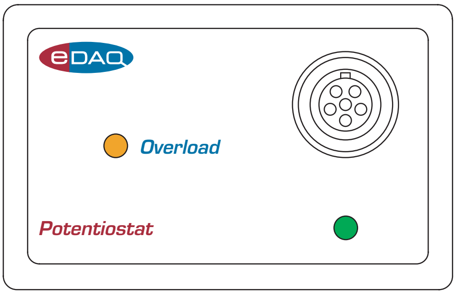
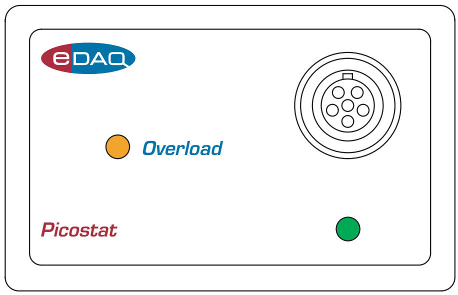
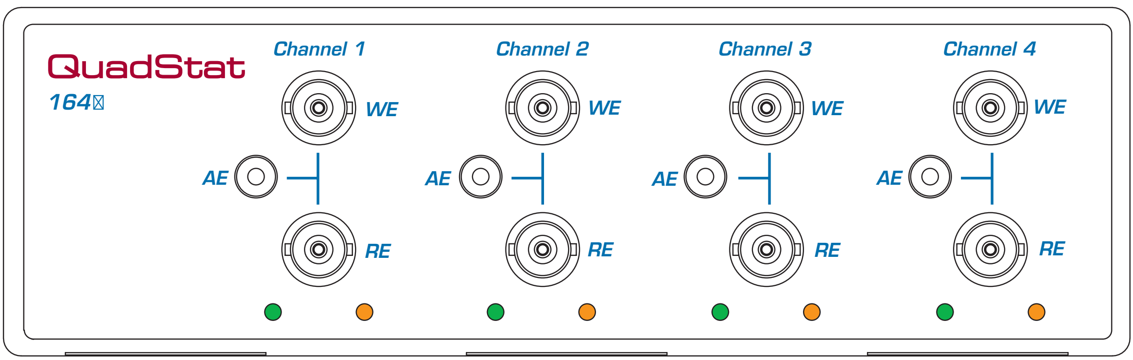
Potentiostat, Picostat & QuadStat







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Products: Potentiostat (EA161)
Picostat (EA162)
QuadStat (EA164)

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Contents

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CHAPTER ONE

Overview

NOTE
This manual is for the EA161 Potentiostat. If you have an older model EA160 Potentiostat then please ask us to send you the appropriate manual.

There are three eDAQ potentiostat models:

- Potentiostat (EA161), Chapter 2. Single channel, three electrode potentiostat/galvanostat with gain ranges of 20 nA to 100 mA;
- Picostat (EA162), Chapter 3. Single channel, three electrode, high sensitivity potentiostat with gain ranges of 10 pA to 100 nA; and
- QuadStat (EA164), Chapter 4. Four channel, three electrode potentiostat with gain ranges of 2 nA to 1 mA with current signal offset.

They are a part of the family of fully–software controlled modular preamplifiers (eDAQ Amps) which are designed for use with the e-corder® system.

Some of the uses of the Potentiostat, Picostat, and QuadStat, are mentioned in Chapter 5, and also 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), Picostat (Chapter 3), or QuadStat (Chapter 4). Their use with Chart and Scope software is also described (Chapter 5).

The appendices provide technical and troubleshooting information.

See the *EChem Software Manual* for a description of the use of these potentiostats with the optional EChem software.

eDAQ Amps

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

The Potentiostat, Picostat, and QuadStat 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 include 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 unit

Before you begin working with the Potentiostat, Picostat, or QuadStat 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* which will be installed as a pdf file on your computer when you install the software.

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CHAPTER TWO

The Potentiostat

This chapter describes how to connect and use your model EA161 Potentiostat. If you have an older model EA160 Potentiostat please refer to the documentation that came with your unit or contact eDAQ at support@edaq.com to obtain the correct document.

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.

NEW FEATURES: If you have used the older EA160 Potentiostat before, then you will notice that the EA161 has new front and back panels, and incorporates several new features: iR compensation; ZRA mode; High Z mode; and also has a High Stability option for stabilization of the Potentiostat in situations where oscillation would otherwise be encountered. Signal accuracy and signal-to-noise ratio have also been improved. Note that the EA 161 Potentiostat now uses the same electrode cable as the EA162 Picostat.

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 electrode lead wires. 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.

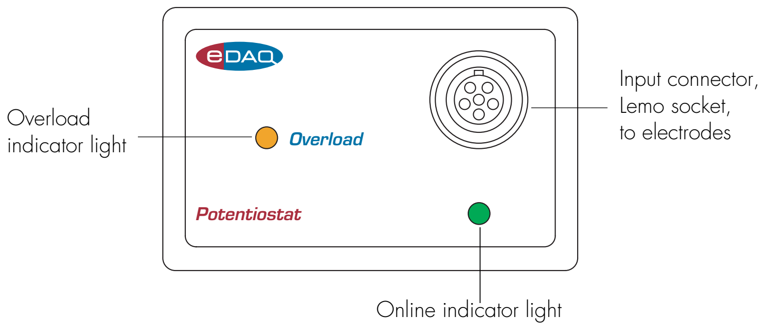


Figure 2–1
The Potentiostat front panel.

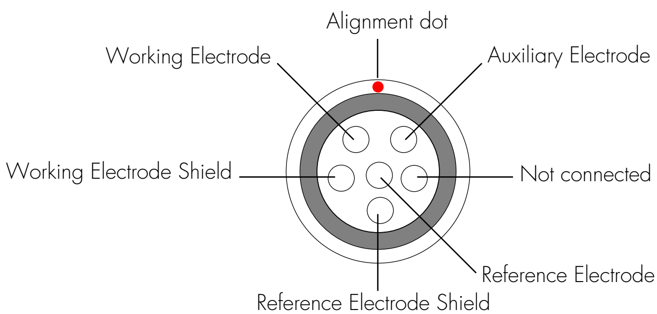


Figure 2–2
The Potentiostat input connector as seen when looking at the front panel.

Table 2–1
Color–coding on the leads of the electrode cable.

Color	*Electrode*
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).

To ensure good grip, the electrode cable alligator clips use a spring made from a good quality steel (stainless steel is unsuitable for springs). Avoid wetting of the alligator clips, especially with electrolyte solutions which can hasten corrosion. If the alligator clips are wetted then immediately disconnect from the Potentiostat, rinse the clips with a little deionized water from a wash bottle, to remove the electrolyte, and immediately dry by patting with paper tissue. The whole cable must then be allowed to dry thoroughly (several hours at least) before reuse.

Never immerse any part of the electrode cable in water, or other liquid!

For normal three–electrode potentiostat, or galvanostat, 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.

When two–electrode potentiostat, or galvanostat, operation is required the auxiliary and reference leads (red and yellow) should be attached to the single 'counter electrode'. The green lead is attached to the working electrode.

When using in **ZRA** (zero resistance ammeter) mode, connect the working (green) and auxiliary (red) leads to the two electrodes (or circuit test points) across which to measure the current. The reference lead (yellow) can be connected to a reference electrode (or circuit test point) to measure the potential difference to the auxiliary (and working) leads.

When using **High Z** (high impedance) mode, connect the working (green) lead to one electrode and the reference lead (yellow) lead to a reference electrode to measure the potential difference between the leads. The auxiliary lead (red) can be connected to a third electrode (or test point) to provide a ZRA current signal at E Out, Figure 2–3.

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, page 91.

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 (or has gone) 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 as soon as there is an overload and will stay on until the recording has stopped.

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.

Figure 2–3
The Potentiostat back panel.

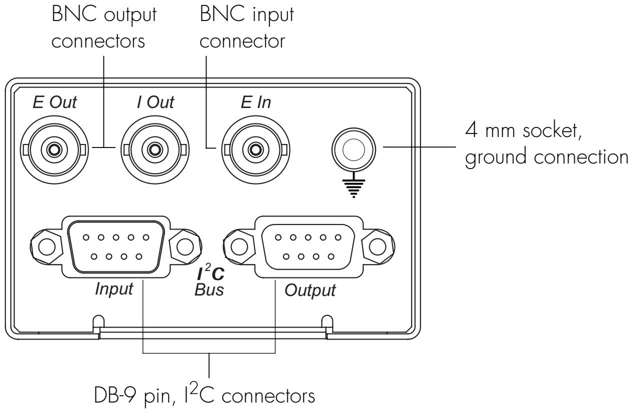
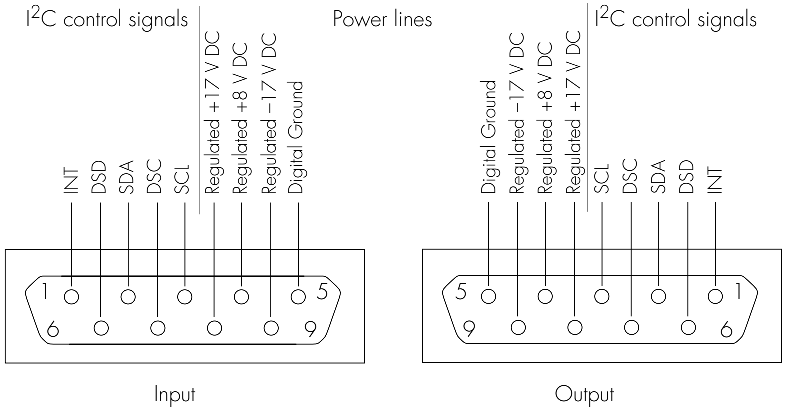


Figure 2–4
The pin assignments for the I²C DB-9 connectors.



The Back Panel

The back panel of the Potentiostat is shown in Figure 2–3.

E Out, I Out and E In Connectors

The Potentiostat 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 – is used. If you need to reverse the polarity of the Potentiostat use e-corder Output +.

The Potentiostat 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 that just two channels you may want to connect the Potentiostat to other e-corder input channels.

I^2C Connectors

▲ WARNING!
The I^2C connectors are for the power and control of *eDAQ Amps, page 2**, and should not be used for connection to any other device.*

The Potentiostat back panel, Figure 2–3, has two DB-9 pin 'I^2C bus' connectors labelled Input and Output. The Input connector provides power to the Potentiostat and carries the various control signals (for gain range and filter selection) to and from the e-corder. A cable is provided with the Potentiostat for this purpose. The pin assignments are shown in Figure 2–4.

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

More information about the I^2C connector can be found in your *e-corder Manual*.

Grounding Connector

The Potentiostat back panel, Figure 2–3, has a 4 mm grounding socket. This enables connection of a Faraday cage (with the green grounding cable included with the Potentiostat) the use of which can greatly diminish electrical noise. The Potentiostat is supplied with a green colored ground cable terminated with a 4 mm pin (attaches to Potentiostat back panel) and an alligator clip (for attachment to Faraday cage). If your Faraday cage is already earthed by its own ground connection then you should not use this cable (otherwise a second pathway to earth would exist which could result in a 'ground loop' and increased signal interference! You can try grounding the Faraday cage via its own connection to earth, *or* via the Potentiostat ground cable — but *not by both* methods simultaneously.

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. But in all cases, it is essential that the Faraday cage be electrically grounded to act as an effective shield against electrical interference.

The Potentiostat 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.

Connecting the Potentiostat

Your Potentiostat will have been supplied with an I^2C 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 I^2C cable to the I^2C connector on the back panel of the e-corder, and the other the other end to the I^2C Input connector on the back panel of the Potentiostat. Use the three BNC cables to connect the back panel of the Potentiostat 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.

Table 2–2
Potentiostat to e-corder connections.

Potentiostat rear panel	*e-corder front panel*
I Out	Input 1
E Out	Input 2
E In	Output –

Table 2–3
Potentiostat to e-corder connections, reverse polarity.

Potentiostat rear panel	*e-corder front panel*
I Out	Input 1
E Out	Input 2
E In	Output +

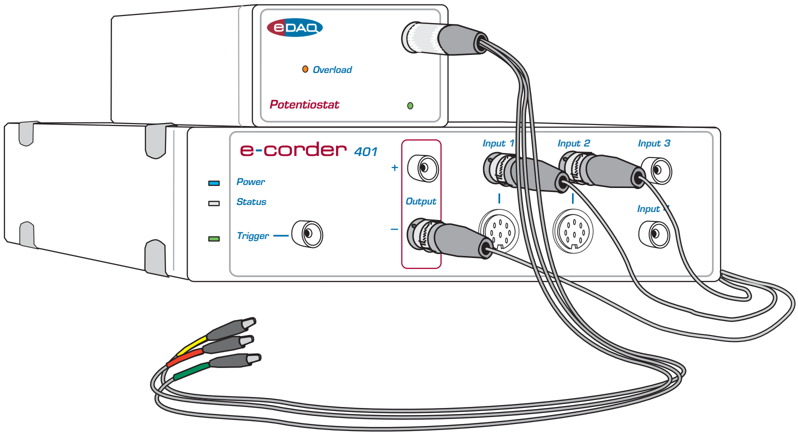


Figure 2–5
The Potentiostat shown connected to an e-corder, front view.

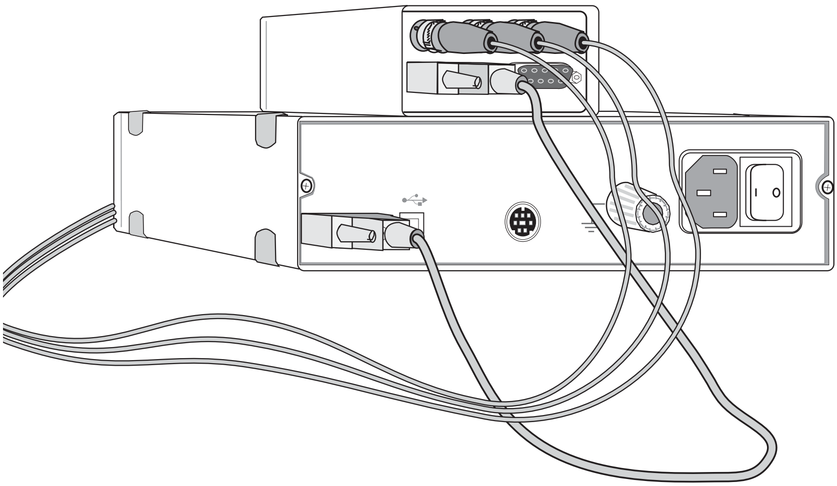


Figure 2–6
The Potentiostat shown connected to an e-corder, back view.

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 reminder 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 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.

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

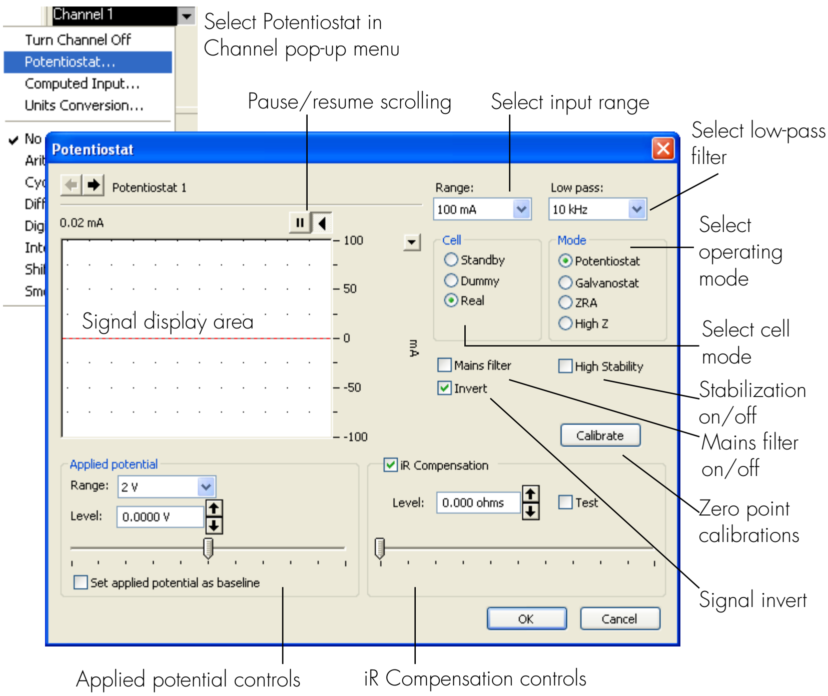
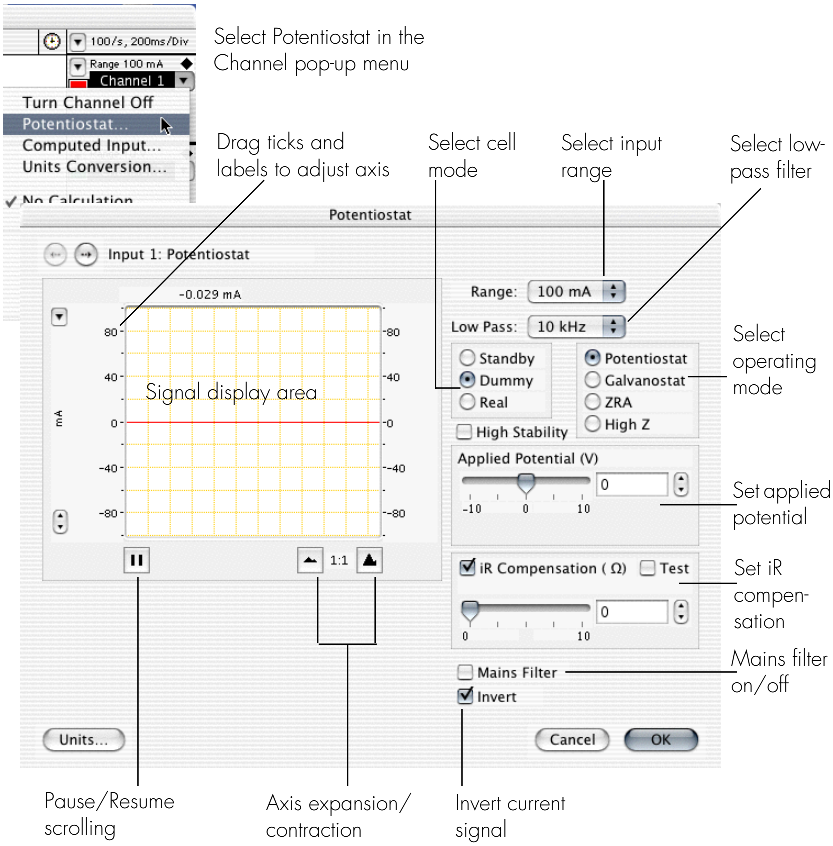


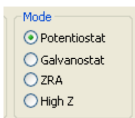
Figure 2–7
Potentiostat controls with Chart software (Windows).

Figure 2–8
Potentiostat controls with Chart software (Macintosh).



[2–8](#) on a Macintosh computer. These windows control the various current ranges and filtering options for the Potentiostat.

Modes of Operation



The EA161 Potentiostat can be operated in several different modes by selecting the appropriate radio button:

- **Potentiostat** (Chart, Scope or EChem software), described below. For three–electrode use connect the working (green), reference and auxiliary (red) leads appropriate electrodes (or circuit test points) The current signal is provided at I Out, Figure 2–3. The potential signal is provided at E Out. When two–electrode potentiostat operation is required the auxiliary and reference leads (red and yellow) should be attached to the single 'counter electrode'.

- **Galvanostat** (Chart and Scope software), page 73 – 78. Connect the electrodes as described for potentiostat operation, above. Note especially that the potential signal is provided at I Out, Figure 2–3. The current signal is provided at E Out.

- **ZRA**, zero resistance ammeter, (Chart and Scope software). Connect the working (green) and auxiliary (red) leads to the two electrodes (or circuit test points) across which to measure the current, the current signal is provided at I Out. The reference lead (yellow) can be connected to a reference electrode (or circuit test point) to measure the potential difference to the auxiliary (and working) leads. The high impedance potential signal (if used) is supplied at E Out, Figure 2–3; or

- **High Z**, high impedance voltmeter (Chart and Scope software). Connect the working (green) lead to one electrode and the reference lead (yellow) lead to a reference electrode to measure the potential difference between the leads. The high impedance potential signal is delivered at I Out. The auxiliary lead (red) can be connected to a third electrode (or test point) to provide a ZRA current signal at E Out, Figure 2–3.

Please make sure the electrode lead wires are connected appropriately to your experiment, before operating in any of these modes. In particular, incorrect placement of leads may damage the reference electrode, if one is being used.

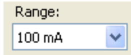
Signal Display

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 will be lost.

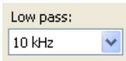
By using the Dummy or Real modes you can investigate the effect of the Applied Potential, page 21, on the current signal.

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.

Setting the Range 

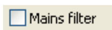
Use the Range pop-up menu to select the input current range (channel sensitivity). The Potentiostat has ranges of 100 mA to 2 nA, while resolution within each range is 16 bits or 0.0015%. You should set the range so that it is larger than the biggest current that you expect to encounter during your experiment. If, during the experiment the current signal exceeds the range, then the signal will go off scale and be lost.

Filtering 

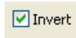
The Potentiostat incorporates four low-pass filters at 10 kHz, 1 kHz, 100 Hz and 10 Hz for removal of high frequency signals ('noise').

In addition the e-corder provides filter settings at 1, 2, 5, 20, 50, 200, 500, and 2000 Hz (Chart software on Windows computers).

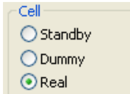
As a general rule the 10 Hz filter setting is highly effective for the removal of mains hum (50 or 60 Hz interference) and should be employed whenever possible. However, it should not be used for pulsed amperometric, or voltammetric experiments, where the pulses are shorter than 100 ms, or for experiments where rapid scan rates (greater than about 100 mV/s) are used.

With Chart and Scope software, there is an additional 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 that it 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 reassign the direction (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 cell modes, controlled by the Cell radio buttons:

- **Standby**: If Standby mode is selected the electrode lead wires are disconnected, and the internal dummy cell is connected. The external (real) 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**: the Potentiostat is connected to the internal 1 MΩ 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**: the external electrodes are connected to the Potentiostat. The Applied Potential slider control, Figure 2–7 and Figure 2–8, can be used to set the potential applied to the electrodes while the Potentiostat control window is open. 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 software, the Potentiostat will remain in Real mode when the dialog is closed — so that when you start and stop recording data the electrodes will remain active. This allows periodic recording of the signal from, for example, amperometric biosensors without disturbing the environment around the electrodes.

High Stability Operation 

If the **High Stability** box is ticked then extra capacitance is introduced into the Potentiostat control loop. This stabilizes the Potentiostat in situations where oscillation is encountered (for example where large surface area electrodes are being used in highly resistive solutions).

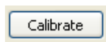
Normally when in Potentiostat mode do NOT use High Stability unless you first encounter stability problems. High Stability decreases the bandwidth of the of the Potentiostat control loop. Thus High Stability mode should never be used when fast sweep rates (> 1 V/s), or when short term pulses (< 0.1 s), are employed as it will produce a noticeable phase lag between the desired and actual applied potential. Also High Stability operation should not be used to try to correct for oscillations introduced by excessive iR compensation.

High Stability operation can be used routinely when performing fixed potential experiments with amperometric sensors where the response time of the sensor is relatively slow (> 0.01 s).

It is likely you will need to use High Stability mode when in Galvanostat mode, especially with highly resistive loads.

Note that High Stability operation is not required for either ZRA or High Z operational modes, because the Potentiostat control loop is disabled.

Current Signal Zero Point Calibration



The Calibrate button is available in Potentiostat and ZRA operating modes, page 15. When the Calibrate button is clicked it corrects for any internal offset error on the current signal. This is only required for very accurate determination of signal values. Current accuracy will be improved from about ±1% of full scale of range to better than ±0.2%. If you do not need this accuracy then you do not need to use the Calibrate button!

For best results allow about 10 minutes after opening powering up the e-corder before using the Calibrate function. This allows the unit to warm up — ambient temperature variation of more than a few degrees during an experiment may require periodic recalibration to maintain maximum accuracy.

When calibrating in ZRA mode you must first remove the Input Connector (Electrode connector) from the Potentiostat.

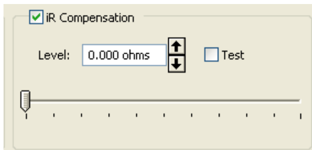
When in Potentiostat mode clicking the Calibrate button will zero the current signal, using the Dummy cell, including any signal due to any small offset from the e-corder Output at E In. Thus it should be considered a 'relative zero'.

Recalibatrion is required after you:

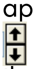
- select a different range for the Potentiostat applied potential, page 21;
- turn iR Compensation on or off, page 20.
- change from Potentiostat to ZRA operating mode;
- change from ZRA to Potentiostat operating mode. However, to get true absolute current measurements in Potentiostat mode (independent of small offsets at E In) first calibrate in ZRA mode and then switch to Potentiostat mode without recalibrating.

Note that, in all cases, the Calibrate button does NOT remove background current signals due to actual electron flow in the real cell.

iR Compensation



iR compensation is available only when in Potentiostat mode. Positive feedback compensation is used.

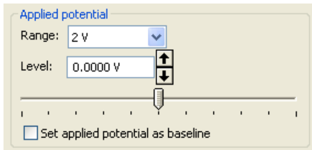
When the iR Compensation panel is on, then the degree of iR Compensation can be adjusted using the slider bar. First adjust the applied potential to a value where no Faradaic process occurs, use the  buttons for fine control. Now use the slider bar to gradually increase the amount of compensation until the current signal goes into oscillation, then decrease the compensation until stability is restored. For very fine control of iR Compensation use the **Test** checkbox. This applies a small perturbation (1 Hz, 10 mV amplitude square wave) to the electrode. The iR Compensation is adjusted until an appropriate amount of ringing is seen on the potential signal.

The maximum amount of iR compensation available depends on the selected gain range, page 99.

Note that iR Compensation is set at the particular applied potential you have chosen. If you then proceed to do an experiment involving a potential sweep, the amount of compensation required for complete compensation will vary during the sweep, and it is possible that the potentiostat will go into oscillation at some point. To avoid this happening it is usual to always slightly undercompensate, that is, to find the point of ideal compensation and then to reduce the setting slightly. The amount of 'undercompensation' is usually determined by trial and error for a particular experiment.

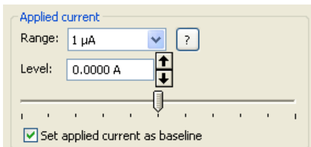
Before using iR Compensation you should always consider other methods of reducing the uncompensated resistance. For example, could the reference electrode be more closely positioned to the working electrode (perhaps by redesigning your reaction chamber), or could the background electrolyte concentration be increased? Also check to ensure that the reference electrode is not clogged or dried out. It is always best to minimize cell resistance within the reaction chamber rather than trying to overcome the problem later with the potentiostat.

Applied Potential



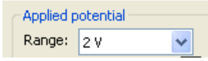
The Applied Potential controls are enabled when either the Dummy or Real cell is selected. It allows you to adjust the voltage applied to either the dummy cell or external electrodes, depending on the mode selected.

Applied Current



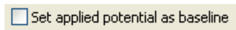
The Applied Current controls appear when in Galvanostat mode (replacing the Applied Potential controls), see Figure 5–17, page 74. The controls are enabled when either the Dummy or Real cell is selected. Use them to adjust the current applied, Figure 5–19, page 75.

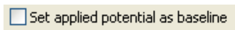
On Windows computers, the  button advises on the correct values to be entered into Units Conversion of the current signal channel, see Figure 5–18, page 74.

Range 

When using Chart software on a Windows computer the Range control limits the range over which the applied potential can be set. Smaller ranges offer finer control with the slider bar of the applied potential, Figure 2–7. In Galvanostat mode this control changes so as to limit the range over which the applied current can be set, Figure 5–17, page 74.

On a Macintosh computer use the values in Range control are affected by the selection in the Stimulator Constant Output dialog box, Figure 5–8, page 64. and Table 5–1, page 77.

Remember Potential 

Check the 

box to remember the value of the applied potential when the Potentiostat control window, Figure 2–7, page 14, is closed. (The potential value is transferred to the Stimulator baseline control, Figure 5–5, page 63).

Maintenance

The Potentiostat will not require maintenance during daily operation. However, you should periodically check the instrument for optimum results by switching to potentiostat mode (with iR Compensation off) and applying a known potential, E, to the Dummy Cell and checking that the resulting current signal value, I, is in accordance with Ohm's law:

$$I = E/R$$

where R is the resistance, and is 1 MΩ for the dummy cell. Thus a signal of 1 µA should be obtained when a potential of 1 V is applied, 1 µA with 2 V, etcetera. Try several different potentials and make sure an appropriate current signal is observed in each case.

If this test produces the expected results then your Potentiostat is likely to be functioning correctly. Next use the Potentiostat in Real Cell mode to check the electrode cables by attaching them to a resistor (usually a resistor of 10^3–10^8 Ω is ideal) with the working electrode lead on one side of the resistor and the auxiliary and reference leads connected to the other. If the current signal does not obey Ohm's law, then it is likely that the electrode leads have become damaged.

However, if both the Dummy Cell and Real Cell tests produce the expected results, but you are still experiencing difficulties with your experiments, then check the electrodes (reference electrodes, in particular, tend to become clogged or dry out with age), 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.

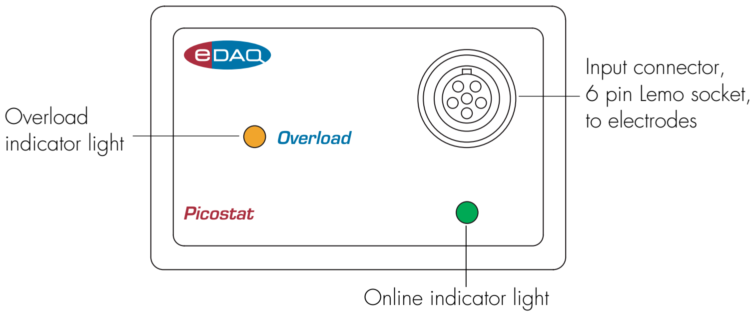


Figure 3–1
The Picostat front panel.

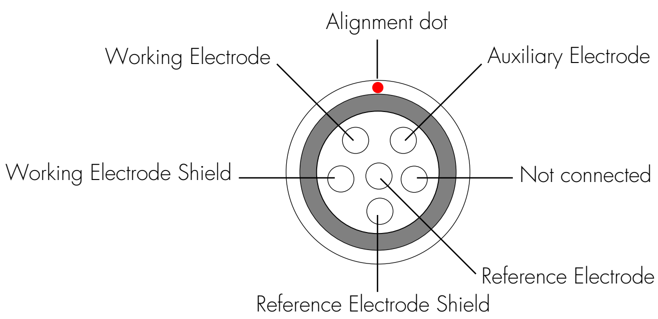


Figure 3–2
The Picostat input connector as seen when looking at the front panel.

Table 3–1
Color-coding on the leads of the electrode cable.

Color	*Electrode*
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 91.

The Overload Indicator

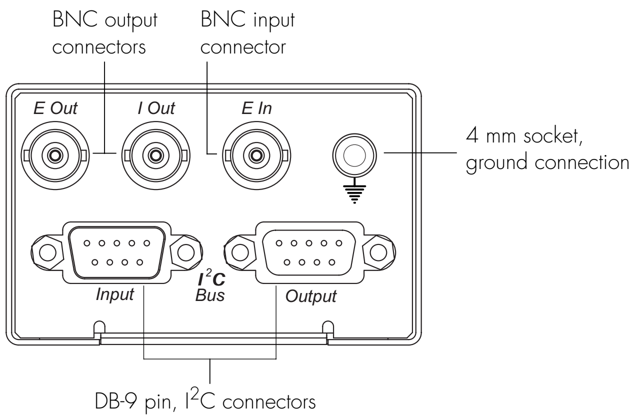
Located on the left–hand side of the front panel is the Overload indicator, Figure 3–1. When lit, this indicates that the Picostat has gone out of compliance, which usually occurs because of an open circuit (such as an unconnected or faulty electrode) or the resistance is too high in the electrochemical 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 you 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 – is used. If you need to reverse the polarity of the Picostat use e-corder Output +.

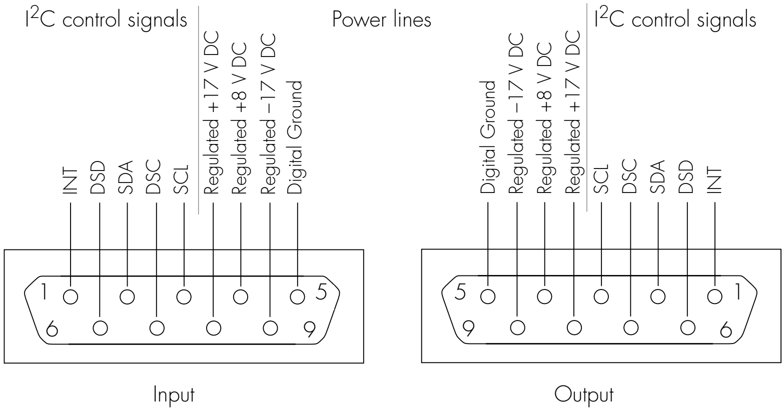
The Picostat provides two signals: the potential signal (E Out) indicating the potential difference between the working and reference electrodes; and the current signal (I Out) indicating the current flow between the working and auxiliary electrodes.

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 that just two channels you may want to connect the Picostat to other e-corder input channels.

I^2C Connectors

The Picostat back panel, Figure 3–3, has two DB-9 pin 'I^2C 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, page 2, 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. 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 I^2C 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 I^2C cable to the I^2C connector on the back panel of the **e-corder**, and the other the other end to the I^2C 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.

Picostat rear panel	*e-corder front panel*
I Out	Input 1
E Out	Input 2
E In	Output –

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

Picostat rear panel	*e-corder front panel*
I Out	Input 1
E Out	Input 2
E In	Output +

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

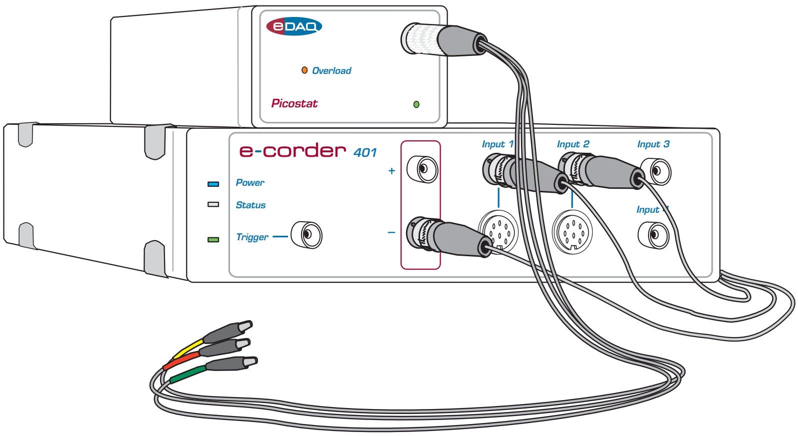
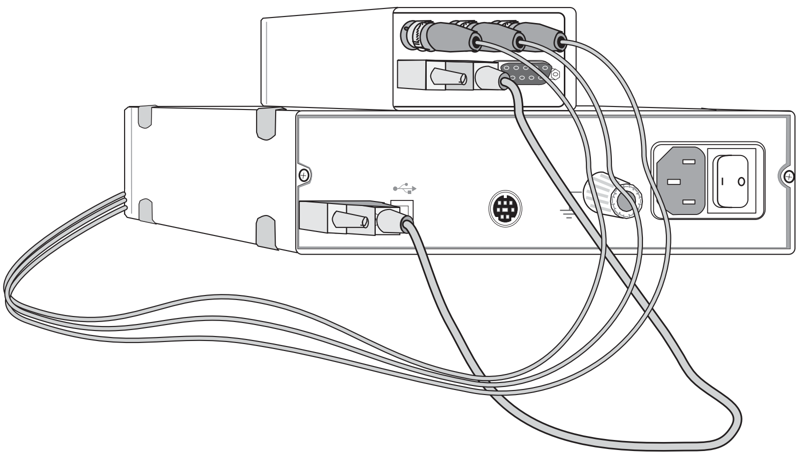


Figure 3–6
The Picostat shown connected to an e-corder, back view.



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 MΩ 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).

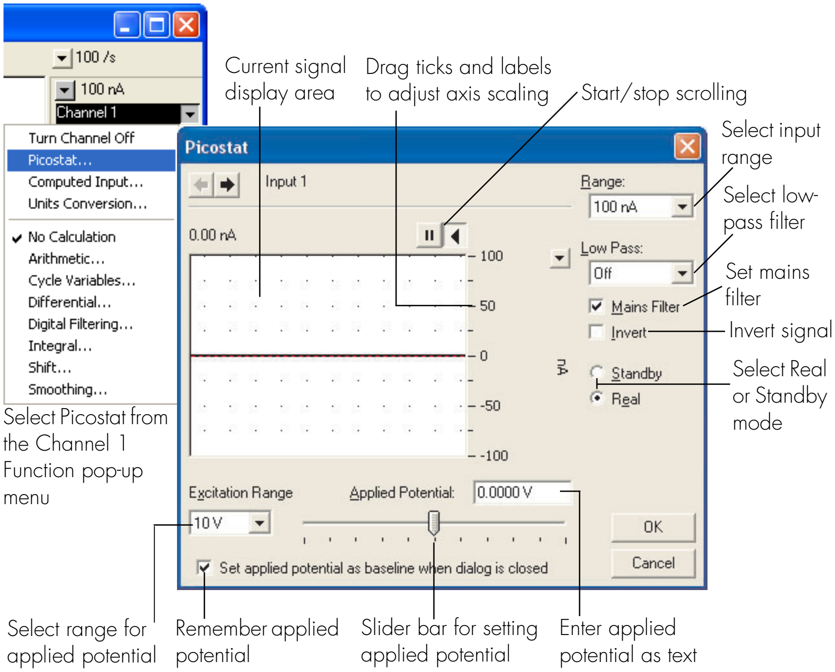
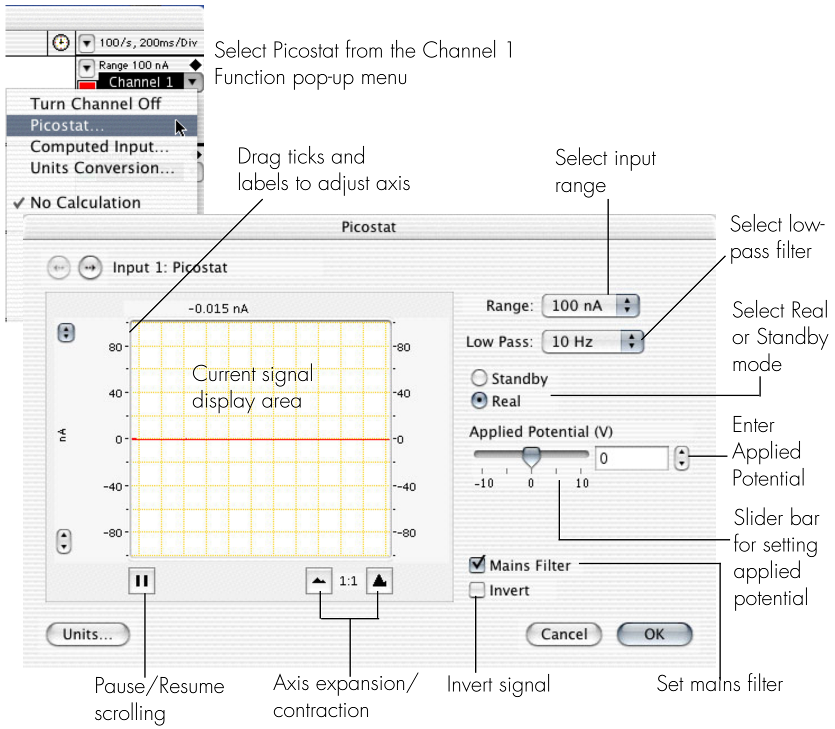


Figure 3–8
Accessing the Picostat controls with Chart software (Macintosh).



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).

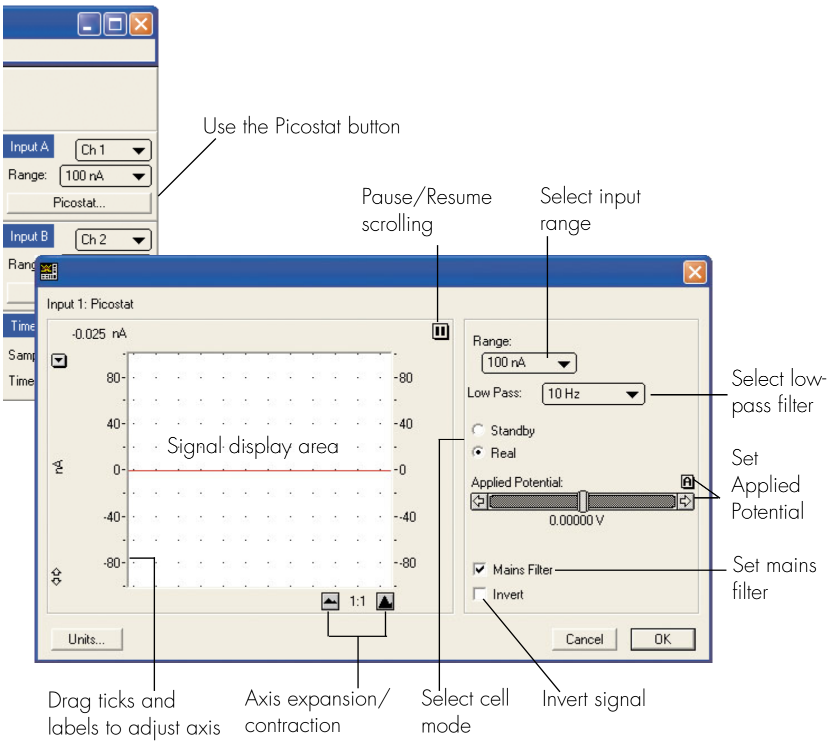
By default, the control window opens with the Picostat in Standby mode, that is with the reference and working electrodes isolated so that no current will flow through your electrodes. To connect to the Picostat lead wires you must select Real mode. When you click Cancel or OK the Picostat will revert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

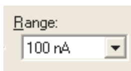
Signal Display

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 .

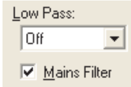
You can shift or stretch the vertical Amplitude axis to make the best use of the available display area. All changes to axis scaling are reflected in the Chart and Scope main window, and vice versa.

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.

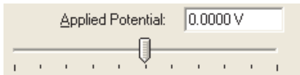
Cell Control

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



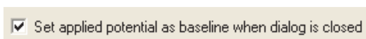
The applied potential slider control is only enabled in Real mode. It allows you to adjust the voltage applied to the electrodes. To change the value simply drag the control left or right to set an appropriate potential, or use the text entry controls to enter a numerical value. When using Chart software 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 5–8.

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 MΩ test resistor, as described in the section on First Use, page 33. If the current signal does not obey Ohm's law, then first recheck your connections of the Picostat to the e-corder, page 31. 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

The QuadStat

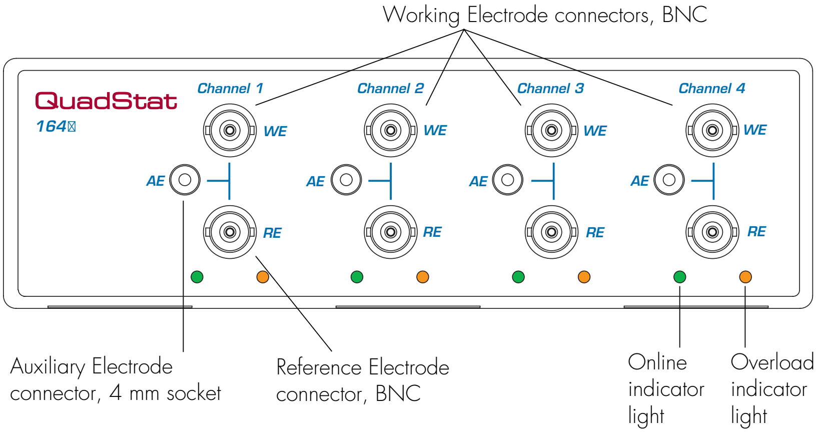
This chapter describes how to connect and use your QuadStat (EA164).

Note that when used with EChem software only a single QuadStat channel can be used. With Scope software one or two channels can be used. With Chart software, one to four QuadStat channels can be used.

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

IMPORTANT: The QuadStat is a highly sensitive current measuring device. To prevent damage by static discharge always make sure you are earthed before touching the QuadStat 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 QuadStat and e-corder) by touching the outer casing of the e-corder or QuadStat. This will connect you to earth (via the electrical grounding of the instrument) and any static charge you have collected will be dissipated.

Figure 4–1
The QuadStat front panel



The Front Panel

The front panel of the QuadStat is shown in Figure 4–1.

Electrode Connectors

The front panel of the QuadStat provides connections for the Working WE), Auxiliary (AE), and Reference (RE) electrodes. BNC connectors are used for the WE and RE leads. The shields of these connectors are driven to the same potential as the electrode.

The connector for the AE lead is a socket for a 4 mm pin.

Electrode Cables

The QuadStat is supplied with appropriate electrode cables, with each lead terminated by an alligator clip which allows 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 4–1). The RE and WE leads are shielded to protect the signals from external interference. The shields are driven to the same potential as the electrode to minimize lead capacitance.

If two-electrode operation is required the auxiliary and reference electrode leads (red and yellow) can be attached to the single ‘counter electrode’.

Table 4–1
Color-coding on the leads of the electrode cables.

Color	*Electrode*
Yellow	Reference
Green	Working
Red	Auxiliary

The Online Indicators

Along the lower edge of the QuadStat front panel are a series Online indicators, Figure 4–1. When lit, they indicate that the software (such as EChem, Chart or Scope) has located and initialised that QuadStat channel. If the light does not go on when the software is run, check that the QuadStat is properly connected. If there is still a problem, please refer to Appendix B Troubleshooting, page 91.

The Overload Indicators

Also along the lower edge of the front panel are the Overload indicators, Figure 4–1. When lit, these indicates that the QuadStat has overloaded, which usually occurs because it has gone out of compliance because of an open circuit (such as an unconnected or faulty electrode), or the resistance is too high in the electrochemical cell. High resistances can be often be encountered when electrodes are fouled by the products of electrolysis reactions. The QuadStat 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 QuadStat Overload indicators will remain lit once an overload has occurred — they will be reset once the scan has finished.

If an overload 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.

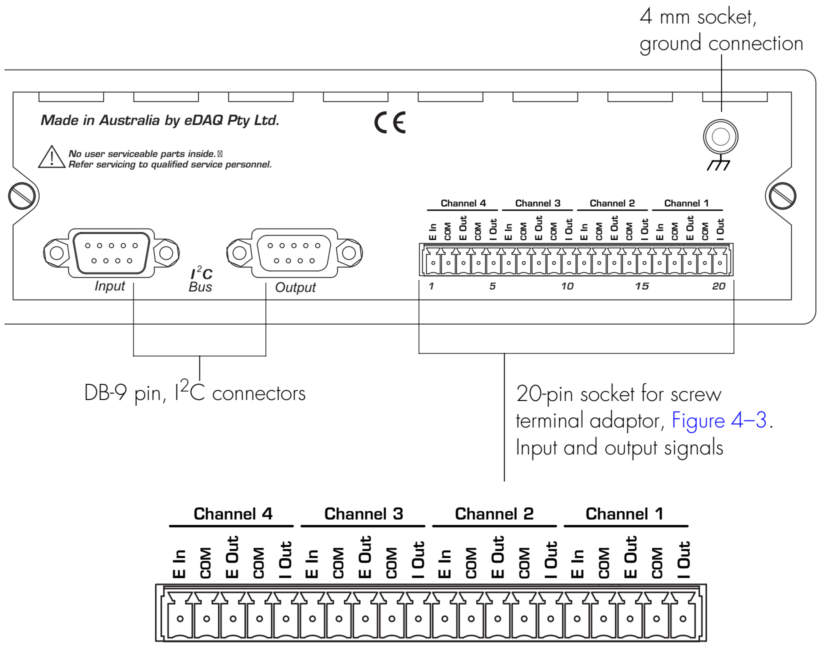


Figure 4–2
The QuadStat back panel.

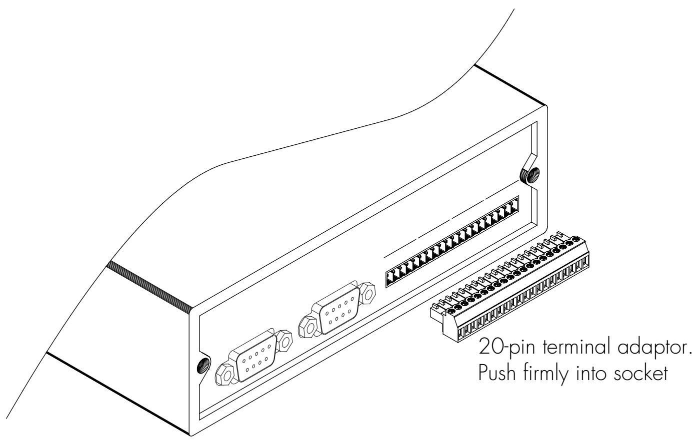


Figure 4–3
The 20-pin screw terminal adaptor.

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. In some circumstances a current overload can also cause the QuadStat overload indicators to light.

The Back Panel

The back panel of the QuadStat is shown in Figure 4–2.

E Out, I Out and E In Connectors

The QuadStat is supplied with a 20 pin screw terminal adaptor, Figure 4–3, which plugs into the 20 pin socket on the back panel. The pin positions are labelled I Out, E Out, E In, and COM, for each QuadStat channel (Channels 1 – 4).

The COM (common) pins are provided for connection to signal ground (black wires of the supplied coaxial cables, Figure 4–5). You can use any COM pin for the ground connection of any I Out, E Out, or E In signal.

▲ ***WARNING!***
The I^2C connectors are for the power and control of eDAQ Amps, page 2, and should not be used for connection to any other device.

I^2C Connectors

The QuadStat back panel, Figure 4–2, has two DB-9 pin 'I^2C bus' connectors labelled Input and Output. The Input connector provides power to the QuadStat and carries the various control signals (for gain

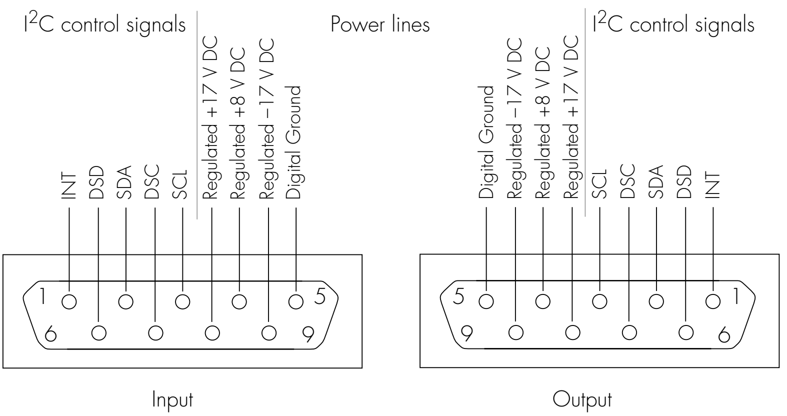


Figure 4–4
The I^2C connectors.

range and filter selection) to and from the e-corder connection. A cable is provided with the QuadStat for this purpose. The pin assignments are shown in Figure 4–4.

The Output connector can be used for the attachment of another QuadStat, or other eDAQ Amp.

More information about the I^2C connector can be found in your *e-corder Manual*.

Grounding Connector

The QuadStat back panel, Figure 4–2, has a 4 mm grounding socket. This enables connection of a Faraday cage (with the green grounding cable included with the QuadStat) 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 QuadStat 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 also important that the power socket that you are using is well earthed.

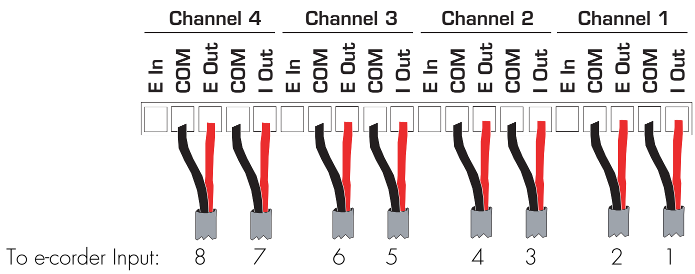
You can try grounding the Faraday cage via its own connection to earth, *or* via the QuadStat ground cable — but *not by both* methods simultaneously. The purpose of this ground cable to the Faraday cage is to provide an easy means of grounding the cage — please note that it is not for grounding the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

The grounding connector is equivalent to the COM pins of the 20 pin terminal socket, Figure 4–2.

Connecting the QuadStat

Your QuadStat will have been supplied with an I^2C cable (DB–9 pin connectors at either end), and nine cables with BNC connectors at one end and bare wires at the other.

Figure 4–5
Signal connections from the terminal adaptor. Black colored wires are connected to COM pins.



For single channel operation use only Channel 1.
For bipotentiostat operation use only Channel 1 and Channel 2.

Figure 4–6
Using the external inputs of the QuadStat. Note connection to E In is only required for potentials of more than ±2.5 V, or for pulsed or ramped waveforms.

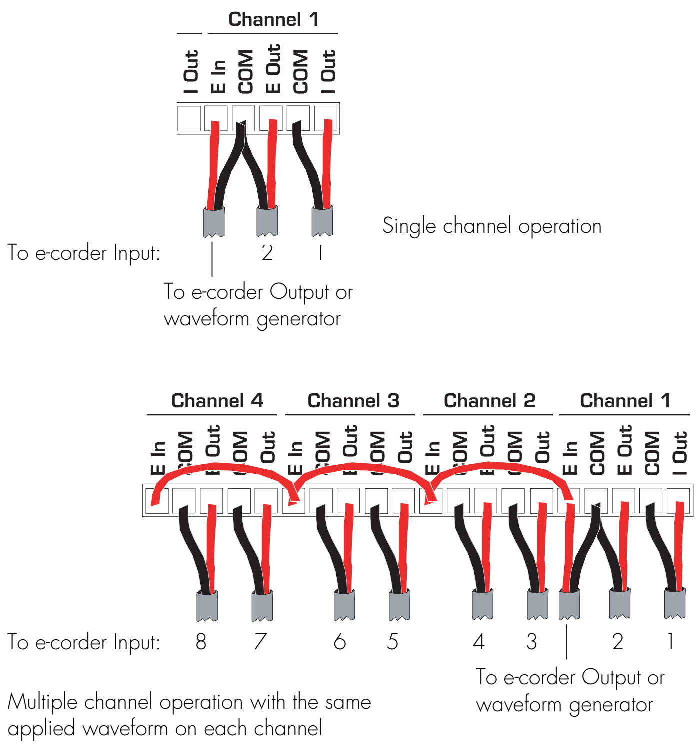


Table 4–2
QuadStat to e-corder BNC connections. See Figure 4–7 for actual appearance.

QuadStat rear panel	*e-corder front panel*
I Out (Ch 1, Ch 2, Ch 3, Ch 4)	Input 1, 3, 5, 7
E Out (Ch 1, Ch 2, Ch 3, Ch 4)*	Input 2, 4, 6, 8
E In †	Output –‡

* It is not always necessary to monitor E Out depending on your experimental requirements.
† Connections to E In are only required if using an external waveform to control the applied potential.
‡ Use Output + to reverse the polarity of the QuadStat.

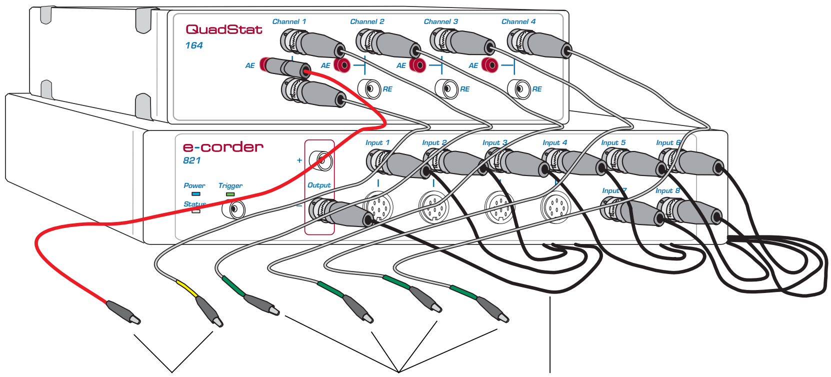
First make sure that the e-corder is turned off. Then connect the I^2C cable to the I^2C connector on the back panel of the e-corder, and the other the other end to the I^2C Input connector on the back panel of the QuadStat.

The QuadStat provides two signals per channel: 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. Use the BNC cables, with bare wires at one end, to connect the terminal strip (Figure 4–3) as described in Table 4–2 and Figure 4–5 or Figure 4–6. Note there are several possibilities depending on how many of the QuadStat channels you wish to use and whether you require the use of the e-corder Output, or an external waveform generator.

For experiments where the working electrode potential is held constant (between ±2.5 V) the E In pin positions are unused, Figure 4–5. If the electrode potential required is greater than ±2.5 V, or is to be pulsed or ramped during the experiment, then the E In input must be connected to a suitable external signal, such as from the Output of the e-corder, or a waveform generator, Figure 4–6. If an e-corder is used, then normally connect to Output –. 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 4–7.

If you need to reverse the polarity of the QuadStat, use e-corder Output +. 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.

Figure 4–7
The QuadStat shown connected to an e-corder, front view, using the connections described in Table 4–2.



By linking the E In positions with short wires you can control the potentials of all electrode potentials simultaneously, Figure 4–6.

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

Each QuadStat channel uses two **e-corder** input channels during normal operation (for recording of the current and potential signals). The remainder of this chapter assumes that you have connected the current signal of QuadStat channel 1 to **e-corder** Input 1 and the potential signal to **e-corder** Input 2, and other channels as shown in Table 4–2 and Figure 4–5. (It is also possible, when using Chart or Scope software, to connect the QuadStat to other **e-corder** input channels in which case the description that follows would change accordingly).

When using EChem software, **e-corder** Input 1 is always set to be the current signal (the I channel), and **e-corder** Input 2 is automatically set to be the potential signal (the E channel). Thus when using EChem software connect the QuadStat Channel 1 current signal (I Out) to **e-corder** Input1, and the QuadStat Channel 1 potential signal (E Out) to **e-corder** Input 2. Other QuadStat channels remain unconnected.

To record the applied potential signals (E Out) of a QuadStat with Chart and Scope software, first configure the settings of the standard Input Amplifier dialog box, described in the *Chart* and *Scope Software Manuals*.

First Use

After you have installed the software, connected the e-corder and computer, and connected the QuadStat as described above, you are ready to begin.

When the e-corder is turned on, and Chart software started, the QuadStat Online indicators (green), Figure 4–1 on page 42, should light for every channel connected.

From the Chart software Channel 1 pop-up menu, select the 'QuadStat' command, (also on Chart software Channels 3, 5, 7 if all four working electrodes are being used) which accesses the QuadStat control window, Figure 4–8, Figure 4–9, or Figure 4–10.

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

By default, the control window opens with the QuadStat 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 QuadStat electrode lead wires you must select Real mode. When you click Cancel or OK the QuadStat will revert to Standby mode until recording is started. For now, select the Dummy cell mode which connects an internal 1 MΩ resistor between the electrodes.

You will need to adjust the gain range to 5 μA to accommodate your signal amplitude. If the signal is noisy select the 10 Hz low-pass filter (and/or Mains Filter).

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:

$$I = E/R$$

so that with a 1 MΩ test resistance, R, an applied potential, E, of 1 V should produce a current, I, of 1 μA, while other potential settings should produce corresponding currents. If this is so, then your QuadStat is working correctly and you can proceed to your experiment.

QuadStat Control Window

With Chart software, the QuadStat Control window is accessed from the QuadStat command in the Channel Function pop-up menu. Figure 4–8 shows the control window on a Windows computer, and Figure 4–9 on a Macintosh computer. These windows control the various current ranges and filtering options for the QuadStat.

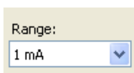
With Scope software, the corresponding controls are shown in Figure 4–10.

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 QuadStat has ranges of 2 nA to 1 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

Figure 4–8
Accessing the QuadStat controls with Chart software (Windows).

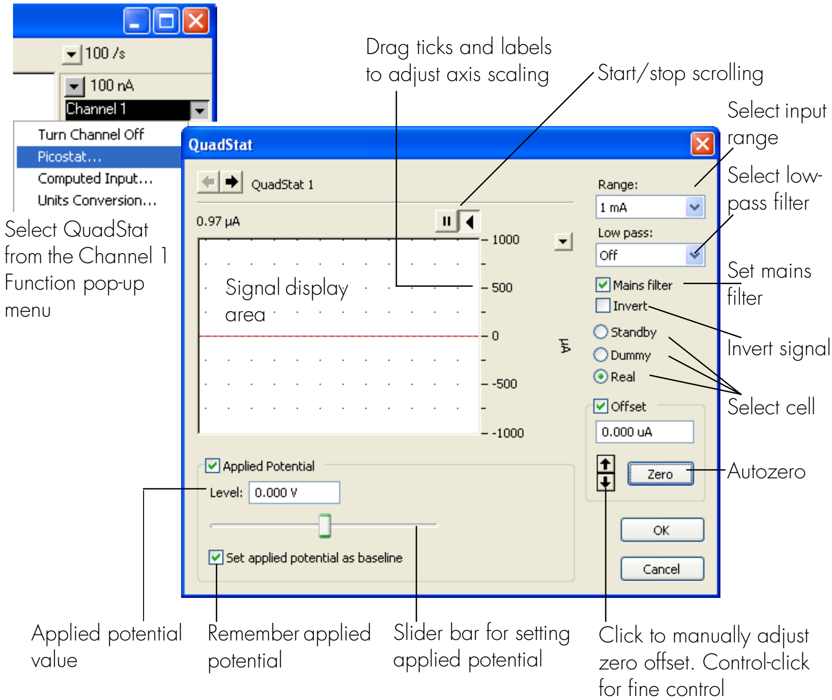


Figure 4–9
Accessing the QuadStat controls with Chart software (Macintosh).

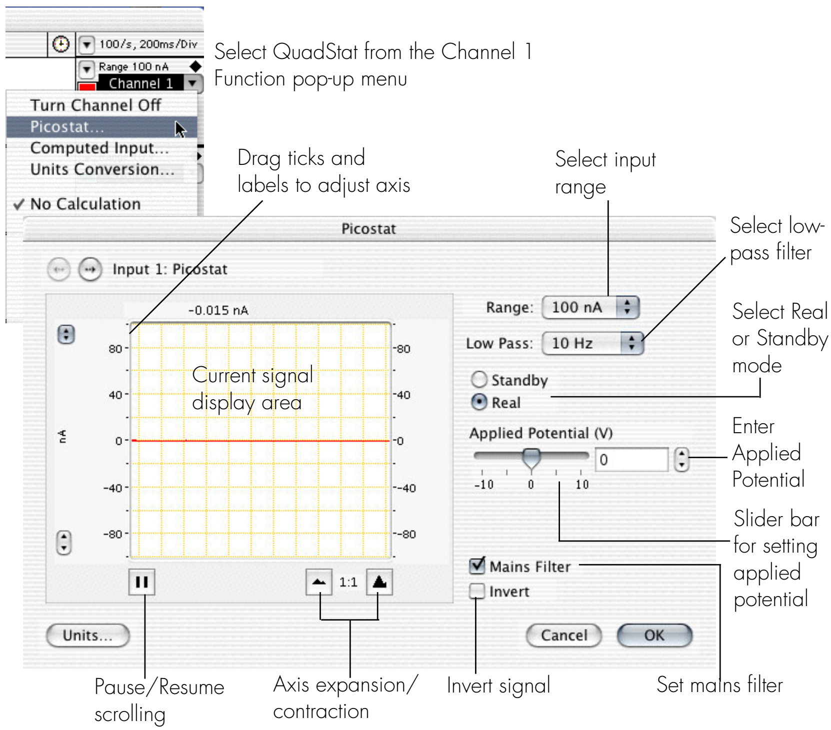
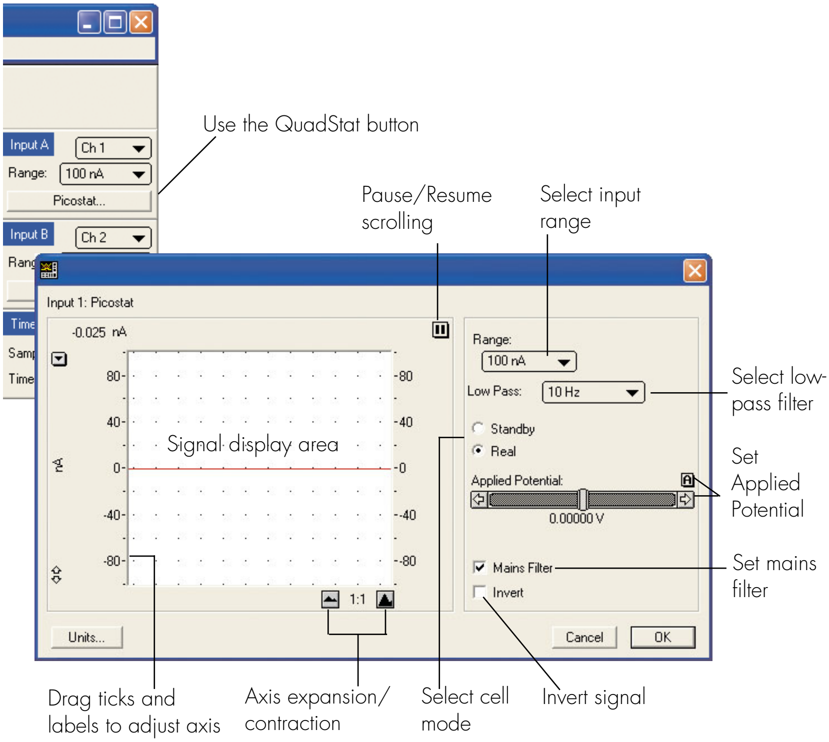
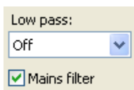


Figure 4–10
Accessing the QuadStat controls with Scope software.



signal exceeds the range, then the data will be truncated and therefore lost.

Filtering



The QuadStat has low-pass filter settings (10 kHz to 1 Hz) for removal of high frequency signals ('noise'). The Off setting gives the full bandwidth of the QuadStat which can be up to 16 kHz (but which may also be limited by the characteristics of your electrodes and sample solution).

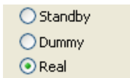
The 10 Hz filter settings, and less, are highly effective for the removal of mains hum (50 or 60 Hz interference) and, as a general rule, should be employed whenever possible. However, low pass filters should be used with care when performing pulse amperometric or voltammetric experiments, or for other signals which are likely to exhibit fast rise or fall times. For example if you are using the 10 Hz filter, then applied potential pulses should be longer be longer than 100 ms, and voltammetric experiments should have scan rates scan rates less than about than 100 mV/s — otherwise excessive smoothing of the signal may occur.

When you use the 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 simple notch filter, and it 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 even be employed 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



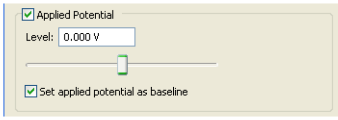
The QuadStat can be in one of three operating modes, controlled by the Cell radio buttons:

- **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 QuadStat 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.

- **Dummy**: When Dummy mode is selected the QuadStat channel is connected to the internal 1 MΩ dummy cell. You can then use the Applied Potential slider control to vary the voltage applied to the dummy cell. The QuadStat will remain connected to the dummy cell even when the QuadStat Control window is closed and Chart, Scope or EChem is recording. This is useful for testing the QuadStat.

- **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 software) the QuadStat will revert to Standby mode until the Start button is clicked to begin a scan. If you are using Chart or Scope software, the QuadStat 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

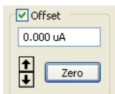


The applied potential slider control adjusts the voltage (up to ±2.5 V) applied to either the dummy cell or external electrodes. This potential, E_Q, is remembered by the QuadStat and will be applied when you start a scan if the "Set applied potential ..." checkbox is ticked. Note that each QuadStat channel may have a different value for E_Q.

This potential value will be summed with any external input waveform, E_w, from the E In connection on the terminal strip connector on the QuadStat back panel. The total potential, $E_Q + E_w$, must be less than ±10 V.

If you wish to use the QuadStat exclusively with an external voltage input (for example with EChem software) then make sure the ☑ Applied Potential checkbox is NOT ticked.

Zero Offset



The Offset control can be used to 'zero' a background signal so that small peaks or transient signals can be more accurately determined in the presence of a large baseline current signal. Each QuadStat channel can have a different amount of offset applied. The maximum amount of offset available is ±400 μA on ranges of 2 μA or more, and ±400 nA on ranges of 1 μA or less.

First tick the ☑ Offset checkbox. Then, while the baseline current is being monitored click the Zero button. It may take a few seconds to zero the signal. Normally this will suffice to accurately zero the signal, and you can then choose a more sensitive current range setting to observe your signals. Use the ↕ buttons to manually adjust the amount of offset if required (use Ctrl-click for fine adjustment, or xxx-click on Macintosh)

The amount of offset is reported in the text box, 0.000 uA. Values can also be directly entered in this box.

Maintenance

Your QuadStat will not require maintenance during daily operation. However, you should periodically check the QuadStat for optimum results by applying a known potential, E, to the Dummy Cell. Open the QuadStat Control window, Figure 4–8 or Figure 4–9. and go to Dummy Cell mode. The current signal, I, should obeys Ohm's law:

$$I = E/R$$

where R is the resistance, and is 10^6 Ω for the dummy cell, and E is the applied potential. Thus a signal of 1 μA should be obtained when a potential of 1 V is applied. Try several different potentials and make sure an appropriate current signal is observed. Repeat this procedure on the different QuadStat channels. If this test produces the expected results then your QuadStat is likely to be functioning correctly.

Also periodically repeat this procedure with the electrode cables connected, and attached to a test resistor, as described in the section on First Use, page 50. If the current signal does not obey Ohm's law, then first recheck your connections of the QuadStat to the e-corder, page 47. If the problem persists then it is possible that the electrode leads or the QuadStat itself has become damaged.

If these tests indicate that the QuadStat 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.

5

CHAPTER FIVE

Techniques

The Chart and Scope software supplied with your e-corder can be used to perform many different electrochemical techniques. 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 staircase 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

NOTE
The QuadStat also has internal potential adjustment of ±2 V. When the e-corder output is connected to a QuadStat channel 'E in', this value is summed with the value set by the Chart or Scope Stimulator controls, to a maximum of ±10 V.

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

This potential difference is determined by a 'command voltage' which is sent from the e-corder output to the 'E In' connector of the Potentiostat, Picostat, Figure 3–3, on page 29, Potentiostat, Figure 2–4, on page 9 or QuadStat, Figure 4–2, on page 44. The QuadStat can also generate a constant command voltage internally. 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, Picostat, or QuadStat with Chart and Scope software to perform the following experiments:

- Linear Scan techniques, page 59 — 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 and QuadStat are sufficient for scan rates up to about 10 V/s
- Chronoamperometry page 61 & page 70, Amperometry, Constant Potential Electrolysis, page 78, — monitor the current signal at fixed potentials
- Chronocoulometry page 71 — monitor and integrate the current signal at a fixed potentials
- Chronopotentiometry page 73, Constant Current Electrolysis page 79 — monitor the potential signal when the Potentiostat is used as a galvanostat to maintain a constant current at the working electrode. Note that the Picostat and QuadStat cannot be used as galvanostats
- Monitoring of amperometric sensors page 80, including dissolved oxygen and nitric oxide electrodes.
- zero resistance ammeter, or high impedance voltmeter, with the Potentiostat, page 15.

Linear Scan Techniques

Linear sweep or cyclic voltammetry are usually best performed with EChem software. However, Scope also 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 these techniques (albeit less conveniently than with the EChem software). 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 5–1.

The base potential is set by using the Stimulator Constant Output dialog box while the waveform is generated using the Stimulator Up & Down, Figure 5–2, or Triangle, Figure 5–3, waveforms. See the *Scope Software Manual* for further details.

In Figure 5–2 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 5–3 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.

Figure 5–1
Scope Setup menu.

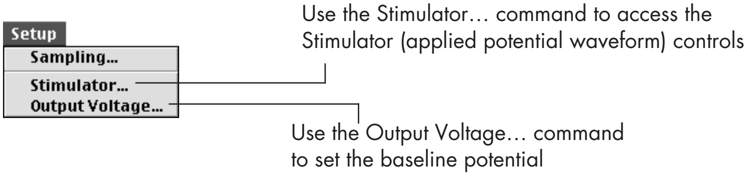


Figure 5–2
Using the Scope Stimulator Up and Down command.

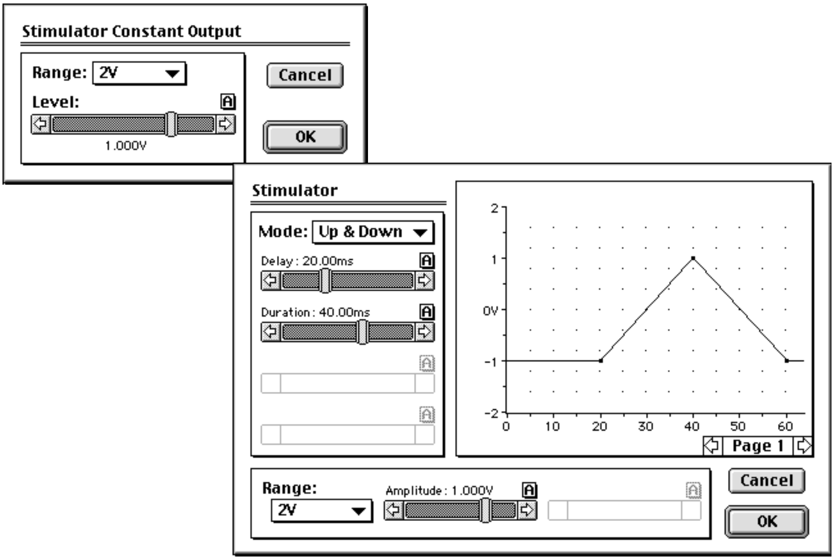
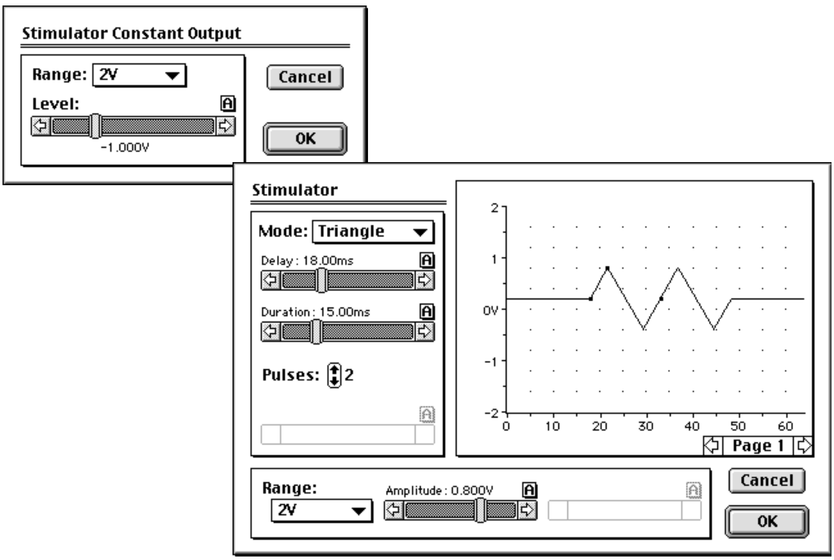


Figure 5–3
Using the Scope Stimulator Triangle command.



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 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 71).

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, or QuadStat (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

If you are using a QuadStat, then most constant potential experiments between ±2.5 V are done by adjusting the internal QuadStat Applied Potential, page 55. If you require applied potentials greater than ±2.5 V, or pulsed waveforms, then you can use the Chart Stimulator controls as described below.

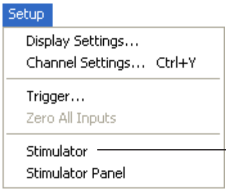
Chart software can be used to set a constant voltage of up to ±10 V (which is known as the command voltage) from the e-corder Output. This is sent to the Picostat or Potentiostat, or QuadStat, via the 'E In' input cable, which then applies this potential across the reference and working electrodes. The software controls are accessed through the Stimulator command in the Setup menu, Figure 5–4.

To adjust the command voltage you will first need to select the range by adjusting the Output Range control in the Stimulator controls Figure 5–5. 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 17 and page 36;
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 5–6. Note that the pulse amplitudes are added to any value set by the Baseline control.

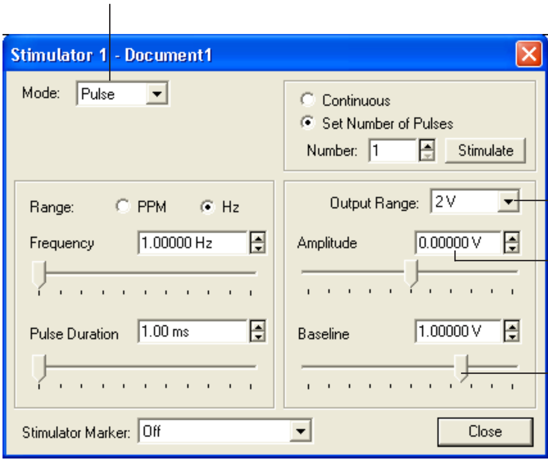
Figure 5–4
Chart Setup menu (Windows).



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

Figure 5–5
Chart Stimulator (waveform output) controls (Windows).

Select stimulator mode

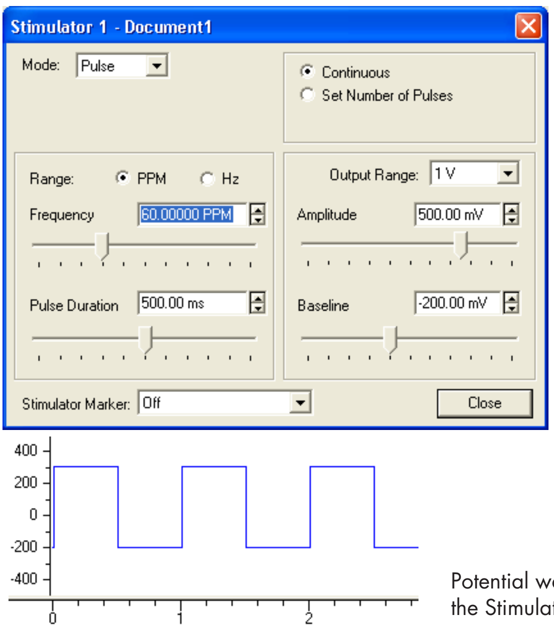


Select output range

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 5–6
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

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

If you are using a QuadStat, then most constant potential experiments between ±2.5 V are done by adjusting the internal QuadStat Applied Potential, page 55. If you require applied potentials greater than ±2.5 V, or pulsed waveforms, then you can use the Chart Stimulator controls as described below.

Chart software can be used to output a constant potential (up to ±10 V) which the Potentiostat, Picostat, or QuadStat will apply at the working electrode. These controls are accessed through the Setup menu, Figure 5–7.

Figure 5–7
Chart Setup menu (Macintosh).

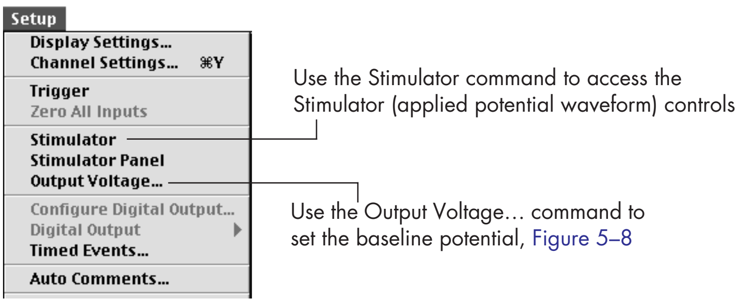
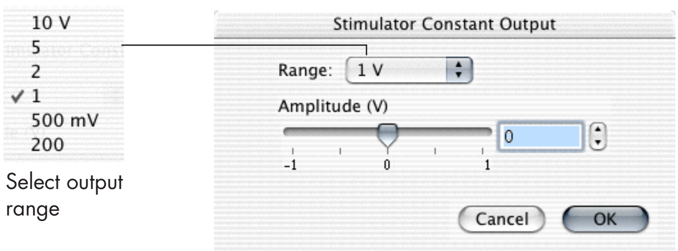


Figure 5–8
Chart Stimulator Constant Output voltage controls (Macintosh).



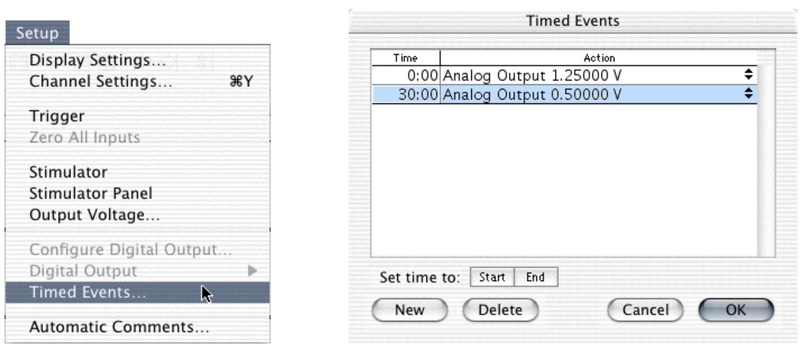
To adjust the potential you will first need to select the range by choosing the Output Voltage command in the Setup menu to activate the Stimulator Constant Output dialog box, Figure 5–8. The smaller the selected output range, the finer the control that you will have when you adjust the potential.

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 5–9 will maintain a potential of 1.25 V for 30 minutes after which the potential will be decreased to 0.50 V in order to reverse the reaction, resulting in a Double Step Chronoamperometric experiment. Any number of steps at any potential could be set up with this feature. 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.

Figure 5–9
Adjusting potential with the Chart Timed Events feature. (Macintosh only)

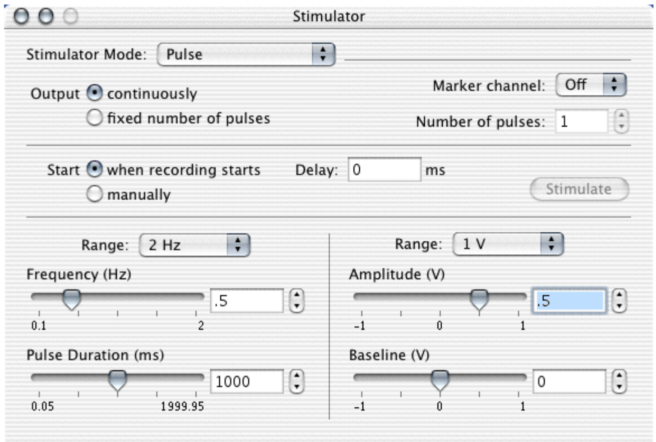


Access Timed Events from the Setup menu

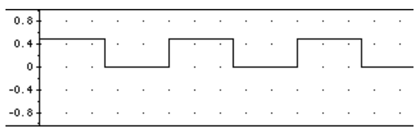
Changing the potential after a period of 30 s

Figure 5–10
Simulator controls for multiple step chronoamperometry (Macintosh).

Using the Stimulator command (Setup menu) it is possible to send and monitor pulses with a precision better than 1 ms, Figure 5–10. 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*.



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



Potential waveform generated by these settings

Analysis of Chronoamperometry

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

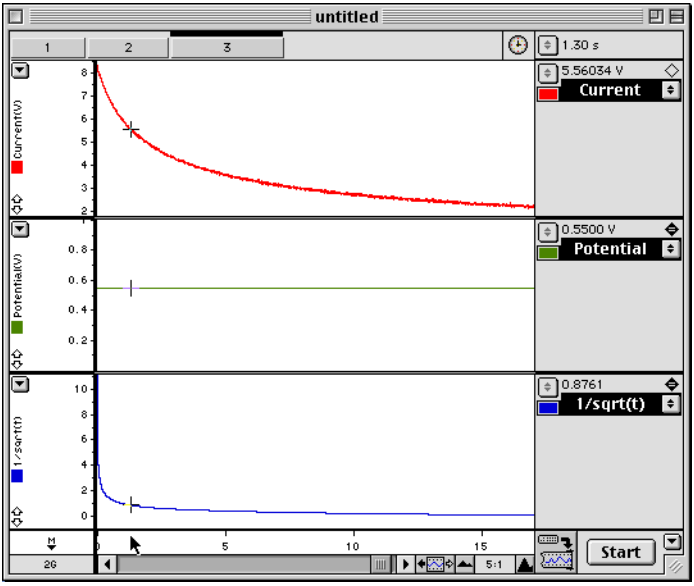
$$i = \frac{nFAC\sqrt{D}}{1000\sqrt{\pi t}}$$

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

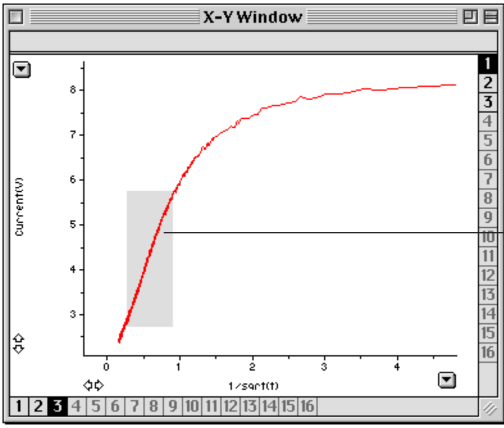
$$i = \frac{a}{\sqrt{t}}$$

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

Figure 5–11
Typical chronoamperometric data, analyzed using the Arithmetic channel calculation and the X–Y window.



Typical experiment with 1/√t data calculated on Channel 3 using the Arithmetic channel



Region of ideal linear response

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

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:

Channel 3 = 1/Sqrt(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 5–11.

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.

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 which is 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 5–12). In this case, to get a well behaved equation when the data selected start at very close to zero time, initially add a small time correction, *c*. This allows 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 5–12.

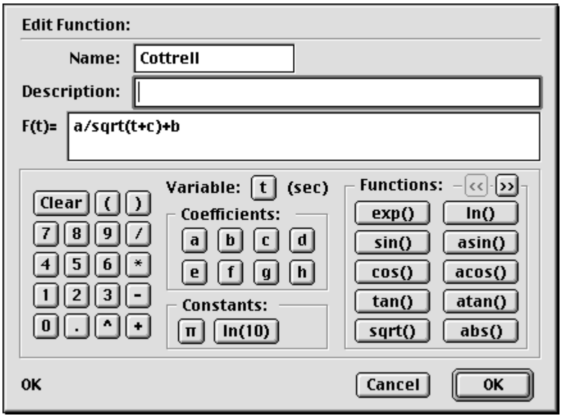
Because of the discontinuity that occurs when the denominator is zero, first try fixing *c* to a small positive value, and iterating for better values of *a* and *b*. Some trial and error will be involved while you make guesses that are suitable for the initial values to iterate. After the better estimates for *a* and *b* have been determined, and iterated, *c* can be unlocked so that it refines during the next iteration, Figure 5–12.

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 some trial and error to determine the time interval to give best results will probably be required.

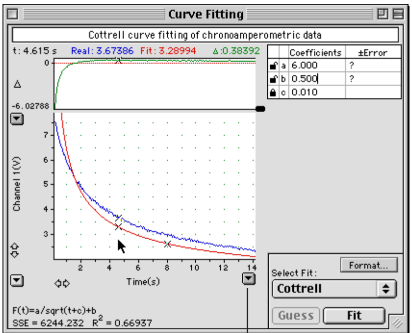
After the file is saved, the Curve Fit Cottrell equation will be available whenever you open Chart data file on the same computer or even when you transfer the data file to another computer on which Chart software

Figure 5–12
Fitting a Cottrell equation to data with the Curve Fit extension.

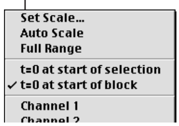
At the time of writing the Curve Fit extension is only available for Chart for Macintosh.



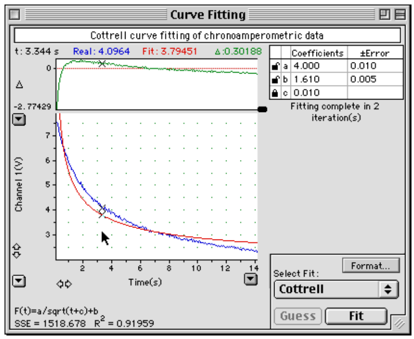
Define the Cottrell relationship as a new equation



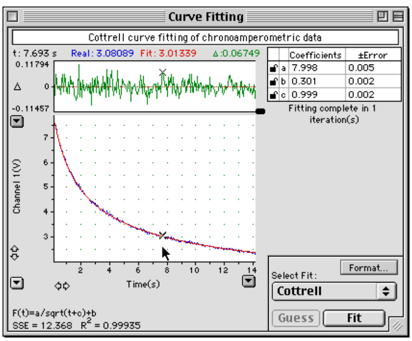
First lock in a value for *c*, then try guesses for *a* and *b* until an approximate fit is obtained



Usually use 't=0 at start of block'



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 vales for *a* and *b* will be obtained.



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

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!

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

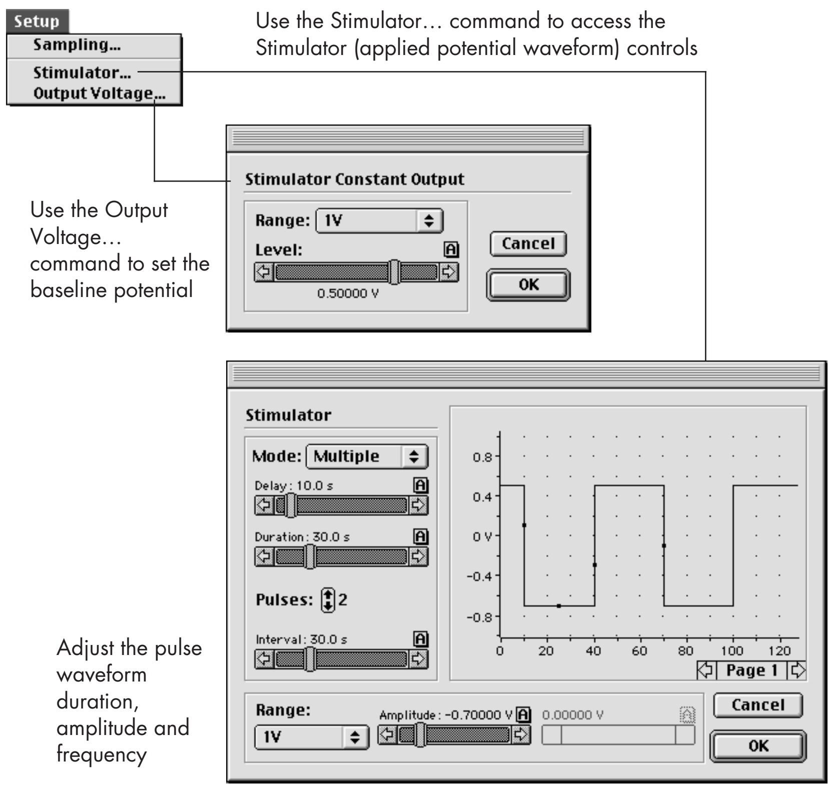


Figure 5–13
Scope controls for multiple step chronoamperometry.

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 5–13.

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 5–13, after a period of 10 s at the base 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 61, 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 5–14 on a Windows computer, and Figure 5–15 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

Figure 5–14
Online integration of the current signal using Chart Computed Input integration (Windows).

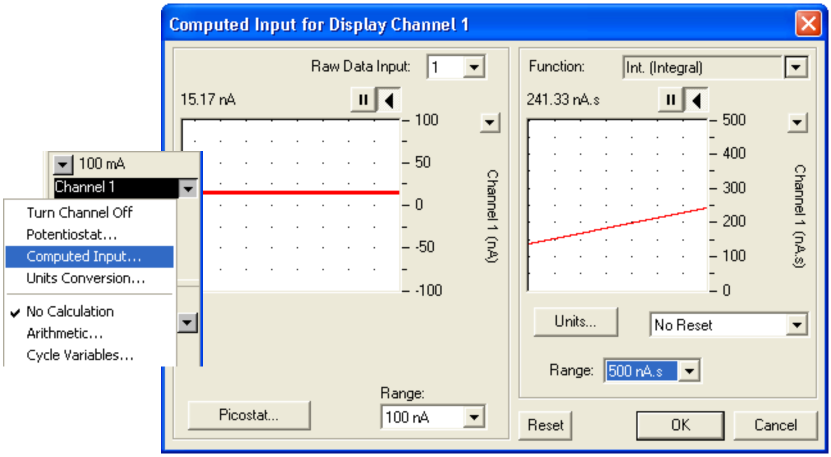


Figure 5–15
Online integration of the current signal using Chart Computed Input integration (Macintosh).

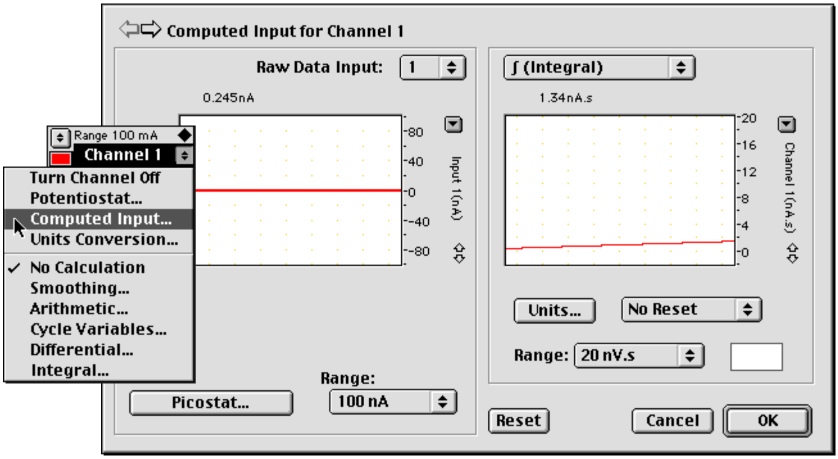
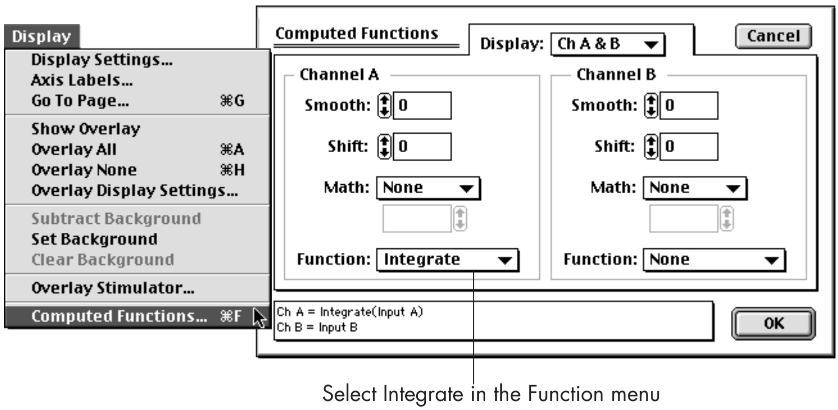


Figure 5–16
Integration of the current signal using Scope Computed Functions.



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 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 5–16. 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 or QuadStat.

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, or use the Potentiostat in High Z mode, page 16.

Figure 5–17
Setting up the Potentiostat as a Galvanostat (Windows).

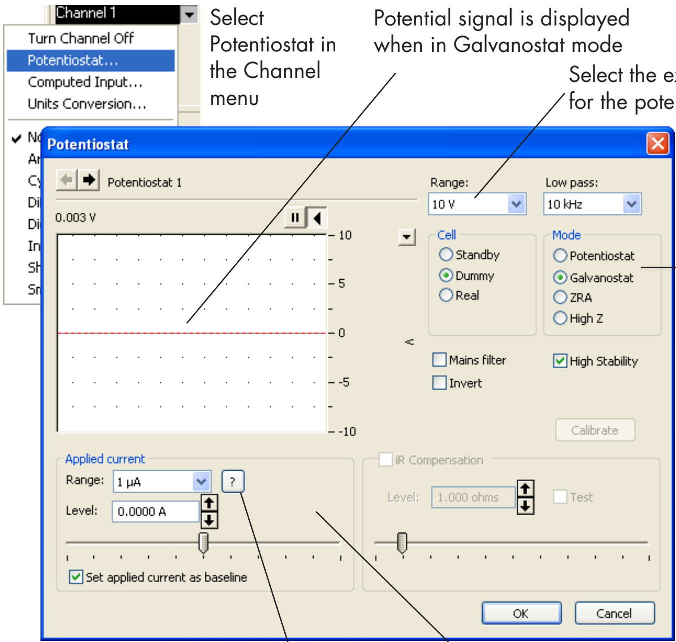


Figure 5–18
The Current channel units conversion dialog box.

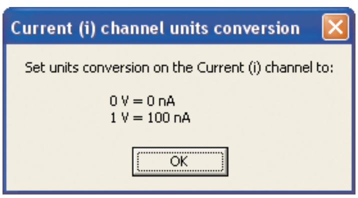


Chart software on Windows computers

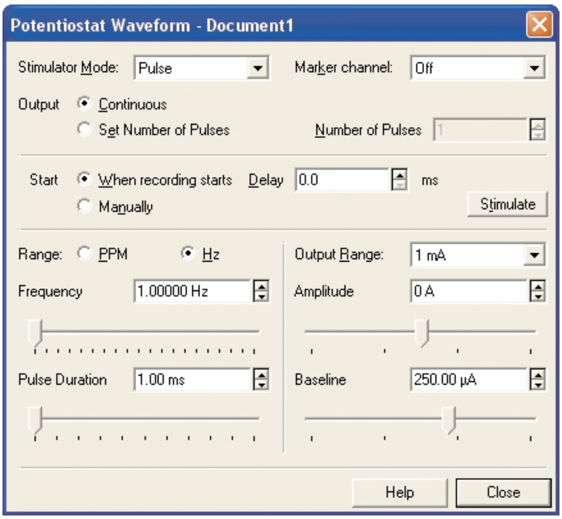
To switch to the Galvanostat mode of operation, choose the Potentiostat command in the Channel Function pop-up menu to open the control window, and turn on the Galvanostat and Dummy radio buttons, Figure 5–17.

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). 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 5–18.

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 5–19.

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.

Figure 5–19
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 5–6.

With highly resistive loads, using a large range setting with a small (close to zero) current can produce unexpected large potential signals 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.

Chart software on Macintosh

Galvanostat mode of operation is accessed by choosing the Potentiostat command in the Channel Function pop-up menu to open the control window. Turn on the Galvanostat and Dummy radio buttons, Figure 5–20.

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

Figure 5–20
Setting up the Potentiostat as a Galvanostat (Macintosh).

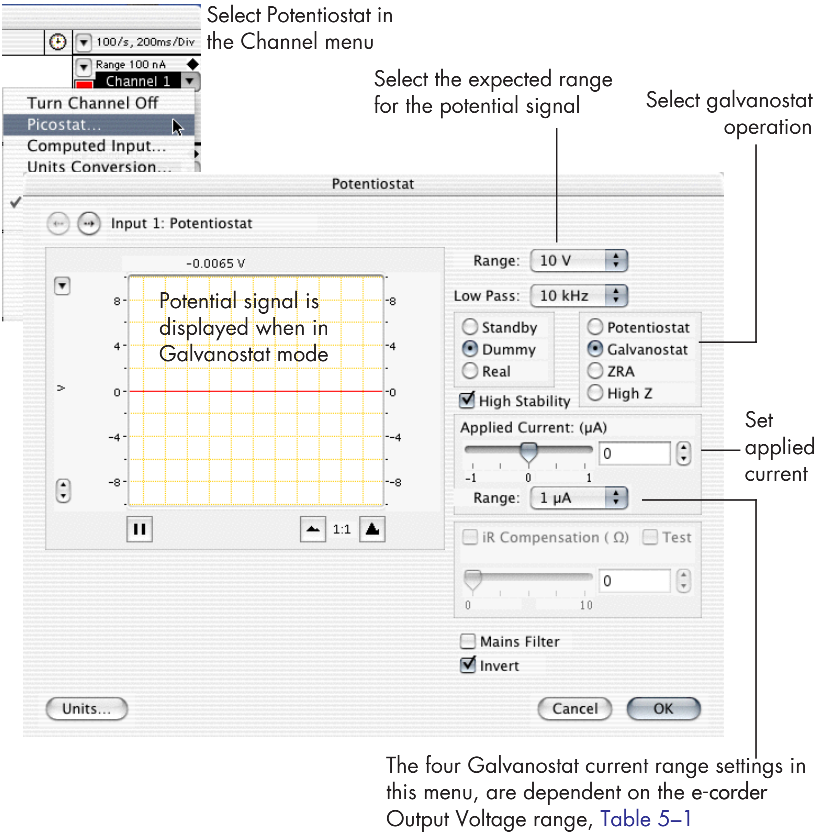


Table 5–1
Galvanostat current range settings of the Potentiostat as a function of e-corder output range.

Galvanostat Current Ranges

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

* Usually it is better to use corresponding settings elsewhere in the table.

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 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 Ω internal dummy cell). Try selecting a more appropriate 1 μA or 10 μA range, where the offset will be correspondingly smaller, and the signal should come on screen and be close to zero volts.

The e-corder Output Voltage can be set as described earlier, Figure 5–8, on page 64. At each of these Output Voltage range settings the Potentiostat offers four current range settings when in Galvanostat mode, Table 5–1. The most accurate control is achieved by using the largest possible Output Voltage range with the smallest possible Galvanostat range setting.

Adjust the current within the selected range. The resulting potential signal is shown in the display area.

During an experiment control the applied current is by adjustment of the Output Voltage controls (Chart Setup menu) — this controls the e-corder output voltage which in turn controls the current applied by the Galvanostat. For example, if you have selected an e-corder Output Voltage range of 500 mV, and a current range of 50 μA, Table 5–1, you might now wish to do an experiment where the current is held at a constant 35 μA (or 35/50 × 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 76. 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 61, 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 71) 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.

To effect the electrolysis of a substrate a potential should be chosen which is at least 50 – 200 mV more oxidising (or reducing) than the half-wave potential 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 formed 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 (< 100 nA) or QuadStat (< 1 mA/channel) 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 greatly increase the conductivity of the solution, without having to add large amounts of electrolyte.

Controlled Current Electrolysis

These techniques are essentially the same as Chronopotentiometry, page 73, 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, or QuadStat, 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 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. Your will also need to determine whether the sensor is of a two or three electrode configuration. The Potentiostat (up to 100 nA), Picostat (up to 100 nA), and QuadStat (up to 1 mA) 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, Picostat, or QuadStat, applies at the working electrode.

Note that the QuadStat can be employed with up to four sensors, each at a different potential, all using the same reference and auxiliary electrode. The QuadStat also has the ability to zero (or offset) a background current signal which can be of use when trying to amplify small peaks on a large background signal, see Zero Offset, page 55.

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 twelve calibration points.

If you are performing a flow injection analysis, or similar experiment, then the Chart Flow Injection Analysis extension (available on Windows computers only) can be used to determine peak areas, prepare a calibration graph, and apply the calibration results to determine the amount of material in the unknown sample peaks. PowerChrom software can also be used with the QuadStat and e-corder hardware as a electrochemical detector for HPLC experiments.

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

If the experiment requires a differential pulse methodology then the MuliPulse 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, QuadStat, or Potentiostat which can then be referred to as ‘biosensor meters’. The first step is to establish the polarising voltage and current measurement requirements of your sensor.

The QuadStat also has the ability to zero (or offset) a background current signal which can be of use when trying to amplify small peaks on a large background signal, see Zero Offset, page 55.

Many biosensors provide a linear signal response over a 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 and QuadStat have suitable current ranges for use with this sensor, and Chart software would normally be used to record data.

Dissolved Oxygen (dO_2) 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, the Potentiostat, QuadStat, 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:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

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. Sampling rates of about 1 /s are usually optimal.

The QuadStat also has the ability to zero (or offset) a background current signal which can be of use when trying to amplify small peaks on a large background signal, see Zero Offset, page 55.

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, or QuadStat, which are suitable for detecting the small currents 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:

$$NO + 2H_2O \rightarrow NO_3^- + 4H^+ + 3e^-$$

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 +1.0 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 in order to minimize any electrical noise. The Mains Filter setting can also be employed to further reduce mains hum. Sampling rates of about 1 /s are usually optimal.

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.

The QuadStat also has the ability to zero (or offset) a background current signal which can be of use when trying to amplify small peaks on a large background signal, see Zero Offset, page 55.

A

APPENDIX A

Technical Aspects

This appendix describes various technical aspects of potentiostat construction — you do not need to understand this material to use the Potentiostat, Picostat or QuadStat. 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, QuadStat and other eDAQ Amps have been designed to be used with an e-corder system. All internal functions (gain ranges, filters, real/standby/dummy cell selection) of the Potentiostat, Picostat or QuadStat are controlled from the e-corder by sending information on a special communications connection called the 'I^2C bus' which also supplies DC power.

Potentiostat

The Potentiostat is designed to function as either a potentiostat (Chart, Scope or EChem software) or galvanostat, ZRA (zero resistance ammeter), or high impedance voltmeter (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 fitted with an internal 1 MΩ dummy cell for use in potentiostat or galvanostat mode. The dummy cell is physically connected whenever the 'Real cell' mode is not being used.

The Potentiostat has gain ranges at decade intervals from 1 nA/V to 10 mA/V, provided by an I to V convertor and PGA. The maximum current output signal (I Out) is 10 V at any gain setting. Secondary

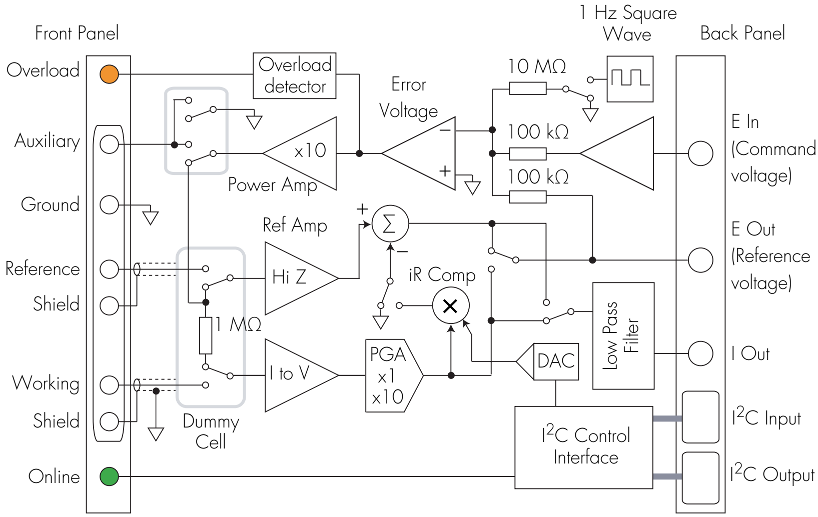


Figure A–1
Block diagram of the Potentiostat.

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 21 current range settings from ±20 nA to ±100 mA in 1:2:5 steps, page 98.

The Potentiostat uses a differential input amplifier to compare the difference in potential between the reference electrode and the excitation potential set using the analog output of the e-corder. The output of this amplifier provides an error signal the feed back circuit tries to zero.

The reference and working 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.

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. The use of DC power allows its use inside Faraday cages.

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–2.

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 29. The use of DC power allows its use inside Faraday cages.

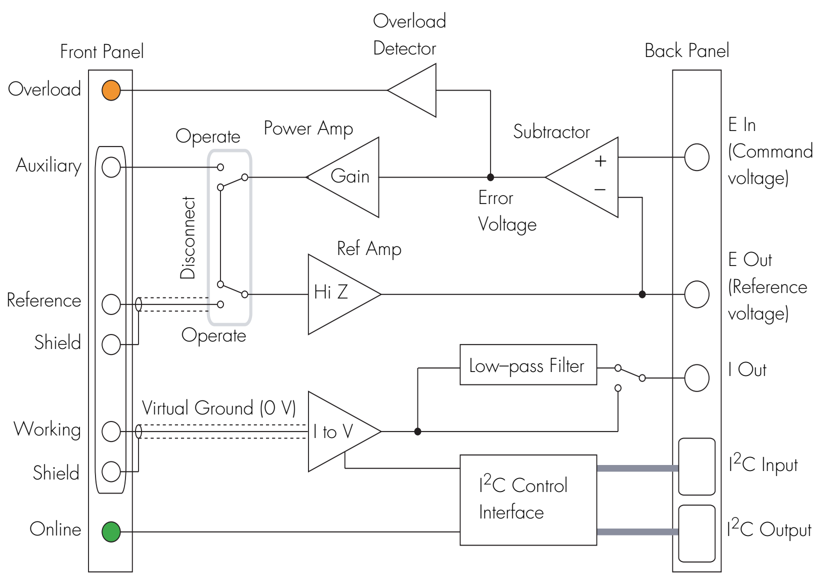
An error voltage is generated from the difference between the voltage on the Reference electrode and the excitation (command) voltage set by the e-corder unit. This difference or error voltage drives a high gain power amplifier (VCVS – voltage controlled voltage source) the output of which is applied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

The Picostat, and the electrochemical cell to which it is connected, forms a composite feedback control system in which the value of the Auxiliary potential 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.

Figure A–2
Block diagram of the Picostat.



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 convertor, 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.

QuadStat

The QuadStat is comprised of four subunits which function in potentiostat mode only — that is the QuadStat cannot be used as a galvanostat. A block diagram of the QuadStat construction is shown in Figure A–3.

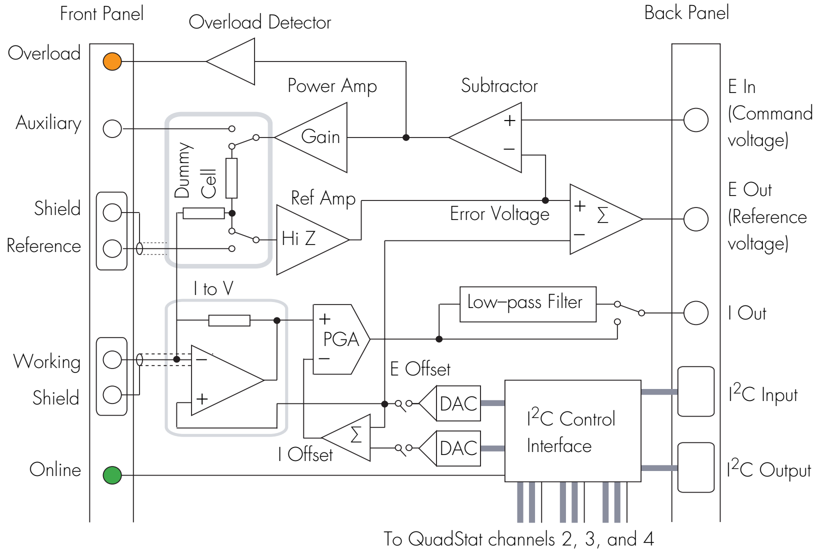


Figure A–3
Block diagram of the QuadStat, Channel 1.

Within the QuadStat an 'error voltage' is generated from the difference between the voltage on the Reference electrode and the sum of the excitation (command) voltage set provided at E In, and the voltage provided by the E Offset DAC. This error voltage drives a high gain amplifier (VCVS – voltage controlled voltage source) the output of which is applied to the Counter electrode (CE) in such a way as to minimise the error voltage.

The QuadStat, and the electrochemical cell to which it is connected, form a composite feedback control system in which the value of the Counter Electrode (CE) voltage is controlled in such a way as to make the Reference voltage with respect to the Working electrode voltage equal to the desired Command voltage. The current flow (I) in the Working Electrode (WE) is the quantity being measured.

When the QuadStat is in Standby mode the CE and RE are disconnected from the cell and connected to an internal dummy cell. This prevents current flowing through the electrochemical cell and allows a simple test of circuit operations.

A steady state, or transient, 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 QuadStat controls are next accessed.

The RE voltage is measured by a high input impedance amplifier whose output is summed with the WE potential to provides a low impedance output to the e-corder unit proportional to the actual potential difference between the RE and WE.

The WE is held at a virtual potential by a voltage-to-current convertor. The different WE's can be individually adjusted (that is the virtual potential can be adjusted) over a range of ±2.5 V. The current measured by the voltage-to-current convertor can be zeroed by means of an offset current — this is useful in situations where a large 'background current' is present, as might occur in a flow injection analysis experiment, or during in vivo neurotransmitter monitoring. The QuadStat has six gain ranges from 100 μA/V to 200 pA/V in 1:2:5 steps. 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 ±2 nA to ±1 mA in 1:2:5 steps.

The coaxial shields of the RE and WE 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.

The QuadStat is powered is powered by regulated +17 V, –17 V and +8 V DC lines from the e-corder, see Figure 4–4 on page 45. The use of DC power allows its use inside Faraday cages.

Multiple electrode potentiostat designs for sensor work have been reported in “Development of a computer controlled multichannel potentiostat for applications with flowing solution analysis”, Tang Fang, Michael McGrath, Dermot Diamond, and Malcolm R. Smyth, *Analytica Chimica Acta*, **305**, 347-358, 1995.

B

APPENDIX B

Troubleshooting

This appendix describes some problems that may arise when using the Potentiostat, Picostat or QuadStat. 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 22, page 39, and page 56. 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, Picostat, or QuadStat 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 11, page 31, and page 48.
- 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 'E In' cable is connected to the e-corder output and the 'I Out' and 'E Out' cables are connected to e-corder Input 1 and 2, see page 11, page 31, and page 47.

• Try using the Potentiostat, Picostat, or Quadstat with another e-corder (if available). If the Online indicator fails to light on the second e-corder, the Potentiostat, Picostat, or Quadstat, may be faulty — contact eDAQ. If it works correctly on a second e-corder then the first e-corder may be faulty — contact eDAQ.

The 'Potentiostat', 'Picostat', or 'QuadStat' 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 Online indicator is illuminated 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 (a potential overload has occurred).

• Check that the electrode cables are firmly attached to the electrodes.

• Check that the surfaces of the electrodes have not become fouled.

• The Picostat or QuadStat Overload indicators 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 page 8, page 28 or page page 43 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, page 27, or page 43.

• 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 11, or Connecting the Picostat, page 31, or Connecting the QuadStat, page 47.

• 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, page 27or page 43. 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 and 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/Hg_2Cl_2)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 18, page 37, or page 54.

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 and 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/Hg_2Cl_2) 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 (or lower) filter of to record your results, see page 17, page 37, and page 53. 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, Figure 3–3 on page 29, and Figure 4–2 on page 44. 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 (which is usual 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).

APPENDIX C

Specifications

Potentiostat

Power Amp

Compliance voltage:	> 10 V
Output current:	±100 mA maximum
Current limit:	±200 mA
Slew rate:	3 V/μs

Electrometer

Input resistance:	10^{13} Ω
Input bias current:	< 1 pA @ 25°C
Input voltage:	±10 V maximum
Output voltage:	±10 V maximum
Output offset voltage:	±0.8 V maximum
Output offset drift:	±0.8 μV/°C
Gain accuracy:	0.1%

Current Measurement and Control

Current Range Setting	Potentiostat gain (μA/V)
±100, 50, 20 mA	10 000
±10, 5, 2 mA	1 000
±1 mA, 500, 200 μA	100
±100, 50, 20 μA	10
±10, 5, 2 μA	1
±1 μA, 500, 200 nA	0.1
±100, 50, 20 nA	0.01

Maximum current signal:	10 V
Low pass filters:	10 000, 1000, 100, 10 Hz 3rd order Bessel
e-corder filter settings:	10 kHz to 1 Hz in 10:5:2 steps
Gain accuracy:	0.2% at ranges 1 mA or smaller 1% at ranges 10 mA or larger
Drift with temperature:	±0.3 mV/˚C

Control Loop

Voltage offset error:	±1 mV
Voltage gain error:	0.1%
Bandwidth (unity loop gain):	16 kHz (@ –90° lag) 160 Hz (high stability mode, @ –90° lag)
Ramp follower error:	±1 mV @ 100 V/s ±1 mV @ 1 V/s (high stability mode)

iR Compensation

Current Range Setting	Compensation Range
±100, 50, 20 mA	0 – 10 Ω
±10, 5, 2 mA	0 – 100 Ω
±1 mA, 500, 200 µA	0 – 1 kΩ
±100, 50, 20 µA	0 – 10 kΩ
±10, 5, 2 µA	0 – 100 kΩ
±1 µA, 500, 200 nA	0 – 1 MΩ
±100, 50, 20 nA	0 – 10 MΩ

Control Port

I^2C input and output:	Male and female DB-9 pin connectors. Provides control and power to the Potentiostat.
Power requirements:	±17 V DC +8 V DC 25 mA typical 2 W

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.

Picostat

Electrometer & Power Amp

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

Current Measurement and Control

Current ranges:	±100, 50, 20, 10, 5, 2, 1 nA ±500, 50, 20, 10 pA
Gain:	10, 1, 0.1 nA/V
DC current error:	< ±1% FS on ranges of 10 pA – 1 nA < ±0.5% FS on ranges of 2 – 100 nA
Filter setting:	10 Hz low-pass. 3rd order Bessel
e-corder filter settings:	10 kHz to 1 Hz in 10:5:2 steps
Bandwidth, unfiltered:	> 10 kHz, on ranges of 20 – 100 nA ~ 1 kHz, on ranges of 10 pA – 10 nA
Drift with temperature:	< 20 μV/˚C

Control Port

I^2C 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.

QuadStat

Electrometer & Power Amp

Compliance voltage:	> 11 V
Maximum control voltage:	±2.5 V using internal control ±10 V using external input
Output current:	±1 mA maximum
Input impedance:	10^{13} Ω ‖ 1 pF
Input bias current:	< 1 pA @ 25˚C

Current Measurement and Control

Current ranges:	±1 mA ±500, 200, 100, 50, 20, 10, 5, 2, 1 µA ±500, 200, 200, 50, 20, 10, 5, 2 nA
I/V Gain:	100, 10, 1 nA/V
I/V Multiplier:	×1, ×1000
DC current error:	< ±1% FS on ranges of 2 µA – 1 mA < ±0.5% FS on ranges of 2 nA – 1 µA
Current signal offset:	±400 µA on ranges 2 µA – 1 mA ±400 nA on ranges 2 nA – 1 µA
Bandwidth, unfiltered:	> 10 kHz, on ranges of 2 µA – 1 mA ~ 1 kHz, on ranges of 2 nA – 1 µA
Low pass filter:	10 Hz, 3rd order Bessel
e-corder filter settings:	10 kHz to 1 Hz in 10:5:2 steps
Drift with temperature:	< 10 µV/˚C

Control Port

I^2C input and output:	Male and female DB-9 pin connectors. Provides control and power.
Power requirements:	±17 V DC, ~ 20 mA +8 V DC, ~ 20 mA ~ 0.6 W quiescent

Physical Configuration

Dimensions (h × w × d):	60 × 150 × 200 mm 2.4 × 5.9 × 7.9 inches
Weight:	1.5 kg (3.3 lb)
Operating conditions:	0 – 35°C 0 – 90% humidity (non-condensing)

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

D

APPENDIX 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:

$$i_{p_a} = 269 n^{3/2} A D^{1/2} C v^{1/2}$$ for an oxidation (anodic scan)

$$i_{p_c} = -269 n^{3/2} A D^{1/2} C v^{1/2}$$ for a reduction (cathodic scan)

The potential where this occurs is given by:

$$E_{p_c} = E_{1/2} - \frac{0.0285}{n} \qquad E_{p_a} = E_{1/2} + \frac{0.0285}{n}$$

where

i_{p_a} = current peak during anodic scan (A)
i_{p_c} = current peak during cathodic scan (A)
E_{p_a} = potential at current peak for anodic scan (V)
E_{p_c} = 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 (cm^2)

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, υ

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 (cm^2)
D = diffusion coefficient of the substrate molecule (cm^2/s).
C = concentration of the substrate molecule (mol/L)
t = time (s).

The factor of 1000 is to bring both cm and dm (1 dm^3 = 1000 cm^3 = 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} cm^2/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

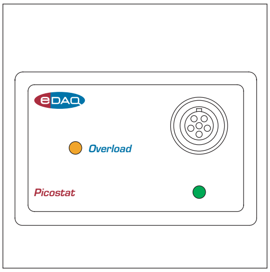
Q = the number coulombs transferred
n = the number of electrons transferred to (or from) the substrate molecule
A = area of the exposed surface of the electrode (cm^2)
D = diffusion coefficient of the substrate molecule (cm^2/s).
C = concentration of the substrate molecule (mol/L)
t = time (s)
k = a 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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