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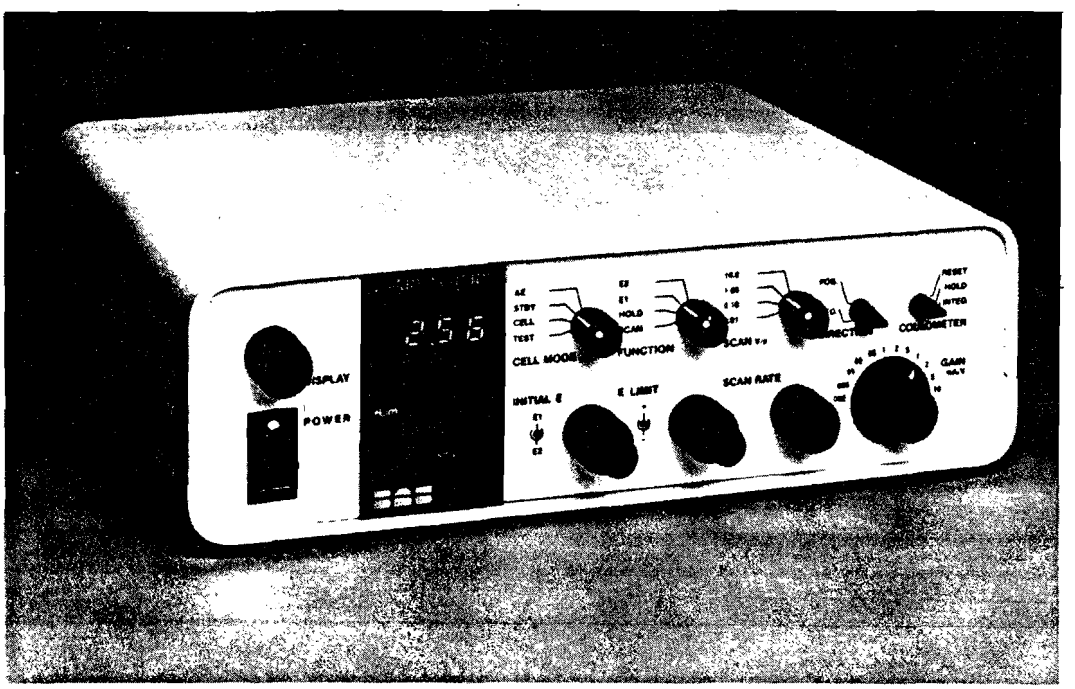
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Find the *Bioanalytical Systems CV-27* at our website: *Click HERE*

OPERATION/INSTRUCTION MANUAL

FOR THE

CV-27
CYCLIC VOLTAMMOGRAPH



Bioanalytical Systems Inc.
Purdue Research Park
2701 Kent Avenue
West Lafayette, IN 47906
(317) 463-4527 telex 276141 BAS WLAF

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BAS CV-27 Series p/n MF9030 05/07/84

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Section 1.0 General Information

1.1 Introduction

The primary reason for forming Bioanalytical Systems Inc. was to manufacture an instrument that solved a problem. This first instrument, the LC-2 electrochemical detector for liquid chromatography, was capable of measuring minute amounts of neurochemically important compounds. LCEC sparked a second Renaissance in electroanalytical chemistry. It fostered among those who knew electrochemistry only by the brand of their pH meter, the idea that electrochemistry had real utility in solving a variety of practical problems. Over the decade since its inception, the BAS philosophy has not changed. Problem solving is still our primary concern. Since we possess significant expertise in electrochemical instrumentation, and since electrochemistry has great potential for solving problems in many areas, the CV-27 Voltammograph® was developed.

Electrochemistry can solve a broad spectrum of analytical problems. These can be fundamental, such as the study of interfacial phenomena, or applied, such as the determination of concentration. Applications exist in biological sciences, physical sciences, material science, chemical synthesis, manufacturing (production/QC/environmental control), and teaching. Electrochemical techniques can be used to illustrate mass transport (diffusion, convection, migration), thermodynamics (Nernst relationships), kinetics (homogeneous and heterogeneous rates), and surface chemistry (adsorption and chemically modified electrodes). Electrochemistry can also be coupled to other techniques, such as spectroscopy. The applicability of electrochemical techniques is diverse.

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Why, then, is electrochemistry not more widely used? There are a number of reasons, but most stem from the fact that analysts have very little background in electrochemical methodologies. The field has been deemed not useful in contrast to the more familiar spectral techniques. To many, their first brush with electrochemistry was as freshman chemistry students, when they tried to make heads or tails (anodes or cathodes as it may have been) out of half cell reactions. Later on, they may have won against a teaching lab's neglected dropping mercury electrode (DME) for the 30 minutes required to determine Pb concentrations in a spiked water sample.

To educate and persuade analysts in the versatility of electrochemistry, there are certain minimum requirements or features of the equipment that must be satisfied. It should be (1) versatile and have broad applicability (i.e. capable of performing many electrochemical techniques) (2) easy to use by the novice and experienced electrochemist alike (3) reliable, and (4) reasonably priced. These requirements have been accomplished in the CV-27 Voltammograph®.

The CV-27 is capable of controlled potential experiments, potential measurements at zero current, and charge measurement experiments. Through the use of modern electronic technology and a unique modular design, operation of the CV-27 is straightforward. The CV-27 electronics are encased in a compact, bench saving package about 1/4 the size of competitive instrumentation. Figure 1.1 illustrates the high density packing of components required to achieve these features.

Many electronic functions have been integrated into the CV-27. These features, illustrated in Figure 1.2, include a potentiostat (±5.00 V applied potential, ±10 V compliance, 120 mA current), a linear ramp and pulse waveform generator, separate controls to fix high

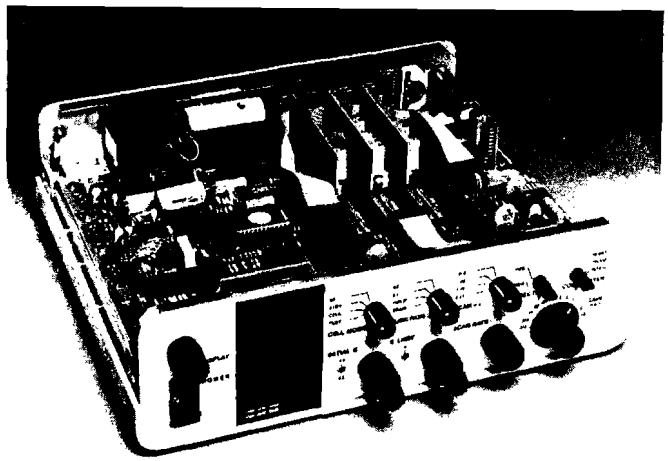


Figure 1.1
PCB and Component Layout in CV-27

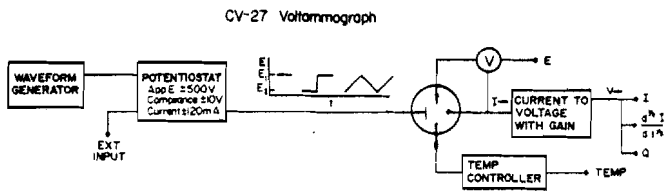


Figure 1.2
Block Diagram of CV-27

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and low scan limits, the ability to bring an external waveform directly into the potentiostat, a current-to-voltage converter with gain (2 μA/V to 10 mA/V), a resident coulometer with an integration time base of seconds for chronocoulometry, to hours for bulk electrolysis, and a voltage follower for the measurement of potential at zero current (i.e. equilibrium or rest potential). Every controlled parameter and output variable may be read, in the proper units of measure, on the 3 1/2 digit front panel display. All the control functions can be actuated by a separate, remote timer using TTL logic. Moreover, in conjunction with the LC-22A Temperature Controller, cell temperature may be controlled and monitored on the CV-27.

With these features, a number of electrochemical techniques can be performed with this instrument. Some of these techniques are noted in Table 1.1. Of particular importance is the general use of this instrument as a tool for compound characterization. Just as one would obtain UV-VIS, IR, mass spectra, etc. to fully characterize an unknown substance, one should consider electrochemistry as a similar qualitative and quantitative tool. The analyst can determine redox centers, electrochemical reversibility, prior and follow-up chemical reactions via cyclic voltammetry. The number of electrons transferred (n) can be measured by bulk electrolysis, adsorption characteristics by chronocoulometry, and diffusion coefficients by chronoamperometry. If the determination of an ultra trace component in solution is required, a stripping voltammetric procedure may be applicable. Titration to an endpoint monitored amperometrically or potentiometrically may be the method of choice. Ion selective electrodes can be used with the CV-27 for selective quantitation. All of the above methods can be combined with spectroscopic techniques, under hydrostatic or dynamic conditions, to broaden the applications even further.

Electrochemical Techniques
Amperometry
Chronoamperometry
Chronocoulometry
Cyclic Voltammetry
Linear Scan Voltammetry
Stripping Voltammetry
Controlled Potential Electrolysis
Potentiometry
Spectroelectrochemistry

Table 1.1

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Does this still sound like so many anodes and cathodes, half cell reactions, and junction potentials? It should't! Consider this instrument as another chemical tool in your analytical arsenal. In this manual we will demonstrate its problem solving capabilities by discussing the principles of electrochemical techniques, the typical applications, and any additional practical comments that would make the development or the understanding of the data easier. We can not cover all the details here. Two excellent, up-to-date, and highly recommended references are: P.T. Kissinger, W.R. Heineman, eds., Laboratory Techniques in Electroanalytical Chemistry, Marcel-Dekker, 1984 (available from BAS), A.J. Bard, L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications John Wiley and Sons, Inc., New York, NY, 1980.

1.1.1 Specifications and Features

Potentiostat and Waveform Generator:

Applied Potential: E1 (Initial), E2 (Step)
Range: ± 5.00V
Compliance Voltage: ±10V
Maximum Current Available: 120 mA typical, 100 mA minimum
Rise Time, 1V potential step: RC Load (10 ohm 1.6 uF): 0.1 ms
Linear Scan Rate Range: 0.1 mV/s to 10.0 V/s, continuously adjustable
Scan Direction: positive or negative going, manual selection
Scan Limit: positive and negative, continuously adjustable ±5.00V range

Current to Voltage Output:

Range: 2 uA/V - 10 mA/V, 1:2:5 sequence in 12 steps
Maximum Measurable Current: 120 mA* typical, 100 mA minimum

*CAUTION: Current values exceeding 120 mA may cause instability in the instrument, e.g. oscillation or loss of potential control.

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Coulometer:

Range: 20 uC/V - 10 C/V, bipolar sum

Semi-Derivative

$d^{\frac{1}{2}}i/dt^{\frac{1}{2}}$ ($I/t^{\frac{1}{2}}$ vs. E or t)
[incorporates inventions embodied in Canadian Letters Patent No. 977,419 and United States Letters Patent No. 3,868,578 and produced under exclusive license from Canadian Patents and Development Limited]

Front Panel Controls:

Display Selector: Single knob
- Pos Scan Limit - ±5V
- Neg Scan Limit - ±5V
  - Error- If scan limits cross, "X Limits" indicated on display
- Scan Rate - 0.1 mV/s - 10 V/s
  - magnitude and direction
- Temperature - 0-99.9 °C
- Equilibrium (Rest) Potential (E)
  - ±1.999V
- Applied Potential (E1, E2) -
  - ±5.00V
- Coulometer - 0.001 mC - 19.99C
- Current Out- 0.01 µA-120mA
- Coulometer Range - Full scale at output jack (48 combinations available through the Gain control and Coulometer Recorder Selection knob), 20 uC/V to 10 C/V (x 10 V)

Scan-Hold-E1-E2 (operation knob)
Test-Cell-Standby- E (operation knob, position indicated on display)
E1-E2 (one knob, dual concentric)
Scan Pos/Neg Limits (one knob, dual concentric)
Scan Range (one knob, 4 position: 0.01, 0.1, 1.0, 10.0 V/S)
Scan Rate (one knob, variable adjust 0-100%, of above 4 ranges)
Scan Direction (toggle switch: +/-)

Current Range (one knob, 12 position: 0.002-10.0 mA/V)
Coulometer (3 position toggle switch: Integ/Hold/Reset)

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Rear Panel Jacks and Switches:

Applied Potential (jacks)
Polarity by toggle switch: +/-
Current Output, (jacks)
Polarity toggle switch: positive for oxidations/positive for reductions
Equilibrium (Rest) Potential, E (jacks) ($W\text{-}R_{grnd}$),
Coulometer Output (jacks)
Coulometer Recorder Selection Knob (4 position A, B, C, D)
Auxiliary Potentiostat Input (jack)
Semi-Derivative Output (jack)
Filter (0.001, 0.1, 2 sec.), (switch)
Temperature Input (jack)
Remote Control Connector (used with external timing device)
E1 (On-Standby), E2 (On-Standby), Scan (On-Hold), Cell (On-Standby), Scan Direction (Pos - Neg), Integrate (On-Off), Reset (On-Off)

1.2 Unpacking and Inspection of Equipment

After carefully unpacking the instrument, check the contents against the inventory lists shown in Table 1.2. Items such as manuals and small components packaged in plastic bags are shipped loose in the box. Examine all packing material before discarding it.

If a shortage exists, call BAS Customer Service and describe the shortage. A replacement part will be sent immediately subject to stock availability

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

Table 1.2

Part Number	Description
EF-1065	CV-27 Voltammograph Power Cord Cell Lead YT or XY Recorder Leads (2) CV-27 Operation/Instruction Manual

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

1. Retain container, packing material, and broken item for inspection by the carrier.
2. Write or phone BAS with our order number, the date received and a description of the damage. BAS will do everything possible to expedite repair or replacement of the items damaged.

Air Freight, Express or Truck

1. Contact the local agent of the transportation company immediately and request an inspection.
2. Retain the container, packing material, and damaged goods until the examining agent has made an inspection report.

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

1.3 Warranty and Service Information

Bioanalytical Systems Inc. products are fully warranted against defects in material and workmanship. Electronic instruments are unconditionally guaranteed for one year, except when failure is due to obvious abuse or neglect, unauthorized tampering, procedures not described in manuals, or improper connection of electronic units to other components. Electrochemical cells and electrodes are warranted for 60 days from date of invoice under the same exclusions.

Products sold but not manufactured by Bioanalytical Systems Inc. carry the

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original manufacturer's warranty. The following items are not covered under any warranty: carbon paste, lamps, panel lights, fuses, seals.

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

Service Information

Bioanalytical Systems provides a skilled service staff available to solve your technical problems if an equipment-oriented problem should arise. For further details, call customer service personnel (317-463-4527) who will route your problem to the correct individual. Following discussion of your specific difficulties, an appropriate course of action will be described and the problem resolved accordingly. Do not return any products for service until a Customer Service Number (CS#) has been obtained. The CS# identifies you as the sender and describes the problem you are having in full detail. All correspondence and shipments should be sent to:

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

Service will normally be completed within ten working days.

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Section 2.0 Introduction to Electrochemical Analysis and Characterization

Electrochemical techniques have become increasingly popular in all fields of chemistry as a means of studying redox states. The electrode potential at which a drug, a metal ion or complex, or some other type of compound undergoes reduction or oxidation can be rapidly located by an electrochemical technique such as cyclic voltammetry. Furthermore, information regarding the stability of the electrogenerated product(s) can be obtained by electrochemical and spectroelectrochemical techniques. Such information is often useful in subsequent experiments involving electrosynthesis, corrosion, coulometry, amperometric titration, and trace analysis. In the latter case, electrochemical techniques such as liquid chromatography/electrochemistry (LCEC), anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), pulse voltammetry and differential pulse voltammetry have proved to be powerful, widely applicable techniques for analysis at the trace level. Electrochemical techniques benefit from the ease with which accurate measurements of very small currents can be made with modern instrumentation.

This instrument is designed to perform electrochemical techniques in which the potential of the working electrode is controlled and the resulting current is measured. The current can be integrated to give the charge passed through the electrochemical cell at any time during an experiment. Also, the instrument enables the cell potential to be measured under the condition of zero current. Thus, this instrument is capable of a wide variety of electrochemical techniques involving potential scan (cyclic voltammetry, polarography, hydrodynamic voltammetry, stripping voltammetry), potential step (chronoamperometry, chronocoulometry), constant potential (controlled potential electrolysis, amperometric titrations, amperometry), hybrid electrochemical

- Potential Scan
  - Linear Scan Voltammetry
    - Polarography
  - Cyclic Voltammetry
  - Hydrodynamic Voltammetry
  - Anodic Stripping Voltammetry
  - Cathodic Stripping
- Potential Step
  - Chronoamperometry
  - Chronocoulometry
- Constant Potential
  - Controlled Potential Electrolysis
  - Amperometry
  - Amperometric Titrations
- Hybrid Electrochemistry
  - Spectroelectrochemistry
- Potentiometric
  - pH
  - Ion Selective Electrode

Table 2.1 Electrochemical Techniques

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techniques (spectroelectrochemistry) and potentiometric techniques (ion selective electrode titrations).

A typical electrochemical cell is shown in Figure 2.1.

The cell consists of a glass container with a cap having holes for introducing electrodes and nitrogen. Solution can be deoxygenated by bubbling with nitrogen gas, then maintained as anaerobic by passing nitrogen over the solution. The reference electrode is typically a saturated calomel (SCE), or Ag/AgCl electrode. The solution is isolated by a salt bridge to prevent contamination from the reference electrode's internal solution. The auxiliary electrode is a platinum wire, which is placed directly into the solution for most techniques. An exception is controlled potential electrolysis for which the auxiliary electrode is isolated by a porous frit to prevent contamination by its by-products in the main cell compartment. Since the current in any type of voltammetry experiment is temperature-dependent, the cell can be thermostated for the most exacting measurements. For most purposes, this is not necessary. A stirring bar is used for hydrodynamic techniques, and for reestablishing initial conditions between experiments performed in quiescent solution.

Many types of working electrodes have been used with voltammetry. Solid electrodes such as platinum, gold, glassy carbon, wax-impregnated graphite, and carbon paste are commonly used. These electrodes have a good positive potential range. An advantage of mercury is its good negative potential range. The voltammetric techniques referred to as polarography utilize the dropping mercury electrode (DME). This electrode consists of mercury drops continuously extruding from the end of a capillary. The hanging mercury drop electrode (HMDE) is commonly used for cyclic voltammetry. Here a drop of mercury is suspended at the end of a

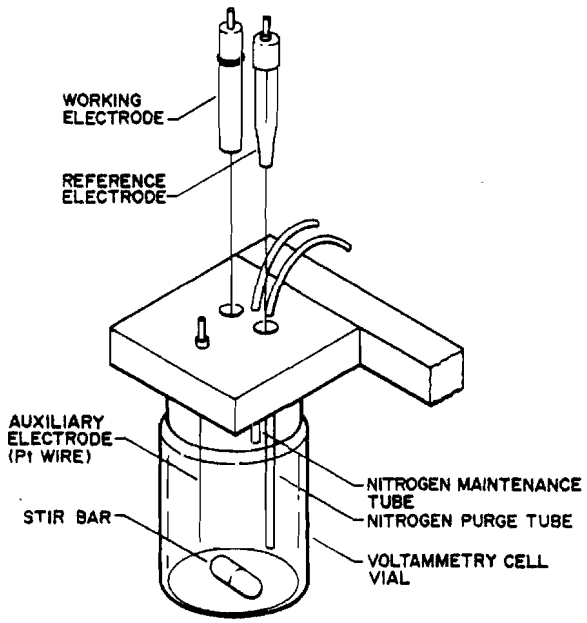


Figure 2.1
Typical Electrochemical Cell Adequate for Many Techniques.

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capillary. A thin coat of mercury can be deposited on a substrate such as graphite to form a mercury film electrode (MFE). For many situations, MFE's are more convenient to use than the traditional DME.

Supporting electrolyte is always added to the sample so that the ionic strength is sufficiently great to minimize solution resistance to charge flow through the cell. Supporting electrolyte also minimizes migration as a means of mass transport to the electrode.

The CV-27 Voltammograph performs a repertoire of electroanalytical techniques in which a potential is applied to the cell and the resulting current is measured. Thus, the applied potential waveform (potential step, potential scan, etc.) is termed the excitation signal and the current is the response signal of the system. The applied potential controls the surface concentration of the two forms of a redox couple as described by the Nernst equation for a reversible couple.

$$O + ne \rightleftharpoons R \qquad (2.1)$$

$$E = E^{\circ\prime}_{O,R} + \frac{0.0591}{n} \log \frac{C^s_O}{C^s_R} - E_{ref} \qquad (2.2)$$

where E = potential applied to cell, volts (V)

$E^{\circ\prime}$ = formal reduction potential of O, R couple, V vs SHE

n = number of electrons transferred per molecule. eq/mol

C^s_O = surface concentration of O, mol/cm^3

C^s_R = surface concentration of R, mol/cm^3

E_{ref} = half cell potential of reference electrode, V vs SHE

0.0591 = conversion factor for 25°C.

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Thus, O can be reduced to R by making E sufficiently negative (relative to $E^{\circ}_{O,R} - E_{ref}$) to cause C^s_O/C^s_R to be very small (typically 10^{-2}); R can be oxidized to O by making E sufficiently positive to cause C^s_O/C^s_R to be very large (typically 100). In other words, the reducing or oxidizing strength of the working electrode is controlled by the applied potential, E. As shown in Figure 2.2, scanning (or stepping) the potential in the negative direction makes the electrode a stronger reductant (causing O to be reduced to R), whereas scanning (or stepping) the potential in the positive direction makes it a better oxidant (causing R to be oxidized to O).

The conversion of O to R by reduction at the electrode surface results in cathodic current, i_c. Oxidation of R to O gives anodic current, i_a.

The axes shown in Figure 2.2 are typically used for the display of the current response vs. potential for many controlled potential techniques. Consequently, these axes will be used for several of the techniques described below.

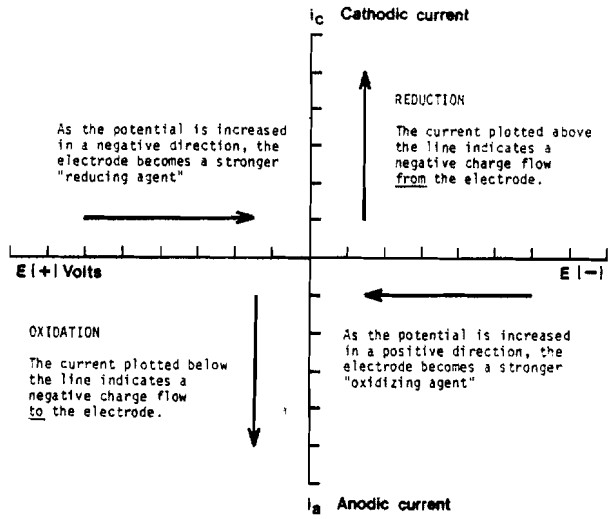


Figure 2.2
Current-potential axes for voltammetric techniques.

Although current is the electrochemical response to the potential applied to a cell, other system responses can be monitored as well. For example, the current can be integrated to give charge.

$$Q = \int_0^t i(t)\ dt \qquad (2.3)$$

where Q = charge, coulombs (C)
i(t) = current, amperes (A)
t = time, seconds (s)

Techniques in which the number of coulombs of charge passed through the cell is measured are termed coulometric experiments. The number of moles of material electrolyzed can be calculated from the charge by Faraday's law.

$$Q = nFN \qquad (2.4)$$

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where n = number of electrons transferred per molecule, eq/mol
F = Faraday's constant, 96,485 C/eq
N = number of moles

System response signals can also be measured by non-electrochemical techniques such as spectroscopy, giving rise to a number of "hybrid" techniques.

The numerous possible combinations of potential excitation signals, and monitored response signals, in either stirred or quiescent solution has led to the development of many electrochemical techniques based on controlled potential. The CV-27 Voltammograph is capable of performing many of these techniques, each of which is described in the following sections.

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Section 3.0 Installation

This section details the physical requirements for installation of the CV-27.

3.1 Power Requirements and Connection of the Power Cord

The CV-27 can be powered by any of the following AC voltages:

100 V
120 V
220 V
240 V

and frequencies of either 50 or 60 Hz. The power supply in your location (i.e. any of the above voltage/frequency combinations) must be the same as the voltage selected in the power cord connector on the rear panel. The CV-27 is usually shipped with the voltage option already matched to the power requirements of the destination. However, the customer should always check this before using the instrument.

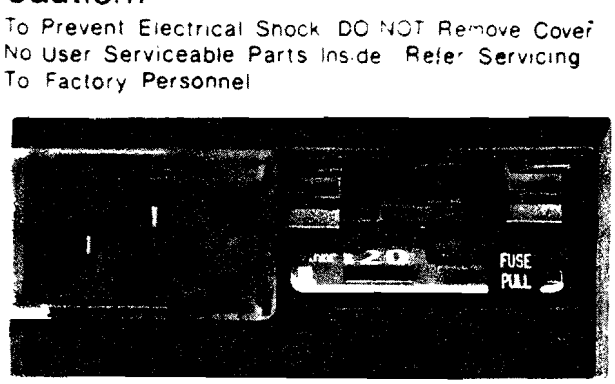


Figure 3.1
Power Cord Connector

Should the power option need to be changed, unplug the line cord and slide the plastic window of the power cord inlet to the left. See Figure 3.1. The orientation of the small circuit board now exposed in the socket determines the voltage option. If the voltage labeled on the outer edge of this board is not that required, pull out the card, and turn it (either by rotation or inversion) such that the desired voltage is readable. Reinsert the board and push the fuse holder back into the cavity. As illustrated in Figure 3.1, the board is oriented for 120 V operation.

If the instrument is operated from a power outlet without safety ground connection, an appropriate adaptor should be used. The ground connection of this adaptor must be securely fastened to an external earth ground for safety purposes. The maintenance of a proper ground connec-

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tion is also very important in the performance of this instrument. A proper ground connection cannot be overemphasized. To insert the power cord into the power socket, slide the plastic window to the right (i.e. over the voltage selection circuit board) and plug the female end of the power cord into this connector. The male end of the power cord is plugged into the power outlet socket. The plug requirements on the male end of the power cord may vary depending on the country of destination. Only one plug type is supplied by BAS.

3.2 Cell Connections

The cell lead cable connects the CV-27 electronics to the electrodes of the electrochemical cell. One end of this cable plugs into the rear panel of the CV-27 and the other end terminates either with the BAS model C-1 Cell Stand or appropriate connectors to the electrodes of the cell.

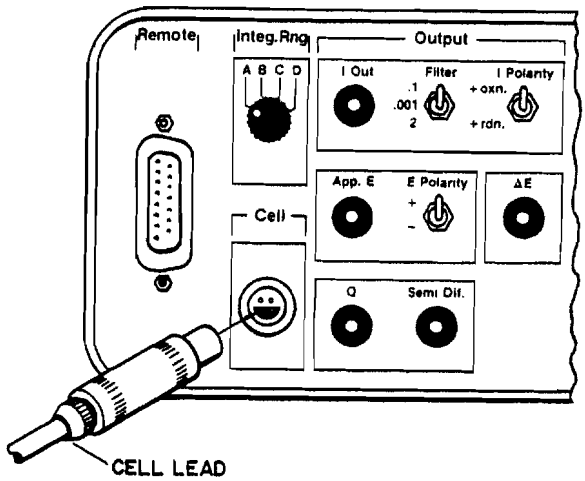


Figure 3.2
Connection of CV-27 to the Cell Cable

3.2.1 CV-27 To Cell Cable

The proper connection of the cell lead is shown in Figure 3.2. The stainless steel connector on the cell lead is inserted into the plug mounted on the rear panel of the unit. Insert the cable connector into the mounted plug and rotate until the cable connector easily slides into the mounted connector. Continue pushing until the pieces "snap" together. To remove. simply pull back on the outer sleeve of the cable connector. The catch will automatically release.

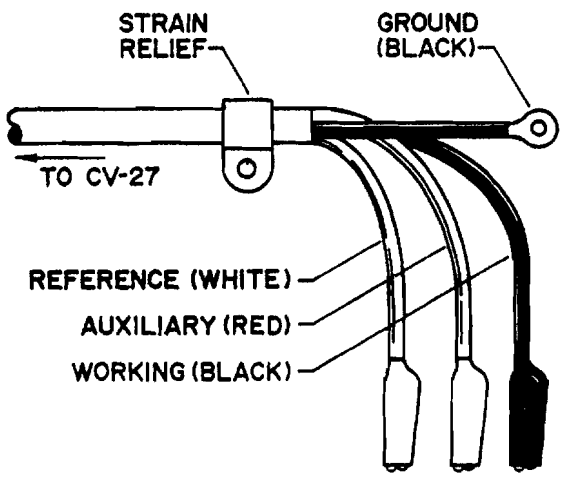


Figure 3.3
Cell (Electrode) End of Cell Cable

3.2.2 Cell Cable to Cell (Electrodes)

A variety of electrochemical cells with variable designs are available commercially. A very versatile electrochemical cell accessories package includes a mounting stand, the BAS C-1B Cell Stand, (with stirring and gas purging capabilities), vials, and electrodes. The BAS

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C-1B Cell Stand contains the cell cable that attaches directly to the CV-27, as described in the previous section. Connection of the cable wires to the individual electrodes is described in the cell stand manual. Note that the CV-27 contains a general purpose cell cable that terminates with connectors that can directly be attached to cell electrodes. The cable contains four color coded connectors (wires); the color code is:

Black wire: working electrode
Red covered wire : auxiliary electrode
White wire: reference electrode
Bare wire or black wire with solder lug: ground connector

A strain relief connector provides a point to affix the cable to prevent jostling of the cell when not in use. Figure 3.3 illustrates the cell end of the CV-27 cell cable.

3.3 Recorder Connections

There are a number of output-to-recorder combinations available depending on the technique used. For each of the techniques discussed in detail in Sections 6-14, the appropriate recorder connections will be noted. A few general considerations are noteworthy at this point.

Two sets of recorder leads are provided with the CV-27 unit. Their use depends on whether a current/potential vs. time or a current vs. potential relationship is to be plotted. Connection to a time base recorder is shown in Figure 3.4. The recording device must be capable of handling the input of analog voltage signals; typically 0 to ± 1 V.

If a response is plotted vs. a specific excitation, an X-Y recorder will be required and the proper connection in such a case is shown in Figure 3.5. Generally the response is plotted on the Y-axis and the excitation on the X-axis. One of the cables provided is used to plot the Y response and the other is used to plot the X excitation.

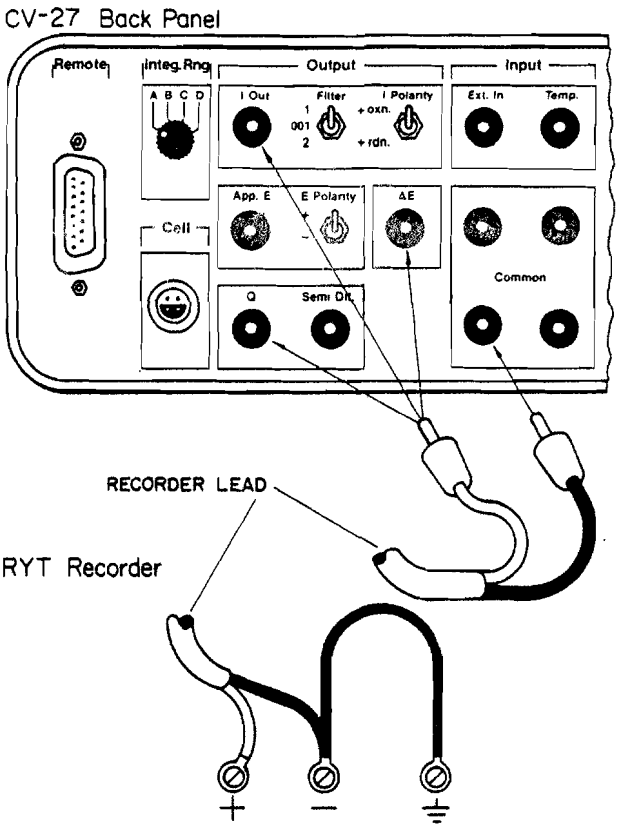


Figure 3.4
Connection of the CV-27 to Y-T Recorder

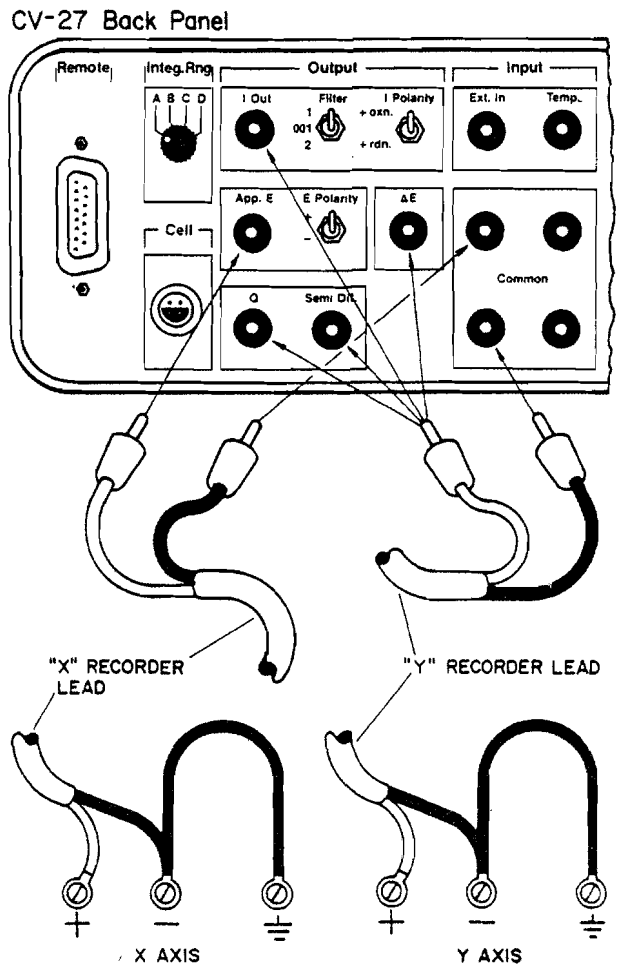


Figure 3.5
Connection of the CV-27 to X-Y Recorder

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3.4 Auxiliary (External) Input

This high impedance input allows an external voltage source to be summed into the voltage of the internal potentiostat. For example, a waveform generator may be used to bring in a sine wave. The limits on this external excitation signal are the same as the limits on the potentiostat as outlined in Section 1.1.1.

This input simply requires a cable with a banana plug on one end and the other end attached to the voltage generator. The circuit is completed by plugging the common of the input device into one of the **Common** jacks.

3.5 Temperature Measurement Input

The CV-27 in combination with the BAS model LC-22A Temperature Controller, auxiliary temperature probe, and connecting cable, can be used to display and monitor the temperature from the electrochemical cell. The proper connection of these units is shown in Figure 3.6.

Note the LC-22A is a temperature controller and as such can provide power to heat up auxiliary heater units such as a knife heater, heating mantle, etc., and will control that temperature to ±0.1°C.

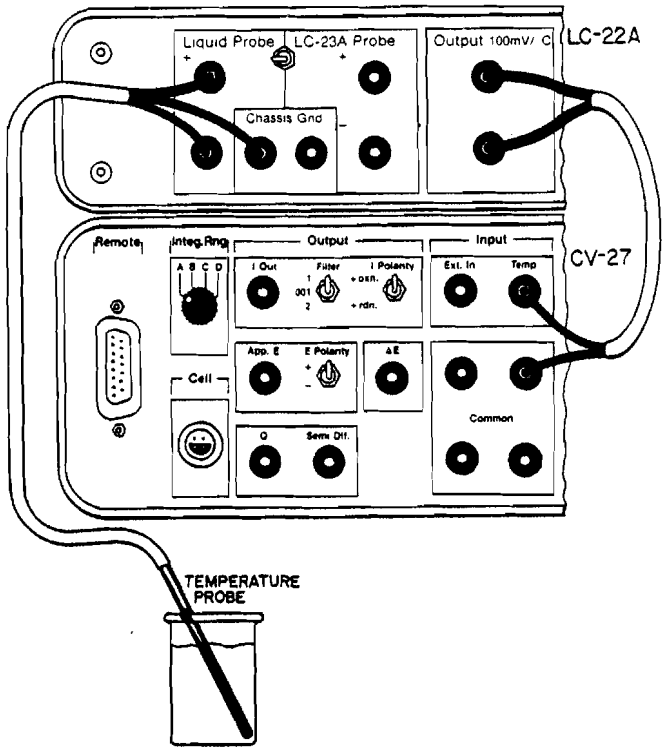


Figure 3.6
Connection of the CV-27 to the LC-22A Temperature Controller and Liquid Temperature Probe

3.6 Remote Timing Input

The following Operational Modes can be controlled remotely:

Cell (on/off)
Scan (on/hold)
E1 (on/standby)
E2 (on/standby)
Scan Direction (pos/neg)
Integrate (on/off)
Reset (on/off)

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Any contact closure to ground will activate these functions.

The connector is attached to the rear panel as shown in Figure 3.7, and the pin designations are as follows:

Operational Function	Low/ High	Pin	Color Code
Digital ground		1	Black
Scan	on/hold	2	Brown
Cell	on/stby	3	Red
E2	on/hold	4	Orange
E1	on/hold	5	Yellow
+ DIR	on/off	6	Green
- DIR	on/off	7	Blue
INTG	on/hold	8	Violet
RESET	on/hold	15	White

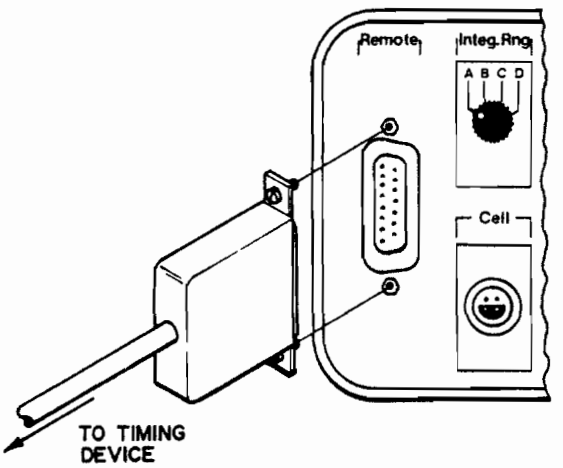


Figure 3.7
Connection of Remote Control Input

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Section 4.0 Operation

This section describes the actual operation of the controls and outputs of the CV-27.

4.1 Identification of Controls/Outputs

4.1.1 Front Panel

The front panel switches and display are used for both control and operation functions of the CV-27. The front panel is shown in Figure 4.1.

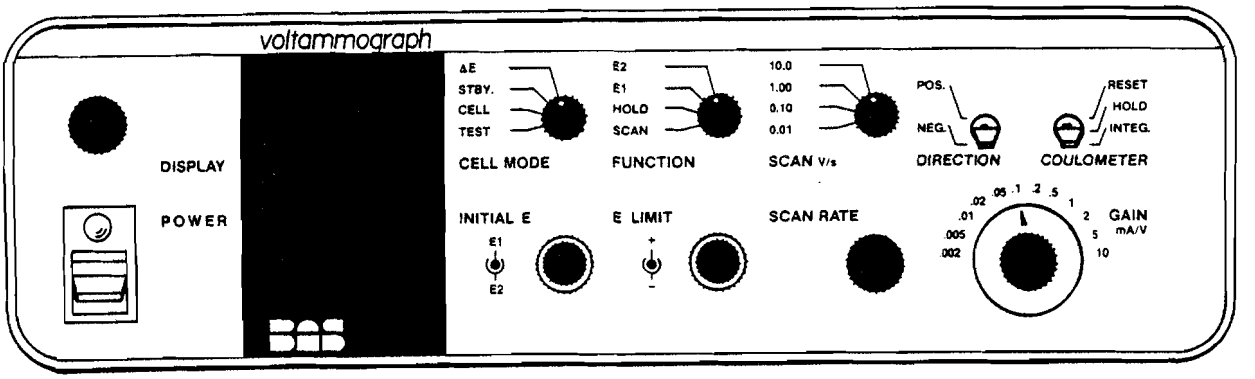
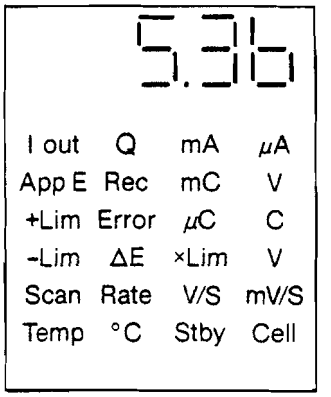


Figure 4.1
Front Panel of CV-27

4.1.1.1 POWER

This switch applies main electrical power to the instrument circuitry. When this switch is pushed up, a small red lamp directly above the switch will become illuminated indicating that power is being supplied. When turning on (or off) the main power, make certain the **CELL MODE** switch, which is discussed in Section 4.1.11, is in the standby, **STBY**, position.



4.1.1.2 DISPLAY

The **DISPLAY** knob is used to choose the function displayed on the meter. There are eight functions that can be shown using this knob. There are a total of 20 indicators (function, status, and functional units) in the display log. The display brightly illuminates the function that is being monitored on the meter.

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Upon switching the display knob to a new position, the new function is brightly lighted but the other functions are dimly lighted, and fade out to dark after approximately 5 seconds. Thus, the operator knows how many switch positions the knob must be advanced to access the desired function.

The display functions are as follows:

I out* is the output current in milliamperes, **mA**, or microamperes, **uA**.

App E is the applied potential in volts, **V**. This potential reading could be control information or output information depending on the **FUNCTION** chosen. The **FUNCTION** control will be described in a following section.

+ Lim is the most positive (this could be a negative number) potential (i.e. positive limit) in volts, **V**, at which the potential scan is reversed from positive going to negative-going.

-LIM is the most negative (this could be a positive number) potential in volts, **V**, in which the potential scan is reversed from negative-going to positive-going. If the **+ Lim** is set more negative than the **- Lim**, two display indicators are illuminated, **Error** and **XLim**. The corrective measure is to adjust either the **- Lim** or the **+ Lim** until the **Error** and **XLIM** lamps shut off.

Scan Rate is the change of the applied potential with time in units of volts/seconds, **V/S**, or millivolts/second, **mV/S**.

Temp is the temperature in **°C** as monitored through the LC-22A Temperature Controller and the "Liquid Probe" transducer.

Q is the charge output in microcoulombs, uC, millicoulombs, **mC**, or coulombs, **C**.

*CAUTION: Current values exceeding 120 mA may cause instability in the instrument, e.g. oscillations or loss of potential control.

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REC is the full scale recorder range for the coulometer in appropriate numerical values of **uC**, **mC**, or **C** per volt, **V**. This is adjustable by a rear panel rotary switch (see section 4.1.2.1.) and the **GAIN** control (see section 4.1.1.8).

4.1.1.3 INITIAL E

The **INITIAL E** is a dual function knob used to vary or adjust two potentials, **E1** and/or **E2**. The application of one or the other of two fixed potentials are numerous and will be discussed in greater detail throughout the following applications section. **E1** is adjusted with the outside knob and **E2** is adjusted with the inside knob. To set **E1**, the **FUNCTION** switch is set at **E1**, and the **DISPLAY** is set to **App E**. Simply turn the outside knob until the desired value, between -5.00 V and +5.00 V, is shown in the display window. **E2** is set in the same manner except the **FUNCTION** switch is set to **E2**, and the inside knob is turned to adjust to the desired potential.

4.1.1.4 E LIMIT

The **E LIMIT** is a dual function knob used to adjust the most positive and the most negative potential scan limits. This function is primarily used in the technique of cyclic voltammetry. The **+ Limit** is set by selecting the **+ Lim** function in the display window and turning the outside **+** knob. This value can be between -5.00 V and +5.00 V but not less than the negative limit, **- Lim**, potential. If the limits cross and an error signal (**Error**, **XLim**) is shown in the display window, then either **+ Lim** must be made more positive or **-Lim** must be made more negative. The negative limit is adjusted in the same way as the positive limit except the **- Lim** must be selected as the display function and the inside knob is turned to adjust to the required value between -5.00 V and +5.00 V.

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4.1.1.5 SCAN V/s

The **SCAN V/s** switch is used to choose the order of magnitude of the potential scan rate. One of four positions can be chosen: the **0.01** position for scan rates from 0.1 to 10.0 mV/s, the **0.10** position for scan rates from 10.0 to 100.0 mV/s, the **1.00** position for scan rates from 0.10 to 1.00 V/s, and the **10.0** position for scan rates from 1.0 to 10.0 V/s. The magnitude of the scan rate is controlled by the **SCAN RATE** knob discussed in the following section, 4.1.1.6.

4.1.1.6 SCAN RATE

The **SCAN RATE** knob is a variable adjust control for setting the scan rate between the limits set by the **SCAN V/s** switch. The CV-27 is adjusted to the desired scan rate as follows: 1) the **SCAN RATE** function is selected in the display window by the **DISPLAY** knob, 2) the correct relative magnitude of the scan rate is chosen by the **SCAN V/s** control switch as described above in Section 4.1.1.5, 3) and finally the **SCAN RATE** knob is turned until the desired value is observed in the display window.

4.1.1.7 DIRECTION

This toggle switch determines the potential scan **DIRECTION**, either positive-going direction, **+**, or negative-going direction, **-**. This switch can change the direction of the scan at any time. It can determine the initial direction setting or change the direction during an experiment. The direction is indicated by either a + or a -, on the **Scan Rate** display.

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4.1.1.8 GAIN mA/V

This switch implies two functions to the CV-27 user; the current to voltage conversion and the amplification factor. The **GAIN** mA/V control is a 12 position switch indicating current-to-voltage conversion in milliamperes of current per volt (mA/V) of output. The actual current is shown in the display when the **I Out** function is selected. Note that the value read in the display is not the voltage at the rear panel output jacks but the actual current in the appropriate units.

4.1.1.9 COULOMETER

This switch controls the current integrating function of the CV-27. There are three positions for this toggle switch. The **RESET** position clears or resets the integrator to zero at the beginning of an experiment. **RESET** is a momentary contact position and must be held in position for approximately 1 second to be assured that all 4 integrators are cleared. The **HOLD** position maintains the values on the integrators. The **INTEG** position starts the summing function.
(See Appendix A for operation)

4.1.1.10 FUNCTION

The **FUNCTION** switch can be thought of as both an operation and a control switch. When the electrodes (cell) are connected to the CV-27 electronics and the experiment is to begin, the user can start the potential scanning function by turning this rotary switch to the **SCAN** position. The switch will also stop and hold at a desired potential by turning to the **HOLD** position. The initial potential conditions can be reestablished by turning to the **E1** position or the potential can be stepped from an initial **E1** value to a second **E2** value by turning the switch to **E2**.

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4.1.1.11 CELL MODE

Rotating this knob to **CELL** connects the electrodes to the CV-27 electronics, and turning the knob to **STBY** disconnects the cell from the electronics. The **TEST** position connects an internal "dummy cell" to the electronics. This is used for testing the electronics of the unit. Section 5.2 will discuss this function in greater detail. The **E** function is used for potentiometric measurements. When the knob is in this position, the potential difference between the reference electrode and the working electrode is displayed.

4.1.2 Rear Panel

The rear panel is used primarily for connection to external devices for input, recording, and power. There is also one control function. This section describes the functions of the components found on the rear panel of the CV-27.

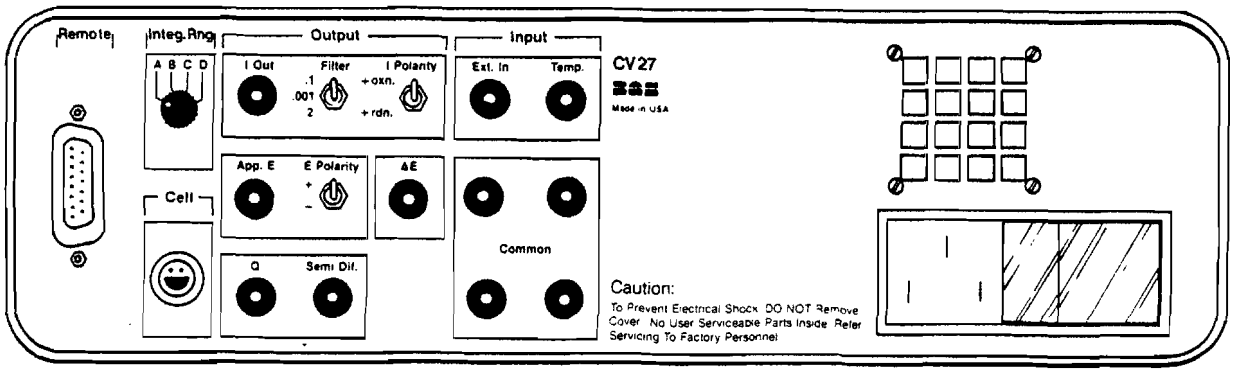


Figure 4.2
Rear Panel of CV-27

4.1.2.1 Integ. Rng

This four position rotary switch is used to select the appropriate integrator range, **Integ. Range.** The **A, B, C,** and **D** settings simply selects one of the four integrators available. The appropriate selection depends on the current generated and the time of the experiment.

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4.1.2.2 Cell

The cell cable connector simply is pushed into this fitting to make contact between the cell and the electronics. When inserting this connector make certain of the correct orientation to prevent damage. See section 3.2.1 for additional installation instructions.

4.1.2.3 Output

There are multiple outputs available on the CV-27 unit. The choice of output will depend on the particular electrochemical experiment and the response desired. The output is selected by plugging the green plug of the recorder cable into the appropriate jack. Complete the circuit by plugging the black plug into any of the common jacks.

I Out is the voltage from the current-to-voltage converter and gain control on the front panel. The voltage is directly proportional to the current being generated by the electrochemical reaction. The conversion factor is the gain setting on the front panel.

The **Filter** is a passive RC network with time constants of 0.1, 0.001, and 2 seconds. The amount of electronic dampening chosen by this three position toggle switch depends on the particular electrochemical experiment under investigation. Fast, pulse type experiments usually require a fast (small) time constant whereas a slow scanning or DC experiment allows for a longer (large) time constant.

I Polarity allows the user to change the polarity of the output current signal. The **+ Oxn.** is a positive-going signal for an oxidation reaction occurring at the working electrode; **+ Rdn.** is a positive-going signal for a reduction reaction. To conform with electrochemical convention, **+Rdn** would be selected.

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App. E monitors the actual applied potential and is commonly used to drive the X-axis on the conventional I vs E plots on X-Y recorders. The **E Polarity** toggle switch allows the choice of output polarities from the **App.E** jack. The **+** position is normal polarity; when toggled to the **-** position, the output is inverted.

E is the equilibrium potential of the working electrode relative to the reference electrode.

Q is the integrator output. Note that this output is dependent on the choice of **Integ. Rng** and the current **GAIN** on the front panel. The actual range for a full scale deflection on the recorder is displayed on the front panel display when **Rec** is chosen by the display indicator.

SEMI DIF is the semi-differential output of the current response. This feature helps resolve closely overlying peaks and eliminates some noise. The amount of filtering and the polarity can be changed using the **Filter** toggle switch and the **I Polarity** toggle switch.

4.1.2.4 Input

There are two jacks in the input section of the rear panel. One, the **Ext. In** plug, is used to connect an external voltage to be summed with the potential on the potentiostat. The other, **Temp.**, monitors a voltage that corresponds to the temperature at a liquid probe. This voltage signal must be from the BAS LC-22A Temperature Controller.

4.1.2.5 Power Cord

The power cord connector allows the unit to be used with multiple input voltages (100 V, 120 V, 220 V, 240 V), and provides power line filtering. The female end of the power cord is simply inserted into the power cord connector, making certain the pins are properly aligned. See Section 3.1 for additional information on the power cord connection and requirements.

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Section 5.0 Maintenance and Service

This section describes general maintenance, electronic troubleshooting, and service procedures for the CV-27.

5.1 Cautions and General Maintenance

This is a very rugged instrument which, with proper care, should give years of service. Following is a brief list of precautions and general maintenance considerations that will extend the lifetime of the instrument.

Follow customary good laboratory practices.

Clean all spills, especially salt solutions, from on or near the cabinet immediately.

Avoid placing the unit in a corrosive atmosphere.

Make sure the **CELL MODE** switch is in **STBY** position whenever making cell changes.

Avoid dropping, shaking, and other forms of mechanical abuse, since this could loosen components or subassemblies.

5.2 Electronic Troubleshooting

This section specifically describes procedures to isolate suspected electronic failure. Each major section of the instrument will be tested. The unit has a built-in "dummy cell," to assist in the testing procedures described below.

Equipment required:

Voltmeter (DVM, 3 1/2 digit is sufficient)

Stop Watch (optional)

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Initial setup conditions:

Rear Panel:

Plug DVM into **App. E** output jacks.

App E polarity to "+" position.

Filter to "0.001"position.

I Out polarity to "+ oxn" position.

Front Panel:

DISPLAY to monitor **App E**

CELL MODE in **STBY** position

Potentiostat test:

Turn **FUNCTION** knob to **E1** position

Turn **INITIAL E, E1** knob both fully clockwise and counterclockwise. The LED display and DVM should monitor a range of > +5.00 to < -5.00 V. The difference between the display and the DVM values should be ± 1% of the value.

Turn **FUNCTION** to **E2** and manually scan the potential range of **E2** by turning the **INITIAL E, E2** knob fully clockwise and counterclockwise. Monitor as above.

Before proceeding further, adjust **E2** to -1.00 V and then turn **FUNCTION** knob to **E1** and adjust **E1** to +1.00 V.

Current-to-voltage converter test:

Connect DVM to **I Out** jack in rear panel.

Turn **GAIN mA/V** to **10** position.

Turn **CELL MODE** to **TEST** position.

Check the current-to-voltage converter by comparing the values from the DVM to those shown in Table 5.1 for the various **GAIN** and **App E.**

Table 5.1

Troubleshooting Current-to-Voltage Converter (I Out) and Logarithm of absolute current value (Log/I/).

App E (E1)	GAIN (mA/V)	I Output (V ± 2%)	Log/I/, (V ± 5%)
+1.00	10	0.10 (±5%)	-2.0
+1.00	5	0.20	
+1.00	2	0.50	
+1.00	1	1.0	-1.0
+1.00	.5	2.0	
+1.00	.2	5.0	
+1.00	.1	10.0	0.0
+0.10*	.1	1.0	-1.0
+0.10*	.05	2.0	
0.10*	.02	5.0	
0.10*	.01	10.0	0.0
+0.020*	.01	2.0 ± 10%	
+0.020*	.005	4.0 ± 10%	
+0.020*	.002	10.0 ± 10%	0.0
†	10	0.01	-3.0
†	10	0.001	-4.0

*This should be adjusted using the DVM because of the ± 10 mV resolution of the DISPLAY value.

†Adjust App E to give the desired I output in these steps.

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Semi-Differential test:

Turn the **GAIN** to **0.1**

Turn **FUNCTION** knob to **E2** (which should be -1.00 V).

The **Semi. Dif.** should read ≈ +1.1 V on the DVM (this reading may take a while to settle).

Filter test:

Move the **DVM** to the **I out jack** and note the reading ≈ -10 V.

Flip the **Filter** toggle switch on the rear panel to **0.1** seconds; the DVM value will change but return to the previous reading.

Flip this switch to **2.0** seconds, again, the value should change but return to the previous reading.

Return the toggle to **0.001** second position.

I Out Polarity test:

Flip **I Polarity** to **+ rdn** and the output should change polarity from -10 V to +10 V (within ±5 mV of previous reading.

Return switch position to **+ oxn** position.

E Output Polarity test

Move the **DVM** to the **E out jack** and note the reading.

Flip the **E Polarity** switch. You should read the same magnitude in the opposite polarity ±1 mV.

Scan Rate test:

Turn **DISPLAY** to **+ Lim**

Adjust to +1.00 V by turning the "+" knob of the **E LIMIT** knob.

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Turn **DISPLAY** to **- Lim.**

Adjust to -1.00 V by turning "-" knob of the **E LIMIT** knob.

Turn **DISPLAY** to **Scan Rate.**

Turn **SCAN V/s** knob to **0.10 V/s** position.

Turn **Scan Rate** knob until 100 mV/s is displayed in readout.

Turn **DISPLAY** to **App E** position.

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The **App E** should be changing with time and should not exceed the ± 1.00 V limits. Toggle the **DIRECTION** switch a few times to make certain the scan direction changes appropriately.

Turn the **FUNCTION** knob from **SCAN** to **E1** position.

Adjust **E1** to + 1.00 V.

Toggle **DIRECTION** switch to **NEG.**

Check the actual scan rate by simultaneously turning the **FUNCTION** knob to the **SCAN** position and starting a stop watch. Monitor the **App E** in the display and as the **App E** value crosses 0.00 V, stop the watch. This time should be approximately 100 seconds (i.e. 1.00 V scan range at 10 mV/s rate = 100 seconds).

Turn **FUNCTION** knob to the **HOLD** position.

Coulometer test:

Turn **FUNCTION** knob to **E1.**

Adjust **E1** to 1.00 V.

Turn **CELL MODE** knob to **TEST** position.

Turn **GAIN mA/V** knob to **1.**

Turn **DISPLAY** knob to **Q** position.

Hold the **RESET** position of the **COULOMETER** switch for approximately 1 second to clear the integrators.

Turn Recorder Range, **Integ. Rng** switch (on rear panel) to the "**C**" position.

Simultaneously, start a stop watch and flip the **COULOMETER** switch to the **INTEG.** position.

The rate of increase of charge of 1 mC/s will be shown in the LED display. Thus after, for example, 30 seconds, 30 mC should be showing on the display and 0.30 V will be the output from the **Q** jack on the rear panel.

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The other three integrators, (A, B, D) can be tested in a similar fashion. Table 5.2 gives some typical values for the other integrators including the appropriate output, "Q", values.

Table 5.2

Troubleshooting Coulometer

App E (V)	Integ. Rng	GAIN (mA/V)	(mC/s)	TIME (Sec)	mC* after	Q* OUTPUT Volts
1.00	C	1	1	100	100.0	1.0
0.10	B	1	0.1	100	10.00	0.10
1.00	A	10	0.1	10	10.00	1.0
1.00	D	0.1	1	100	100.00	1.0

*An error of ±5% is not unreasonable, it can be greater if the App E is not set to ±2 mV.

Section 5.3 Service Procedure

There are no user serviceable parts in this unit and all service requests should be referred to BAS service personnel. In certain cases, BAS will provide electronic schematics and extended electronic service procedures to qualified electronic maintenance facilities, but only upon written request to the BAS Service Coordinator.

If a problem arises and appears equipment oriented, call BAS at (317) 463-4527 and ask for Customer Service. The operator will route you to the Service personnel. Be prepared to give the following information:

1. Model number of the instrument
2. Serial number of the instrument
3. Approximate date of purchase
4. Description of the problem in detail, including reference to specific errors made by your unit in the above tests.

If the Service personnel can not resolve your problems, he/she will take your name, institution, address, and phone number and forward the above information to the Service Coordinator. The Service Coordinator will work with you to get a satisfactory answer to your service problem. He/she has other, more specific, technical personnel available to him/her to solve all problems, i.e. electronic problems will be directed forward to electronic engineers, chemical problems to staff chemists, etc. If required, a person from one of these departments will call you back and further discuss your problem.

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All correspondence and shipments should be sent to

Bioanalytical Systems Inc.
2701 Kent Avenue
Purdue Research Park
West Lafayette, IN 47906 USA

Items being returned for service must clearly show the CS# on the outside of the package.

Service will normally be completed and the unit returned to you within 10 working days.

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Section 6.0 Cyclic Voltammetry

6.1 Principles

In cyclic voltammetry the potential is scanned linearly from an initial value, E_i, to a second value and then back to E_i (or some other potential). This potential excitation signal is illustrated in Figure 6.1 for a scan from 0 to +0.8 to -0.4 V vs a reference electrode (i.e. SCE, Ag/AgCl). One or more potential cycles can be performed, hence the term "cyclic" voltammetry. Figure 6.2 illustrates the current response signal obtained when the potential excitation signal in Figure 6.1 is applied to a Pt electrode immersed in 1.0 mM Fe^{2+}, 1 M H_2SO_4. As the potential is scanned positively, anodic current occurs when the electrode becomes a sufficiently strong oxidant to oxidize Fe^{2+} to Fe^{3+}. The anodic current increases rapidly until the concentration of Fe^{2+} at the electrode surface approaches zero, causing the current to peak. The current then decays at a $t^{-\frac{1}{2}}$ rate as the solution surrounding the electrode is depleted of Fe^{2+} due to its electrolytic conversion to Fe^{3+}.

The scan direction is switched to negative at +0.8 V for the reverse scan. When the electrode becomes a sufficiently strong reductant, Fe^{3+}, which has been accumulating adjacent to the electrode, can now be reduced back to Fe^{2+}. This causes cathodic current, which rapidly increases until the surface concentration of Fe^{3+} approaches zero. The current then peaks and decays as the solution adjacent to the electrode is depleted of Fe^{3+}. The first cycle is completed when the potential reaches 0.0 V.

In summary, Fe^{3+} is electrogenerated from Fe^{2+} in the forward scan as indicated by the anodic current. In the reverse scan this electrogenerated Fe^{3+} is reduced back to Fe^{2+} as indicated by the cathodic current. Thus, cyclic voltammetry is capable of rapidly generating a new species during the forward scan and then monitoring its fate on the reverse scan.

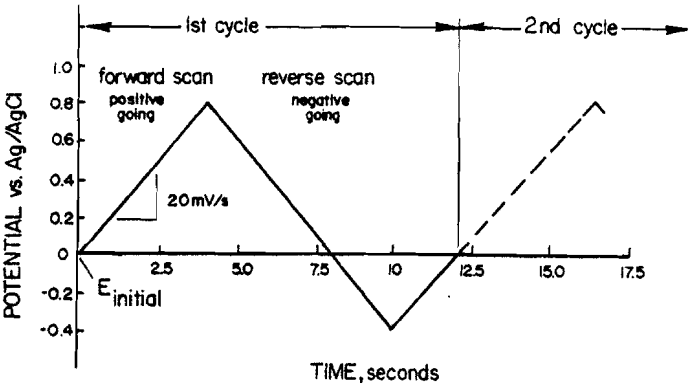


Figure 6.1
Triangular waveform for cyclic voltammetry.

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The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (i_{pa}), the cathodic peak current (i_{pc}), the anodic peak potential (E_{pa}), and the cathodic peak potential (E_{pc}). One method for measuring i_p involves extrapolation of a baseline current, as shown in Figure 6.2.

A redox couple in which both species are stable and rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. The formal reduction potential (E°') for a reversible couple is centered between E_{pa} and E_{pc}:

$$E^{\circ\prime} = \frac{E_{pa} + E_{pc}}{2} \qquad (6.1)$$

The number of electrons transferred in the electrode reaction (n) for a reversible couple can be determined from the separation between the peak potentials:

$$E_p = E_{pa} - E_{pc} = \frac{0.058}{n} \qquad (6.2)$$

Thus, a one-electron process, such as the oxidation of Fe^{2+} to Fe^{3+}, should ideally exhibit a E_p of 0.058 V.

The peak current for a reversible system is described by the Randles-Sevcik equation for the forward sweep of the first cycle:

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \qquad (6.3)$$

where i_p = peak current, amperes
n = electron stoichiometry, eq/mol
A = electrode area, cm^2
C = concentration, mol/cm^3
v = scan rate, volts/second

According to this equation, i_p increases with $v^{\frac{1}{2}}$ and is directly proportional to concentration.

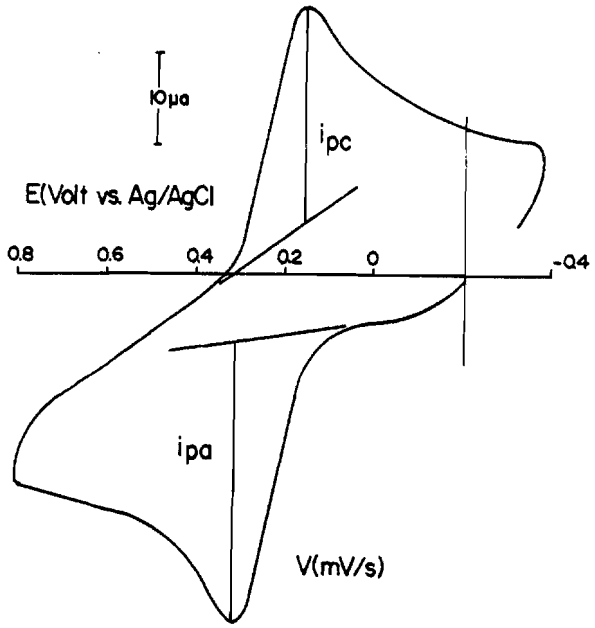


Figure 6.2
Typical Cyclic Voltammogram showing method of extrapolating baselines and determining peak currents.

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For a reversible couple, i_{pa} is approximately equal to i_{pc}, or

$$\frac{i_{pa}}{i_{pc}} \cong 1 \qquad (6.4)$$

One of the most useful aspects of cyclic voltammetry is its application to the qualitative diagnosis of homogeneous chemical reactions that are coupled to the electrode surface reaction. An example of this is the electrochemical oxidation of thyronine. A cyclic voltammogram is shown in Figure 6.3.

A positive potential scan initiated at 0.0 V gives anodic current (peak A) due to oxidation of thyronine to thyronine quinoid cation, some of which reacts with H_2O to form quinone (Q) and tyrosine. The tyrosine produced can then be oxidized at the more positive potential, peak B. Additionally, the chemically formed Q is reduced in peak C to p-hydroquinone (H_2Q), which is oxidized at peak D in the forward scan of the second cycle.

6.2 Typical Applications

Cyclic voltammetry is commonly used as the initial electrochemical technique to characterize a redox system. The redox couples are typically located by potential scans encompassing the entire accessible potential window. The scan range is then narrowed for the study of a particular couple.

CV is used extensively to determine E°' values by means of Equation 6.1 and n values by Equation 6.2. Frequently, the value of n cannot be determined due to contribution to E_p from slow electron transfer. In such cases, Equation 6.1 is also not strictly applicable, although useful estimates of E°' can be obtained. Typically v (scan rate) is varied over a wide range to determine the applicability of Equations 6.1 and 6.2 (i_p a $v^{\frac{1}{2}}$).

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Many electrochemical reductions/oxidations generate an intermediate which rapidly reacts with components of the medium. One of the most useful aspects of CV is its application to the qualitative diagnosis of these homogeneous chemical reactions that are coupled to the electrode surface reaction. CV provides the capability for generating a species during the forward scan and then probing its fate with the reverse scan and subsequent cycles, all in a matter of seconds or less, since the time scale of the experiment is easily adjustable over several orders of magnitude by changing the scan rate. An example of the qualitative use of CV to elucidate an electrode mechanism is described above for thyronine (Figure 6.3).

A collection of CV Notes has been provided with the CV-27 Voltammograph. These introduce several practical examples.

6.3 Practical Considerations

A conventional way to measure i_p is by extrapolation of a baseline current as shown in Figure 6.2. The establishment of a correct baseline is important for the accurate measurement of peak currents. This is not always easy, particularly for more complicated systems. An alternative method involves obtaining a voltammogram of the supporting electrolyte alone and using the residual current at the appropriate potential as the baseline.

In most experiments, little additional information is gained by cycling the potential more than 2 or 3 times.

A lowpass filter is often employed to minimize unwanted noise. However, filtering must be done with caution or distortion of the voltammogram may result. Too large a filter time constant will cause attenuation of the peak current and an apparent shift in the peak potential. The criterion used to relate the maximum time constant [RC, s] of the filter to a

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given scan rate [v, V/s] for minimal signal distortion is:

$$2 \quad RC \quad \frac{1}{40\ nv} \qquad [1]$$

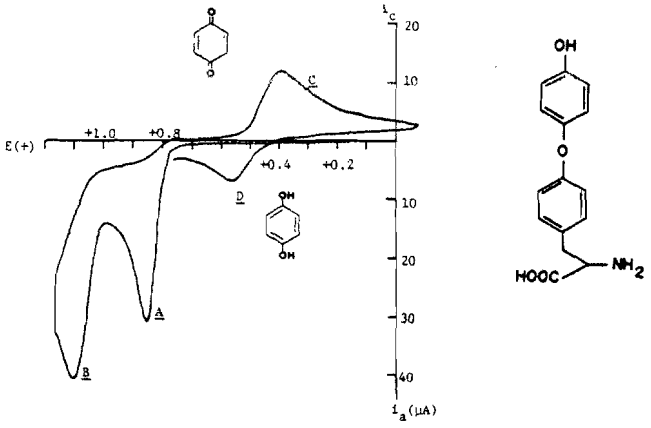
Following Equation 1 will cause less than 1% distortion as determined by Fourier Transform Analysis.

The criterion was tested with a BAS CV-27 Voltammograph at time constants of 0.1 s and 0.001 s. According to Equation 1, the maximum scan rate that may be used with a 0.1 s time constant is 40 mV/s. Superimposed voltammograms for the reversible one-electron oxidation of ferrocene at a scan rate of 40 mV/s obtained with each of the filters are shown in Figure 1. The data show that the peak height is slightly attenuated and the peak potential is shifted a few millivolts with the 0.1 s time constant filter. The distortion is insignificant for most studies.

Voltammograms obtained at a scan rate of 100 mV/s [Figure 2] with each of the filters is shown for comparison. There are significant differences between the voltammograms at 100 mV/s, both in the peak current and the peak potential.

The data demonstrate that adherence to Equation 1 results in voltammograms with maximum signal-to-noise and minimal distortion. The further the deviation from the condition given by Equation 1, the more pronounced the distortion will be.

The frequency response requirements must also be applied to the recording device. Scan rates of 10-200 mV/s are typically used when the recording device is an X-Y recorder. Faster scan rates are possible with computer or oscilloscope displays. Scan rates greater than 100 V/s are generally impractical because of iR drop and large charging current.



POTENTIAL, V vs. Ag/AgCl
Figure 6.3
Cyclic Voltammogram of Thyronine at a glassy carbon electrode.

A: $2e^-$ oxidation of thyronine producing p-benzoquinone and tyrosine.
B: oxidation of the tyrosine generated from thyronine.
C: reduction of p-benzoquinone to p-hydroquinone.
D: Oxidation of p-hydroquinone produced via wave C (not present on initial positive scan).

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Peak separations greater than predicted by equation 6.2, 58/n mV, are typically caused by iR drop due to high resistance between working and reference electrodes. This is especially a problem at fast scan rates where i can be large and in non-aqueous solvents where R can be large. Also, slow heterogeneous electron exchange with the electrode can increase E_p. Thus, the use of E_p to determine n must be performed with caution.

The initial potential for a voltammogram should be chosen with care. It is important to select E_i so that its application does not initiate any electrolysis of the species of interest. For example, E_i in Figure 6.3 is 0.0 V, which does not initiate oxidation of thyronine. If an E_i of approximately +1.2 V had been used with a negative scan to 0 V as the forward scan, the application of E_i would have caused immediate oxidation of thyronine before the voltammogram was recorded. If this occurs unknown to the experimenter, the resulting voltammogram can be considerably more difficult to interpret. Often it is best to measure the open circuit potential (E), and select this value as E_i. Application of E_i should then give only a brief current spike to charge the double layer. A large current that decays slowly is a sure indication that application of E_i has caused electrolysis.

Always record a cyclic voltammogram on the solvent/supporting electrolyte alone to locate the potential window. This window is usually limited on the negative end by reduction of supporting electrolyte or solvent and on the positive end by oxidation of supporting electrolyte, solvent, or of the electrode itself (especially in the case of mercury). Any waves due to electroactive impurities, the formation of surface oxides on the electrode, or dissolved oxygen can be positively identified as such and not mistakenly attributed to the compound of interest.

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Section 6.4 Typical Installation/Operation

This section describes a cyclic voltammetry experiment with the redox couple ferrocyanide/ferricyanide in aqueous solution at a glassy carbon electrode.

Materials:
Equipment:
- CV-27 Voltammograph
- C-1B Cell Stand
- GCE Glassy Carbon Working Electrode
- RE-1, Ag/AgCl Reference Electrode
- RXY, Analog X-Y Recorder with leads

Sample Solution: 1.15 mM $K_4Fe(CN)_6$ in 0.1 M KNO_3
0.1 M KNO_3
Make solutions immediately prior to the experiment.

Procedure:
Instrumentation Set-up

1. Connect the "App E" output to the "Hi" or "+" input of the X-axis of the X-Y recorder.
2. Connect a "Common" output to the Lo or "-" input of the X-axis on the X-Y recorder.
3. Connect "I out" to the "Hi" or "+" input of the Y-axis on the X-Y recorder.
4. Connect a "common" output to the "Lo" or "-" input of the Y axis on the X-Y recorder.
5. Set the "Filter" switch to the 0.001 position.
6. Flip the "I Polarity" switch to "+ rdn" position.
7. Flip the "E Polarity" switch to the "-" position.
8. Plug the Cell Lead cable into the CELL jack.

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9. Zero the X and Y axis somewhere near the center of the paper using the zero position and controls for each axis. Push the DIV switch to either cm or inch (depending on the divisions on your graph paper) and the X and Y axis range to 0.1V/division.

Front Panel

1. Turn the CELL MODE switch to the STBY position.

2. Turn the POWER switch on. The red light in the switch will be illuminated.

3. Turn the DISPLAY knob to "App E".

4. Turn the FUNCTION knob to the E1 position and adjust the INITIAL E, E1 knob until the number in the display window shows -0.20 V.

5. Following the operation sequence of step 3 and 4, adjust all other experimental parameters to the pre-set numbers as in Table 6.1.

6. Turn the DISPLAY knob counterclockwise to the Appl E. position.

7. Push the DIRECTION toggle switch upward for positive scan.

8. Set the GAIN switch to the 0.050 mA/V position,

9. Place the sample solution in the glass cell and mount this on the C-1B Cell Stand.

10. Place the Ag/AgCl reference and glassy carbon working electrodes through the cell top and into the solution.

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Table 6.1

Turn Display:	Use this Control:	to set this valve:
Appl E.	a) FUNCTION Knob to E1	
	b) INITIAL E, E1 to	-0.20 V
+Lim	E LIMIT, +Knob (outer) to	+0.80 V
-Lim	E LIMIT, -Knob (inner) to	-0.40 V
Scan Rate	a) SCAN v/s Rotary Switch to	0.10
	b) SCAN RATE Knob to	20 mV/s

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11. Connect electrode leads: WHITE to reference; BLACK to working; RED to mounted platinum auxiliary electrode.

12. Degas the solution for 5 - 15 minutes. This operation has been substantially simplified with the C-1B Cell Stand which is recommended for all experiments in conjunction with the CV-27.

The experiment: Make sure the X-Y recorder is On, Pen Up, and Record-Standby switch in the Record position.

13. Turn the FUNCTION knob to the HOLD position.

14. Turn the CELL MODE knob to the CELL position. (The recorder pen will jump to the initial potential selected on the X-axis and there will be a momentary current pulse.)

15. Put the recorder pen down.

16. Turn the FUNCTION knob to the SCAN position.

NOTE: The recorder pen will start to move to the left (positive direction) at the scan rate of 20 mV/s. Notice the current response for the ferrocyanide oxidation traced on the recorder paper. The scan will continue until it reaches the positive limit of 0.80 V where the potential scan is reversed. The scan is then continued in the negative direction until the negative limit of -0.40 V is reached. On this reverse scan a cathodic current should be observed which is due to the reduction of the ferricyanide generated on the initial scan. A cyclic voltammogram for the oxidation of ferrocyanide is shown in Figure 6.4

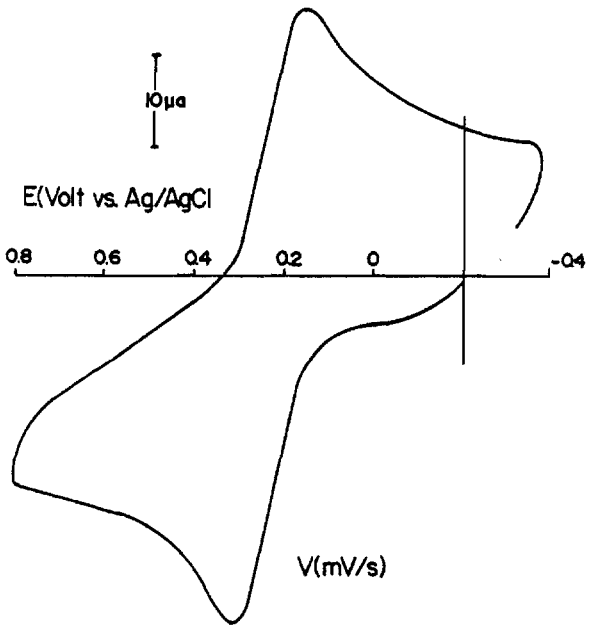


Figure 6.4
Cyclic Voltammogram of Ferrocyanide

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17. At the completion of the reverse scan, lift the pen on the recorder while turning the FUNCTION knob to HOLD to stop the experiment.

18. Remove the paper from the recorder and measure the anodic and cathodic peak current for the oxidation of ferrocyanide as illustrated in Figure 6.4

19. Gently move the working electrode up and down several times. Put a new piece of paper in the recorder and repeat steps 13 to 18 at scan rates of 50, 100, 200, 300, and 400 mV/s.

20. Calculate and tabulate the electrochemical data for the ferrocyanide oxidation at a glassy carbon electrode as in Table 6.2.

21. Plot i_{pa} vs. $V^{1/2}$. A linear plot should be observed for the oxidation of ferrocyanide as shown in Figure 6.5.

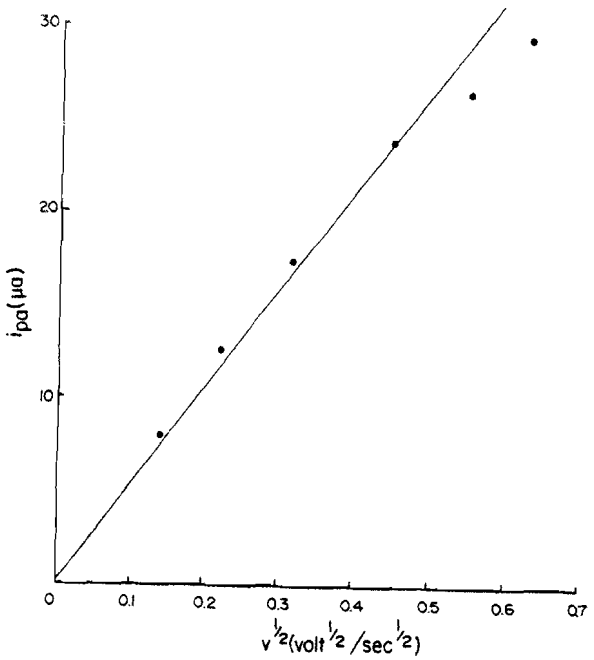


Figure 6.5
Linear dependency of peak current on the square root of scan rate for the ferrocyanide oxidation on a glassy carbon electrode.

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Table 6.2

V(mV/s)	$V^{1/2}$ $(V/s)^{1/2}$	i_{pa}(ua)	i_{pc}(ua)	i_{pc}/i_{pa}	E_{pc}(V)	E_{pa}(V)	E_p(mV)
20	0.141	8.0	7.5	0.938	0.380	0.460	80
50	0.223	12.50	12.2	0.976	0.375	0.468	93
100	0.316	17.30	15.3	0.884	0.373	0.475	102
200	0.447	33.80	21.0	0.882	0.375	0.480	105
300	0.548	26.3	22.5	0.856	0.350	0.495	145
400	0.632	29.3	25.0	0.853	0.350	0.500	150

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7.0 Chronoamperometry

7.1 Principles

In chronoamperometry the potential is stepped from an initial value, E_i, to E_f, and the accompanying current is recorded as a function of time for an electrode in an unstirred solution. If the potential is then stepped back to E_i after time T, the technique is termed double-potential step chronoamperometry. A double potential step excitation signal and a typical current response are shown in Figures 7.1 and 7.2. In a typical experiment the potential is stepped from a value at which no redox process occurs at the electrode (i = 0) to a value at which a diffusion-controlled reduction or oxidation occurs. This is illustrated on the cyclic voltammogram in Figure 7.3, for a solution containing R.

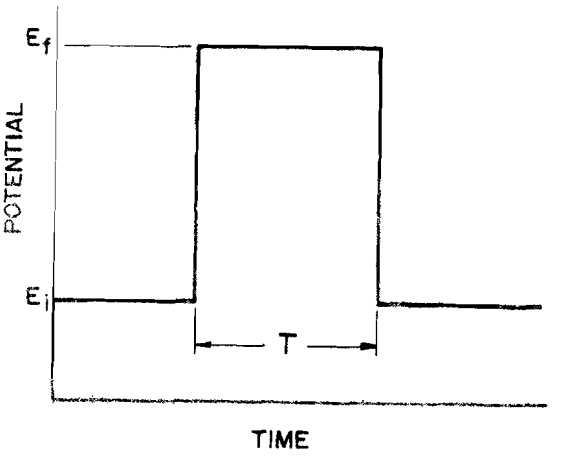


Figure 7.1
Excitation signal for double potential step chronoamperometry.

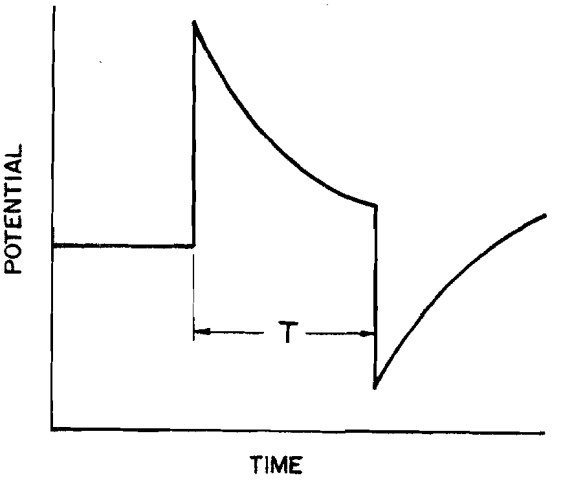


Figure 7.2
Chronoamperogram (current-time response) for double-potential step chronoamperometry.

As shown in Figure 7.3, the potential step initiates current, due to the electrolysis needed to change the ratio C_R^s/C_O^s to the ratio required by E_s. The current decays as the electrolysis proceeds to deplete the solution near the electrode of electroactive species. This current response is described by the Cottrell equation for a planar electrode

$$i = \frac{nFA\,D^{1/2}C}{\pi^{1/2}\,t^{1/2}} \qquad (7.1)$$

Where

i = current, amperes
n = number of electrons per molecule, eq/mol
F = Faraday's constant, 96,485 C/eq
A = electrode area, cm^2
C = concentration of O, mol/cm^3
D = diffusion coefficient of O, cm^2/s
t = time, s

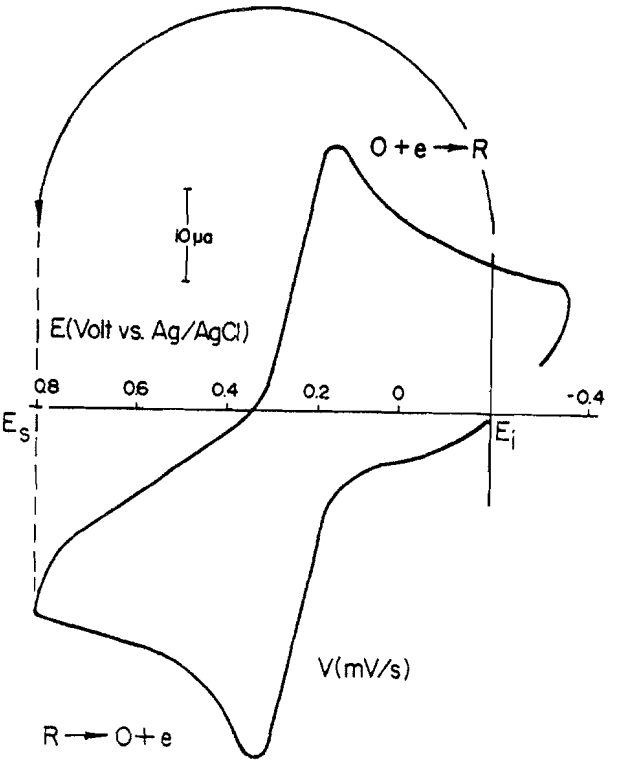


Figure 7.3
Cyclic voltammogram showing the processes occuring during chronoamperometry. E = initial potential where no oxidation occurs; E_f = final potential where oxidation procedes at a diffusion limited rate.

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7.2 Typical Applications

Chronoamperometry is commonly used to determine electrode area, A; diffusion coefficient, D; and electron stoichiometry n. These parameters are determined from the slope of an i vs. $t^{-\frac{1}{2}}$ plot, i.e. the Cottrell equation. For example, the effective electrochemical area of an electrode, A, can be determined by chronoamperometry on a system for which D and n are known, e.g. $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$ in water. Once A is known, that electrode can be used to measure values of D for other redox couples for which n is known (perhaps from thin-layer coulometry). Chronoamperometry is rarely used to measure concentration; other electroanalytical techniques have superior detection limits.

The constancy of $it^{\frac{1}{2}}$, as predicted by the Cottrell equation, is very useful to define the "time window" in which an electrochemical system exhibits the characteristics of planar diffusion. A typical plot of $it^{\frac{1}{2}}$ vs t for a simple redox system with no chemical complications is shown in Figure 7.4. The negative deviation observed at short times is often representative of the time required by the potentiostat to charge the electrode to E_s. The positive deviation at long times is typically caused by convection from slight vibrations or density gradients near the electrode surface when O and R have different densities. The approximation of planar diffusion for spherical and cylindrical electrodes is lost at sufficiently long times (typically for time greater than 1 second for a Hanging Mercury Drop Electrode, HMDE).

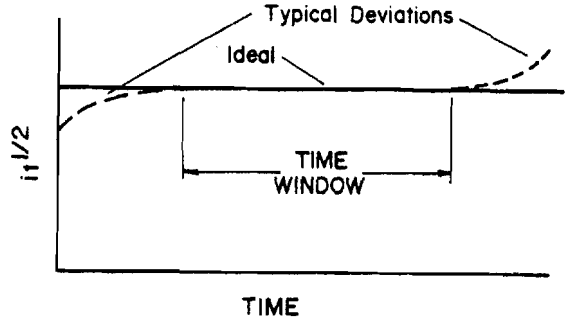


Figure 7.4
Plot of $it^{\frac{1}{2}}$ vs. t for chronoamperometry illustrating "time window" for condition of planar diffusion for an electrochemical system.

7.3 Practical Considerations

As described in Section 7.0, a cyclic voltammogram is usually recorded prior to the chronoamperometry experiment. Values for E_i and E_s are then chosen from the position of E_{pc} and E_{pa} on the potential axis. In order to reduce the

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concentration of electroactive species at the electrode surface to a value approaching zero, the potential is stepped a minimum of 100 mV beyond the appropriate value of E_p on the voltammogram. For the example in Figure 7.3, E_i would be at least 100 mV positive of E_{pa} and E_s 100 mV negative of E_{pc}. Although 100 mV is a rough guideline for a minimum potential step beyond E_p, values of 200 and 300 mV are commonly used to ensure the condition of essentially zero surface concentration of electroactive species upon which Equation 7.1 is based. However proximity to another redox couple or to background current can impose a practical limitation on the magnitude of the potential step.

Chronoamperograms are usually recorded under identical conditions on supporting electrolyte alone. The contributions from charging and residual current can then be subtracted from the experimental chronoamperogram to give a "Faradaic" current-time response for the electroactive species.

Between repetitive experiments on the same solution, initial conditions should be reestablished by 30 s of stirring followed by a 2 minute rest period to ensure solution quiesence.

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Section 7.4 Installation/Operation

This section describes a chronoamperometric experiment with ferrocyanide. This is the same system as studied by CV in Section 6.3.

Materials: see Section 6.3 except use an RY-T i.e. time or strip chart recorder.

Procedure

1. Connect the "I out" output to the "Hi" or "+" input of the RY-T recorder.

2. Connect a "common" output to the "Lo" or "-" input of the RYT recorder.

3. Set the "Filter" switch to the 0.001 position.

4. Set the "I Polarity" switch to "+ rdn".

5. Turn on the power switch of the RYT recorder. Set the time base knob to 20 cm/min and the voltage input control to the CHECK position. Zero the recorder pen at the position of one-tenth full scale deflection on the right. Reset the voltage input switch to 1 volt full scale.

Front Panel

1. Turn the CELL MODE switch to the STBY position

2. Turn the POWER switch to the ON position. The red light in the switch will be illuminated.

3. Turn the DISPLAY knob to the "Appl. E" setting.

4. Turn the FUNCTION switch to E1 and adjust E1 to -0.20 V.

5. Turn the FUNCTION switch to E2 and adjust E2 to -0.70 V.

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6. Reset the FUNCTION switch to E1.

7. Set the GAIN switch to 0.050 mA/V full scale.

8. The sample solution and the cell setup are the same as in the cyclic voltammetric experiment. Degas the solution for 5-10 minutes with nitrogen and make sure no gas bubbles adhere to the surface of the working electrode.

Experiment: Make sure the recorder is on, the pen is up, and the chart is off.

9. Turn the CELL MODE knob to the CELL position.

10. Put the recorder pen down and turn on the CHART SPEED switch of the RYT recorder.

11. Switch the FUNCTION knob from E1 to E2. The recorder pen will be immediately deflected to the left. The current spike, due to the charging of the working electrode as its potential is stepped to E2 will be followed by a slow current decay in accordance with the depletion of ferrocyanide ions near the electrode surface. After 30 sec. switch the FUNCTION knob back to the E1 position.

12. Lift the recorder pen, turn off the CHART SPEED switch and turn the CELL MODE switch to STBY position. (The recorder pen should immediately return to the preset zero position). Figure 7.5 (curve A) shows the chronoamperometric i vs. time curve for the oxidation of ferrocyanide solution at the GC electrode.

13. Disconnect the cell and electrode from the cell stand. Rinse the whole set of accessories thoroughly with distilled water before returning them to the cell stand.

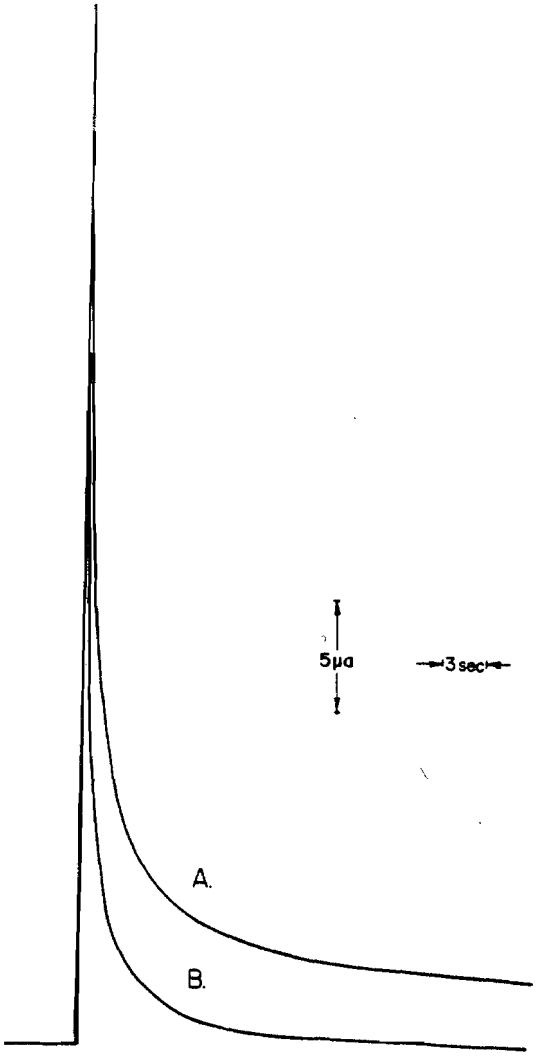


Figure 7.5
Chronoamperometric current vs. time curves on a glassy carbon electrode. E_{in} = 0, E_{final} = 0.8 Volt. Curve A, 0.2 mM ferrocyanide in 0.1 M KCl solution. Curve B, supporting electrolyte only.

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14. Place 0.1 M KNO_3 solution free of ferrocyanide ions in the cell and repeat steps 8 to 12. A current vs. time chronoamperometric curve will be traced on the recorder for the background as shown in Figure 7.5 (curve B).

15. Calculate the net current by subtracting the background from the sample current at each $t^{-1/2}$. Tabulate these i_{net}, t, $t^{-1/2}$ as well as the $i\ t^{1/2}$ produced as shown in Table 7.1

16. Plot i_{net} vs. $t^{1/2}$ as in Figure 7.6. Calculate the slope and linear correlation coefficient of this curve.

17. Using equation 7.1, calculate the electrochemical area of the glassy carbon electrode. Use $D_s = 0.63 \times 10^{-5}$ cm^2/sec.

18. Compare this number with the geometric area (0.071 cm^2).

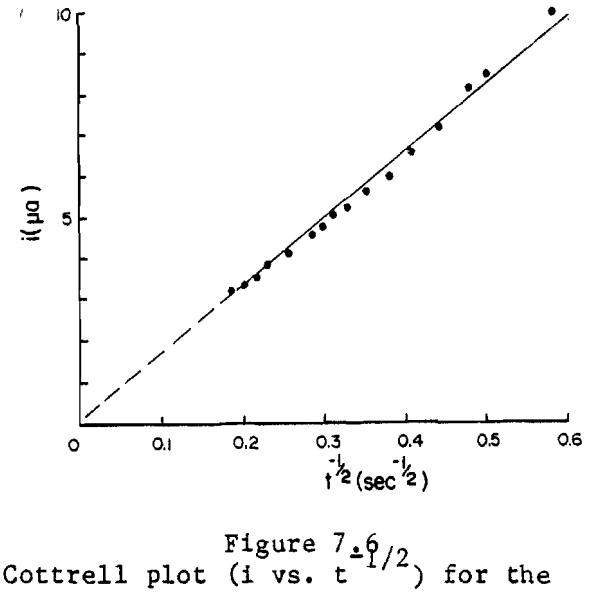


Figure 7.6
Cottrell plot (i vs. $t^{-1/2}$) for the oxidation of 0.2 mM ferrocyanide solution on a glassy carbon electrode.

Table 7.1
Chronoamperometric data for the oxidation of 0.2 mM ferrocyanide solution on a glassy carbon electrode. Potential step from E_{in} = 0 Volt to E_{final} = +0.8 Volt (vs Ag/AgCl).

TIME (sec)	$t^{-1/2}$ ($sec^{-1/2}$)	i (ua)	$i\ t^{1/2}$ (ua $sec^{1/2}$)
3	0.577	10.0	17.3
4	0.500	8.46	16.9
5	0.477	7.18	16.1
6	0.408	6.56	16.1
7	0.378	6.00	15.9
8	0.354	5.55	15.7
9	0.333	5.22	15.7
10	0.316	4.96	15.7
11	0.302	4.76	15.8
15	0.258	4.53	15.7
12	0.289	4.07	15.8
18	0.236	3.78	16.0
21	0.218	3.50	16.0
24	0.204	3.35	16.4
27	0.192	3.23	16.8

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8.0 Chronocoulometry

8.1 Principles

Chronocoulometry is chronoamperometry in which the current response to the potential step excitation signal (Figure 7.1) is integrated. The monitored response is now charge, Q.

$$Q = \int_0^t i(t)\, dt \qquad (8.1)$$

A typical chronocoulogram (Q vs. t plot) for a double-potential step excitation signal is shown in Figure 8.1. The charge recorded at a given time is from three sources

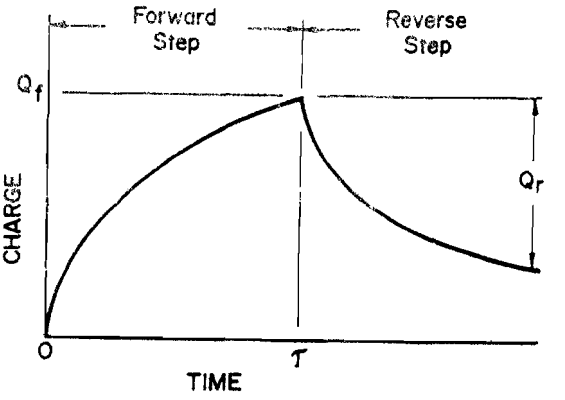


Figure 8.1
Chronocoulogram for double-potential step excitation signal. Q_f = charge for forward step, Q_r = charge for reverse step, T = duration of potential step.

total charge = diffusing component + adsorbed component + double layer charging

$$Q = \frac{2nFAC_o^* D_o^{1/2} t^{1/2}}{\pi^{1/2}} + nFA\Gamma_o + Q_{dl} \qquad (8.2)$$

where Γ_o = surface concentration of adsorbed O, mol/cm^2 and Q_{dl} = double layer charging, C (other terms identified in Eq. 7.1). A plot of Q vs. $t^{1/2}$ has an intercept equal to $nFA\Gamma_o + Q_{dl}$ as shown in Figure 8.2 for Q_f. Q_r can be plotted in an analogous manner vs. $[T^{1/2} + (t-T)^{1/2} - t^{1/2}]$ where T is the time of the reverse step.

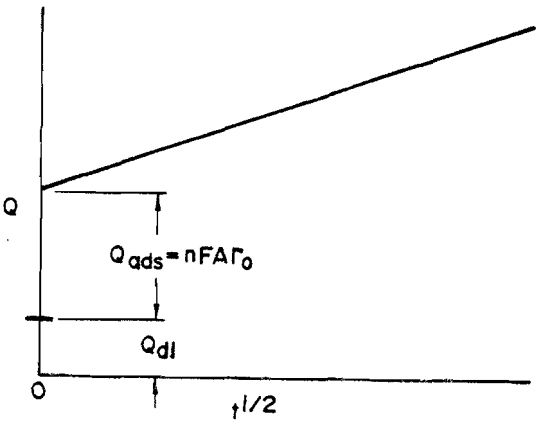


Figure 8.2
Plot of Q vs. $t^{1/2}$ for chronocoulometry equipment.

8.2 Typical Applications

Chronocoulometry is used primarily to determine surface concentrations of electroactive species adsorbed on the electrode from the intercept of the plot in Figure 8.2. The experiment is repeated in a solution containing only supporting electrolyte in order to obtain Q_{dl}, the charge for the nonFaradaic current required to change the electrode potential. Q_{dl} is then subtracted from the charge-intercept to obtain Q_{ads} from which the surface concentration, Γ_o, can be calculated.

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8.3 Practical Considerations

Since chronocoulometry is essentially chronoamperometry in which the current is integrated, the same general considerations described in Section 7.3 apply to this technique.

Additional consideration should be given to the selection of E_i and E_s. For example, obtaining chronocoulograms for a series of E_i values can give information regarding the variation in adsorption of electroactive reactant as a function of potential. Similar information can be obtained from Q_r from the reverse potential step if E_s is varied.

Sufficient time for equilibration of adsorption should be allowed between repetitive experiments.

The frequency response of the coulometer limits its application to experiment times greater than 100 ms.

8.4 Installation/Operation

This section describes a chronocoulometry experiment with ferrocyanide. This is the same system as studied by CV in Section 6.3.

Materials: See section 6.3 except use an RY-T recorder.

Procedure:

Instrument Setup, The setup procedures for chronocoulometry are identical to those for chronoamperometry except as follows:

3. Connect "Q out" to the "Hi" or "+" input of the Y-axis on the RY-T recorder.

4. Connect a "Common" output to the "Lo" or "-" input of the Y-axis on the RY-T recorder.

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Front Panel

1. Turn the CELL MODE switch to the STBY position

2. Flip the POWER switch to the ON position. The red light in the switch will be illuminated.

3. Turn the DISPLAY knob to the "Appl. E

4. Turn the FUNCTION switch to E1 and adjust to -0.20 V.

5. Turn the FUNCTION switch to E2 and adjust to -0.70 V.

6. Reset the FUNCTION switch to E1.

7. Turn the DISPLAY knob to read "Rec", set the gain switch to 0.2 mA/V, and turn the integrator recorder range switch (rotary) on the back panel to position A. The LED should display 0.2 mC at the indicator "Rec"; 0.2 mC corresponds to the full scale recorder deflection for charge.

8. The sample solution and the cell setup are the same as in the cyclic voltammetric experiment. Degas the solution for 5-10 minutes with nitrogen and make sure no gas bubbles adhere to the surface of the working electrode.

Experiment: Make sure the recorder is on, the pen is up, and the chart speed off.

9. Turn the CELL MODE knob to the CELL position.

10. Put the recorder pen down and turn on the CHART SPEED switch of the RY-T recorder.

11. RESET the integrator by momentarily pushing the switch upward.

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12. Switch the FUNCTION knob from E1 to E2 while pushing down the integrator switch to record the charge. Be sure both operations are synchronized. The recorder pen will rise slowly to the left. At t = 30 sec after the potential step, switch the FUNCTION knob back to the E1 position.

13. Lift the recorder pen, turn off the CHART SPEED and turn the CELL MODE knob to the STBY position. Reset the integrator by pushing the switch upward. (The recorder pen should immediately return to the preset zero position.) Figure 8.3 shows the chronocoulometric Q vs t curve for the oxidation of ferrocyanide at a GC electrode.

14. Disconnect the cell and electrode from the cell stand. Thoroughly rinse the whole set of accessories with distilled water before returning them to the cell stand.

15. Place 0.1 M KNO_3 solution free of ferrocyanide ions in the cell and repeat steps 8 to 12. A charge vs. time chronocoulometric curve will be traced on the recorder for the electrolyte only. This is the experimental background signal.

16. Tabulate the chronocoulometric data from the experiments with ferrocyanide and pure electrolyte solution as in Table 8.1.

17. Plot Q vs $t^{1/2}$ curves for the forward steps of both ferrocyanide and supporting electrolyte solution on the same graph paper. See the example in Figure 8.4. Calculate the slope from the Q vs t curve for ferrocyanide oxidation. Measure the double layer charge Q_{dl} from the intercept.

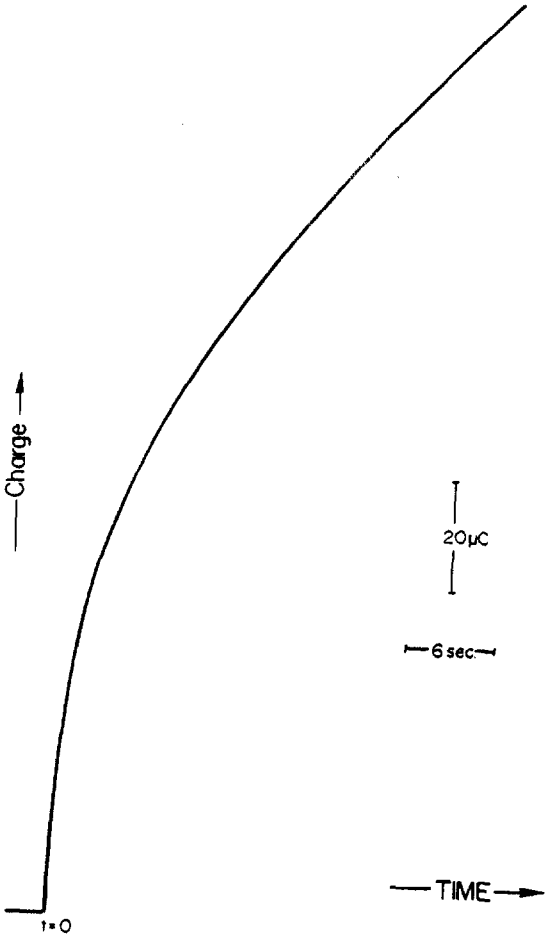


Figure 8.3
Chronocoulometric, Q vs. t, plot for the oxidation of ferrocyanide at glassy carbon electrode.

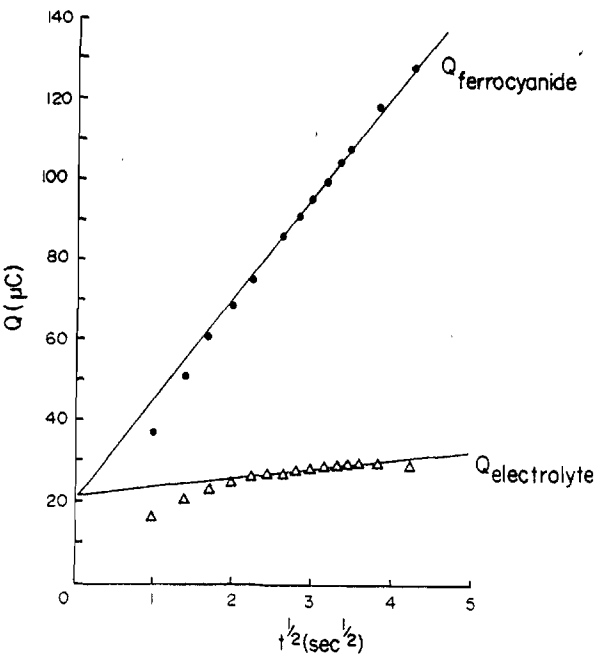


Figure 8.4
Plot of Q vs t; Anson Plot, of ferrocyanide and electrolyte.

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Table 8.1 Chronocoulometric Data for the Oxidation of Ferrocyanide and Electrolyte at a glassy carbon electrode. Potential Step from E_{in} = 0 Volt to E_{final} = 0.8 Volt (vs. Ag/AgCl).

Q_f (μC)	$Q_{electrolyte}$ (μC)	t (sec)	$t^{1/2}$ ($sec^{1/2}$)
36.6	16.1	1	1.000
51.2	20.5	2	1.414
60.6	23.2	3	1.732
68.5	24.9	4	2.000
74.8	26.2	5	2.236
80.7	27.0	6	2.449
85.8	27.6	7	2.646
90.9	27.9	8	2.828
95.4	28.3	9	3.000
100.0	28.5	10	3.162
104.9	28.4	11	3.316
107.5	28.7	12	3.464
111.4	28.8	13	3.606
118.1	29.0	15	3.873
127.9	29.0	18	4.243

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18. Using equation 8.2, calculate the electrochemical area of the glassy carbon electrode. Use $D_s = 0.63 \times 10^{-5}$ cm^2/sec.

19. Compare this number with that from the chromoamperometric experiment.

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9.0 Stripping Voltammetry

9.1 Principles

Stripping voltammetry is commonly used for the trace determination of electroactive metals because of its excellent detection limit (typically 10^{-9} ~ 10^{-10} M).

The stripping voltammetry experiment consists of two parts. During the first step, the analyte is deposited at the electrode by controlled potential electrolysis in a stirred solution. This step serves to electrochemically "extract" metal ions from solution and preconcentrate them at the electrode. In the case of many metal ions, the electrolysis product is the elemental form, which is soluble in mercury. Consequently, these analyses are commonly performed with a mercury film electrode (MFE) or a hanging mercury drop electrode (HMDE). After a sufficient amount of analyte has been deposited at the electrode, the stirring is switched off. The potential of the electrode is then scanned so that the deposited metals are electrolyzed from the mercury electrode, i.e., stripped from the electrode. This experiment is illustrated in Figure 9.1 for the determination of lead (Pb^{2+}). In this case the potential is scanned in the positive direction, which produces anodic current when Pb is stripped, and the technique is termed "anodic stripping voltammetry" (ASV). The concentration of Pb^{2+} in the sample can be determined by means of a standard curve of i_p vs. $C_{Pb^{2+}}$ from a series of standards or by means of standard addition techniques. Several metals can be determined simultaneously, if the peak potentials of their stripping waves are sufficiently resolved. In "cathodic stripping voltammetry" (CSV) the deposited analyte is stripped by means of a negative potential scan which gives a cathodic current peak.

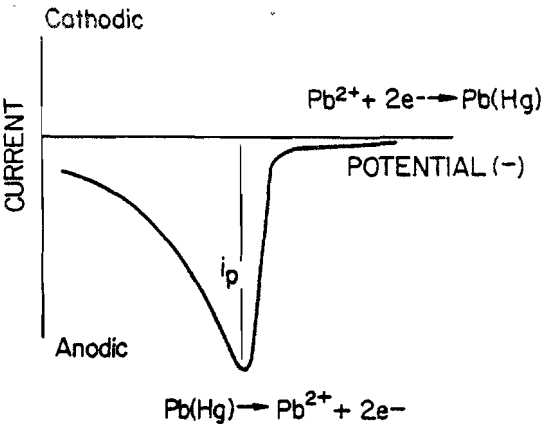


Figure 9.1
Anodic stripping voltammogram for determination of Pb^{2+}.

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9.2. Typical Applications

ASV is commonly used for the determination of metal ions at the trace level. The determination of lead (especially lead in blood) and cadmium are perhaps the most widespread applications. Other commonly determined metals are Bi, Cu, Ga, In, Sn, Tl, Zn, Sb, Ag. ASV has been used extensively for the analysis of environmental samples such as water from numerous sources. A more recent application in forensic chemistry is the detection of firearm discharge residues by the determination of Sb and Pb.

CSV procedures have been developed for a number of anions (e.g. Cl^-, Bi^-, I^-, S^{2-}, Se^{2-}, CrO_4^{2-}, oxalate) that can be preconcentrated as insoluble salts at Hg and Ag electrodes.

9.3 Practical Considerations

A general procedure for analysis by stripping voltammetry is outlined below.

(a) Deoxygenate sample/supporting electrolyte in the cell with solvent-saturated nitrogen by bubbling for 5-10 minutes.

(b) Divert nitrogen over solution to blanket cell.

(c) Activate stirring and apply deposition potential for a carefully measured time interval.

(d) Switch off stirring and allow convection to cease during a rest period (typically 10 to 60 s).

(e) Activate potential scan for stripping and record voltammogram.

It is important to reproduce parameters such as deposition time, stirring rate, rest time, scan rate, and electrode area as

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carefully as possible for a series of measurements. This ensures that the same fraction of sample is deposited at the electrode for all standards and samples.

As with all analytical methods that are capable of analysis at the trace level, contamination of the sample must be avoided. At low detection levels stringent cleaning of cell components and all glassware used for sample preparation is necessary. Pre-electrolysis of supporting electrolyte used to prepare samples and standards is usually necessary to lower the background level of metals for trace analysis.

Lower detection levels are achieved by longer deposition times that enhance preconcentration. In general, a longer deposition time is required for the HMDE compared to the MFE to achieve a given detection level.

9.4 Installation/Operation

Anodic stripping voltammetry will be illustrated in this section for the determination of Pb^{2+} and Cd^{2+}. An advanced experiment for the determination of Pb^{2+} in human hair is also described.

Materials

Equipment: CV-27 Voltammograph

C-1B Cell Stand (This apparatus is strongly recommended for this experiment as it has specifically tailored degassing/blanketing and stirring in its design).

GCE, Glassy Cabon Working Electrode.

RE-1, Ag/AgCl Reference Electrode.

RX-Y, Analog X-Y Recorder with leads.

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A timing device

Volumetric flasks: 25 mL and 100 mL

Sample Solutions:

1. 0.015 M Hg^{2+} stock solution: Dissolve 0.3 g of triple distilled mercury with several drops of concentrated nitric acid (in the HOOD) and dilute it to 100 ml with distilled water.

2. 1×10^{-4} M Hg^{2+}/0.1 M KNO_3 solution: Dilute 6.7 ml of stock Hg^{2+} solution with about 900 mL of H_2O. Add 10.1 g of KNO_3 and dilute to 1.0 L.

3. 25 ppm standard Pb^{2+} solution: Dilute 2.5 ml of Fisher standard Pb^{2+} solution (1000 ppm) to 100 ml with 0.001 M HNO_3 solution. Repeat for the 25 ppm Cd^{2+} solution.

4. 25 ppm standard Cd^{2+} solution. Dilute 2.5 ml of Fisher standard Cd^{2+} solution (1000 ppm) to 100 add with 0.001 M HNO_3.

5. 400 ppb standard Pb^{2+}/Cd^{2+} solution: Dilute 400 ul each of 25 ppm Pb^{2+} and 25 ppm Cd^{2+} to 25 ml with 1×10^{-4} M Hg^{2+}/0.1 M KNO_3 solution.

Procedure:

Instrument Set-up: Connect the CV-27 voltammograph to an X-Y recorder in the same manner as described in Section 6.3 for cyclic voltammetry.

Front Panel

1. Follow the same sequence (Steps 1 to 7) as described in Section 6.3 adjusting the exerimental parameters as shown in Table 9.1.

2. Turn the GAIN setting to the 0.020 mA/V position

Table 9.1 Experimental Conditions for the ASV of Lead and Cadmium.

DISPLAY	Controls	Pre-Set Number
Appl E.	a) FUNCTION Switch to E1 b) INITIAL E, E1 Knob to	-1.00
+LIM	E LIMIT, + Knob (outside) to	-0.1 V
-LIM	E LIMIT, - Knob (inside)	-1.20 V
Scan Rate	a) SCAN v/s switch to 0.10 b) SCAN RATE Knob to	5 mV/s

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3. Place the sample solution of Pb^{2+} and Cd^{2+} (400 ppb e.g.) and a stirring bar in the glass cell and mount this onto the C-1B Cell Stand.

4. Place the Ag/AgCl reference and glassy carbon working electrodes through the cell top and into the solution.

5. Connect electrode leads: WHITE to reference; BLACK to working; RED to platinum auxiliary electrode.

6. Degas the solution for 5-15 minutes. This operation has been substantially simplified with the C-1B Cell Stand which is recommended for all experiments in conjunction with the CV-27.

7. Stop degassing. Note: The C-1B automatically blankets the solution with a nitrogen atmosphere. Turn on the magnetic stirrer. Remember that the stirring speed must be constant throughout all experiments.

8. Turn the CELL MODE knob to the CELL position while simultaneously starting the timer.

9. At the end of the deposition time (t_d = 240 sec in this case), stop the stirring. Put down the recorder pen and wait for the solution to become stationary (this is the quiet time, t_q = 60 sec).

10. At the end of t_q, turn the FUNCTION knob to the SCAN position.

Note: 1) The recorder pen will slowly move to the left at a scan rate of 5 mV/sec. Stripping peaks will appear at E_p = -0.65 and -0.45 Volt vs. Ag/AgCl for Cd^{2+} and Pb^{2+} respectively. An actual anodic stripping voltammogram is shown in Figure 9.2. 2) The ASV experimental parameters are summarized in Table 9.2 for reference.

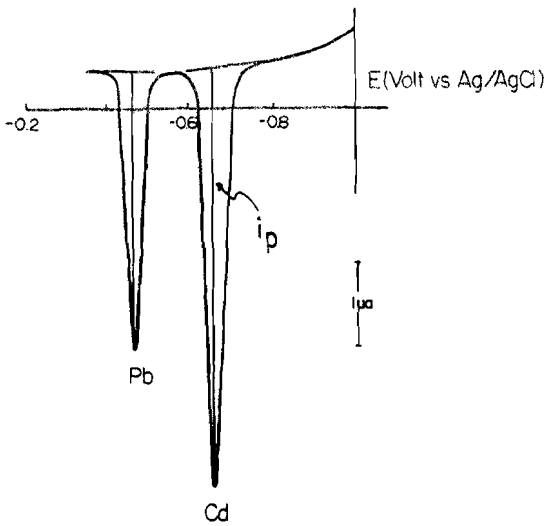


Figure 9.2

Anodic Stripping Voltammetry of 400ppb Pb^{2+} and Cd^{2+}, t_d = 240 sec., t_q = 60 sec. 0.1M KNO_3 and $[Hg^{2+}]$ = 0.1mM

Table 9.2 Stripping Voltammetric Parameters.

Stripping Voltammetric Parameters
$E_{deposition}$ = -1.0 V
t_d = 240 sec (manually timed)
tq = 60 sec (manually timed)
Scan rate = 5 mV/s.

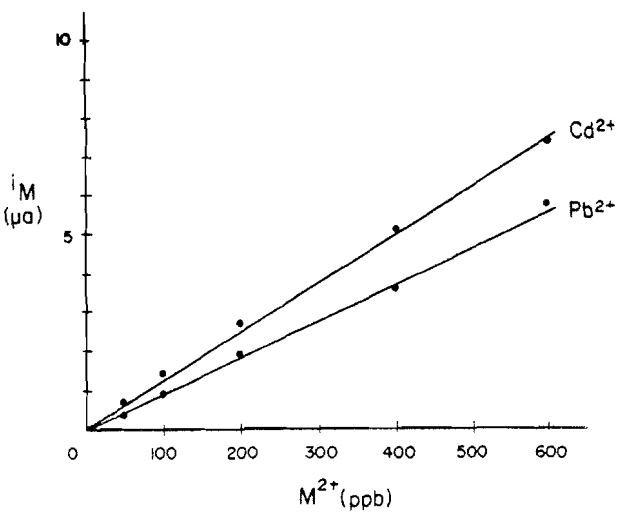


Figure 9.3
Calibration curves for the ASV determination of lead and cadmium.

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11. At the end of the potential scan, lift the recorder pen, turn on the magnetic stirrer and switch the FUNCTION knob to E2. This is preset at +1.0 V to strip all of the Hg^{2+} and other adsorbed species from the GC electrode.

12. Repeat the ASV experiment (step 6 to 11) for a series of Pb^{2+} and Cd^{2+} mixtures with 50, 100, 200 and 600 ppb concentrations.

13. For each sample solution, measure the peak heights, i_p, for Pb^{2+} and Cd^{2+} as illustrated in Figure 9.2.

14. Plot i_p vs. concentration for Pb^{2+} and Cd^{2+} (in ppb) as shown in Figure 9.3.

Honor Experiment: This appendix is included for those who want further practice in anodic stripping voltammetry. The sample is human hair, digested with concentrated nitric acid prior to the ASV analysis. The procedure is simple and can be repeated in any laboratory with minimum facilities. Quantitation is by the method of standard additions.

1. Weigh a 0.2 g hair sample into a 25 ml beaker.

2. Deliver 1 ml of concentrated HNO_3 with a disposable pipet to the beaker and cover it with an evaporating dish.

3. On a hot plate, slowly heat the beaker (IN THE HOOD) until all of the hair sample is dissolved. Continue to warm the solution to evaporate to a residue.

4. Redissolve the residue with 1 ml of dilute HNO_3 solution (0.1% V/V) and pour the solution into a 100 ml volumetric flask. Carefully rinse the beaker with distilled water and transfer the rinse solution into the flask. Dilute to the 100 ml mark.

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5. Transfer 1 ml of solution 4 to a 25 ml volumetric flask and dilute it to the mark with the supporting electrolyte (0.1 M KNO_3 with 1.0×10^{-4} M Hg^{2+})

6. Pipette 10 ml of the sample aliquot to the voltammetric cell. On a polished glassy carbon electrode, perform anodic stripping voltammetry as described in the previous section. Conditions: $E_{deposition} = -1.0$ V for 240 sec; scan at 5 mV/sec to -0.10 V.

7. From working standards, add known amounts of Pb and Cd using appropriate syringes to the sample solution. The volumes should be sufficient to generate peak heights about double those of run #6.

8. Repeat procedure 7 with 2 more additions of working standard solution to the same sample solution.

9. For each analyte, plot the peak height (uA) on the y-axis versus added concentration on the x-axis. Be certain to include the dilution factor when computing the concentration added.

10. Extrapolate the linear plot of peak height vs. concentration added to the x-axis intercept to determine the concentration of analyte in the original sample aliquot. This is shown in Figure 9.4

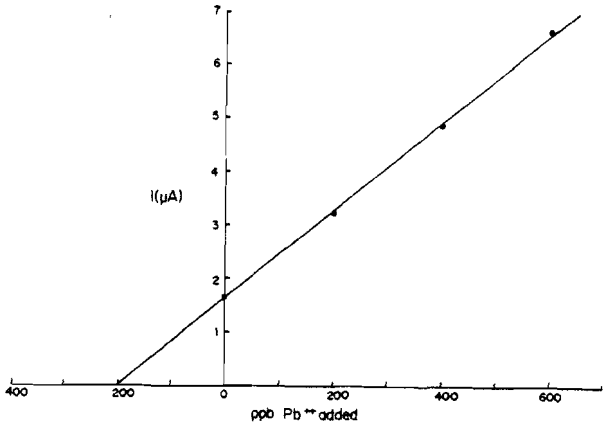


Figure 9.4
Standard addition curve for the ASV determination of lead.

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10.0 Controlled Potential Electrolysis

10.1 Principles

In this technique the analyte is completely electrolyzed by applying a fixed potential to an electrode. The solution is stirred and the electrode usually has a large surface area to minimize electrolysis time. The current (Figure 10.1) is integrated during the course of the experiments. When the electrolysis of sample is 100% complete, the total charge is used to calculate the amount of material electrolyzed by means of Faraday's Law:

$$Q = nFN \qquad (10.1)$$

where,

Q = charge, coulombs (C)
F = Faraday's number, 96,485 coulombs/equivalent (C/eq)
n = equivalents/mole, (eq/mol), i.e., the number of electrons transferred per molecule or ion.

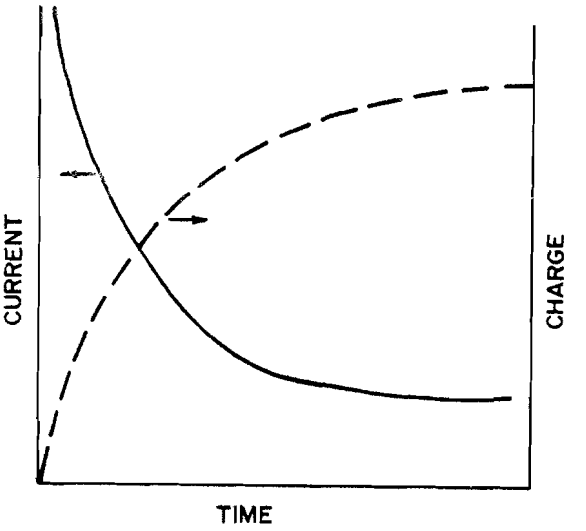


Figure 10.1
Current-time and charge-time response for controlled-potential electrolysis.

10.2 Typical Applications

Controlled potential electrolysis is also commonly used for the electrochemical synthesis of compounds on a preparative scale.

Controlled potential analysis is known as an analytical technique with excellent precision and accuracy for assays, rather than as a method for trace analysis.

Controlled potential electrolysis in a thin-layer cell (typically referred to as thin-layer coulometry) is commonly used as a quick means of establishing n-values. Electrolysis times on the order of a few minutes are typical of thin-layer cells that are usually less than 0.2 mm thick and contain less than 100 uL of solution.

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10.3 Practical Considerations

Selectivity for this technique can be achieved by judicious choice of the deposition potential. A voltammogram performed on the sample will show where electroactive components reduce/oxidize. For example, a cyclic voltammogram with a micro-electrode can be useful for determining the optimum potential for electrolysis.

The condition of 100% electrolysis is usually achieved when the current has dropped to a residual level.

Electrolysis time can be minimized by efficient stirring and a large-area working electrode. For example, a pool of mercury in the bottom of the electrolysis cell gives a large surface area for this electrode.

The auxiliary electrode must be isolated from the sample compartment of the cell in a complete electrolysis experiment. This procedure prevents species that are electrogenerated at the auxiliary electrode from interfering with electrolysis of the sample at the working electrode.

An identical experiment performed on supporting electrolyte alone enables a correction for background charge to be made.

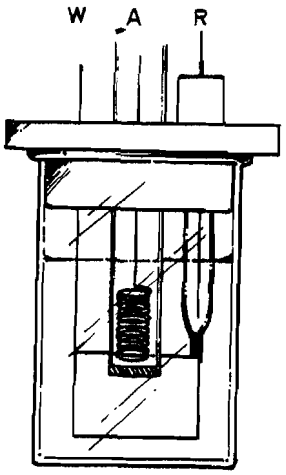


Figure 10.2
Typical cell for bulk electrolysis.

10.4 Installation/Operation

Materials:
Equipment: see Section 8.4

Procedure:
Instrumentation Set-up

Step 1. Set-up as in Section 8.4

Step 2. Set E2 to the electrolysis potential

Step 3. Set E1 to the initial potential

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Step 4. Turn the Display knob to "I Out"

Step 5. Turn the Cell Mode knob to "Cell"

Step 6. To initate electrolysis turn Function knob from E1 to E2 and push down the Coulometer switch.

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11.0 Amperometry

11.1 Principles

In amperometry, the potential of the working electrode is held at a constant value and the resulting current is measured. The electrodes are usually in a stirred or flowing solution. Analytical determinations are made from the current, which is proportional to the concentration of electroactive species. Usually, the potential is held on the limiting current region of the electroactive species of interest. For example, a hydrodynamic voltammogram of Pb^{2+} is shown in Figure 11.1. Such a voltammogram is obtained by scanning the potential. The voltammogram plateaus when Pb^{2+} is reduced as rapidly as it is transported to the electrode surface. The resulting current is termed the limiting current, i_L. Concentrations of Pb^{2+} in unknown samples can be determined by means of the standard curve shown in Figure 11.2. Alternatively, the concentration can be determined through a titration.

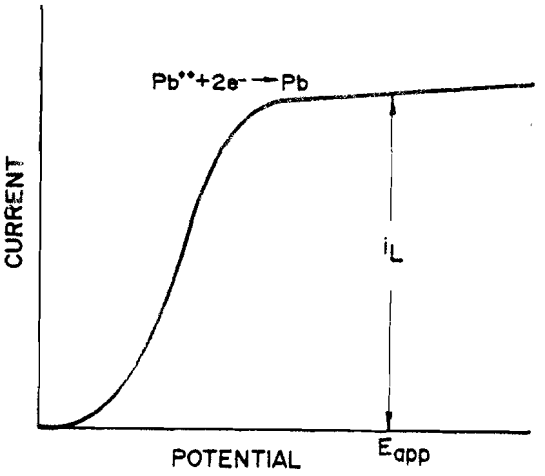


Figure 11.1
Hydrodynamic voltammogram of Pb^{2+} showing limiting current i_L.

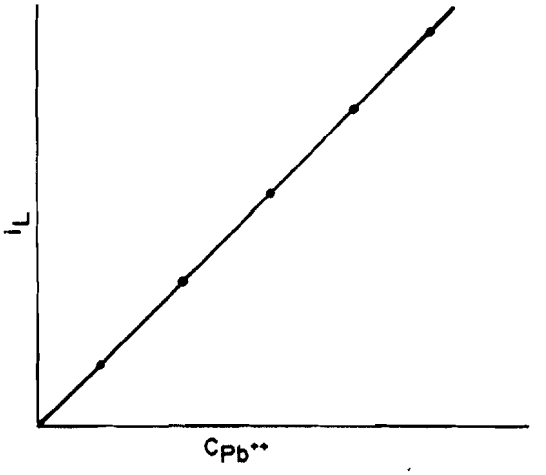


Figure 11.2
Standard curve obtained at E_{app} in Figure 11.1.

11.2 Typical Applications

Amperometry is now commonly used as a means of detection for flow injection analysis (FIA) and liquid chromatography. In these techniques, the sample is injected into a flowing stream of electrolyte, and a current peak is recorded as it passes through the electrochemical cell.

Amperometry can also be used for end-point detection in a titration (amperometric titration). For example, the precipitation titration of Pb^{2+} with a standard SO_4^{2-} solution.

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4\ (s)$$

can be monitored by applying a potential such that the decrease in $C_{Pb}{}^{2+}$ is followed. A titration curve such as that shown in Figure 11.3 is obtained.

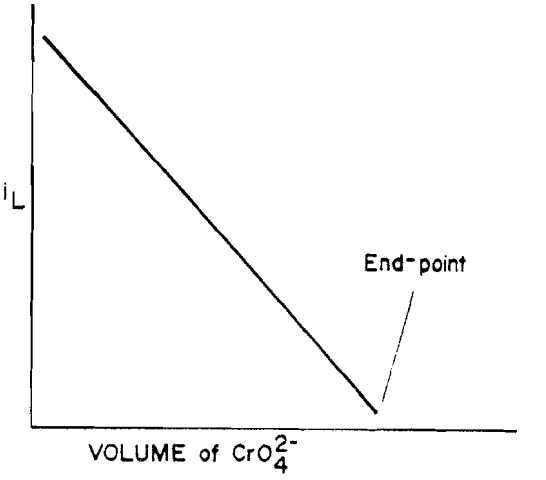


Figure 11.3
Amperometric titration of Pb^{2+} with CrO_4^{2-} titrant.

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11.3 Practical Considerations

An important consideration in the successful implementation of amperometry is the selection of E_{appl} so that the species of interest is monitored with optimum selectivity and current sensitivity. The selection of E_{app} is best done by considering voltammograms (such as shown in Figure 11.1) that have been obtained with a potential in the limiting current region.

Electrochemical detection with FIA and liquid chromatography is capable of determinations at the picogram level. Consequently, the current responses can be in the nanoampere range. The CV-27 is not designed for the measurement of such low currents. Other instrumentation has been developed by BAS (LC-4B and LC-3A) specifically for this application.

11.4. Installation/Operation

In its conventional and/or most common form, the amperometric titration consists of a polarizable microelectrode e.g. a platinum flag in combination with a large non-polarizable reference electrode. A constant potential is impressed across the indicating system such that it is on the diffusion current pleatau for either the titrant, reactant or both. The titration experiment is measuring the current as a function of the volume of titrant.

With its three electrode configuration, the CV-27 voltammograph is a suitable controller for this application. This will be illustrated with the titration of ferrous ion using the ceric ion as the titrant.

Equipment and Materials

1. CV-27 Voltammograh
2. C-1B Cell Stand
3. 50 mL buret
4. Platinum flag electrode (2 cm^2 in area) sealed in a glass tube.

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5. A two-compartment electrochemical cell (75 mL) separated with a fritted disk.
6. 0.025 M ferrous ammonium sulfate
7. 0.050 M ceric sulfate

Experimental Procedures

1. Turn the CELL MODE switch to the STBY position. Flip the POWER switch to the ON position and adjust INITIAL E, E1 to +0.80 V. A recorder will not be needed for this experiment; all results will be recorded manually from values read directly from the LED Display.

2. Deliver 50 mL of ferrous ammonium sulfate solution to the cell. Place the platinum flag working electrode and the Ag/AgCl reference electrode in the main compartment. The other compartment should have a platinum wire as an auxiliary electrode. Connect these three electrodes to the CV-27 with a cell cable. (RED-auxiliary, BLK-working, and WHITE-reference). Place the cell on the C-1B Cell Stand.

3. Fill a 50 mL, mounted buret with the ceric sulfate solution to 30 mL mark. Position the tip of the buret above the cell.

4. Switch the DISPLAY to the I out position. Turn on the magnetic stirrer.

5. Turn the CELL MODE switch from the STBY position to the CELL position. Read and record the amperometric current (I out response) at zero volume of titrant.

6. Slowly deliver the titrant solution into the cell. Record the corresponding current readout at each volume increment.

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7. On a graph paper, plot the current, I (ua) vs. volume (mL) titrant added. A titration curve for this system is illustrated in Figure 11.4

8. Adjust the INITIAL E, E1 to +0.1 Volt and repeat this experiment. The titration curve under these conditions are also shown in Figure 11.4 curve B.

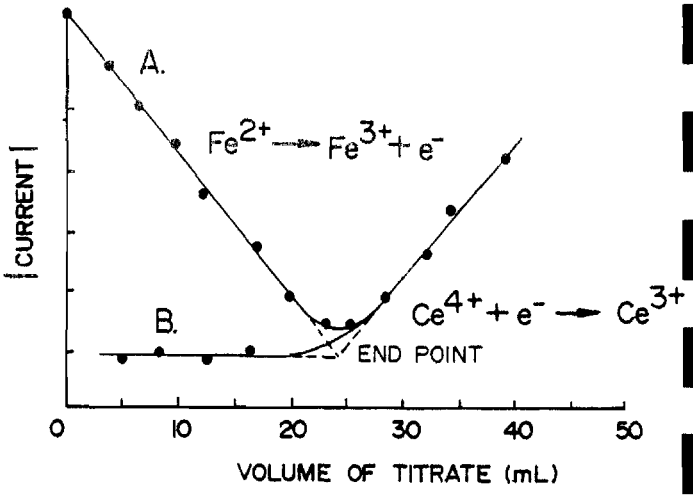


Figure 11.4
Amperometric titration curve for the determination of ferrous ion. The titrant solution is 0.050 M ceric culfate. Curve A, +0.80 Volt; Curve B, +0.1 Volt.

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12.0 Potentiometry

12.1 Principles

Potentiometry refers to those electrochemical techniques in which the potential of an electrochemical cell is measured under the condition of zero current. Thus, in contrast to the other methods described here, this is an equilibrium technique. The potential of the cell (E_{cell}) is determined by the electrode potentials of the two half-reactions constituting the cell ($E_{cathode}$ and E_{anode}) such that:

$$E_{cell} = E_{cathode} - E_{anode} \qquad 12.1$$

Of particular interest to electroanalytical chemists is the relationship between E_{cell} and concentration (or, more accurately, activity) as described by the Nernst equation. For example, if a platinum electrode and an SCE are immersed in a solution of Fe^{3+} and Fe^{2+} the potential of the cell is

$$E_{cell} = E_{SCE} - E^{o'}_{Fe^{3+}/Fe^{2+}} + \frac{.0591}{1} \log \frac{C_{Fe^{2+}}}{C_{Fe^{3+}}} + E_{lj} \qquad (12.2)$$

where

$E^{o'}_{Fe^{3+}/Fe^{2+}}$ = formal reduction potential

E_{SCE} = potential of the SCE

E_{lj} = liquid junction potentials

Since E_{SCE}, $E^{o'}_{Fe^{3+}/Fe^{2+}}$, and E_{lj} are constant in a given solution,

$$E_{cell} = K + 0.0591 \log \frac{C_{Fe^{2+}}}{C_{Fe^{3+}}} \qquad (12.3)$$

Thus, E_{cell} can be used to monitor the ratio of concentrations, as with a potentiometric titration of Fe^{2+}.

Potentiometry is perhaps most useful from an analytical point of view when used in conjunction with ion selective electrodes. In these electrodes, the potential across a selective membrane is

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measured with two reference electrodes. Membranes such as glass of special composition (for H_3O^+), crystals (LaF_3 for F^-), insoluble pellets (AgCl for Cl^-), and liquid membranes (for NO_3^-) have been developed for the selective determination of many ions. More recently, enzymes have been coated on the ion-selective membranes to extend their applicability to numerous enzyme substrates such as urea (urease coating). Gas-sensing electrodes are also available.

Ion selective electrodes can be used for direct potentiometric measurements or potentiometric titrations. For example, the Nernst equation that is applicable to the fluoride electrode is

$$E_{cell} = K - 0.0591 \log C_{F-} \qquad (12.4)$$

C_{F-} can be determined by measuring E_{cell}. Unknown solutions are usually determined by means of a standard curve, such as shown in Figure 12.1, or by the method of standard additions. Fluoride can also be determined by a potentiometric titration with La^{3+} by the precipitation reaction

$$La^{3+} + 3F^- \text{ ---- } LaF_3 \text{ (s)}$$

as shown in Figure 12.2.

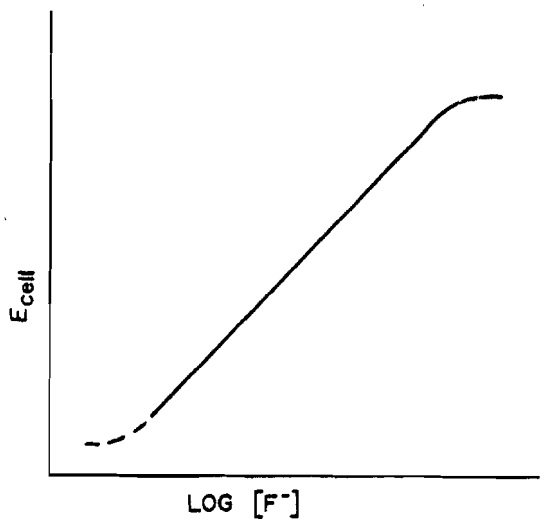


Figure 12.1
Standard curve for F^- by direct potentiometry with F^- selective electrode.

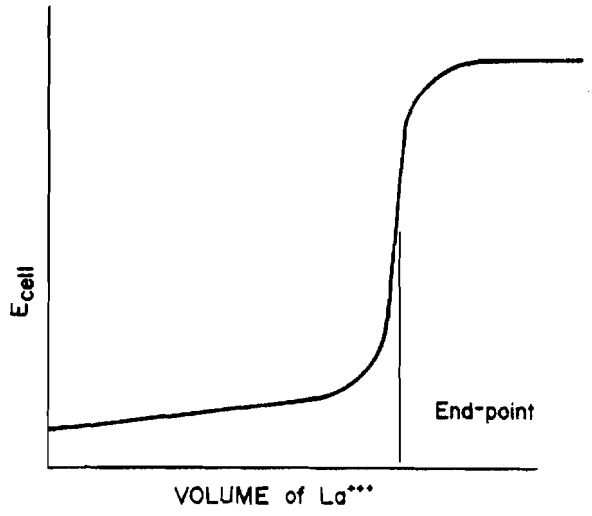


Figure 12.2
Potentiometric titration of F^- with Ta^{3+}.

12.2 Typical Applications

Direct potentiometry is used extensively for the determination of pH, Na^+, K^+, Ca^{2+}, Cl^-, F^-, CO_2, NH_3 and water hardness. Direct potentiometry is highly advantageous when speed of measurement is important and moderate precision is acceptable. The technique is typically applicable over a range of 10^{-7} - 10^{-2} M. Potentiometric titrations can be used when greater precision is required.

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12.3 Practical Considerations

Potentiometric measurements are typically performed with pH meters, which are specifically designed for this purpose. Although the CV-27 Voltammograph was designed as an instrument for implementing Faradaic electrochemical techniques, the ΔE function can be used to measure the potential of a cell under the condition of no current.

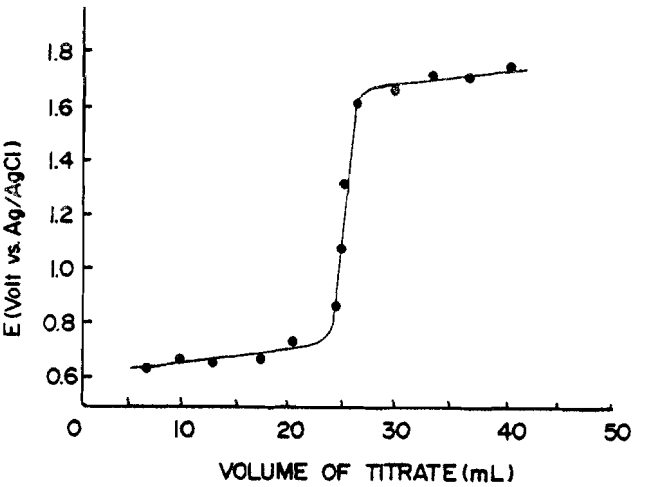


Figure 12.3
Potentiometric titration curve for the determination of ferrous. The titrant is 0.050 M ceric sulfate solution.

12.4 Installation/Operation

The potentiometric mode can be used for both direct potentiometric measurements or potentiometric titration. In this mode the CV-27 can be used with ion selective electrodes (ISE's).

Materials:
Equipment: CV-27 Voltammograph
Indicating Electrode or ISE
RE-1, Ag/AgCl Reference Electrode

Procedure:
Instrumentation Set-up

Step 1. Connect the black electrode lead to the indicating electrode (or ISE).

Step 2. Connect the white electrode lead to the reference electrode.

Step 3. Turn the Cell Mode knob to " ΔE". The difference in potential between the indicating and reference electrodes will be displayed.

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Appendix A

Operation of Coulometer

The output of the "Q" jack in the back of the CV-27 will depend upon both the integrator switch on the back of the CV-27 and on the gain switch on the front panel. Table 1 gives the outputs with the various settings. Note that the units are in charge/volt. Since the output can go to 10V before saturation, the maximum charge that can be measured for each setting is ten times the value in the table. The four integrators A, B, C, and D are charged simultaneously. The integrator can be changed during an experiment and not affect the experimental data. The gain switch cannot be changed during an experiment.

As shown in the table, there are a variety of settings which can give the same output of the coulometer. Best results would be obtained with gain switch set to higher sensitivity and the integrator set to later letter. For example, for an output of 10 mC/V, settings of 0.01 mA/V and integrator D would be better than 10 mA/V and integrator A. However, if the charge becomes greater than 100 mC then the output with the first setting will become saturated and the experiment must be repeated. With the second setting, the integrator could be switched to B during the exeriment.

Table 1. Coulometer output

Gain	Integrator A	B	C	D
10 mA/V	10 mC/V	100 mC/V	1 C/V	10 C/V
5 mA/V	5	50	500 mC/V	5
2	2	20	200	2
1	1	10	100	1
0.5	500 μC/V	5	50	500 mC/V
0.2	200	2	20	200
0.1	100	1	10	100
0.05	50	500 μC/V	5	50
0.02	20	200	2	20
0.01	10	100	1	10
0.005	5	50	500 μC/V	5
0.002	2	20	200	2

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