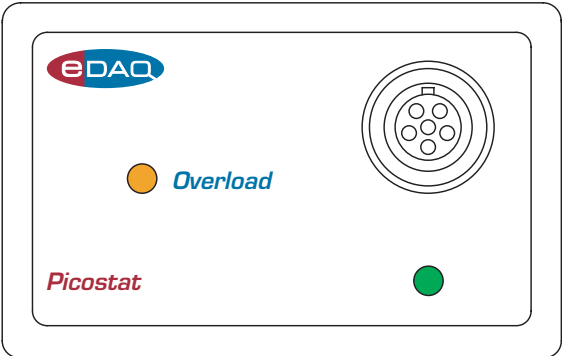
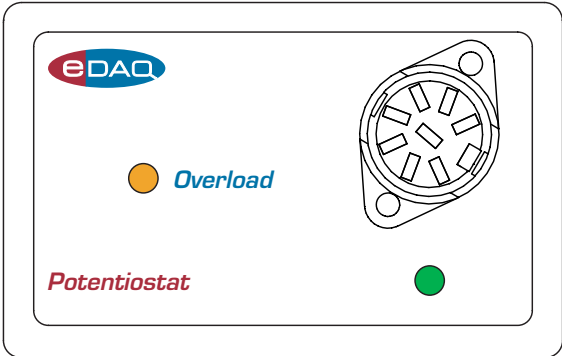


Potentiostat & Picostat



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Products: Potentiostat (EA160); Picostat (EA162)

Document Number: UM-EA160/162-1203

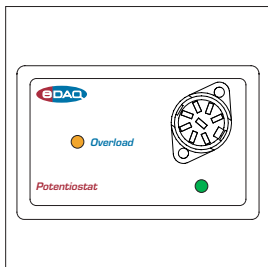
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eDAQ Pty Ltd
6 Doig Avenue
Denistone East, NSW 2112
Australia

<http://www.eDAQ.com>
email: info@eDAQ.com

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1

CHAPTER ONE

Overview

The eDAQ Potentiostat and Picostat can perform various electrochemical voltammetric and amperometric experiments. They are a part of a family of fully–software controlled modular preamplifiers (eDAQ Amps) which are designed for use with the e-corder® system.

Many of the additional uses of the Potentiostat and Picostat for electroanalytical chemistry are described in the *EChem Software Manual* which describes the use of the optional EChem software.

How to Use this Manual

This manual describes how to set up and begin using your Potentiostat ([Chapter 2](#)) or Picostat ([Chapter 3](#)). Their use with Chart and Scope software is also described ([Chapter 4](#)). The appendices provide technical and troubleshooting information. See the *EChem Software Manual* for a description of the use of the Potentiostat and Picostat with the optional EChem software.

eDAQ Amps

The Potentiostat and Picostat are part of a family of preamplifiers known as eDAQ Amps.

The Potentiostat and Picostat are designed for performing voltammetric and amperometric experiments. As with other eDAQ Amps, they are designed to be operated under full software control and are automatically recognised by Chart, Scope or EChem software which control their gain range, signal filtering, and other settings.

The eDAQ Amp family also includes the:

- pH Amp, suitable for connection of pH, ion selective, and potentiometric (ORP) electrodes
- Bridge Amp, suitable for sensors requiring a DC Wheatstone bridge connection. Also provides DC excitation
- GP Amp, suitable for high output sensors requiring a high impedance DC Wheatstone bridge. Also provides DC excitation.

See our web site at www.eDAQ.com for more information.

Checking the Potentiostat or Picostat

Before you begin working with the Potentiostat or Picostat, please check that:

- all items described in the packing list are included; and that
- there are no signs of damage that may have occurred during transit.

Contact your eDAQ distributor if you encounter a problem.

You should also become familiar with the basic features of your e-corder system, which are discussed in the *e-corder Manual* on the Installer CD.

2

C H A P T E R T W O

The Potentiostat

This chapter describes how to connect and use your Potentiostat.

IMPORTANT: Always make sure that the e-corder is turned off before you connect or disconnect the Potentiostat. Failure to do this may result in damage to the e-corder and/or the Potentiostat.

The Front Panel

The front panel of the Potentiostat is shown in [Figure 2-1](#).

The Input Connector

The input connector of the Potentiostat provides connection pins for the Working, Auxiliary and Reference electrodes. The connector also provides connections for the lead shields which protect the signals in the cable wiring from electrical interference (noise pickup).

The pin assignments of the Potentiostat input connector are shown in [Figure 2-2](#). The Auxiliary and Reference electrode leads have coaxial shields which are maintained at the respective electrode potential.

Figure 2-1
The Potentiostat front panel.

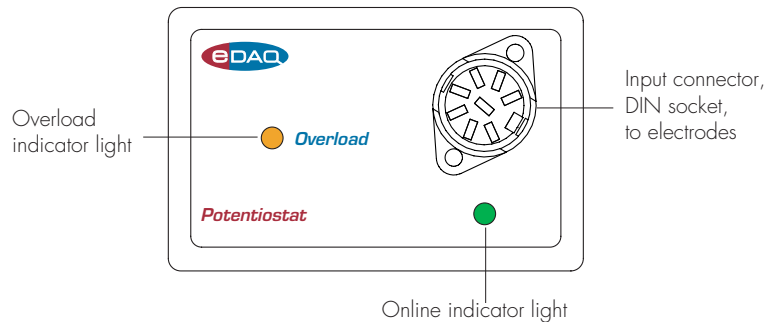


Figure 2-2
The Potentiostat input connector as seen when looking at the front panel.

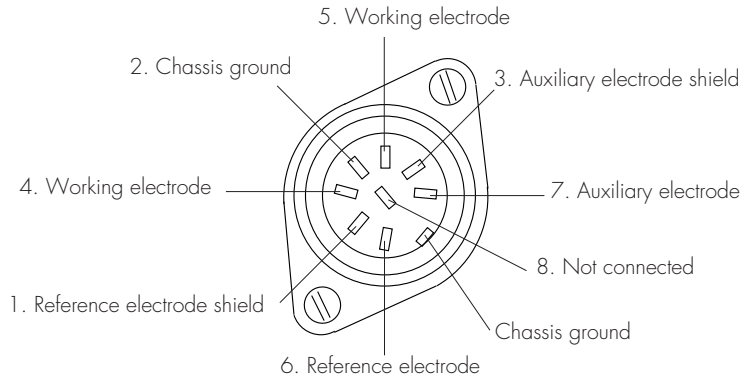


Table 2-1

Color-coding on the leads of the electrode cable.

<i>Color</i>	<i>Electrode</i>
Yellow	Reference
Green	Working
Red	Auxiliary

Electrode Cable

The Potentiostat is supplied with an electrode cable comprising three leads, with each lead terminated by an alligator clip. The Reference and Working electrode leads are shielded to protect the signals from external interference. The alligator clips allow connection to a wide variety of electrodes, and the leads are color-coded to indicate the type of electrode to which they should be attached (Table 2-1).

For normal three-electrode use, the reference electrode must never be connected to either the auxiliary (red) or working (green) leads, otherwise the current that would be passed through the electrode could effectively destroy it as a reference potential source.

If two-electrode operation is required the auxiliary and reference electrode leads (red and yellow) should be attached to the single 'counter electrode'. The green electrode lead is attached to the working electrode.

The Online Indicator

Located at the bottom right of the front panel is the Online indicator., Figure 2-1. When lit, it indicates that the software (such as EChem, Chart or Scope) has located and initialised the Potentiostat. If the light does not go on when the software is run, check that the Potentiostat is properly connected. If there is still a problem, please refer to Appendix B B, page 67.

The Overload Indicator

Located on the left-hand side of the front panel is the Overload indicator, Figure 2-1. When lit, this indicates that the Potentiostat is out

of compliance, which usually occurs because of an open circuit or excessive resistance in the electrochemical cell. Higher resistances can be often be encountered when electrodes are fouled by the products of electrolysis reactions. The Potentiostat tries to compensate by increasing the compliance potential (that is, the potential between the auxiliary and working electrodes). If the compliance voltage exceeds specification (about 11 V) potential control of the cell is lost and drifting, or oscillation, of the signal can be seen. Any data collected during this period is unreliable and should be discarded.

The Overload indicator will light when there is an overload and will go out once the overload is removed.

If the indicator light comes on repeatedly, and your connections are good, then try bringing your electrodes closer together, and/or increasing electrolyte concentration, and/or modifying your experimental conditions to avoid fouling of the electrodes. Redesigning your electrochemical cell may be necessary. Normally cells are designed to keep the reference and working electrodes very close together, however, when a potential overload occurs, you also need to consider the distance between the auxiliary and working electrodes.

Note that a potential overload is quite different from a current overload condition. A current overload is caused when the current signal exceeds the full scale limits of the range setting of the current channel, and is usually caused by a low resistance between the electrodes.

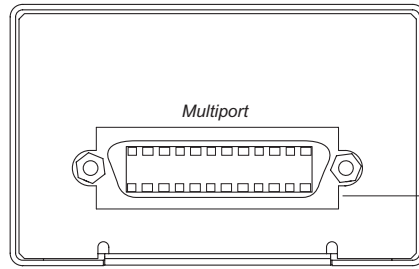
The Back Panel

The back panel of the Potentiostat is shown in [Figure 2-3](#).

Multiport Connector

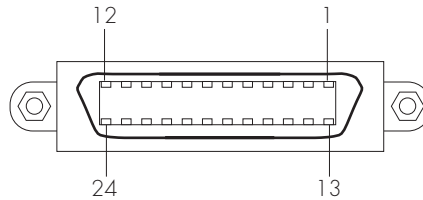
The Potentiostat back panel has a single 'Multiport' 24 pin connector that connects it to the e-corder. A cable is provided with the Potentiostat for this purpose. This connection provides power to the Potentiostat and carries the various analog and control (gain range and filter settings) signals between the two. The pin assignments of the Multiport are shown in [Figure 2-4](#).

Figure 2-3
The Potentiostat back panel.



Multiport connector, Centronics 24 pin, I²C, power, and analog input and outputs

Figure 2-4
The Potentiostat Multiport pin assignments.



1 Not connected	9 Not connected	17 I Out, analog signal
2 SDA (I ² C control)	10 Analog ground	18 Not connected
3 SCL (I ² C control)	11 Digital ground	19 Not connected
4 Not connected	12 Not connected	20 Not connected
5 Not connected	13 Regulated +8 V	21 Not connected
6 MPDSD (I ² C control)	14 Not connected	22 Regulated +17 V
7 DSC (I ² C control)	15 Not connected	23 Regulated -17 V
8 Not connected	16 E Out, analog signal	24 E In, analog signal

Connecting the Potentiostat

Your Potentiostat will have been supplied with a cable that is terminated by a 'Multiport' (Centronics 24 pin) connector at one end and, at the other end, terminated by a I²C (DB-9 pin) connector and three BNC connectors.

First make sure that the e-corder is turned off. Connect the Multiport end of the cable to the matching connector on the rear panel of the Potentiostat.

Table 2-2

Potentiostat to e-corder connections.

<i>Cable labelled</i>	<i>e-corder front panel</i>
CH1 (I) or I Out	Input 1
CH2 (E) or E Out	Input 2
OUTPUT (E In)	Output -

Table 2-3

Potentiostat to e-corder connections, reverse polarity.

<i>Cable labelled</i>	<i>e-corder front panel</i>
CH1 (I) or I Out	Input 1
CH2 (E) or E Out	Input 2
OUTPUT (E In)	Output +

Connect the other end of the cable to the I²C connector on the rear panel of the e-corder. Use the three BNC terminated cables to connect to the front panel of the e-corder as shown in [Table 2-2](#).

With these connections, when you use the software to set a more positive voltage, a more oxidising potential will be applied at the working electrode.

Such an arrangement is shown in [Figure 2-5](#) and [Figure 2-6](#).

To operate the Potentiostat with the reverse polarity make the connections as shown in [Table 2-3](#).

With these connections, when you use the software to set a more positive voltage, a more reducing potential will be applied at the working electrode.

Check that all connectors are firmly attached. Loose connectors can cause erratic behaviour, or may cause the Potentiostat to fail to work.

The Potentiostat uses two e-corder input channels during normal operation. The remainder of this chapter assumes that you have connected the current signal to e-corder Input Channel 1 and the potential signal to e-corder Input Channel 2. (It is possible when using Chart or Scope software to connect the Potentiostat to other e-corder

Figure 2-5
The Potentiostat shown connected to an e-corder, front view.

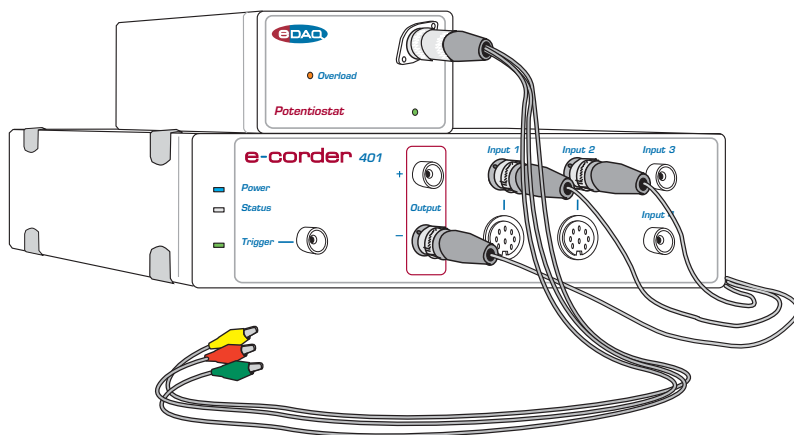
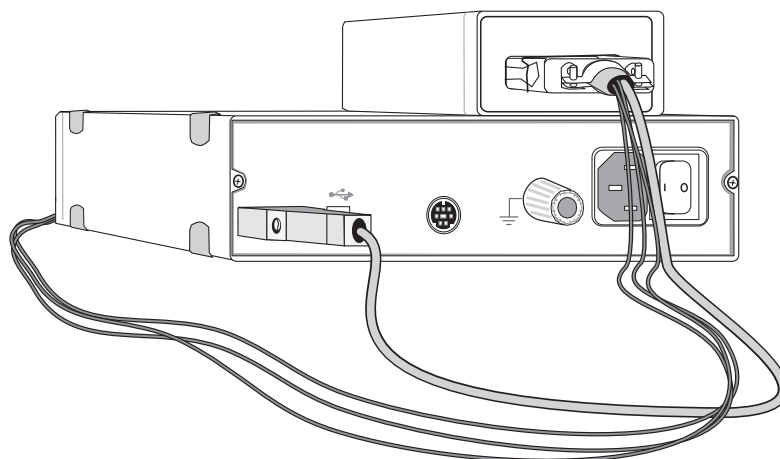


Figure 2-6
The Potentiostat shown connected to an e-corder, back view.



input channels, in which case the description that follows would change accordingly).

When using EChem software, Channel 1 is always set to be the current signal (the I channel), and Channel 2 is automatically set to be the potential signal (the E channel). Thus when using EChem software you *must* always connect the current signal (I Out) to Input Channel 1, and the potential signal (E Out) to Input Channel 2 of the e-corder.

Channel 2 normally displays the applied potential, and its settings are controlled using the standard Input Amplifier dialog box, described in the *Chart Software Manual* and *Scope Software Manual* on the eDAQ Installer CD.

First Use

After you have installed the software, connected the e-corder and computer as described with the booklet supplied with the *e-corder* system, and connected the Potentiostat as described above, you are ready to begin.

When the e-corder is turned on, and Chart software started, the Potentiostat Online indicator (green) should light.

From the Channel 1 Function pop-up menu, select the 'Potentiostat' command, which opens the Potentiostat Control window, [Figure 2-7](#) (Windows), or [Figure 2-8](#) (Macintosh).

This window allows you to preview the current signal without actually recording the signal to your computer's hard disk. (If the menu says 'Input Amplifier' instead of 'Potentiostat' then the software has not recognised the Potentiostat. Exit the software, check all your connections and try again).

By default, the control window opens with the Potentiostat in Standby mode, that is with the reference and working electrodes isolated so that no current will flow through your electrodes. To connect to the Potentiostat lead wires you must select Real mode. When you click Cancel or OK the Potentiostat will revert to Standby mode until recording is started.

Now select Dummy mode operation. You will need to adjust the gain range to 20 μA to accommodate your signal amplitude. You can now adjust the applied potential with the slider bar, or by entering the exact potential with the A-button. The resulting current signal should obey Ohm's law:

$$I = E/R$$

so that an applied potential of 1 V should produce a current of 10 μA , while other potential settings should produce corresponding currents.

Figure 2-7
 Accessing the Potentiostat controls with Chart software (Windows).

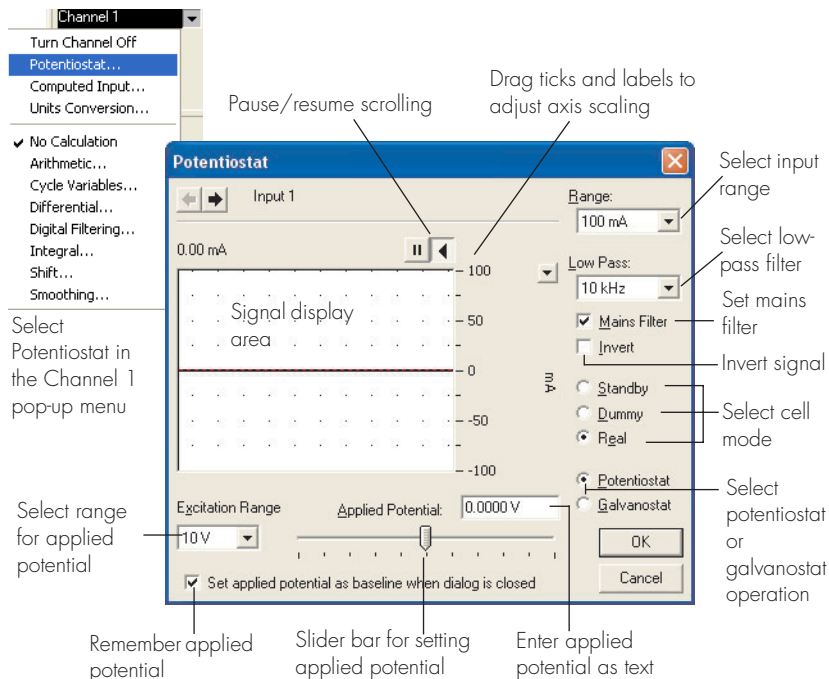
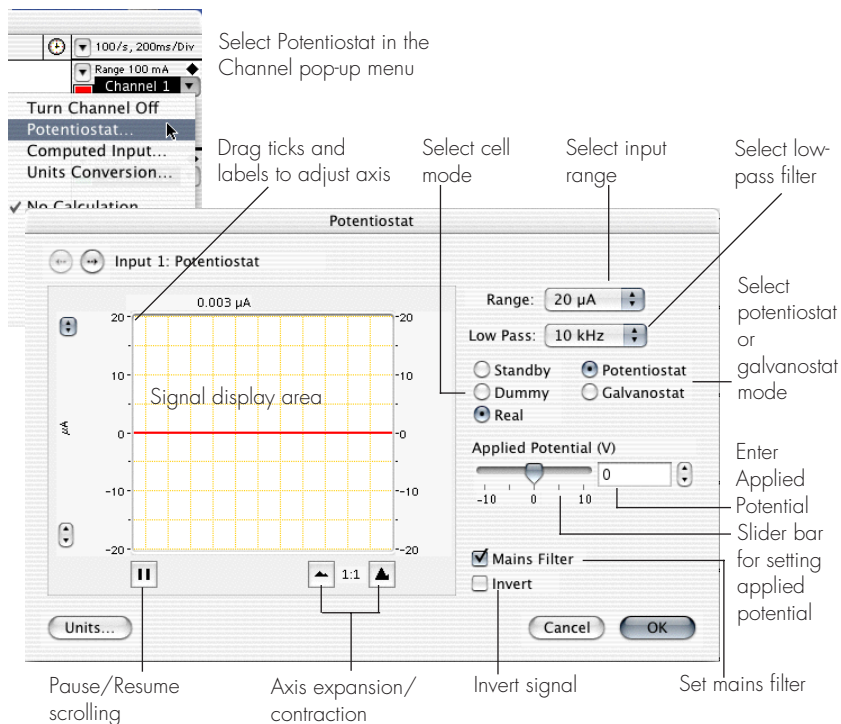


Figure 2-8
 Accessing the Potentiostat controls with Chart software (Macintosh).



Potentiostat Control Window

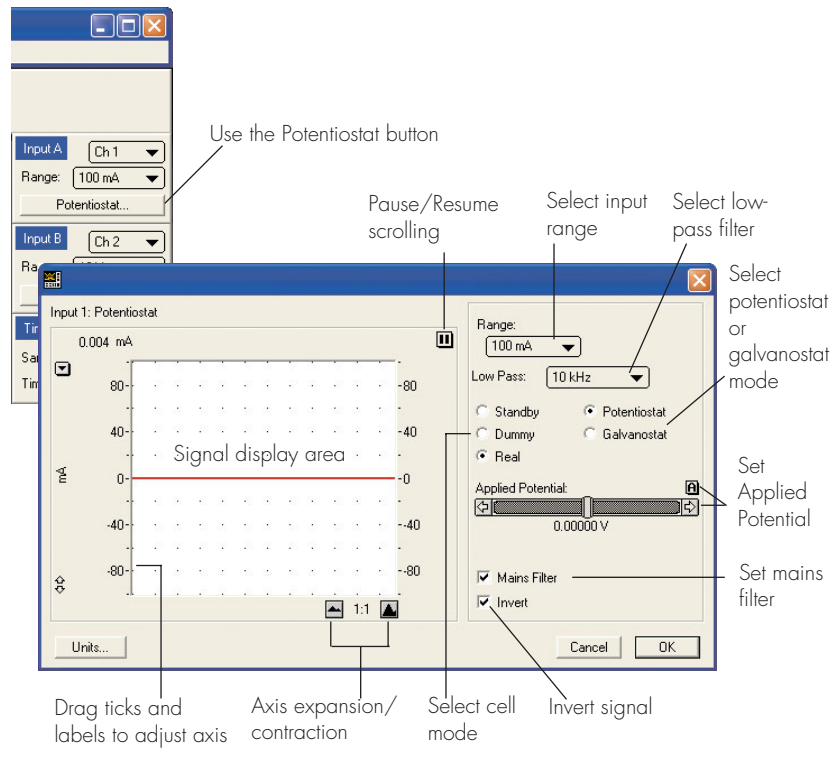
With Chart software, the Potentiostat Control window is accessed from the Potentiostat command in the Channel Function pop-up menu. Figure 2-7 shows the control window on a Windows computer, and Figure 2-8 on a Macintosh computer. These windows control the various current ranges and filtering options for the Potentiostat.

With Scope software, the corresponding controls are shown in Figure 2-9.

Potentiostat/Galvanostat Operation Potentiostat Galvanostat

The Potentiostat can be operated in either potentiostat (Chart, Scope or EChem software) or galvanostat mode (Chart and Scope software only) by selecting the appropriate radio button.

Figure 2-9
Accessing the Potentiostat controls with Scope software.




The rest of this chapter deals with potentiostatic operation. The use of galvanostat mode is dealt with on [page 52 – 56](#).

Signal Display

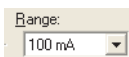
The current signal is previewed in the scrolling display area. Note that the signal is not being recorded to hard disk at this stage, and that when the window is closed the signal trace is lost.

By using the Dummy or Real modes the effect of an applied potential can be seen.

You can stop/start the signal scrolling by clicking the Pause/Resume button .

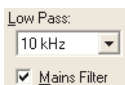
You can shift or stretch the vertical Amplitude axis to make the best use of the available display area — similar to the amplitude axis in the main Chart, Scope or EChem window. All changes made in the Potentiostat Control window are reflected in Chart, Scope or EChem and vice versa.

Setting the Range



Use the Range pop-up menu to select the input current range (channel sensitivity). The Potentiostat has ranges of 100 mA to 20 nA, while resolution within each range is 16 bits or 0.0015%. You should set the range so that it is larger than the biggest current that you expect to encounter during your experiment. If, during the experiment the current signal exceeds the range, then the signal will go off scale and those data points effectively lost.

Filtering



The Potentiostat incorporates four low-pass filters at 10 kHz, 1 kHz, 100 Hz and 10 Hz for removal of high frequency signals ('noise'). In addition the e-corder provides filter settings at 1, 2, 5, 20, 50, 200, 500, and 2000 Hz (Chart software on Windows computers).

As a general rule the 10 Hz filter setting is highly effective for the removal of mains hum (50 or 60 Hz interference) and should be employed whenever possible. However, it should not be used for pulse

amperometric or voltammetric experiments where the pulses are shorter than 100 ms, or for experiments where rapid scan rates (greater than about 100 mV/s) are used, or else the signal you collect may be excessively smoothed.

In addition, with Chart and Scope software, there is a Mains Filter checkbox. If this is ticked, then the e-corder will apply a mains filtering algorithm to the incoming signal which removes repetitive signals occurring at 50 or 60 Hz which are typical of mains interference. Note that the mains filter is not a notch filter, and can remove a 50 or 60 Hz interference even if it is not a pure sinusoidal function. However, the mains filter does take a few seconds to 'learn' the pattern of the interference so that you will need to record for longer than this for it to take full effect. The mains filter can be employed even for experiments in which there are sudden potential jumps.

Inverting the Signal

The Invert checkbox, allows you to invert the incoming signal. It provides a simple way to reassign the directions (up or down) of an anodic (or cathodic) current. Please note that this affects the display of the signal only — it does not reverse the direction of actual current flow at the electrodes!

Cell Control

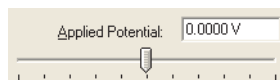
The Potentiostat can be in one of three operating modes, controlled by the Cell radio buttons:

- **Standby:** If Standby mode is selected the electrode lead wires are disconnected (With the Potentiostat the internal dummy cell is connected). The external cell is not connected until the Potentiostat Control window is closed and the Chart, Scope or EChem Start button is clicked. This mode is used if you do not wish to alter the state of the external cell until the method is actually performed. The Applied Potential slider bar control is disabled in this mode.
- **Dummy:** When Dummy mode is selected the Potentiostat is connected to the internal 100 k Ω dummy cell. You can then 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 Control window is closed and Chart,

Scope or EChem is recording. This is useful for testing the Potentiostat.

- **Real:** In Real mode the external electrodes are connected to the Potentiostat while the Potentiostat Control window is open, [Figure 2-7](#) and [Figure 2-8](#). The Applied Potential slider control can be used to set the potential applied to the electrodes. When you close the control dialog (using EChem or Scope software) the Potentiostat will revert to Standby mode until the Start button is clicked to begin a scan. If you are using Chart or Scope software, the Potentiostat will remain in Real mode when the dialog is closed — this allows you to start and stop recording data while the electrodes remain active, which allows periodic recording of the signal from amperometric biosensors or *in vivo* electrodes without disturbing the environment around the electrodes.

Applied Potential



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 electrodes, depending on the mode selected.

Excitation Range



When using Chart software on a Windows computer you have the option of limiting the range over which the applied potential can be set. Smaller ranges offer finer control with the slider bar, or text entry, of the applied potential, [Figure 2-7](#).

On a Macintosh computer use the Range control in the Stimulator Constant Output dialog box, [Figure 4-8](#), [page 42](#).

Remember Potential

Set applied potential as baseline when dialog is closed

When using Chart software you can check the box labelled 'Set applied potential as baseline...' This causes the potential set with the slider bar or text entry to be transferred to the Stimulator baseline control when the window is closed.

Maintenance

Your Potentiostat will not require maintenance during daily operation. However, you should periodically check the Potentiostat for optimum results by applying a known potential, E , to the Dummy Cell and checking that the resulting current signal, I , is in accordance with Ohm's law:

$$I = E/R$$

where R is the resistance, and is $10^5 \Omega$ for the dummy cell. Thus a signal of $10 \mu\text{A}$ should be obtained when a potential of 1 V is applied. Try several different potentials and make sure an appropriate current signal is observed. If this test produces the expected results then your Potentiostat is likely to be functioning correctly and if you are experiencing difficulties with your experiments then you should now check the electrode cables.

Attach the electrode cables to a resistor (usually a resistor of 10^3 – $10^6 \Omega$ is ideal) with the working electrode lead on one side and the auxiliary and reference leads connected to the other side. If the current signal does not obey Ohm's law, then it is likely that the electrode leads have become damaged. However, if this test produces the expected results, but you are experiencing difficulties with your experiments, then you should now check the electrodes you are using, and the design and condition of the reaction vessel, and any salt bridges that you are using.

3

CHAPTER THREE

The Picostat

This chapter describes how to connect and use your Picostat (EA162).

IMPORTANT: Always make sure that the e-corder is turned off before you connect or disconnect the Picostat. Failure to do this may result in damage to the e-corder and/or the Picostat.

IMPORTANT: The Picostat is a highly sensitive current measuring device. To prevent damage by static discharge always make sure you are earthed before touching the Picostat input connector, connecting the lead wires, or before you connect the lead wire alligator clips to the electrodes. You can do this (after first connecting the Picostat and e-corder) by touching the outer casing of the e-corder or Picostat. This will connect you to earth (via the electrical grounding of the instrument) and any static charge you have collected will be dissipated.

The Front Panel

The front panel of the Picostat is shown in [Figure 3-1](#).

Input Connector

The Input connector of the Picostat provides connection pins for the Working, Auxiliary and Reference electrodes. The connector also provides connections for shields which protect the signals in the cable wiring from electrical interference (noise pickup).

The pin assignments of the Picostat Input connector are shown in [Figure 3-2](#). The Working and Reference electrode leads have coaxial shields which are maintained at the respective electrode potentials to minimise lead capacitance.

Figure 3-1
The Picostat front panel.

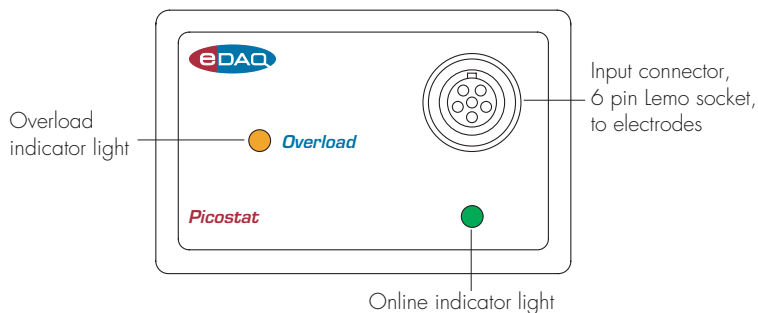


Figure 3-2
The Picostat input connector as seen when looking at the front panel.

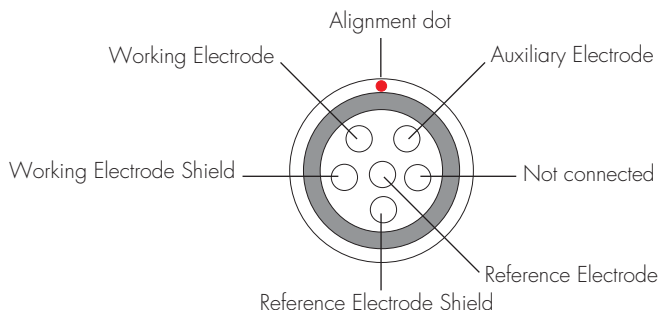


Table 3-1

Color-coding on the leads of the electrode cable.

<i>Color</i>	<i>Electrode</i>
Yellow	Reference
Green	Working
Red	Auxiliary

Electrode Cable

The Picostat is supplied with a three lead electrode cable, with each lead terminated by an alligator clip. The Reference and Working electrode leads are shielded to protect the signals from external interference. The alligator clips allow connection to a wide variety of electrodes. The leads are color-coded to indicate the type of electrode to which they should be attached (Table 3-1).

For normal three-electrode use, the reference electrode must never be connected to either the auxiliary or working leads, otherwise the current that would be passed through the reference electrode could effectively destroy it as a reference potential source.

If two-electrode operation is required the auxiliary and reference electrode leads (red and yellow) can be attached to the single 'counter electrode'. The green electrode lead is attached to the working electrode.

When attaching the cable to the Picostat make sure that the red dot on the cable connector is aligned with the red dot on the Picostat Input Connector, Figure 3-2. Insert the cable connector and push gently until it locks into position. To remove the cable pull the cable connector gently until it disengages. Do NOT twist the connector.

The Online Indicator

Located at the bottom right of the front panel is the Online indicator, Figure 3-1. When lit, it indicates that the software (such as EChem, Chart or Scope) has located and initialised the Picostat. If the light does not go on when the software is run, check that the Picostat is properly connected. If there is still a problem, please refer to Appendix B [Troubleshooting](#), page 67.

The Overload Indicator

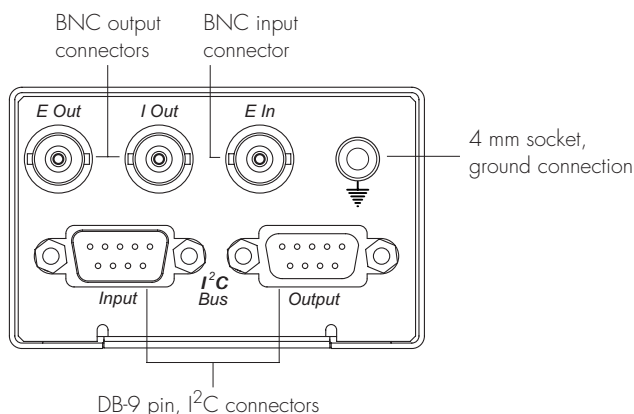
Located on the left-hand side of the front panel is the Overload indicator, [Figure 3-1](#). When lit, this indicates that the Picostat has gone out of compliance, which usually occurs because of an open circuit (such as an unconnected or faulty electrode) or the resistance is too high in the electrochemical cell. Higher resistances can be often be encountered when electrodes are fouled by the products of electrolysis reactions. The Picostat tries to compensate by increasing the compliance potential (that is, the potential between the auxiliary and working electrodes). If the compliance voltage exceeds specification, about 13 V, potential control of the cell is lost and drifting, or oscillation, of the signal can be seen. Any data collected during this period is unreliable and should be discarded.

The Picostat Overload indicator will remain lit once an overload has occurred — it will be reset once the scan has finished.

If the indicator comes on repeatedly, and your connections are good, then try bringing your electrodes closer together, and/or increasing electrolyte concentration, and/or modifying your experimental conditions to avoid fouling of the electrodes. Redesigning your electrochemical cell may be necessary. Normally electrochemical cells are designed to keep the reference and working electrodes very close together, however, when a potential overload occurs, you also need to consider the distance between the auxiliary and working electrodes.

NOTE: A potential overload is quite different from a current overload condition. A current overload is caused when the current signal exceeds the full scale limits of the sensitivity setting of the current channel. This is, in turn, due to a low resistance between the electrodes.

Figure 3–3
The Picostat back panel.



The Back Panel

The back panel of the Picostat is shown in [Figure 3–3](#).

E Out, I Out and E In Connectors

The Picostat back panel has three BNC connectors labelled E Out, I Out, and E In. The E In is connected to the Output of the e-corder, usually Output – (or Output 2 on SP e-corders) is used. If you need to reverse the polarity of the Picostat use e-corder Output +.

The Picostat provides two signals: the potential signal (E Out) indicating the potential difference between the working and reference electrodes; and the current signal (I Out) indicating the current flow between the working and auxiliary electrodes.

For most situations I Out is connected to e-corder input channel 1, and E Out to e-corder input channel 2. However, when you are using Chart software and recording data from various sources on more than just two channels you may want to connect the Picostat to other e-corder input channels.

I²C Connectors

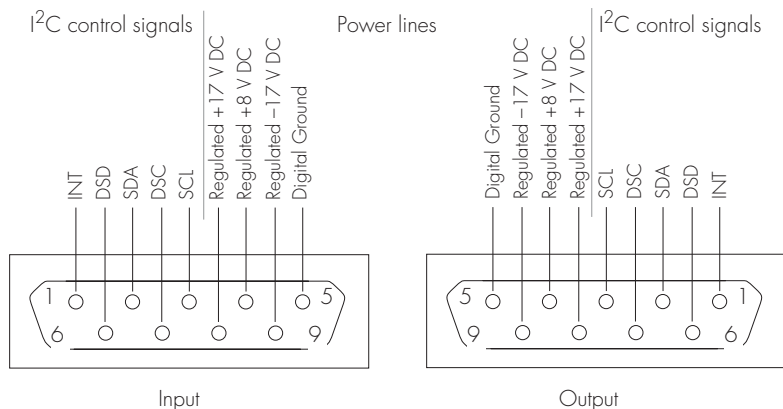
The Picostat back panel, [Figure 3–3](#), has two DB-9 pin 'I²C bus' connectors labelled Input and Output. The Input connector provides

Figure 3-4

The pin assignments for the Input I²C DB-9 connectors.

▲ WARNING!

The I²C connectors are for the power and control of eDAQ Amps and should not be used for connection to any other device.



power to the Picostat and carries the various control signals (for gain range and filter selection) to and from the e-corder connection to the e-corder. A cable is provided with the Picostat for this purpose. The pin assignments are shown in [Figure 3-4](#).

The Output connector can be used for the attachment of other eDAQ Amps.

More information about the I²C connector can be found in your *e-corder Manual*.

Grounding Connector

The Picostat back panel, [Figure 3-3](#), has a 4 mm grounding socket. This enables connection of a Faraday cage (with the green grounding cable included with the Picostat) the use of which can greatly diminish electrical noise. The construction of the Faraday cage can range from a simple cardboard box covered with aluminium foil, in which the electrochemical cell is located, to a more sophisticated copper mesh enclosure or sheet-metal box.

In all cases, it is essential that the Faraday cage be electrically grounded to act as an effective shield against electrical interference. The Picostat is supplied with a green colored ground cable terminated with a 4 mm pin (attaches to Picostat back panel) and an alligator clip (for attachment to Faraday cage) for this purpose. The Picostat itself is grounded via its connection to the e-corder unit which is in turn earthed

via the three pin mains power connector. It is of course important that the power socket that you are using is well earthed.

The purpose of this ground cable to the Faraday cage is to provide an easy means of grounding the cage — please note that it is not for grounding the Picostat. If your Faraday cage is already earthed by its own ground connection then you should not use this cable! Use of the cable in this instance will provide a second pathway to earth which could result in a 'ground loop' which can actually increase signal interference! You can try grounding the Faraday cage via its own connection to earth, *or* via the Picostat ground cable — but *not by both* methods simultaneously.

Connecting the Picostat

Your Picostat will have been supplied with an I²C cable (DB-9 pin connectors at either end), and three cables with BNC connectors at either end.

First make sure that the e-corder is turned off. Then connect the I²C cable to the I²C connector on the back panel of the e-corder, and the other the other end to the I²C Input connector on the back panel of the Picostat. Use the three BNC cables to connect the back panel of the Picostat to the front panel of the e-corder as in [Table 3-2](#).

Table 3-2
Picostat to e-corder BNC connections.

<i>Picostat rear panel</i>	<i>e-corder front panel</i>
I Out	Input 1
E Out	Input 2
E In	Output –

Table 3-3
Picostat to e-corder BNC connections, reverse polarity.

<i>Picostat rear panel</i>	<i>e-corder front panel</i>
I Out	Input 1
E Out	Input 2
E In	Output +

Figure 3-5
The Picostat shown
connected to an
e-corder, front view.

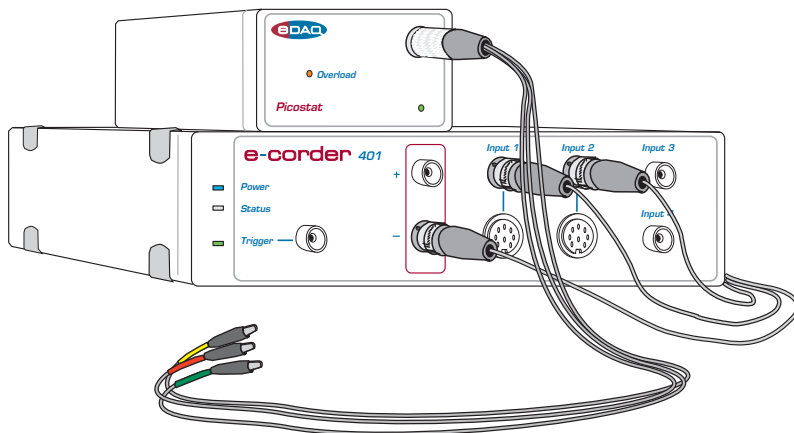
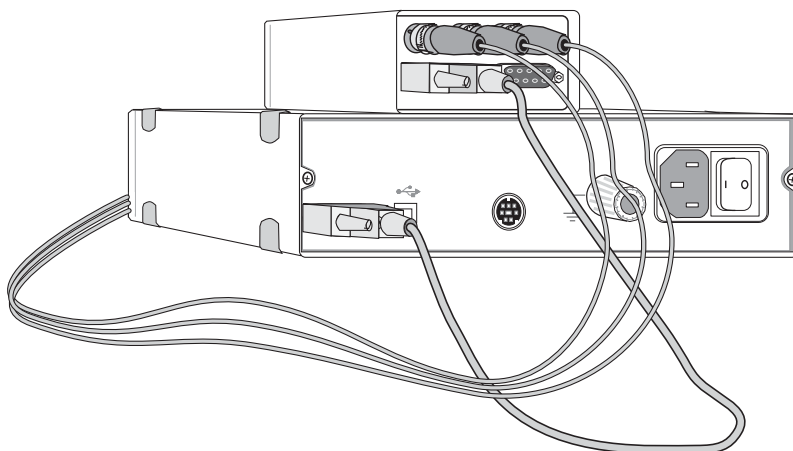


Figure 3-6
The Picostat shown
connected to an
e-corder, back view.



With these connections, when you use the software to set a more positive voltage, a more oxidising potential will be applied at the working electrode. Such an arrangement is shown in [Figure 3-5](#) and [Figure 3-6](#).

To operate the Picostat with the reverse polarity make the connections shown in [Table 3-3](#).

With these connections, when you use the software to set a more positive voltage, a more reducing potential will be applied at the working electrode.

Check that all connectors are firmly attached. Loose connectors can cause erratic behaviour, or may cause the Picostat to fail to work.

The Picostat uses two e-corder input channels during normal operation. The remainder of this chapter assumes that you have connected the current signal to e-corder Input Channel 1 and the potential signal to e-corder Input Channel 2. (It is possible when using Chart or Scope software to connect the Picostat to other e-corder input channels in which case the description that follows would change accordingly).

When using EChem software, Channel 1 is always set to be the current signal (the I channel), and Channel 2 is automatically set to be the potential signal (the E channel). Thus when using EChem software you *must* always connect the current signal (I Out) to Input Channel 1, and the potential signal (E Out) to Input Channel 2, of the e-corder.

Channel 2 normally displays the applied potential and its settings are controlled using the standard Input Amplifier dialog box, described in the *Chart and Scope Software Manuals* on the eDAQ Installer CD.

First Use

After you have installed the software, connected the e-corder and computer as described in the booklet that is supplied with the e-corder system, and connected the Picostat as described above, you are ready to begin.

When the e-corder is turned on, and Chart software started, the Picostat Online indicator (green) should light. Touch the body of the Picostat or e-corder (to discharge any static charge that you may have accumulated), then attach the 100 M Ω test resistor (supplied with the Picostat) to the electrode leads so that the Working electrode lead is connected to one end of the resistor, and Reference and Auxiliary electrode leads to the other).

From the Channel 1 Function pop-up menu, select the 'Picostat' command, which accesses the Picostat control window, [Figure 3-7](#), [Figure 3-8](#), or [Figure 3-9](#).

The Picostat control window allows you to preview the current signal without actually recording the signal to the computer hard disk. (If the

Figure 3-7
Accessing the Picostat controls with Chart software (Windows).

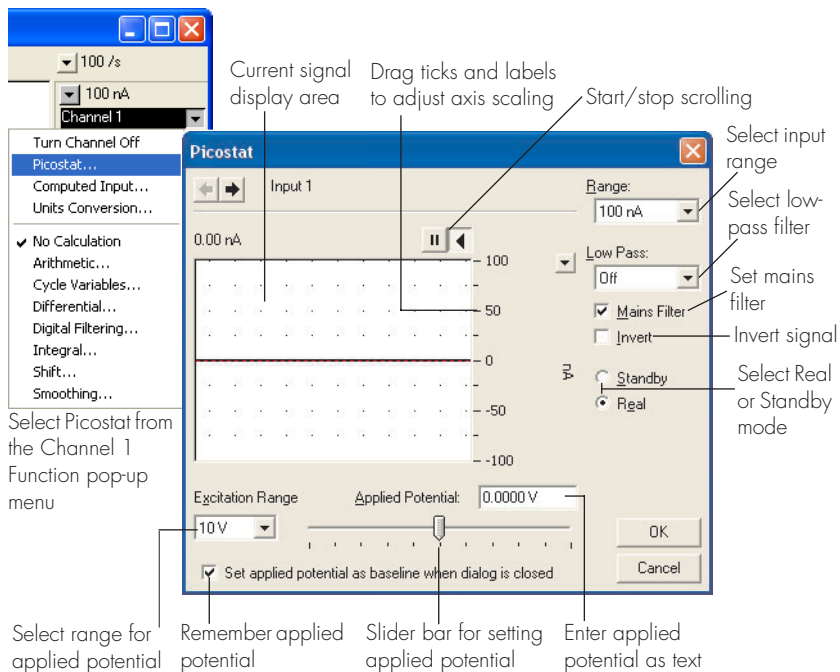
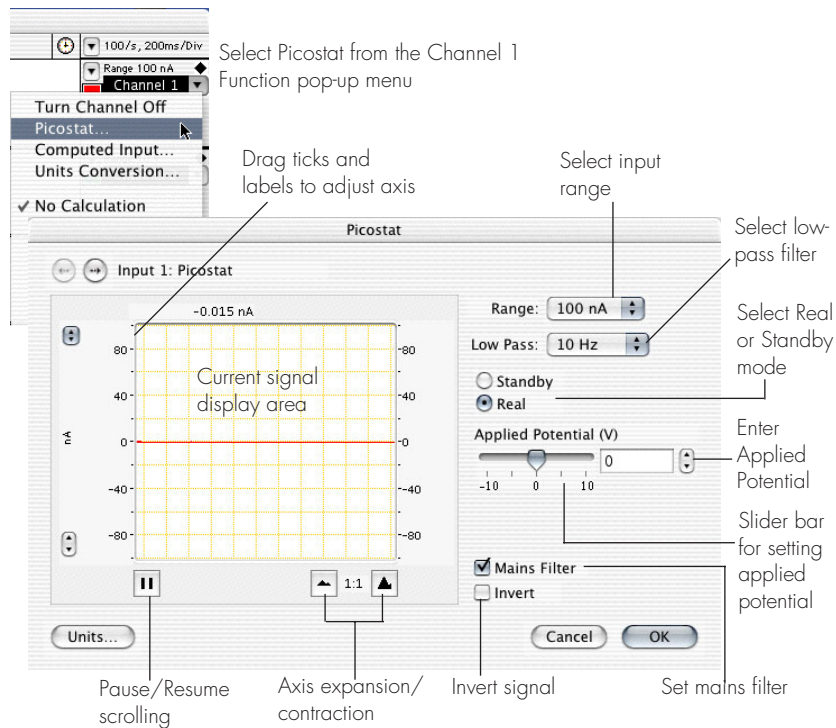


Figure 3-8
Accessing the Picostat controls with Chart software (Macintosh).



menu says 'Input Amplifier' instead of 'Picostat' then the software has not recognised the Picostat. Exit the software, check all your connections and try again).

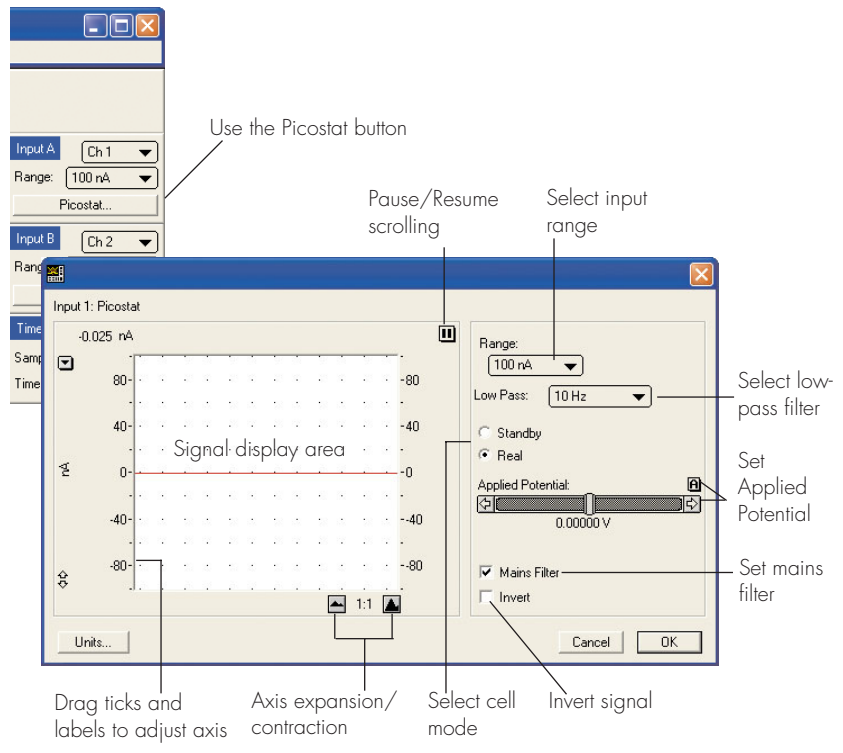
By default, the control window opens with the Picostat in Standby mode, that is with the reference and working electrodes isolated so that no current will flow through your electrodes. To connect to the Picostat lead wires you must select Real mode. When you click Cancel or OK the Picostat will revert to Standby mode until recording is started.

You will need to adjust the gain range to 20 nA to accommodate your signal amplitude, and to select the 10 Hz low-pass filter (and/or Mains Filter) to minimise high frequency noise on the signal — especially if you are working outside a Faraday cage.

You can now adjust the applied potential with the slider bar, or by entering the exact potential with text entry. The resulting current signal should obey Ohm's law:

$$I = E/R$$

Figure 3–9
Accessing the Picostat controls with Scope software.



so that with the 100 M Ω test resistor, R, in place, an applied potential, E, of 1 V should produce a current, I, of 10 nA, while other potential settings should produce corresponding currents.


Picostat Control Window

With Chart software, the Picostat Control window is accessed from the Picostat command in the Channel Function pop-up menu. [Figure 3-7](#) shows the control window on a Windows computer, and [Figure 3-8](#) on a Macintosh computer. These windows control the various current ranges and filtering options for the Picostat.

With Scope software, the corresponding controls are shown in [Figure 3-9](#).

Signal Display

The current signal is previewed scrolling across the display area. Note that the signal is not being recorded to hard disk at this stage, and that when the window is closed the signal trace is lost.

You can stop/start the signal scrolling by clicking the Pause/Resume button .

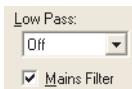
You can shift or stretch the vertical Amplitude axis to make the best use of the available display area. All changes to axis scaling are reflected in the Chart and Scope main window, and vice versa.

Setting the Range



The Range pop-up menu lets you select the input current range or sensitivity. The Picostat has ranges of 10 pA to 100 nA (if you require a system to monitor larger currents, the Potentiostat has ranges of 20 nA to 100 mA). You should set the range so that it is larger than the biggest current that you expect to encounter during your experiment. If, during the experiment the current signal exceeds the range, then the data will be truncated and therefore lost.

Filtering



The Picostat has an internal 10 Hz low-pass filter for removal of high frequency signals ('noise'). The Off setting gives the full bandwidth of the Picostat which can be up to 16 kHz (but which may also be limited by the characteristics of your electrodes and sample solution).

The 10 Hz filter setting is highly effective for the removal of mains hum (50 or 60 Hz interference) and, as a general rule, should be employed whenever possible. However, it should not be used for either pulse amperometric or voltammetric experiments where the pulses are shorter than 100 ms, or for voltammetric experiments where fast scan rates (greater than 100 mV/s) are used, or for other signals which are likely to exhibit fast rise or fall times — otherwise excessive smoothing of the signal may occur.

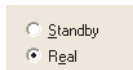
In addition, with Chart and Scope software, there is a Mains Filter checkbox. If this is ticked, then the e-corder will apply a mains filtering algorithm to the incoming signal which removes repetitive signals occurring at 50 or 60 Hz which are typical of mains interference. Note that the mains filter is not a notch filter, and can remove 50 or 60 Hz interference even if it is not a pure sinusoidal function. However, the mains filter does take a few seconds to 'learn' the pattern of the interference so that you will need to record for longer than this for it to take full effect. The mains filter can be employed even for experiments in which there are sudden potential jumps.

Inverting the Signal



The Invert checkbox allows you to invert the incoming current signal. It provides a simple way to redefine the directions (up or down) of an anodic (or cathodic) current signal. This control *does not* affect the direction of current flow at the electrodes.

Cell Control



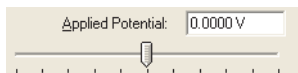
The Picostat can be in one of two operating modes, controlled by the Cell radio buttons:

- **Standby:** If Standby mode is selected the auxiliary and reference electrodes are isolated by an internal relay which effectively means that all the electrodes are at a 'floating' potential and that no current

will be passed through your experimental solution. The electrodes will not be connected until the Picostat control dialog is closed and the Chart, Scope or EChem Start button is clicked to begin a scan. The Applied Potential control is disabled in this mode.

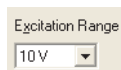
- **Real:** In Real mode the electrodes will be active and the Applied Potential slider control can be used to adjust the potential. When you close the control dialog (using EChem or Scope software) the Picostat will revert to Standby mode until the Start button is clicked to begin a scan. If you are using Chart or Scope software, the Picostat will remain in Real mode when the dialog is closed — this allows you to start and stop recording data while the electrodes remain active, which allows periodic recording of the signal from amperometric biosensors or *in vivo* electrodes without disturbing the environment around the electrodes.

Applied Potential



The applied potential slider control is only enabled in Real mode. It allows you to adjust the voltage applied to the electrodes. To change the value simply drag the control left or right to set an appropriate potential, or use the text entry controls to enter a numerical value. When using Chart software on a Windows computer the default potential will be the same as the Baseline value in the Stimulator control.

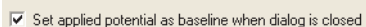
Excitation Range



When using Chart software on a Windows computer you have the option of limiting the range over which the applied potential can be set. Smaller ranges offer finer control with the slider bar or text entry of the applied potential.

On a Macintosh computer use the range control in the Stimulator Constant Output dialog box, [Figure 4–8](#).

Remember Potential



When using Chart software on a Windows computer you can select the checkbox labelled 'Set applied potential as baseline...' This causes the potential set with the slider bar or text entry to be transferred to the Stimulator baseline control when the window is closed.

Maintenance

Your Picostat will not require maintenance during daily operation. However, you should periodically check the Picostat for optimum results.

First set up the Picostat and e-corder as outlined earlier in this Chapter. Disconnect the electrode cable from the Picostat. Open the Picostat Control window, [Figure 3-7](#) or [Figure 3-8](#). Adjust the current range to 10 pA, the Low Pass filter to 10 Hz, and select Real mode. After a couple of seconds the resulting current signal should have stabilised and be close to zero. If the current signal is drifting significantly, or is greater than ± 5 pA, then contact your eDAQ representative — it is possible that stray static discharge may have damaged the Picostat's electrometer chip.

Also periodically repeat this procedure with the electrode cable connected, and attached to the 100 M Ω test resistor, as described in the section on [First Use](#), [page 27](#). If the current signal does not obey Ohm's law, then first recheck your connections of the Picostat to the e-corder, [page 25](#). If the problem persists then it is possible that the electrode leads or the Picostat itself has become damaged.

If these tests indicate that the Picostat is working correctly, but you are still experiencing difficulties with your experiments, then you should now check the electrodes you are using, the connections to them, and the design and condition of the reaction vessel, and any salt bridges that you are using.

4

CHAPTER FOUR

Techniques

The Chart and Scope software supplied with your e-corder can be used to perform many different electrochemical techniques with the Potentiostat and Picostat. This chapter provides an overview of these techniques, but you will need to also refer to the *Chart Software Manual* and *Scope Software Manual* (which are installed on the computer hard disk, with the software, or can be found on the eDAQ Installer CD).

Also discussed is the use of the Potentiostat when configured as a galvanostat.

Additional experiments such as current-sampled staircase linear sweep, differential pulse, normal pulse, square wave and cyclic voltammetry, and pulse amperometry can be performed with the optional EChem software — see the *EChem Software Manual*, or contact eDAQ for more details.

Introduction

The Potentiostat and Picostat apply a potential difference across a pair of working and reference electrodes whilst monitoring the current flow between the working and auxiliary electrodes.

The potential difference is determined by a 'command voltage' which is sent from the e-corder output to the 'E In' connector of the Picostat, [Figure 3–3, on page 23](#), or the E in pin of the Multiport connector of the Potentiostat, [Figure 2–4, on page 9](#). Chart and Scope software control the e-corder output via the 'Stimulator' controls in their Setup menus. For a full description of these controls, and the waveforms that can be produced, you should consult the *Chart Software Manual* and *Scope Software Manual*.

You can use your e-corder and Potentiostat, or Picostat, with Chart and Scope software to perform the following experiments:

- Linear Scan techniques — use Scope software with the Potentiostat to provide a potential ramp (up to 500 V/s) and to subtract charging current contributions. The bandwidth of the Picostat is sufficient for scan rates up to about 10 V/s
- Chronoamperometry, Amperometry, Constant Potential Electrolysis — monitor the current signal at fixed potentials
- Chronocoulometry — monitor and integrate the current signal at a fixed potentials
- Chronopotentiometry, Constant Current Electrolysis — monitor the potential signal when the Potentiostat is used as a galvanostat to maintain a constant current at the working electrode
- Monitoring of amperometric sensors including dissolved oxygen and nitric oxide electrodes.

Linear Scan Techniques

Linear sweep or cyclic voltammetry are usually best performed with EChem software. However, Scope incorporates Stimulator... and Output Voltage... commands which can be used to control the analog output of the e-corder to create a waveform suitable for driving the Picostat or Potentiostat. With Scope software up to 2560 points can be

collected on one channel at a rate of up to up to 100 kHz on both channels.

Fast Cyclic Voltammetry

Scope software has a number of features that can perform Fast Cyclic Voltammetry (FCV). These are accessed via the Stimulator... and Output Voltage... commands in the Setup menu, [Figure 4-1](#).

The base potential is set by using the Stimulator Constant Output dialog box while the waveform is generated using the Stimulator Up & Down, [Figure 4-2](#), or Triangle, [Figure 4-3](#), waveforms. See the *Scope Software Manual* for further details.

In [Figure 4-2](#) 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.

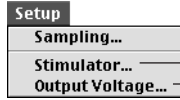
[Figure 4-3](#) shows an example of a positive and negative cyclic waveform. The base potential has been set to $+0.20$ V and a potential ramp has been set up to go from $+0.20$ to $+0.80$ V back again to -0.40 V and finally return to $+0.20$ V, over a period of 20 ms using the Triangle waveform option. 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, of the potential limits.

Ideally, FCV requires a smooth analog ramp, and so it is desirable to make the steps in the applied waveform output as small as possible. The e-corder output is controlled by a DAC (digital-to-analog convertor) is the value of which is updated whenever a new data point acquired. Thus, by setting the data acquisition rate to be as fast as possible for a particular experiment, you will also ensure that the waveform has steps that are as small as possible.

When performing FCV, a large background charging current is often recorded. This can be many times larger than the signal you are

Figure 4-1
Scope Setup menu.



Use the Stimulator... command to access the Stimulator (applied potential waveform) controls

Use the Output Voltage... command to set the baseline potential

Figure 4-2
Using the Scope Stimulator Up and Down command.

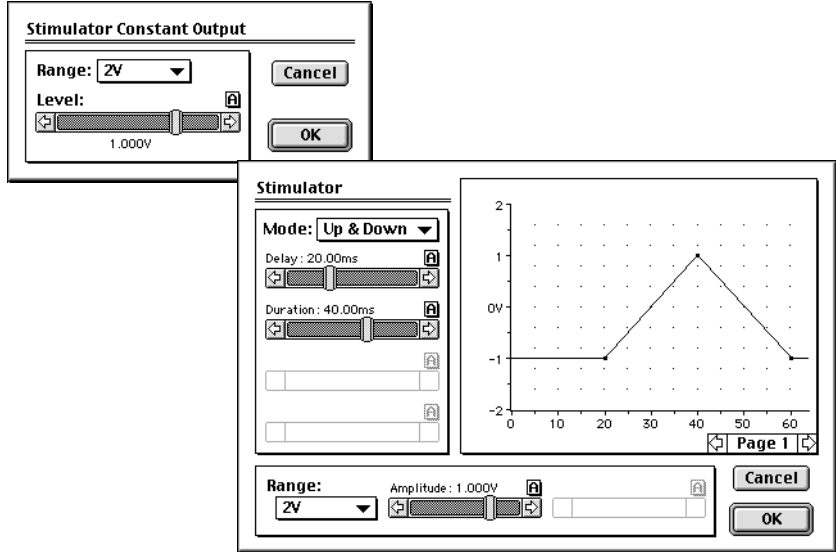
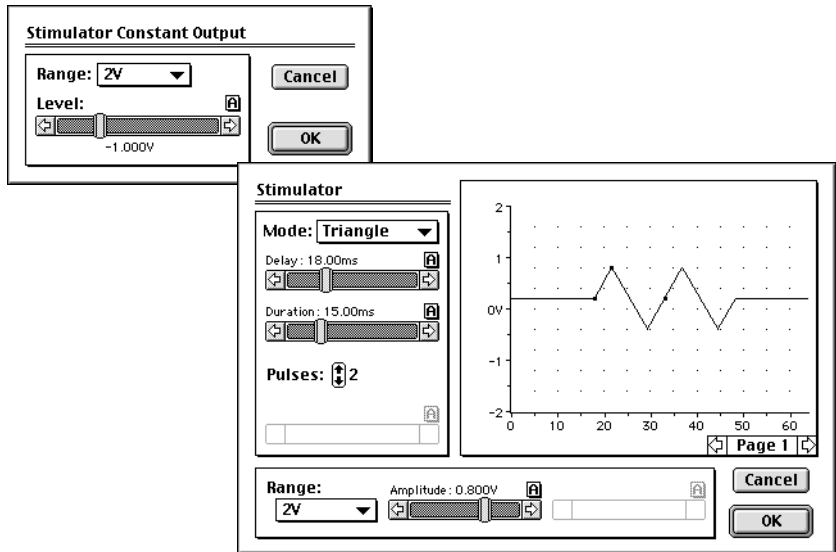


Figure 4-3
Using the Scope Stimulator Triangle command.



looking for. Fortunately the charging current is usually reproducible between scans and can be subtracted from the final result:

1. first a background scan is obtained with a 'blank' solution (that is, a solution containing only the background electrolyte);
2. next a scan is performed of the solution in which the substrate is present; and finally
3. the Scope 'page' that contains the background scan is selected using the Display > Set Background command which will subtract this scan from all other pages in the file. Use the Display > Don't Subtract Background command to cancel subtraction, and Clear Background to cancel the subtraction and clear the background sweep.

The background scan must be run under the same conditions (sweep width and stimulator settings) as the substrate solution to be effective. See the *Scope Software Manual* for more information.

Chronoamperometry with Chart

Chronoamperometric techniques require that a constant potential is maintained for a defined period while the current is monitored. If the current signal is integrated with respect to time then the total charge transferred at the electrode can be calculated ([Chronocoulometry, page 49](#)).

Single, double and even multi-step chronoamperometry, can be performed with Chart or Scope software, in a time frame from a millisecond to hours, or even days, if need be. For experiments involving sudden changes in potential you should use the full bandwidth of the Potentiostat or Picostat (that is, if possible, do not use the low-pass filters) or the response of the current signal may be modified by the low-pass filter time response characteristics.

On Windows computers

Chart software can be used to set a constant voltage of up to ± 10 V (which is known as the command voltage) from the e-corder Output. This is sent to the Picostat or Potentiostat via the 'E In' input cable, which then applies this potential across the reference and working

electrodes. The software controls are accessed through the Stimulator command in the Setup menu, [Figure 4-4](#).

To adjust the command voltage you will first need to select the range by adjusting the Output Range control in the Stimulator controls [Figure 4-5](#). The smaller the selected output range, the finer the control that you will have when you adjust the potential with the Baseline control. To monitor the current signal at a constant potential:

1. set the **Stimulator** to Pulse mode;
2. set the **Pulse Amplitude** to zero volts;
3. set the **Baseline** control to the desired voltage;
4. adjust the current input range to an appropriate value, [page 15](#) and [page 30](#);
5. set the speed of recording (that is the number of data points to be collected per second) to an appropriate value — you will usually require at least several hundred data points over the lifetime of your experiment. The *Chart Software Manual* has detailed descriptions on setting the recording speed; and finally
6. begin the experiment by clicking the Start button in the main Chart window.

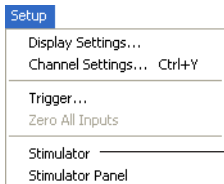
The Stimulator command can be used to alter the applied potential with a precision better than 1 ms. Pulses up to 30 s long may be created by this method. For further details on using the Stimulator in Chart refer to the *Chart Software Manual*. An example using the Chart Stimulator is shown in [Figure 4-6](#). Note that the pulse amplitudes are added to any value set by the Baseline control.

Chart macros can be used to keep the potential constant for a fixed period of time, or to drive the reaction backwards by first applying one potential and then subsequently applying a second potential to perform an oxidation/reduction cycle. Refer to the *Chart Software Manual* for more information.

On Macintosh

Chart software can be used to output a constant potential (up to ± 10 V) which the Picostat or Potentiostat will apply at the working electrode. These controls are accessed through the Setup menu, [Figure 4-7](#).

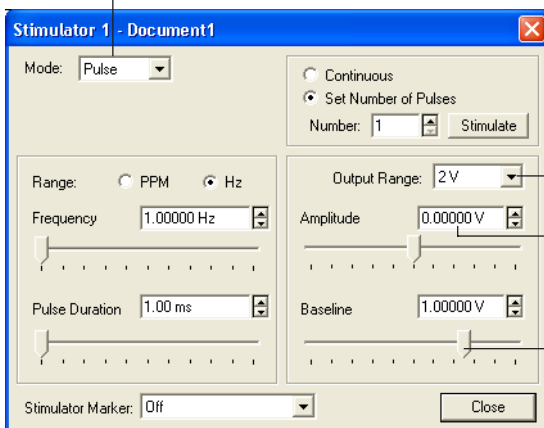
Figure 4-4
Chart Setup menu
(Windows).



Use the Stimulator command to access the Stimulator (applied potential waveform) controls, Figure 4-5 & Figure 4-6

Figure 4-5
Chart Stimulator
(waveform output)
controls (Windows).

Select stimulator mode

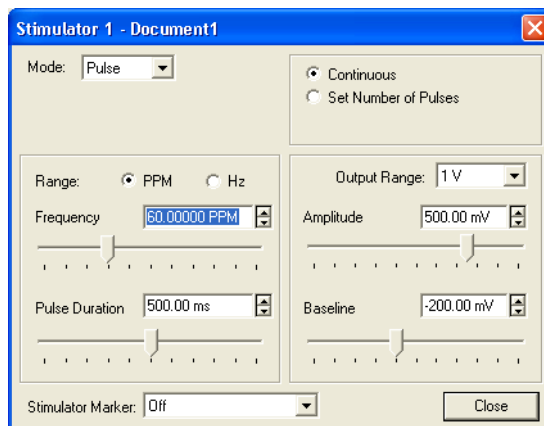


Select output range

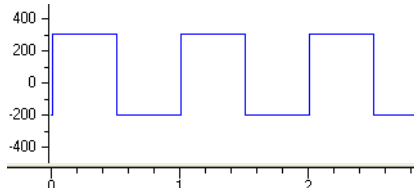
Enter exact values as text.
Use zero amplitude for
constant output

Baseline control can be used for constant
output — drag slider
controls to adjust
value

Figure 4-6
Stimulator controls for
multiple step
chronoamperometry
(Windows).



Settings to produce a 500
mV amplitude 1 Hz square
wave, on a base potential
of -200 mV



Potential waveform generated by
the Stimulator settings above

To adjust the potential you will first need to select the range by choosing the Output Voltage command in the Setup menu to activate the Stimulator Constant Output dialog box, [Figure 4–8](#). The smaller the selected output range, the finer the control that you will have when you adjust the potential.

The Timed Events (Setup menu) feature and macros can be used to keep the potential constant for a fixed period of time, or to drive the reaction backwards by applying an opposite potential to perform an oxidation/reduction cycle.

The Chart software Stimulator command (in the Setup menu) can also be used to set up pulses, stepped pulses, and staircase ramp waveforms for the Potentiostat or Picostat. See the *Chart Software Manual* for more details.

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 4–9](#) will maintain a potential of

Figure 4–7
Chart Setup menu
(Macintosh).

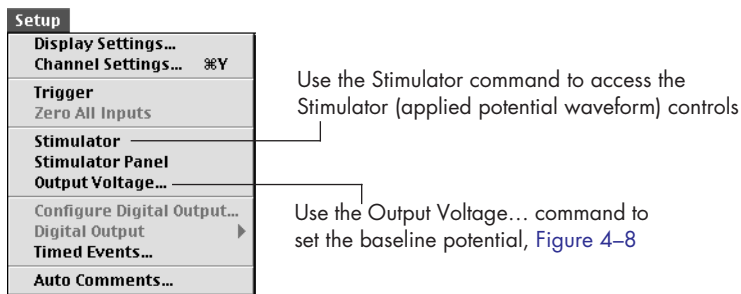
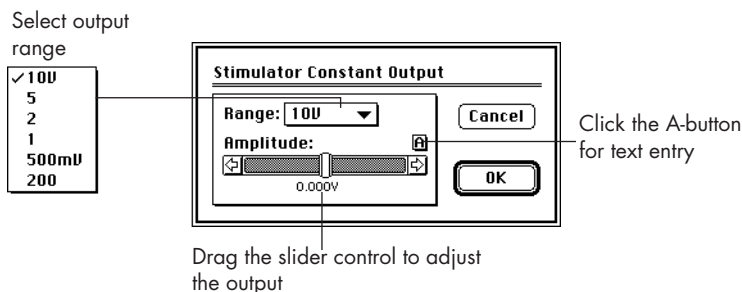


Figure 4–8
Chart Stimulator
Constant Output voltage
controls (Macintosh).



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. However, Timed Events can be slightly delayed (by up to 0.1 s) depending on the model of computer and what else is happening in the computer operating system. For accurate timing it is better to use the Chart Stimulator which is fully under the control of the internal e-corder clock.

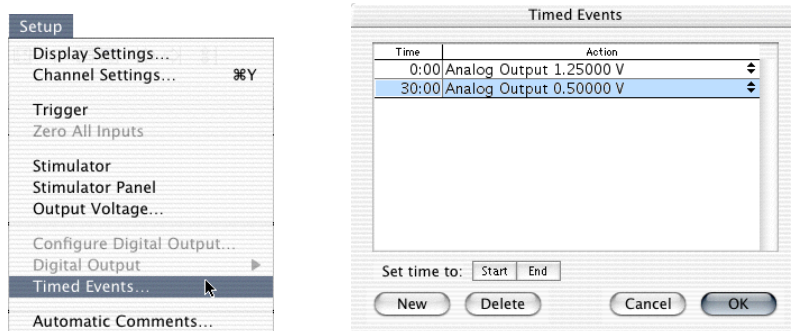
Using the Stimulator command (Setup menu) it is possible to send and monitor pulses with a precision better than 1 ms, [Figure 4–10](#). Pulses up to about 30 s may be created by this method. For further details on using the Stimulator in Chart refer to the *Chart Software Manual*.

Analysis of Chronoamperometry

Chronoamperograms obtained from a planar disk electrode should exhibit a current/time relationship governed by the Cottrell equation, (see Appendix D for definition of terms)

$$i = \frac{nFAC\sqrt{D}}{1000\sqrt{\pi t}}$$

Figure 4–9
Adjusting potential with the Chart Timed Events feature. (Macintosh only)

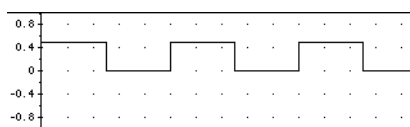
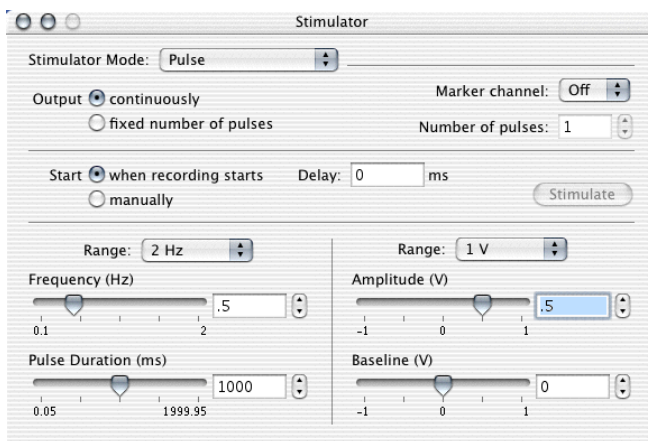


Access Timed Events from the Setup menu

Changing the potential after a period of 30 s

Figure 4-10

Simulator controls for multiple step chronoamperometry (Macintosh).



Stimulator settings to produce a 500 mV high, 0.5 Hz square wave

It is usually easier to first simplify the Cottrell equation thus:

$$i = \frac{a}{\sqrt{t}}$$

where a is treated as an empirical constant to be determined.

You can use the Chart's Arithmetic channel calculation (see the *Chart Software Manual*) to create 'data' on an unused channel (usually Channel 3) according to the equation:

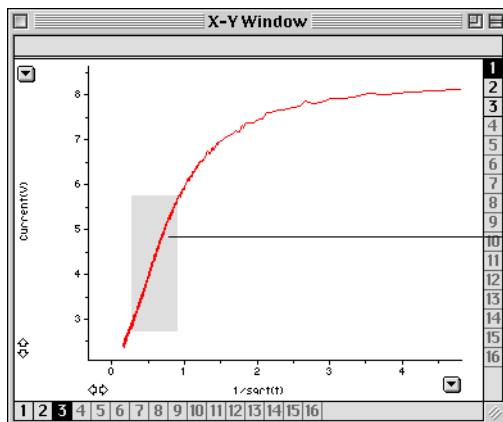
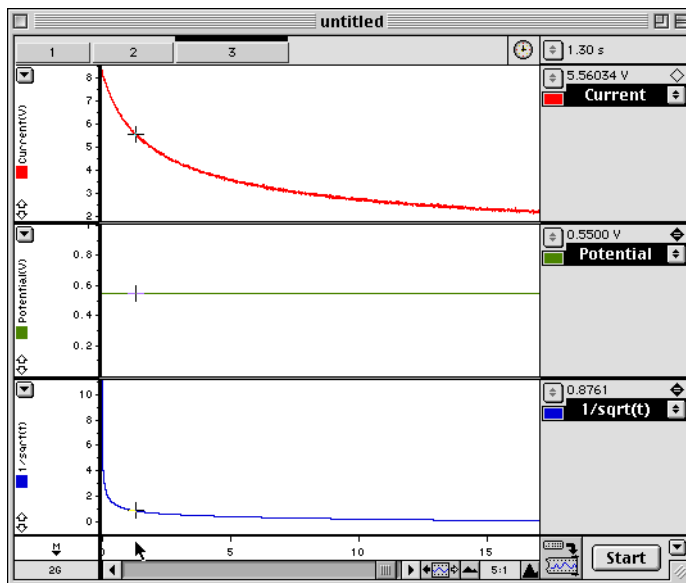
$$\text{Channel 3} = 1/\text{Sqrt}(\text{SampleTime})$$

You can now use the X-Y window to plot the current signal (usually on Channel 1) versus Channel 3, and a near straight line should be obtained with a slope of a , [Figure 4-11](#).

With the Curve Fit extension installed, you can use the Curve Fitting command (Windows menu) to fit your current signal data with an idealised curve. The Curve Fit analysis extension and accompanying documentation can be downloaded free from the eDAQ web site, www.eDAQ.com. The extension file should be put into the Chart Extensions folder, inside the Chart folder on your hard disk.

Figure 4-11

Typical chronoamperometric data, analyzed using the Arithmetic channel calculation and the X-Y window.



Typical experiment with $1/\sqrt{t}$ data calculated on Channel 3 using the Arithmetic channel

Region of ideal linear response

Cottrell graph of current versus $1/\sqrt{t}$ prepared in the XY Window. Deviations from linearity typically occur at very small and very large t values.

It is unlikely that the current signal will decay to exactly zero (due to convection currents in the vessel causing non-ideal diffusion) so a small non-zero constant, b , is added. Also 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 (in the Curve Fitting window, it is usually best to use the 't=0 at start of block' option as shown in Figure 4-12). 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 the estimation of time zero, and the fact that the Potentiostat has a finite bandwidth and so

the current signal will take a small amount of time to register a true value after a sudden change in potential.

Thus a better form of the equation to be fitted is:

$$i = \frac{a}{\sqrt{t+c}} + b$$

This must be entered as a New Equation in the Curve Fit extension the very first time you use it, [Figure 4-12](#).

Because of the discontinuity that occurs when the denominator is zero, first try fixing c to a small positive value, and iterating for better values of a and b . Some trial and error will be involved while you make guesses that are suitable for the initial values to iterate. After the better estimates for a and b have been determined, and iterated, c can be unlocked so that it refines during the next iteration, [Figure 4-12](#).

Also your data selection should not include points very close to zero time (the Potentiostat will require some time to settle), 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 time interval to give best results will probably be required.

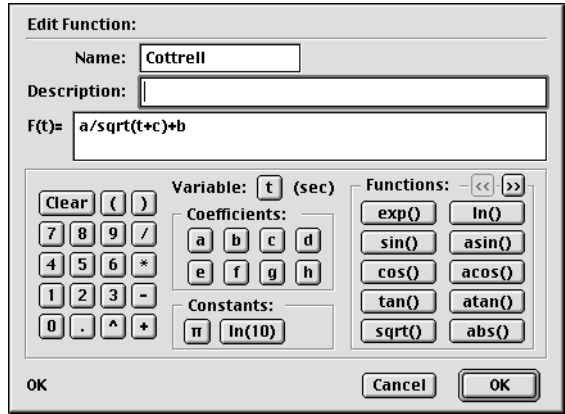
After the file is saved, the Curve Fit Cottrell equation will be available whenever you open Chart data file on the same computer or even when you transfer the data file to another computer on which Chart software and the Curve Fit extension are installed.

Remember to operate the Potentiostat or Picostat at full bandwidth (that is do not use the low-pass filters if possible) or else your results may be dominated by the low-pass filter response!

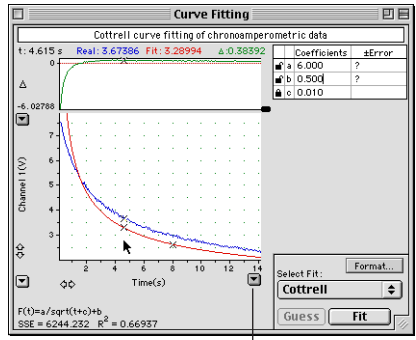
Figure 4-12

Fitting a Cottrell equation to data with the Curve Fit extension.

At the time of writing the Curve Fit extension is only available for Chart for Macintosh.



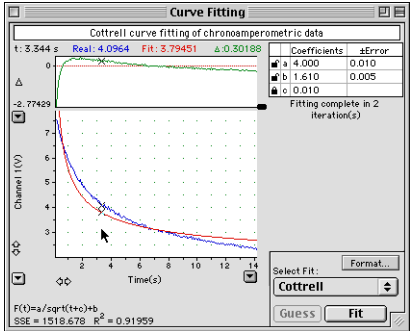
Define the Cottrell relationship as a new equation



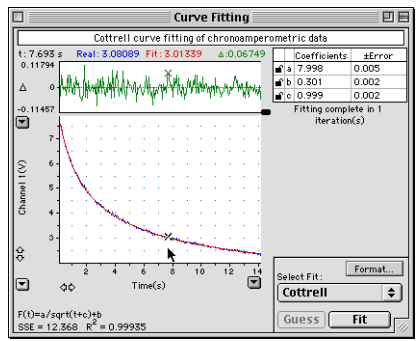
First lock in a value for c, then try guesses for a and b until an approximate fit is obtained

Usually use 't=0 at start of block'

Set Scale...
 Auto Scale
 Full Range
 t=0 at start of selection
 t=0 at start of block
 Channel 1
 Channel 2



Iterate by clicking the Fit button, refining a and b only. If the initial guesses are close enough, then a curve of better fit with new values for a and b will be obtained.



Unlock c, and iterate again. A curve of best fit should be obtained.

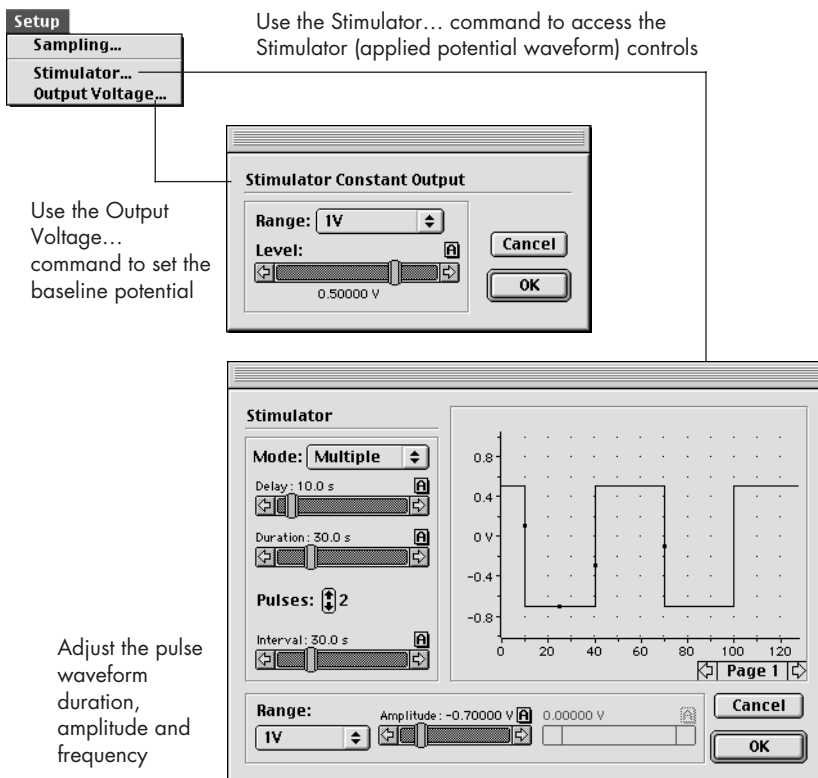
Chronoamperometry with Scope

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. Up to 2560 data points can be collected in a period of up to 128 s long. You should normally use the full bandwidth of the Potentiostat or Picostat (that is, do not use the low-pass filters) or the response of the current signal may be dominated by the low-pass filter time response characteristics. The base potential is adjusted with the Output Voltage... command (Setup menu) shown in Figure 4-13.

A potential that will cause the reaction to proceed (and the period for which it will be applied) is set using the Stimulator command. In the example shown in Figure 4-13, after a period of 10 s at the base

Figure 4-13
Scope controls for multiple step chronoamperometry.



potential of +0.5 V, 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' data subtracted with the Set Background command. You can then copy and paste the scan to a spreadsheet so that the differences can be plotted against $1/\sqrt{t}$ in a Cottrell graph.

For further details refer to the *Scope Software Manual*.

Chronocoulometry

Chart and Scope software have the ability to integrate an incoming signal both online (that is, in real time as you are collecting data), or offline (that is after the experiment is completed). Since the total charge transferred (the total number of coulombs, or electrons, transferred) is equal to the integrated current, the settings used for chronoamperometry, [page 39](#), can also be used for chronocoulometry.

With Chart software it also necessary to set up an unused channel (usually Channel 3) to be the integral of the current signal channel (usually Channel 1).

With an online function you need to actually be recording data to obtain the integral. To configure Channel 3 you need to choose the Computed Input command from the Channel Function pop-up menu, which opens the Computed Input dialog box ([Figure 4-14](#) on a Windows computer, and [Figure 4-15](#) on a Macintosh). For more information refer to the Computed Input section in the *Chart Software Manual*.

Post-acquisition integration of a signal is also possible with the Chart Integral channel calculation, which is accessed via the Integral command in the Channel Function pop-up menu — further details are in the *Chart Software Manual*. This is particularly useful when you want to recalculate the integral from the original current signal. The real time methods will give good results only if the appropriate sensitivity range has been pre-selected — and it is not always possible to determine this beforehand. A good strategy is often to use the real time integral

Figure 4-14

Online integration of the current signal using Chart Computed Input integration (Windows).

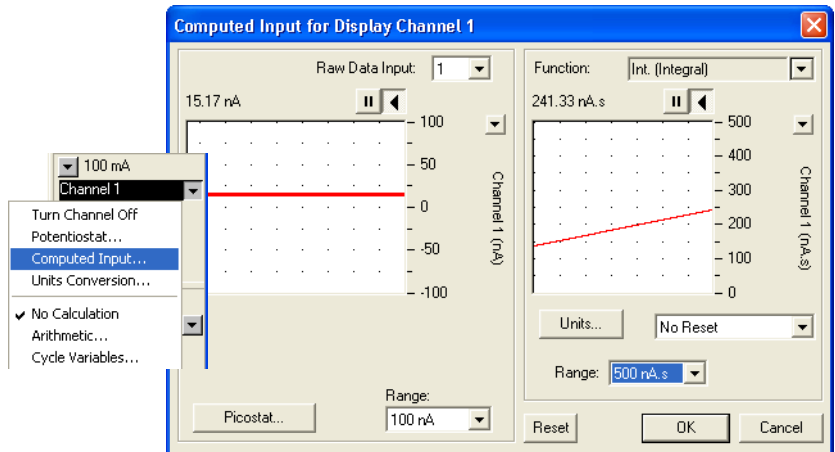


Figure 4-15

Online integration of the current signal using Chart Computed Input integration (Macintosh).

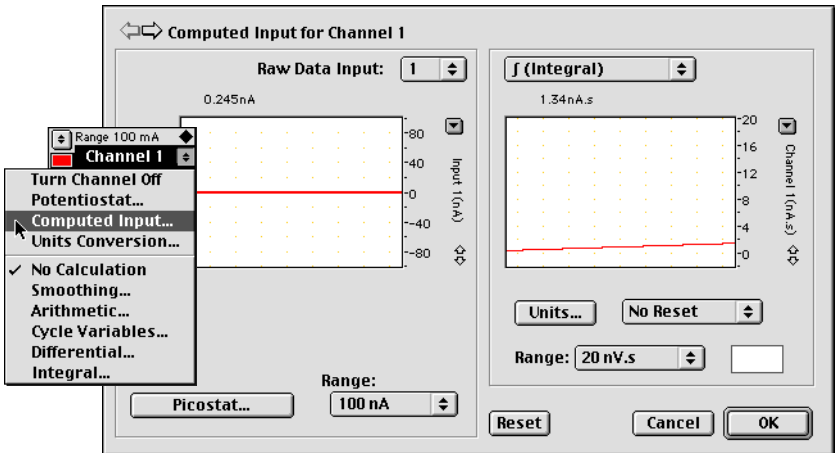
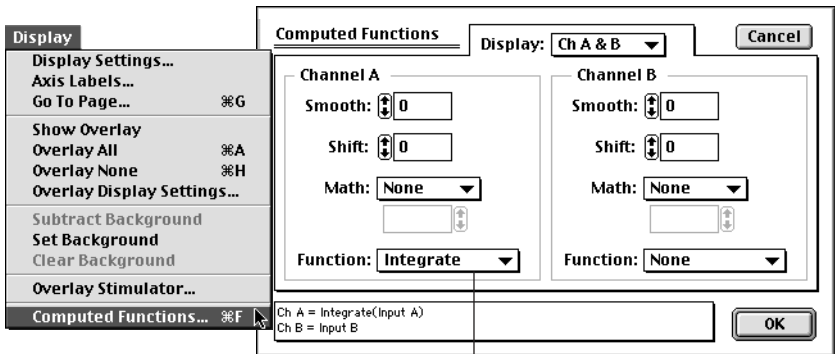


Figure 4-16

Integration of the current signal using Scope Computed Functions.



Select Integrate in the Function menu

function to get an idea of what is happening during an experiment and the use post-acquisition integration to prepare data for a final report.

With Scope software the current signal can be integrated by using the Computed Functions... command, [Figure 4-16](#). The Integrate item is chosen from the Function menu. This is actually a post-acquisition function — you can always cancel it afterwards to look at the underlying current data. Refer to the *Scope Software Manual* for more information.

Chronopotentiometry

Chronopotentiometry 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, after which there will be a sudden change in the potential.

For this type of experiment it will be necessary to run the Potentiostat in Galvanostat mode with Chart or Scope software. For correct operation make sure that the 'CH 1 (I)' cable of the Potentiostat is connected to Input 1 of the e-corder, and the 'CH2 (E)' cable of the Potentiostat is connected to Input 2.

Note that galvanostat mode is not available with the Picostat.

When using the Potentiostat as a galvanostat, the applied current can be set within ranges up to 100 mA. Select the smallest range setting consistent with your desired current to ensure maximum accuracy. For example, if a current of 750 μA is required then a range setting of 1 mA (1000 μA) should be used, and then exact current value adjusted accordingly.

The current values used should ensure that the resulting potentials do not exceed ± 10 V (the maximum limit of the Potentiostat) — highly resistive loads can easily produce large potentials, even with small currents.

Remember that when setting zero, or very small, currents there is always a small amount of offset (error) in the system. If you are trying to measure the potential of a system under zero current conditions then it

would generally be more accurate to use a zero current potentiometer (or pH meter) than a galvanostat.

Chart software on Windows computers

To switch to the Galvanostat mode of operation, choose the Potentiostat command in the Channel Function pop-up menu to open the control window, and turn on the Galvanostat and Dummy radio buttons, [Figure 4-17](#).

When in Galvanostat mode, the current and potential signals will be reversed from normal (potentiostatic) operation. That is, the 'I Out'

Figure 4-17
Setting up the Potentiostat as a Galvanostat (Windows).

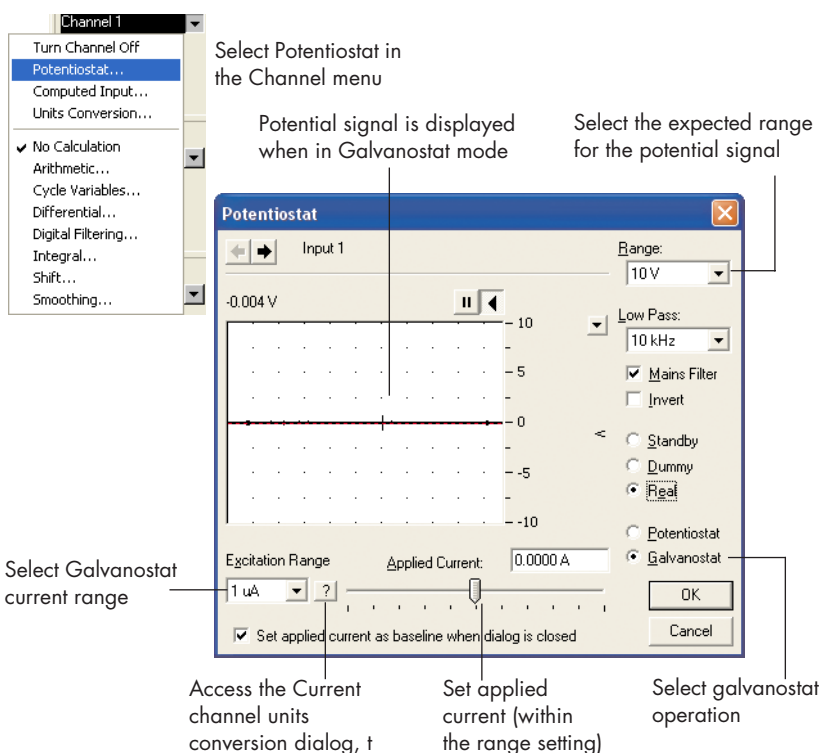
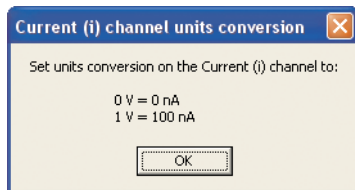


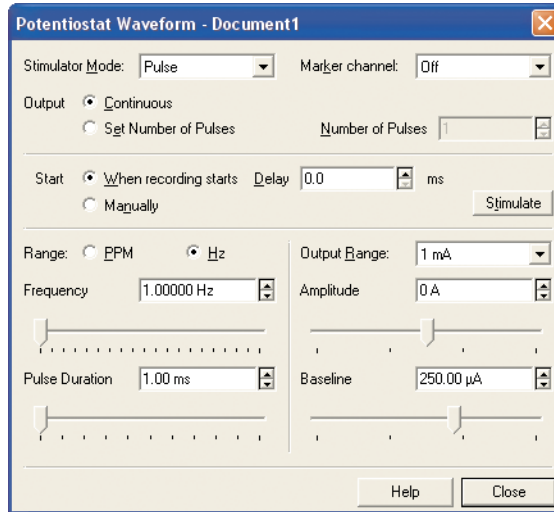
Figure 4-18
The Current channel units conversion dialog box.



Use these values to set Units Conversion for the Current channel

Figure 4–19

The Chart Stimulator dialog box when the Potentiostat is in Galvanostat mode



When in Galvanostat mode the Stimulator controls are used to adjust the applied current. Compare with Potentiostat mode where the Stimulator is used to adjust applied potential, Figure 4–6.

cable will be carrying the potential signal (which will now appear on Channel 1) and the 'E Out' cable the current signal (which will now appear on Channel 2). You will need to configure the Units Conversion of Channel 2 so as to ensure that the current signal is recorded in the correct current units, Figure 4–18.

When the Chart Stimulator command (Setup menu) is selected it accesses the Stimulator dialog box which, when using galvanostat mode, allows a baseline and various current waveforms to be configured, Figure 4–19.

Always select an appropriate current range for your system. While it is possible to set an applied current of up to 100 mA, the Potentiostat/ Galvanostat cannot supply a potential much greater than ± 10 V. Even relatively small applied currents, with a highly resistive load, may require potentials in excess of this. If in doubt, start with a small test current and observe the resulting potential.

Using a large range setting with a small (close to zero) current can produce unexpected results (large potential signals) with highly resistive loads because of small offsets in the current control circuitry. If you require very small currents always use a small range setting as well, this will ensure a minimum offset error. For example, to apply a current of only 25 nA use the 100 nA range setting for best results.

Figure 4-20
Setting up the Potentiostat as a Galvanostat (Macintosh).

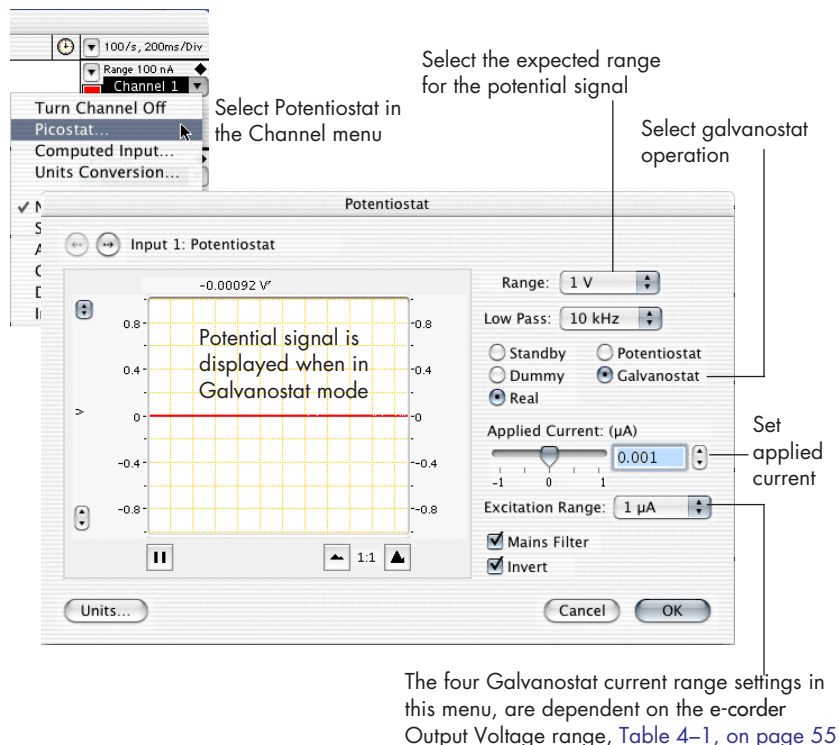


Chart software on Macintosh

To switch to the Galvanostat mode of operation, choose the Potentiostat command in the Channel Function pop-up menu to open the control window, and turn on the Galvanostat and Dummy radio buttons, [Figure 4-20](#).

When in Galvanostat mode, the current and potential signals will be reversed from normal (potentiostatic) operation. That is, the 'I Out' cable will be carrying the potential signal (which will now appear on Channel 1) and the 'E Out' cable the current signal (which will now appear on Channel 2). When you start to record data you will find that the Units Conversion on Channel 2 has been set to appropriate value so that the signal is automatically displayed with the correct current units.

The default setting is to have the applied current on the 100 mA range. It is likely that there will be a small residual offset at this setting which

Table 4-1
Galvanostat current range settings of the Potentiostat as a function of e-corder output range.

e-corder Output Voltage Range	Potentiostat/Galvanostat primary gain			
	100 nA/V	1 μ A/V	100 μ A/V	10 mA/V
10 V	1 μ A	10 μ A	1 mA	100 mA
5 V	500 nA	5 μ A	500 μ A	50 mA
2 V	200 nA	2 μ A	200 μ A	20 mA
1 V	100 nA	1 μ A *	100 μ A	10 mA
500 mV	50 nA	500 nA *	50 μ A	5 mA
200 mV	20 nA	200 nA *	20 μ A	2 mA

* It is better to use the corresponding settings with the 100 nA/V primary gain.

will cause the Potentiostat/ Galvanostat to go off scale (over 10 V) in Standby mode (as it is connected to the relatively low resistance $10^5 \Omega$ internal dummy cell). Try selecting a more appropriate 1 μ A or 10 μ A range, where the offset will be correspondingly smaller, and the signal should come on screen and be close to zero volts.

The e-corder Output Voltage can be set as described earlier, [Figure 4-8, on page 42](#). At each of these Output Voltage range settings the Potentiostat offers four current range settings when in Galvanostat mode, [Table 4-1](#). The most accurate control is achieved by using the largest possible Output Voltage range with the smallest possible Galvanostat range setting.

You can use the slider bar, or the text entry to adjust the current within the selected range. The resulting potential signal is shown in the display area.

You control the current passed by the Potentiostat/ Galvanostat by adjusting the Output Voltage controls (Setup menu) — this adjusts the e-corder control voltage which is reinterpreted as a current value by the Potentiostat/ Galvanostat. For example, if you have selected an e-corder Output Voltage range of 500 mV, and a current range of 50 μ A xxx, you might now wish to do an experiment where the current is held at a constant 35 μ A (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. A positive or

negative Output Voltage determines 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. You can also use the Timed Events feature (Setup menu) to adjust the current at predetermined time intervals after the start of recording.

Consult the *Chart Software Manual* for more details of the Output Voltage, Stimulator, and Timed Events features.

Scope software

Operation of the Potentiostat as a Galvanostat with Scope software is similar to using Chart software (Macintosh version), see [page 54](#). However, a wider variety of applied waveforms can be generated with the Scope Stimulator command.

Controlled Potential Electrolysis

This technique is essentially the same as [Chronoamperometry with Chart, page 39](#), and is also known as amperometry. 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 software in the same way as for chronoamperometry. The integrated current (that is, the total charge transferred) can also be determined by integrating the current signal (see [Chronocoulometry, page 49](#)) and this can be used to determine the extent of reaction.

If the solution is being stirred during the procedure then eventually all the substrate can be oxidized, or reduced, to a new material and the technique may be referred to as electrosynthesis rather than chronoamperometry.

If the reaction causes the formation of a polymer film on the electrode (for example pyrrole to polypyrrole, or aniline to polyaniline) then the technique may be referred to as electropolymerisation.

A potential should be chosen which is at least 50 – 200 mV more oxidising (or reducing) than the half-wave potential of the substrate in order to ensure complete reaction. It is usually important to separate the auxiliary (counter) electrode from the main body of the electrochemical cell by means of a salt bridge. This is to prevent the reduction products in the region of the auxiliary electrode reacting with the products of oxidation at the working electrode (or if reducing the substrate, to prevent the products of oxidation forming around the auxiliary electrode from reacting with the reduction products at the working electrode). The working electrode is usually constructed to have relatively 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, although reticulated vitreous carbon (RVC) which has an open pore foam structure, is also a popular choice.

The conversion of large amounts of substrate (> 100 mg) in reasonable times requires relatively high currents to be passed through the cell. Thus the Potentiostat (maximum current 100 mA) is usually more suitable than the Picostat (maximum current 100 nA) for electrosynthesis. The production of organic compounds in highly resistive non-aqueous solvents often requires the addition of large amounts of electrolyte to sustain the current flow (and which can lead to difficulties in later separation of the product). For studies using water, or other protic 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

These techniques are essentially the same as [Chronopotentiometry, page 51](#), and require the use of a galvanostat. The Potentiostat, when operated in Galvanostat mode, is suitable for experiments where currents less than 100 mA and potentials less than 10 V are anticipated. (Please note that the Picostat cannot be operated as a galvanostat). 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 (that is, the total charge

transferred) can also be determined which can be used to determine the extent of reaction.

Electrosynthesis and electropolymerization reactions are often more quickly carried out under constant current conditions than under constant potential conditions, but there is a greater risk of side reactions occurring as the potential changes. Ideally there should be no competing redox reactions at nearby potentials.

A sudden change in the potential usually indicates when the substrate is fully consumed.

It is important to limit the current so that the potential stays within the compliance voltage (10 V) of the Potentiostat/Galvanostat, at least until the reaction of interest is complete. Electropolymerization reactions can be problematic as a non-conducting polymer film adhering to the working electrode will increase its electrical resistance causing the Potentiostat to eventually go out of compliance and experience a potential overload.

Amperometric Sensors

Amperometric sensors require a potentiostat of appropriate gain range. You will also need to determine whether the sensor is of a two or three electrode configuration. Both the Potentiostat (currents greater than 100 nA) and Picostat (currents less than 100 nA) can be used in three electrode mode (working, reference and auxiliary electrode), or in two electrode mode (working and counter electrodes) by connecting the reference and auxiliary leads of the electrode cable together. You will also need to determine the correct 'polarising voltage' to use with your sensor. The 'polarising voltage' is the potential at which the Potentiostat or Picostat applies at the working electrode.

Normally Chart software (rather than Scope) is the better choice of recording software for these types of sensor. The Units Conversion feature of Chart can be used to perform two point calibration of the signal in the units of your choice, which is satisfactory for most uses — see the *Chart Software Manual* for more information. If multiple point, or non-linear, calibration is required then the Chart Multiple Point Calibration extension can be used with up to 12 calibration points. You

can download the extension and accompanying documentation from the eDAQ web site at www.eDAQ.com.

If the experiment requires a differential pulse methodology then the MultiPulse Amperometry techniques of the EChem software can be used for various pulse amperometric experiments. See the *EChem Software Manual* for more details.

Biosensors

Biosensors are often amperometric sensors and so can be used with the Picostat or Potentiostat which can be used as 'biosensor meters'. The first step is to establish the polarising voltage and current measurement requirements of your sensor.

Many biosensors provide a linear signal response over a limited range of concentrations. The Chart software Multiple Point Calibration extension can be used to extend the useful range over which a biosensor can be used by compensating for a non-linear signal response.

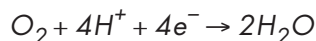
Microdialysis Sensor

The Sycopel™ Microdialysis Biosensor is available in several configurations for both in vivo or in vitro detection of analytes including glutamate, glucose, glycerol, ascorbate and acetylcholine. The Picostat has suitable current ranges for use with this sensor, and Chart software would normally be used to record data.

Dissolved Oxygen (dO₂) Sensors

Usually a polarographic (Clark) oxygen sensor electrode and meter are purchased from the same manufacturer to ensure matching sensitivity. However, depending on the current requirements of your oxygen sensor, either the Potentiostat or Picostat may be a suitable alternative to a standard meter as they have adjustable sensitivity and can be matched to a wide range of current signal requirements. In addition you can use them to alter the polarising voltage to 'fine tune' your sensor.

Most polarographic oxygen electrodes comprise a gold or platinum cathodic working electrode (to which the working electrode lead is attached) and a silver anodic counter electrode (to which the reference and auxiliary electrode leads are attached). Usually a reducing polarising voltage (applied potential) of between -0.7 to -0.8 V is required at the working electrode to effect the reaction:



The exact potential can be varied to suit the sample being measured and to minimise side reactions. A smaller potential reduces sensitivity but is usually more selective for oxygen.

Most oxygen sensors exhibit a slow response time and will take at least several seconds to stabilise. Thus you would normally employ a 1 – 10 Hz filter setting on the Potentiostat or Picostat in order to minimise any electrical noise. The Mains Filter setting can also be employed to further reduce mains hum.

If you intend to monitor oxygen concentrations over a wide range then you can calibrate the electrode at several concentrations and use the Chart software Multiple Point Calibration extension to compensate for a non-linear electrode response. You can download the extension from www.edaq.com.

Nitric Oxide (NO) Sensors

Most polarographic nitric oxide sensors can be used with the Picostat, which is suitable for detecting the small currents (<100 nA) expected from the low concentrations of nitric oxide found in natural biological systems.

Most commercial nitric oxide sensors comprise a carbon fibre anodic working electrode (to which the working electrode lead is attached) and a cathodic counter electrode (to which the reference and auxiliary electrode leads are attached). Usually an oxidising polarising voltage

(applied potential) of up to +1.0 V is required at the working electrode, to effect the reaction:



The exact potential can be varied to suit the type of electrode (many electrodes have special catalytic surface coatings), the sample being measured, and to minimise side reactions.

At potentials smaller than +0.7 V, the current signal is usually dependent on the polarising voltage, but between +0.7 and +0.1 V the current signal tends to plateau as the reaction is limited by the rate at which nitric oxide can diffuse to the anode surface. At potentials greater than +1.0 V the hydrolysis of water gradually becomes the dominant source of the current signal.

Most nitric oxide sensors exhibit a slow response time and will take at least several seconds to stabilise. Thus you would normally employ a 1 – 10 Hz filter setting with the Picostat in order to minimize any electrical noise. The Mains Filter setting can also be employed to further reduce mains hum.

It is recommended in most cases to calibrate the electrode at several nitric oxide concentrations covering your range of interest. Use the Chart software Multiple Point Calibration extension which can be downloaded from the eDAQ web site at www.edaq.com.

Vertical line

A

A P P E N D I X A

Technical Aspects

This appendix describes some of the technical aspects of the Potentiostat — you do not need to understand the material here to use the Potentiostat or Picostat. Please note that this information is not intended as a service manual and that user modification of the equipment voids your rights under warranty.

The Potentiostat, Picostat and other eDAQ Amps have been designed to be used with a e-corder system. All internal functions (gain ranges, filters, real/standby/dummy cell selection) of the Potentiostat or Picostat are controlled from the e-corder by sending information on a special communications connection called the 'I²C bus' which also supplies power to the Potentiostat or Picostat.

Potentiostat

The Potentiostat is designed to function as either a potentiostat (Chart, Scope or EChem software) or a galvanostat (Chart and Scope software only). The mode of operation is under software control. A block diagram of the Potentiostat circuitry is shown in [Figure A-1](#).

The Potentiostat is also fitted with an internal 100 k Ω dummy cell shown in [Figure A-2](#). The dummy cell is physically connected whenever the 'Real cell' mode is not being used.

The Potentiostat is powered by regulated +17 V, -17 V and +8 V DC lines from the e-corder, see [Figure 2-3 on page 9](#).

Figure A-1
Block diagram of the Potentiostat.

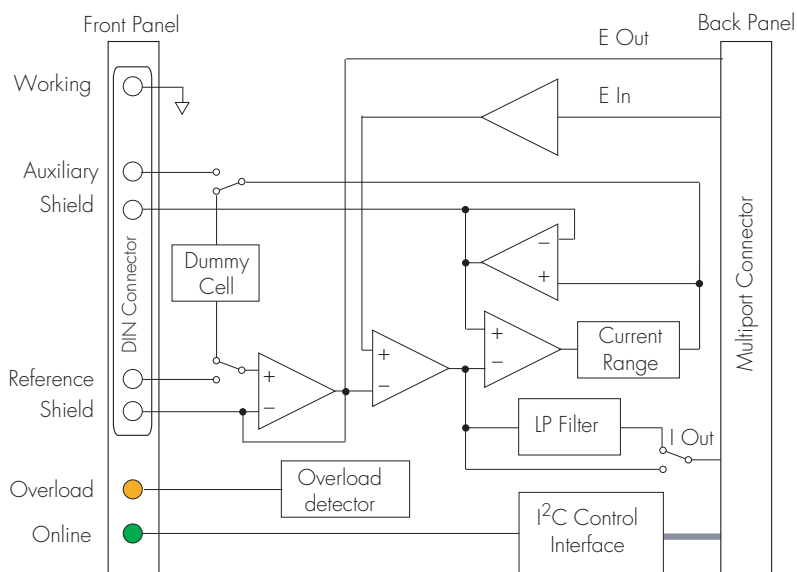
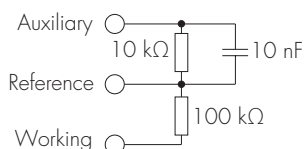


Figure A-2
The Potentiostat 100 kΩ Dummy Cell.



The Potentiostat has four gain ranges of 100 nA/V, 1 μ A/V, 100 μ A/V, and 10 mA/V. The maximum current output signal (I Out) is 10 V at any gain setting. Secondary amplification of the current signal is done by the e-corder. The gain and secondary amplification are set by the single 'range' menu in the software which offers a combined total of 19 current range settings from ± 20 nA to ± 100 mA in 1:2:5 steps.

The Potentiostat uses a VCCS (Voltage Controlled Current Source) design based on a Howland current pump. A differential input amplifier compares the difference in potential between the reference electrode and the excitation potential set on the analog output of the e-corder. The output of this amplifier provides an error signal to the VCCS which drives a current through the auxiliary electrode to try to zero the error signal. By using a VCCS the working electrode of the cell can be directly connected to ground. This is a safe configuration particularly

suitable for student use. Further information on the basic design can be obtained from 'A Potentiostat Based on a Voltage-Controlled Current Source for use with Amperometric Gas Sensors', J. C. Fidler, *IEEE Transactions on Instrumentation and Measurements*, **41**, 1992.

The high impedance reference and auxiliary electrode lead wires are actively shielded (that is, the shield is driven at the same potential as the lead wire itself) to minimise electrical interference.

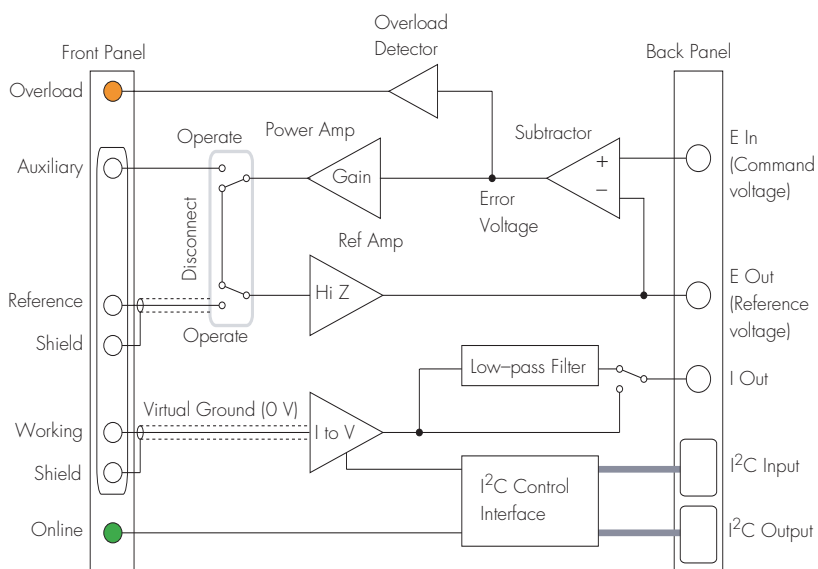
Picostat

The Picostat is designed to function in potentiostatic mode only, that is it cannot be used as a galvanostat. A block diagram of its construction is shown in [Figure A-3](#).

The Picostat is powered by regulated +17 V, -17 V and +8 V DC lines from the e-corder, see [Figure 3-3 on page 23](#).

An error voltage is generated from the difference between the voltage on the Reference electrode and the excitation (command) voltage set by the e-corder unit. This difference or error voltage drives a high gain power amplifier (VCVS – voltage controlled voltage source) the output of which is applied to the Auxiliary electrode in such a way as to minimise the error voltage.

Figure A-3
Block diagram of the Picostat.



The Picostat, and the electrochemical cell to which it is connected, forms a composite feedback control system in which the value of the Auxiliary voltage is controlled in such a way as to make the Reference voltage equal to the desired Command voltage. The current flow in the Working electrode is the quantity being measured.

When the Picostat is in Standby mode the Working and Reference electrodes are disconnected by an internal relay. This prevents unwanted current flowing through your electrochemical cell.

An overload condition is indicated when the error voltage exceeds a small non-zero value. This indicates that the system could not establish or sustain a balanced state. The Overload light will be reset when scanning is stopped or when the Picostat controls are next accessed.

The reference voltage is measured by a high input impedance amplifier which provides a low impedance output to the e-corder unit.

The voltage at the working electrode is effectively held at a virtual ground potential (zero volts) by a voltage-to-current converter, the output of which reads directly in current units and is also applied to the e-corder unit. The Picostat has three gain ranges of 100 pA/V, 1 nA/V, and 10 nA/V. The maximum current output signal (I Out) is 10 V at any gain setting. Secondary amplification of the current signal is done by the e-corder. The gain and secondary amplification are set by the single 'range' menu in the software which offers a combined total of eleven current range settings from ± 10 pA to ± 100 nA in 1:2:5 steps.

The coaxial shields of the reference and working electrode lead wires (which carry a high impedance signal) are maintained at the same potential as the lead wire itself to minimise electrical interference, and reduce lead capacitance.

B

A P P E N D I X B

Troubleshooting

This appendix describes some problems that may arise when using the Potentiostat or Picostat. There is also help in your *e-corder Manual* and *Software Manuals*, located on the *eDAQ Software Installer CD*.

In many cases, a problem can be fixed by turning the e-corder and computer off, checking connections, and starting again. Also try performing the maintenance checks on [page 18](#) and [page 33](#). If you cannot correct the problem, then please contact your eDAQ representative.

The On-line indicator fails to light when the software is opened.

- Check that the e-corder is connected to the mains power and that it is turned on.
- Check that Potentiostat or Picostat is properly connected to the e-corder and that the cables are not loose. Especially check that the 'E in', 'I Out' and 'E Out' cables are correctly connected, see [page 10](#), and [page 25](#).
- If possible, change cables and try again. If a second cable works and you find that the first cable is faulty, you should contact eDAQ for a replacement.
- If you are using EChem software, check that the Potentiostat or Picostat 'E In' cable is connected to the e-corder output and the 'I Out' and 'E Out' cables are connected to Input Channels 1 and 2, see [page 10](#), and [page 25](#).
- Try using the Potentiostat or Picostat with another e-corder (if available). If the Online indicator fails to light on the second

e-corder, the Potentiostat or Picostat may be faulty — contact eDAQ. If the Potentiostat or Picostat works correctly on a second e-corder then the first e-corder may be faulty — contact eDAQ.

The 'Potentiostat' or 'Picostat' controls cannot be accessed in Chart, Scope or EChem software (that is only the standard 'Input Amplifier' dialog box of the e-corder can be accessed)

- Check that the Potentiostat or Picostat Online indicator is on after the software has been opened. If not, then proceed as in the previous problem.
- Check that you have connected the 'E In', 'I Out' and 'E Out' cables correctly to the appropriate e-corder connectors.

The Overload indicator is on (the Potentiostat or Picostat is experiencing a potential overload).

- Check that the electrode cables are firmly attached to the electrodes.
- Check that the surfaces of the electrodes have not become fouled.
- The Picostat Overload indicator may come on when the software is started — this is normal. The Overload indicator light should go out when you open the Picostat controls, or start recording.
- See Chapter 2 [page 7](#), and Chapter 3 [page 22](#) for more details.

The current signal goes off scale.

- Increase the full scale current range setting.
- Make sure each electrode is connected to the correct lead wire, [page 7](#) and [page 21](#).
- Make sure the electrodes (and the alligator clips connecting them to the lead wires) are not touching each other.
- Decrease the surface area of your working electrode.
- Decrease the concentration of the background electrolyte.
- Decrease the concentration of the substrate.
- Check that a potential overload (see previous section) has not occurred.

The results show peaks or steps at the inverse polarity I expect to see (i.e. a peak may be occurring at 0.5 V when it should be at -0.5 V).

- Check that you are connected to the correct Output (+ or -) of the e-corder. See [Connecting the Potentiostat, page 9](#), or [Connecting the Picostat, page 25](#).
- If you are using Chart or Scope, software check that the Invert box is checked or not, as appropriate, for the potential recording channel.

The results show peaks (or steps) at different potentials than you expect.

- See previous section.
- Make sure the reference electrode is connected to the correct (yellow) lead wire, [page 7](#) and [page 21](#). Connection of the reference electrode to either the working or auxiliary leads can also cause rapid electrode deterioration requiring electrode replacement.
- Check the condition of the reference electrode. All reference electrodes age. For example an Ag/AgCl electrode will age with exposure to light. Eventually the white/light grey coating of AgCl on the central silver wire will be replaced by a brown/black coating of silver oxide. As this process takes place the apparent positions of your voltammetric peaks will appear to shift to different potentials. Most Ag/AgCl electrodes can be quickly regenerated by placing the silver wire in 1 M hydrochloric acid solution for a minute or two (any silver oxide is quickly reconverted to AgCl), although you may wish to remove the old coating completely and re-chloridize the silver wire to ensure a good coating of fresh AgCl. In either case replace the newly coated wire back into the electrode casing with freshly prepared KCl solution. Aged calomel (Hg/Hg₂Cl₂) electrodes should usually be replaced. Reference electrodes using a gelled electrolyte will deteriorate if the gel dries out.

The results show peaks in the negative current direction when you want them in positive direction.

- Check that the Invert box is checked or not, as appropriate, for the current recording channel. See [Inverting the Signal on page 16](#) and [page 31](#).

The results show peaks (or steps) at different potentials than you expect.

- See previous section.
- Make sure the reference electrode is connected to the correct (yellow) lead wire!
- Check the condition of the reference electrode. All reference electrodes age. For example an Ag/AgCl electrode will age with exposure to light. Eventually the white/light grey coating of AgCl on the central silver wire will be replaced by a brown/black coating of silver oxide. As this process takes place the apparent positions of your voltammetric peaks will appear to shift to different potentials. Most Ag/AgCl electrodes can be quickly regenerated by placing the silver wire in 1 M hydrochloric acid solution for a minute or two (any silver oxide is quickly reconverted to AgCl) — although you may wish to remove the old coating completely and re-chloridize the silver wire to ensure a good coating of fresh AgCl. Replace the newly coated wire back into the electrode housing and refill with freshly prepared KCl solution. Aged calomel (Hg/Hg₂Cl₂) electrodes should usually be replaced. Reference electrodes using a gelled electrolyte will deteriorate if the gel dries out.

The results are contaminated by 'noise'.

- Most often the noise encountered in electrochemical experiments is a manifestation of mains hum (50 or 60 Hz interference) from power lines and mains-powered equipment. Note that, depending on the sampling rate, aliasing can make such interference appear as a low frequency oscillation superimposed on your data. Ensure common grounding by attaching the e-corder and computer to the same power board which is then attached to a three pin (grounded) power socket. If consistent with the bandwidth required by your experiment, use the 10 Hz filter of the Potentiostat or Picostat to record your results, see [page 15](#) and [page 31](#). Get an electrical technician to check that the grounding of the power socket itself is in good condition. Try the Mains Filter setting (Chart and Scope software) which is very effective at removing main induced artifacts
- Check electrode connections. Poor electrical contact to the electrodes will act as a source of noise. Particularly check the electrode cables: cables age, especially at the alligator clips where they are subject to mechanical wear. Use a multimeter to ensure that the clips are still in good electrical contact with the correct pins in

the input connector of the electrode cable, see [Figure 2–2 on page 6](#), and [Figure 3–3 on page 23](#). Also check that the shield pins have not shorted to any of the alligator clips.

- Ensure that the reaction vessel (and electrodes) are positioned as far as possible from power leads, computers, monitors and other mains-powered equipment. Ideally the reaction vessel (and even the Potentiostat or Picostat) should be enclosed by a Faraday cage. A Faraday cage (or other electrical shielding) is almost always required when measure small currents with the Picostat.
- Random spikes occurring during your experiment are more likely to be due to nearby electrical equipment switching on and off. Equipment with high current drain such as electric motors in vacuum pumps, refrigerators, or air-conditioner compressors should be particularly suspect. Try turning such equipment off during your experiment to identify the source of the problem. You may have to change your location (try a power socket on another circuit in the same room, or even move rooms completely).

Vertical line

C

A P P E N D I X C

Specifications

Potentiostat

Electrometer & Power Amp

Potentiostat type: Voltage Controlled Current Source.
Galvanostat mode available.

Compliance voltage: > 10 V

Output current: ± 100 mA maximum

Input resistance: $10^{13} \Omega$

Input bias current: < 10 pA @ 25°C

Current Measurement and Control

Current range settings: $\pm 100, 50, 20, 10, 5, 2, 1$ mA
 $\pm 500, 100, 50, 20, 10, 5, 2, 1$ μ A
 $\pm 500, 100, 50, 20$ nA

Gain: 10000, 100, 1, 0.1 μ A/V

Maximum current signal: 10 V

Low pass filters: 10000, 1000* Hz, 4th order Bessel
100*, 10* Hz, 2nd order Bessel
* These settings are used alone with Scope and EChem software and with the corresponding e-corder digital filters with Chart software.

Slew rate: 3 V/ μ s
Drift with temperature: < 10 μ V/ $^{\circ}$ C

Control Port

Multiport/I²C: Centronics 24 pin. Provides control and power to the Potentiostat along with analog signal connections to the e-corder.

Power requirements: \pm 17 V DC
+8 V DC
25 mA typical
2 W

Physical Configuration

Dimensions (h \times w \times d): 50 \times 76 \times 260 mm
1.96 \times 3.0 \times 10.2 inches

Weight: 0.8 kg (1.8 lb)

Operating conditions: 0 – 35 $^{\circ}$ C
0 – 90% humidity (non-condensing)

eDAQ reserves the right to alter these specifications at any time.

Picostat

Electrometer & Power Amp

Compliance voltage:	> 13 V
Maximum control voltage:	± 10 V
Output current:	± 100 nA maximum
Input impedance:	$10^{13} \Omega \parallel 1$ pF
Input bias current:	< 250 fA @ 25°C (60 fA typical)

Current Measurement and Control

Current ranges:	$\pm 100, 50, 20, 10, 5, 2, 1$ nA $\pm 500, 50, 20, 10$ pA
Gain:	10, 1, 0.1 nA/V
DC current error:	< $\pm 1\%$ FS on ranges of 10 pA – 1 nA < $\pm 0.5\%$ FS on ranges of 2 – 100 nA
Filter setting:	10 Hz low-pass. Used alone with Scope and EChem software, and with the corresponding e-corder setting with Chart software.
Filter type:	3rd order Bessel
Bandwidth, unfiltered:	> 10 kHz, on ranges of 20 – 100 nA ~ 1 kHz, on ranges of 10 pA – 10 nA
Drift with temperature:	< 20 μ V/°C

Control Port

I ² C input and output:	Male and female DB-9 pin connectors. Provides control and power to the Picostat.
Power requirements:	± 17 V DC, ~ 20 mA +8 V DC, ~ 20 mA ~ 1 W quiescent

Physical Configuration

Dimensions (h × w × d): 50 × 76 × 260 mm
1.96 × 3.0 × 10.2 inches

Weight: 0.8 kg (1.8 lb)

Operating conditions: 0 – 35°C
0 – 90% humidity (non-condensing)

eDAQ reserves the right to alter these specifications at any time.

D

A P P E N D I X 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:

$$i_{pa} = 269n^{3/2}AD^{1/2}C_V^{1/2} \quad \text{for an oxidation (anodic scan)}$$

$$i_{pc} = -269n^{3/2}AD^{1/2}C_V^{1/2} \quad \text{for a reduction (cathodic scan)}$$

The potential where this occurs is given by:

$$E_{pc} = E_{1/2} - \frac{0.0285}{n} \quad E_{pa} = E_{1/2} + \frac{0.0285}{n}$$

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

A = area of the exposed surface of the electrode (cm²)

D = diffusion coefficient of the substrate molecule (cm^2/s)

C = concentration of the substrate molecule (mol/L)

ν = the scan rate (V/s).

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:

$$i_p \propto \sqrt{\nu}$$

E_p independence of the scan rate, ν

In addition cyclic voltammograms will exhibit:

$$|E_{p_a} - E_{p_c}| = \frac{57}{n} \text{ mV (at 298 K)}$$

$$\left| \frac{i_{p_a}}{i_{p_c}} \right| = 1$$

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 $|E_{p_a} - E_{p_c}|$ to become larger than predicted, the peaks to be broader, and the peak currents to be smaller.

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

A = area of the exposed surface of the electrode (cm²)

D = diffusion coefficient of the substrate molecule (cm²/s).

C = concentration of the substrate molecule (mol/L)

t = time (s).

The factor of 1000 is to bring both cm and dm (1 dm³ = 1000 cm³ = 1 L) in the equation to common units.

Thus a plot of i versus $1/\sqrt{t}$ should produce a straight line.

In aqueous solution the coefficient of diffusion usually has a value of between 10⁻⁵ and 10⁻⁶ cm²/s.

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).

C = concentration of the substrate molecule (mol/L)

t = time (s)

k = a constant.

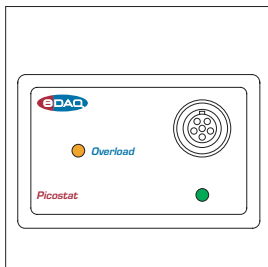
Thus a plot of Q versus $t^{1/2}$ should produce a straight line with an intercept of k , which in turn can be defined as:

$$k = nFA\Gamma + Q_{dl}$$

where

Γ = surface concentration of adsorbed substrate (mol/cm^2)

Q_{dl} = double layer charging.



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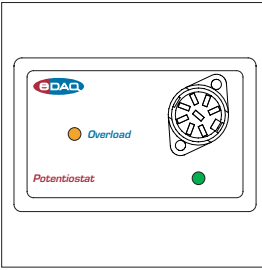
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License & Warranty

Trademarks

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Responsibilities

You and any others using any eDAQ product agree to use it in a sensible manner for purposes for which it is suited, and agree to take responsibility for their actions and the results of their actions.

If problems arise with an eDAQ product, eDAQ will make all reasonable efforts to fix them. This service may incur a charge, depending on the nature of the problems, and is subject to the other conditions in this Agreement.

Hardware Warranty

eDAQ Pty Ltd warrants the Potentiostat or Picostat, to be free of defects in material and workmanship for one year from the date of purchase. eDAQ Pty Ltd will repair or replace defective equipment as appropriate.

To obtain a warranty repair/replacement you must first notify us before return of the instrument and we

will issue you with a RAN (return authorization number). You must ship the defective product at your expense. We will pay return shipping. The product should be packed safely (preferably in its original packaging) and have the RAN on the shipping label. Returns sent without a RAN may be refused delivery.

This warranty does not cover hardware that has:

- been modified by the user in any way;
- been subjected to unusual physical, electrical, or environmental stress. This includes damage due to faulty power sockets, inadequate earthing, or power spikes or surges;
- been damaged because of incorrect wiring to ancillary equipment, or because of substandard, connectors or cables; or
- had the original identification marks removed or altered.

Software License

You have the non-exclusive right to use the supplied eDAQ software (Chart, Scope etc). Your employees or students, for example, are entitled to use it, provided they adhere to this agreement. Each separate purchase of the eDAQ software licenses it to be used on two computers at any given time (on one computer for data acquisition with a e-corder hardware unit, and on a second computer for the analysis of existing data files). Although multiple

copies of a program may exist on several computers, more than two copies must not be used simultaneously. Departmental/company licences are available if you wish to run more than two copies simultaneously.

Technical Support

Please register your unit to receive technical support. Technical assistance is available via email. Please describe the problem with as much detail as possible. Include a small example data file, if appropriate. Please also state:

- the model and serial number of your e-corder unit and Potentiostat or Picostat.
- the type of computer and operating system being used (for example Windows XP, or Macintosh OS 10.2)
- the software version you are using (for example Chart v5.1.2)

We endeavor to answer all your questions, but in some cases, for example where the problem relates to the other equipment that you are using, a nominal fee may be charged.

Jurisdiction

eDAQ Pty Ltd is bound by the laws of New South Wales in Australia, and any proceedings shall be heard by the Supreme Court of New South Wales in Australia.

Disclaimer

eDAQ reserves the right to alter specifications of hardware and software without notice.

No liability can be accepted for consequential damages resulting from use of eDAQ products.