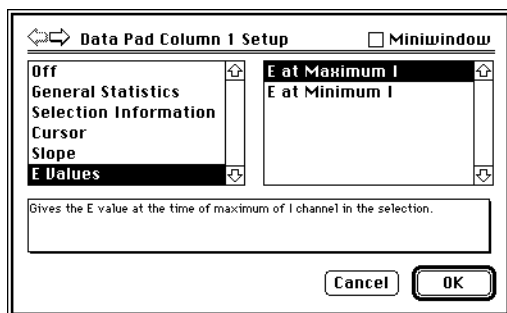
To move to the dialog boxes of adjacent columns (and set up many columns quickly), click the arrows by the dialog box title, or press the right or left arrow keys on the keyboard.

The channel that data is taken from is selected in the Channel pop-up menu at the right of the dialog box. Two scrolling lists let you select from the many forms of information that could be recorded, whether derived or direct. The left-hand list gives the general information type, and the right-hand one options available in that set. The selected option is briefly explained in a box beneath the two lists.

Off simply turns the column off: no data is recorded in it.

General Statistics offers calculation of the mean, standard deviation, standard error of the mean, or integration (with respect to time, $\int i.dt$) of the selected region of the current signal. The value of the largest or smallest data points in the selection (or the difference between them), the times at which they were recorded, or the number of data points in the selection can also be obtained for the current signal.

Selection Information. If there is a selection, this function will report the start time, end time, or duration.

Cursor. These functions report the time, current and/or potential (t, I and E values) at the active point, if there is one. It does nothing if there is a selection of more than one point.

Slope gives the maximum or minimum slopes (with respect to time, di/dt) found in a selected area of the voltammogram (or amperomogram), the average slope of a selection (the equivalent of fitting a straight line through a selection of data points), or the slope of the curve at the active point.

**E values** can return the magnitude of the potential at the points at which the maximum or minimum current signal (i values) in a selection.

Its various functions make the Data Pad very useful for quickly extracting information about a voltammogram. You can leave the Data Pad, set up to display the required information, as a small visible background window that will be updated as you skip from page to page or as new entries are made.

Data Pad Miniwindow

Miniwindows can be created to display the current values of statistics or measurements set up in the Data Pad, Figure 4–21. Click the Miniwindow checkbox in the Data Pad Column Setup dialog box to show or hide the miniwindow for a column, or drag a column heading to the main EChem window. Drag the miniwindow by its title bar to where you want it, click the close box to dismiss it, or click its body to bring up the dialog box again.

Figure 4–21
Data Pad Miniwindows
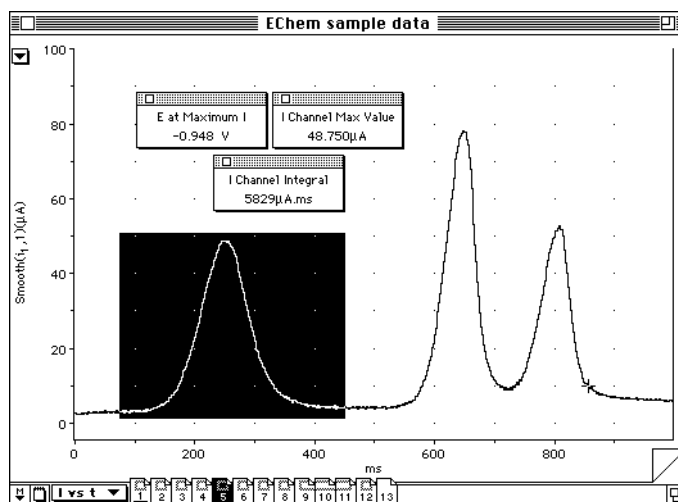
Printing the Data Pad

When the Data Pad window is active, then the Print option in the File menu changes to Print Data Pad…, so that the contents of the Data Pad window are printed rather than those of the EChem window. The Data Pad will print across two or more pages if it is wide enough, but individual columns will remain intact.
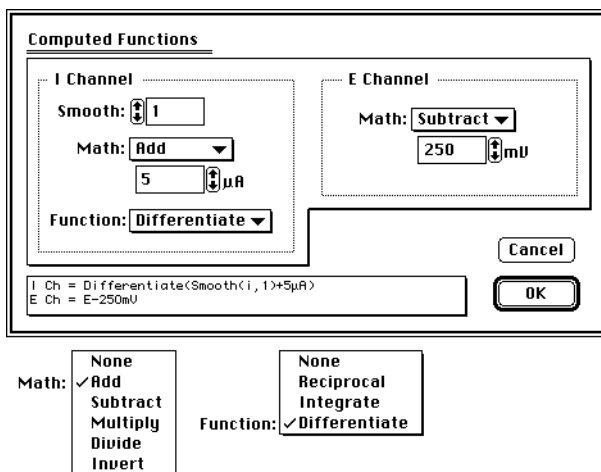
Computed Functions

By default, EChem records the raw current data in the I Channel and does not apply any computed function. Sometimes, though, some

derived or altered signal is of more interest or use, or can throw more light on the original signal. For instance, you could measure the charge transferred at the working electrode by integrating the current signal with respect to time. EChem has a number of computed functions that can be applied singly or in combination, before or after recording. EChem always retains the raw data in memory, so the unaltered voltammogram (or amperomogram) can be retrieved at any time simply by turning all computed functions off. The E Channel allows only one computed function – to add or subtract a constant value.

The Computed Functions dialog box, Figure 4–22, lets you set up data manipulation of various sorts. Choose the Computed Functions… command from the Display menu, or type Command-F (Macintosh) or Control-F (Windows PC). The function, or functions, chosen will apply to all pages in the file until you change the settings.

Figure 4–22
The Computed Functions dialog

Sampling Speed

Computed functions do not affect sampling speeds, or scan rates, but they may affect the delay between consecutive sweeps. The speed with which computations are applied to the data is directly related to the speed of the computer, so slower models will give longer delays. If this proves to be a problem, perform computed functions after the data has been collected.

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Channel Functions

The dialog box has one panel for I Channel and one for the E Channel, in which functions for the two channels can be set independently. If multiple functions are applied, their order is from the top to the bottom of the panel: the waveform is first smoothed, then shifted, and so on. The display panel at the bottom of the dialog box indicates this order (and the display settings, as well).
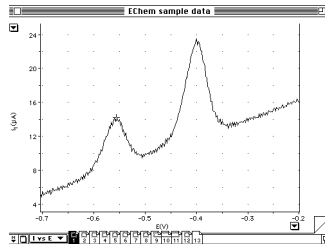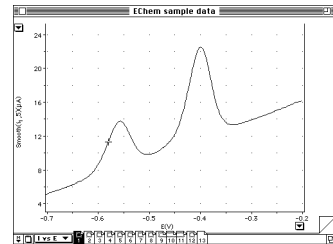
No smoothing

Smoothing value of 1
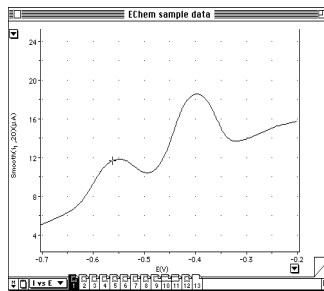
Smoothing value of 20 – too much
smoothing gives distorted peak shapes

Smooth

Data can be smoothed to remove noise in the current signal. If the control is set to zero, then smoothing is off (the default); the larger the number entered, the greater the smoothing, Figure 4–23. Click the up/down arrow buttons to alter the degree of smoothing; hold the mouse down continuously to increase or decrease the number

rapidly; or type a value in the text box to directly set the degree of smoothing, from 1 to 50. For 'n' point smoothing, at each data point 'p' the values of the data points in the range p±n are averaged (i.e. a moving point average is taken). At the very start and end of the voltammogram (or amperomogram) there may be insufficient points to complete a full 'n' point smoothing and the amount of smoothing will not be as great. Smoothing will affect different waveforms in different ways: voltammograms with sharp peaks cannot be smoothed too much without distortion, but those with broad peaks can be smoothed a lot more.

Math
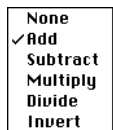
The Math control lets you add, subtract, multiply or divide the data by a constant amount. By default, the setting is None (no operation is applied) and the text entry box and units control are dimmed. Choose an operation from the Math pop-up menu, Figure 4–22

Add or Subtract. If you choose one of these, the text entry box and units control become usable. You can add or subtract a constant amount from the signal. Type the value in the text box: it can be up to ±30,000, and be set to four decimal places. The units are set by using the up/down arrow buttons. You may want to add or subtract a constant value to the E Channel if you have recorded a voltammogram with a Ag/AgCl electrode but want to change the display so that zero volts corresponds to use of a calomel or standard hydrogen electrode.

Multiply or Divide. If you choose one of these, the text entry box becomes usable. (The units control does not, since you are multiplying by a scalar number.) Type the value in the text box: it can be up to ±30,000, and be set to four decimal places, although you cannot enter zero.

Invert. If you choose Invert, the text entry box and units control remain dimmed. Invert changes the sign of the signal, effectively multiplying it by minus one: positive values become negative, and vice-versa. This is usefulness the E channel if you recorded data with one polarity convention (say, more negative potentials mean greater reduction) but then later want to display data with the opposite polarity convention (more negative potentials mean greater reduction).
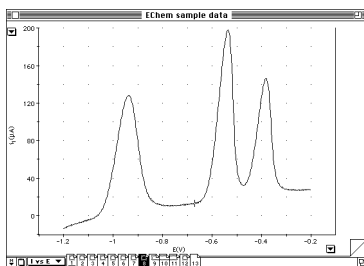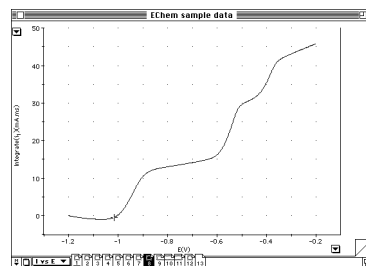
Function

The Function pop-up menu gives a range of available functions that can be applied to a signal. By default, the setting is None; if you want a function applied, choose it from the pop-up menu.

Reciprocal. This function displays the reciprocal of the current signal, that is, $1/i$ for any data point of value i (so zero values will become infinite).

Figure 4–24
Integration of data

Original voltammogram

Integrated voltammogram
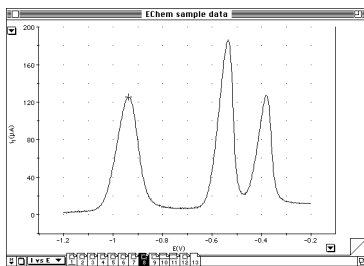
Voltammogram after 'blank' page subtraction
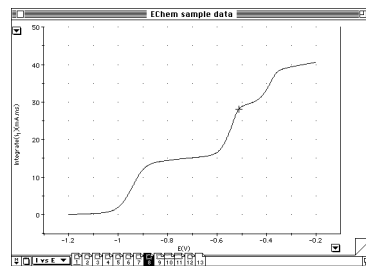
Integration of subtracted voltammogram

Integrate. The Integrate function measures the area under a waveform, calculated as the sum of the data points multiplied by the sample time interval. The integral over a time with of the current signal will have units of charge (an ampere.second is a coulomb).

The integral function works best when the voltammogram or amperomogram has a flat baseline close to zero current, Figure 4–24.

Apply the Integrate function first, then use the Subtract Background command to subtract a blank run to achieve a better result. If you Subtract Background first, then integrate this will NOT work!

.**Differentiate**. This function gives the first-order derivative of the current signal with respect to time (di/dt), Figure 4–25. It is useful when the voltammogram shows ill defined peaks or shoulders where the differential may give a resolved signal. The Differentiate function is particularly sensitive to noise, so its use with the Smooth function, is often necessary.
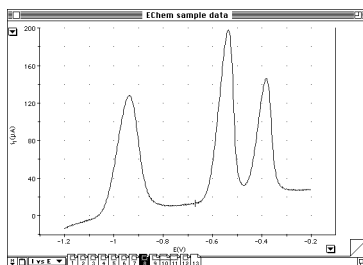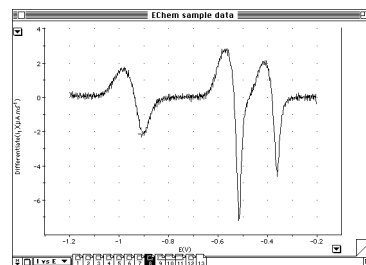
Figure 4–25
Differentiation of data

Original voltammogram

Differentiated voltammogram

The Notebook

You can enter your observations and notes in the Notebook, Figure 4–26, which is saved along with the EChem file. To use the Notebook, choose Notebook from the Windows menu.

The Notebook has a total of eight numbered pages that can be used for general notes about a file. Each page can contain up to 32,000 characters, and you can scroll vertically through the contents using the up and down arrow keys on your keyboard.

Clicking the 'dog-ears' at the lower left of the window turns the pages back and forth. Click the Date or Time buttons at the bottom of the window to add the date or time to your notes at the insertion point. The commands Cut, Copy, Paste, and Clear can be used to edit text normally, although you cannot paste graphics into the Notebook. You can also paste text from the Notebook into word processor documents.

Figure 4–26
The Notebook window

Write your notes here

Click here to move to next page

Click here to move back a page

Click this button to add the time at the insertion point

Click this button to add the date at the insertion point

Notebook

Analysis for zinc, lead, and cadmium in river water using a mercury film on a glassy carbon electrode and an Ag/AgCl reference electrode. Method: Anodic stripping linear sweep voltammetry. Standards prepared as chloride salts in 0.010 mol/L 1-ascorbic acid over the range 1-100 ppb.

1

Printing the Notebook

When the Notebook window is active, then the Print option in the File menu changes to Print Notebook…, and if the command is selected, the contents of this window are printed rather than those of the EChem window. The Print dialog box allows you to print the entire contents of the Notebook, or any selected page range (EChem will not print empty Notebook pages). The pages are printed out as they appear on screen. You can copy the contents of the Notebook to the Clipboard for pasting into a word processor if this is more convenient.

The Page Comment window

The page comments feature allows you to annotate your individual voltammograms. (The Notebook, above, allows you to make more general comments about the recording as a whole.) Comments must be entered after recording, and once entered, can be edited.

The Page Comment button can be found at the bottom left of the EChem window, to the right of the Marker (Figure 2–3). When there are comments noted down for the active page, the button icon changes from a blank note to a marked one. Click the button to bring up the Page Comment window, Figure 4–27.

Figure 4–27
The Page Comment window

The Page Comment window shows comment text ("The subject was showing signs of lassitude and impaired higher cognitive function. Note the immediate increase in brain activity here, though, when the adverts on the TV stopped.") and "Modified: Tue, 27 Apr 1993, 3:53 PM" with annotations:

Comment text can be typed in here and edited normally

Information on the date the page was modified or the number of pages averaged is given here

A comment can be typed in (or pasted into) the window, and text there can be edited normally. For practical purposes, the text should not be too lengthy (say over 300 characters), since more than that will make the comments difficult to read in the window, although you can autoscroll up and down through them using the arrow keys.

The box at the bottom of the window shows the time and date the page was recorded or otherwise modified.
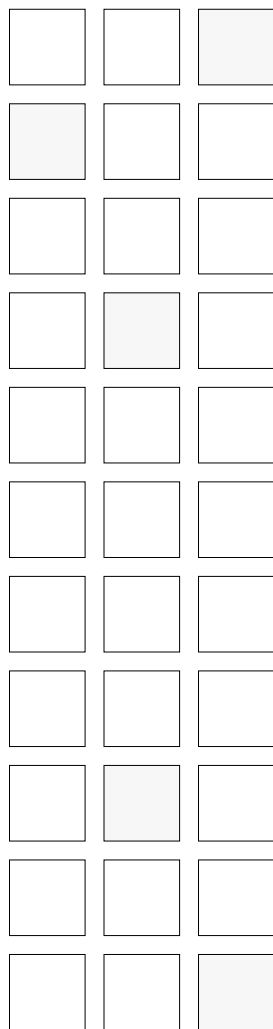
Printing Page Comments

Whenever a EChem page is printed, Page Comments are printed beneath the waveform pictures. If comments are lengthy, the voltammograms will be printed in a reduced area. If the comments are very lengthy, they may also be truncated.

5

Working With Files

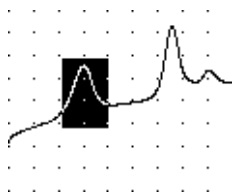EChem data files can be edited, printed, and saved to disk in various formats. This chapter describes these operations, and such features as creating a single file summarising results from many files, and saving settings to allow easy repetition of an experiment. Other topics covered include the transfer of data to other programs, such as spreadsheets and graphing software, and the use of page comments and the Notebook.
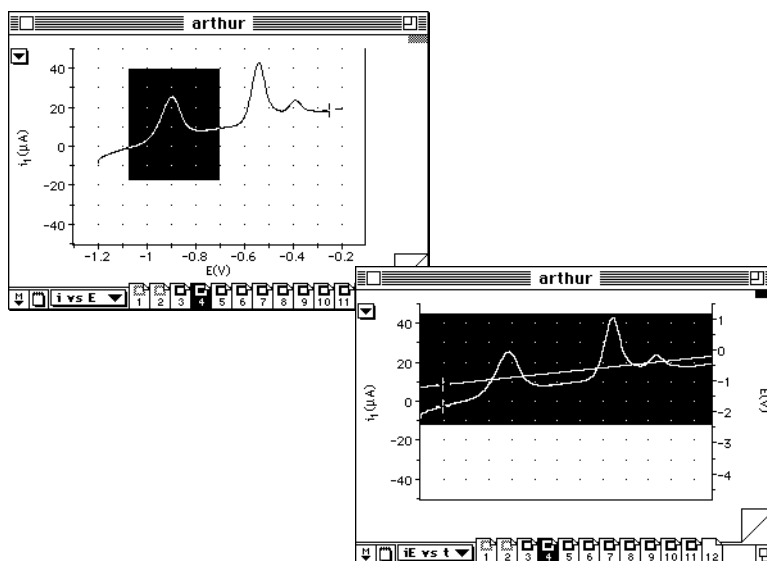
Selecting Data

To select a region of data position the pointer, then click and drag to highlight a rectangular area. When in the i vs E display mode, the minimum horizontal extent of any selection in the Main window is four data points.

When in the iE vs t mode only the vertical extent of the selection rectangle can be varied, with the horizontal extent being the whole page. If the channels are split (not overlaid) then you can select a region on the first channel then, holding the Shift key, select a region on the second channel. If the two channels are overlaid, simply drag to create a common selection rectangle over both channels.

Figure 5–1
A selection rectangle in the Main window

Figure 5–2
Examples of selection rectangles in the two different display modes: above is the i vs E mode, and at bottom the iE vs t mode

Editing Data

The Cut, Copy, Paste, and Clear commands appear in the Edit menu. These commands can be used to copy selection of the text entries in the Page Comment or Notebook windows and to paste the text into word processor or spreadsheet documents.

When the Main window is active, the commands work with whole pages of EChem data rather than selections. Cut removes the active page from the file and places it on the Clipboard. Copy places a copy of the active page on the Clipboard. Paste adds a page already on the Clipboard to the file before the currently selected page. Clear removes the active page from the file. If the Zoom window is active, the active page is still affected rather than the selection that the Zoom window is showing, for most purposes.

All these commands are able to be undone (only a single level of undo is supported). The Undo command, appears in the Edit menu, and changes to reflect your last action. If you have just, for instance, removed a page from the file by choosing Clear from the Edit menu, then the menu command will change to Undo Clear Data. (Should you choose the command again, it becomes Redo Clear Data.)

The editing commands allow you to move pages about and to delete those you do not want. You can move a page between files by placing it on the Clipboard and opening another file (closing the current one, since Scope can only have one file open at a time), then pasting it where it is wanted. Paste inserts the page on the clipboard immediately before the active page.

Transferring Data

You can transfer graphs from EChem to other applications, such as a spreadsheet or drawing program. The Cut and Copy commands place the Main and Zoom windows on the Clipboard as a picture. (The same pictures you would see if the windows were printed, with title, page comments, and so on, but without overlaid pages.) The Clipboard contents can then be pasted into drawing software such as Canvas or CorelDraw which have extra features to modify the picture for presentation purposes. However the best results are usually obtained by transferring the data itself to a specialist graphing program.

An EChem data file can be saved as an ASCII text file able to be opened by any application that can import text, such as a word processor, spreadsheet, or graphing program such as Igor Pro, Kaleidagraph or Origin (to do this, choose the Save As… menu command from the File menu.)

Special Copying

EChem also has a more powerful method of copying text or graphics to the Clipboard for data transfer, the Copy Special… command, in the Edit menu. It allows the copying of overlays in pictures (which the Copy command itself does not), and the copying of multiple pages or even an entire file, as text. Choosing the Copy Special… command when the Main window is active brings up the Copy to Clipboard dialog box (Figure 5–3).

Figure 5–3
The Copy to Clipboard dialog box.
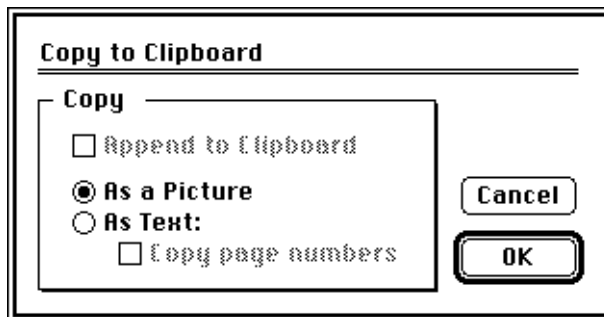
The dialog box lets you choose one of two options: copying the Main window as a picture; or copying it as text. If the Append to Clipboard checkbox is turned on, data in text form from the Main window can be appended to the contents of the Clipboard, rather than replacing its contents. The control is dimmed and unavailable if you are copying a picture.

As a Picture. If this radio button is on, then the EChem window, including visible overlaid pages, is placed on the Clipboard as a QuickDraw picture. (The same picture you would see if the window were printed, with title, page comments, and so on.)

As Text. If this radio button is on, then the data from the EChem file is placed on the Clipboard as tab-delimited text. The 'Copy page numbers' checkbox allows you to precede the data with the page number if required. If page overlaying is turned on, then the data for entire file will be copied to the clipboard, regardless of which overlaid pages are visible (if any); if it is off, only the active page will be copied. Use this option for pasting data into spreadsheet or graphing applications.

A similar dialog box appears when you choose Copy Special… with the Zoom window active. When the Zoom window is active, the picture copied is confined to the selection that the Zoom window displays.

The Clipboard

Whenever data is cut or copied from EChem, it is stored in the Clipboard. You can choose Show Clipboard from the Edit menu to see what is copied: the Clipboard window appears (Figure 5–4). The Clipboard window is a normal window with a close box, zoom box, size box, and title bar, and can be moved around the screen or left in the background while the EChem window is active.

Figure 5–4
The Clipboard window as it might appear after copying: Copy from the EChem window produces a picture (near right); Copy Special, as text, with potential values in volts and current in amperes (far right). Other text format options allow time and page number to be copied as well.
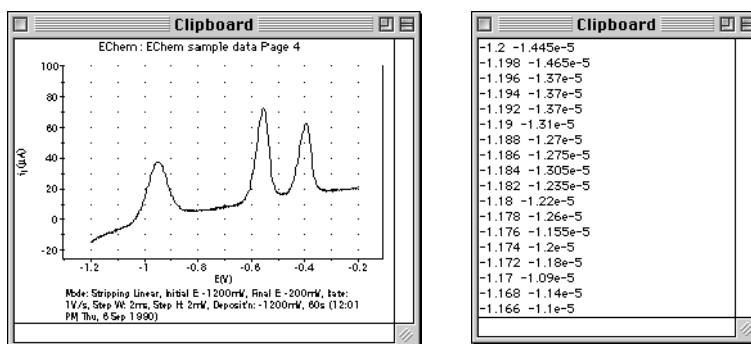
The Clipboard window shows either a representation of a picture (sized to fit the window), or rows and columns of data in text format, depending on what has been copied. If a very large selection is made, the process of copying may take some time.
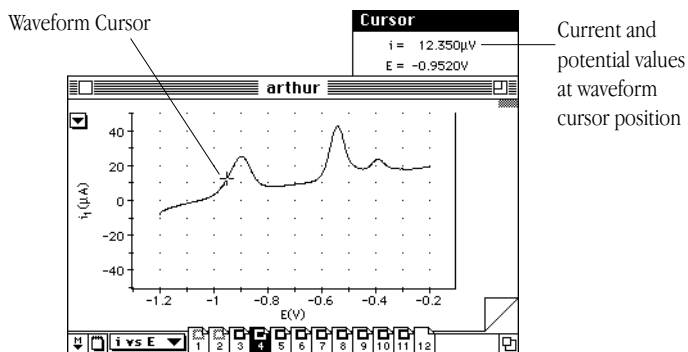
Measuring From the Waveform

When you have finished recording, you can go though your data and make measurements directly from the recording — since everything is digital, you are given a direct read-out, with no chance of the errors in reading that could occur in analysing a paper-and-ink record. You can make direct or relative measurements.

When the pointer is over the data display area, the Waveform Cursor tracks the waveform. The display in the Cursor panel shows the

current and potential value at the waveform cursor location. This is irrespective of the display mode.

The pointer appears as a cross over the data display area. The Waveform Cursor only gives discrete measurements, jumping from data point to data point (you can see this more clearly in the Zoom window). It cannot provide a reading on the line that is drawn between the points.
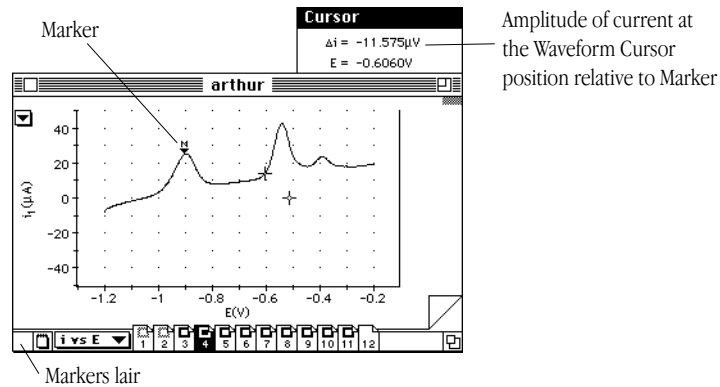
Using the Marker

The Marker can be found in a box at the bottom left of the Main window (Figure 5–6). It is used to set a particular data point as a zero reference point, so that relative measurements can be made with respect to that point. To set the reference point, drag the Marker from its lair into the main window: it will lock onto the waveform when you release the mouse button (Figure 5–6). Option-drag to position the Marker independently of the waveform. Use the Waveform Cursor display in the Cursor panel to help to select a data point. If you need finer control of where the Marker ends up, use the Zoom window to look at a selection in more detail: the Marker is duplicated there, and can more easily be assigned to a particular data point.

When moving between pages, the Marker will remain at the same time position: if locked to the waveform, it will lock to the new waveform amplitude at that time; if independent, it will remain static. Double-clicking the Marker or clicking its box at the bottom left of the main (or Zoom) window sends it back home.

Once the Marker is in position, current measurements relative to it (preceded by Δ) are given in the Waveform Cursor display. The potential at the Waveform Cursor position is absolute. The 'Δ' symbol before the current value indicates that it is a difference, not a direct reading.

Figure 5–6
The operation of the marker and waveform cursor in the main window.

Marker

Cursor
Δi = −11.575µV
E = −0.6060V

Amplitude of current at the Waveform Cursor position relative to Marker

Markers lair

Setting and Removing Baselines

In iE vs t display mode the Marker can also used for setting relative amplitude measurements where the baseline of a channel is not zero. Once you have recorded a waveform, you may find that the baseline value is not at zero potential (or set units) when it should be –that is, there is some slight offset. You may want to measure features of a waveform relative to a series of other features. In either case, a baseline should be set up for the channel of interest. To do this, place the Marker at a point you want the baseline to intersect. Then Command-drag from the Marker lair or the Marker itself: this creates a duplicate Marker, which can be placed in the same channel to set the second point the baseline intersects (Command-Option-drag to place this duplicate independently of the waveform). The baseline is displayed as a dotted line passing through the two Markers.

The value along the baseline is set at zero: the Waveform Cursor display in the Cursor panel shows the absolute potential, and the amplitude of the current relative to the baseline (Figure 5–7).

Note that the baseline is set for a particular page of data. When moving between pages, the baseline may move considerably if locked to the waveform; if independent, it will remain static. Removing one Marker removes both Markers, and the baseline.

Figure 5–7
Setting a baseline in the main
window in iE vs t display mode
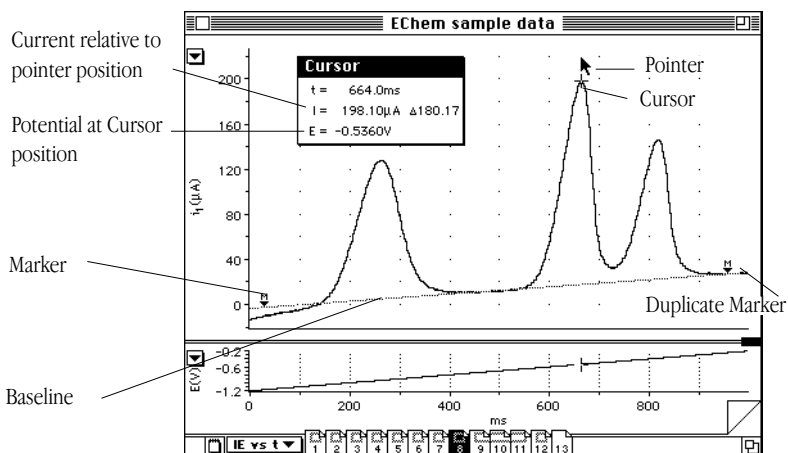
Attempting to set a vertical or near-vertical slope will also remove the
baseline and send the Marker and its duplicate home. The marker has
no effect if placed on the potential (E) waveform.

Saving Options

To save a file of recorded data, choose Save from the File menu, or
type Command-S. When this is done, an already existing file will
have any changes made to it saved to disk. The first time that you
save a file, or on any occasion that you choose Save As… from the File
menu, the Save As dialog box will appear (Figure 5–8).

Figure 5–8
The Save As Text dialog box

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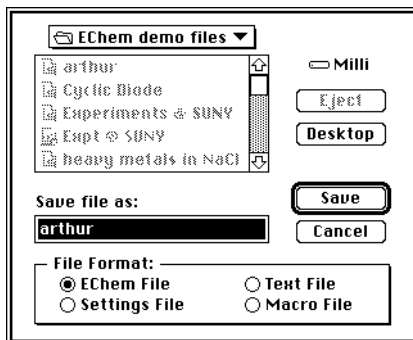
The dialog box allows you to navigate through the file system of the Macintosh to choose where your file will be saved. (You should be familiar with this process; if not, see your *Macintosh User's Guide* for directions.) Once you have typed in a name for the file, you can select a file format by clicking one of the radio buttons in the lower portion of the dialog box, and then save the file by clicking the Save button. You can save multiple copies of a file in any format or formats, provided that the copies have different names or are in different folders.

Data File

In this format, which is the default, both data and settings (including macros) are saved. The file chronicles the entire recording, and is the usual way you would want to save data. EChem can open only one file at a time. Opening a data file will close an already opened file.

Echem Data File

Settings File

This format does not save any recorded data, only the settings. Settings include the technique, current range, and those that affect the way the data looks, such as the window size, display settings, and menu configuration. Macros are also stored as settings. Using settings files, you can build up a library of settings for many different experiments, to enable quick and easy preparation for recording.

EChem Settings

Settings files have a different icon from other EChem files. Double-clicking on a settings file icon from the Finder will automatically load the settings from that file into a new untitled EChem file. Opening a settings file using the Open directory dialog box with the Load Settings checkbox selected loads the settings into the current file.
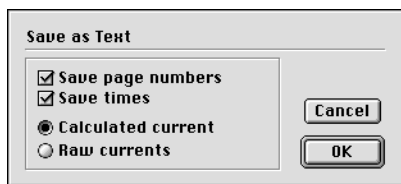
Text File

This format saves data as a standard text file able to be opened by any application that can import text, such as a word processor, spread-sheet, or statistics package. Each data point is stored as a row of numbers comprising the page number, time (t, in seconds), potential (E, in volts) and current (I, in amperes) values, in that order, separated by tabs.

Text File

Figure 5–9
The Save as Text dialog box

Save as Text

☑ Save page numbers
☑ Save times
◉ Calculated current
○ Raw currents

Cancel

OK

Before the a text file is saved, you will be presented with the Save as Text dialog box (Figure 5–9). The save page numbers checkbox allows you to omit or include the page number and time data from the file. Additionally you can save the calculated current (i.e. the currents as they are displayed) or the raw current data. There may be up to four current sampling periods, i1, i2, i3, and i4 for each displayed data point. Differential methods (for example differential pulse voltammetry) require two of these sampling periods but normally only display the difference (for example i1 -i2). Usually you want to save the data as it is displayed but by selecting 'Raw currents' you can save the actual data collected separately for the i1 and i2 periods. See Chapter 7 for more details about sampling periods.

Thus at most one row of the text file could have seven items: page number, time, potential, i1, i2, i3, and i4. For simple regraphing of a voltammogram using a spreadsheet, however, you only require three items: page number, potential and calculated current. If you only want to regraph a few voltammograms from a file then it will probably be easier to use the Copy Special command in the Edit menu and to paste the data directly into the spreadsheet or graphing program.

The size of a text file is typically much greater than the size of the EChem data file it is created from, and saving the data of a file as text can be relatively slow. While a file is being saved as text, the percentage of the file currently saved is displayed. To stop the creation of a text file, type Command–period (or Control–period).

The EChem 'Data File' format actually contains much more information (names of the techniques used, date and time of experiment, user annotations, range settings etc.) and all in a much more compact format than a text file, so you should always keep the original data as an EChem 'Data File' and only ever use a text file to transfer data to another application. You can always regenerate a text file from an original EChem 'Data File' if required.

Macro File

This format saves any macros currently in memory as a separate file, which can be opened by EChem as required. It is useful to save particular groups of macros together.

Macro files have a different icon from other EChem files. Double-clicking on a macro file icon from the Finder will automatically load the macros from that file into a new untitled EChem file. Opening a macro file using the Open directory dialog box (whether or not the Load Settings checkbox is on) loads the macro into the current file.

Appending Files

This feature allows any EChem data file to be appended to the end of an already open file in order to produce a single file with the desired contents. By combining this feature with EChem's ability to cut and paste pages of data in a file or between files, summary files can be created using only those segments of recordings that have significance. Appending a file is an option provided in the Open directory dialog box: choose Open… from the File menu. (If you have made changes to your file since last you saved, you will be asked if you want to save them.) The Open directory dialog box appears (Figure 5–10) and by default only EChem files are shown in the scrolling list. You can navigate through your hard disk using the Macintosh hierarchical file system to find the file you want.

Click the Append to Current File checkbox to turn it on. Note that the Load Settings checkbox becomes dimmed and unusable, since the appended file takes on the settings currently in memory. This may result in some scale changes, but the raw data will not be altered. Select the EChem file you wish to append to the currently open file, and click the Open button to perform the operation. The pages will be added on to the end of the current file.

Text Files

EChem can open text files, or append them to already open files. To do this, choose Open… from the File menu. The Open directory dialog box appears (Figure 5–10) — click the Text Files radio button

Figure 5–10
The Open dialog box with the
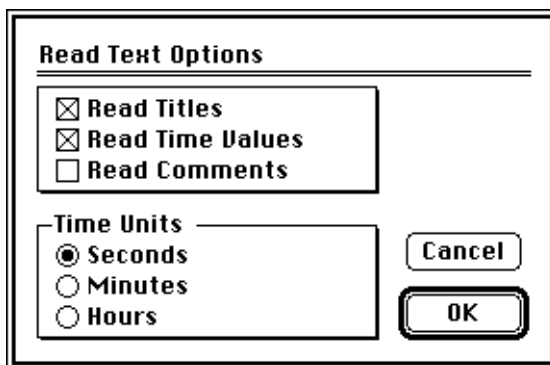Append option selected
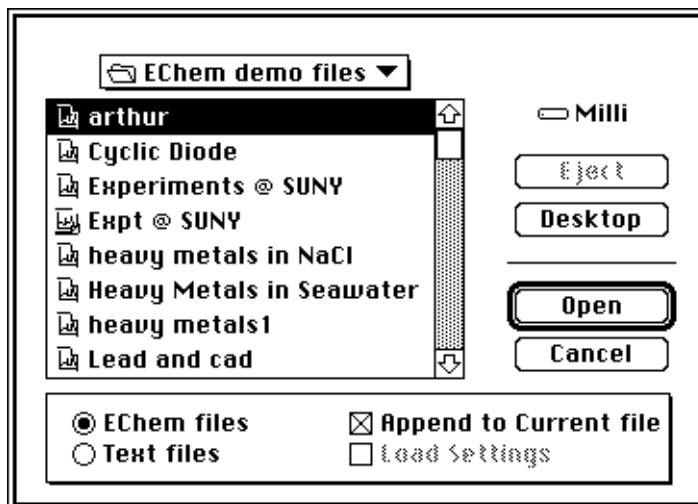
so that only text files will appear in the scrolling list. The Load Settings checkbox becomes dimmed and unusable, since text files cannot contain settings data. The text file must can have several different formats and the items in each row must be separated by tabs, commas, or semicolons. Typical formats are:

- potential (E, in volts) in column 1, and current (I, in amperes) in columns 2.

- current (I, in amperes) in column 1, and potential (E, in volts) in columns 2.

- time (t, in seconds) in column 1, potential (E, in volts) in column 2, and current (I, in amperes) in columns 3, 4, 5, and 6 (these will be read as current sampling periods i1, i2, i3, and i4). Columns 4, 5, and 6 are optional.

You can navigate through your hard disk using the Macintosh or Windows file system to find the file you want. After a text file has been selected in the Open directory dialog box and the OK button has been clicked, the Read Text Options dialog box appears (Figure 5–11).

Read Time Values. If this checkbox is on, EChem reads in the first column of numbers as time values. EChem expects a constant difference between time values: a discontinuity is treated as the start of a new page of data. The minimum selection in EChem is four data

Figure 5–11
The Read Text Options
dialog box

Read Text Options

☒ **Read Titles**
☒ **Read Time Values**
☐ **Read Comments**

Time Units
◉ Seconds
○ Minutes
○ Hours

[Cancel]
[OK]

points: thus any times read in must have at least three consecutive intervals the same to create a new EChem page of data. If times are not read in, then the EChem Time axis will have no units.

The Time Units radio buttons allow you to specify the time units of the time values.

EChem first scans the file to see if it is in order. If there is a problem, such as erratic time values or text where it expected numbers, it alerts you and does not load the file. It also allows you to

Pasting in Text

Copied text from data files (such as Scope software) of other software can be pasted into EChem directly. The text copied to the clipboard must be in a correct format.

Printing

Printing an EChem file or parts of it will give you a hard copy of your data for use in reports and presentations. There are two menu commands in the File menu concerned with printing: Page Setup… and the basic Print… command (with a keyboard equivalent of Command-P, or Control-P), which may change depending on what can be printed at the time.

Page Setup

The Page Setup dialog box that appears when you select the Page Setup… command will depend on your chosen printer (and system software). A typical Page Setup dialog is shown in Figure 5–12. The user's guide that came with your printer will explain most of what is involved. Choose the paper size that you will be using, page orientation, and so on.

Figure 5–12
A Page Setup dialog box for an Apple LaserWriter 12/640 on Macintosh (upper) and on a Windows PC (lower). Other printers will exhibit different options.
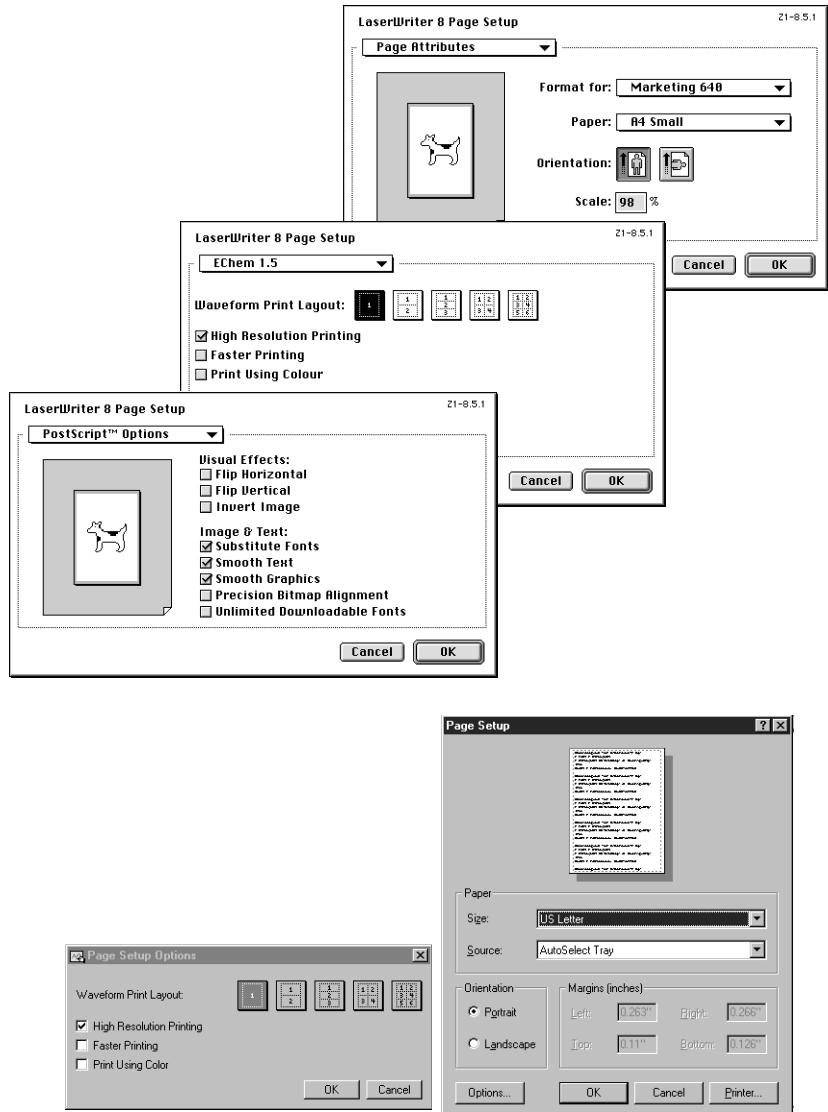
Waveform Print Layout

Click the appropriate Waveform Print Layout buttons to print one, two, three, four, or six EChem pages per printed sheet of paper. By default, the leftmost button is selected, and one EChem page appears on a printed sheet. The page range specified when printing refers to EChem pages, not pieces of paper produced: printing six pages would, if the rightmost Waveform Print Layout button were selected, produce one printed sheet with the six data pages on it.

On a Macintosh this feature will work in conjunction with the Layout option in the LaserWriter 8 Print dialog box, which gives you the choice of one, two, or four, eight or sixteen pages per sheet of paper, so that you could print up to 48 EChem pages per sheet — but this would results in tiny graphs!

High-Resolution Printing

Note

For the best possible printing, ensure that you are using the latest version printer driver for your particular printer. Many manufacturers allow you to download the latest printer drivers from their web sites.

Some printers support several modes of resolution. Checking this option allows you to print the EChem or Zoom windows at the maximum resolution of the printer. For example, if you are using a 600 dpi laser printer, EChem will print with a resolution of 600 dots per inch. This will result in output of the best possible quality, but, since every data point and connecting line is drawn at full resolution, printing may be slow.

Without high-resolution printing, the accuracy of positioning items (data points, axis tick marks and labels, etc.) is not as accurate on the printed page. This may still be adequate for drafts and overviews, and will result in quicker printing.

Faster Printing

If Faster Printing is not selected, EChem passes the recorded data to the printer driver, which generates a set of instructions which are passed to the printer. If there are many data points in the file, the printer driver software has to work harder at converting the data points into the printer instructions, which will take more time.

When Faster Printing is selected, EChem attempts to speed up printing by creating a bitmapped image of the data to be printed.

Since the file itself, the chosen resolution, the printer, and the type of computer all have a bearing on the speed of the process, this will not always result in faster printing. Try a few pages with your setup to establish relative speeds using this method and printing normally.

When faster printing and high-resolution printing are both selected, EChem determines the resolution of the printer and generates a bitmap at that resolution (if the printer resolution cannot be determined EChem just generates a low resolution bitmap). This rasterised image is then transferred to the printer directly rather than having to be converted to PostScript, or other printer instructions. The time saving can be quite significant on files with large numbers of data points, with little or no loss in resolution, but it is possible that it could take longer with some systems. On Macintosh computers EChem must be given enough memory to image the data at high resolution. An alert box will warn you if memory is insufficient.

Print Using Color

Checking this option enables color printing of your data. You can set the data display colors using the Display Settings dialog box (and similar dialog boxes). Some colors may not be supported by certain color printers, or the colors actually printed may differ from those that appear on a color monitor. Try a few samples with your equipment to establish color compatibility.

The Print Command

If the Page Comment or Clipboard windows are active, the Print command is dimmed and cannot be chosen. In other circumstances the command will be enabled and will appear slightly differently depending on which window is active (Table 5–1).

Table 5–1
The results of the various print commands

| Print Command	Active (Top) Window	What Prints
Print…	Main	Page range or current page
Print…	Zoom	Zoom window contents
Print Data Pad...	Data Pad	Data Pad contents
Print Notebook…	Notebook	Notebook contents

When a Print… command is chosen, the Print dialog box for your printer appears. EChem provides special options: the Print Current Page Only and Print Sweep Description checkboxes.When the Print Current Page Only checkbox is on, the active page prints regardless of the specified page range. To print a range of pages, turn off the checkbox and enter the page numbers as usual. When the Print Sweep Description checkbox is on, the parameters displayed in the Technique Description panel (Figure 2–3) are also printed underneath each graph.

Figure 5–13

A Print dialog box for an Apple LaserWriter 12/640 on Macintosh (upper) and on a Windows PC (lower). Other printers will exhibit different options.
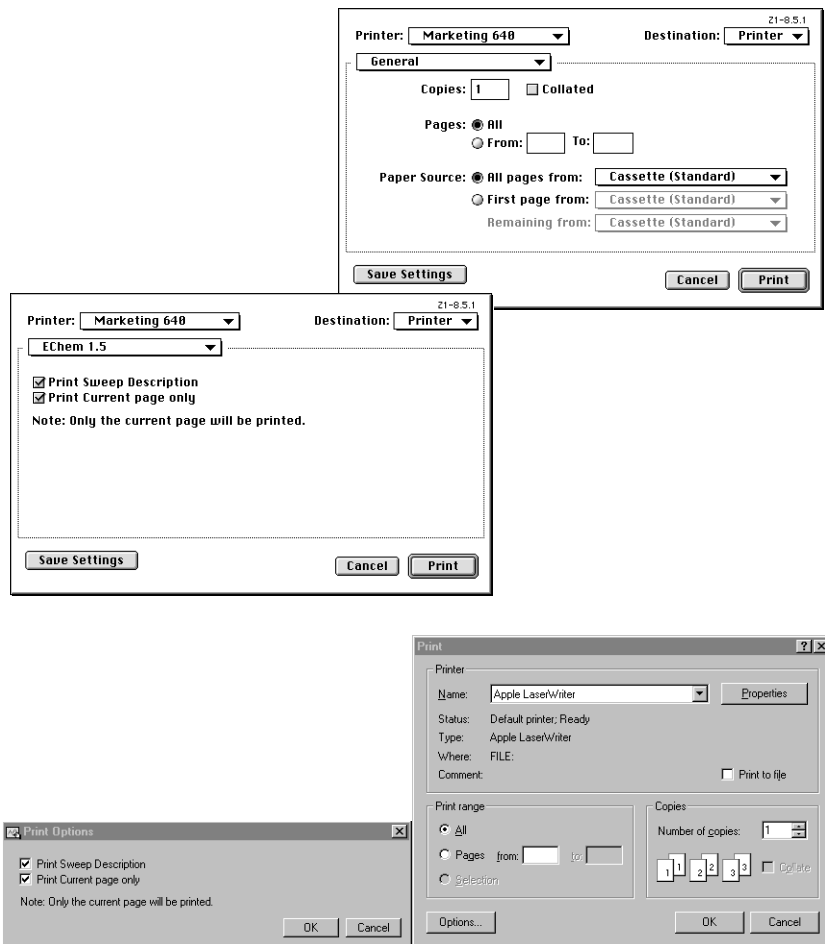
When printing the contents of the EChem or Zoom windows, the Page Layout dialog box pops up after you click OK in the Print dialog box. This dialog box lets you adjust the size, location, and proportions of the image. Drag the image to reposition it on the page (the gray border shows where it will go), and drag the gray box at the bottom right of the image to adjust its size.

Drag the image to where you want it on the page

Turn off this checkbox to reshape the image

Drag the gray box to resize the image

You can also double-click the image to scale it to the maximum size that will fit on the page. If the Keep Shape checkbox is checked, then the image is scaled in proportion to its original dimensions (which depend on the window settings), otherwise it can be reshaped at will. If, however, you are printing multiple EChem pages on a page (using the Waveform Print Layout controls in the Page Setup dialog box), you will see a number of rectangles in the page area rather than the image of one page, and the Keep Shape checkbox will not appear.

The file title, page number, and any page comments are included in the printed EChem page. Long comments mean the area used for the drawing is reduced; very long comments will be truncated.

The Notebook is printed out looking much like it does on screen, but empty columns are not included in the hard copy.

On a Macintosh printed text will appear in the Geneva font, unless you have a PostScript LaserWriter and check Font Substitution in its Page Setup dialog box, in which case Helvetica will be used. If you are using the TrueType Geneva font in your Mac OS, the text will be printed at the maximum resolution of the printer on any printer. Faster printing always produces a bitmap with no substitution of fonts taking place.

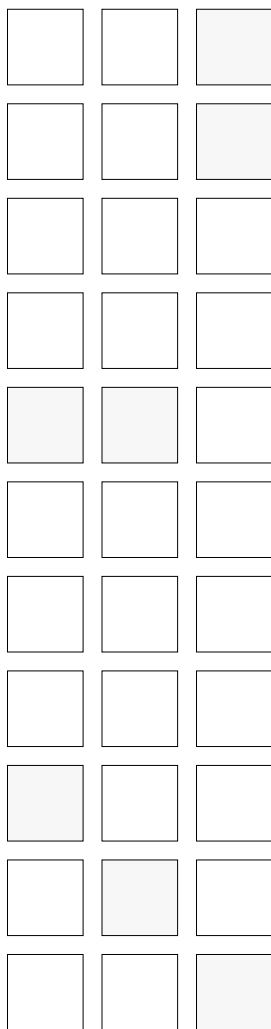On a Windows PC a default font will be used.

While the file is printing (or being spooled, if you are printing in the background) a small dialog box appears. Click its Cancel button to stop printing (or type Command-period, or Control-Period, or press the Return, Enter, or Esc keys).

EChem User's Guide

C H A P T E R   S I X

6

Customizing & Automating EChem

You can to customise and to automate functions within EChem, greatly increasing its convenience and ease of use. It can be simplified or modified by:

- locking or hiding menus or commands with the Menu Editor

- altering controls, menus, and menu commands, and moving control panels then store your changes as a Settings File or as the Default Startup.

- storing techniques with preconfigured parameters (initial and final potentials, scan rates, pulse heights etc.) as Settings Files.

- automate complex tasks by creating multi-step Macro commands which can be stored as new commends in new or existing menus.

This chapter looks in detail at these various ways of altering EChem to suit your experimental requirements.

Preferences

The options in the display settings and recording controls allow basic customizing of EChem. You can also choose to lock, hide, or alter controls, menus, and menu commands (and their keyboard equivalents). This can be particularly useful in simplifying EChem for teaching purposes.

The Preferences submenu in the Edit menu contains four menu commands: Options; Menus; Controls; and Start-Up. These allow you to alter various aspects of EChem performance and display.

Menus

The six EChem menus (File, Edit, Technique, Display, Windows, Macro: see Appendix A–1) and their commands can be modified from the default settings by using the Menus dialog box (Figure 6–1), which appears on selecting the Menus… submenu command. You can hide or lock any menu or menu command to create a very simple EChem setup, limiting the actions that can be performed. This is particularly useful when you want inexperienced students or technicians to be able to use some features of EChem, but not to edit, delete, or change the data in files.
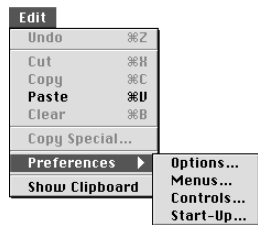
Figure 6–1
The Menus dialog box
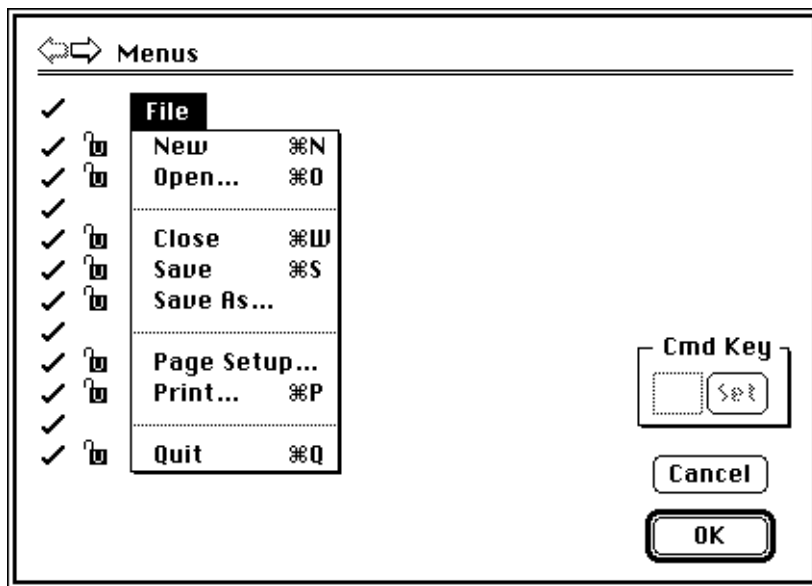
The dialog box will initially display the File menu. To move to the dialog boxes of adjacent menus, click the arrows by the dialog box title, or press the right or left arrow keys on the keyboard. Click the OK button to apply any changes you have made.

Menus that are too long to fit entirely within the dialog box will have a downwards pointing arrow at their base: click it (or press the down arrow key on the keyboard) to move through the menu; click the arrow that appears at the top of the menu (or press the up arrow key) if you need to move up again. By default, the menu title and all items within the menu will have a tick to their left, and all menu commands will have an open padlock beside them, indicating that everything is visible and unlocked.

Clicking the tick beside the menu title will hide the menu (a cross appears): it will not appear in the menu bar when you return to the EChem window. Clicking the tick beside a menu command or a dividing line will hide it: it will not appear in the menu, and neither will any Command-key equivalent work. Clicking a cross will change it to a tick, and show the previously hidden item beside it.

✔ Show
✗ Hide
🔓 Unlocked
🔒 Locked

Clicking an open padlock changes it to a closed padlock, and locks the menu command beside it. The command will still appear in the menu, but it will be dimmed and cannot be activated (if there is a Command-key then this will also be inactivated). Clicking a closed padlock changes it to an open padlock, and unlocks the previously locked menu command beside it.

Command-Key Equivalents

Some menu commands have Command-key equivalents. The equivalent key appears selected in the text entry box, and you can either change it, or delete it so that no Command-key equivalent is available.
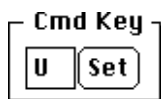
Cmd Key
U Set

Command-key equivalents for menu commands can also be added or changed. Click a menu command to select it: the Cmd Key area of the dialog box becomes active. Type a single lower-case letter (a, b, c, ...) or number (1, 2, 3, ...) in the text entry box (letters are automatically capitalized; invalid characters will be rejected) and click the Set button to assign a keyboard equivalent. If you choose a character in

use elsewhere, an alert box will warn you. If you choose the character anyway, your choice overrides the previous assignment.

Controls

On selecting the Controls… submenu command, the Control Options dialog box appears, Figure 6–1. It lets you modify the display of the various EChem Control Panels, Figure 2–3. By default, all items will have a tick to their left, and the icons show the tall window to the left in front of the panel to the right, indicating that everything is visible and that panels will appear behind the Main window in case of overlap. You can hide any EChem panel to create a very simple EChem setup, if you want to limit the actions that can be performed.

Figure 6–2
The Control Options dialog
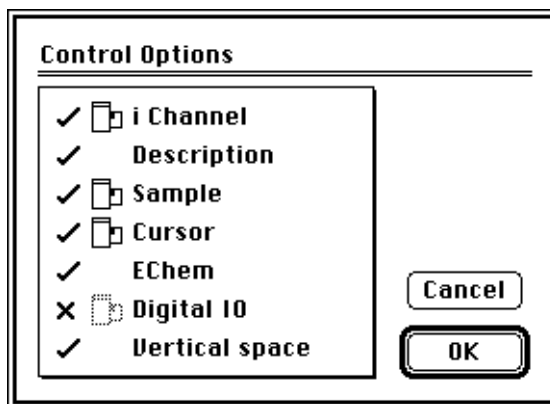
Clicking a tick will change it to a cross, and deactivate the panel: it will not be visible when you return to the EChem window. Clicking a cross will change it to a tick, and return the previously hidden item to view.
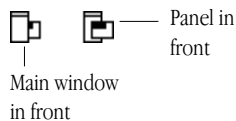
The icons show two overlapping rectangles. By default, the tall left rectangle is in front (the panel to appear behind the main EChem window in case of overlap). Click the icon, to make the short right rectangle appear in front, if you want the panel to appear on top of the EChem window. Click it again to revert to the default setting.

Panel in front

Main window in front

You can also change the overlap order can be by Option-clicking the tile of a panel in the main EChem window.

The vertical space (the blank space above the sample panel), and EChem title can also be hidden.

Moving Control Panels

The panels represented in the Control Options dialog box can all be moved around your Macintosh screen if you want to alter the default arrangement. When you hold the Shift key down you can drag a panel by its title to move it. The pointer changes to an arrow-headed cross, and as you drag, a gray outline indicates where the panel will go.

The vertical space and description panels can be Shift-dragged from any point in them.

Options

The EChem Options dialog box, Figure 6–3, is opened by the Preferences/Options command in the Edit menu.
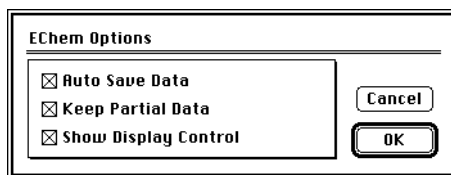
The Auto Save Data checkbox will cause the EChem file to be saved immediately after every sweep. It is on by default. You may wish to turn it off if you want to do a succession of sweeps with the minimum delay period between each sweep, or if you have set up a series of macro commands and want to also set up the Save command from within a macro.
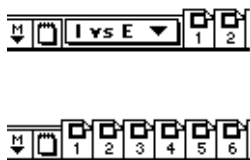
The Keep Partial Data checkbox is also on by default. It will keep a partially completed voltammogram if you prematurely halt scanning by clicking the Stop button in the main display before an experiment has finished.

The Show Display Control checkbox allows you to show or hide the Display pop-up menu, Figure 6–4. So that the user can no longer alter the display (I vs. E, IE vs. t t, etc.)

Start-Up

When EChem first starts up, it will use its factory default settings, taking the whole screen for its display, with the current range on the lowest sensitivity, and so on. You can alter these defaults so that EChem will always start with your preferred settings.

Settings are of two sorts: those that affect recording, such as the technique and channel ranges; and those that affect the way the data looks, such as the window size, channel areas, display settings, and menu configuration. To save or clear customized settings, select the Start-Up… submenu command: the Start-Up Settings dialog box appears (Figure 6–5).

Figure 6–5
The Start-Up settings dialog
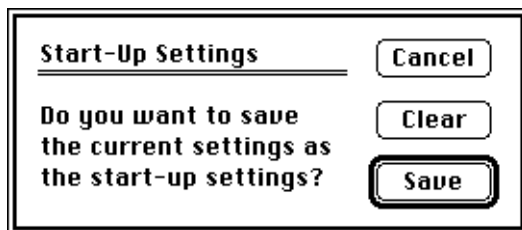
Clicking the OK button will save all current settings in the EChem Settings file in the Preference folder in the System folder so that they are used each time you start up EChem. Clicking the Clear button will clear any settings currently stored in the EChem Startup file.

Emergency Access!

Note
If you have created start-up settings but want start up EChem with its factory default settings, on a one-time basis, hold down the Command key as you open it (straight after double-clicking the icon). Release the key when the alert box appears, and click the OK button.

Because it is possible to change menu preferences so that vital menu commands are locked or menus themselves hidden, it is necessary to be able to have a way to get them back. Emergency access to dialog boxes is available through the Show Dialog Box dialog box (Figure 6–6), which appears on typing Command-\ (backslash).

Clicking the Menu Editor… button will bring up the Menus dialog box (Figure 6–1), allowing you to show hidden menus, and to unlock menu commands.

Figure 6–6
The Emergency Access
dialog box

Show Dialog:

[Menu Editor...]   [Cancel]
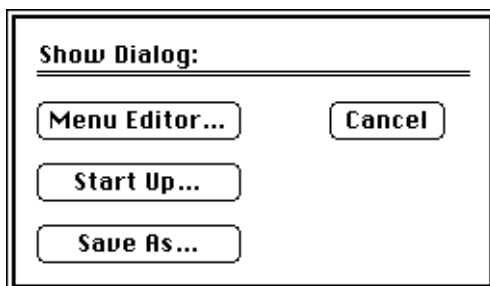
[Start Up...]

[Save As...]

Clicking the Start Up… button will bring up the Start-Up Settings dialog box (Figure 6–5), allowing you to save the current settings in the file (including menu layouts and so on) as those EChem will use when it starts up.

Clicking the Save As… button will bring up the Save As dialog box (Figure 5–8), which allows you the complete range of options in saving a EChem file. This is useful to save the file as a Settings file with the hidden or locked menu items remaining as specified when the file is saved.

Macros

Macros are used to group sets of commands together conveniently, enabling you to speed up repetitive and tedious tasks, such as changing the settings for various parts of an experiment, and to automate recording and analysis. They record the results of your actions step by step, then reproduce them when played back. If you find yourself regularly doing the same series of operations in EChem macros can automate things considerably.

Macros can record any EChem operation: setting dialog box and window controls; changing the display format; saving data as a new file; printing the Zoom window; and so on. There are some differences involved in recorded and real operations, but in general, dialog boxes will guide you through your options.

It is important to understand how macros work: they record the results of your actions, not individual keystrokes and mouse clicks, and record the simplest possible interpretation of those actions. Even if you spend some time fiddling with control settings during the recording of a macro, only the final settings you obtain will be used. Macros are not able to be edited.
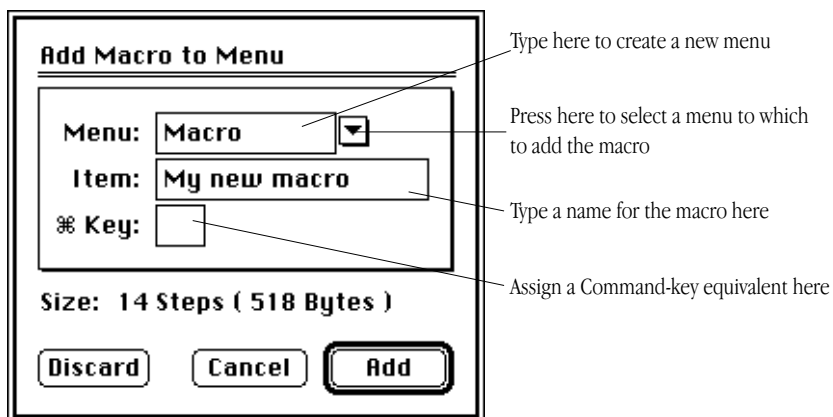
You should keep a written record, in a notebook, HyperCard stack, or whatever you find most convenient, of the steps involved in your macros, and their purpose: it is easy to forget which macro does what when you haven't used them for a few weeks. Noting the steps down before actually recording will help when constructing complex macros, since it can prove easy to miss out a step or end a repeated sequence in the wrong place, with detrimental effects.

Macros are saved as part of a normal data file, or can be saved as a separate file on their own. In either case, any macros currently in memory are saved to the file. They are loaded into memory whenever data or settings from the file that contains them are loaded, effectively adding to the EChem application (this is one reason why they are stored in as compact a way as possible). Hence if you load three files in succession, with a different macro in each, then all three macros will be available until you quit and restart EChem, or delete the macros. When a file is saved, all currently available macros are saved with it, becoming part of the file.

Macro Hint

Macros cannot be edited but they can activate other macros. It is usually better to write several small macros and to use a master macro to call each of them in turn. If you make a mistake then you will only have to rewrite the macro the error is in.

Recording a Macro

To record a macro, choose Start Recording from the Macro menu, or type Command-R (the menu command then changes to Stop Recording…). During the process, a small indicator changes in the display panel, and the message 'Recording…' is displayed to remind you that your actions are being recorded, not effected. Perform each action to be recorded, then choose Stop Recording… from the Macro menu, or type Command-R again. Once you stop recording, the Add Macro to Menu dialog box appears (Figure 6–7). When a macro is being recorded, for the most part EChem remembers rather than executes operations, but operations such as changing current ranges, for example, are done as you record.

Figure 6–7
The Add Macro to Menu
dialog box

Type here to create a new menu

Press here to select a menu to which to add the macro

Type a name for the macro here

Assign a Command-key equivalent here

The pop-up Menu button allows you to select the menu in which your macro will appear from a list of existing menus. By default, the macro will be added as a new menu command to the Macro menu. You can create a new menu by entering its title in the Menu text entry box: the menu will be added to the right of existing menus in the menu bar. The name of the macro (up to 20 characters) should be entered in the Item text entry box.

An optional Command-key equivalent can be assigned to the macro as well: type a single lower-case letter or number in the text entry box (letters are automatically capitalized and invalid characters will be rejected). If you choose a character already in use, an alert box will warn you of the fact and tell you where it is assigned. If you choose this character anyway, your choice overrides the previous assignment

and the Command-key equivalent will only work for (and appear beside) the menu command that you have just created.

The Size indicator tells you the number of steps recorded (useful if you can't remember which step you are up to in the middle of a complex macro), and the memory taken by the macro, so far. The amount of memory used depends on the complexity of the procedure. Click the Discard button to discard the macro you have just recorded. Click the Cancel button to continue recording more steps in the macro. Click the Add button to add the macro to the bottom of the selected menu; the Add button is only active and undimmed when the macro is named and a menu is chosen.

Until you save the file, the macro exists only in memory and is not permanently stored. If you open another file and save that, the macro (and all other currently available macros) will become part of the new file. When you quit EChem, you will not be asked to save changes if you have created new or altered existing macros. So it is a good idea to save the file each time you create a macro (or save it as various macro files).

Playing a Macro

Once assigned a name and location, macros act much as if they were menu commands. Select them from their menu or type their Command-key equivalent to use them. While a macro plays, the title of the menu in which it resides is highlighted, and no other functions can be performed within EChem, nor can one switch to another application and leave EChem in the background. To stop a macro playing, hold down the Command key and press Period (.). The macro will stop at its current step.

Deleting a Macro

To delete existing macros, choose the Delete Macro menu command in the Macro menu which brings up the Delete Macro dialog box (Figure 6–8).

A scrolling list displays the name of the menu that the macro is in, a colon, and the name of the macro, for all available macros. To delete a macro, select it and click the Delete button. To delete multiple macros,

Figure 6–8
The Delete Macro dialog box

Delete Macro

File: Periodic Save
File: Transfer Page Data
Macro: Click Whirr Fertangg
Macro: Percent
Protocols: Experiment TTK4
Protocols: Experiment TTN 2
Tests: Motor Nerve Stimulus

[Cancel] [**Delete**]
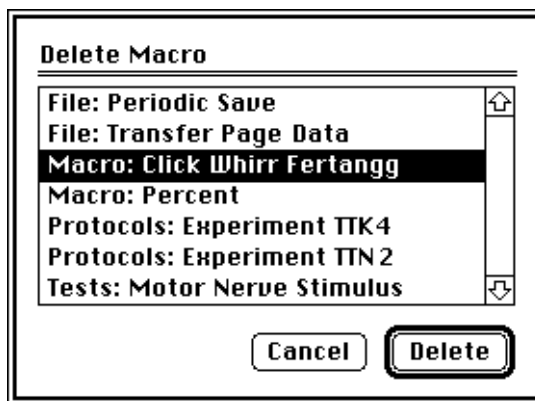
Shift-click or Shift-drag to select contiguous macros, or Command-click (or Control-click) to select or deselect multiple macros individually. The dialog box will close and the macro or macros will be gone. As a shortcut, double-click a macro to delete it and close the dialog box in one step.

As was mentioned, when a file is saved, all currently available macros are saved with it. When you delete a macro, you delete it from memory. If the macro is part of the current file, it is permanently deleted from that file only when the file is saved. Copies of the same macro that are part of other files will not be deleted.

Macros That Call Other Macros

Once a macro has been created, it can then be used by other macros that you create. When constructing multistep procedures it is usually best to call a series of small macros from a single master macro. Macros can be nested up to ten deep. An alert box will appear during the playing of your macros if the combination of macros becomes too recursive.

If a macro is called by another macro, EChem will warn you if you attempt to delete it. If you delete it without replacing it then, when the deleted macro is called, an alert box will tell you that it cannot be found.

Options When Recording Macros

Operations involving files and dialog boxes can be made to behave in different ways when playing macros, depending on whether you want to do the same thing all the time, allow user modification, and so on.

Changing Dialog Box Settings

Macros can be used to change dialog box settings to the values specified when you record the macro, or to open a dialog box for the user to change settings when the macro is played.

If you want a macro that changes the settings in a dialog box, then select the dialog box as you would normally while recording the macro. Change the settings, and then click OK in the dialog box. (If you click Cancel, the changes made in the dialog box will be ignored.) When playing the macro, the settings are changed without displaying the dialog box.

If you want a macro that opens a dialog box for the user to change settings when the macro is played, hold down the Option key when selecting the command that shows the dialog box while recording the macro, then click the OK button. Do not make any setting changes. When you play back the macro, the dialog box is displayed so that its settings can be changed by the user. Clicking the OK or Cancel buttons in the dialog box will allow the macro to continue, with the user-defined settings or the original settings respectively.

When changing control values in dialog boxes, absolute values are recorded, not relative changes. For example, if you move a scroll bar that increases potential by 50%, from 1V to 1.5 V, the new potential (1.5 V) is recorded, not the change in voltage (+0.5 V) or the percentage change in potential (+50%).

Starting Sampling

Macros can be used to control when sampling starts and stops: you simply click the Start button when recording the macro, and EChem will start sampling at the appropriate point when the macro is played.

Opening Files

A macro can be used to open the same file each time it is played, or to allow the user to choose which file to open. To open a particular file with a macro, choose Open… from the File menu while the macro is being recorded: the Macro Open directory dialog box is displayed (Figure 6–9).

To allow the user to choose which file is to be opened when the macro is played, press the Option key when selecting the Open… command while recording the macro. The Open directory dialog box will be displayed when the macro is played.
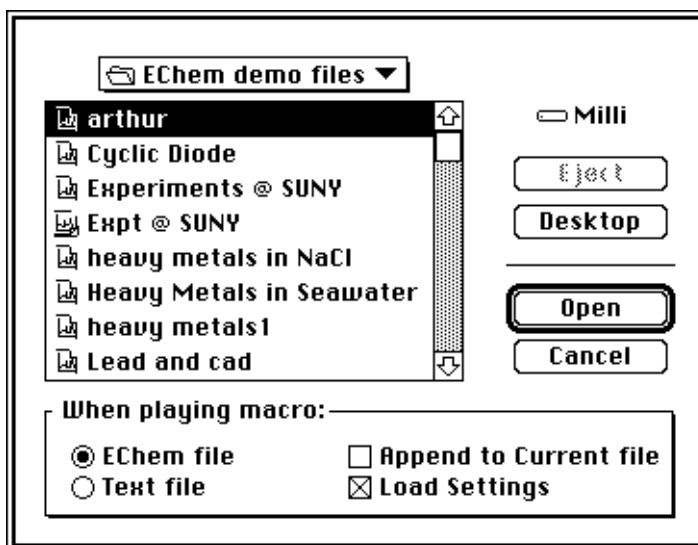
When opening the same file each time, the full hierarchical file name (the 'pathname') of the file, from the disk through any number of folders, is noted. If the file has been moved (or deleted) since the macro was recorded, then EChem searches in the most recently used folder and in the same folder as EChem. If the file is in neither of these locations, an alert box lets you know that EChem cannot find the file, and the Open directory dialog box is displayed to allow you to find it yourself. If you choose a different file at this stage, it will be opened instead and if you click the Cancel button, the macro will abort.

Saving Files

When playing a macro, you can save data in a file or in a series of files. Choosing the plain Save command will save a named file (you might want to do this at specified intervals to minimize data loss in case of possible power loss; just remember that data is not recorded during the time it takes to save a file to disk).

You can specify where and in what form you want the data to be saved by using the Save As… command when recording the macro. The Macro Save As directory dialog box will appear (Figure 6–10).
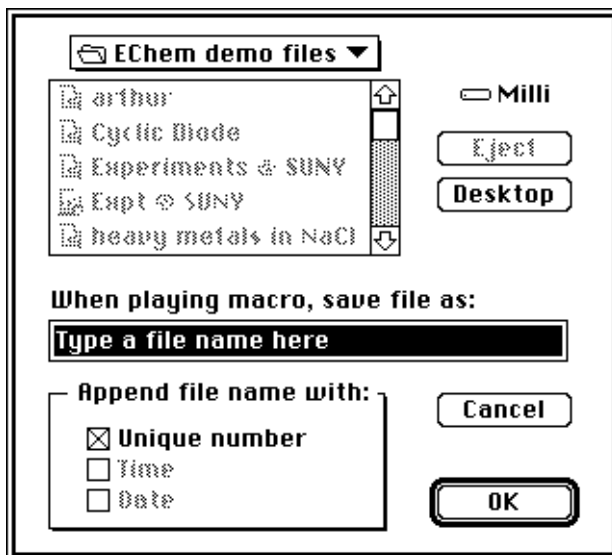
Three checkboxes in the 'Append file name with' section of the directory dialog box allow you to specify unique file names. If no checkboxes are selected, then each time you play the macro, the file will be overwritten, just as it is when saved normally.

If the Unique number checkbox is selected, a different number is added to the end of the given file name each time the file is saved during the playing of the macro. Numbers are added in numerical sequence starting with '1'. For example, if the file name is CoolData, then the next files generated will be CoolData1 and CoolData2.

Selecting the Time checkbox appends the current time to the file name. Selecting the Date checkbox appends the current date to the file name. Both time and date are appended if both boxes are checked. These checkboxes are dimmed and unavailable if the Unique number checkbox is selected.

Macro Commands

Control structures for macros are provided in the Macro Commands submenu in the Macro menu (see Appendix A–1). The macro commands are only available while recording a macro. They allow you to provide user feedback in the form of dialog boxes or sounds, set up repeat sequences, and so on.

Menu:
```
✓Update Screen

Wait...
Play Sound...
Message...
Speak Message...
AppleScript...

Repeat for Each Page
Begin Repeat...
End Repeat
```
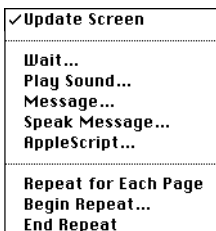
Update Screen

Normally, when a macro is played, the screen is updated after each macro step (a tick beside the Update Screen menu command indicates that it is active). Choosing the command from the menu as the first step in a macro causes the macro to play without redrawing the screen each time the data display is altered in some way (the tick disappears). Update Screen can be turned off or on at any stage of a macro (the settings toggle). If Update Screen is off, the screen will be redrawn only when the macro is finished, or it is turned on again.

This may considerably speed up some macros, for example, those involving multiple changes to view and display settings: in this case, the data on screen will still be seen to be selected, but data off screen will not be scrolled through before selection, as would occur if Update Screen were off. Since you cannot edit macros, you cannot change the Update Screen settings once the macro is finalized. You can, however, record another macro that consists of two steps: turning update screen off, then calling the original macro.

Wait…

Selecting the Wait… macro command brings up the Wait dialog box (Figure 6–11). A pop-up menu lets you select from Wait For, Wait Until, and Wait Until the Next, to wait for a set length of time (say, 55 seconds), wait until a certain time (say, 11:20 a.m.), or wait until the next time division (say, at the next hour) before the macro continues.

Figure 6–11
The Macro Wait dialog box,
with the three options
selected
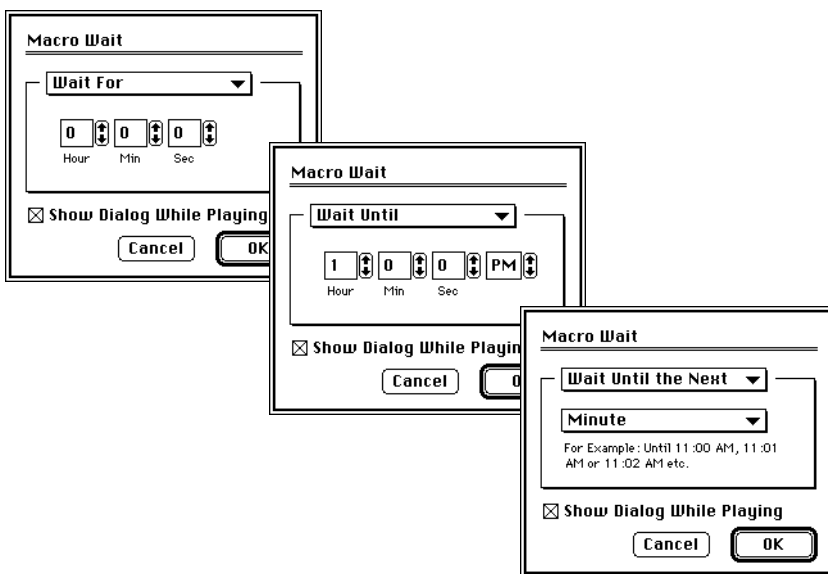
The checkbox allows you to choose whether a dialog box with a
progress bar appears during the wait (Figure 6–12). The dialog box
gives a visual indication of wait progress, and gives you the options
of proceeding immediately to the next step of the macro by clicking
the Skip the Wait button, or aborting the macro by clicking the Stop
Macro button (equivalent to typing Command-period).

Figure 6–12
The Macro Wait dialog box
during the playing of the Wait
step of a macro
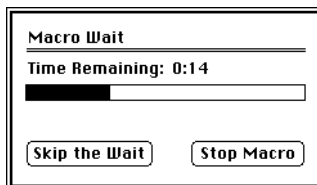
This feature is useful if you want to perform some steps of an
experiment at certain intervals, or to record multiple samples with a
specific interval between samples.

Play Sound…

Selecting the Play Sound… macro command brings up the Macro
Play Sound dialog box (Figure 6–12), which allows you to select from
the range of sounds in your Macintosh System to set audible alerts in
macros.

Figure 6–13
The Macro Play Sound dialog box

```
Macro Play Sound
┌──────────────────────────────┐
│ Simple Beep                  ⇧│
│ Quack                         │
│ Droplet                       │
│ Indigo                        │
│ Wild Eep                      │
│ Sosumi                        │
│                              ⇩│
└──────────────────────────────┘

( Play )        ( Cancel )  (( OK ))
```

Click the name of a sound in the scrolling list to select it. If you wish to hear the selected sound, click the Play button. To have it actually played in the macro, click the OK button. To choose more than one sound option, Shift-click or Shift-drag to select contiguous sounds in the list, or Command-click to select or deselect multiple sounds individually. Sounds appear in the list in the order they were installed in the system, and are played back in that order. To save time in creating multiple sounds, you can create a library of sound combination macros, and simply incorporate one or more of them in the macro that needs them.

You might wish to have three beeps signal when EChem starts recording data, or a bell and a whistle at the end of a scan. You can even record short verbal cues using the Sound control panel (if your Macintosh has a microphone input) and use these in your macros.

If a macro attempts to play a sound not in the System file (created on a computer with a different setup, or since removed from the System), then an ordinary system beep will be substituted for the sound originally specified.

Message…

If you select the Message… macro command, the Macro Message dialog box appears (Figure 6–12). This allows you to cause alert boxes requiring user response to appear at certain stages within the macro.

Figure 6–14
The Macro Message dialog
box
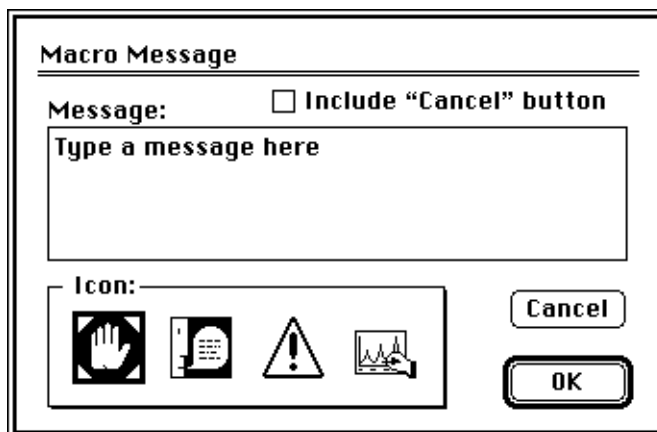
You can type in the message of your choice (up to 255 characters). The dialog box produced will have an OK button, and if the checkbox at the top is highlighted, a 'Cancel' button as well (for exiting the macro).

There are four choices of icon: the default shape (a hand) is highlighted with a heavy border. Click one of the icon buttons to choose it. You can use the icons to indicate the urgency of an important message (hand, exclamation mark, and face, in order of decreasing urgency), and the EChem icon for general messages which indicate EChem's state. Click the OK button when you have chosen an icon and typed in the message.

Speak Message…

Note
The Speak Message
command is only available
on Macintosh systems.

If you select the Speak Message… macro command, the Speak Message dialog box appears (Figure 6–15). Using it, you can give spoken messages in macros, if your Macintosh has speech abilities. Type in the phonetic equivalents to allow non-English words to be spoken. After the message is spoken, the macro carries out subsequent steps.

You can type in the message of your choice (up to 255 characters). If the Macintosh on which the macro plays has no speech abilities then, if the checkbox is off, a standard system beep will be used in place of the spoken message. If the checkbox is on, an alert box appears, just as if the Macro message dialog box were used: this will stop the macro until its OK button is clicked.

The volume at which the message is spoken can either be the default system volume set in the Sound control panel, or can be set independently to any of the sound levels, from 1 to 7, available in the Sound control panel, by clicking or pressing the arrow controls.

Begin Repeat

The Begin Repeat macro command brings up the Begin Repeat dialog box (Figure 6–16). This is used to repeat groups of steps in a macro. You may repeat any group of commands up to 100,000 times. This could be used, for example, to set up sampling at staggered intervals overnight. For each Begin Repeat you should specify an End Repeat. If you do not specify enough End Repeats, they are automatically added when you select Stop Recording…, but if you have a complex macro, the repeated sequences might not end up in the right places. Writing down the macro before recording it will help avoid such problems.

Repeat for Each Page

This macro command allows you to perform some operation on each overlaid page of data in turn in the EChem file. The blank (last) page, and pages not in the overlay, will be ignored.

When this macro command plays, it will go through the EChem file and display each page it operates upon, which may take a while: turn off the Update Screen command to avoid this. As with the Begin Repeat macro command, you should specify an End Repeat after the instructions you want performed in the repeated sequence.

End Repeat

Each Begin Repeat or Repeat for Each Page macro you specify should be paired with an End Repeat. If you do not specify enough End Repeats, they are automatically added when you select Stop Recording…, but if you have a complex macro, the repeated sequences might not end up in the right places. Writing down the macro before recording it will help avoid such problems.

AppleScript…

This macro command allows you to insert an AppleScript as a macro step. AppleScript is a scripting language for automating tasks, and controlling applications and their interactions through Apple events. To use it, you must have AppleScript installed on your Macintosh. On selecting the AppleScript… macro command, the AppleScript from Macro dialog box appears. You will also need to be familiar with using AppleScript.

For more information read the AppleScript section of your *Scope User's Guide*. The EChem software has similar capability.

7
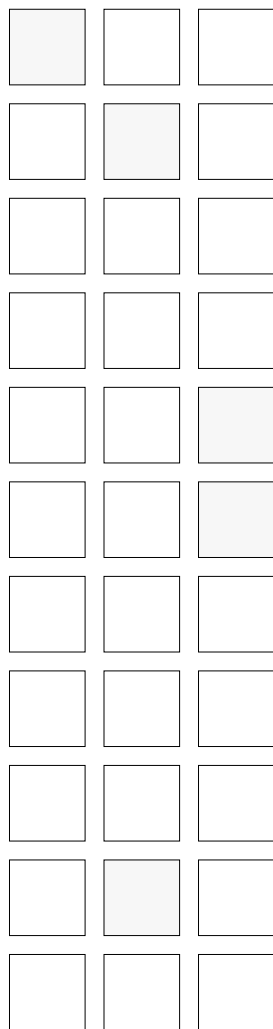
EChem Techniques

This chapter describes each of the items in the EChem Techniques menu and the experiments that can be performed. Unnecessary Techniques can be deleted from the menu by use of the Menu Editor (discussed in Chapter 6).

Commonly performed experiments can be quickly configured with the technique and exact parameters (scan rate, upper and lower potential limits, pulse duration etc.) by the use of Settings Files or Macros (Chapter 6).

In addition, other electrochemical experiments can be performed with the Chart and Scope software, and these techniques are discussed in Chapter 8. Chapter 8 also describes the use of EChem for AC voltammetry and AC cyclic voltammetry.

Introduction

*The EChem Technique
menu*

EChem software supports a variety of voltammetric and amperometric techniques:

Standard techniques
- Linear sweep voltammetry
  - potentiodynamic polarization
  - polarization resistance
- Differential pulse voltammetry
- Square wave voltammetry
- Normal (and reverse) pulse voltammetry

Stripping techniques
- Linear sweep stripping voltammetry
- Differential pulse stripping voltammetry
- Square wave stripping voltammetry
- Normal pulse stripping voltammetry

Special techniques
- Cyclic voltammetry
  - cyclic potentiodynamic polarization scanning
- MultiPulse voltammetry
  - non-standard sampling for linear sweep voltammetry
  - non-standard sampling for cyclic voltammetry
  - cyclic square wave voltammetry
  - cyclic differential pulse voltammetry
- Pulse Amperometry
  - differential pulse amperometry
  - double pulse amperometry
  - constant potential electrolysis
  - differential normal pulse voltammetry
  - double pulse voltammetry

The bulleted headings (•) can be selected from the Techniques menu in EChem. This will activate the appropriate dialog box so that the parameters for the experiment (scan rate, upper and lower potential limits, pulse duration, etc.) can be entered.

All 'Stripping' and 'Special' techniques include controls that enable a pre-scan deposition and a post-scan cleaning potential to be applied.

Multi Pulse Voltammetry is a general purpose technique allowing you to define any potential waveform that may be constructed from a combination of a stepped ramp with one or two pulses superimposed on each step. Up to four current signal sampling periods may be defined for each step/pulse cycle. This technique can also be used to set up nonstandard linear sweep, cyclic, square wave and differential pulse voltammetry experiments where the current signal is sampled at non standard times. It can also be used to perform cyclic square wave and cyclic differential pulse voltammetry.

The 'Pulse Amperometry' technique allows a fixed potential to be set with up to two pulses to be performed over a pre-set interval. The potential/pulse interval can be repeated up to 16000 times, to create a continuous scan.

Support for polarography experiments with a dropping mercury electrode is provided by means of synchronized TTL pulse signals (available on PowerLab S series units only).

Each of these techniques is discussed in greater detail in the following sections.

Other techniques, which can be performed with Chart and Scope software, are discussed in Chapter 8.

EChem software can also be used in conjunction with an AC waveform generator and lock-in amplifier to drive a potentiostat for AC voltammetry and AC cyclic voltammetry (also discussed in Chapter 8).

General Considerations

Voltammetric experiments involve measuring the current signal while the potential difference between the working and reference electrode is varied. Results are usually presented as a plot of current versus potential.

Amperometric techniques use a fixed base potential, i.e. they have a scan rate of 0 V/s. However pulses may be superimposed on the base potential. The results are usually plotted as current signal versus time.

The Voltammetric Ramp

Voltammetric techniques require that the potential between the reference and working electrodes be increased or decreased at a constant rate. If the potential at the electrode is plotted against time then the resulting graph has the appearance of a smooth ramp (Figure 7–1).
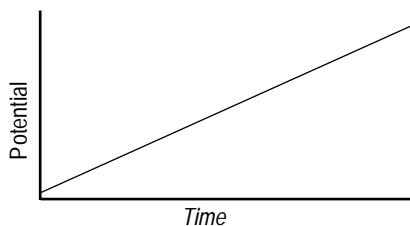
Figure 7–1
Typical potential/time profile of a voltammetric ramp

With digital instrumentation, such as the PowerLab system, the ramp actually consists of a series of discrete steps (and thus is often called a staircase or stepped ramp) defined by the step width (t_s) and step height (E_s) as shown in Figure 7–2.

The coarseness of this staircase is a function of the step width (t_s) and step height (E_s). Step widths should be chosen to keep the step height to a minimum (generally the step height should be less than 10 mV with 1 or 2 mV being ideal). Then minimum step width and height available depend on the potential range and sampling speed selected.

Figure 7–2
The digitally generated
'staircase' ramp
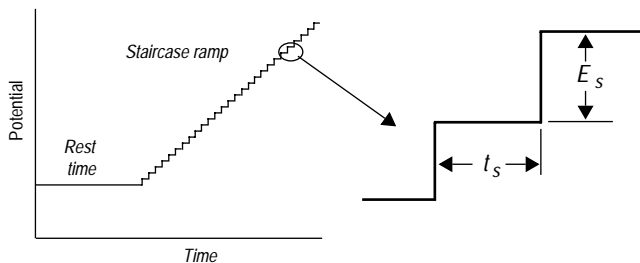
Table 7–1   Dependence of Step Height resolution on selected Potential Range. The Step Height at any range setting must be a multiple of the resolution.

Potential Range	Step Height resolution
±1 V	0.5 mV
±2 V	1.0 mV
±5 V	2.5 mV

Table 7–2   Dependence of time base on selected Sampling Speed. The Step Width, Sampling Period, and Pulse Width at any speed setting must be multiples of the time base.

Sampling speed	Time Base
100 Hz	10 ms
400 Hz	2.5 ms
1 kHz	1 ms
4 kHz	0.25 ms
10 kHz	0.1 ms

Table 7–3 Commonly selected scan rates (mV/s) as a function of Step Height and Step Width.

Width, ms	Height, mV				
	0.5	1	1.5	2	2.5
0.1	5000	10000	15000	20000	25000
0.2	2500	5000	7500	10000	12500
0.25	2000	4000	6000	8000	10000
0.3	1666.6667	3333.3333	5000	6666.6667	8333.3333
0.4	1250	2500	3750	5000	6250
0.5	1000	2000	3000	4000	5000
0.6	833.3333	1666.6667	2500	3333.3333	4166.6667
0.7	714.2857	1428.5714	2142.8571	2857.1429	3571.4286
0.75	666.6667	1333.3333	2000	2666.6667	3333.3333
0.8	625	1250	1875	2500	3125
0.9	555.5556	1111.1111	1666.6667	2222.2222	2777.7778
1.0	500	1000	1500	2000	2500
1.1	454.5455	909.0909	1363.6364	1818.1818	2272.7273
1.2	416.6667	833.3333	1250	1666.6667	2083.3333
1.25	400	800	1200	1600	2000
1.5	333.3333	666.6667	1000	1333.3333	1666.6667
1.6	312.5	625	937.5	1250	1562.5
1.8	277.7778	555.5556	833.3333	1111.1111	1388.8889
2.0	250	500	750	1000	1250
2.5	200	400	600	800	1000
3.0	166.6667	333.3333	500	666.6667	833.3333
3.3	151.5152	303.0303	454.5455	606.0606	757.5758
4.0	125	250	375	500	625
5.0	100	200	300	400	500
7.5	66.6667	133.3333	200	266.6667	333.3333
8.0	62.5	125	187.5	250	312.5
10.0	50	100	150	200	250
11.1	45.045	90.0901	135.1351	180.1802	225.2252
12.5	40	80	120	160	200
14.3	34.965	69.9301	104.8951	139.8601	174.8252
15.0	33.3333	66.6667	100	133.3333	166.6667
16.7	29.9401	59.8802	89.8204	119.7605	149.7006
20.0	25	50	75	100	125
25.0	20	40	60	80	100
30.0	16.6667	33.3333	50	66.6667	83.3333
33.3	15.015	30.03	45.045	60.0601	75.0751
40.0	12.5	25	37.5	50	62.5
50.0	10	20	30	40	50
62.5	8	16	24	32	40
66.7	7.4963	14.9925	22.4888	29.985	37.4813
80.0	6.25	12.5	18.75	25	31.25
83.3	6.0024	12.0048	18.0072	24.0096	30.012
90.9	5.5006	11.0011	16.5017	22.0022	27.5028
100.0	5	10	15	20	25
111.1	4.5005	9.0009	13.5014	18.0018	22.5023
125.0	4	8	12	16	20
142.9	3.499	6.9979	10.4969	13.9958	17.4948
166.7	2.9994	5.9988	8.9982	11.9976	14.997
200.0	2.5	5	7.5	10	12.5

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Table 7–3 Commonly selected scan rates (mV/s) as a function of Step Height and Step Width.

Width, ms	Height, mV				
	0.5	1	1.5	2	2.5
250.0	2	4	6	8	10
333.3	1.5002	3.0003	4.5005	6.0006	7.5008
500.0	1	2	3	4	5
1000.0	0.5	1	1.5	2	2.5
1250.0	0.4	0.8	1.2	1.6	2
1500.0	0.3333	0.6667	1	1.3333	1.6667
2000.0	0.25	0.5	0.75	1	1.25
3333.3	0.15	0.3	0.45	0.6	0.75
5000.0	0.1	0.2	0.3	0.4	0.5
6666.7	0.075	0.15	0.225	0.3	0.375
10000.0	0.05	0.1	0.15	0.2	0.25
100000.0	0.005	0.01	0.015	0.02	0.025

Scan Rate

The scan rate is determined by the ratio of the step height to the step width:

$$ScanRate = \frac{E_s}{t_s}$$

This means that only certain scan rates, albeit a very large number, can be entered. Table 7–3 contains a small selection of scan rates for various combinations of step height and width.

In most techniques the easiest way to enter a legal scan rate is to type in the desired scan rate, then to alter the Step Width to the nearest exact multiple of the time base, Table 7–2. The scan rate will be automatically updated to a legal value.

Pulse Techniques

Pulse techniques require sudden increases in potential to be superimposed on the staircase for short periods of time. Each pulse is characterized by a Pulse Width and Pulse Height (Figure 7–3).
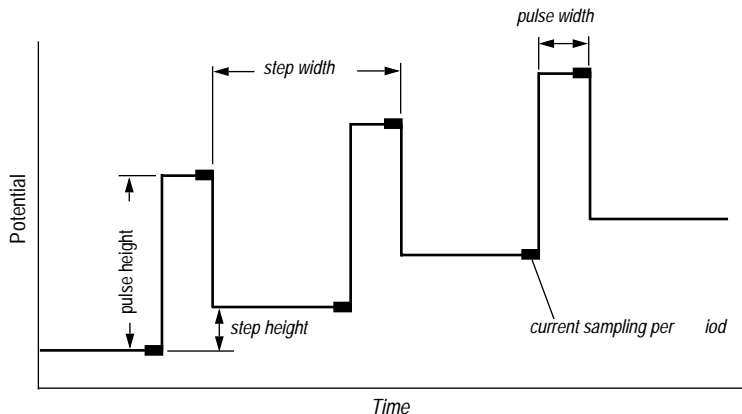
The Sampling Period

The EChem software samples the current signal at discrete periods during each step. During these sampling periods data is collected at a user selected rate of 100 Hz to 10 kHz. Sample periods are defined as the period over which current readings are taken and then averaged. The sampling period can be as short as 0.1 ms if sampling at 10 kHz.

There can be up to 4095 individual points in a sampling period which can be as long as 409.5 ms (in the 10 kHz mode) to 40.95 s (in the 100 Hz mode)

Thus if you have defined a sampling period to be 2 ms long then EChem can take 20 current measurements (at 0.1, 0.2, ... 1.9, 2.0 ms) when in the 10 kHz sampling mode. At the end of the period the current values are averaged to give a single value representative of the current flowing during the sample period.

The slower modes are used for very slow scanning, for example with corrosion techniques, where very long step widths and sampling periods are used. If the 100 Hz speed is selected scan rates as slow as 0.00016 mV/s can be used.

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When using slower scan rates the sampling period can be set to minimize mains noise. If you are operating on a mains frequency of 50 Hz (Europe, Australia, Chile, Argentina, and most of Africa, Asia) then use sampling periods that are a multiple of $1/50$ Hz = 20 ms, i.e. a single mains AC cycle. If you are operating at 60 Hz (North America, South Korea, Taiwan, most of South America, and parts of Japan, Peru and Saudi Arabia, etc.) then make your sample period a multiple of $1/60$ Hz ≈ 16.7 ms. This will cause the current data to be sampled over an integral number of mains AC cycles and thus any noise arising from this source will be effectively filtered out.

With most techniques the sampling period is located at the end of the pulse or step. But with the more flexible MultiPulse Voltammetry and Amperometry techniques you may set the sample period to be at the beginning, middle or end of a step or pulse.

The Rest Time

Before data is recorded it is common to bring the working electrode to the initial potential of the applied potential ramp. The potential is then held at this value for a short period of time, the rest time, (usually several seconds or longer) for the current flow to stabilise, and for the solution to settle after stirring.

Linear Sweep Voltammetry

In linear sweep voltammetry (LSV) a linearly increasing (or decreasing) potential staircase ramp is applied to the working electrode (Figure 7–4). The average current flowing during the sample periods (at the end of each step of the potential ramp) is recorded and plotted against the voltage. Note that the peaks may appear positive or negative depending on your definition of the direction of current flow. The invert check box in the Potentiostat/Input Amplifier setup dialog can be used to alter the direction (up or down) of the peaks.

Figure 7–4
Waveform terminology for the Linear Sweep technique
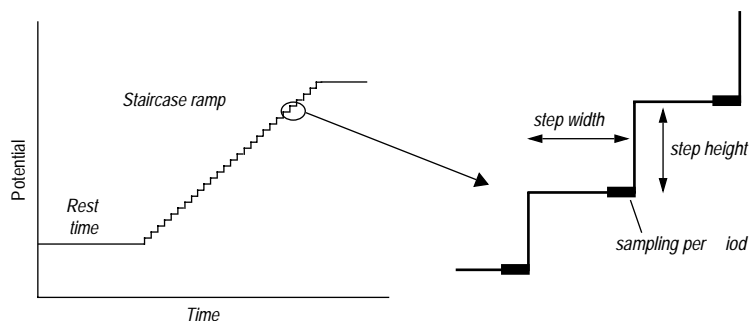
The position of the current sampling period in LSV is fixed by software at the end of each potential step. At this point the faradaic component is still significant whereas the charging current has decayed. If you require a different position of the sampling period then you can use the Multi Pulse method to set up your own customized LSV run.

Since this technique is designed to mimic linear sweep behavior obtained with analog instruments, the idea is to select parameters such that the coarseness of the potential staircase ramp is minimized. To achieve this the step height should be kept as small as possible. With EChem this places an effective limit on the scan rate of about 50 V/s for a potential range of 1 V. The scan rate can exceed this limit but close adherence to results obtained from true analog linear sweep voltammetry is no longer retained. Note that higher scan rates are achieved with PowerLab/4s, /8s, and /16s models.

Parameters

When Linear Sweep Voltammetry is chosen from the techniques menu the Linear Sweep Voltammetry dialog box appears (Figure 7–5). This allows the user to adjust the parameters for the technique. The first time the technique is chosen the parameters will be default values.

Figure 7–5
The Linear Sweep
Voltammetry dialog box

Each parameter is altered by entering a new value in the appropriate box, selecting a new menu item, or clicking the control arrows. Changes take effect when the OK button is clicked. Click the Cancel button to exit without altering the parameters. It is usually best to adjust the parameters in the following order:

Speed

The data acquisition rate is normally set at 10 kHz in the Speed pop-up menu. Very slow rates (less than 1 mV/s) may require slower speeds so that appropriately long step widths can be used.

Range

The range pop-up menu selects the full scale range of the applied potential. Three ranges are available, ±1000 mV giving 0.5 mV resolution, ±2000 mV giving 1 mV resolution, or ±5000 mV giving 2.5 mV resolution, Table 7–1. Usually the 2000 mV range is chosen.

Height 2 mU

(Step) Height

This is the amplitude of each potential step. The minimum step available depends on the selected range, Table 7–1. Values from 0.5 to 2.5 mV are ideal for work where accurate peak positions, heights and areas are required. Values over 5 mV may give insufficient potential resolution, and also lead to excessively high charging currents at macro electrodes, for most voltammetric and pulse techniques.

Initial (Potential)

Initial -1000 mU

This is a text box that sets the initial or starting potential of the ramp. This can be chosen anywhere between the limits of the range setting.

Final (Potential)

Final 0 mU

The potential voltage at which the ramp waveform finishes.This can be chosen anywhere between the limits of the range setting. The final potential may be either more negative than the initial potential (negative scan) or more positive than the initial potential (positive scan).

Steps

The number of steps in the ramp is derived from the initial and final potentials and the step height:

$$Steps = \frac{|FinalPotential - InitialPotential|}{StepHeight}$$

This number must be an integer. If it is not then you will have to adjust the Upper and / or Lower Limit so that the difference is an exact multiple of the Step Height.

(Scan) Rate

Rate 100 mU/s

This sets the rate at which the ramp will be generated. Faster scan rates lead to a higher background signal unless a microelectrode is used. This is usually set between 5 and 1000 mV / s for ordinary macro electrodes. The scan rate is the ratio of the step height to the step

width. When the rate is adjusted the step width is also adjusted to maintain the selected step height.

(Step) Width

Width [20] ms

The time that the potential is kept constant at each step. The value must be a multiple of the time base, Table 7–2. Step width, step height and scan rate are interrelated:

$$StepWidth = \frac{StepHeight}{ScanRate}$$

After you adjust the scan rate, adjust the step width to the nearest exact multiple of the time base, Table 7–2. This may alter the scan rate slightly.

Rest Time

Rest Time [2] s

This is the length of time the initial potential is maintained before the scan is started. A time of around 1 to 60 seconds is usually appropriate, although much longer times may be necessary for corrosion experiments (potentiodynamic polarization or polarization resistance experiments).

Figure 7–6
Waveform Overview dialog box for a typical LSV technique
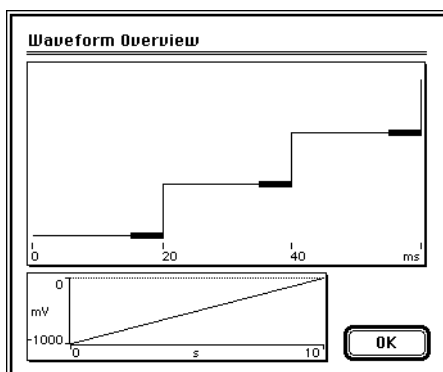
The View Button

View...

You can get an idea of what effect the present parameters will have on the waveform by clicking the View button. If the parameters are set correctly then the Waveform Overview dialog will appear (Figure 7–6). This displays a small section of the waveform showing

the steps and the sampling period (the thick, red, line segments). If the parameters are above the maximum limits or do not make sense then you will see an error dialog describing what is wrong

EChem User's Guide

Square Wave Voltammetry

In Square Wave Voltammetry (SWV) a square wave cycle is added to each step of the staircase potential ramp. This technique is also called Osteryoung Square Wave Voltammetry. A variation where a number of square wave cycles occur at each step is called Baker Square Wave Voltammetry and this is not available in EChem.

SWV has the advantage of showing the signals from a reversible redox reaction while partially suppressing signals of irreversible processes, and can be a very powerful technique for compound characterization. It is also extremely useful for high speed, yet sensitive, stripping analysis

The wave-form used in square wave voltammetry is shown in Figure 7–7 Note that the square wave amplitude is defined as half the

Figure 7–7
Waveform terminology for
Square Wave Voltammetry
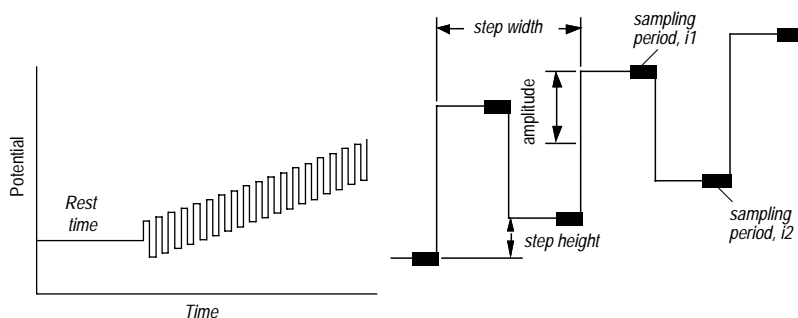
peak to trough separation (similar to the definition of the amplitude of a sine wave). The current is sampled and averaged at the end of the forward step and again at the end of the reverse step. The two data points at each step can be described by the potential/current coordinates (E1, i1) and (E2, i2).

SWV is quite popular for analysis as it combines the speed of linear sweep techniques with the ability to discriminate against charging currents (similar to differential pulse voltammetry). The difference between the current at the forward step, i1, and the current at the reverse step, i2, is displayed against average potential during the step width. Thus at each step of the experiment the coordinates of the data points displayed on the screen are given by:

$$([i1\text{-}i2], [E1+E2]/2)$$

The actual values of the two currents, i1 and i2 are stored in the arrays of these names and can be viewed separately by choosing Sampling Display in the Display menu, to present the dialog in Figure 7–8.

Figure 7–8
The Data Selection dialog box.
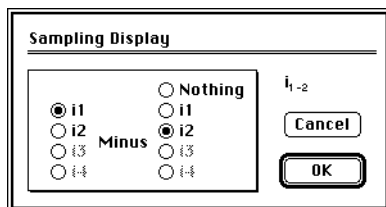
The default settings for SWV displays i1–i2 (i3 and i4 are not used for Square Wave Voltammetry). Selecting 'i2 Minus Nothing' would change the graph on display so that you would see the current values at the top of each pulse.

You may occasionally find that a SWV run gives you small peaks and that on attempting to run the experiment at a slightly higher gain you find that much of the signal is off scale. Remember that the default display is i1–i2, i.e. the difference between the current values in i1 and i2. It is possible that the arrays i1 and i2 contain many large current values and so need to be recorded on low gain settings to be on scale. You can check that this is so by using the Sampling Display command. If corresponding values in i1 and i2 are both large and nearly equal then the difference, i1–i2 will be small but you will not be able to select higher gains to collect the data.

Parameters

When Square Wave Voltammetry is chosen from the techniques menu the Square Wave Voltammetry dialog box appears (Figure 7–9). Suitable parameters can be entered in the relevant spaces to alter the technique as needed for the experiment being conducted.

Changes take effect when the OK button is clicked. Click the Cancel button to exit without saving.

Figure 7–9 z
The Square Wave
Voltammetry dialog box.

Square Wave Voltammetry   Range: 2000mV ▼

Ramp

Initial	-1000	mV
Final	0	mV
Freq	25	Hz
Rate	50	mV/s
Height	↕2	mV
Steps	500	

S.W. Ampl.

25 mV

S. Period

5 ms

Rest Time

2 s

Speed: 10kHz ▼

View...

Cancel

OK

The Speed Menu

| 100 Hz |
| 400 |
| 1 kHz |
| 4 |
Speed: | ✓10 |
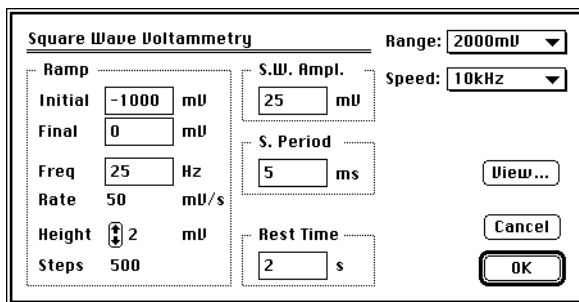
The data acquisition rate is normally set at a speed of 10 kHz.

Range

| 5000mV |
Range: | ✓2000mV |
| 1000mV |

The range pop-up menu selects the full scale range of the applied
potential. Three ranges are available, ±1000 mV giving 0.5 mV
resolution, ±2000 mV giving 1 mV resolution, or ±5000 mV giving 2.5
mV resolution, Table 7–1. Usually the 2000 mV range is chosen.

Initial (Potential)

Initial [-1000] mV

Enter the initial or starting potential of the ramp in this text box. This
can be chosen between anywhere between the extremes of the
selected range. The Initial Potential is the mid point of the first square
cycle.

Final (Potential)

Final [0] mV

The potential voltage at which the ramp waveform finishes. This can
be chosen anywhere between the extremes of the selected range. The
final potential may be either more negative than the initial potential
(negative scan) or more positive than the initial potential (positive
scan). The Final Potential is the mid point of the last square wave
cycle.

Frequency

Freq [15] Hz

This is the frequency of the square wave. Frequencies in the range
5– 60 Hz usually give good results, but with microelectrodes, or RAM
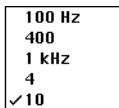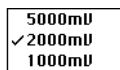
electrodes, frequencies of hundreds (or even thousands) of Hertz may be employed. With a PowerLab S model, frequencies of up to 5000 Hz can be used. With PowerLab e, and earlier, models you should not exceed 500 Hz.

The frequency of the square wave is related to the step width by:

$$StepWidth = \frac{1}{Frequency}$$

For square wave voltammetry the step width must be twice some multiple of the time base, so that not all frequencies are allowed.

(Step) Height

Height [⇕] 2   mV

Typical values of 1 – 2.5 mV are ideal. Values over 10 mV usually give insufficient potential resolution for precise analytical work. The step height and frequency are related to the scan rate by:

$$ScanRate = Frequency \times StepHeight$$

Steps

This value is automatically calculated and shows the number of steps in the ramp according to the formula:

$$Steps = \frac{|FinalPotential - InitialPotential|}{StepHeight}$$

S.W. Ampl. (Square Wave Amplitude)

S.W. Ampl.
25   mV

This is the half-height of the pulses of the square wave. Typical amplitudes are in the range of 10 – 50 mV. Use a negative amplitude if you want the initial square wave cycle to begin in the negative direction.

S.(ampling) Period

S. Period
10   ms

Current data will be collected and averaged over this period which occurs at the end of each step (upper and lower). The sampling period should normally be shorter than the step width (= 1/Frequency) in order for the charging current to decay. For

example at a frequency of 25 Hz the step width is 40 ms. Therefore the sampling period should be set to 40 ms or less (preferably 16.7 or 20 ms to minimize mains 60 Hz or 50 Hz noise interference).

Rest Time

Rest Time

| 2 | s |

This is the length of time the initial potential is maintained before the scan is started. A time of around 1 to 60 seconds is usually appropriate.

The View button

[View...]

The quickest way to determine if the parameters you have set will work is to click the view button. If the parameters you have set are logically consistent then the Waveform overview window will appear (Figure 7–10) with a representation of the potential waveform. If for any reason the values you have set are out of range, or otherwise inappropriate, you will be prompted by a dialog box telling you what the problem is.
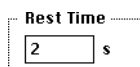
Figure 7–10 Waveform Overview for a typical Square Wave Voltammetry technique
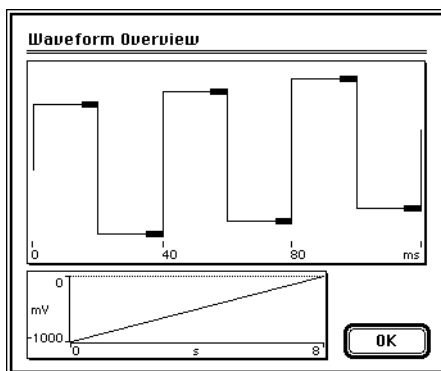
Normal Pulse Voltammetry

In Normal Pulse Voltammetry, a series of pulses of successively larger potential are applied above a base potential to the working electrode. Alternatively this can be thought of as an applied ramp interrupted at regular intervals by a return to the baseline value.

Reverse Pulse Voltammetry is similar except that the base potential is chosen to electrolyse the electroactive substrate. The pulses that are then applied cause the reverse reaction to take place. This may be useful if parallel competing reactions take place when the original species is electrolysed. The waveform used in normal pulse voltammetry is depicted in Figure 7–11. The current is sampled at the end of each pulse, and plotted against the potential.

Figure 7–11
Waveform terminology for Normal Pulse Voltammetry
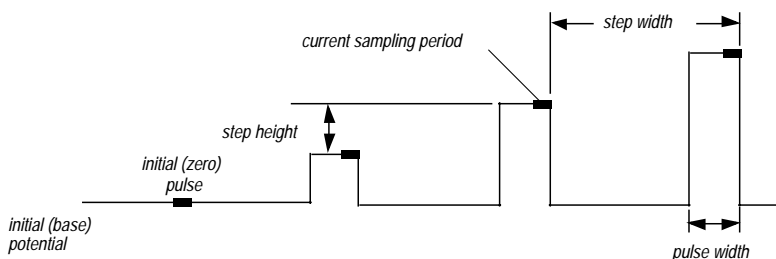
Parameters

A Typical dialog box for setting up a normal pulse experiment is shown in Figure 7–12. Each parameter is altered by entering a new value in the appropriate box, selecting a new menu item, or clicking the control arrows. Changes take effect when the OK button is clicked. Click the Cancel button to exit without saving.
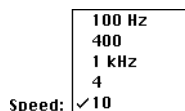
Speed

The data acquisition rate is normally set at 10 kHz. Very slow rates (less than 1 mV/s) may require slower speeds so that appropriately long step widths can be used.

Figure 7–12
The Normal Pulse
Voltammetry dialog box

```
Normal Pulse Voltammetry          Range: 2000mV  ▼
┌ Ramp ─────────┐ ┌ Pulse Width ┐  Speed: 10kHz  ▼
  Initial  -1000  mV    10     ms
  Final    0      mV   ┌ S. Period ┐
  Rate     50   mV/s    5      ms        (View...)
  Width    40     ms
  Height  ⇕2    mV   ┌ Rest Time ┐       (Cancel)
  Steps    500         2      s          ┌ OK ┐
```

Range


```
         5000mV
Range: ✓ 2000mV
         1000mV
```

The range pop-up menu selects the full scale range of the applied potential. Three ranges are available, ±1000 mV giving 0.5 mV resolution, ±2000 mV giving 1 mV resolution, or ±5000 mV giving 2.5 mV resolution, Table 7–1. Usually the 2000 mV range is chosen.

Initial (Potential)


```
Initial  -1000  mV
```

This is the initial or starting potential of the ramp. This can be chosen between ± 2000 mV if on the 2000 mV range or ± 5000 mV when on the 5000 mV range. This value is usually chosen to be a value at which the electrode reaction of interest does not occur (so that the current is close to zero). For Reverse Pulse Voltammetry this potential is chosen to cause complete oxidation (or reduction) of the substrate, and the pulses then cause the reverse reaction.

Final (Potential)


```
Final  0  mV
```

The potential voltage at which the ramp waveform finishes. This can be set between ± 2000 mV if on the 2000mV range or ± 5000 mV when on the 5000 mV range. The final potential may be either more negative than the initial potential (negative scan) or more positive than the initial potential (positive scan). This is the height of the last pulse to be applied. It can be thought of as the height of an imaginary ramp passing through the tops of the pulses.

(Scan) Rate


```
Rate  100  mV/s
```

This sets the rate at which the ramp will be generated in mV per second. This is usually set between 5 and 100 mV s^{-1} for macro

electrodes. Generally this parameter is allowed to vary as the Initial and Final Potentials and the Step Width and Height are set.

(Step) Width

`Width  20    ms`

The time that the potential is kept constant at each step. The value cannot be set less than 0.2 ms. Times of around 2 – 4 ms are usually satisfactory. Step Width is related to Step Height and Scan Rate by:

$$StepWidth \ = \ \frac{StepHeight}{ScanRate}$$

(Step) Height

`Height  2    mV`

This defines the increase in height (mV) of successive pulses. The minimum step available is 1 mV. Typical values of 1 – 2 mV are ideal.

Steps

This value is automatically calculated and shows the number of steps in the ramp according to the formula:

$$Steps \ = \ \frac{|FinalPotential - InitialPotential|}{StepHeight}$$

Pulse Width

`Pulse Width
10   ms`

The length of time of the applied pulse. Values between 5 and 100 ms are commonly used, with a minimum of 0.1 ms possible. The pulse width should be wide enough to allow the non-faradaic components of the current to decay before sampling. For a 1 mm^2 macro electrode allow the pulse to be at last several milliseconds longer than the sample period.

Rest Time

`Rest Time
2   s`

This is the time that the initial potential will be applied to the cell before the actual ramp is applied. This allows you to leave the cell electrodes at a preset potential in order for charging currents and other disturbances to settle. This time is usually in the range of 1 – 60 seconds. Setting the rest time to zero will start the technique immediately.

S.(ampling) Period

Current data will be collected and averaged over this period which occurs at the end of each pulse. A suitable sampling width is 20 ms, or 16.7 ms where mains frequency is 60 Hz. This effectively discriminates against mains frequency interference.

The View button

The quickest way to determine if the parameters you have set will work is to click the view button. If the parameters you have set are OK then the Waveform overview window will appear (Figure 7–13) with a representation of the potential waveform. If for any reason the values you have set are out of range or inappropriate you will be prompted by a dialog box telling you what the problem is.

View...

Figure 7–13
The Waveform Overview dialog box for the Normal Pulse Voltammetry technique
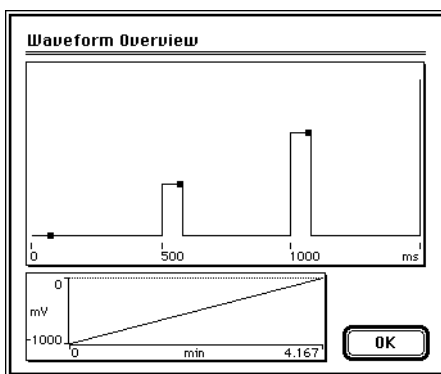
Differential Pulse Voltammetry

Differential Pulse Voltammetry (DPV) uses a series of short, small amplitude pulses (typically 50 mV) superimposed on a linearly increasing or decreasing potential ramp (Figure 7–14). The current is sampled just prior to each pulse (i1) and at the end of the pulse (i2). The difference in current (i2–i1) is plotted versus the potential at the base ramp.
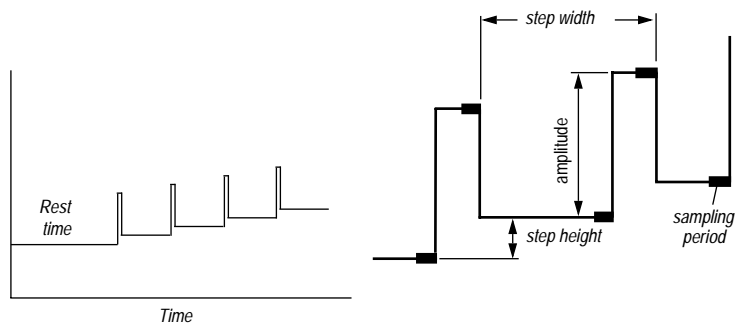
Remember that you are viewing the difference between two current signals. The actual values of the two currents, i1 and i2 are stored in the arrays of these names and can be viewed by choosing Sampling Display in the Display menu.
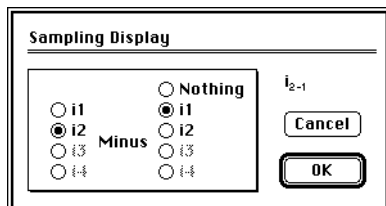
This brings up the Data Selection Dialog (Figure 7–15) which is set to display 'i2 Minus i1' (i3 and i4 are not used for DPV). Selecting 'i2 Minus Nothing' would change the graph on display so that you would see the current values at the top of each pulse.

You may occasionally find that a Differential Pulse Voltammetry run gives you small peaks and that on attempting to run the experiment at a slightly higher gain you find that much of the signal is off scale. Remember that the default display is 'i2 – i1', i.e. the difference

between the current values in i2 and i1. It is possible that the arrays i1 and i2 contain many large current values and so need to be recorded on low gain settings to be on scale. You can check that this is so by using the Sampling Display command to view i1 and i2 separately. If the values in i1 and i2 are both large and nearly equal then the difference, i1 – i2, will be small but you may not be able to select higher gains to collect the data because i1 and/or i2 will go off scale.

Increasing the pulse height for DPV experiments may give you larger peaks but resolution will be decreased.

Note that if you make the Pulse Width exactly half the Step Width then you will actually have a waveform that is identical to that used for Square Wave voltammtery. However, there are two important differences. Firstly the default display of DPV is 'i2 – i1' while for SWV it is 'i2 – i1'. Thus you will need to alter the DPV Sampling Display appropriately. Secondly DPV results are plotted against the potential at base of each pulse, whereas in SWV the average potential over each square wave step is used.

Parameters

When Differential Pulse is chosen from the Techniques menu the Differential Pulse Voltammetry dialog box appears (Figure 7–16).

Each parameter is altered by entering a new value in the appropriate box, selecting a new menu item, or clicking the control arrows. Changes take effect when the OK button is clicked. Click the Cancel button to exit without saving.

The Speed Menu

The data acquisition rate is normally set at 10 kHz. Very slow rates (less than 1 mV/s) may require slower speeds so that appropriately long step widths can be used.

Range

Range:
5000mV
✓2000mV
1000mV

The range pop-up menu selects the full scale range of the applied potential. Three ranges are available, ±1000 mV giving 0.5 mV resolution, ±2000 mV giving 1 mV resolution, or ±5000 mV giving 2.5 mV resolution, Table 7–1. Usually the 2000 mV range is chosen.

Initial (Potential)

Initial   -1000   mV

This is the initial or starting potential of the ramp. This can be chosen between ± 2000 mV if on the 2000 mV range or ± 5000 mV when on the 5000 mV range.

Final (Potential)

Final   0   mV

The potential voltage at which the ramp waveform finishes. This can be set between ± 2000 mV if on the 2000 mV range or ± 5000 mV when on the 5000 mV range. The final potential may be either more negative than the initial potential (negative scan) or more positive than the initial potential (positive scan). The final potential cannot be the same as the initial potential.

(Step) Height

Height ↕2   mV

This is the amplitude of each voltage step in millivolts. The minimum step available is 1 mV. Typical values of 1–10 mV are ideal. Keep this parameter as small as possible.

(Scan) Rate

Rate   100   mV/s

This sets the rate at which the ramp will be generated in mV per second. This is usually set between 1 and 25 mV s^{-1}. Increasing the scan rate decreases peak resolution. However very slow scan rates mean inordinately long analysis times.

Width [20] ms

(step) Width

The time of each step (including the pulse time). This is also the period between pulses. This parameter is usually allowed to vary while the Scan Rate and Step height are set. This parameter is usually set between 0.5 to 4 s. Step Width is related to Step Height and Scan Rate by the following relationship.

$$StepWidth = \frac{StepHeight}{ScanRate}$$

Steps

This is simply a readout value showing the number of steps in the ramp according to the initial and final voltages and the step height set in these text boxes. The relationship between the number of steps and the other parameters is:

$$Steps = \frac{|FinalPotential - InitialPotential|}{StepHeight}$$

Pulse Width

The width of the pulse superimposed upon the potential ramp. This parameter is usually set in the range of 5 to 100 ms. The pulse should last long enough to allow the non-faradaic components of the current to decay before sampling. For a standard glassy carbon electrode with an area of ~1 cm^2 where sampling is to be carried out over a wide enough window to reject mains noise (20 ms @ 50 Hz) then a pulse width of 50 ms would be appropriate.

Pulse
Width [50] ms
Ampl. [25] mV

Pulse Amplitude

The height of the pulse superimposed upon the potential ramp. This is usually set in the range of 50 – 100 mV. Larger values increase sensitivity (i.e. you get bigger peaks), smaller values improve resolution.

The Pulse Height must be greater than Step Height, or else the next step will be higher that the previous pulse!

Rest (time)

This is the period between when the deposition potential is applied and the scan commences. This is usually set to between 1 and 5 s.

S.(ampling) Period

Current data will be collected and averaged over this period which occurs just prior to the pulse and at the end of each pulse. Usually this parameter is set to between 1 and 20 ms. Multiples of 20 ms (at 50 Hz mains) or 16.7 ms (at 60 Hz mains) will discriminate against mains noise. In general there will be less noise for longer sampling periods.

The View button

View...

The quickest way to determine if the parameters you have set will work is to click the view button. If the parameters you have set are OK then the Waveform overview window (Figure 7–17) will appear with a representation of the potential waveform. If for any reason the values you have set are out of range or inappropriate you will be prompted by a dialog telling you what the problem is.

The thick line segments just prior to the pulse and at the end of the pulse represent the sampling period. Note that the waveform overview dialog box shows a magnified portion of the entire waveform (upper) as well as the whole ramp (lower).
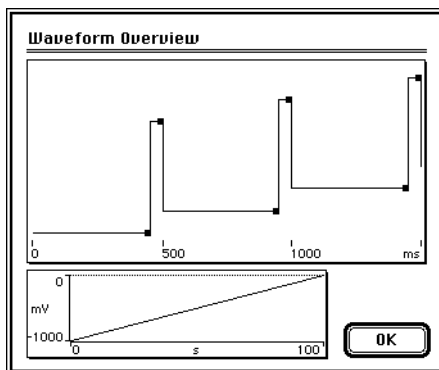
Figure 7–17
The Waveform Overview Dialog box for a typical Differential Pulse Voltammetry experiment

Stripping Techniques

EChem allows you to perform stripping type techniques using any one of the five standard methods just described. EChem supports;

- Linear sweep stripping voltammetry
- Differential pulse stripping voltammetry
- Square wave stripping voltammetry
- Normal pulse stripping voltammetry

In addition non-standard stripping experiments can also be set up in the Cyclic and MultiPulse Techniques. Stripping techniques involve fixing the analyte to the working electrode in some way. This has the advantage of concentrating the analyte at the electrode and giving a dramatic increase in sensitivity.

The two main methods in this area are cathodic stripping voltammetry and anodic stripping voltammetry. Both methods make use of a constant deposition potential applied prior to beginning of the experiment proper. Similarly after the experiment a constant cleaning potential can be maintained for a fixed time period.

Anodic Stripping Voltammetry

Anodic stripping techniques usually involve the use of mercury as a working electrode. This may be in the form a hanging mercury drop electrode (HMDE), or a mercury film electrode (MFE). The function of the mercury is to amalgamate with (dissolve) metals that plate out on the electrode surface when metal ions in solution are reduced. Solid electrodes can also be used but mercury usually gives superior performance.

Prior to the experiment a reduction step takes place when a deposition potential is applied to the mercury working electrode. This potential is maintained, usually while stirring the solution, so that the metal ions of interest in the sample are concentrated within the mercury electrode. The deposition potential should be at least 0.2 V more reducing than the peak potential of the most electropositive metal to be detected.

The deposition process can involve a concentration increase of many orders of magnitude and allows the measurement of metal ion concentrations in extremely dilute (ppb or ppt) solutions. The more dilute the original sample the larger it should be, and the longer the deposition step will take. While you will have to work out your own parameters for any given sample some suggested values to start with are shown in Table 7–4.

Table 7–4   Typical deposition times for analytes of various concentrations.

Concentration mol L^{-1}	Deposition time min
10^{-7}	5
10^{-8}	20
10^{-10}	60

After the metals have been deposited within the mercury electrode stirring is stopped and a rest potential is applied for at least 30 s. Linear sweep voltammetry or one of the standard pulsed techniques can be applied. At the end of the ramp an oxidizing cleaning potential is applied to remove any residual metals from the mercury electrode. This potential should be at least 0.2 V more oxidizing than the peak potential of the most electronegative metal being measured.

It is not necessary to deposit all the metal ions in solution. It is simply necessary to repeat the experiment under exactly the same conditions (deposition time and potential, scan rates and limits etc.) for a series of standards followed by the unknown(s) so that a useful graph of concentration versus signal can be prepared. If the concentration of the metal ion is relatively high then it is important to either dilute the solution before measuring and/or to ensure that deposition times are short. This is to ensure that the build up of metal analyte in the mercury does not change the properties of the amalgam too far from that of a dilute mixture. A concentrated amalgam may give peaks at unexpected values or even multiple peaks for a single analyte, or may give a current that overloads the potentiostat.

Closely overlapping peaks arising from metal ions with a similar reduction potential can sometimes be separated by the addition of a complexing agent (such as EDTA, or dimethylglyoxime). The metal is

then no longer present in solution as an aquated metal ion but as a complex ion with a different reduction potential.

Cathodic Stripping Voltammetry

Anions can be fixed to an electrode as an insoluble metal salt. In the case of analyzing for halides an oxidizing deposition potential is first applied at a silver electrode:

$$Ag_{(s)} \; + \; I^{-}_{(aq)} \; \rightarrow \; AgI_{(s)} \; + \; e^{-}$$
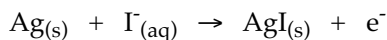
A subsequent scan to reducing potential can be used to detect the halide(s) present as the silver halide is reduced:

$$AgI_{(s)} \; + \; e^{-} \rightarrow \; Ag_{(s)} \; + \; I^{-}_{(aq)}$$
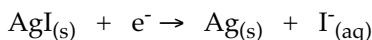
Other anions that can be detected include sulfide, phosphate, arsenate, and arsenite. The working electrode is usually made of mercury, gold or silver.

Setting Parameters

When any of the stripping techniques are chosen from the Technique menu, a dialog box will appear (Figure 7–18). The dialog is similar to the non-stripping technique dialog except that extra controls for Deposition and Cleaning appear at the bottom of the dialog box. You can set a potential, and a time period, for both deposition and cleaning. All the Stripping techniques carry out deposition first, followed by the actual technique and then cleaning takes place.

Both the deposition and Clean Time periods can be turned off using the check boxes next to their titles. By tuning off both the Deposition and Clean Time periods then only the basic technique will be left. For example, when using Cyclic Voltammetry you should leave both check boxes off unless you are attempting an unconventional experiment.

The ramp and pulse parameters are set up in the same way as for the corresponding non-stripping technique. Refer to the corresponding non-stripping technique for information on these parameters.

Figure 7–18
An example of the Stripping
version of the standard Linear
Sweep Voltammetry technique
dialog box

Linear Sweep Stripping Voltammetry dialog box showing: Range: 2000mV, Speed: 10kHz; Ramp — Initial -1200 mV, Final -200 mV, Rate 100 mV/s, Width 20 ms, Height 2 mV, Steps 500; S. Period 5 ms; Rest Time 2 s; Deposition — Pot. -1200 mV, Time 60 s, Stirrer checked, Gas; Clean Time — Pot. -200 mV, Time 2 s; View..., Cancel, OK buttons.

Deposition potential

Pot. [-1000] mV

This potential is applied for a fixed period (usually several minutes) and can be set between extremes of the Range setting.

Deposition Time

Time [60] s

This is the time in seconds for which the deposition potential will be applied. You can enter times from 0.01 seconds up to 9999 seconds (about 2 h 47 min).

Clean Time Potential

Pot. [   ] mV

At the end of a scan a cleaning potential can be applied (usually for a minute or so). This can be set anywhere between the extremes of the range setting.

Cleaning Time

Time [   ] s

This is the time in seconds for which the cleaning potential will be applied. You can enter times from 0.01 seconds up to 9999 seconds (about 2 h 47 min).

Stirrer & Gas Controls

☐ Stirrer
☐ Gas

Use of a stirrer and gas purge is facilitated by the provision of TTL logic control signals carried by carried by Output 1 and Output 2 of

TTL logic signals are a simple means of on/off communication between instruments. 'TTL high' corresponds to a voltage level of about 5 V, while 'TTL low' corresponds to a signal of about 0 V. These states are controlled in software by a single bit variable which is referred to as being set on or off.

the PowerLab digital output, page 160. The Stirrer check box controls digital output 1 and the Gas check box controls digital output 2 of the PowerLab. Refer to your *PowerLab Owners Guide* for details of the digital output signals and how to connect to them. Note that on PowerLab/200 /400 and the older /2e and /4e units the digital output signals are provided on the Multiport connector on the rear of the unit. Other PowerLab models have a dedicated digital output connector. The digital I/O ports provide 0 – 5 V at about 1 mA. This is enough to act as an on/off signal but is not sufficient to power a stirrer or other equipment.

Checking the Gas and/or Stirrer checkboxes allows you to control the state of an external stirrer motor or solenoid gas valve during deposition. These check boxes control two of the digital output (TTL) lines provided by the PowerLab. Activating these controls (click the check box) will set the corresponding digital output on at appropriate times during the experiment. Output 1 is on during the Deposition and Cleaning periods, while Output 2 is on during the Deposition time only. A cable can be made to use these signals to turn a stirrer and solenoid gas valve on and off during the stripping experiment.

You can monitor the state of the digital output lines by displaying the Digital Output panel, Figure 7–32.

Cyclic Voltammetry

The potential is driven between two limits at a constant rate, similar to linear sweep voltammetry. When a limit is reached the potential is swept back again at the same rate. The experiment can start at any potential (initial potential) between the two limits and usually finishes at the initial potential so that an integral number of cycles are performed. This technique is usually used for qualitative purposes and is valuable in the characterization of new compounds.

The ideal waveform used in cyclic wave voltammetry is depicted in Figure 7–19. For computer driven systems like EChem/PowerLab the ramp is stepped (shown below right) and this method is often called staircase cyclic voltammetry.
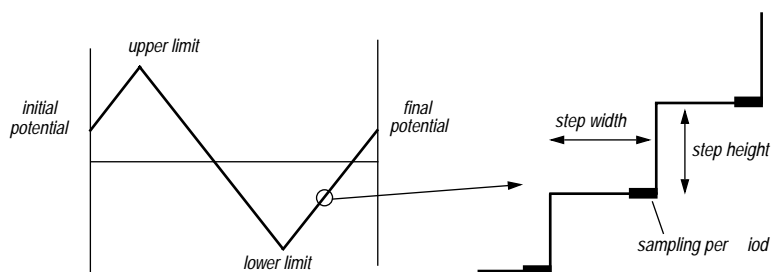
Different workers have sampled at 25%, 50%, 75%, or 100% of each step, depending on the experimental requirements. For qualitative work this will usually not give significant differences. The Cyclic Voltammetry method in EChem always samples current at the end of each step. Thus a 100 ms step with a sampling period of 25 ms would be sampled at 75.0 – 99.9 ms at 0.1 ms intervals (when the 10 kHz speed mode is used) and the values then averaged. If you require to sample the current values over different regions, say halfway through the step, then you can use the Multi Pulse Voltammetry command.

The upper and lower potential limits will often be constrained by the choice of solvent and electrolyte. Background sweeps (of solvent and electrolyte) are necessary to determine the window region in which measurements can be made. Remember to perform these sweeps at the same gain setting as will be used in your experiment. When using

non-aqueous solvents ensure that adequate purification and drying are undertaken. See Appendix E for more information.

Parameters

Choose Cyclic Voltammetry from the Techniques menu. The Staircase Cyclic Voltammetry dialog will appear (Figure 7–20).

Each parameter is altered by entering a new value in the appropriate box, selecting a new menu item, or clicking the control arrows. Changes take effect when the OK button is clicked. Click the Cancel button to exit without saving.

The Speed Menu

The data acquisition rate is normally set at 10 kHz. Very slow rates (less than 1 mV/s) may require slower speeds so that appropriately long step widths can be used.

Range

The range pop-up menu selects the full scale range of the applied potential. Three ranges are available, ±1000 mV giving 0.5 mV resolution, ±2000 mV giving 1 mV resolution, or ±5000 mV giving 2.5 mV resolution, Table 7–1. Usually the 2000 mV range is chosen.

Initial -1000 mV

Initial (Potential)

This is the initial or starting potential of the ramp. This can be set anywhere between the Upper and Lower Potential Limits. It is normally chosen to be a value at which oxidation or reduction of the substrate does not occur.

Final (Potential)

The potential voltage at which the ramp waveform finishes. It is automatically set to be the same as the initial potential (so as to complete a full cycle).

Upper (Potential Limit)

Limits
Upper 1000 mV
Lower -1000 mV

The maximum potential that will be achieved in a cycle and this can be set anywhere between the extremes of the Range.

Lower (Potential Limit)

The minimum potential that will be achieved in a cycle and this can be set anywhere between the extremes of the Range. Note that the difference, 'Upper–Lower' will be less than 2 V if the ±1000mV range is selected, 4 V if the ±2000 mV range is selected, and less than 10 V if the ±5000 mV range is selected.

(Step) Height

Height 2 mV

Click the arrows to adjust the Step Height, usually 1 or 2 mV is ideal. More than 10 mV will not give adequate resolution on the potential axis.

(Scan) Rate

Rate 100 mV/s

This sets the rate at which the ramp will be generated in units of mV/s. It is usually set in the range 10 – 1000 mV/s for normal macro electrodes (1 mm diameter or greater). Microelectrodes (diameters from less than 1 μm to 100 μm) are usually employed for faster scan rates.

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(Step) Width

Width [20] ms

This is the time that the potential is kept constant at each step. In general first adjust the Step Height, next enter the Scan Rate, then finally adjust the Step Width to the nearest allowed resolution increment, Table 7–2

Step Width is related to Step Height and Scan Rate by the following relationship.

$$StepWidth = \frac{StepHeight}{ScanRate}$$

Steps

The number of Steps in a cycle is determined automatically and is given by the formula:

$$Steps = \frac{UpperPotential - LowerPotential}{StepHeight} \times 2$$

If Steps is not an integer then EChem will not perform the experiment and a warning dialog will appear when you click the View or OK button. In this case you will need to adjust Step Height or the Upper and Lower Potentials to make Steps an integer.

Rest Time

Rest Time
[2] s

This is the period after the deposition potential has been applied and before the scan commences. This is usually set to between 1 and 60s.

(Deposition) Pot(ential)

Pot. [-1000] mV

Not normally used for Cyclic Voltammetry. This is the deposition potential applied for a fixed period prior to the scan. This can be set anywhere between the extremes of the Range.

(Deposition) Time

Time [60] s

Not normally used for Cyclic Voltammetry. This is the time in seconds for which the deposition potential will be applied. You can enter

times from 0.01 to 9999 seconds (about 2h 47 min). This a period before the Rest Time.

(Cleaning) Pot(ential)

Pot. [_____] mV

Not normally used for Cyclic Voltammetry. The potential applied during the Cleaning Time. The Cleaning Potential can also be set so as to oxidize (or reduce) any material that has plated out on the working electrode. This can be set anywhere between the extremes of the Range.

(Cleaning) Time

Time [_____] s

Not normally used for Cyclic Voltammetry. At the end of a scan a cleaning potential can be applied for a period defined by the Cleaning Time (usually a few seconds to a minute or so).

Cycles

Enter the number of cycles required in this text box, this number must be an integer less than 100. You can also choose the initial direction of the cycle (if the Initial Potential lies between the Upper and Low Potential Limits) by using the 'Initial Direction' check box.

The maximum number of data points that can be stored during one experiment is set at 65000. Thus number of cycles that can be performed in the one experiment is limited by the formula:

$$Steps \times Number\ of\ Cycles \leq 65000$$

Usually this will enable you to collect a maximum of between 8 and 100 scans (depending on your parameters). Of course if you require more cycles you can always start the experiment over again or set a Macro to repeat the experiment as many times as you like. There will however be a short interval between each experiment.

The View button

View...

The quickest way to determine if the parameters you have set will work is to click the view button. If the parameters you have set are OK then the Waveform Overview window will appear (Figure 7–21)

---

with a representation of the potential waveform. If for any reason the values you have set are out of range or inappropriate you will be prompted by a dialog box telling you what the problem is:

Figure 7–21
The Waveform Overview dialog box for Cyclic Voltammetry.
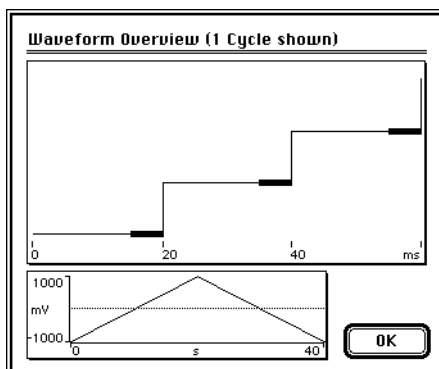
Cyclic Voltammetry with 3rd Party Potentiostats

The PowerLab Potentiostat will automatically isolate the electrodes after the scan but if you are using a third party potentiostat you may wish to set the Cleaning Potential equal to the Final Potential for some seconds. This will give you time to isolate the electrodes before the signal from the PowerLab is switched to zero volts. Similarly the rest time can be extended to give you time to switch the potentiostat from 'standby' to 'real' mode before the scan commences.

MultiPulse Voltammetry

The MultiPulse Voltammetry technique allows you to generate your own waveform. This is constructed by the addition of a staircase ramp and one or two pulses per step of the ramp. These pulses may be either positive or negative and may be increased or decreased throughout the scan. Using this dialog the operator is able to define any one of a number of regularly used techniques. There is also the added flexibility of being able to define an unusual pulse sequence. In addition up to four current sampling windows can be selected with their position and duration independently set.

A library of different signals, that can be used at any time, can be achieved by writing Macros that include the Multi Pulse method or by storing MultiPulse parameters in Settings files. This will allow you to automate your experiments.

Note that if you want to set up a non-standard or cyclic Square Wave voltammetry experiment then you will need to make the Pulse Width exactly half the Step Width. Remember to adjust the Sampling Display to i1-i2. Also MultiPulse Voltammetry results the default display is to plot current against the potential at the base of each pulse, whereas in the Square Wave Voltammetry technique the average potential over each step is used.

Parameters

To use the MultiPulse technique, select the Multi Pulse method from the Techniques menu. The MultiPulse dialog will appear (Figure 7–22).

Each parameter is altered by entering a new value in the appropriate box, selecting a new menu item, or clicking the control arrows. Changes take effect when the OK button is clicked. Click the Cancel button to exit without saving.

Ramp parameters

First the Ramp parameters are adjusted. These have a similar function to the parameters used for linear sweep voltammetry.

Figure 7–22
The Multi Pulse Voltammetry
Technique dialog box

Multi Pulse Voltammetry	Range: 2000mV ▼	Speed: 10kHz ▼

Ramp

Initial	-1000	mV
Final	-1000	mV
Rate	10	mV/s
Width	200	ms
Height	↕ 2	mV
Steps	2000	

☒ **Pulse 1**

Start	75	ms
Height	15	mV
Inc.	0	mV
Width	20	ms

☒ **Pulse 2**

Start	180	ms
Height	30	mV
Inc.	0	mV
Width	20	ms

Rest Time

| | 2 | s |

☒ Cyclic

[Params...]

[Sampling...]

[View...]

☐ **Deposition**

| Pot. | | mV | ☐ Stirrer |
| Time | | s | ☐ Gas |

☐ **Clean Time**

| Pot. | | mV |
| Time | | s |

[Cancel]

[OK]

Speed

The data acquisition rate is normally set at 10 kHz. Very slow rates (less than 1 mV/s) may require slower speeds so that appropriately long step widths can be used.


```
          100 Hz
          400
          1 kHz
          4
Speed: ✓ 10
```

Range

The range pop-up menu selects the full scale range of the applied potential. Three ranges are available, ±1000 mV giving 0.5 mV resolution, ±2000 mV giving 1 mV resolution, or ±5000 mV giving 2.5 mV resolution, Table 7–1. Usually the 2000 mV range is chosen.


```
             5000mV
Range: ✓ 2000mV
             1000mV
```

Initial (Potential)

This is the initial or starting potential of the ramp. This can be chosen between ± 2000 mV if on the 2000 mV range or ± 5000 mV when on the 5000 mV range.

| Initial | -1000 | mV |

Final (Potential)

| Final | 0 | mV |

The potential voltage at which the ramp waveform finishes. This can be set between ± 2000 mV if on the 2000 mV range or ± 5000 mV when on the 5000 mV range. It must not be the same as the initial potential. The final potential may be either more negative than the initial potential (negative scan) or more positive than the initial potential (positive scan).

(Scan) Rate

Rate `100` mV/s

This sets the rate at which the ramp will be generated in mV per second. It is usually set less than 1 mV s^{-1} for corrosion work or in the range of 5 to 1000 mV s^{-1} for other work. Faster scan rates lead to a higher background signal.

(Step) Width

Width `20` ms

The time that the potential is kept constant at each step. Step Width is related to Step Height and Scan Rate by:

$$StepWidth = \frac{StepHeight}{ScanRate}$$

(Step) Height

Height `2` mV

The size of each step. The value of this parameter will depend on the experiment being performed. But it is usually less than 10 mV.

Steps

This is simply a readout value showing the number of steps in the ramp according to the initial and final voltages and the step height set in these text boxes. The relationship between the number of steps and the other parameters is:

$$Steps = \frac{|FinalPotential - InitialPotential|}{StepHeight}$$

Rest Time

Rest Time `2` s

This is the period between when the deposition potential is applied and the scan commences. This is usually set to between 1 and 5 s, or longer for corrosion work.

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Cyclic

Clicking the Cyclic checkbox will activate the Params... button. This also automatically sets the Final Potential equal to the Initial Potential (so that the cycle will be complete)

Params...

Clicking the Params... button brings up the Cyclic Parameters dialog box, Figure 7–23, so that a cyclic waveform can be set up. You can enter the Upper and Lower Limits of the scan, the Number of Cycles to be performed, and the Initial Direction of the scan (if the Initial Potential lies between the extremes of the Upper and Lower Potential. See the section on Cyclic Voltammetry for more information on the operation of these parameters.

Figure 7–23
The Cyclic Parameters dialog box

Defining pulses
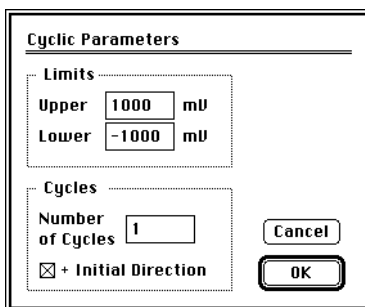
⊠ Pulse 1
Start   75   ms
Height   15   mV
Inc.   0   mV
Width   20   ms

For each step of the staircase ramp two pulses may be used. Each pulse is activated by clicking the box in the upper left-hand corner of the pulse panel, and now the relevant parameters can be entered.

(Pulse) Start

Start   75   ms
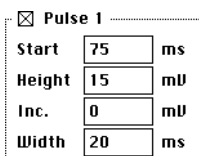
The timing of each pulse is linked to the start of each step in the base ramp. For example if you enter 20 ms in the Start box it means the pulse will be activated 20 ms after the beginning of the step. The pulse can begin at any time during each step and must be less than the Step Width. If you are using a PowerLab/200, /400, /800 or /2e, /4e or /8e then try to avoid starting pulses at 0 ms or starting two

pulses at the same time when constructing a waveform. There will be a short delay (a few microseconds) between the beginning of apparently concurrent events. Often a waveform of the same shape can be construct by placing the pulse towards the end of the step. The PowerLab/4s, /4SP, /8s and /16s do not suffer these limitations.

(Pulse) Height

Height 15 mV

The height of the pulse superimposed upon the potential ramp. Note that the value for the height of the pulse is added to the potential of the staircase ramp. If two pulses are made to overlap then the ramp and pulse potentials are all added together over this period.

Inc(rement)

Inc. 0 mV

Pulses on successive steps will be incremented by this amount.

Width

Width 20 ms

The duration of the pulse must be such that the entire pulse occurs within one step of the potential ramp.

This is best explained by examples. The dialog box shown in Figure 7–24 sets up two simple pulses, each 100 ms long, on each 500 ms step of the ramp. Clicking the View... button Waveform Overview window displays the appearance of several steps of the ramp, Figure 7–25.
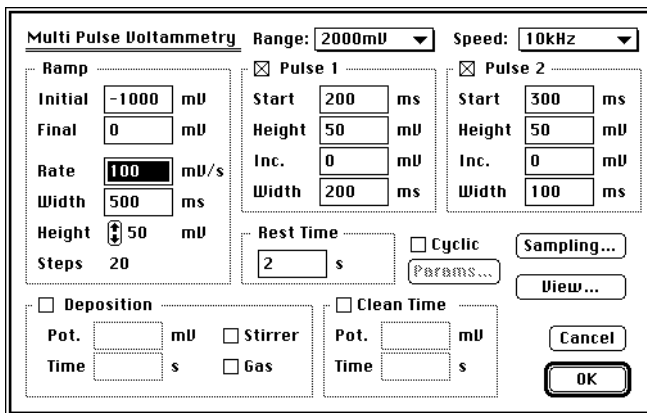
The Sampling Dialog

Sampling...

By clicking the Sampling... button in the Multi Pulse dialog the Sampling Time dialog in Figure 7–26 is activated. This dialog box allows you to nominate the current sampling periods. This involves choosing the time and duration of each of up to 4 sampling periods (i1, i2, i3, and i4).

The dialog box is divided into four panels which control each of the four sampling periods available.

Figure 7–24
An example of settings for the Multi Pulse dialog box.

Figure 7–25 the Waveform Overview dialog generated by the settings shown in Figure 7–24

Figure 7–26
The Sampling Time dialog box for Multi Pulse voltammetric techniques.

Each sampling period is activated by clicking the check box in the top corner of each panel. The Start text box defines the commencement of each sampling period with respect to the beginning of each step of the ramp. The relative position of each sample period on the step can be seen at the bottom of the dialog box (Figure 7–26).
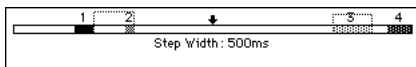
Note that all sampling periods must be in chronological order. That is point 1 must precede point 2 and so on. Also it is not possible to overlap sampling periods.

Sampling periods that are multiples of 20 ms will discriminate against 50 Hz mains frequency noise (or use a multiple of 16.7 ms for 60 Hz mains).

EChem normally plots the current versus the computed potential of the base ramp within each step. However it is also possible to actually measure the potential at any time along the step. To sample the potential at a specific point use the 'E sample' sub dialog

Select either Calculated (to used the computed potential) or Sampled. Selecting Sampled then allows you to nominate the position along each step that the potential is sampled. These sampled potentials are then used when you display your results in I vs E, E vs I, or IE vs t modes.
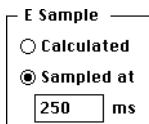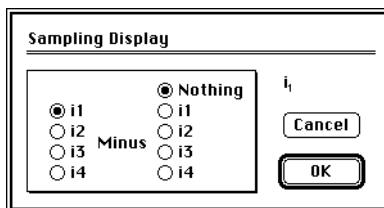
Displaying Multi Pulse Data

Selecting Sampling Display... in the Display menu brings up the corresponding dialog, Figure 7–28, which can be set to display a graph of the values in i1, i2, i3 or i4, or the difference between any

two of these. If you require to display more complicated functions you will need to transfer the data to a spreadsheet or graphing application.

MultiPulse Amperometry

The MultiPulse Amperometry technique allows you to perform constant potential and pulsed amperometric, and some voltammetric experiments. The applied waveform is constructed by the addition of up to two pulses on a base potential. These pulses may be either positive or negative and may be increased or decreased throughout the scan for voltammetric work. You are able to define any one of a number of regularly used methods. There is also the added flexibility of being able to define an unusual pulse sequence. In addition up to four current sampling windows can be selected with their position and duration independently set.

A library of different signals, that can be used at any time, can be achieved by writing Macros that record your methods or by storing parameters in Settings files. This will allow you to automate your experiments.

Parameters

To use this technique, select the Multi Pulse Amperometry from the Techniques menu. The dialog shown in Figure 7–29 will appear.

Figure 7–29
The Multi Pulse Amperometry dialog box.

Each parameter is altered by entering a new value in the appropriate box, or selecting a new menu item. Changes take effect when the OK button is clicked. Click the Cancel button to exit without saving.

Base potential

First the base potential is set. This must be within the extreme values of the Range setting.

Potential `500` mV

Speed

The data acquisition rate is normally set at 10 kHz. Very long sampling periods may require slower speeds. Up to 4095 samples can be averaged in one sampling period.

```
100 Hz
400
1 kHz
4
Speed: ✓10
```

Range

The range pop-up menu selects the full scale range of the applied potential. Three ranges are available, ±1000 mV giving 0.5 mV resolution, ±2000 mV giving 1 mV resolution, and ±5000 mV giving 2.5 mV resolution.

```
         5000mV
Range: ✓2000mV
         1000mV
```

Steps

The total number of steps taken during the experiment is entered here and must be less than or equal to 16000.

Steps `1000`

Step Width

The time taken for a single step of the experiment (base potential + pulse 1 + pulse 2) during the experiment:

Width `20` ms

Duration

The Duration is the total time taken for the experiment and is automatically calculated:

Duration 3 min 20 s

$$Duration = Steps \times StepWidth$$

Rest Time

This is the period after the deposition potential is applied and the scan commences. This is usually set to between 1 and 60 s, or longer for corrosion experiments.

Rest Time `2` s

Defining pulses

For each step up to two pulses may be applied. Each pulse is activated by clicking the box in the upper left-hand corner of the pulse panel, and now the relevant parameters can be entered.

(Pulse) Start

The timing of each pulse is linked to the start of each step. For example if you enter 100 ms in the Start box it means the pulse will be activated 100 ms after the beginning of the step. The pulse can begin at any time during each step but the start time must be less than the Step Width

(Pulse) Height

The height of the pulse. Make sure that the sum of the base and pulse potentials does not exceed the Range setting.

Note that the value for the height of the pulse is added to the base potential. If two pulses are made to overlap then the base and two pulse potentials are all added together over this period.

Inc(rement)

Pulses on successive steps will be incremented by this amount. If you enter a non zero value you will probably be doing a pulsed voltammetric experiment ie the potential will be changing in a ramp-like manner during the experiment.

Width

The duration of the pulse must be such that the entire pulse occurs within one step of the experiment.

This is best explained by examples. The dialog box shown in Figure 7–30 sets up two simple pulses, each 100 ms long, on each 500 ms step of the experiment.

Figure 7–30
Example settings for Multi Pulse Amperometry experiment.

Figure 7–31
Waveform overview for the settings in Figure 7–30.
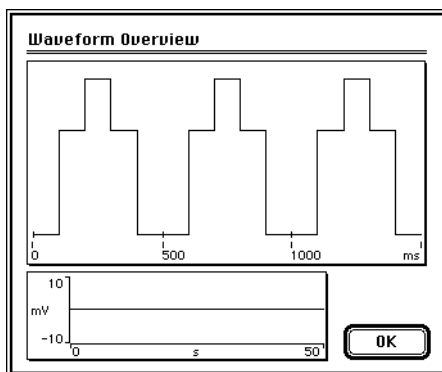
By clicking the View... button the Waveform Overview window displays the appearance of several steps of the ramp, Figure 7–31.

The Sampling Dialog

[Sampling...]

By clicking the Sampling... button in the Multi Pulse dialog the Sampling Time dialog in Figure 7–26 is activated. This dialog allows you to nominate the current sampling periods during each step by entering the time and duration of each of up to four periods (i1, i2, i3, and i4).

The dialog box is divided into four panels which control each of the four sampling periods. Adjust the parameters in the same manner as

described for the Sampling Dialog in the MutiPulse Voltammtery Technique.

Sampling periods that are multiples of 20 ms will discriminate against 50 Hz mains frequency noise (use a multiple of 16.7 ms if your main power is at 60 Hz).

Displaying MultiPulse Amperometric Data

Display

Display Settings...	
Go To Page...	⌘G
Show Overlay	
Overlay All	⌘A
Overlay None	⌘H
Overlay Display Settings...	
Sampling Display...	
Don't Subtract Background	
Set Background	
Clear Background	

For existing data the Sampling Display... command, in the Display menu, brings up the Data Selection dialog, Figure 7–28, which is can be set to display i1, i2, i3 or i4, or the difference between any two of these. If you require to display more complicated functions you will need to transfer the data to a spreadsheet or graphing application.

The Apply Technique... command

An EChem file may contain many different types of experiment that have employed one or more techniques with different parameters. You may occasionally want to use the technique and parameters of a particular page (run) for your next scan. Click on the page button of the that required to display it. Next go to the Apply Technique... command in the Techniques menu. This will bring up the parameter entry dialog with the settings used for that run. You can modify any of the parameters if desired. When you click OK you are ready to begin the next scan using these parameters.

Polarographic Techniques

TTL logic signals are a simple means of on/off communication between instruments. 'TTL high' corresponds to a voltage level of about 5 V, while 'TTL low' corresponds to a signal of about 0 V. These states are controlled in software by a 'bit' variable which is referred to as being set on or off.

Figure 7–32
The Digital IO panel. Output 3 is shown on, while outputs 1, 2, and 4, are shown off. On most PowerLab e models only Outputs 1 and 2 are shown.

If you are using a PowerLab S or ST model or PowerLab/800, or MacLab/8e, then the use of dropping mercury electrode (DME) is facilitated by the provision of a synchronized TTL pulse signal (of about 5 V amplitude and 10 ms duration) at the beginning of each step. This pulse is carried by 'Output 4' of the TTL digital output lines accessed at the back of the PowerLab unit. Consult your *PowerLab Owners Guide* for pin connection information.

This signal is provided for all EChem techniques all the time. However, as the duration of the TTL pulse is 10 ms, your technique must employ a step width of greater than 10 ms so that the signal can return to its resting state between steps. Thus the drop rate must be significantly less than 100 per second. Note that the TTL signal is provided for timing purposes only, and that there is not enough current available (about a milliampere) to actually drive a solenoid drop hammer directly. In such cases you will need to construct a suitable amplifier/power source for your DME.

In addition 'Output 3' of the digital output (PowerLab S and ST models and PowerLab/800 or MacLab/8e only) is set 'on' at the beginning of each scan and turned 'off' at then end of the experiment. If you want to do a series of sweeps with a hanging mercury drop electrode (HMDE), with a new drop for each experiment, then this signal can be used. Outputs 1 and 2 are described on page 138.

You can monitor or manually control the digital output signals by activating the Controls subcommand in the Preferences command in the Edit menu (ie Edit/Preferences/Controls), Figure 6–1, and then select the Digital IO display panel control. The Digital IO panel, Figure 7–32, will now be shown at the right of the screen. When EChem is scanning the indicators for outputs 1, 2, 3, and 4 will turn green when they are active. When EChem is not scanning you can click on the indicators, this will turn on the relevant output and the indicator will be shown as green. Manual operation of the outputs is useful for testing you connection cable, but it is overridden by automatic operation when a scan is commenced. The indicator for Output 4, (10 ms pulses for drop hammer synchronisation) usually appears off during a scan because the 10 ms pulses are too short for the screen display.

8 Additional Techniques
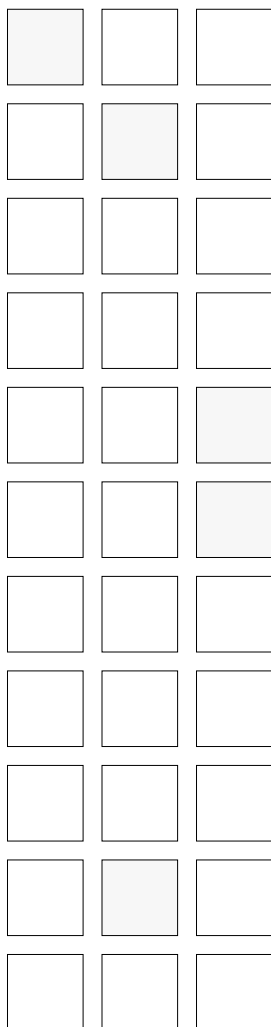
Apart from the EChem software, additional electrochemical techniques can be performed with PowerLab using the Chart and Scope software.

Also discussed is the use of the ADInstruments Potentiostat when configured as a Galvanostat with Chart and Scope software.

Introduction

In addition to the EChem techniques, you can also use the Chart and Scope applications to perform or monitor the following experiments:

- AC voltammetry — use Chart or Scope to monitor, or Echem to provide a staircase ramp waveform;

- Chronoamperometry — use Chart or Scope to monitor or to provide a square wave signal;

- Chronocoulometry — use Chart or Scope to monitor and integrate the current signal or to provide a square wave signal;

- Chronopotentiometry — use Chart or Scope to monitor the potential signal or to provide square wave signal;

- Fast scan techniques — use Chart or Scope to monitor, or use Scope to provide a potential ramp (up to 500 V/s) signal to potentiostat, and to subtract charging current contributions;

- Controlled Potential or Controlled Current Electrolysis and Electrosynthesis — use Chart or Scope to monitor or to provide a potential signal to the potentiostat;

- Rotating Ring Disk Electrodes — use Chart to monitor up to two current and two potential signals with, for example, a PowerLab/400 or /4SP;

- Titrimetry — use Chart or Scope to monitor the current signal from the amperometric or potentiometric sensor. The ADInstruments μPump can be used as an autoburette;

- Quartz Crystal Microbalance experiments — use Chart software to monitor potential current and mass changes;

- Amperometric detection (for chromatography) — use Chart to monitor the output from the detector; and

- Monitoring of meters for biosensors, pH and ion selective electrodes, conductivity electrodes and dO_2 sensors.

AC Voltammetry

EChem is not specifically designed for AC voltammetric studies but there are several ways to use your PowerLab with this technique. If your existing potentiostat or waveform generator system can perform AC voltammetry then you can use your PowerLab with Chart or Scope to record the results. Your PowerLab now replaces a conventional chart recorder.

Alternatively EChem can drive such a potentiostat using the Linear Sweep or Cyclic Voltammetry modes. The potentiostat can be used to provide an AC waveform. Provided the step width of the staircase ramp generated by EChem is very much longer than the period of the AC waveform then you will get good results. For example if your AC excitation is 20 Hz, with a period of 50 ms, then you should ensure that the step width is at least 200 ms.

You can also use EChem and a PowerLab connected to a potentiostat, AC waveform generator and AC lock in amplifier. Both the EChem and the AC waveform can be summed into the potentiostat. Again make sure that the step width of the staircase ramp is much longer than the period of the AC waveform.

Fast Scan Techniques

Some techniques using microelectrodes require very fast scan rates. EChem is designed for electrochemical techniques where very high speeds are not required. The minimum step width allowed in EChem is 0.1 ms, Table 7–1. You will find that this will allow scan rates of up to about 80 V/s (with PowerLab 's' models) or about 30 V/s (with other PowerLab models) and still maintain adequately small step heights in the applied potential ramp. If you require faster scan rates for linear sweep or cyclic voltammetry, then you should use Scope or Chart. Both Chart and Scope incorporate Stimulator and Output Voltage commands which can be used to control the analog output of the PowerLab and to create a waveform suitable for driving a potentiostat.

Chart and Scope can sample up to 40,000 points per second on two channels or up to 10^5 points per second on one channel. You can make use of these features in a number of ways:

- if you are using a third party potentiostat capable of fast scan rates then you can use Scope as a storage oscilloscope for recording data. Up to 2560 points can be collected on one channel at a rate of up to 100 kHz, or up to 40 kHz on two channels.

- with Chart software you can monitor one channel continuously up to 200 kHz (PowerLab/4SP, /8SP, or /16SP) or 1 kHz (PowerLab/200, /400, /800). On the slower models you can also record in snapshot mode up to 16000 points at up to 100 kHz on a single channel.

Remember that Chart or Scope data is not averaged from a series of readings over a finite 'sampling period', as it is in EChem. Each data point corresponds to only one sampling of the signal, thus you may find that noise is more troublesome when recording at high speeds.

Read the Chart and Scope *User Guides* for further information on how to set up your experiment.

The PowerLab/4SP, /8SP, and /16SP models have extended high speed sampling:

- using Chart a single channel can be recorded at 200 kHz indefinitely to hard disk (or 100 kHz if using USB interface). Similarly 2 channels can be recorded at 100 kHz, 3 or 4 channels at 40 kHz, and 5–8 channels at 20 kHz, and 8–16 channels at 10 kHz, all continuously to hard disk.

- in both Chart and Scope the PowerLab stimulator (waveform generator) can be used at even the fastest sampling rates.

Fast Cyclic Voltammetry

Scope software has a number of features that facilitate Fast Cyclic Voltammetry (FCV). The base potential is set by using the Constant Output dialog box while the waveform is generated using the Stimulators Up & Down or Triangle waveforms (Figure 8–1). See the *Scope User Guide* for further details.

Figure 8–1
Setting up the Stimulator in
Scope to perform Fast Cyclic
Voltammetry
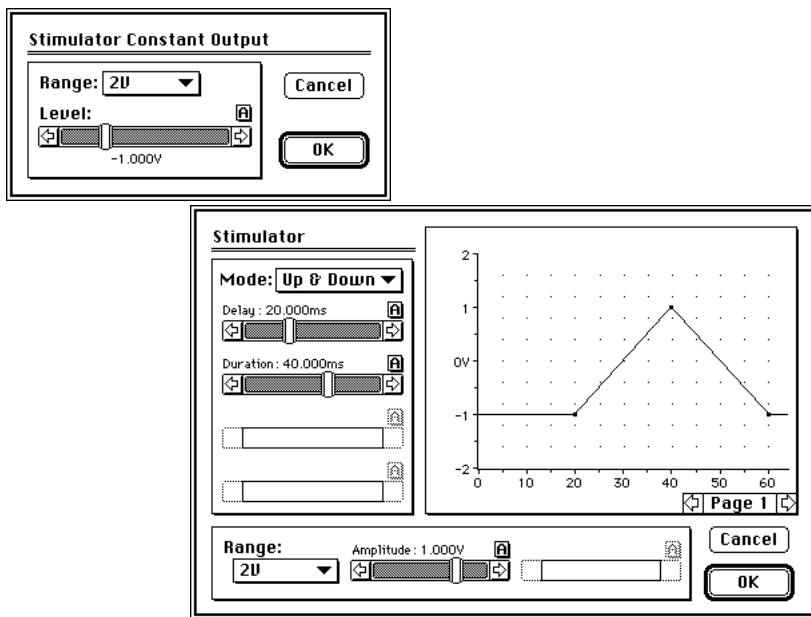
The base potential has been set to –1.00 V and a potential ramp has
been set up to go from –1.00 to +1.00 V and back again over a period
of 40 ms using the Up & Down waveform option. This corresponds to
a scan rate of 50 V/s.

Figure 8–2 shows an example of a positive and negative cyclic
waveform. The base potential has been set to +0.20 V and a potential
ramp has been set up to go from +0.20 to +0.80 V back again to -0.40
V and finally return to +0.20 V, over a period of 20 ms using the
Triangle waveform option. This corresponds to a scan rate of 120 V/s.

The Triangle waveform option always starts a scan in the centre of the
potential limits, while the Up & Down waveform option starts a scan
at one or the other potential limits.

When performing FCV a large background charging current is often
recorded. This can be a hundred times larger than the signal you are
looking for. Fortunately the charging current is highly reproducible
between scans and can be subtracted out: a background scan is
obtained, and then the run repeated on a new 'page' where the
compound of interest (often a neurotransmitter) is present. Make sure

Figure 8–2
Cyclic voltammetry using
Scope and the Stimulators
Triangle waveform option
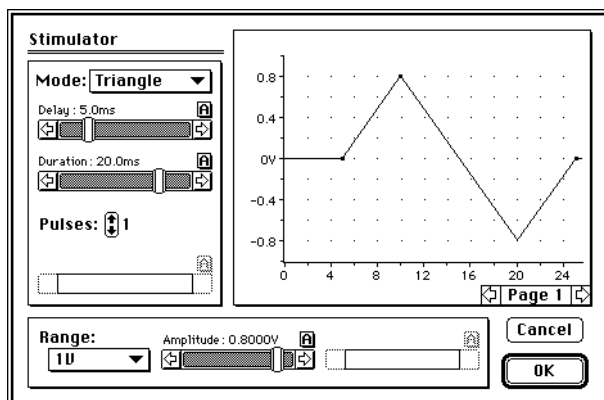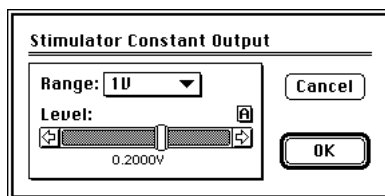
that the two scans are run at the same gain setting. Select the Scope page that contains the background scan then use the Set Background command — this will subtract this scan from all other pages in the file. Use the Don't Subtract Background command to cancel subtraction, and the Clear Background de-identifies the background page. See the *Scope User's Guide* for more information.

Low Current Experiments

Some experiments using microelectrodes (especially when used in organic solvents, or for in vivo studies) require the measurement of extremely small currents. You can use the PowerLab system to perform electrochemistry on such systems provided that you have a suitable potentiostat available.

If you are using microelectrodes the you may need the ADInstruments Picostat™ (under development at the time of writing) This has a thousand times the sensitivity of the ADInstruments Potentiostat. To minimize interference from noise, try to position the Picostat as close to the electrodes as possible, and shield the experiment well (usually by enclosure in a Faraday cage).

Another suitable instrument for microelectrode work is the BAS Low Current Module (available from Bioanalytical Systems Inc.). This system can be supplied with its own Faraday cage (the BAS C–2 Cell Stand) and has current ranges from 10 pA/V to 1 µA/V, with a maximum current of 12 µA. The current signal is amplified near the electrodes inside the Faraday cage. Your ADInstruments dealer can supply the necessary cables to connect your PowerLab unit to this system (see Chapter 9). Please note that the Low Current Module is directly connected to the PowerLab unit — no other potentiostat is required.

Chronoamperometry

These techniques require that a constant potential is maintained for a defined period while the current is monitored (chronoampero-metry). If the current signal is integrated with respect to time then the total charge transferred at the electrode can be calculated (chrono-coulometry).

For these techniques Chart and Scope (supplied with the PowerLab unit) can be used. PowerLab with Chart or Scope will allow you to perform Single, Double and even Multi-Step Chronoamperometry, with data collection taking place in milliseconds or over hours or even days if need be.

Chronoamperometry and Chart

Chart software can be used to output a constant potential (up to ±10 V) with a suitable potentiostat equipped with an external input (or the ADinstruments Potentiostat). The Timed Events (Setup menu) feature can be used to keep the potential constant for a fixed period of time, or even to drive the reaction backwards after the initial oxidation/reduction.

To adjust the potential you will first need to select the range by choosing the Constant Voltage command in the Setup menu to activate the Constant Output dialog, Figure 8–3. You can set the control voltage sent to the potentiostat by setting the slider bar or entering a value after clicking the A-button. The slider control, and the direct text entry available with A-button, both offer 12 bit resolution (0.024%) within each range (selected by the pull down).

This equates to 1 mV resolution if you use the ±2 V range, which is suitable for most experiments employing aqueous solutions.

Figure 8–3
The Constant Output Dialog box.

At the time of writing the control of the Stimulator with Chart software on Windows computers was still under development. There may be significant differences in its use.

Output Voltage control for PowerLab S series models)

Output Voltage control for PowerLab e series models
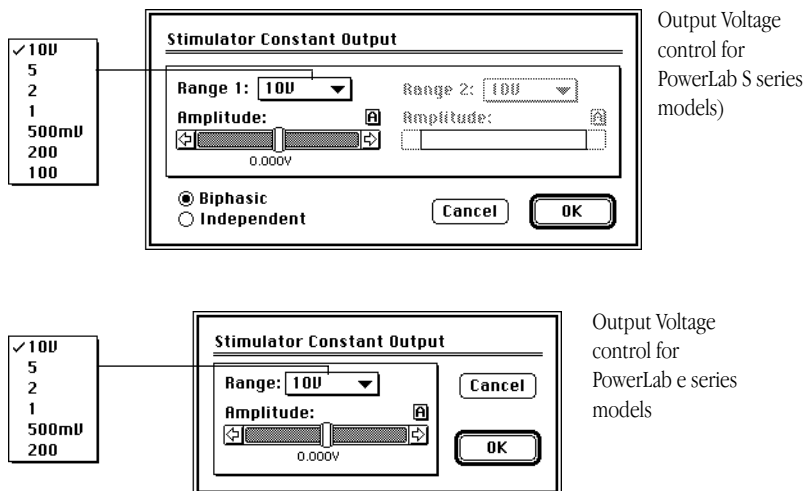
If you are using a bipotentiostat with a PowerLab S series model then clicking the Independent radio button, Figure 8–3, allows you to set two output voltages which can be sent to the two external inputs of the bipotentiostat.

The Chart software Stimulator command (in the Setup menu) can also be used to set up pulses, stepped pulses, and staircase ramp waveforms which the potentiostat will follow. PowerLab S series models can also be configured in Chart software to provide sinusoidal and triangular wavefunctions).

You can also use the Timed Events feature (Setup menu) to adjust the current at predetermined time intervals after the start of recording. For example the settings shown in Figure 8–4 will maintain a potential of 1.25 V for 30 minutes after which the potential will be decreased to 0.50 V in order to reverse the reaction, resulting in a Double Step Chronoamperometric experiment. Any number of steps at any potential could be set up with this feature.

At the time of writing the Timed Events feature was only available for Macintosh systems.

Timed Events can be slightly delayed by up to (0.1 s) depending on the model of computer and what else is happening. For fast charging and discharging systems it is better to use the Chart Stimulator.
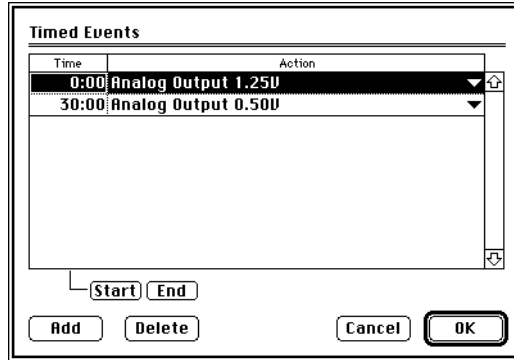
Using the Stimulator command in the Setup menu it is possible to
send and monitor pulses with a precision better than 1 ms. Pulses up
to 29.9 s may be created by this method. For further details on using
the Stimulator in Chart refer to the *Chart User's Guide*. An example
using the Chart Stimulator is shown in Figure 8–4.
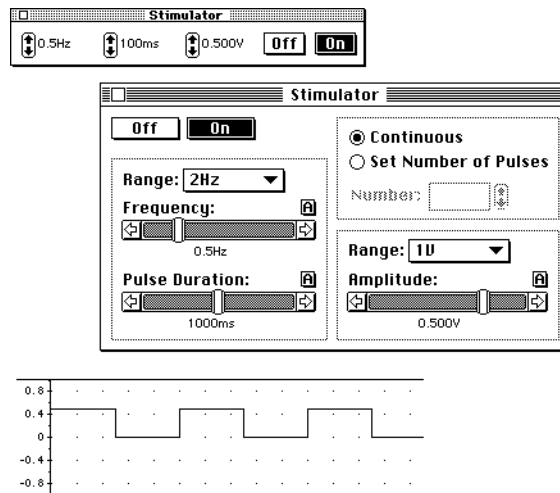
CurveFit

Curve fitting extension icon
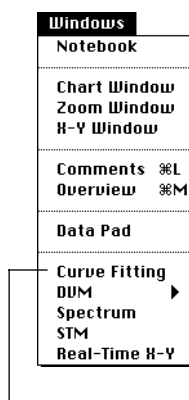
The Curve Fitting command is added to the Chart Windows menu if the Curve Fitting extension is installed

Analysis of Chronoamperomograms

The resulting chronoamperomograms obtained from a planar disk electrode should exhibit a current/time relationship governed by the Cottrell equation, Appendix D.

$$i = \frac{nFAD^{1/2}C}{1000\pi^{1/2}t^{1/2}}$$

You can use the Chart Curve Fitting command (Windows menu) to fit your data with a an idealised curve. This command will only be present if the Curve Fitting analysis extension is correctly installed in the Chart Extensions folder (adjacent to the Chart software icon on your hard disk). For instructions on the use of the extension also see Application note AN003 which can be downloaded from our web site at http://www.adinstrumnets.com.

It is usually easier to first simplify the Cottrell equation to:

$$i = \frac{a}{t^{1/2}}$$

where a is treated as an empirical constant to be determined. In addition it is unlikely that the results will decay to exactly zero current (due to convection currents in the vessel causing non-ideal diffusion) so a small non-zero constant, b, is added. Finally the equation is very sensitive to the exact instant when t is zero. This can be a problem if you have selected data very close to zero time (it is best to use the 't = 0 at start of block' option, Figure 8–7). To get a well behaved equation when the data selected start at very close to zero time it is usually best to initially add a small time correction, c, which will allow for the errors in your estimation of time zero, and the fact that the potentiostat will take a finite time to stabilise after the change in potential. Thus the final form of the equation to be fitted is:

$$i = \frac{a}{(t+c)^{1/2}} + b$$

This must be entered as a New Equation in the Curve Fitting extension the very first time you use it, Figure 8–6.

Figure 8–6
Entering an equation suitable
for the Cottrell equation

Figure 8–7
Fitting a Cottrell equation to
chronoamperometric data
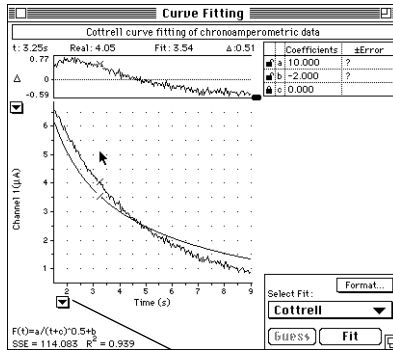
Usually use 't=0 at start of block'
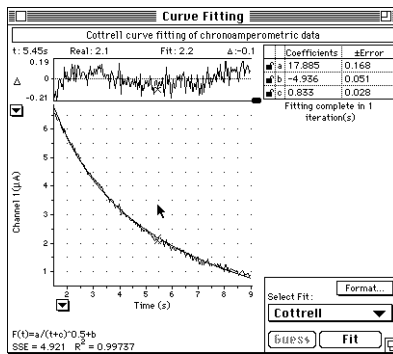
First lock the value for c, then type in guesses
for a and b until an approximate fit is obtained
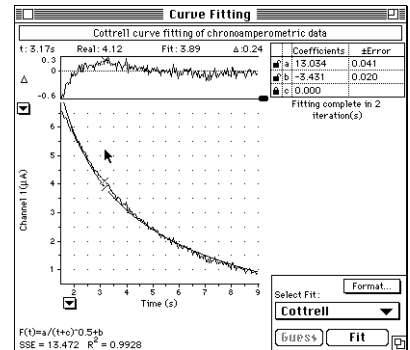
Iterate by clicking the Fit button, refining a and
b only. If the initial guesses are close enough
then better vales for a and b will be obtained.

Unlock c, and iterate again. A curve
of even better fit should be obtained.

After the file is saved the equation will be available whenever you open Chart data file on the computer or even when you transfer the data file to another computer. Some trial and error will be involved while you make guesses that are suitable for the initial values to commence iteration.

Because of the discontinuity that occurs when the denominator is zero problems can occur if the selected data starts at zero time (or close to zero time). In this case first try fixing c to a small positive value, and iterating for better values of a and b. Usually your data selection should not include data points very close to zero time (the potentiostat will require some time to settle — remember to have the potentiostat low pass filters turned off otherwise you may only be measuring the filter response time!), nor points taken at very long times when convection aided diffusion will produce non-ideal behaviour. The exact time period that is suitable will depend on the size of the electrode and the quality of the potentiostat and some trial and error to determine the best time interval will be required. After the better estimates for a and b have been determined c can be set free to refine during the next iteration cycle, Figure 8–7

Chronoamperometry and Scope

For chronoamperometric measurements, where you need to overlay the results of successive experiments, Scope will generally be the program of choice.

The total length of the experiment is chosen in the Time Base panel (128 s is usually sufficient, this is given by the 100 s setting). Up to 2560 data points can be collected in this period. The base potential is adjusted with the Output Voltage command (Setup menu) and is similar in function to the corresponding Chart software control shown in Figure 8–3.

The potential that will cause the reaction to proceed (and the time that it will be applied) is set using the Stimulator command in the Setup menu. In the example shown in Figure 8–9, after a period of 10 s at the base potential, two 30 s pulses of –0.70 V are to be applied each followed by a 30 s return to the base potential.

The experiment is usually first done on a blank solution containing only electrolyte, followed by a sample solution containing the
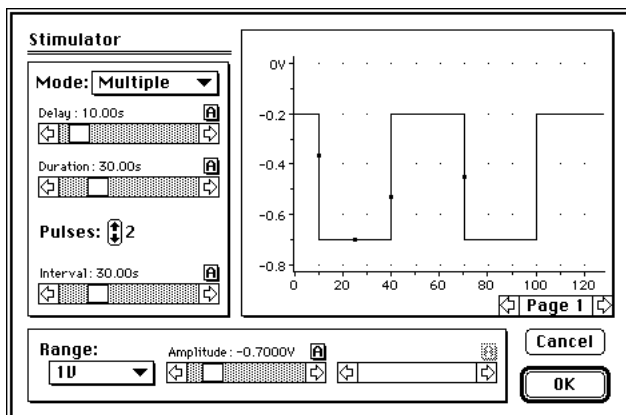
substrate. The data is collected on separate pages in Scope and the
blank subtracted with the Set Background command then cut and
pasted to a spreadsheet application so that the differences can be
plotted against $1/(\sqrt{t})$ in a Cottrell graph. For further details on using
Scope refer to the *Scope User's Guide*.

If you want to fit chronoamperomograms, that were collected with
Scope software, to the Cottrell equation the first import the data to
Chart software (see Application Note AN010 which can be
downloaded from our web site at http://www.adinstruments.com)
and then use the Curve Fitting extension discussed in the previous
section.

Chronocoulometry

Chart and Scope software have the ability to integrate an incoming
signal both in real time or off line. Since the total charge transferred
(the total number of coulombs, or electrons, transferred) is equal to
the integrated current, the settings used for chronoamperometry can
also be used for chronocoulometry. It is only necessary to set up an
unused channel (usually channel 3 if using Chart software) to be the
integral of the current monitor channel (usually channel 1). Note,
however, that the accuracy of this method is not as good as the results
that can be obtained from a precision coulometer. If you require very
precise results you should record the signal directly from such a
device.

In Scope software either of the two input channels can be integrated by choosing the Computed Functions option (Figure 8–9) in the Display menu. The Integrate function is chosen from the functions pop-up menu. The integrated channel will reset itself automatically if the integral goes off scale. This works in the same way as an integrating pen recorder would. Refer to the *Scope User's Guide* for more information.
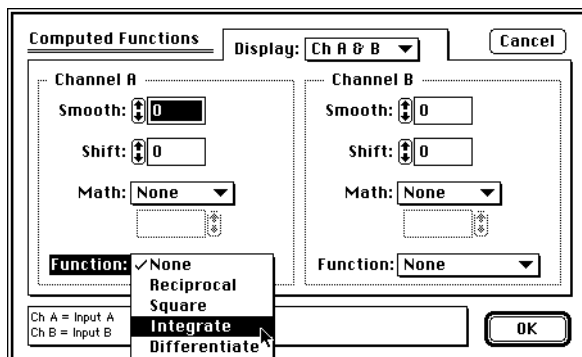
When using Chart software, any one of the unused channels can be setup to be the integral of the current channel. This is an on-line function so you need to record to display the integral. To setup integration you need to choose the Computed Input command from the Channel pop-up menu which brings up the Computed Inputs dialog box (Figure 8–10). Several integration options are available. For more information refer to the Computed Inputs sections in the *Chart User's Guide*.

EChem User's Guide
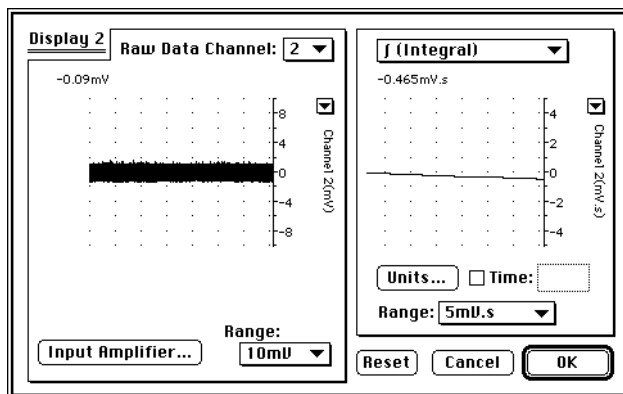
For post-acquisition integration of a signal recorded with Chart the 'Integral extension' can be used. This is particularly useful since the results can be recalculated from the original current signal at will. The on-line method will give good results only if the appropriate sensitivity range has been selected and it is not always possible to decide on this beforehand.

Chronopotentiometry

This technique requires that a constant current be maintained between the working and auxiliary (counter) electrodes. The potential at the working electrode is monitored. For many systems the potential will remain approximately constant until the electroactive species is consumed in the region of the electrode.

For this type of experiment it will be necessary to use a specialist galvanostat or to run your potentiostat in galvanostat mode (check the potentiostat's manual to see if your potentiostat can be used in this mode) and use Chart to record the data. The ADinstruments Potentiostat can be used in galvanostat mode using Chart or Scope software. If you are using a third party potentiostat/galvanostat you can set the potential from the front panel of the potentiostat and use Chart or Scope software to record the current and potential with time.

Alternatively once the galvanostat is set up, adjust Chart or Scope as you would for chronoamperometry. Remember, however, that the PowerLab output voltage will be converted to a current value by the galvanostat. In most cases this means that only small values should be used, < 100 mV, which would correspond to < 100 mA if a 1:1 correspondence is maintained by the galvanostat. This is because most galvanostats will not be able to generate voltages big enough to pass larger currents.

The ADInstruments Potentiostat as a Galvanostat

Like many other potentiostats, the ADInstruments Potentiostat can be configured for galvanostat operation (with Chart or Scope software). However since it is primarily designed for potentiostatic operation

you will need to take some extra care when setting it up as a galvanostat.

At the time of writing the control of the Potentiostat with Chart software on Windows computers was still under development.
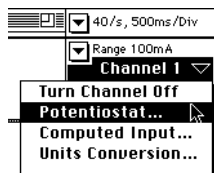
First find the Potentiostat menu item in the Chart software Channel menu
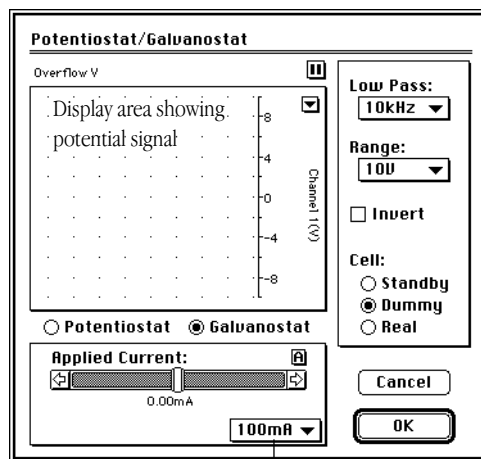
At each PowerLab control Output Voltage setting there are four current range settings available

First switch to the galvanostat mode of operation. Choose the Potentiostat item in the Channel menu to open the control window and turn on the Galvanostat and Dummy radio buttons, Figure 8–11.

The default setting is for zero current on the 100 mA range. It is likely that there will be a small residual offset at this setting which will cause the Potentiostat/Galvanostat to go off scale (over 10 V) in standby mode (as it is connected to the internal 100 kΩ dummy cell). Try selecting the 1 µA or 10 µA range, where the offset will be correspondingly smaller, and the signal should come on screen and be close to zero volts.

The PowerLab control voltage can be set using the Chart software Output Voltage command in the Setup menu. You can select a range of 100 mV to 10 V in 1:2:5 increments on most models, or 200 mV to 10 V on PowerLab /200 and /400 models, Figure 8–3.

At each of the Output Voltage range settings the ADInstruments Potentiostat/ Galvanostat offers four current range settings when in Galvanostat mode, Table 8–1. The most accurate control is achieved by using the largest possible Output Voltage range with the smallest

possible Galvanostat range setting. The resolution within each range is 12 bits or 0.024% of the range setting.

You can use the slider bar, or the A-button to adjust the current within the selected range. The resulting potential signal is shown in the display area. Remember to set the radio button back to Standby before you return to the main Chart window.
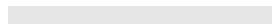
Table 8–1   Galvanostat range settings available for each Output Voltage range of the PowerLab unit, when using the ADInstruments Potentiostat in galvanostat mode.

Output Voltage Range	Galvanostat Range Settings			
10 V	1 µA	10 µA	1 mA	100 mA
5 V	500 nA	5 µA	500 µA	50 mA
2 V	200 nA	2 µA	200 µA	20 mA
1 V	100 nA	1 µA	100 µA	10 mA
500 mV	50 nA	500 nA	50 µA	5 mA
200 mV	20 nA	200 nA	20 µA	2 mA
100 mV *	10 nA	100 nA	10 µA	1 mA

* This setting not available on some PowerLab models (for example PowerLab/200 and /400).

If you are using a PowerLab/200 or /400 with Multiport connection to the Potentiostat/Galvanostat then when you return to the main Chart window and begin recording — the potential signal will be shown on channel 2 and the current signal on Channel 1. If you are not using a Multiport cable then the current and potential signals will be recorded on the channels you have used to connect the Potentiostat/Galvanostat. The current channel will automatically have had Units Conversion applied to it so that the display is correctly shown in units of nA, µA or mA.

You can now control the current passed by the Potentiostat/Galvanostat by setting the Output Voltage slider bar or entering a value after clicking the A-button. However you will be adjusting the PowerLab control voltage which is reinterpreted as a current value by the galvanostat. For example if you have selected a PowerLab Output Voltage of 500 mV, and a current range of 50 µA you might now wish

to do an experiment where the current is held at a constant 35 μA (or $35/50 \times 100 = 70\%$ of the range setting). You should now set the slider control of the Output Voltage control to a value of 70% of 500 mV, that is to 350 mV. Remember that the use of + and – voltages determine the direction of current flow (into or out of the working electrode).

The Chart software Stimulator command (Setup menu) can also be used to set up pulses, stepped pulses, and staircase ramp waveforms which the galvanostat will follow (PowerLab/4sp, /8sp, or /16sp models can also be configured in Chart software to provide sinusoidal and triangular wavefunctions). You can also use the Timed Events feature (Setup menu) to adjust the current at predetermined time intervals after the start of recording.

Operation of the Potentiostat/Galvanostat with Scope software is similar but a wider variety of waveforms can be used.

Consult the Chart and Scope User's Guides for more details of the Output Voltage, Stimulator, and Timed Events features.

Controlled Potential Electrolysis and Electrosynthesis

These techniques are essentially the same as chronoamperometry. A constant potential is applied at the working electrode which is sufficient to oxidize or reduce the substrate. As the electrolysis continues the substrate is eventually completely consumed and the current will decrease to a residual value. Both the potential and the current flow can be monitored with Chart in the same way as for chronoamperometry. The integrated current (i.e. the total charge transferred) can also be determined which can be used to determine the extent of reaction.

A potential should be chosen which is at least 50 – 200 mV more oxidizing (or reducing) than the half potential in order to ensure complete reaction of the substrate. It is important to separate the auxiliary (counter) electrode from the electrochemical cell by means of a salt bridge. This is due to the build up of reduction products in the region of the auxiliary electrode which could react with the products of oxidation at the working electrode (or conversely

products of oxidation will build up around the auxiliary electrode if reduction is taking place at the working electrode). The working electrode is constructed to have a large surface area so that a greater amount of material can be electrolyzed in a small time, thus a plate or gauze electrode is usually chosen.

It is usual to stir the solution during electrolysis in order to bring a fresh supply of substrate into contact with the working electrode.

For the conversion of large amounts of substrate (> 100 mg) in reasonable times relatively high currents must be passed through the cell. A potentiostat capable of a maximum current of at least 100 mA, or even 1 A is required. For the electrosynthesis of organic compounds in highly resistive non-aqueous solvents the addition of a large amount of electrolyte is necessary to sustain the current flow (which can sometimes lead to difficulties in later separation of the product), as is the use of a high compliance potentiostat. For studies using water as the solvent the addition of a small quantity of acid (or base) can increase the conductivity of the cell greatly, without having to add large amounts of electrolyte.

Controlled Current Electrolysis and Electrosynthesis

These techniques are essentially the same as chronopotentiometry and require the use of a galvanostat (or constant current source and voltmeter). A constant current is applied between the working and auxiliary electrodes and the potential at the working electrode is monitored as the substrate is oxidized or reduced. As the electrolysis continues the substrate is eventually completely consumed and the potential will alter as the galvanostat tries to maintain a constant current. Both the potential and the current flow can be monitored with Chart software. The integrated current (i.e. the total charge transferred) can also be determined which can be used to determine the extent of reaction.

Electrosynthesis reactions are often more quickly carried out under constant current conditions (especially if there are no competing redox reactions at nearby potentials) than under constant potential conditions.

It is important to limit the current so that the potential stays within the compliance voltage of the galvanostat, at least until the reaction of interest is complete.

Many potentiostats can be used in galvanostat mode — consult the instrument manual to see if this is possible. The use of the ADInstruments Potentiostat in galvanostat mode is discussed above: See "The ADInstruments Potentiostat as a Galvanostat" on page 175.

Rotating Ring Disk Electrodes

A rotating ring disk electrode (RRDE) consists of two electrodes: an inner circular cross section electrode; and an outer, concentric, annular electrode. Both the disk and the ring can be controlled independently by two separate potentiostats or with a bipotentiostat. Rotation of the electrode causes hydrodynamic flow such that the solution is moved onto the disk from the bulk solvent then pushed outwards towards the ring. Thus the RRDE can be used to measure rates of various redox reactions, using the ring as a detector and the disk as a generator of various electroactive substances.

Much RRDE work will require at least a four channel PowerLab unit (for example a PowerLab/400) as the potential and current flows of both (or either) the ring or disk will need to be monitored.

A typical experiment would use a PowerLab/400 with Chart to record the results. The current at the ring is held at a constant oxidizing potential to detect any reduced species formed at the disk. The disk potential is swept over a range of potentials in order to generate various reduced species in solution. Because the ring potential is held constant it does not need to be monitored. But we will need to plot both the disk and ring currents against the disk potential so each of these must be recorded. The Chart X-Y Window command (Windows menu) can be used to plot the results on one channel versus another.

Amperometric Titrimetry

Titrations can be performed in an electrochemical cell where the working electrode is held at a constant potential while the current is

monitored. As the electroactive species is consumed during the titration the current decreases.

The ADInstruments µPump, can be used to deliver 50 µL aliquots of titrant to a vessel with a coefficient of variability of 0.3%. It is suitable (after calibration) for performing titrations on a scale similar to that used with a conventional 25 or 50 mL burette. Monitoring such a titration is best achieved with Chart software, plotting volume and current flow on separate channels. Chart also has the ability to perform XY plots so that current can be plotted against volume of titrant added.

Liquid Chromatography Detectors

Electrochemical detection can be an extremely sensitive technique for liquid and high–pressure liquid chromatography (LC and HPLC). The method is essentially chronoamperometry on a flowing sample. A flow–through cell must be purchased or constructed.

Chart can be set up to drive the potentiostat at a constant potential for an indefinite period. Alternatively the potentiostat can be set to provide a fixed potential. The potential is chosen such that the substrate will be oxidised or reduced as it passes through the electrochemical cell. The current is monitored continuously. As the substrate passes through the cell an increase in the current occurs, the current then peaks and subsides as the substrate is pushed out of the cell by new carrier solution.

Chart can also be used to monitor the outputs of other detectors connected to other channels of the PowerLab. Thus using a PowerLab/400 you could monitor output from an electrochemical, uv-visible, refractive index, and fluorescence detector, simultaneously. In addition four virtual channels of data can be constructed using the computed functions dialog to monitor the integrated signals (or their differentials) from each of the detectors. Refer to the *Chart User's Guide* for further details.

For more extensive chromatographic use, PowerChrom software is also available for use with PowerLab units. It can acquire and analyze

data, and supports autosamplers and fraction collectors. The ADinstruments Potentiostat can be used as a low cost electrochemical detector for chromatography systems when used in conjunction with Chart or PowerChrom software. Ask your ADInstruments dealer for more information.

Biosensors

Biosensors are usually of the potentiometric, amperometric or conductiometric varieties (see the following sections). Usually ordinary pH meters or high impedance voltmeters can be used for the potentiometric type. The amperometric variety usually require a special meter that has an adjustable polarizing potential and a variable gain ranges suitable for the currents being measured (see Appendix F). The conductiometric types may work with an ordinary conductivity meter but may have special requirements in terms of the frequency of AC excitation or the range of conductances to be measured. Any 'biosensor' meter with an analog recorder output can be connected to a PowerLab unit.

Potentiometric sensors

As their name suggests these sensors measure potential, and there output can always be monitored in units of millivolts or volts. In some cases it is more convenient to convert this signal to alternative units such a pH or log[Na] to give a more direct indication of the type of measurement being carried out. Virtually all these sensors can be monitored by connection to a pH meter or other high impedance voltmeter.

pH Electrodes

The impedance of the PowerLab inputs is 10^6 Ω which is unsuitable for direct connection to the very high impedance signals produced by glass pH electrodes. For these electrodes a high impedance preamplifier (a pH or ISE meter with an impedance of $>10^{12}$ Ω) must be used between the electrodes and the PowerLab. The ADinstruments pH Amp is also suitable for most pH and

combination pH electrodes – contact your local ADInstruments dealer for details.

Some pH meters give an output which is directly proportional to the pH reading on the meter. If this is the case then refer to the meter manual to find the relationship between the analog signal (in mV) and pH. Often the correspondence is 0 mV = pH 0, and 1400 mV = pH 14, in which case the units conversion feature of Chart can be set up as show in Figure 8–12

Figure 8–12
Setting up Units Conversion for a meter with a known voltage/pH relationship of pH 14 = 1400 mV.

If the pH meter outputs a raw millivolt signal (as does the ADInstruments pH Amp) then you can calibrate the signal with the specially designed Chart 'pH extension'. See the section entitled pH and Ion Selective Electrode Calibration, p. 189. This method also has the advantage of reporting the percentage Nernstian response of the electrode. If multiple point or non-linear calibration is required then the Chart 'MPCalibration extension' can be used. See Application Notes AN006 and AN112 (downloadable in Adobe Acrobat[®] 'pdf' format from the ADInstruments home page at http://www.adinstruments.com).

Ion Selective Electrodes

Ion selective electrodes, like pH electrodes, normally require to be connected to a high impedance preamplifier such as a pH meter or the ADInstruments pH Amp, which can in turn be connected to the PowerLab unit. Usually the recorder signal is provided as a raw millivolt signal which is recorded with Chart software. The Chart 'pH extension' can be used to calibrate the signal directly in units of pNa, pCl, etc. If multiple point or non-linear calibration is required then the Chart 'MPCalibration extension' can be used. See Application Notes AN006 and AN112 (downloadable in Adobe Acrobat[®] 'pdf' format from the ADInstruments home page at http://www.adinstruments.com).

Potentiometric Redox Electrodes

Depending on the design of the electrode it may be possible to connect a reference and redox electrode directly to the PowerLab inputs. However, for best quality results it is usually better to use a high impedance preamplifier such as a pH meter or the ADInstruments pH Amp, which can in turn be connected to the PowerLab unit. Chart software is usually the best choice to record the signal.

Dissolved CO_2 and NH_3 Electrodes

These electrodes measure the pH of an internal solution which is separated from the bulk solution by a gas permeable membrane. As CO_2 (or NH_3) concentration equilibrates on either side of the membrane, the pH of the internal solution will change. The resulting signal is usually measured with a conventional pH meter. The recorder signal of the pH meter can be monitored with Chart software on a PowerLab unit. The Units Conversion feature of Chart can be used to perform two point calibration of the signal which is satisfactory for most uses. If multiple point or non-linear calibration is required then the Chart 'MPCalibration extension' can be used. See Application Note AN112 (downloadable in Adobe Acrobat® 'pdf' format from http://www.adinstruments.com).

Electrode Behaviour

The behaviour of an ideal pH, or ion sensitive, electrode is characterised by the Nernst equation. This describes the relationship between observed potential and ion activity.

$$E \; = \; E_0 - \left(\frac{RT}{nF}\right)pY$$

where

- E is the observed potential (in volts)
- E_0 is the potential when pY is zero
- R is the gas constant (8.314 J K^{-1} mol^{-1})
- T is the temperature in Kelvin
- F is the Faraday constant (96487 C mol^{-1})

n is the number of electrons transferred at the electrode (usually the charge of the ion)

$pY = -\log_{10}[Y]$ where $[Y]$ is the activity of the ionic species, Y (for a pH electrode $pY = $ pH)

If pY is plotted against E then a straight line should be obtained of intercept E_0 and a slope of $-(RT/nF)$. For pH measurements ($n=+1$) at 25°C and the expression RT/nF has a value of 59.16 mV.

If two solutions of known pY are measured then these values can be used to construct a graph of a straight line to determine E_0 and the slope. The percentage Nernstian response of the electrode is given by:

$$response \ = \ \frac{100 \times slope_{observed}}{slope_{calculated}}$$

where $slope_{observed}$ is the observed slope and $slope_{calculated} = (-RT/nF)$

Such a graph, with the Nernstian response is calculated by the Chart pH extension.

High quality pH electrodes will have a response in the range 95 – 102%. Cheaper, older, or poorly maintained, electrodes will most likely have a response below this range. Ion selective electrodes exhibit a wider variation which should be taken into account when characterising electrode types.

Non-Linear Multiple Point Calibration

Both single and two point calibration assume that the electrode has a linear response to ion activity. Experimentally there will always be some deviation from linearity in the response. This is most noticeable at very high or low concentrations. In these instances a non-linear calibration technique must be used for accurate work.

At the time of writing the MP Calibration extension is only available for Macintosh systems.

If you need to calibrate an electrode directly in terms of ionic concentration (or log of concentration) rather than activity, a non-linear calibration is also needed. The Chart Mutipoint calibration extension can perform this sort of non-linear calibration.

MPCalibration

Mutipoint calibration
extension icon
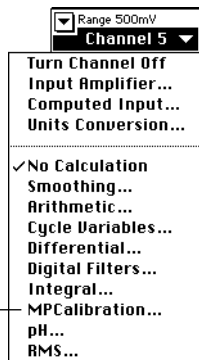
The MPCalibration command is
added to each of the Channel
menus if the Mutipoint
calibration extension is installed

The Mutipoint Calibration extension should be installed in the Chart Extensions Folder (adjacent to the Chart software icon) on the hard disk of your computer. When the Chart software is next run the MPCalibration command will appear in each of the channel menus.

In a typical calibration experiment your sensor probe (pH electrode, biosensor, etc.) might be immersed in a series of solutions of increasing analyte substrate as you record data, or if you have a flow system you might make regular injections of the calibration solutions. The input gain range of the PowerLab channel should be set so as to accommodate the largest signal you expect to record. If your signals will cover a very large dynamic range then you can record signals from different concentration of analyte at different gain ranges.

Recording is continued at each concentration until a steady reading is obtained or, if a flow injection analysis system is used, until the peak of interest has passed the sensor. After the calibration solutions have been recorded the signal will have units of raw millivolts. You can select a region of data to perform multipoint calibration, Figure 8–13. A good idea is to annotate the file with the Chart comments feature (see your *Chart User's Guide*) so that each concentration level is written in the data file.

Choose the MPCalibration command from that channel pop-up menu. The Multi Point Calibration dialog box, Figure 8–13, will appear. Make sure that the correct units (if any) are entered and that an appropriate number of decimal places is selected.

Figure 8–13
Selection of data from
potassium selective electrode

Concentrations used can be entered
as comments
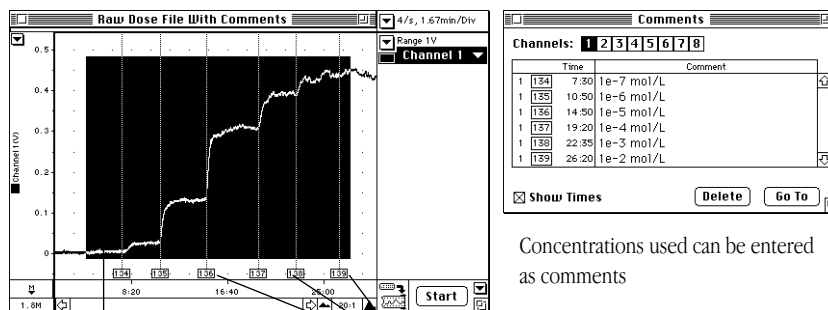
Select the data region of interest   Comments are marked on the signal

Figure 8–14
Setting up multiple point
calibration

Enter the signal value   Enter the concentration value, or log of concentration

Set the number of decimal places

Select a region of the signal
that represents a steady signal.
(Clicking would set just one
pint)

Enter the unit name or other identifier such as pH or $\log[K^+]$

Each calibration solution is
selected and entered separately

Use the arrow buttons to enter
the average of the selected
signal value

Use the Fit button to show the
calibration graph

While in the Multi Point Calibration dialog box select a calibration
level. Enter the mean value in the left hand column (use the arrow
button) and enter the corresponding concentration value in the right
hand column. In most cases the logarithm, base 10, of the
concentration is used if the concentrations are to vary by several
orders of magnitude. Repeat for each calibration level. Next click the
Fit... button to show the calibration graph (Figure 8–15). Different
functions, can be used to achieve a best fit for the data. For difficult
functions use the Point-to-Point function which does linear
interpolation between pairs of points, and extrapolates the first and
last interval beyond the calibration region. Beware of polynomial
functions which can give unexpected results outside the region of
calibration.

Figure 8–15
Selecting a calibration
function.

Multipoint Calibration Curve for Channel 1

0.446V   −1.93log[K+]

	V	log[K+]
1	0.004	-7
2	0.025	-6
3	0.131	-5
4	0.308	-4
5	0.392	-3
6	0.443	-2

Raw signal(V)

Point to point

Fit:
Point to point
☐ Force Origin

SSE=0   R²=1

Copy...   Print...   Cancel   OK
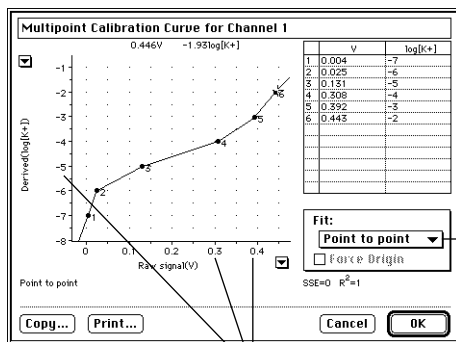
The calibration points are shown as a
graph and in spreadsheet format

Fit:
Point to point
Linear
Quadratic
✓Cubic
Quartic
Quintic
Logarithmic
Exponential

Choose the
function to fit
the calibration
data

Drag the axis tick labels to stretch
and compress the axes

Multipoint Calibration Curve for Channel 1

0.223V   −4.44log[K+]

	V	log[K+]
1	0.004	-7
2	0.025	-6
3	0.131	-5
4	0.308	-4
5	0.392	-3
6	0.443	-2

Raw signal(V)

Linear fit
y=9.668x−6.6

Fit:
Linear
☐ Force Origin

SSE=0.711   R²=0.95935

Copy...   Print...   Cancel   OK
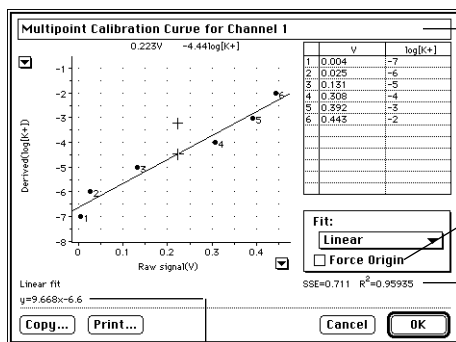
Type in you own title

Check this box if you want
the fitted function to pass
through the graph origin

Goodness of fit parameters
are reported

The equation of the calibration
function is shown

Multipoint Calibration Curve for Channel 1

0.354V   −3.571log[K+]

	V	log[K+]
1	0.004	-7
2	0.025	-6
3	0.131	-5
4	0.308	-4
5	0.392	-3
6	0.443	-2

Raw signal(V)

3rd order polynomial
$y=145.9x^3-96.48x^2+25.17x-6.873$

Fit:
Cubic
☐ Force Origin

SSE=0.154   R²=0.99118

Copy...   Print...   Cancel   OK
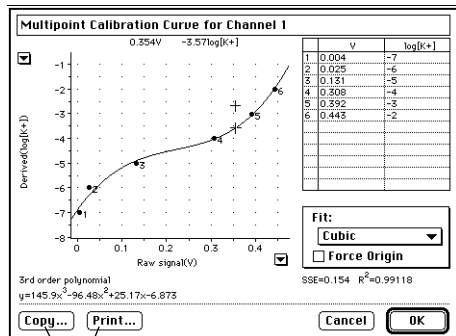
Copy or Print the results
for a quick report

The Print button allows printing of the calibration curve for quick reports, while the Copy... button allows the graph to be copied either as a picture, or as the text of the calibration data in the small spreadsheet. Clicking OK returns you to the main Multi Point Calibration dialog Figure 8–14.

When the OK button is clicked in the main Multi Point Calibration dialog, Figure 8–14, then the calibration calculation will be applied to the entire channel, Figure 8–16. You can always revert to the original, uncalibrated, data by selecting No Calculation in the channel menu.

Figure 8–16
A view of the calibrated data in Figure 8–13.
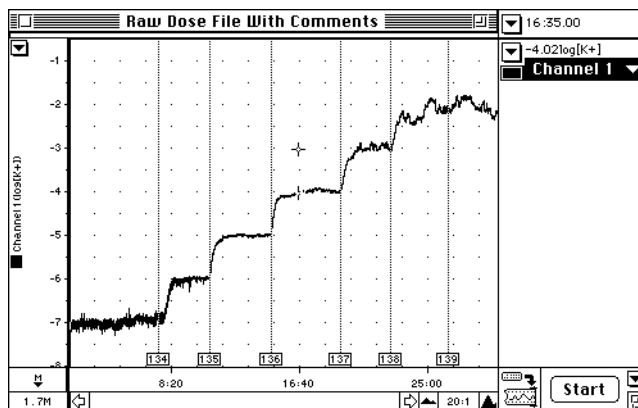
pH extension icon
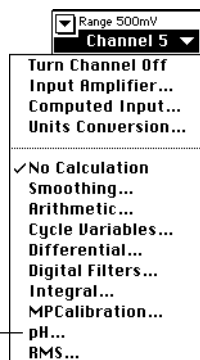
The pH... command is added to each of the Channel menus if the pH extension is installed

Also see Application Note AN006. Application Notes can be downloaded from our web site at http://www.adinstruments.com.

pH and Ion Selective Electrode Calibration

If you need to calibrate a pH or electrode then usually a single or two buffer (single or two point) calibration procedure is used based on the Nernst equation. The Chart pH extension can perform this sort calibration. The pH extension should be installed in the Chart Extensions Folder (adjacent to the Chart software icon) on the hard disk of your computer. When the Chart software is next run the pH... command will appear in each of the channel menus.

If you are using a conventional pH meter with analog outputs, connect the electrode to the meter input and then connect the meter output to one of the analog inputs of the PowerLab. The meter should have a minimum impedance of 10^{12} Ω and be set to read absolute millivolts. Any temperature compensation on the meter should be

turned off unless you want to use it. If you are using an ADInstruments pH Amp then follow the instructions in its *Owner's Manual* to set it up.

Set the PowerLab channel input range to an appropriate range (usually 500 mV for pH readings in the range pH 0 – 14). Because readings from pH and ISE electrodes take several seconds or even minutes to stop drifting, slow sampling rates in Chart are usually employed (2 samples per second or less is adequate).

The electrode is placed in a buffer solution of known pH and the response is recorded using Chart until a steady reading is obtained. If you are performing two point calibration the electrode is then placed in a second buffer solution while still recording.

Figure 8–17
Signal from a pH electrode in two different calibration buffer solutions

Select a region of data to be used for calibration
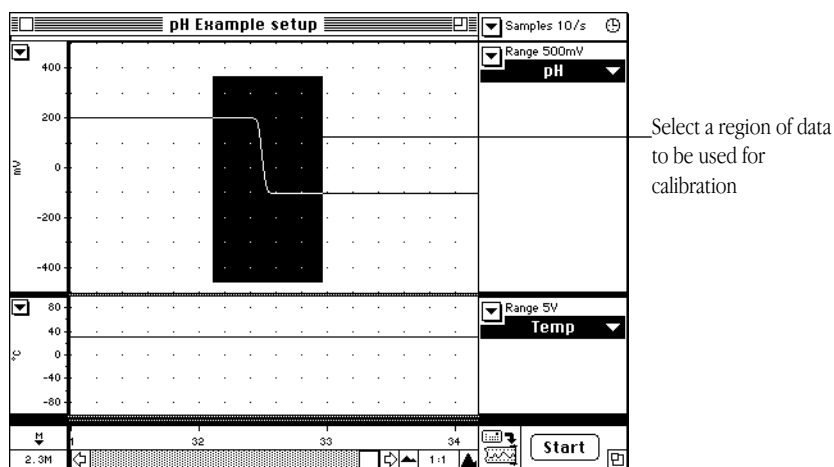
A selection of data covering the two pH regions of interest is made in the Chart window by dragging a selection to include both pH values. For single point calibration you will only need to record one pH value. A typical recording of two pH values and an appropriate selection for use in calibration is shown in Figure 8–17.

Choose the 'pH...' command from that channel pop-up menu. The Electrode Calibration dialog box, Figure 8–18, will appear. Make sure that the correct units are entered (in this case the units are pH), that the correct choice for n is made (+1 for pH) and that an appropriate number of decimal places is selected.

Figure 8–18
Setting up electrode
calibration with the pH
extension

Use the arrow button to enter the average selected signal value

Enter the value of the first buffer

Select units

Set number od decimal places to be displayed

The E_0, slope and percentage Nernstian response are displayed. For a single buffer a 100% Nernstian response is assumed.
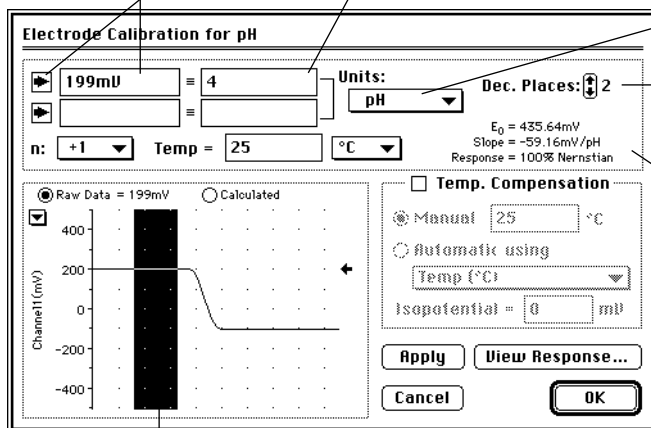
Select a region of constant signal for the first buffer

Select value of 'n'

Enter temperature and units

Click the View Response button to see the calibration graph
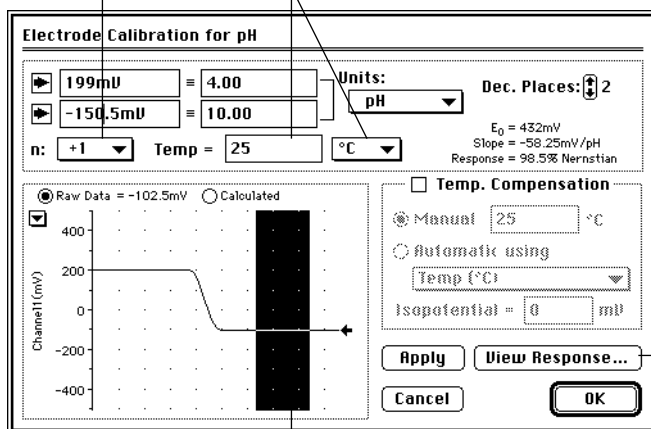
Select a region of constant signal for the second buffer

Select an area in the data display region that corresponds to recorded voltage of one of the pH buffer solutions. Click the arrow icon to the left of the first text entry box to put the mean value of the selected region of the trace into the adjacent box. Now type in the value of the buffer (in this example a pH of 4.00). The dialog box is updated assuming the electrode has 100% Nernstian behavior and the E_o value for the electrode is zero volts. This is equivalent to single point

calibration. An example of this process is shown in the top dialog in Figure 8–18.

Next select a region of the trace in the data display area which represents the value of the second buffer. You only need to do this if you are performing a two point calibration. Click the arrow button to the left of the second row of boxes to enter the mean value into the second entry box. Type in the value of the second buffer (pH 10.00). The slope, E_o value, and percentage Nernstian response of the electrode is then calculated and displayed. An example of this process is shown in the bottom dialog in Figure 8–18.

The calibration data entered will only be applied to the raw millivolt data in the Chart window when the OK or Apply button is clicked. Note that this calibration will be applied to all data in the channel, whether it is pH (or pNa, pCl etc.) data or not. It is therefore important to remember to use one electrode per channel per data file.

The pH calibration can be turned off at any time by choosing the No Calculation command from the channel pop-up menu. This allows you to return to the raw millivolt electrode signal at any time.
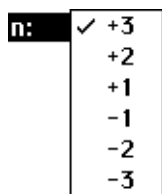
Ionic Charge

The *n* pop-up menu lets you set the value for the number of electrons transferred at the electrode. This usually corresponds to the charge of the ion be measured. You can choose a value between ±3. For pH measurements this value should be set to +1. The value of *n* is used internally to calculate the response of the electrode using the Nernst equation.

Calibration Temperature

The temperature of the solutions used for calibration is entered in this text box. Units of Celsius, Kelvin or Fahrenheit can be selected. The buffer solutions you use should have accurately known values at the temperature at which the calibration is performed.

Viewing the Electrode Response

To confirm the calibration calculation use the View Response...
button. The calibration point(s) will be shown and parameters used in
the Nernst equation are also tabulated. The graph can be printed by
simply clicking the print button. You can also copy either the graph or
the text of the small spreadsheet showing the calibration points. The
graph axes are scalable (drag the axis tick labels, or the area between
the ticks) so that smaller ranges can be plotted, which is particularly
useful for ISE work.

Figure 8–19 shows two typical electrode responses, one for a single
point calibration, and one for a two point calibration. The default
value for the isopotential point is zero.

Figure 8–19
Viewing the response graph

Calibration point   Type in your own title

Electrode parameters are reported

Print or copy the calibration

Calibration point coordinates are reported

Calibration points

Drag the tick labels to stretch and compress the axes
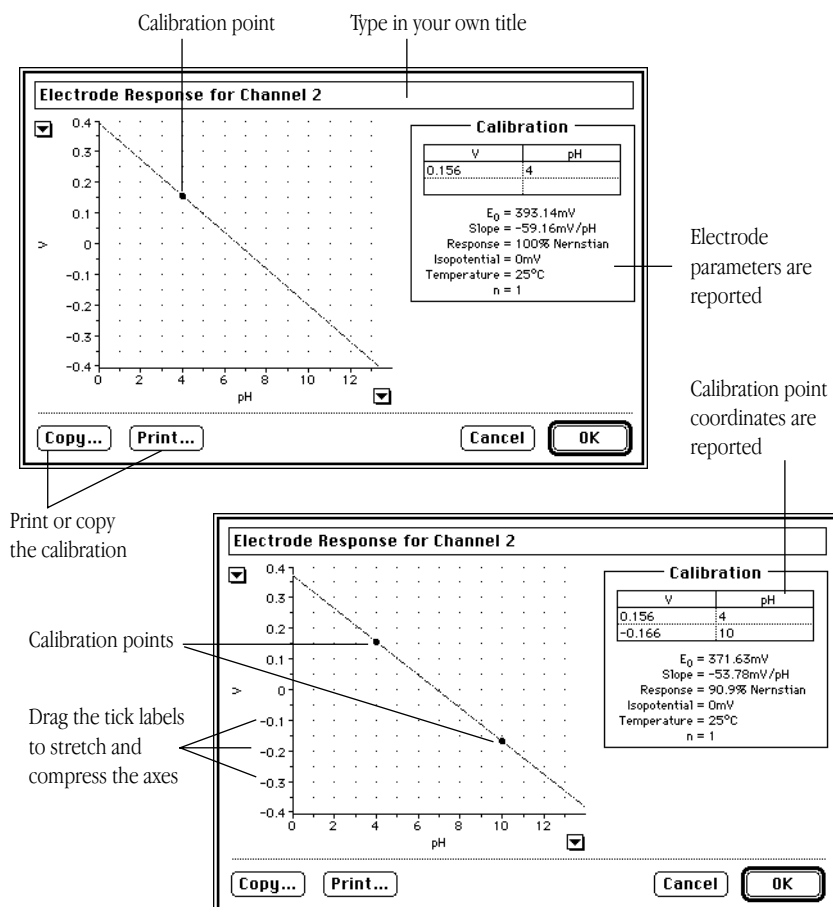
The vertical axis of the plot will be automatically scaled to the full scale range that the data was recorded at. So, for instance, if you were recording on the 500 mV range then the scale would have a range of ± 500 mV. If the response does not go anywhere near the current full scale range you can drag or stretch the vertical axis to obtain a more detailed plot.

The horizontal axis represents the ionic concentration and is by default pH. In the case of pH the horizontal scale will be automatically scaled to be between 0 and 14 pH. This scale can also be dragged or stretched to view the response plot in more detail. The small arrow pop-up menu next to the horizontal axis allows you to use the set scale feature to adjust the axis between two values.

The electrode response dialog can be copied to the Clipboard for export to a word processor or another application or can be printed for a permanent record. The title area at the top of the dialog is editable so that an electrode serial number or other information can be entered instead of the default title.

Temperature Compensation

There will be times when pH or other ISE measurements will be made at temperatures other than the temperature under which calibration was performed. The greater the change in temperature from the calibration temperature the greater the error in the electrode reading. Also the further away from the isopotential point the greater the error. To overcome this problem most pH meters provide a method for temperature compensation using the Nernst equation as a basis for compensation.

The pH extension offers both Manual and Automatic Temperature Compensation (MTC and ATC). Both MTC and ATC corrections can be turned off so you can return to the uncompensated data.

Manual Temperature Compensation (MTC)

The MTC option is for use when you need to make your measurements at a temperature other than that at which the electrode was calibrated. For instance the calibration may have taken place at 25°C but you need to record a solution that will be at 65°C. MTC will

alter the electrode response to suite the new temperature using the Nernst equation. Note that this mode is not suitable if the temperature is going to change significantly during recording. You should use the ATC mode in this case.

To use MTC make sure that temperature compensation is enabled by placing a tick mark in the Temp. Compensation check box. Then select the Manual radio button. The temperature at which recording will take place or has taken place should be entered in the text entry box next to the Manual option.

A temperature (other than the calibration temperature) is entered. When the View Response button is clicked the electrode response dialog will display two plots: one representing the response at the calibration temperature; and a second plot showing the response at the specified temperature, Figure 8–20.

The calibration response can be identified as the line with one or two calibration points on it. These are represented as large dots. The information displayed on the right of the dialog shows the calibration points and the values used for the Nernst equation.

Figure 8–20
Electrode response graph with Manual Temperature Compensation
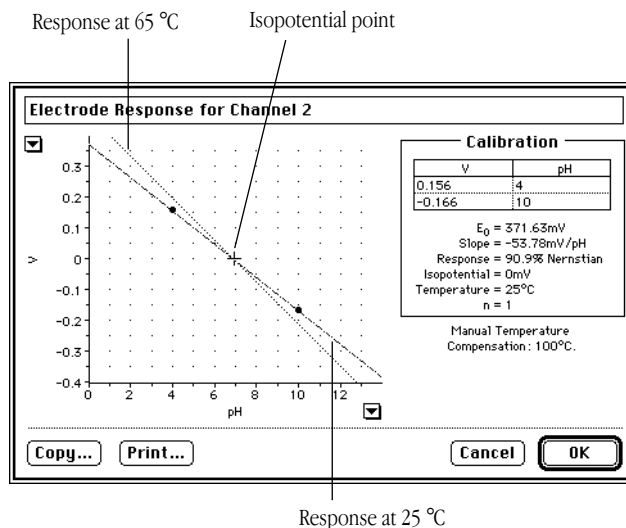
Automatic Temperature Compensation (ATC)

There may be circumstances where the temperature of the solution being measured cannot be maintained at a constant temperature. In this case the pH extension provides the necessary functionality to perform real-time, or automatic, temperature compensation.

Using the Temperature amplifier of the pH Amp, or a temperature signal from a third party temperature measurement device, the temperature signal can be recorded on a second PowerLab channel. When the Automatic option is chosen, the pH extension will use temperature data from one of the Chart channels to correct the pH channel for variations in temperature. To choose the automatic temperature compensation option click in the radio button next to the Automatic option. The channel selection pop-up menu will no longer be grayed out and you can choose the channel on which temperature was recorded.

Recording Temperature for ATC

To record and use a temperature channel with the ATC, the channel must be appropriately calibrated using the Units Conversion feature. The units must be set to either °C, °F, or K. If you have not calibrated the temperature channel you will be warned by the dialog box shown in Figure 3–7. This is necessary because the pH extension will look at the units first to determine the conversion factor required the Nernst equation.

Isopotential Point

The isopotential point of the electrode is that potential which remains constant as the temperature changes. Most pH electrodes are constructed so that the isopotential point is about 0 mV (which for most pH electrodes also corresponds to pH 7). But it is usual, even in

new pH electrodes, that the isopotential point is actually anywhere between ±50 mV and that this value changes as the electrode ages.

Ion selective electrodes may have an isopotential completely outside the measuring range of the electrode.

Most pH meters assume an isopotential point of 0 mV (at pH 7) and then apply either manual or automatic temperature compensation. The Chart pH extension however allows you to set the isopotential point to an appropriate value. To calculate the isopotential point, two calibration runs must be made at two different temperatures, T_1 and T_2.

From the Nernst equation:

$E = E_{01} + (\text{slope}_1)\,\text{pH}$ 　　or　　 $\text{pH} = (E - E_{01})/\text{slope}_1$
$E = E_{02} + (\text{slope}_2)\,\text{pH}$ 　　or　　 $\text{pH} = (E - E_{02})/\text{slope}_2$

where

$\text{slope}_1 = -RT_1/nF$ 　　and　　 $\text{slope}_2 = -RT_2/nF$

At the isopotential point both potential and pH are constant for both T_1 and T_2, that is $E = E_{ip}$, and $\text{pH} = \text{pH}_{ip}$. From the above equations we derive:

$$\frac{(E_{ip} - E_{01})}{slope_1} = \frac{(E_{ip} - E_{02})}{slope_2}$$

which can be solved for E_{ip}:

$$E_{ip} = \frac{(E_{01} - E_{02})}{slope_1 - slope_2}$$

or:

$$E_{ip} = \frac{(E_{01} - E_{02})nF}{R(T_1 - T_2)}$$

For best results ensure that T_1 and T_2 are at least 20 degrees apart.

Potentiometric Titrimetry

The ADInstruments µPump, can be used to deliver 50 µL aliquots of titrant to a vessel with a coefficient of variability of 0.3%. It is suitable

(after calibration) for performing titrations on a scale similar to that used with a conventional 25 or 50 mL burette. Monitoring such a titration is best achieved with Chart software, plotting volume and current flow on separate channels. Chart also has the ability to perform XY plots so that current can be plotted against volume of titrant added.

Dissolved Oxygen, dO_2, Sensors

Usually the sensor electrode and meter will be purchased from the same manufacturer because the gain settings of the meter must be appropriate for the current signal from the electrode. The recorder output of the dO_2 meter can be connected to your PowerLab unit. On line measurements can be made over periods of less than a second to weeks if need be. This can be an ideal way to monitor water quality over a long period of time, or for monitoring of fermentation reactors.

Most oxygen sensors exhibit a slow response time and will take at least 20 s to stabilize. The Units Conversion feature of Chart can be used to perform two point calibration of the signal which is satisfactory for most uses. If multiple point or non-linear calibration is required then the Chart 'MPCalibration extension' can be used. See Application Note AN112 (downloadable in Adobe Acrobat[®] 'pdf' format from http://www.adinstruments.com).

Conductivity Sensors

Conductivity measurements are usually performed with a pair of platinum plate electrodes. The conductivity meter provides a small amplitude AC signal from 50 – 1000 Hz (to prevent hydrolysis of the solution) and should provide a recorder type signal that is proportional to the conductivity of the solution. The Units Conversion feature of Chart can be used to perform two point calibration of the signal which is satisfactory for most uses. If multiple point or non-linear calibration is required then the Chart 'MPCalibration extension' can be used. See Application Note AN112 (downloadable in Adobe Acrobat[®] 'pdf' format from http://www.adinstruments.com)

Simple Galvanic Cells

Simple galvanic cells used in undergraduate and high school experiments, for example a Zn | 1 M $ZnSO_4$ | | 1 M $CuSO_4$ | Cu system set up in two beakers joined by a salt bridge can be connected by wiring the electrodes (anode and cathode) directly to the PowerLab inputs. There are two ways to do this for a galvanic cell:

• connect one electrode to the centre wire of a shielded cable with a BNC connector at the other end. The second electrode should be connected to the shield of the cable. The BNC connector of the cable can now be plugged into the Channel 1 (or Channel 2 etc.) of a PowerLab unit.

• connect one electrode to the centre wire of a shielded cable with a BNC connector at the other end, and plug this into Channel 1+ of two or four channel PowerLab unit (these units feature differential inputs). Connect the second electrode to the centre wire of a second cable and plug this into Channel 1– of the PowerLab. Make sure that the + and – checkboxes are both checked in the Input Amplifier window to enable differential input.

The second configuration is the one to be preferred as it allows easy reversal of the polarity of the system and allows maximum shielding of the wiring which may be important where small potentials are being measured.

However, for highest precision work for small potentials, or if your cell has a high internal resistance, then your electrodes should be connected to a ADInstruments GP Amp (input impedance 10^8 Ω, ±200 mV maximum), or to a pH meter, or to an ADinstruments pH Amp (±2 V maximum, input impedance 3×10^{12} Ω), which in turn is connected to the PowerLab. If in doubt always use a pH meter or the ADInstruments pH Amp.

Quartz Crystal Microbalance

The use of a potentiostat to control the potential of an electrode which is also the sensor of a Quartz Crystal Microbalance (QCM) allows mass changes to be detected during a voltammetric experiment.

You will need a QCM with analog recorder output. A PowerLab (with at least four channels) with Chart software to monitor current, potential and mass signals is also required. If you want to control the potentiostat then a PowerLab/4SP, /8SP, or /16SP is recommended as these units can be configured with Chart software to provide a triangular waveform (sent to the potentiostat for a cyclic voltammetric experiment) while recording on all channels. EChem software can only record current and potential and is not suitable for QCM use.

Electrochemical Noise Experiments

PowerLab units with Chart software can be used to measure the current and/or potential signals from potentiostats, galvanostats and potential meters. If you are measuring the noise associated with these signals then you should consult Application Notes AN002 and AN007 which discuss the determination of RMS (root mean square) and Noise (the standard deviation) functions of a signal, and the application of digital filtering of a signal. Also of interest is the Spectrum command in Chart (Windows menu) which can be used for frequency (FFT) analysis of the signal. This can be us use in determining if the 'noise' seen is actually a high frequency interference. Make sure that you are recording at a rate at least twice as fast as the highest frequency component that you need to detect.

At the time of writing these features are only available on Macintosh systems.

Application notes can be downloaded from our web site at http://www.adinstruments.com.

Corrosion Measurements

EChem can be used to drive a potentiostat to perform simple electrochemical corrosion experiments. Because very slow scan rates are employed make sure that you are running EChem in slower speed mode (100 Hz, 400 Hz, or 1000 Hz) when attempting these experiments or you are likely to encounter warning messages saying that the sampling periods are too long.

In addition PowerLab with Chart and Scope software can be used to monitor potentiostat systems replacing existing XYT plotters and chart recorders. In general Chart will be more useful than Scope for these techniques as the slowest Scope can be run at is 2 Hz for 2560 points, a total of 20 minutes per scan. Chart can be run as slow as 12 points per hour for an indefinite period.

Choice of Potentiostat

The American Society for Testing and Materials (ASTM) has put forward several standard protocols performing corrosion experiments. The ADinstruments' Potentiostat meets the requirements of ASTM G5–87 for potentiostatic and potentiodynamic polarization measurements ASTM G61–86 for cyclic potentiodynamic polarization measurements, and ASTM G59–91 for polarization resistance measurements. However you should note that this requires that the potentiostat have a maximum current rating of only 100 mA. If you require a potentiostat with greater capability then consult Chapter 9 for a suitable instrument that will be compatible with PowerLab. Also the ADinstruments Potentiostat provides a signal that is proportional to current. Some third party potentiostats have an option so that a recorder signal proportional to log of the absolute current can be obtained. By using such a potentiostat with EChem, Chart, or Scope, the PowerLab system will be able to present data as log of current versus potential.

See ASTM Designation G15 – 90a for standard terminology relating to corrosion experiments, and also ASTM G3: Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing.

For most experiments the value of E_{corr} must first be determined by measuring the resting potential of your system. This is usually done

by connecting a high impedance digital voltmeter (or pH meter in millivolt mode) across the working and reference electrodes before the potentiostat is connected. You may have to wait a few minutes for the reading to stabilize.

Potentiodynamic Polarization

This is essentially Linear Sweep Voltammetry at very slow scan rates, typically 0.6 V/hour ≈ 0.16667 mV/s, over a potential range that is up to E_{corr} ± 500 mV.

The potential range should be limited so that extensive water hydrolysis does not occur as this is likely to produce large currents that may overload the potentiostat, while bubbles on the working electrode may alter the rate and type of corrosion taking place, as well as interrupting current flow and causing a noisy signal. Also the use of larger potentials than necessary may also accelerate corrosion to the extent that the surface of the working electrode is altered sufficiently so that results cannot be reproduced.

This type of scan can also be set up using the Multi Pulse technique. EChem should be run at slower speeds (100 Hz – 1 kHz mode) for these types of experiment to enable longer step widths and data sampling periods to be used.

The output from EChem is displayed as current versus the potential. If you wish to display the results as the log of current density versus potential then the data should be transferred to a third party graphing program, for example IGOR Pro. A set of macros for IGOR Pro are available from your ADInstruments dealer to facilitate plotting of the data in this format.

If you are used to performing this type of experiment with analog potentiostats then you may wish to do several comparison runs with known materials to compare results. EChem generates a staircase ramp and samples the current over a fixed period of time at a constant potential then averages the current value at each potential. This may lead to smoother graphs and more reproducible results than you are accustomed to. Make the sampling period a multiple of 20 ms (if you use 50 Hz mains) or 16.7 ms (if you use 60 Hz mains) to eliminate noise due to mains hum.

Cyclic Potentiodynamic Polarization

See ASTM Designation G61 – 86 for a description of the standard test method. This experiment can be set up with the Cyclic Voltammetry in EChem using very slow scan rates typically 0.6 V/hour (0.1667 mV/s). EChem should be run at slower speeds (100 Hz – 1 kHz mode) for these types of experiments. If the results need to be plotted as the log of current density versus potential then the data will need to be transferred to a specialist graphing program, or you will need to employ a third party potentiostat with a recorder output proportional to the log of current flow.

If you require more control over the sampling period use the Multi Pulse technique with the Cyclic Parameters setting to define your own forward and reverse scan procedures.

Polarization Resistance

See ASTM Designation G59 – 91 for a description of the standard practice. This experiment is simply Linear Sweep (or Cyclic) Voltammetry over a restricted potential range (usually E_{corr} ± 30 mV) at slow scan rates, typically 0.6 V/hour. This can be performed using EChem software after first determining E_{corr} with a potentiodynamic polarization scan, or with a high impedance voltmeter.

Make sure that EChem is running in a slower mode (100Hz – 1kHz) when performing these experiments. This technique can also be set up in the Multi Pulse technique. Results are usually plotted as current versus potential.

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Using 3rd Party Equipment

You may wish to use you PowerLab with a potentiostat other than the ADInstruments Potentiostat. This is necessary for:

- very low current situations; or for

- high current/ high power situations.

- or you may have existing potentiostats in your laboratory that you want to use with a computer.

This chapter takes a look at some of the third party equipment that is compatible with a PowerLab unit using EChem, Chart, or Scope software. PowerLab units can also be used with many patch, voltage, or current clamps such as those made by Axon, Warner, or WPI.

Connection of third party potentiostats to your PowerLab unit is discussed in Chapter 3.

For very low current (picoampere range) work look for the release of our special low current Picostat (under development at time of writing).

Introduction

There is an extensive range of potentiostats manufactured by third parties that are compatible with PowerLab. In most cases all that is required is a simple cable connection to the PowerLab.

A range of adaptor cables can also be purchased from your ADInstruments dealer.

EG&G PARC

Many of the potentiostat models made by EG&G Princeton Applied Research (PAR) are suitable for connection to PowerLab systems. A brief summary of the different PAR models that can be connected to PowerLab is given in Table 7–1 at the end of this section. More information can be found at http://www.egginc.com/par.

Model 170 potentiostat

This model has been superseded but if you already own one it can be connected to a PowerLab system using Chart and Scope for plotting, or using EChem to drive the potentiostat and plot the data. The 170 has a very high compliance (100 V) and due caution should be taken in its use. The 170 allows AC polarography/voltammetry. Your electronics workshop can construct a cable to enable EChem to drive the 173, otherwise an MLC–01 Cable Kit can be used to record data with Chart and Scope.

Model 173 potentiostat

This model has been superseded but if you already own one it can be connected to a PowerLab system using Chart or Scope for plotting, or using EChem to drive the potentiostat and plot the data. The 173 potentiostat has a very high compliance (100 V) and due caution should be taken in its use. Your electronics workshop can construct a cable to enable EChem to drive the 173, otherwise an MLC-01 Cable Kit can be used to record data with Chart and Scope.

CAUTION

Please remember that many of these potentiostats are high power models capable of producing dangerous voltages. They should only be used after reading the manufacturer's instruction manuals and becoming thoroughly acquainted with the hazards.

Model 174 potentiostat

This model has been superseded but if you already own one it can be connected to a PowerLab system using Chart and Scope for plotting, or using EChem to drive the potentiostat and plot the data. The 174 has a very high compliance and due caution should be taken in it use. If you have a 174/51 dual cell differential operation is possible. The 174/50 configuration allows AC polarography.

Model 175 Universal Programmer

The 175 is essentially a waveform generator capable of outputting pulses or a potential ramp. It can be used to drive potentiostats capable of accepting a waveform input. It would normally be used with a potentiostat and the PowerLab system could be used with Chart or Scope to replace an XY plotter or oscilloscope. The MLC-01 Cable Kit is available to connect your PowerLab to this instrument.

The use of a PowerLab unit as a waveform generator with EChem, Chart or Scope software renders the Model 175 largely redundant but it is still useful if you require true analog ramps.

Models 263, 273, and 273A potentiostats

The 263, and 273 series of potentiostats would normally used with PAR's own programs via their inbuilt GPIB IEEE interfaces and an IBM clone computer. However, they can also be used with a Macintosh computer and a PowerLab. You may prefer to use the potentiostat in its stand alone mode and use the combination of Scope/Chart and a PowerLab for plotting your data rather than a standard XY plotter, or you can control the potentiostat by generating stepped and pulsed waveforms with EChem. The MLC–01 Cable Kit is available to connect your PowerLab to this instrument.

Model 264A potentiostat

The 264A Polarographic Analyser/Stripping Voltammeter can benefit by using a PowerLab/200 with Scope or Chart in place of its standard XY plotter. Alternatively it can be used with EChem to drive it and replace its inbuilt techniques. The MLC–01 Cable Kit is available from to connect your PowerLab to this instrument.

Model 363 potentiostat

The 363 is a non–scanning potentiostat/galvanostat with a maximum current rating of 1 A and 30 V compliance making it ideal for corrosion and plating studies, and electrosynthesis. Combining this potentiostat with a PowerLab/EChem system will enable it to become a scanning instrument. All the techniques offered by EChem will then be available with this potentiostat. Newer models of the 363 have inbuilt positive feedback iR compensation. The MLC–02 Cable Kit is available to connect your PowerLab to this instrument.

Model 362 potentiostat

This model has similar specifications to the 362 potentiostat with the added advantage that it can provide its own analog ramp. This means that techniques that require a true analog ramp can be monitored with a PowerLab controlled with Chart or Scope. The 362 comes equipped with positive feedback iR compensation. The MLC–02 Cable Kit is available to connect your PowerLab to this instrument.

Model 366 Bipotentiostat

Ring /disk work requires a bipotentiostat (or two single potentiostats). The model 366 bipotentiostat can be used with a PowerLab in several ways, including:

- a PowerLab/200 or /400 could be used to drive the ring or disk electrode with EChem (via the external input) while a constant potential is applied to the disk (or ring) with the other half of the bipotentiostat. When using EChem only two channels of data can be recorded.

- a PowerLab/400 and Chart could monitor current and potential at the ring as the ring potential is ramped, while simultaneously monitoring current at the disk as it is held at constant potential. A total of three channels of data would be recorded.

For maximum recording flexibility with this instrument a four (or more) channel PowerLab unit is recommend. The MLC–03 Cable Kit is available to connect your PowerLab to this instrument.

Model 400 electrochemical detector

The Model 400 electrochemical detector is designed for liquid chromatography. Both outputs on the Model 400 can conveniently be monitored with a PowerLab/200 and Chart. With a PowerLab/400 the signals from two Model 400's could be monitored. The MLC–01 Cable Kit is available to connect your PowerLab to this instrument.

If you are using a Model 400 detector and a UV-visible or fluorescence detector you can monitor the outputs of any two detectors simultaneously with Chart and a PowerLab/200. With a PowerLab/400 you can monitor the output of up to four detectors. Extra virtual channels are provided which can be used for on-line integration of the incoming signals (using the Computed Input feature).

The Model 400 is also suitable for connection to our PowerChrom system which offers many more features suitable for chromatographic data analysis.

Model 303A Static Mercury Drop Electrode

The PAR 303A Static Mercury Drop Electrode (SMDE) can also be used as a Hanging Mercury Drop Electrode or Dropping Mercury Electrode (HMDE or DME). It can be used with a PowerLab/EChem system, either with a third party potentiostat, or with a ADInstruments Potentiostat.

Table 10–1

Comparison table for EG & G PARC equipment. [1]

Feature	Model										
	363	362	366	263	VersaStat	170	173	174	273 & 273A	264A	400 LC Detector
PowerLab as plotter	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
PowerLab as waveform generator	yes	yes	yes	yes	yes	yes[2]	yes	yes	yes	yes	no
Inbuilt scanning	no	yes	yes	yes	yes	yes	no	yes	yes	yes	no
Inbuilt scan rate	–	0.1 mV/s to 5 V/s	0 to 1 V/s	Processor controlled	Processor controlled	0.1 mV/s to 500 mV/s	–	0.1 mV/s to 500 mV/s	Processor controlled	1 mV/s to 10 V/s	1 mV/s to 100 mV/s
External input	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	no
Voltage range	±10 V	±10V	±2V	±8 V	±10 V	±5 V	±5 V	±5 V	±10 V	±10 V	±2 V
Compliance	30 V	30 V	10 V	20 V	20 V	100 V	100 V	80 V	100 V	10 V	10 V
Current ranges (full scale)	1 µA to 1 A	1 µA to 1 A	1 µA to 1 A	100 nA to 100 mA	1 µA to 250 mA	1 nA to 5 A	100 µA to 1 A	20 nA to 10 mA	100 nA to 100 mA[3]	100 nA to 5 mA	100 nA to 100 µA
iR compensation	feedback	feedback	none	feedback/ current interrupt	current interrupt	feedback	feedback	feedback with /50 option	feedback/ current interrupt	none	none

Notes: 1. These specifications should be verified by the manufacturer, specifications may change at short notice; 2. The external input should be modified to accept DC signals as described in section III, pages 1 & 2 of the PAR 170 instruction manual; 3. Ranges of 10 A and 1 nA can be selected if the instrument is controlled by PAR's own software.

BAS Equipment

Refer to Table 9–2 at the end of this section for a table of equipment made by Bioanalytical Systems Inc. (BAS) at its compatibility with PowerLab. Also see http://www.bioanalytical.com/.

Model CV-1B potentiostat

The CV–1B is BAS's most basic unit and is widely used in teaching laboratories. It is greatly enhanced by connecting its recorder outputs to a PowerLab and recording data with Chart or Scope software. It is not suitable for control with EChem. The MLC–06 Cable Kit is available to connect your PowerLab to this instrument.

To set up scan limits, connect the CV–1B to the PowerLab, I output to Channel 1 and E output to Channel 2. Now open the Input Amplifier on Channel 2. Adjust the scan limits of the CV-1B while using the Input Amplifier window to monitor the value of the potential.

Models CV-27 and CV-37 potentiostats

The CV-27 and CV-37 can both be connected to a PowerLab, with Chart and Scope, to replace a conventional XY plotter. These units can also be controlled with EChem and a PowerLab, allowing full use of stepped ramp and pulse techniques. The MLC-06 Cable Kit is available to connect your PowerLab to these instruments.

Model PWR-3 Power Module potentiostat

The PWR-3 Power Module can be used directly with a PowerLab and EChem or Chart or Scope, or you may use it with one of BAS's other potentiostats in combination with PowerLab. Remember that this instrument can produce dangerous voltages and should only be used after thoroughly reading its instruction manual. The MLC-06 Cable Kit is available to connect your PowerLab to this instrument.

Low Current Module potentiostat

The BAS Low Current Module is designed to be used with a waveform generator. This module can be directly attached to a

PowerLab unit, and with EChem, Chart, or Scope, software you can perform very low current (sub nA) work with microelectrodes. Note that you do not need to purchase a separate potentiostat! Low current work generally requires the use of a Faraday cage and the low current module is designed to be compatible with BAS's C–2 Cell Stand. The MLC–04 Cable Kit is available to connect your PowerLab to this instrument.

Models 100A and 100B potentiostat workstations

The BAS 100A, and 100B are both equipped with analog recorder outputs which can be connected directly to a PowerLab and the data recorded with Chart or Scope. In addition an analog input is provided so that control of the instrument is possible with a Macintosh computer using a PowerLab and EChem. The MLC–06 Cable Kit is available to connect your PowerLab to these instruments.

Model LC-44

The LC–44 electrochemical detector is designed for liquid chromatography. Both generator and detector current outputs can be monitored with a PowerLab/200 and Chart, or the detector outputs from two LC–44's. With a PowerLab/400 the generator and detector currents from two LC–44's could be monitored. The MLC–07 Cable Kit is available to connect your PowerLab to this instrument.

If you are using an LC–44 detector and a UV-visible or fluorescence detector you can monitor the outputs of any two detectors simultaneously with Chart and a PowerLab/200. With a PowerLab/400 you can monitor the output of up to four detectors. Extra virtual channels are provided which can be used for on-line integration of the incoming signals (using the Computed Input feature).

Model RDE-1

The BAS Rotating Disk Electrode can be used with most potentiostats. If your potentiostat is being used with a PowerLab/EChem system then you can connect the RDE–1 to the potentiostat and you will be able to drive the RDE–1 with EChem.

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Table 10–2
Comparison table for BAS equipment.[1]

Feature	Model								
	CV-1B	CV-27	CV-37	PWR-3	Low Current Module	50W	100	100A & B	LC-44 LC Detector
PowerLab as plotter	yes	yes	yes	yes	yes	no	no	yes	yes
PowerLab as waveform generator	no	yes	yes	yes	yes	no	no	yes	yes
Inbuilt scanning	yes	yes	yes	no	no	yes	yes	yes	no
Inbuilt scan rate	0 to 10 V/s	0.1 mV/s to 4 V/s	0.1 mV/s to 400 mV/s	–	–	Processor controlled	Processor controlled	1 mV/s to 10 V/s	–
External Input	no	yes	yes	yes	yes	no	no	yes	yes
Voltage range	±3.75 V	±5 V	±5 V	±10 V	–	±3.276 V	–	±3.276 V	±2 V
Compliance	–	12 V	10 V	85 V	12 V	10 V	–	12 V	–
Current ranges (full scale)	0.5 µA to 500 µA	2 µA to 120 mA	0.2 nA to 12 µA	10 mA to 1 A	10 pA to 12 µA	100 nA to 100 mA	–	100 nA to 100 mA	0.1 nA to 50 µA
iR compensation	none	none	none	none	none	feedback	–	feedback	none

Notes: 1. These specifications should be verified. Specifications may change at short notice.

PINE Equipment

Table 9–3 provides a comparison of different potentiostats offered by the PINE Instrument Company, http://www.pineinst.com/.

Model AFCBP1 bipotentiostat

This model operates on 110 V/60 Hz (the AFCBP1E is the corresponding 220 V/50 Hz model). It is a true analog bipotentiostat suitable for cyclic voltammetry and dual electrode hydrodynamic studies. It is capable of being interfaced to an IBM type computer and controlled with PINE's own software. It is equipped with analog outputs and can be used with a PowerLab to replace an XY plotter or chart recorder. It also has an external waveform input and can be used with EChem. The MLC-01 Cable Kit is available to connect your PowerLab to this instrument.

Model AFRDE5 bipotentiostat

This model operates on 110 V /60 Hz (the AFRDE5E is the corresponding 220 V/50 Hz model). It is a true analog bipotentiostat similar to the AFCBP1 in features but without the option of connecting to an IBM computer. It can be used with PowerLab and Chart, Scope, and EChem. The MLC-01 Cable Kit is available to connect your PowerLab to this instrument.

Table 9–3
Comparison table for PINE equipment

Feature	AFCBP1 & AFCBP1E	AFRDE5 & ARFDE5E
PowerLab as plotter	yes	yes
PowerLab as waveform generator	yes	yes
inbuilt scanning	yes	yes
inbuilt scan rate	0 to 1 V /s	0.01 to 10 V /s
external input	yes	yes
voltage range	±10 V	±10 V
current ranges (full scale)	100 nA to 1 A	100 nA to 1 A
iR compensation	no	no

Note: These specifications should be verified. Specifications may change at short notice.

While many experiments can be performed with a PowerLab/200, for maximum flexibility these PINE bipotentiostats should be used with a PowerLab/400. PINE also makes a variety of rotators, and disk and ring disk electrodes. these are also compatible for use with PowerLab systems.

Metrohm Equipment

Model 506 Polarecord with 663 VA Stand

The Metrohm 506 Polarecord™ is found in many analytical laboratories using polarography for trace analysis. It has provision for attachment to an external XY recorder and so Scope or Chart can be used with PowerLab to record data directly to a Macintosh.

It is also possible to use EChem to drive a Polarecord but the pilot voltage connection on the Polarecord has an attenuation of 1:10. Thus the maximum potential range that EChem is capable of (±5 V) will be interpreted as ±0.5 V. To overcome this you can use a 1:10 amplifier to boost the signal before feeding it into the Polarecord, or, if your experiment can be run in a ±0.5 V range, put up with the X-axis being out by a factor of 10.

Model 690 Ion Chromatograph

The Metrohm 690 is a conductivity detector system for ion chromatography. It is ideal for use with PowerLab and Chart to replace a conventional strip chart recorder. The program Peaks can then be used to analyse the data and extract peak heights and areas.

For more advanced chromatography our PowerChrom system is available.

Schlumberger Equipment

Model 1186 potentiostat

Schlumberger potentiostats (such as the 1186) are compatible with PowerLab and EChem. The MLC-01 Cable Kit is available from your ADinstruments representative to help you connect your PowerLab to these systems.

Radiometer Equipment

Model PGP201 potentiostat

This instrument is a potentiostat/galvanostat which can be used with Chart, Scope, and EChem. The MLC-01 Cable Kit is available from your ADinstruments representative to help you connect your PowerLab to these systems.

Table 9–4
Features of the Radiometer PGP201 potentiostat/galvanostat

Feature	PGP201
PowerLab as plotter	yes
PowerLab as waveform generator	yes
inbuilt scanning	yes
inbuilt scan rate	25 μV/s to 2.5 V/s
external input	yes
voltage range	±4.095 V
compliance	20 V
current ranges (full scale)	1 μA to 1 A
iR compensation	none

Note: These specifications should be verified. Specifications may change at short notice

HEKA Equipment

Models PG28.. series potentiostats

The HEKA™ potentiostats in the PG28 system are all compatible with PowerLab and Chart and Scope for data collection. In addition they can also be used with a PowerLab and EChem so that you can use them as part of a computer controlled system. The MLC-01 Cable Kit is available from your ADinstruments representative to help you connect your PowerLab to these Heka systems.

The basic system comprises modules from the series 100 control amplifiers and the series 200 current amplifiers. In addition the 300 series modules, trigger pulse and scan generators; 400 series modules, current integrators; and 500 series module, digital display; can also be added. Consult http://www.heka.com/ more details.

Table 9–5
Features of HEKA potentiostats

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Feature	PG28	PG28../5A	PG28.B	PG284	PG285	PG287
PowerLab as plotter	yes	yes	yes	yes	yes	yes
PowerLab as waveform generator	yes	yes	yes	yes	yes	yes
Inbuilt scanning	no	no	no	yes	yes	yes
Inbuilt scan rate	–	–	–	1 mV/s to 1 kV/s	1 mV/s to 1 kV/s	1 mV/s to 1 kV/s
External Input	yes	yes	yes	yes	yes	no
Voltage Range	±10 V	±5 V	±2 V	±10 V	±90 V	±10 V
Current Ranges (full scale)	1 µA to 2 A	1 µA to 2 A	1 µA to 200 mA	1 µA to 1 A	1 µA to 1 A	1 µA to 1 A
iR Compensation	feedback	feedback	feedback	feedback	feedback	feedback

Note: These specifications should be verified. Specifications may change at short notice.

Cypress Systems Equipment

Cypress Systems make a variety of potentiostats and related information. Latest information can be found at http://www.cypresshome.com/.

Omni 90 Potentiostat

The Omni 90 is a simple potentiostat with inbuilt analog scanning and also able to accept an external input. It can be used with PowerLab replacing the XY plotter or chart recorder with Scope and Chart software, or can be used with EChem software so that stepped ramp and pulse voltammetry can be performed. The MLC-01 Cable Kit is available to connect your PowerLab to this instrument.

Omni 101 Potentiostat

The Omni 101 is a stand alone microprocessor controlled analog potentiostat with inbuilt analog scanning and also able to accept an external input. It can be used with PowerLab replacing the XY plotter or chart recorder with Scope and Chart software, or can be used with EChem software so that stepped ramp and pulse voltammetry can be performed. The MLC-01 Cable Kit is available to connect your PowerLab to this instrument.

CS 1000 Galvanostat/Coulometer

The CS1000 can be used with PowerLab replacing the chart recorder with Chart software.

EI 400 Bipotentiostat

The EI 400 is an analog bipotentiostat (which can also be used as a single potentiostat) with inbuilt analog scanning and also able to accept an external input. It can be used with PowerLab replacing the XY plotter or chart recorder with Scope and Chart software, or can be used with EChem software so that stepped ramp and pulse voltammetry can be performed. It is also suitable for use with microelectrodes.

Table 9–6
Features of Cypress
Systems instruments.

Feature	Model			
	Omni 90	Omni 101	CS 1000	EI 400
PowerLab as plotter	yes	yes	yes	yes
PowerLab as waveform generator	yes	yes	no	yes
Inbuilt scanning	yes	yes	no	yes
Inbuilt scan rate			–	<100 mV/s to 1000 V/s
External Input	yes	yes	no	yes
Voltage range	±2.5 V	±2 V		±10 V
Compliance	10 V	15 V	18 V	10 V
Current ranges	0.01µA to 100mA	100nA/V to 100mA/V	100 µA/V to 1 A	100 pA/V to 100 nA/V
iR Compensation	no	no	no	no

Note: These specifications should be verified. Specifications may change at short notice.

AMEL Equipment

Latest information on AMEL potentiostats can be found at http://www.amelsrl.com/.

Model 2049 Potentiostat

The 2049 has an external input and can be used with PowerLab replacing the XY plotter or chart recorder with Scope and Chart software, or can be used with EChem software so that stepped ramp and pulse voltammetry can be performed. The MLC-01 Cable Kit is available to connect your PowerLab to this instrument.

Model 2051 Potentiostat/Galvanostat

The 2051 has an external input and can be used with PowerLab replacing the XY plotter or chart recorder with Scope and Chart software, or can be used with EChem software so that stepped ramp and pulse voltammetry can be performed. The MLC-01 Cable Kit is available to connect your PowerLab to this instrument.

Model 2053 Potentiostat/Galvanostat

The 2053 has an external input and can be used with PowerLab replacing the XY plotter or chart recorder with Scope and Chart software, or can be used with EChem software so that stepped ramp and pulse voltammetry can be performed. The MLC-01 Cable Kit is available to connect your PowerLab to this instrument.

Model 2053 High Current Potentiostat

The Omni 101 is a high current (up to 12 A) potentiostat/galvanostst able to accept an external input. It can be used with PowerLab replacing the XY plotter or chart recorder with Scope and Chart software, or can be used with EChem software so that stepped ramp and pulse voltammetry can be performed. The MLC-01 Cable Kit is available to connect your PowerLab to this instrument.

Table 9–7
Features of AMEL
instruments.

Feature	Model			
	2049	2051	2053	2055
PowerLab as plotter	yes	yes	yes	yes
PowerLab as waveform generator	yes	yes	yes	yes
Inbuilt scanning	no	no	no	no
External Input	yes	yes	yes	yes
Voltage range	±5 V	±5 V	±5	±5 V
Compliance	22 V	27 V	50 V	30 V
Current ranges	1µA to 1 A	1µA to 1 A	1µA to 1 A	100 µA to 10 A
iR Compensation	no	no	yes	no

Note: These specifications should be verified. Specifications may change at short notice.

EChem User's Guide

A

Menus & Commands

Menus

The menus shown here are similar to how they will appear when you first use EChem. If your copy of EChem has previously been used by someone else it may appear differently if the EChem menus have been customized. EChem has six standard menus: File, Edit, Technique, Display, Windows, and Macro. Some of the menu commands shown will change or be disabled depending on the active window and what, if anything, is selected. An ellipsis, three dots (…), after a menu command indicates that it brings up a dialog box; a tick to the left of the command indicates that it is currently active; and a keyboard equivalent, if there is one, is shown to the right.

Figure A–1
The File menu

File		
New	⌘N	Create a new EChem file
Open...	⌘O	Open an existing file
Close	⌘W	Close the current file
Save	⌘S	Save the current file
Save As...		Save the file with a new name, elsewhere, or in various forms
Page Setup...		Set up page size and so on to suit the printer
Print...	⌘P	Print one or more pages of data
Quit	⌘Q	Quit EChem

Figure A–2
The Edit menu

Edit

Undo Load Data	⌘Z

Undo previous action (if possible)

Cut	⌘H
Copy	⌘C
Paste	⌘U
Clear	⌘B

Cut page or selected data to the Clipboard
Copy page or selected data to the Clipboard
Paste page or selection
Clear page or selection

Copy Special...

Copy text or graphics to the Clipboard

Preferences ▶

Customise EChem options (see Figure A–3)

Show Clipboard

Show contents of Clipboard

Figure A–3
The Preferences submenu

Preferences ▶

Options...
Menus...
Controls...
Start-Up...

Modify various EChem settings
Modify EChem menus
Modify appearance of control panels
Save current settings as default settings

Figure A–4
The Technique menu

Technique

✓Linear Sweep...	⌘E
Square Wave...	
Normal Pulse...	
Differential Pulse...	
Linear Sweep Stripping...	
Square Wave Stripping...	
Normal Pulse Stripping...	
Differential Pulse Stripping...	
Cyclic Voltammetry...	
Multi Pulse Voltammetry...	
Multi Pulse Amperometry...	
Apply Technique...	

Command- E (or Control-E) signifies the active technique

'Apply Technique' makes uses old parameters for the next page

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Figure A–5
The Display menu

Display

Display Settings...	Modify display colours, grids, lines, and so on
Go To Page... ⌘G	Go to a particular page of a file quickly
Show Overlay	Show or hide an overlaid page
Overlay All ⌘A	Turns all overlays on
Overlay None ⌘H	Turns all overlays off
Overlay Display Settings...	Modify the way overlaid waveforms are displayed
Sampling Display...	Sets the current sampling display method
Don't Subtract Background	Keep selected background but don't subtract
Set Background	Select a scan to be background
Clear Background	Deselect background scan

Figure A–6
The Windows menu

Windows

Notebook	Display Notebook window. Write general notes on the file
Main Window	Return to, or open the main EChem window
Zoom Window ⌘M	Display a selection in the Zoom window
Selection	Define selection area
Marker	Define marker position
Data Pad	Bring up Data Pad window
Add to Data Pad ⌘D	Log results to Data Pad

Figure A–7
The Macro menu

Macro

Start Recording ⌘R	Start or stop recording a macro
Delete Macro...	Delete a macro from the current list of macros
Macro Commands ▶	Choose macro control actions (see Figure A–8)

Figure A–8
The Macro Commands submenu. The Speak Message and AppleScript commands are available only on Macintosh systems.

Macro Commands ▶

Redraw the screen during the playing of a macro	**✓Update Screen**
Pause the macro for a set time	**Wait...**
Set an audible alert using the System sounds	**Play Sound...**
Display a message dialog box (requiring user action)	**Message...**
Speak a written message (if the computer can do this)	**Speak Message...**
Add an AppleScript as a macro step	**AppleScript...**
Select each page of data to perform some action to	**Repeat for Each Page**
Start a repeat sequence	**Begin Repeat...**
Finish a repeat sequence	**End Repeat**

Keyboard Shortcuts

The Command-key (or ⌘) on Macintosh, or the Control-key on Windows PC, menu command equivalents are shown in Table A–1. Your copy of EChem may be set up differently if it has been customized. Some of the Command-key equivalents will also change or be disabled depending on the active window and what, if anything, is selected. Their functions are discussed elsewhere in this user's guide.

Table A–1
EChem keyboard short-cuts for Macintosh. Use the Control key on a Windows PC, or the - or ⌘ -key on a Macintosh. The list is alphabetical so that you can see at a glance which keys have been used for menu commands

Keystrokes	Function
Command–A	Overlay all
Command–B	Clear data
Command–C	Copy to Clipboard
Command–E	Edit active technique
Command–H	Overlay none
Command–N	New
Command–O	Open
Command–P	Print
Command–Q	Quit EChem
Command–R	Start/stop macro recording
Command–S	Save file
Command–V	Paste
Command–W	Close active window
Command–X	Cut page
Command–Z	Undo/redo (if possible)
Command–\	Access to dialog boxes (Menu, Save As, Start-up)
Command–Period (.)	Stop sampling, stop macro recording or playing
Command–Spacebar	Start/stop sampling
Command–Right arrow	Go to last page
Command–Left arrow	Go to first page

Standard keyboard short-cuts for dialog boxes also apply: Tab moves the insertion point to next text entry box; Enter or Return is the same as clicking the OK button; and Esc or Command-period (.) or Control-period, is the same as clicking the Cancel button.

B

Troubleshooting

Technical Support

EChem has been extensively tested to make sure that it runs smoothly and without difficulties. Occasionally, however, problems may arise or something unexpected may occur. The second part of this appendix gives a list of possible problems and likely solutions: you should look there first to see if your needs are addressed specifically.

If you are experiencing difficulties with EChem that are not covered in this user's guide, or you need technical assistance with your system, then ADInstruments and its authorised distributors are glad to help. The About EChem dialog box provides dealer and distributor addresses and the required system configuration information. To access this information, select the About EChem… command from the Apple ( ) menu on a Macintosh, or go to the Help menu on a Windows computer (click the dialog box when you have finished to make it go away).

Figure B–1
The About EChem dialog box

Release date

Click this button for information on hardware configuration

Click this button for information on dealer contacts

Dealer and Distributor Information

If you need help or information from an authorised PowerLab distributor, click the Telephone button, Figure B–1, to bring up the PowerLab Dealer and Distributor Addresses dialog box. Click in the scrolling list on the right of the dialog box to select your country, or the nearest one to it, and contact information will appear to the left. Feel free to contact your PowerLab dealer to discuss hardware and software requirements generally, and find out more about the latest releases, upgrades, and software maintenance information.

System Configuration Information

In general, you will need to provide specific information about your hardware and software to help to isolate and to solve problems effectively. Since this type of information can be tedious to collate, EChem does it all for you. Click the computer icon-shaped button, Figure B–1,to activate the About This Computer dialog box. There will be a short delay while it gleans the required information from your system.

The dialog box gives information on which version of EChem is running, together with a list of system extensions and 'inits'. Also provided is a detailed description of your Macintosh, your PowerLab and how it is connected, special hardware configurations, and other peripheral devices connected to the computer.

Click the Print button to print the picture (it brings up the Print dialog box), or the Copy to Clipboard button to copy the picture for pasting into a letter or fax to your PowerLab dealer.

Figure B–3
The About This Computer dialog box

Model of PowerLab (if connected)

Information about computer

List of system extensions (Macintosh only)

Click to copy information

Click to print information
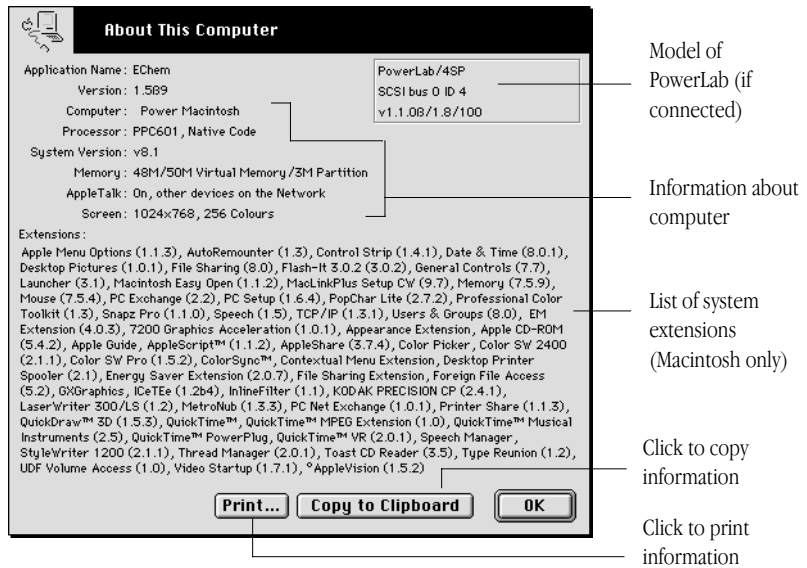
General

We welcome customer comment. You don't have to wait until you can send a software problem report or return damaged hardware! If you have comments or suggestions you would like to make about the EChem application or this user's guide, please feel free to write to us directly in Australia or New Zealand, or through your local PowerLab dealer. We value your responses, and they are taken into account when future releases are being worked on.

Solutions to Common Problems

EChem has an extensive array of dialog and alert boxes, and these will probably appear in most cases where problems arise. Very often they will suggest appropriate courses of action. Where they do not, or where the actions they suggest fail to alleviate the problem, this section of the guide should prove useful.

Starting Up

Start-up errors are mostly hardware problems, and are dealt with in detail in your *PowerLab Owner's Guide*, but are briefly covered here.

The computer can't find the PowerLab unit

The PowerLab is off or the power is switched off at the wall, the power cable is not connected firmly, or a fuse has blown.

- Check switches, power connections, and fuses.

Poor cable connection between the PowerLab and the computer, or a bad cable.

- Ensure that the cable is firmly attached at both ends and try again. If there is still a problem, try a new cable.

The PowerLab has an internal problem or has 'hung'

- Turn off the computer and PowerLab (and any other devices in the SCSI chain), and then turn the PowerLab back on again after at least ten seconds. Turn on the computer and try using EChem again.

SCSI problems: two SCSI devices on the bus have the same SCSI ID, or termination is incorrect.

- Check that each device has a unique ID number and that the SCSI chain is terminated correctly.

EChem 'hangs' or gives an alert on start-up

SCSI problems: two SCSI devices on the bus have the same SCSI ID, or termination is incorrect.

- Check that each device has a unique ID number and that the SCSI chain is terminated correctly.

It may be that the application has become damaged in some way.

- Try reinstalling EChem from the original CD

EChem starts up with strange settings and macros

You started EChem by opening a data file with custom settings or a settings file, or the start-up settings have been customised.

- Start up again from the application itself. To start up EChem with its default settings, hold down the Command key as you open the application (straight after double-clicking it). Release the key when an alert box appears.

To revert to the default start-up settings, choose the Start-Up… submenu command from the Preferences submenu of the Edit menu and click Clear in the dialog box that appears. The next time EChem starts up, it will open with the default settings.

Interface Problems

Some data display areas show gray

The Zoom window needs a selection (at least four data points) in the EChem window before it can display anything. Zooming within the Zoom window changes the selection in the EChem window, and may reduce the selection too far.

- Select data in the EChem window if there is no selection or change the extent of the selection if the Zoom window is gray.

Defined units display incorrectly

EChem will deal with a unit prefix correctly only if it is chosen from the Prefix pop-up menu in the dialog box for defining units: if defined as part of a unit, it is ignored. For example to define a milliampere — if you type in 'mA' as one word with no prefix, then EChem will display a signal of a microampere in units of mmA (millimillliampere). If the prefix 'm' were chosen, and the units as 'A', EChem would scale the unit prefix properly, to give the correct units of μA.

The indented position of defined units in the Units pop-up menu in the Units Conversion dialog box will show if a prefix has been used properly.

Commands seem to have no effect, or a strange one

Macro recording might have been turned on, so that you record what you are doing rather than actually doing it. If so, then an indicator will be turning in the title panel, with the word 'Recording…' beside it.

• Choose Stop Recording… from the Macro menu, and discard the macro, since it will likely be of little use.

Command-key equivalents don't work, or do strange things

Menu commands may have been deleted, or reassigned to other menu commands or macros.

• Look at the menus and compare them with Table A–1. See below for resetting procedures.

Menus, controls, or settings don't resemble those in this guide

If you started EChem by opening a data file with custom settings or a settings file, or the copy of EChem you are using has been extensively customised, and the settings saved as start-up settings. (Some menu commands may be disabled, or have disappeared altogether, some or all may be replaced by macros.)

• Start up again from the application itself. To start up EChem with its default settings, hold down the Command key as you open the application (straight after double-clicking it). Release the key when an alert box appears.

To revert to the default start-up settings, choose the Start-Up… submenu command from the Preferences submenu of the Edit menu and click Clear in the dialog box that appears.

I've altered menus and locked myself out, can't save, and so on

• Type Command-/ to bring up a dialog box that allows emergency access to the menu settings, start-up settings, and saving options.

Dialog boxes don't appear where I want them

EChem dialog boxes usually appear on the main monitor (the one with the menu bar). There are times, however, when you want one to appear on a secondary monitor, for instance, if that monitor is colour and you are changing display colours.

- EChem in fact brings up dialog boxes on the monitor where the pointer is positioned. To make a dialog box appear on a secondary monitor, place the pointer there and use a Command-key equivalent to bring up the dialog box (or if there is no keyboard equivalent, define a macro with one to do it).

The computer 'hangs' while recording, or there is data loss

There may be a poor cable connection between the PowerLab unit and the computer, or a bad cable, or incorrect SCSI termination. Network connection problems or a strange system extension could also be causing the problem.

- Ensure that the cable is firmly attached at both ends and try again. If there is still a problem, try a new cable.

- If you are using a SCSI interface ensure that the SCSI chain is terminated correctly.

- Check your network connections, if you are on a network.

- Check for strange system extensions, or software, especially obscure ShareWare or FreeWare.

I keep running out of memory

EChem records to RAM. If you increase its memory allocation (Macintosh only), you will have more of the RAM in your System available to record data.

- To increase available memory (Macintosh only), quit EChem, select the EChem icon in the Finder and choose Get Info in the File menu (or type Command-I). Type in a new value in the 'Preferred size' box.

- If the Macintosh has little free RAM space, you might want to turn off unused applications, reduce the size of the RAM cache or remove non-standard extensions or 'inits' from the system. See your computer's *User's Guide* for more details.

- If the Windows computer is running more than one piece of software turn off these other programs while EChem is running.

When multiple sweeps are taken, data compression is only done *after* all the pages have been sampled. EChem uses a reasonable amount of memory for an off-screen buffer: if the EChem window is large and the display is grayscale or color, more memory is used, especially if thousands or millions of colors (16 bit or more) are selected for display.

- Shrink the EChem window and change the display from colour or grayscale to black and white, or at least reduce the colour depth.

Printing Problems

Only one page printed, although a page range was specified

EChem adds to the bottom of the Print dialog box a dividing line and the Print Current Page Only checkbox, which is on by default. When the checkbox is on, the active page prints regardless of the range, if any, specified in the dialog box.

- To print a range of pages, turn off the Print Current Page Only checkbox, and enter the numbers as usual.

Printing is slow

If getting a hard copy of your EChem pages quickly is important, there are a number of things you can do.

- First, work in black and white, not gray-scale or color, and use the Waveform Print Layout buttons to minimize the number of sheets of paper to printed. On Macintosh turn off Background Printing in the Chooser: although it is useful to print in the background, spooling the document takes time. Ensure that you are using the latest printer driver (the LaserWriter 8 software, for instance, is considerably faster than the LaserWriter 7 software).

- The Page Setup options affect printing speed. For a PostScript laser printer, Faster Printing should be on, and Color and High-Resolution Printing off. If you have another type of printer, you should experiment with the Page Setup options to see which give greatest speed. (Remember that the Faster Printing option in the EChem Page Setup dialog box is not necessarily a panacea, in fact, depending on your particular setup, it is possible that it could make printing slower.) If using the LaserWriter 8 software, leave the Layout option in the Page Setup dialog box at '1 Up' (printing one page per sheet) — rescaling is quite slow.

The quality of printed work using these settings should be sufficient for most routine purposes, although, for publication quality diagrams, you may want to transfer data to a specialist graphing program such as IGOR Pro.

Printing speed depends on hardware as well: the faster the computer and printer, the faster that material can be printed.

Graphs are shrunk or comments truncated when printed

The file title, page number, and any page comments are included in the printed EChem page. Long comments mean the area used for the drawing is reduced; very long comments will be truncated.

- You cannot prevent page comments from printing, so keep them short (300 characters at most). Transfer longer comments as text to a word-processing program.

Macro Problems

Macros behave unexpectedly

- Make sure that you have the right macro, not a different one of the same name (in the case of name conflicts, the latest macro loaded into memory is used).

- Check that you have the steps and effects recorded somewhere, and that you haven't remembered them incorrectly–it is very easy to do.

- If the macro is a new one, it is possible that a step was not recorded correctly, and in particular, that a repeated sequence was ended in the wrong place. Try recording the macro again.

I have macros in files where I don't want them

A macro, once created, floats around in memory until you save a file, whereupon a copy is saved with the file (not necessarily the original file where it was created). If you have opened many files with macros in them, you will likely have a lot in memory.

- Delete unwanted macros from a file using the Delete Macro… menu command and then save the file. (Delete Macro… removes the macros from memory — the changes do not permanently take effect until the file is saved.)

I created a macro, but lost it on quitting EChem

As mentioned above, macros float around in memory until a file is saved. Your macro may have been attached to another file, or lost if you saved no files before quitting EChem.

- Save a file where you want macros stored before quitting EChem.

Crashes

EChem quits unexpectedly, crashes, or freezes

If EChem quits unexpectedly or crashes (you get a dialog box with a bomb in it), or the pointer freezes, then there may be a operating system problem. If the behaviour is repeated, then the problem may be coming from other software on you hard disk.

- Turn off screen savers. On a Macintosh try also turning off system extensions to see if this fixes the problem. See your computer's manual for more details on this problem and how to deal with it.

The data or settings file you are using may have become corrupted, possibly through disk damage, especially if it is on a floppy disk.

- Use disk-checking software to find and attempt to fix any problems in this area.

It may be that the EChem software itself has become damaged in some way.

• Try reinstalling EChem from the original CD.

It could be that a computer virus is causing the problems.

• Check your disk with anti-viral software. If you find a virus, you should check all potentially affected computers, disks, and backups, and eliminate the infection. See if you can find the cause of the outbreak (poor network security or student copying of software onto lab machines, for example) and try to prevent future occurrences.

Noise

The detection of small current signals can be hampered by a relatively large amount of noise. The determination of the source(s) of the noise and its elimination can be a time consuming task. The following advice is meant only as a guide to the likely sources of noise and is by no means a comprehensive list.

If you are using the ADInstruments Potentiostat, much high frequency noise can be effectively removed by setting the 10 Hz filter setting. Remember, however, that this filter will affect results from experiments that use short pulses (< 0.1 s), or fast scan times and should not be used under such conditions.

EChem voltammograms show unexpected oscillations

The noise on the raw signal is probably large. Check by opening the Input Amplifier or Potentiostat dialog and examining the raw signal at the same gain range as your experiment.

If the 'noise' is 50 Hz or 60 Hz mains interference then the regular sampling periods of EChem can cause an aliasing effect which may produce low frequency oscillations in the voltammogram. In this case:

• Set the sampling period to an exact multiple of 20 ms (if using 50 Hz mains power) or 16.7 ms (if using 60 Hz mains power). The mains induced noise will be eliminated when the signal is averaged over each sampling period; or

- Adjust the filter setting on your potentiostat to less than 50 Hz so that the noise is reduced to an acceptable level. This will only be possible at slower scan rates as filtering will distort peak shapes at faster scan rates. A 10 Hz filter setting can be used even for quantitative linear sweep or cyclic voltammetry up to about 100 mV/s and for qualitative work up to about 500 mV/s. For pulse techniques the pulse widths should be longer than about 100 ms if a 10 Hz filter setting is employed.

- Make sure that power cables are positioned well away from your experiment and the electrodes.

Other high frequency noise

Other high frequency noise may come from fluorescent lighting, air conditioners, electric motors (in laboratories these are found in hotplate-stirrers, water bath thermostat-stirrers, and refrigerators). Occasionally equipment in adjacent rooms may be the cause of the problem.

- Turn off lights, and nearby equipment, one at a time to locate noise source(s) by trial and error

The computer itself, or other nearby computers, are likely sources of high frequency noise. The computer monitor and the floppy and hard disk drives are the most common origins.

- Reposition the potentiostat and reaction vessel as far from the computer as possible. Especially avoid having the electrodes in front of the computer monitor.

Occasional spikes or intermittent noise

Occasional spikes or intermittent noise are more likely to be caused by nearby electrical instrumentation being turned on or off. Remember that many instruments have internal relays that may be switching on and off during normal operation. The computer hard disk and floppy disk drives may also give rise to this type of noise.

- Install a surge suppressor/line filter power board on your power socket and plug the computer, MacLab/PowerLab and

potentiostat all into this one board. Try running your experiment with nearby equipment switched off.

Noise with no apparent cure

Aluminium foil wrapped around the electrochemical cell and grounded at a single common place may help. Placing the experiment, potentiostat, MacLab or PowerLab, and even the computer on a single large grounded copper sheet may reduce noise levels markedly. In very low current or very noisy situations you may have no alternative but to enclose your experiment in a Faraday cage. Commercial cages are available but they will work no better than one made by a local tradesperson from sheet metal or copper mesh. It may also be useful to position the potentiostat within the cage. In a large laboratory a small garden shed could be used as a walk-in cage.

EChem User's Guide

A P P E N D I X   C

Technique Summary

This Appendix provides a quick reference to the techniques provided in then EChem Technique menu. It is not a replacement for the detail given in Chapter 7. If you need more detail please refer to the appropriate technique in Chapter 7.

This Appendix does not cover the additional techniques described in Chapter 8.

Linear Sweep Voltammetry

In linear sweep voltammetry (LSV) a linearly increasing (or decreasing) potential staircase ramp is applied to the working electrode (Figure C–1). The average current flowing during the sample periods (at the end of each step) in the potential ramp is recorded and plotted against the voltage.

The current is usually sampled at the end of each potential step. If you use the Multi Pulse Technique to set up a linear sweep run then you can alter the position of the sampling period.

Table C–1
Linear Sweep Voltammetry parameter reference

Parameter	Values	Comments
Range	1000, 2000 or 5000 mV full scale	The 2000 mV range is typical
Initial Potential	between ±1, 2 or 5 V	
Final Potential	between ±1, 2 or ±5 V	Must not be the same as the initial potential. It can be more negative or positive than the initial potential.
Scan Rate	usually 5–1000 mV/s	Faster scan rates lead to a higher background signals unless microelectrodes are employed.
Step Width	≥ 0.1 ms	The time that the potential is kept constant at each step
Step Height	1-2 mV is ideal	Values over 10 mV give insufficient potential resolution and lead to excessively high charging currents
Samplig Period	≥ 0.1 ms	Use 20 ms at 50 Hz power, or 16.7 ms at 60 Hz power, to minimise mains hum interference (visible as oscillations on voltammogram)
Steps	automatically set	
Rest Time	1–5 s is usual	The length of time the potential is kept at the initial potential before the scan is started.

Square Wave Voltammetry

In Square Wave Voltammetry a square wave is superimposed upon a staircase potential ramp so that one square wave cycle occurs on each step. The Square Wave technique in EChem uses this method which is sometimes called Osteryoung Square Wave Voltammetry.

The current is sampled at the end of the forward step and again at the end of the reverse step.

Table C–2
Square Wave Voltammetry parameter reference

Parameter	Values	Comments
Range	1000, 2000 or 5000 mV	2000 mV is typical
Initial Potential	between ±1, 2 or 5 V	This potential is usually chosen so as to not oxidise or reduce the substrate
Final Potential	between ±1, 2 or 5 V	must be different to the initial potential
Frequency	10–60 Hz is typical	frequency of the square wave
Step Height	≥ 1 mV	This is the height by which the staircase base ramp increments
Steps	automatically set	
SW Ampl.	10–50 mV is typical	This is the half-height of the pulses of the square wave
Sampling Period	≥ 0.1 ms	Current data will be collected and averaged over this period which occurs at the end of each step (upper and lower). The sampling period should be significantly shorter than the step width in order for the charging current to decay. Use 20 ms at 50 Hz power, or 16.7 ms at 60 Hz power, to minimise mains hum interference (visible as oscillations on voltammogram).
Rest Time	1–5 s is typical	

Normal & Reverse Pulse Voltammetry

In Normal Pulse Voltammetry, a series of pulses of successively larger potential are applied above a base potential to the working electrode. Reverse Pulse Voltammetry is similar except that the base potential is chosen to electrolyse the electroactive substrate. The pulses that are then applied cause the reverse reaction to take place. The current is sampled at the end of each pulse, and plotted against the potential.

Table C–3
Pulse Voltammetry parameter reference

Parameter	Values	Comments
Range	1000, 2000 or 5000 mV	2000 mV is typical
Initial Potential	between ±1, 2 V or 5 V	Usually chosen to be a value at which the electrode reaction of interest does not occur. For Reverse Pulse Voltammetry this potential is chosen to cause complete oxidation (or reduction) of the substrate, and the pulses then cause the reverse reaction.
Final Potential	between ±1, 2 or 5 V	This is the height of the last pulse to be applied. It can be thought of as the height of an imaginary ramp passing through the tops of the pulses.
Scan Rate	usually 5–100 mV/s	Usually this parameter is allowed to vary as the Step Width and Step Height are set.
Step Width	2–4 s is typical	This is the period of a single step (including the pulse time). Much shorter times can be used with microelectrodes.
Step Height	10 mV is typical	This defines the increase in height (mV) of successive pulses. The minimum increment available is 1 mV
Steps	automatically set	
Pulse Width	5–100 ms is typical	Should be wide enough to allow the non-faradaic components of the current to decay before sampling. Much shorter times can be used with microelectrodes.
Rest Time	several seconds	This is the period between when the deposition potential is applied and the scan commences. It allows the solution to come to equilibrium after the initial potential is applied.
Sampling Period	≥0.1 ms	The current is always sampled at the end of the pulse. Use 20 ms at 50 Hz power, or 16.7 ms at 60 Hz power, to minimise mains hum interference (visible as oscillations on voltammogram)

Differential Pulse Voltammetry

Differential pulse voltammetry uses a series of short, small amplitude pulses (typically 50 mV) superimposed on a linearly increasing or decreasing potential ramp (Figure 7–14). The current is sampled just prior to each pulse (i1) and at the end of the pulse (i2). The difference in current (i2–i1) is plotted versus the potential at the base ramp.

Parameter	Values	Comments
Range	1000, 2000 or 5000 mV	2000 mV is typical
Initial Potential	between ±1, 2 or 5 V	
Final Potential	between ±1, 2 V or 5 V	Must not be the same as the initial potential
Scan Rate	1–25 mV/s is typical	Increasing the scan rate decreases peak resolution. However very slow scan rates mean inordinately long analysis times
Step Width	0.5–4 s is typical	The time of each step (including pulse time). This is also the period between pulses. This parameter is usually allowed to vary while the Scan Rate and Step Height are set. Much horter times can be used with microelectrodes.
Step Height	1–10 mV is typical	keep as small as possible
Steps	automatically set	
Pulse Height	50–100 mV is typical	The height of the pulse superimposed upon the potential ramp. A positive peak height indicates a pulse in the direction of the applied ramp. Larger values increase sensitivity (bigger peaks). Smaller values improve resolution. The Pulse Height must be greater than the Step Height or the next step will be bigger than the previous pulse.
Pulse Width	20–100 ms is typical	The pulse should last long enough to allow the non-faradaic components of the current to decay before sampling, this usually requires that the Pulse Width is at least 5 ms longer than the sampling period - the larger the area of the electrode the longer this will need to be. For a standard glassy carbon electrode with an area of ~1 mm the pulse should be at least 20 ms wide. Much shorther times can be used with microelectrodes.
Rest Time	1–5 s	The period before the scan commences when the initial potential is applied.
Sampling Period	1–20 ms typically	Use 20 ms at 50 Hz power, or 16.7 ms at 60 Hz power, to minimise mains hum interference (visible as oscillations on voltammogram).

Cyclic Voltammetry

The potential is driven between two limits at a constant rate, similar to linear sweep voltammetry. When a limit is reached the potential is swept back again at the same rate. The experiment can start at any potential (initial potential) between the two limits. The current is sampled at the end of each potential step.

Parameter	Values	Comments
Range	1000, 2000 or 5000 mV	2000 mV is typical
Initial Potential	between ±1, 2 or 5 V	Chosen to be a value at which oxidation or reduction of the substrate does not occur. The potential might correspond to either the Upper or Lower potential or be somewhere in this range.
Final Potential		must be the same as the initial potential (to complete a cycle).
Upper (Potential Limit)	between ±1, 2 or 5 V	maximum potential that will be achieved in a cycle and can be any value
Lower (Potential Limit)	between ±1, 2 or 5 V	minimum potential that will be achieved in a cycle. Note that the difference, Upper-Lower potential, must be less than 4 V if the 2000 mV range is selected, and less than 10 V if the 5000 mV range is selected.
Scan Rate	10–1000 mV/s	Faster scan rates can be selected but (depending on the scan width) you may find that the step height is unacceptably high.
Step Height	≥ 1 mV	the step height to a minimum (between 1 or 2 mV is ideal. More than 10 mV will not give adequate potential resolution.
Step Width	≥ 2 ms	The time that the potential is kept constant at each step.
Samplig Period	≥ 0.1 ms	Use 20 ms at 50 Hz power, or 16.7 ms at 60 Hz power, to minimise mains hum interference (visible as oscillations on voltammogram)
Rest Time	≥ 1 s	Period between when the Potential is applied and the scan commences.
Deposition Potential	not normally used	potential applied during the deposition time.
Deposition Time	not normally used	This is a period before the Rest Time. Can be used for stripping methods.
Cleaning Potential	not normally used	The Cleaning Potential can also be set to a value to oxidise (or reduce) any material that has plated out on the working electrode. The potential applied during the Cleaning Time.
Cleaning Time	not normally used	This is a period after the Final Potential has been reached. Can be used for stripping methods.

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Multi Pulse Voltammetry

The Multi Pulse Voltammetry technique allows you to generate your own waveform. This is constructed by the addition of a staircase ramp and one or two pulses per step of the ramp. In addition up to four current sampling windows can be selected with their position and duration independently set.

Ramp Parameter	Values	Comment
Range	1000, 2000 or 5000 mV	Usually the 2000 mV range is chosen.
Initial Potential	between ±1, 2 or 5 V	
Final Potential	between ±1, 2 or 5 V	Must not be the same as the initial potential. The final potential may be either more negative than the initial potential (negative scan) or more positive than the initial potential (positive scan).
Scan Rate	< 1 mV/s for corrosion work otherwise 5–1000 mV/s	Faster scan rates lead to a higher background signal.
Step Width	≥ 2 ms	The time that the potential is kept constant at each step.
Step Height	dependent on experiment	
Steps	automatically set	
Rest Time	1–5 s is typical, longer for corrosion work	the length of time the potential is kept at the initial potential before the scan is started

Defining Pulses

Pulse Parameters	Values	Comments
Pulse Start	< Step Width (ms)	The timing of each pulse is linked to the start of each step in the base ramp. For example if you enter 20 ms in the Start box it means the pulse will be activated 20 ms after the beginning of the step. The pulse can begin at any time during each step
Pulse Height		this is the height of the pulse above (or below) the step.
Increment		pulses on successive steps will be incremented by this amount
Duration	< (Step Width – Pulse Start)	the duration of the pulse must be such that the entire pulse occurs within one step of the potential ramp

D

Electrochemical Equations

Linear Sweep and Cyclic Voltammetry

The Randles-Sevcik Equation

For a substrate with a reversible redox reaction, at a planar disk electrode, in an unstirred solution, the peak current during linear sweep, or cyclic voltammetry, is given by the Randles–Sevcik equation:

$$i_{Pa} = 269 \, n^{3/2} A D^{1/2} C v^{1/2} \qquad \text{for an oxidation (anodic scan)}$$

$$i_{Pc} = -269 \, n^{3/2} A D^{1/2} C v^{1/2} \qquad \text{for a reduction (cathodic scan)}$$

The potential where this occurs is given by:

$$E_{Pc} = E_{1/2} - \frac{0.0285}{n} \qquad\qquad E_{Pa} = E_{1/2} + \frac{0.0285}{n}$$

where

i_{Pa} = current peak during anodic scan (A)
i_{Pc} = current peak during cathodic scan (A)
E_{Pa} = potential at current peak for anodic scan (V)
E_{Pc} = potential at current peak for cathodic scan (V)
$E_{1/2}$ = half potential as determined by cyclic voltammetry (V)
n = the number of electrons transferred to (or from) the substrate molecule

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A = area of the exposed surface of the electrode (cm^2)
D = diffusion coefficient of the substrate molecule ($cm^2\,s^{-1}$).
C = concentration of the substrate molecule ($mol\,L^{-1}$)
υ = the scan rate ($V\,s^{-1}$)

The factor of 269 is a parameter that derives from using a planar electrode at a temperature of 298 K

Thus a truly reversible reaction can be identified by examining the adherence of the system to the following functions:

- $i_p \propto \sqrt{\upsilon}$

- E_p independence of the san rate, υ

In addition cyclic voltammograms will exhibit:

$$|E_{Pa} - E_{Pc}| = \frac{57}{n} \quad mV\ (at\ 298\ K)$$

$$\left| \frac{i_{Pa}}{i_{Pc}} \right| = 1$$

When working in highly resistive solutions, which is often the case when using organic solvents for cyclic voltammetry, the reference electrode should be kept as close as possible to the working electrode to minimise iR drop. Nonetheless there may still be an appreciable uncompensated resistance which will cause $|E_{pc} - E_{pa}|$ to become larger than predicted, the peaks will be broader and the peak currents smaller.

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Differential Pulse Techniques

The Parry-Osteryoung Equation

Differential pulse techniques require that the sampling periods be chosen so that the current is only due to a Faradaic component (i.e. only due to a redox reaction and not the charging current which dominates immediately after the application of a pulse)

The observed potential of the peak when studying a reversible system is given by:

$$E_P = E_{1/2} - \frac{h_p}{2}$$

where

E_p = potential at which the peak occurs

$E_{1/2}$ = the half wave potential (as might determined by cyclic voltammetry)
h_p = the height of the pulse.

The peak current is given by the Parry-Osteryoung equation:

$$i_P = \frac{nFAD^{1/2}C(1-\theta)}{1000\pi^{1/2}(\tau-t)^{1/2}(1+\theta)}$$

where

$t =$ time at which the current is first sampled in each cycle
$\tau =$ time at which the current is sampled second in each cycle

$\theta = e^{\frac{(nFAh_p)}{2RT}}$

n = the number of electrons transferred to (or from) the substrate molecule
F = Faraday's constant, 96485 C mol^{-1}
A = area of the exposed surface of the electrode (cm^2)
D = diffusion coefficient of the substrate molecule (cm^2 s^{-1}).
C = concentration of the substrate molecule (mol L^{-1})
R = the gas constant, 8.314 J K^{-1} mol
T = the temperature (K)

Chronoamperometry

The Cottrell Equation

When chronoamperometry is performed on an unstirred solution at a planar electrode the faradaic current response is described by the Cottrell equation

$$i = \frac{nFAD^{1/2}C}{1000\pi^{1/2}t^{1/2}}$$

where

n = the number of electrons transferred to (or from) the substrate molecule

F = Faraday's constant, 96485 C mol^{-1}

A = area of the exposed surface of the electrode (cm^2)

D = diffusion coefficient of the substrate molecule (cm^2 s^{-1}).

C = concentration of the substrate molecule (mol L^{-1})

t = time (s)

The factor of 1000 is to bring both cm and dm (1 L = 1 dm^3) in the equation to common units.

In aqueous solution the coefficient of diffusion usually has a value of between 10^{-5} and 10^{-6} cm^2 s^{-1}.

Chronocoulometry

The Integrated Cottrell Equation

The current response equation at a planar electrode for a chronocoulometric experiment is the time integrated form of the Cottrell equation:

$$Q = \int_0^t i\, dt = \frac{2nFAD^{1/2}Ct^{1/2}}{1000\pi^{1/2}} + k$$

where
   Q = the number coulombs transferred
   n = the number of electrons transferred to (or from) the substrate molecule
   A = area of the exposed surface of the electrode (cm^2)
   D = diffusion coefficient of the substrate molecule ($cm^2\,s^{-1}$).
   C = concentration of the substrate molecule (mol L^{-1})
   t = time (s)
   k = a constant.

Thus a plot of Q versus $t^{1/2}$ should produce a straight line with an intercept of k.

The constant k can be defined as: $k = nFA\Gamma + Q_{dl}$

where
   Γ = surface concentration of adsorbed substrate (mol cm^{-2})
   Q_{dl} = double layer charging.

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E

Cyclic Voltammetry, Solvents & Electrolytes

Common organic solvents for cyclic voltammetry include methanol, ethanol, propylene carbonate, 1,2-dimethoxyethane, acetonitrile, acetone, dimethylsulfoxide (dmso), dichloromethane, dichloroethane, and toluene. Polar and protic solvents exhibit lower resistivities than non-polar and/or aprotic solvents. Unfortunately it is the more resistive solvents in which common electrolytes are least soluble.

Remember that many of the constituent ions (both cations and anions) of electrolytes are toxic and that when dissolved in organic solvents they can be carried across the skin. Similar aqueous solutions are usually much less of a hazard if skin contact occurs. However, in all cases of accidental spillage where you do not know the specific treatment, all contaminated skin areas should be continuously flushed with copious amounts of water for at least several minutes.

For a a good general introduction to the use of non-aqueous solvents see the 'Chapter 7, Solvents and Electrolytes' in 'Electrochemistry for Chemists', 2nd edition, D. T. Sawyer, A. Sobkowiak, and J. L. Roberts, Wiley-Interscience New York, 1995.

Solubility Rules

Some generalised rules for solubility of electrolytes in organic solvents are:

* perchlorates (care! explosion hazard), chlorides, nitrates, and tosylates are most soluble in alcohols;

- perchlorate in the presence of potassium ions will give a precipitate of $KClO_4$;

- electrolytes comprising large cations and anions will be more soluble in non-polar solvents and less soluble in polar solvents;

- dimethylsulfoxide is a very good solvent for most electrolytes;

- fluoroborate and hexafluorophosphate salts exhibit particularly good solubility in acetone and acetonitrile;

- dichloromethane and similar solvents usually require tetra-n-butylammonium hexafluorophosphate.

- electrochemistry in toluene an be performed using liquid tetrabutylammonium tetrafluoroborate toluene solvate. See *J. Chem. Soc. Chem. Commun*, 323 (1985).

Solvent Stability

Amides, esters, nitriles, strained ethers, etc. are subject to hydrolysis especially if traces of acid or base are present. Hydrolysis reactions can be very slow (hours or days) and often manifest themselves as an increase in background currents or a reduced redox stability window. Remember that only a small fraction of the solvent need hydrolyze to generate impurities that can be detected electrochemically but which will remain unseen by nmr or infrared spectroscopy.

Use of Large Ions as Electrolytes

A wide variety of large cations and anions are available so that in practice it is nearly always possible to find an electrolyte that will be suitable for a given solvent. Common electrolytes are commercially available but others will need to be prepared by the user. Purity of both commercial and home made electrolytes should be checked by performing a blank run at the same sensitivity setting of the potentiostat that is used when the analyte is present. Remember that purity is a relative term – electrolyte and solvent that has been used satisfactorily with high concentrations of analyte at low sensitivity settings may prove to hopelessly contaminated when used with much lower concentrations of analyte at very high sensitivity settings.

Cations

Complex cations are typically subject to reduction at sufficiently large potential, oxidation is usually less of a problem. Remember that only a small proportion of the electrolyte needs to be electrolyzed to produce a signal that will interfere with the analyte's signal. Some large cations that can be employed are shown in Table E–1.

Tetraalkylammonium salts are the most commonly used for organic solvent work because of their relatively low cost and because they are fairly resistant to reduction.

Table E–1
Complex cations used in background electrolytes

Cation	Formula	M_r	Comments
tetramethylammonium	$[N(CH_3)_4]^+$	74.15	
tetraethylammonium	$[N(CH_2CH_3)_4]^+$	130.3	
tetra-n-butylammonium	$[N(CH_2CH_2CH_2CH_3)_4]^+$	242.5	PF_6^- salt used in dichloromethane.
tetraphenylphosphonium	$[P(C_6H_5)_4]^+$	339.4	Easily reduced. Hydrolyzed by hydroxide.
benzyltriphenylphosphonium	$[P(CH_2C_6H_5)(C_6H_5)_3]^+$	353.4	Easily reduced. Hydrolyzed by hydroxide.
bis(triphenylphosphino)imminium	$[(C_6H_5)_3P=N=P(C_6H_5)_3]^+$	538.6	
tetraphenylarsonium	$[As(C_6H_5)_4]^+$	383.3	
(18-crown-6)potassium	$[K(C_{12}H_{24}O_6)]^+$	303.4	Can be prepared in situ from potassium salts.
(dibenzo-18-crown-6)potassium	$[K(C_{20}H_{24}O_6)]^+$	399.5	Can be prepared in situ from potassium salts. Soluble in benzene, toluene etc.

WARNING

Perchlorates are a known explosion hazard and their use should be avoided wherever possible. Especially avoid evaporation of perchlorate containing solutions and clean up all spills immediately.

Anions

Large anions may be subject to reduction or oxidation. Some anions that can be employed as shown in Table E–2. Perchlorate salts are a known explosion hazard and should be avoided wherever possible. Note that while nitrate is often considered safe to use, it is an oxidizing agent. Its use as an electrolyte (at relatively high concentrations) in organic solvents is a potential explosion/fire hazard, especially if traces of acid are present, or if the solution is left to evaporate.

Table E–2
Complex anions used in background electrolytes

Anion	Formula	M_r	Comments
nitrate	NO_3^-	62.00	Potential explosion hazard.
perchlorate	ClO_4^-	99.45	Explosion hazard, easily reduced.
triflate	$CF_3SO_3^-$	149.1	
methanesulfonate	$CH_3SO_3^-$	95.09	
tosylate	$CH_3C_6H_4SO_3^-$	171.2	
trifluoroacetate	CF_3COO^-	113.0	
tetrafluoroborate	BF_4^-	86.80	May hydrolyze to HF.
tetraphenylborate	$B(C_6H_5)_4^-$	319.2	
hexafluorophosphate	PF_6^-	145.0	May hydrolyze to HF.

Electrode and Cell Design for Organic Solvents

Cyclic voltammetry can be carried out in ordinary sample tubes (2.5 × 5 cm) with the electrodes placed through holes in the plastic cap. Air can be excluded with an argon or nitrogen purge. Argon is more expensive but because of its greater density tends to blanket the sample more efficiently.

The purity of the solvent and the electrolyte can be established by looking for spurious signals in the cyclic voltammogram — but make sure that you run at the same gain range you will be using for your samples. In many cases both the solvent and electrolyte will need to be thoroughly dried as traces of water may limit the scan range or react with the substrate or electrolysis products.

Electrochemistry in dichloromethane or 1,2-dichloroethane (less volatile) can be performed using a 0.10 mol L^{-1} solution of tetra-n-butylammonium hexafluorophosphate. Other common combinations are 0.1 mol L^{-1} tetra-n-butylammonium tetrafluoroborate in acetonitrile, or benzonitrile; or 0.1 mol L^{-1} tetraethylammonium perchlorate in propylenecarbonate, tetrahydrofuran, or dimethyl formamide. Where possible perchlorates (explosion hazard) should be substituted with salts containing non-oxidizing anions.

While many workers go to great length to dry their solvents this is really only necessary if the compound or its redox products are water sensitive or if you wish to explore outside the redox inactive region of water. There is nothing inherently wrong in using mixed aqueous/organic solvent mixtures if this is convenient. However, remember that many molecules, or their redox products, are acids or bases and, that if your aqueous solutions are not adequately buffered, you may have difficulty in getting reproducible results. The addition of a small amount of acid or base to an aqueous solvent mixture can both serve to buffer the solution and to act as a background electrolyte.

Many studies require only a simple determination of $E_{1/2}$ values for compound characterisation. In these cases some liberties can be taken with electrode design. A 0.5 mm diameter platinum wire can be used

as the working electrode. The wire should be embedded in a soft (soda) glass rod which can be polished at its end. Soda glass matches the thermal coefficient of platinum more closely than borosilicate — if the platinum wire and glass rod separate in the working electrode solution may seep into the electrode and give old signals. Allowing the wire to protrude by as much as 1–3 mm will increase the current but this is usually not necessary.

The auxiliary (counter) electrode is usually a simple platinum wire.

The reference Ag/AgCl electrode can be as simple as a silver wire previously anodized in 1 M hydrochloric acid, rinsed with water, then allowed to dry. The wire is then immersed in electrolyte solution in a thin glass or Teflon tube with a sintered frit at the bottom which acts as a small salt bridge.

If there is any doubt about the stability of the reference then the ferrocene/ferrocinium (Fc/Fc$^+$) couple can be used as reference potential to calibrate the reference electrode: a small amount of ferrocene is added to the reaction mixture after the experiment is finished (the peak to peak separation is usually about 70 mV). Alternatively the electrode can be calibrated at the beginning of each day by measuring the Fc/Fc$^+$ couple in fresh electrolyte. Cleaning and re-anodizing of the silver wire will be necessary from time to time. It is not uncommon for inorganic and organic chemists to report redox potentials relative to ferrocene.

The reference electrode should be placed as close as possible to the working electrode. Distances between the working and auxiliary electrodes should also be kept to a minimum to keep the required compliance voltage small (see Appendix F).

Synthesis of Selected Electrolytes

Tetraethylammonium perchlorate, $[(CH_3CH_2)_4N]ClO_4$, $M_r = 229.7$

Acid-Bromide method

Tetraethylammonium bromide, $M_r = 210.2$, (100 g, 0.48 mol) is dissolved in water (100 mL) with slight warming, then 1.0 M perchloric acid (600 mL, 0.60 mol) is added. White crystals form immediately and are filtered off after cooling the mixture to below 5 °C. The crude product is washed with ice cold 1.0 M perchloric acid (100 mL) then recrystallised from 1.0 M perchloric acid (300 mL). The product is filtered off, washed first with ice cold 1.0 M perchloric acid (100 mL), then ice cold ethanol (200 mL). Recrystallisation from boiling ethanol (300 mL) with sufficient water to ensure complete dissolution (about 30 mL) gives the final product which is washed with ice cold ethanol (200 mL). The product can be checked for purity by dissolving about 0.5 g in warm water (2 mL) and testing the pH of the solution, and for any reaction with silver nitrate. A further recrystallisation from ethanol may be necessary. The product is dried under vacuum (0.1 mm Hg), to yield 70.3 g (64%) of white needles. The solid compound should be treated as an oxidising agent and stored away from reducing (organic) materials.

Acid-Base method

Aqueous 1 M perchloric acid (250 mL, 0.25 mol) is added to a solution of 1 M tetraethylammonium hydroxide (250 mL, 0.25 mol). The mixture is adjusted to pH 7 (use a narrow range pH indicator paper, not litmus paper) by the addition of more acid or base solution as required, and stirred while cooling in an ice bath.The resulting precipitate is removed from the cold suspension by suction filtration and washed with cold water. The crude product can be recystallised from water and dried at 100°C for 24 h in vacuo. M.p. 351–352.5°C with decomposition. The solid compound should be treated as an oxidising agent and stored away from reducing (organic) materials.

The purity of the product should be checked by cyclic voltammetry.

Tetra-n-butylammonium hexafluorophosphate, [n-Bu$_4$N]PF$_6$

Bromide method

A solution of tetra-n-butylammonium bromide (100 g, 0.31 mol) in acetone (250 mL) is mixed with a solution of ammonium hexafluorophosphate (50 g, 0.4 mol) in acetone (350 mL). The resulting precipitate of ammonium bromide is removed by suction filtration. The filtrate is concentrated, with a rotary evaporator, to approximately 200 mL. Water is added to the acetone solution to precipitate tetra-n-butylammonium hexafluorophosphate (final volume approximately 2 L). The precipitate is removed by suction filtration, washed with water, and then redissolved in a solution of ammonium hexafluorophosphate (5 g, 0.04 mol) in acetone (200 mL) — more acetone can be added to complete dissolution if required. Addition of water (final volume approximately 2 L) causes the precipitation of the crude product which is removed by suction filtration and washed with water.

Acid-base method

An aqueous solution of 0.5 M hexafluorophosphoric acid (600 mL, 0.3 mol) is added to an aqueous 0.5 M solution of tetra-n-butylammonium hydroxide (600 mL, 0.3 mol). The mixture is adjusted to pH 7 (use a narrow range pH indicator paper, not litmus paper) by the addition of more acid or base solution as required. The crude product is removed from the cooled mixture by suction filtration and washed with water.

Recrystallisation

The crude product, produced by either the bromide or acid-base method, is recrystallized three or four times from a 3:1 mixture of ethanol/water and then dried for at least 24 h at 100°C in a vacuum oven. The yield is usually about 95 g.

The purity of the product should be checked by cyclic voltammetry.

Tetra-n-butylammonium tetrafluoroborate, [n-Bu$_4$N]BF$_4$, M$_r$ = 391.5

Acid-Bromide method

Aqueous fluoroboric acid (48%, 36 mL) is added to a solution of tetra-n-butylammonium bromide (84 g, 0.25 mol) in water (180 mL) and the mixture stirred for 1 minute. The resulting precipitate is removed by suction filtration and washed with water until the washings are no longer acid (use a narrow range pH paper). The crude product can be recrystallised from ethyl acetate/cyclohexane. M.p. 162–162.5°C.

The purity of the product should be checked by cyclic voltammetry.

Tetra-n-butylammonium fluoroborate toluene solvate, [n-Bu$_4$N]BF$_4$.3(C$_6$H$_5$CH$_3$)

Tetrabutylammonium fluoroborate is stirred in toluene between 22–25°C. A two phase mixture results. The lower layer has an approximate formula of [n-Bu$_4$N]BF$_4$.3(C$_6$H$_5$CH$_3$). (Below 22°C the solvent-free fluoroborate salt crystallises.) This layer an be separated and used, without further purification, as the solvent for electrohemical work. Reference: *J. Chem. Soc. Chem. Commun*, 323 1985.

Tetra-n-butylammonium triflate [n-Bu$_4$N]CF$_3$SO$_3$, M$_r$ = 391.5

Triflic acid (trifluoromethanesulfonic acid), M$_r$ = 150.1, (600 mL, 0.15 mol) is slowly added, with stirring, and cooling, to a commercially available 40% solution of tetrabutylammonium hydroxide (M$_r$ = 259.5) (100 mL 0.15 mol) until the pH drops to 6.5 (use a narrow range indicator paper). Water is added if necessary to allow adequate stirring. The crude product is suspended in ice cold water and filtered 5 times to wash it, then dried and recrystallised from a mixture of dichloromethane and diethyl ether. Reference: *J. Org. Chem.*, **37**, 3968, 1972.

The purity of the product should be checked by cyclic voltammetry.

Purification of solvents

For guidelines on the purification of many solvents see "Purification of Laboratory Chemicals", 4th edition, W. L. F. Armarego and D. D. Perrin, Butterworth-Heinemann, 1997, ISBN 0750637617.

Solvents should be of at least AR (analytical reagent) grade otherwise they may be grossly wet or otherwise need a preliminary purification step. Further drying and purification is then usually necessary before the solvent can be used for cyclic voltammetry or other electroanalytical techniques.

Distillation of solvents should always take place using a short fractionating column filled with glass rings to prevent an aerosol of the boiling solvent being carried through the condensor. A dedicated still for each solvent is ideal.

Ethers (including tetrahydrofuran, diethyl ether, 1,4-dioxan, and 1,2-dimethoxyethane), as well as aromatic hydrocarbons (benzene, toluene, xylenes) can be first dried over sodium wire then distilled from freshly drawn sodium wire with a little benzophenone added to the distillation pot. A dark blue or purple color should develop and persist during reflux, for at least 10 minutes, which signals the presence of sodium benzophenone ketyl (a radical anion). The ketyl can only exist in the absence of water. The anhydrous solvent can then be distilled. Excess sodium wire is destroyed by allowing the distillation pot to cool and cautiously adding absolute ethanol.

Dichloromethane, 1,2-dichloroethane, cyclohexane, or hexane, can be dried by distillation from either P_2O_5 or from CaH_2.

Acetonitrile should be predried using a molecular sieve with a pore size of not greater than 4 Å. Distillation can take place after reflux with a small quantity of P_2O_5 (about 0.5% w/v) to remove the residual water. Avoid using too much P_2O_5 to prevent excessive formation of an orange polymeric material.

Dimethyl sulfoxide or dimethylformamide should be predried using a molecular sieve with a pore size of not greater than 4 Å, followed by distillation at reduced pressure (10 – 20 mmHg).

Supercritical Fluids

The use of supercritical fluids as solvents for cyclic voltammetry has also been investigated. For an example of a recent paper see "Electrochemical investigations in liquid and supercritical 1,1,1,2-tetrafluoroethane (HFC 134a) and difluoromethane (HFC 32)", Andrew P. Abbott, Christopher A. Eardley, John C. Harper, and Eric G. Hope, *Journal of Electroanalytical Chemistry,* **457**, 1–4, 1998. In particular HFC 134a, with tetra-n-butyl ammonium tetrafluoroborate as electrolyte, was shown to be have an extraordinarily wide redox stability window of 9 volts.

The Mercury Electrode

At times it may be of use to perform cyclic voltammetry experiments in organic solvents using a mercury working electrode. Mercury dropping electrodes (MDE's) can be used but commercial models are expensive, cumbersome to set up, require periodic cleaning and maintenance, and require the use of relatively large amounts of elemental mercury. However they do have the advantage of being able to provide a clean mercury electrode by dislodgment of the old mercury drop and allowing a new drop to form, all at the press of a button, in any solvent you require.

Mercury film electrodes (MFE's) use much less mercury (often much less than 1%) than a MDE, and are relatively low cost. The mercury is usually electrodeposited as a thin film on a glassy carbon, or carbon–fiber, support electrode. However the mercury coating must be removed and replated if it is fouled or oxidised. Some workers prepare the MFE by electrodeposition from aqueous mercuric ion solutions and then wash the electrode to replace the solvent. However it is also possible to electrodeposit mercury directly in suitable organic solvents: G. Alarnes-Varela, A.L. Suárez-Fernández, A. Costa-García, *Electrochimica Acta*, **44**, 763–772, 1998.

F

Potentiostat Designs

Potentiostats are designed to maintain a known potential difference across a pair of electrodes while measuring the resulting current flow. While this sounds simple in theory, the practice of electrochemistry has demanded a variety of designs to cope with different types of experiment.

Two electrode systems

The simplest potentiostat is a two-electrode unit that connects to a working and reference electrode. A battery connected to two electrodes with an ammeter in series could be considered as a very simple example.

However, to maintain a known potential at the working electrode the reference electrode must exhibit a steady response. This is not easy as the current passing through the electrode will electrolyze (reduce or oxidize) either the electrode material itself or material around the electrode, which in turn will alter the half cell potential. In days gone by the effects of this were usually minimized by making a very large reference electrode which would not be significantly disturbed by the currents flowing through it.

Today two electrode potentiostats masquerade under a variety of different names, such as:

- dissolved oxygen meters which measure the current that passes between a gold or platinum working electrode (at which a preset reducing potential is maintained, usually about –0.8 V, which is

called the 'polarizing voltage') with respect to a silver counter electrode. This is the classic Clarke type cell;

- nitric oxide meters, which are very similar to oxygen meters, but which reduce NO.

- amperometric 'biosensor' meters, which are very similar to the previous two types of meter but which can usually have their polarizing voltages adjusted to suit the system being measured.

- voltage clamps, which are used by neurophysiologists to study inter- and intracellular processes. These are usually exceptionally high gain instruments employing head stage amplification, capacitive compensation, and exhibiting very fast response times.

The common feature amongst all these devices is that they are used for experiments in which the current flowing through the (relatively large) reference electrode is usually measured in nanoamperes or less. These tiny currents are not sufficient to cause enough electrolysis to seriously disrupt the environment around the reference electrode.

Some of these potentiostats will also have an external input so that they can except an external voltage signal to alter the electrode potential.

Three electrode systems

Most voltammetric experiments for analytical chemistry involve currents of microamperes or greater and make use of a three electrode instrument. The ADinstruments Potentiostat is of this type.

The electrodes are identified as the:

- working electrode, where the redox reaction of interest takes place;

- reference electrode, at which a constant potential is provided by a known half reaction. Virtually no current flows through this electrode because it is connected to the working electrode across a very large resistance (typically greater than 10^{12} Ω). This ensures

that concentrations around (and the potential of) the reference electrode is constant throughout the experiment; and an

- auxiliary (or counter) electrode, where a counter reaction takes place to maintain the electroneutrality of the solution. Thus if reduction occurs at the working electrode then oxidation must occur at the auxiliary electrode.

Compliance voltage

For most experiments involving such a potentiostat, at any given instant the potential between the working and reference electrodes is being held at a predetermined value while current flow is measured across the working and auxiliary electrodes. These are the current and potential values that are actually plotted.

But to do this some other potential must be maintained between the auxiliary and working electrodes. This potential is called the compliance voltage and, depending on the internal resistance of the cell (which in turn depends on type of solvent, total electrolyte concentration, distance between the electrodes, porosity and size of frits used to separate cell compartments, etc.) may be much greater than the observed potential of the working electrode. During an experiment it may happen that the potentiostat is unable to provide a sufficiently large voltage across the auxiliary and working electrodes to achieve the desired potential across the reference and working electrodes. In this situation the potentiostat is said to be out of compliance (or overloaded) and the results from such an experiment will be meaningless in the non-compliance region. The ADInstruments Potentiostat has a non-compliance light on its front panel which will illuminate if this occurs.

High compliance potentiostats are an electrical shock hazard unless used strictly in accordance with the correct procedure. Read the manufacturer's manual!

The greater the compliance voltage of a potentiostat the greater the number of cell designs with which it will be able to cope. Also, because this voltage can actually occur across the working and auxiliary electrodes, the greater the hazard from electric shock if the instrument is not used in accordance with the correct safety procedure. Most standard electronic componentry can handle ±10 V as a matter of course, and most potentiostats will exhibit a compliance voltage within this range. Greater compliance voltages will require the use of more specialist componentry, and such instruments will necessarily command a higher price.

It may also occur that the current flowing between the auxiliary and working electrodes is greater than the potentiostat is capable of delivering and/or measuring. This is a current overload condition. Currents can be decreased by using electrodes with a smaller surface area, using lower concentrations of analyte, or (for stripping methods) using a shorter deposition period. If EChem is being used with an ADinstruments Potentiostat and the current capability of the potentiostat (100 mA) is exceeded then an overload message appears in the Cursor Panel.

By connecting the reference and auxiliary electrode leads together most three electrode potentiostats can also be used as a two electrode system. Check with the potentiostat manufacturer if you are unsure whether your instrument can be used the way. The ADinstruments Potentiostat can be used in this way

Many manufacturers make three electrode potentiostats such as EG&G PAR, BAS, Radiometer, Solartron, AMEL, Metrohm, HEKA, Cypress, Sycopel, and ADInstruments.

Four electrode systems

The most common four electrode potentiostat is the bipotentiostat. This is designed to work with two working electrodes and a common reference and auxiliary electrode, and can be considered a simple variant of the three electrode design. Advanced bipotentiostats can sweep the potential at each working electrode independently of one another while simpler units only allow the working electrode potentials to be adjusted independently and then held steady.

The bipotentiostat is used with a rotating ring disk electrode where the potentials of the ring and disk electrodes need to independently controlled. The most widely known manufacturer of these devices is PINE Instruments.

Another type of four electrode design makes use of two reference and two counter electrodes. These instruments can be employed to control the potential across a membrane or interface and to measure the resulting current flow. This type of potentiostat is not readily commercially available but a good design has been published: T. J. VanderNoot and D. J. Schiffrin, 'Design and Evaluation of a Four-

Electrode Potentiostat/ Voltage Clamp Suitable for AC Impedance Measurements at the Interface of Immiscible Electrolytes', *Journal of Electroanalytical Chemistry,* **278**, 137 – 150 (1990), and M. C. Wiles, D. J. Schiffrin, and T. J. VanderNoot, 'Experimental Artifacts Associated with Impedance Measurements at Liquid–Liquid Interfaces', *Journal of Electroanalytical Chemistry,* **278**, 151 – 159 (1990).

EChem User's Guide

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Electrochemistry is a large field and there are many specialised and general texts available, as well as journals and on line information. The following list is meant as only as a general introduction to the literature.

The Internet

Much useful information can be obtained from various internet web sites such as:

http://www.electrochem.org/ — The Electrochemistry Society, Inc.

http://seac.tufts.edu/ — The Society for Electroanalytical Chemistry

http://electrochem.cwru.edu/estir/ — Electrochemical Science and Technology Information Resource. Lists of text books, journals,hand books, graduate schools, societies, meetings, etc

http://www.soton.ac.uk/~slt1/EchemGate.html — The Electrochemistry Gateway

http://www.yahoo.com/Science/Chemistry/Electrochemistry/ — Yahoo search engine

http://www.anachem.umu.se/jumpstation.htm — The Analytical Chemistry Springboard

http://chemweb.com/ecos/ — Electrochemistry Online Services (ECOS) from Elsevier. Includes liks to Elsevier's electrochemistry journals.

http://www.nace.org/ — NACE Internaional (National Association of Corrosion Engineers)

Text Books

For an extensive listing of text books, from 1950 to present, consult the Electrochemical Science and Technology Information Resource (ESTIR) web site at http://electrochem.cwru.edu/estir/books.htm. Many other monographs and proceedings are available from the Electrochemical Society.

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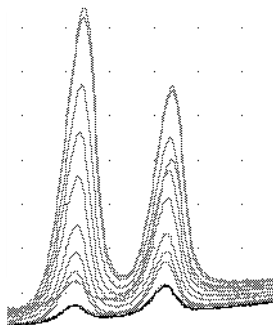
Glossary

amperometric titrimetry. A titration technique where a constant potential is held at the working electrode and the resulting current measured during a titration.

amperometry. Techniques that monitor the current signal versus time. The potential is held constant, or pulses are applied on a base potential.

amperomogram. Graph of current signal (usually on the Y axis) versus time (usually on the X axis).

analyte. Substance that an analytical procedure is trying to detect.

anion. Negatively charged ion.

anode. Electrode at which oxidation takes place.

charging (or capacitive) current. Current that flows due to charging of the electrode and the interfacial region.

cation. Positively charged ion.

cathode. Electrode at which reduction takes place.

compliance. The compliance (or compliance voltage) of a potentiostat is the potential it is capable of generating across the working and auxiliary (counter) electrodes. This may be much greater than the potential across the working and reference electrodes.

controlled potential electrolysis. Technique where a constant potential is held at the working electrode in order to completely electrolyse a substance in solution. Usually the solution is stirred and either the resulting current, or total charge transferred, is measured in order to determine the extent of reaction.

chronoamperometry. Technique where a constant potential is held at the working electrode and the resulting current measured.

chronocoulometry. Technique where a constant potential is held at the working electrode and the resulting transferred charge measured. It is equivalent to integrating a chronoamperometric trace.

current sampling. With digital techniques the current flow is sampled (and averaged) for discrete intervals at exact times. This can greatly reduce noise.

deposition potential. For stripping techniques an initial deposition potential is applied to a mercury film or hanging drop electrode. This potential must be sufficiently reducing to ensure that the metal ions of interest are deposited from solution as metal atoms which then dissolve in the mercury electrode.

double step chronoamperometry. Technique where a constant potential is held at the working electrode and the resulting current measured. This is followed by switching the potential to a new value (usually to reverse the reaction) and the current is again monitored at the new potential value. The potential switching may be repeated a number of times.

electroactive. Capable of undergoing reduction or oxidation

electrolytic cell. An electrochemical cell in which an applied potential causes a chemical reaction.

electrochemistry. A rather general term covering just about all techniques where electrodes of any description are used. Usually current, potential, charge, conductivity, (or some combination of these) is measured as a function of one of the others, or of time, or of addition of titrant etc.

electrode. Solid or liquid (usually of mercury) material at which a potential is

measured, or at which an electrochemical reaction takes place.

electrolyse. Chemical reaction (oxidation or reduction) induced by the passage of an electric current

electrolyte. substance which forms cations and anions when dissolved. Also a solution containing cations and anions.

electronegative. Tending to be reduced

electropositive. Tending to be oxidised

electrosynthesis. Synthesis using the passage of electric current through a solution

emf. Electromotive force (often used interchangeably but incorrectly with the terms 'potential' and 'voltage'). The emf of a cell is determined by a potentiometer with zero current drain.

faradaic current. Current that flows due to the occurrence of a redox reaction.

frit. Porous disk, usually made of sintered glass, used to partially separate two solutions.

galvanic cell (also a voltaic cell). An electrochemical cell in which electricity is produced by a spontaneous redox reaction.

galvanostat. Device to maintain a known current flowing between two electrodes.

half-wave potential ($E_{1/2}$). The potential which produces half the diffusion limited polarographic current. For a reversible redox reaction, maintaining the working electrode at $E_{1/2}$ will ultimately result in equal

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concentrations of the oxidised and reduced forms of the analyte.

iR compensation. Methods which attempt to correct for the 'uncompensated resistance' in an electrochemical cell. This may be useful when highly resistive cells are being used. The most common techniques are positive feedback (offered on many brands of potentiostat) and current interrupt (offered with some EG&G PAR potentiostats). However iR compensation is no substitute for careful cell design and electrode placement!

polarography. Electrochemical techniques involving the use of a dropping mercury electrode.

potential. The potential energy difference between two electrodes.

potentiometer. Device or component for measuring the potential between two points with zero current drain.

potentiostat. Device for maintaining a known potential between two electrodes.

salt bridge. Often a tube containing an electrolyte solution sealed at either end with a sintered glass frit. (Sometimes a rolled filter paper soaked in electrolyte solution is used). A salt bridge connects the solutions in two separate containers in which the anode and cathode are placed.

stripping voltammetry. Technique whereby the analyte is first concentrated by deposition on the working electrode. A subsequent voltametric scan then measures the oxidation (or reduction) of the deposited material.

voltammetry. Techniques involving the control potential and measuring the resulting current flows.

voltammogram. Graph of current (usually on the Y axis) versus potential (on the X axis).

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