

Unit 2 B

Voltammetry and Polarography

Voltammetric methods of Analysis

What is Voltammetry?

A time-dependent potential is applied to an electrochemical cell, and the current flowing through the cell is measured as a function of that potential.

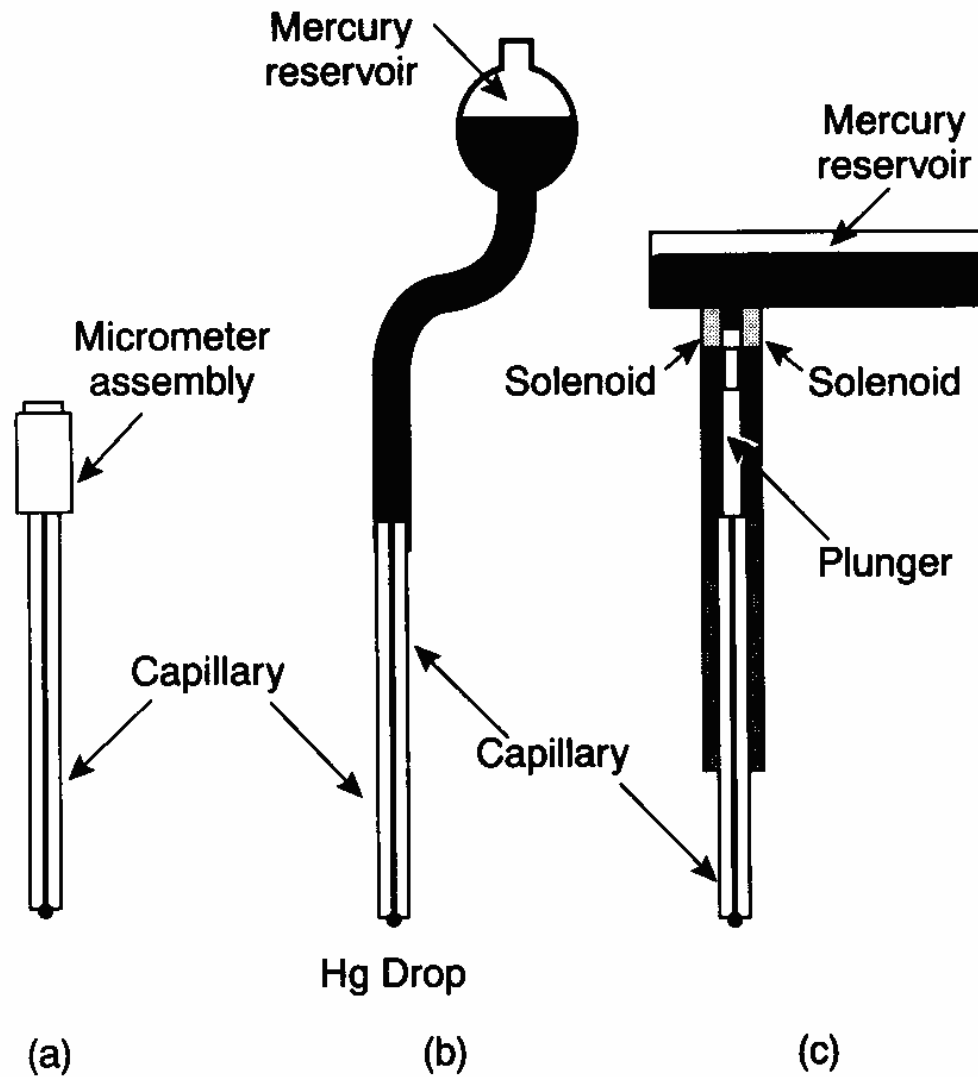
- A plot of current as a function of applied potential is called a voltammogram and is the electrochemical equivalent of a spectrum in spectroscopy, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction.**

Voltametric Measurements

- **Three electrode system potentiostat mentioned earlier is used as a device that measures the current as a function of potential**
- **Working electrodes used: Hg, Pt, Au, Ag, C or others**
- **Reference electrode: SCE or Ag/ AgCl;**
- **Auxiliary electrode: Pt wire**

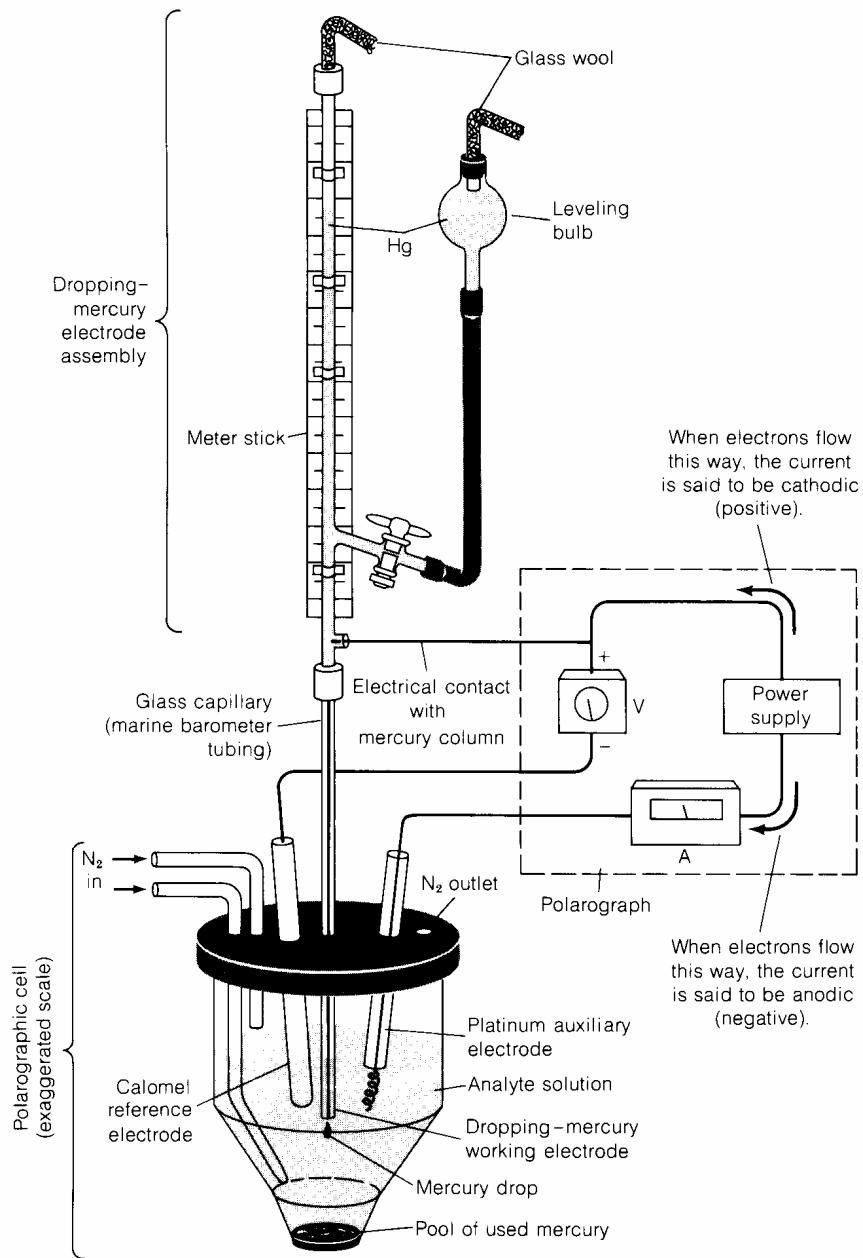
Polarography

- In polarography, the current flowing through the cell is measured as a function of the potential of the working electrode.
- Usually this current is proportional to the concentration of the analyte.
- Apparatus for carrying out polarography is shown below.
- The working electrode is a dropping mercury electrode or a mercury droplet suspended from a bottom of a glass capillary tube.
- Analyte is either reduced (most of the cases) or oxidized at the surface of the mercury drop.
- The current –carrier auxiliary electrode is a platinum wire.
- SCE or Ag/AgCl reference electrode is used.
- The potential of the mercury drop is measured with respect to the reference electrode.

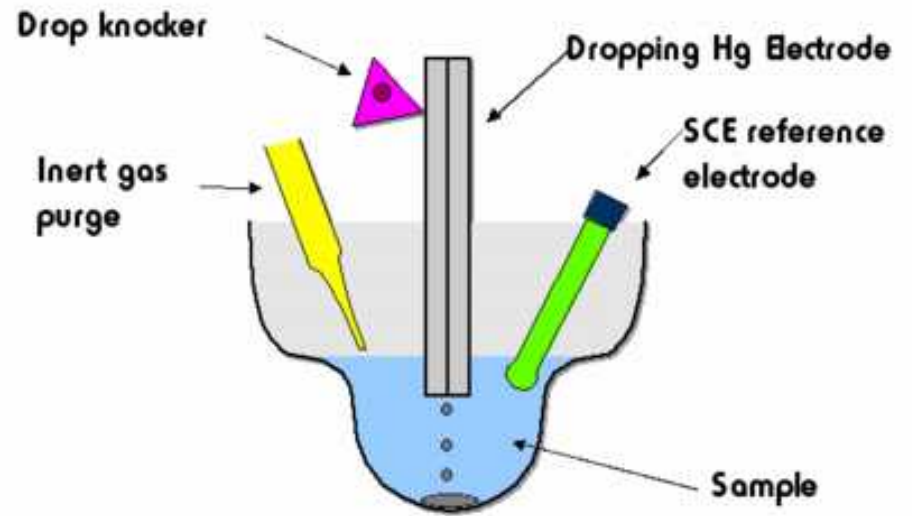


Mercury electrodes: (a) hanging mercury drop electrode; (b) dropping mercury electrode; (c) mercury pool electrode

Typical electrochemical cell used in polarography



Sample cell



Sample cell



Why Dropping Mercury Electrode?

- Hg yields reproducible current-potential data.
- This reproducibility can be attributed to the continuous exposure of fresh surface on the growing mercury drop.
- With any other electrode (such as Pt in various forms), the potential depends on its surface condition and therefore on its previous treatment.
- The vast majority of reactions studied with the mercury electrode are reductions.
- At a Pt surface, reduction of solvent is expected to compete with reduction of many analyte species, especially in acidic solutions.
- The high overpotential for H^+ reduction at the mercury surface. Therefore, H^+ reduction does not interfere with many reductions.

Problems with mercury electrode

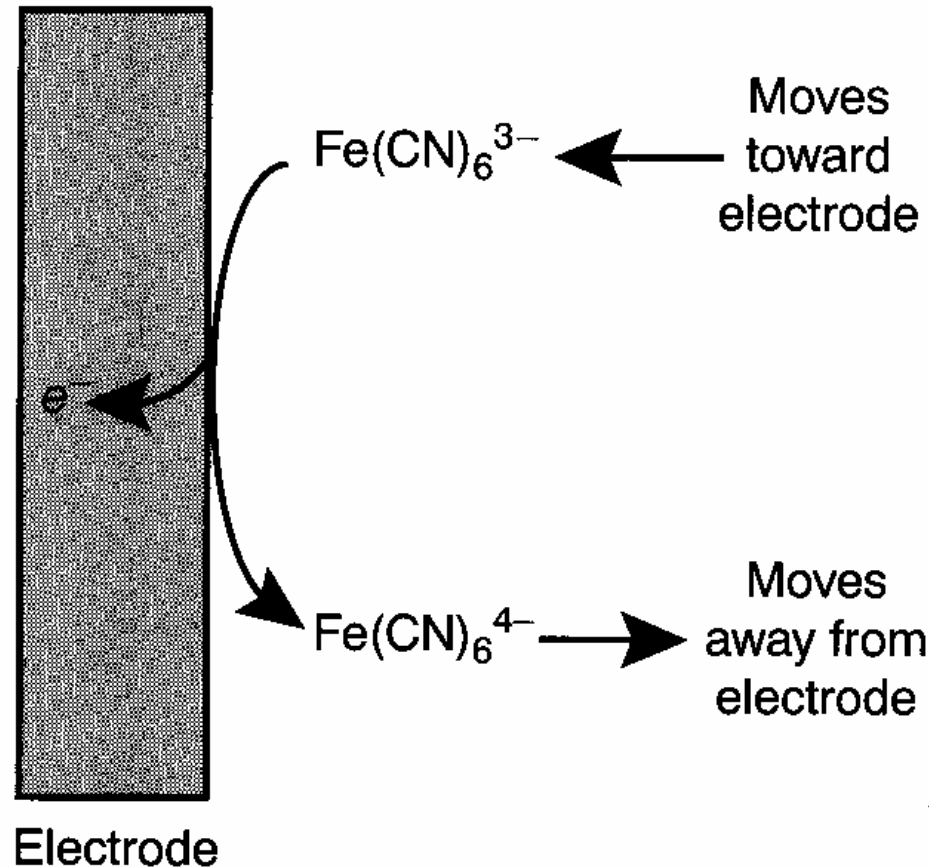
- A mercury electrode is not very useful for performing oxidations, because Hg is too easily oxidized.
- In a noncomplexing medium, Hg is oxidized near + 0.25 V (versus S.C.E.).
- For most oxidations, some other working electrode must be employed.
- Pt electrode Vs SCE; works for a range of +1.2 to – 0.2 in acidic solution +0.7 V to –1 V in basic solution. Carbon paste electrode is also used in voltammetry
- Mercury is toxic and slightly volatile, and spills are almost inevitable. a good vacuum cleaner.
- To remove residual mercury, sprinkle elemental zinc powder on the surface and dampen the powder with 5% aqueous H_2SO_4
- Mercury dissolves in the zinc. After working the paste into contaminated areas with a sponge or brush, allow the paste to dry and then sweep it up. Discard the powder appropriately as contaminated mercury waste

Current in Voltammetry

- When an analyte is oxidized at the working electrode, a current passes electrons through the external electric circuitry to the auxiliary electrode.
- This current flows from the auxiliary to the working electrode, where reduction of the solvent or other components of the solution matrix occurs .
- The current resulting from redox reactions at the working and auxiliary electrodes is called a **faradaic current**.
- **Sign Conventions** A current due to the analyte's reduction is called a **cathodic** current and, by convention, is considered **positive**. **Anodic** currents are due to oxidation reactions and carry a **negative** value.

Influence of applied potential on the faradaic current

- **When the potential applied to the working electrode exceeds the reduction potential of the electroactive species, a reduction will take place at the electrode surface**
- **Thus, electroactive species diffuses from the bulk solution to the electrode surface and the reduction products diffuse from the electrode surface towards the bulk solution. This creates what is called the faradaic current.**



Schematic showing transport of $\text{Fe}(\text{CN})_6^{3-}$ toward the electrode and $\text{Fe}(\text{CN})_6^{4-}$ away from the electrode following the reduction of $\text{Fe}(\text{CN})_6^{3-}$.

- **The magnitude of the faradaic current is determined by the rate of the resulting oxidation or reduction reaction at the electrode surface.**
- **Two factors contribute to the rate of the electrochemical reaction:**
 - **the rate at which the reactants and products are transported to and from the surface of the electrode (mass transport)**
 - **and the rate at which electrons pass between the electrode and the reactants and products in solution. (kinetics of electron transfer at the electrode surface)**

Influence of Mass Transport on the Faradaic Current

There are three modes of mass transport to and from the electrode surface: diffusion, migration, and convection.

- **Diffusion** from a region of high concentration to a region of low concentration occurs whenever the concentration of an ion or molecule at the surface of the electrode is different from that in bulk solution.
- **Convection** occurs when a mechanical means is used to carry reactants toward the electrode and to remove products from the electrode.
 - The most common means of convection is to stir the solution using a stir bar. Other methods include rotating the electrode and incorporating the electrode into a flow cell.
- **Migration** occurs when charged particles in solution are attracted or repelled from an electrode that has a positive or negative surface charge.
 - Unlike diffusion and convection, migration only affects the mass transport of charged particles

- The flux of material to and from the electrode surface is a complex **function of all three modes** of mass transport.
- In the limit in which **diffusion** is the only significant means for the mass transport of the reactants and products, the current in a voltammetric cell is given by

$$i = \frac{nFAD(C_{\text{bulk}} - C_{x=0})}{\delta}$$

where n is the number of electrons transferred in the redox reaction, F is Faraday's constant, A is the area of the electrode, D is the diffusion coefficient for the reactant or product, C_{bulk} and $C_{x=0}$ are the concentration of the analyte in bulk solution and at the electrode surface, and δ is the thickness of the diffusion layer.

- For the above equation to be valid, migration and convection must not interfere with formation of diffusion layer around the electrode surface.
- **Migration** is eliminated by adding a **high concentration of an inert supporting electrolyte** to the analytical solution.
- The large **excess of inert ions**, ensures that few reactant and product ions will move as a result of migration.
- Although **convection** may be easily eliminated by not physically agitating the solution, in some situations it is desirable either to stir the solution or to push the solution through an electrochemical flow cell. Fortunately, the dynamics of a fluid moving past an electrode results in a small diffusion layer, typically of 0.001 - 0.01-cm thickness, in which the rate of mass transport by convection drops to zero.

Influence of the Kinetics of Electron Transfer on the Faradaic Current

- When electron transfer kinetics at the electrode surface are fast, the redox reaction is at equilibrium, and the concentrations of reactants and products at the electrode are those specified by the Nernst equation.
- Such systems are considered electrochemically reversible.
- In other systems, when electron transfer kinetics are sufficiently slow, **the concentration of reactants and products at the electrode surface, and thus the current**, differ from that predicted by the Nernst equation. In this case the system is electrochemically irreversible.

Non faradaie Currents

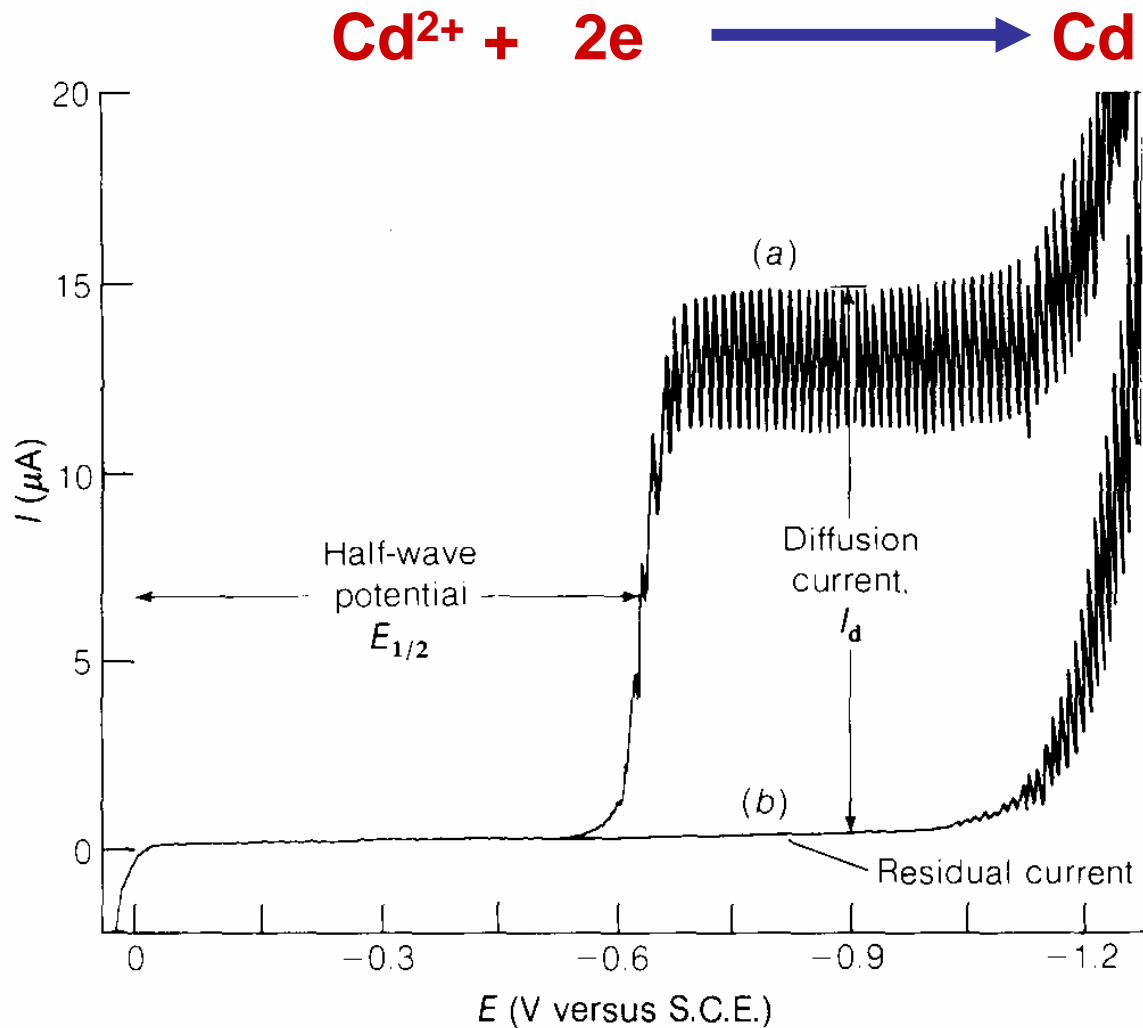
- Currents other than faradaic may also exist in an electrochemical cell that are unrelated to any redox reaction.
- These currents are called **nonfaradaic currents**
- The most important example of a nonfaradaic current occurs whenever the electrode's potential is changed.
- When mass transport takes place by migration negatively charged particles in solution migrate toward a positively charged electrode, and positively charged particles move away from the same electrode.
- When an inert electrolyte is responsible for migration, the result is a structured electrode-surface interface called the electrical double layer, or EDL,
- The movement of charged particles in solution, gives rise to a short-lived, nonfaradaic charging current.
- Changing the potential of an electrode causes a change in the structure of the EDL, producing a small charging current.

Residual Current

- Even in the absence of analyte, a small current flows through an electrochemical cell.
- This current, which is called the residual current, consists of two components:
 - a **faradaic current** due to the oxidation or reduction of trace impurities,
 - a **charging current**. it is the current needed to charge or discharge the capacitor formed by the electrode surface-solution interface. This is called the condenser current or charging current.
 - It is present in all voltammetric and polarographic experiments, regardless of the purity of reagents.
 - As each drop of mercury falls, it carries its charge with it to the bottom of the cell. The new drop requires more current for charging.

SHAPE OF THE POLAROGRAPH

A graph of current versus potential in a polarographic experiment is called a polarogram.



- **When the potential is only slightly negative with respect to the calomel electrode, essentially no reduction of Cd^{2+} occurs. Only a small residual current flows.**
- **At a sufficiently negative potential, reduction of Cd^{2+} commences and the current increases. The reduced Cd dissolves in the Hg to form an amalgam.**
- **After a steep increase in current, concentration polarization sets in: The rate of electron transfer becomes limited by the rate at which Cd^{2+} can diffuse from bulk solution to the surface of the electrode.**
- **The magnitude of this diffusion current I_d is proportional to Cd^{2+} concentration and is used for quantitative analysis. The upper trace in the Figure above is called a polarographic wave.**

- When the potential is sufficiently negative around -1.2 V, reduction of H^+ begins and the curve rises steeply.
- At positive potentials (near the left side of the polarogram), oxidation of the Hg electrode produces a negative current. *By convention, a negative current means that the working electrode is behaving as the anode with respect to the auxiliary electrode. A positive current means that the working electrode is behaving as the cathode.*
- *The oscillating current in the Figure above is due to the growth and fall of the Hg drops.*
- *As the drop grows, its area increases, more solute can reach the surface in a given time, and more current flows.*
- *The current increases as the drop grows until, finally, the drop falls off and the current decreases sharply.*

Shape of the voltammetric Wave

- $E_{\text{electrode}}$ is related to the current during the scan of a voltammogram by the equation

$$E_{\text{electrode}} = E_{\text{appl}} = E_{1/2} - (0.059/n) \log (i / i_d - i)$$

where i is the value of the current at any applied potential.

- This equation holds for reversible systems. Thus, the value of n can be calculated if E_{appl} is plotted versus $\log (i / i_d - i)$ derived from the polarogram during the rising portion.
- The relationship is a straight line with a slope of $(-0.059/n)$ V.
- $E_{1/2}$ in most cases is the same as the reaction's standard state potential

Diffusion Current

- When the potential of the working electrode is sufficiently negative, the rate of reduction of Cd^{2+} ions



- is governed by the rate at which Cd^{2+} can reach the electrode.
- In the Figure above, this occurs at potentials more negative than -0.7 V .
- In an unstirred solution, the rate of reduction is controlled by the rate of diffusion of analyte to the electrode.
- In this case, the limiting current is called the diffusion current.
- The solution must be perfectly quiet to reach the diffusion limit in polarography.
- Thus, the diffusion current is the limiting current when the rate of electrolysis is controlled by the rate of diffusion of species to the electrode.

- **Current \propto rate of diffusion $\propto [C]_o - [C]_s$**
The $[C]_o$ and $[C]_s$ are the concentrations in the bulk solution and at the electrode surface.
- **The greater the difference in concentrations the more rapid will be the diffusion.**
- **At a sufficiently negative potential, the reduction is so fast that the $[C]_s \ll [C]_o$ and equation above reduces to the form**
- **Limiting current = diffusion current $\propto [C]_o$**
- **The ratio of the diffusion current to the bulk solute concentration is the basis for the use of voltammetry in analytical chemistry**

- The magnitude of the diffusion current, is given by the Ilkovic equation:
- $I_d = (7.08 \times 10^4)nCD^{1/2} m^{2/3} t^{1/6}$
- where I_d = diffusion current, measured at the top of the oscillations in the Figure above with the units μA
- n = number of electrons per molecule involved in the oxidation or reduction of the electroactive species.
- C = concentration of electroactive species, with the units mmol/L
- D = diffusion coefficient of electroactive species, with the units M^2/s
- m = rate of flow of Hg, in mg/s
- t = drop interval, in s
- The number 7.08×10^4 is a combination of several constants whose dimensions are such that I_d will be given in , μA

- Thus, i_d is proportional to the concentration of a certain species under specific conditions and the above equation may be expressed as follows:

$$i_d = kc$$

- where k is constant under the specific conditions.
- If k is constant for a series of standard solutions of various concentrations and an unknown, a calibration plot can be constructed and the unknown concentration can be determined.
- Clearly, the magnitude of the diffusion current depends on several factors in addition to analyte concentration.
- In quantitative polarography, it is important to control the temperature within a few tenths of a degree.
- The transport of solute to the electrode should be made to occur only by diffusion (**no stirring**).

Supporting electrolyte

- **Current flow due to electrostatic attraction (or repulsion) of analyte ions by the electrode is reduced to a negligible level by the presence of a high concentration of supporting electrolyte (1 M HCl in the Figure above).**
- **Increasing concentrations of electrolyte reduces the net current, since the rate of arrival of cationic analyte at the negative Hg surface is decreased.**
- **Typically, a supporting electrolyte concentration 50-100 times greater than the analyte concentration will reduce electrostatic transport of the analyte to a negligible level.**

Half-wave Potential, $E_{1/2}$

- Half wave potential, $E_{1/2}$ is an important feature can be derived from the polarogram.
- It is the potential corresponding to one half the limiting current i.e. $i_d/2$.
- $E_{1/2}$ is a characteristic for each element and thus used for qualitative analysis.

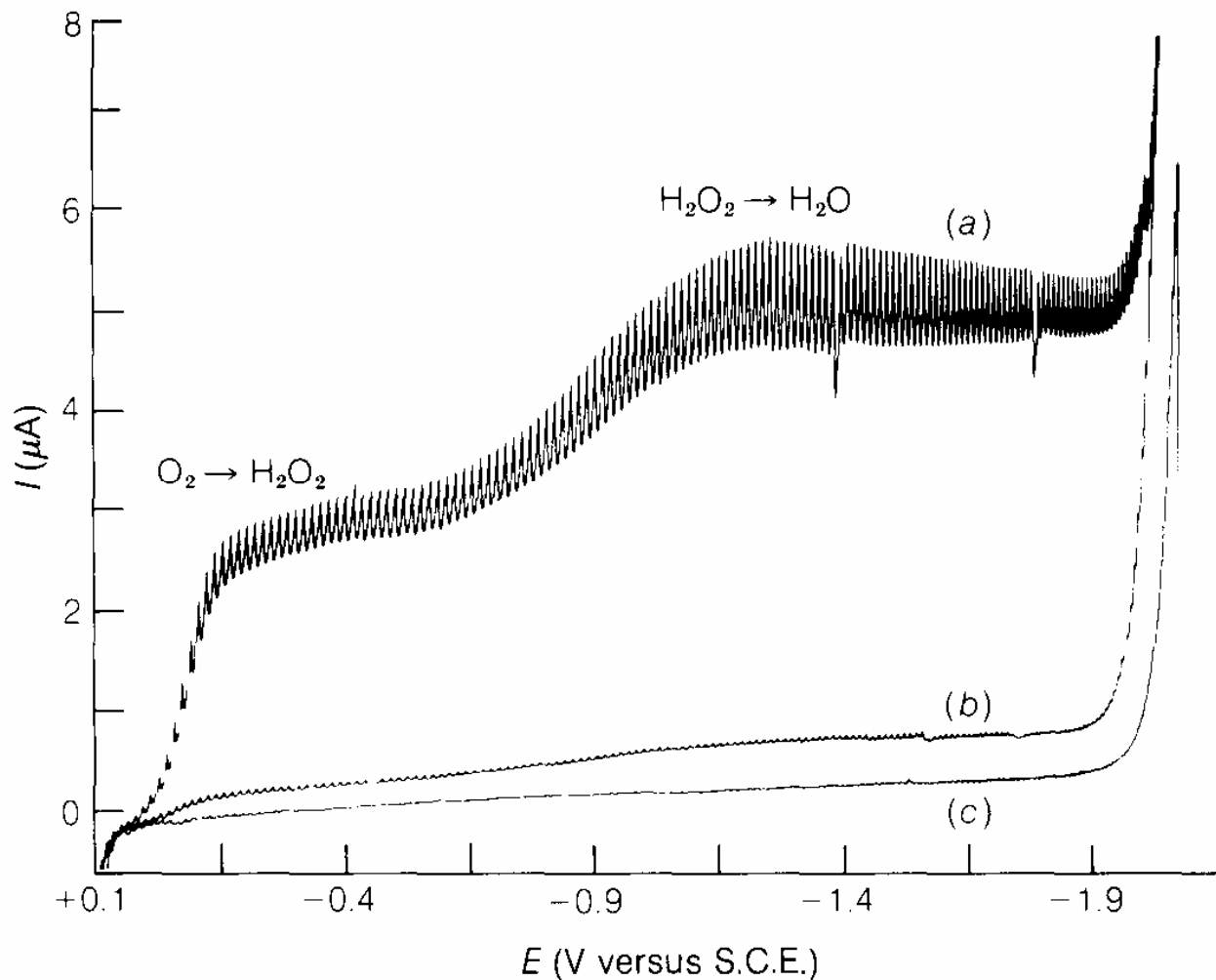
Polarographic data

Reaction	$E_{1/2}$ vs SCE	Supporting electrolyte
$\text{Cu}^{2+} \rightarrow \text{Cu}$	0.04	0.1 M KCl
$\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}$	-0.25	4 M NH_4Cl , 1 M HCl
$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.40	0.1 M KCl
$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.50	0.4 M Na tartrate
$\text{Pb}^{2+} \rightarrow \text{Pb}$	-0.76	1 M NaOH

Note how the $E_{1/2}$ value can be shifted by changing the supporting electrolyte.

Effect of Dissolved Oxygen

- Oxygen dissolved in the solution will be reduced at the DME leading to two well defined waves which were attributed to the following reactions:
- $\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2$; $E_{1/2} = -0.1\text{V}$
- $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$; $E_{1/2} = -0.9\text{V}$
- $E_{1/2}$ values for these reductions in acid solution correspond to -0.05V and -0.8V versus SCE.
- This indicates that dissolved oxygen interferes in the determination of most metal ions.
- Therefore, dissolved O_2 has to be removed by bubbling nitrogen free oxygen into the solution before recording the polarogram.



Polarogram of 0.1 M KCl. (a) Saturated with air. (b) After partial deaeration. (c) After further deaeration. [L. Meites, *Polarographic Techniques*, 2nd ed. (New York: Wiley, 1965).]

Voltammetric Techniques

Normal Polarography

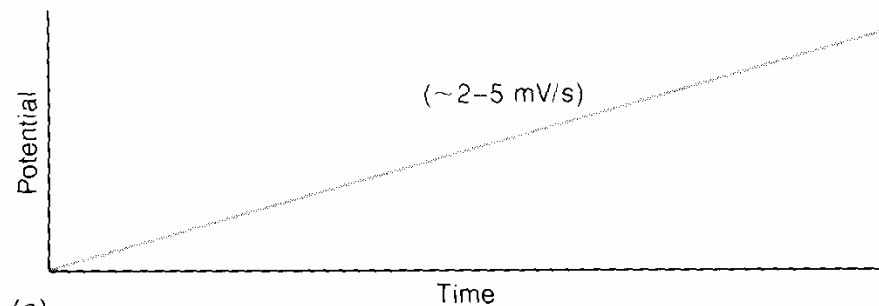
- The earliest voltammetric experiment was normal polarography at a dropping mercury electrode. In normal polarography the potential is linearly scanned, producing voltammograms (**polarograms**) such as that shown in Figure above.
- This technique is discussed above and usually called **Direct Current (DC) polarography**

Differential Pulse Polarography

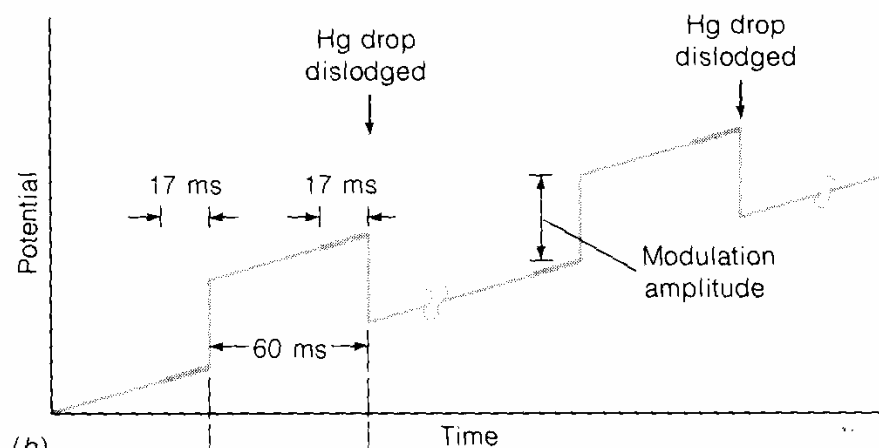
- In direct current polarography, the voltage applied to the working electrode increases linearly with time, as shown above. The current is recorded continuously, and a polarogram such as that shown above results. The shape of the plot is called a linear voltage ramp.
- In differential pulse polarography, small voltage pulses are superimposed on the linear voltage ramp, as in the Figure below.
- The height of the pulse is called its modulation amplitude.
- Each pulse of magnitude 5-100 mV is applied during the last 60 ms of the life of each mercury drop.

- The drop is then mechanically dislodged.
- The current is not measured continuously. Rather, it is measured once before the pulse and again for the last 17 ms of the pulse.
- The polarograph subtracts the first current from the second and plots this difference versus the applied potential (measured just before the voltage pulse).
- The resulting differential pulse polarogram is nearly the *derivative of* a direct current polarogram, as shown in the Figure below

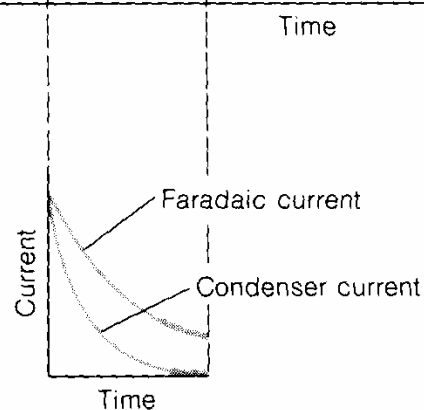
(a) Linear voltage ramp used in direct current polarography. (b) Pulsed ramp of differential pulse polarography. Current is measured only during the intervals shown by heavy lines. (c) Behavior of faradaic and condenser currents during each pulse.



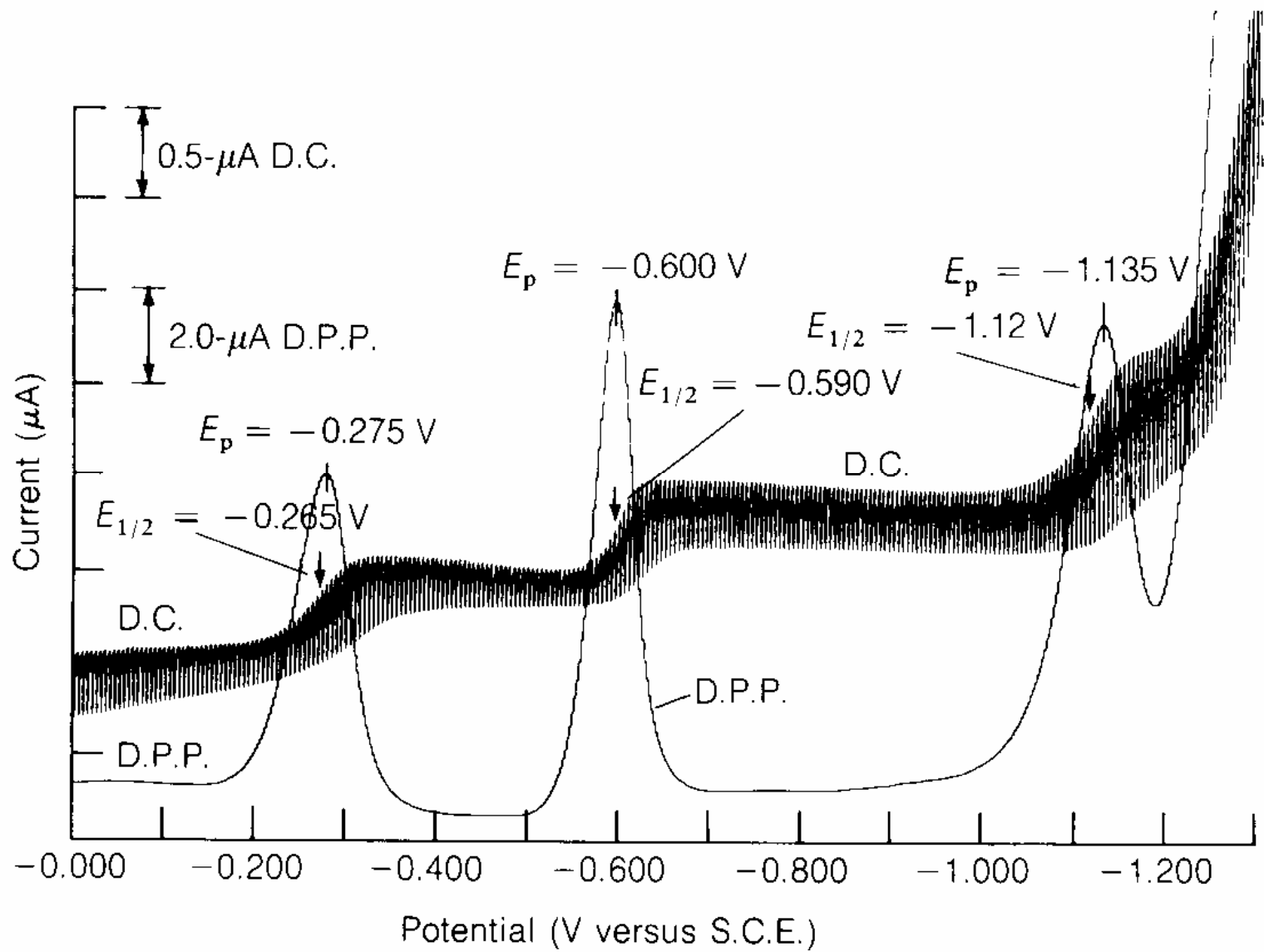
(a)



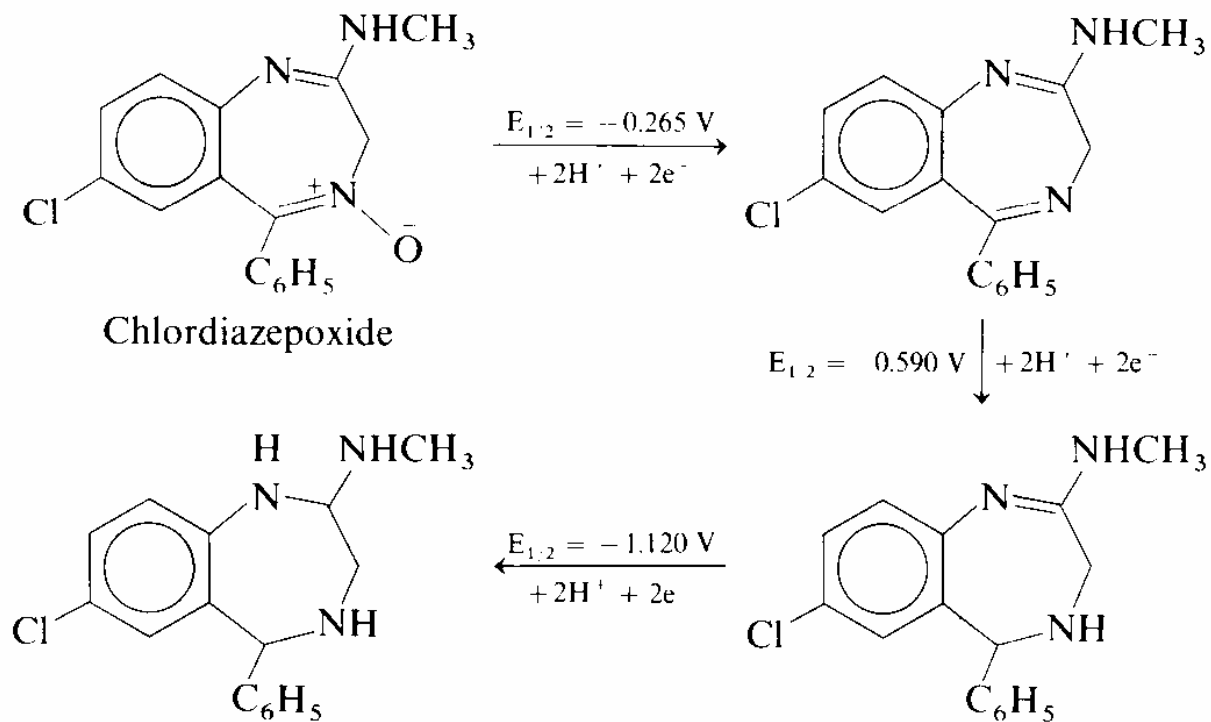
(b)



(c)



Comparison of direct current (D.C.) and differential pulsed polarography (D.P.P.) of 1.2×10^{-4} M chlordiazepoxide (the drug Librium) in 3 mL of 0.05 M H_2SO_4 . Modulation amplitude = 50 mV. Note the different current scales for each curve. [M. R. Hackman, M. A. Brooks, J. A. F. de Silva, and T. S. Ma, *Anal. Chem.*, **46**, 1075 (1974).] The chemistry responsible for each wave is believed to be as shown below. [E. Jacobsen and T. V. Jacobsen, *Anal. Chim. Acta*, **55**, 293 (1971).]

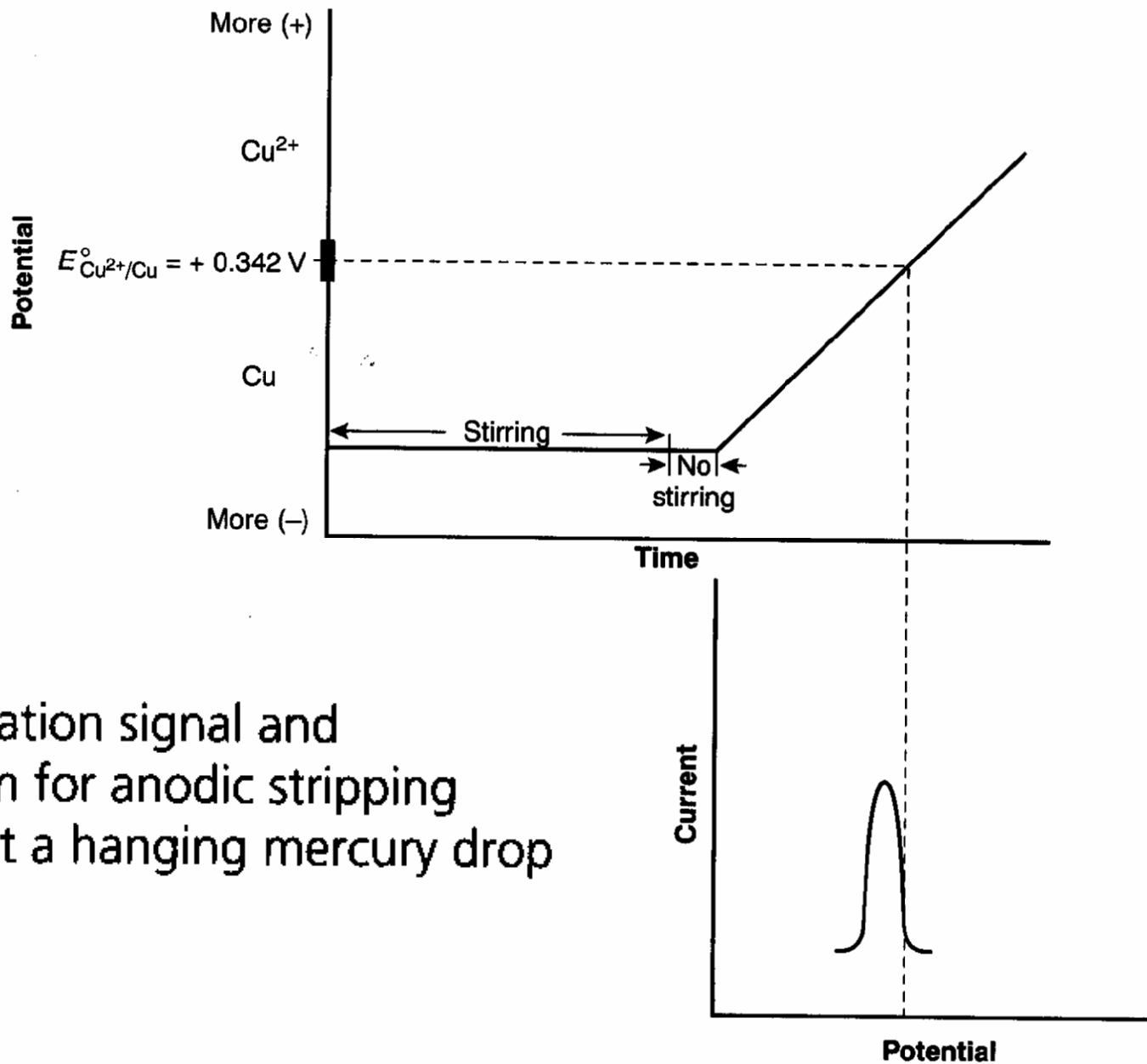


Hydrodynamic Voltammetry

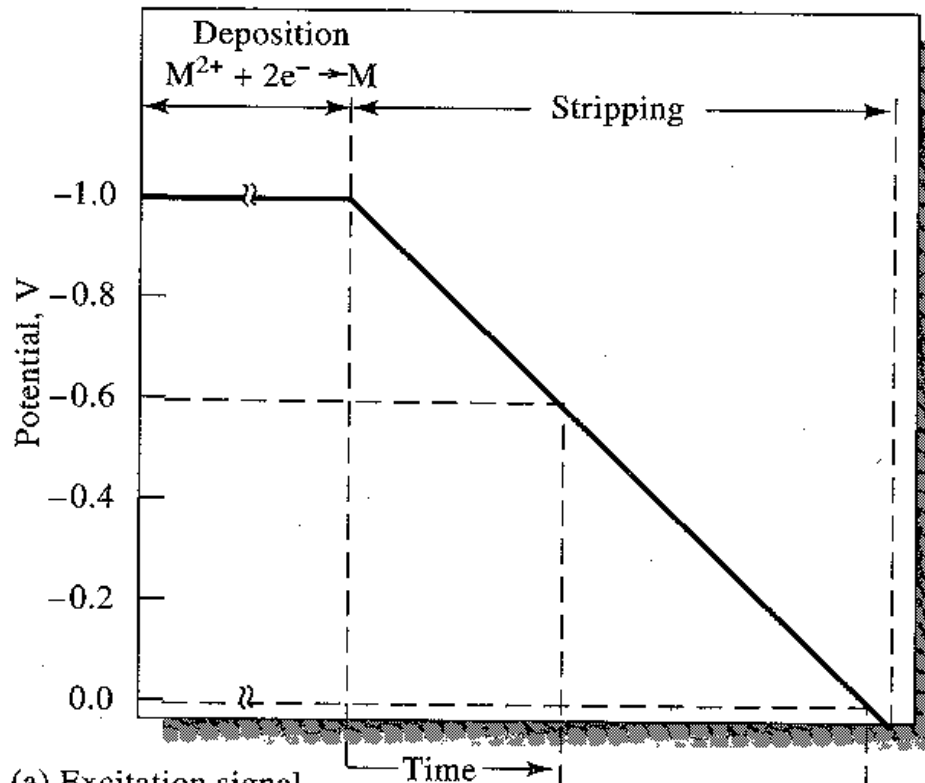
- In hydrodynamic voltammetry the solution is stirred by rotating the electrode.
- Current is measured as a function of the potential applied to a solid working electrode.
- The same potential profiles used for polarography, such as a linear scan or a differential pulse, are used in hydrodynamic voltammetry.
- The resulting voltammograms are identical to those for polarography, except for the lack of current oscillations resulting from the growth of the mercury drops.
- Because hydrodynamic voltammetry is not limited to Hg electrodes, it is useful for the analysis of analytes that are reduced or oxidized at more positive potentials.

Stripping Analysis

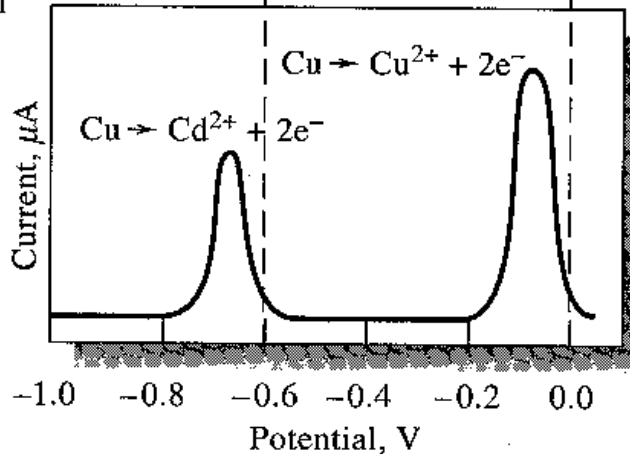
- The analyte from a **dilute** solution is first concentrated in a single drop of Hg (or any micro-electrode) by electroreduction or electro-oxidation.
- The electroactive species is then *stripped* from the electrode by reversing the direction of the voltage sweep.
- The potential becomes more *positive*, *oxidizing* the species back into solution (**anodic stripping voltammetry**) or more negative reducing the species back into solution (**cathodic stripping voltammetry**)
- The current measured during the oxidation or reduction is related to the quantity of analyte
- The polarographic signal is recorded during the oxidation or reduction process.
- The deposition step amounts to an electrochemical preconcentration of the analyte; that is, the concentration of the analyte in the surface of the microelectrode is far greater than it is in the bulk solution.



Potential-excitation signal and voltammogram for anodic stripping voltammetry at a hanging mercury drop electrode.



(a) Excitation signal



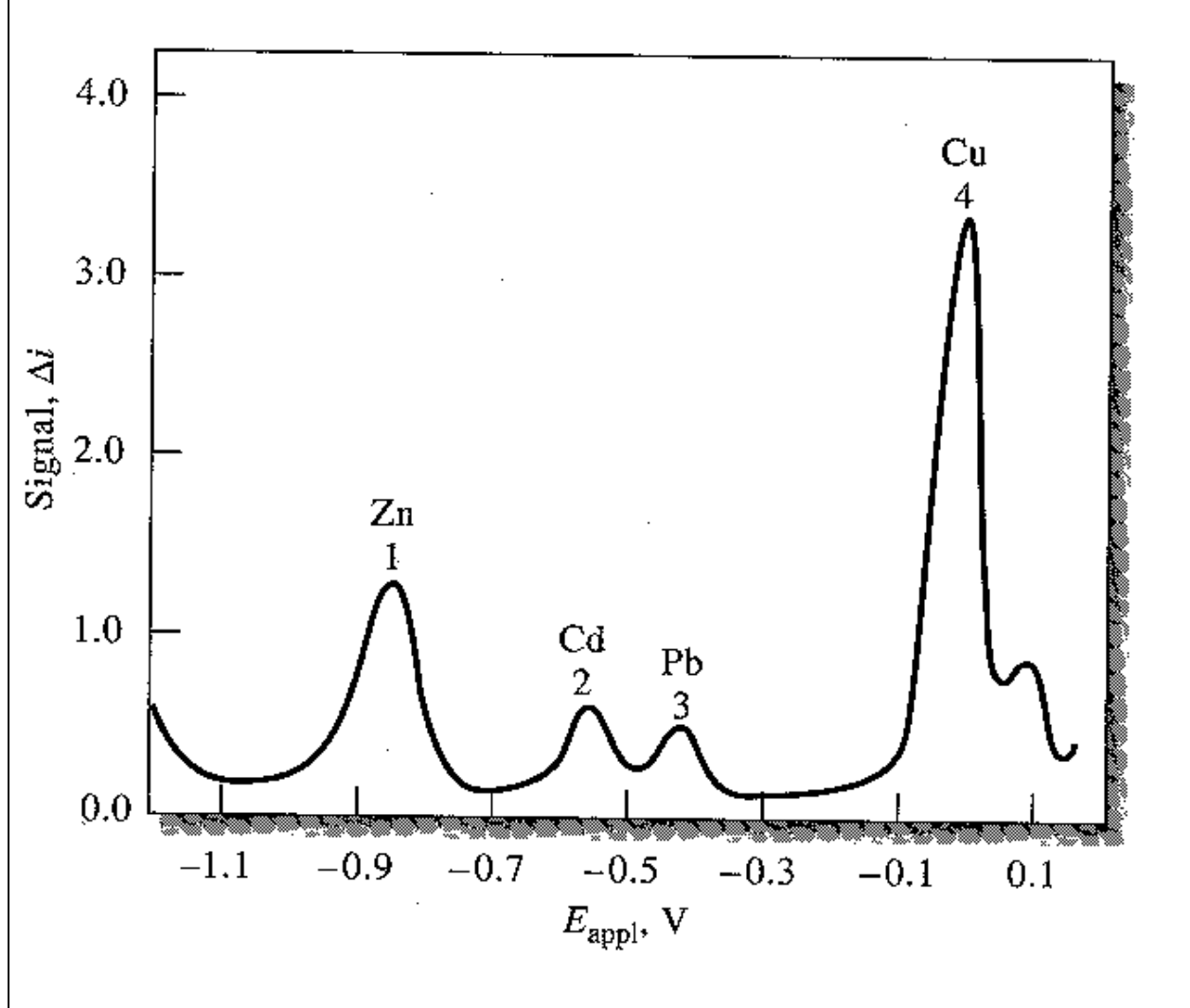
(b) Voltammogram

(a) Excitation signal for stripping determination of Cd^{2+} and Cu^{2+}

(b) Voltammogram.

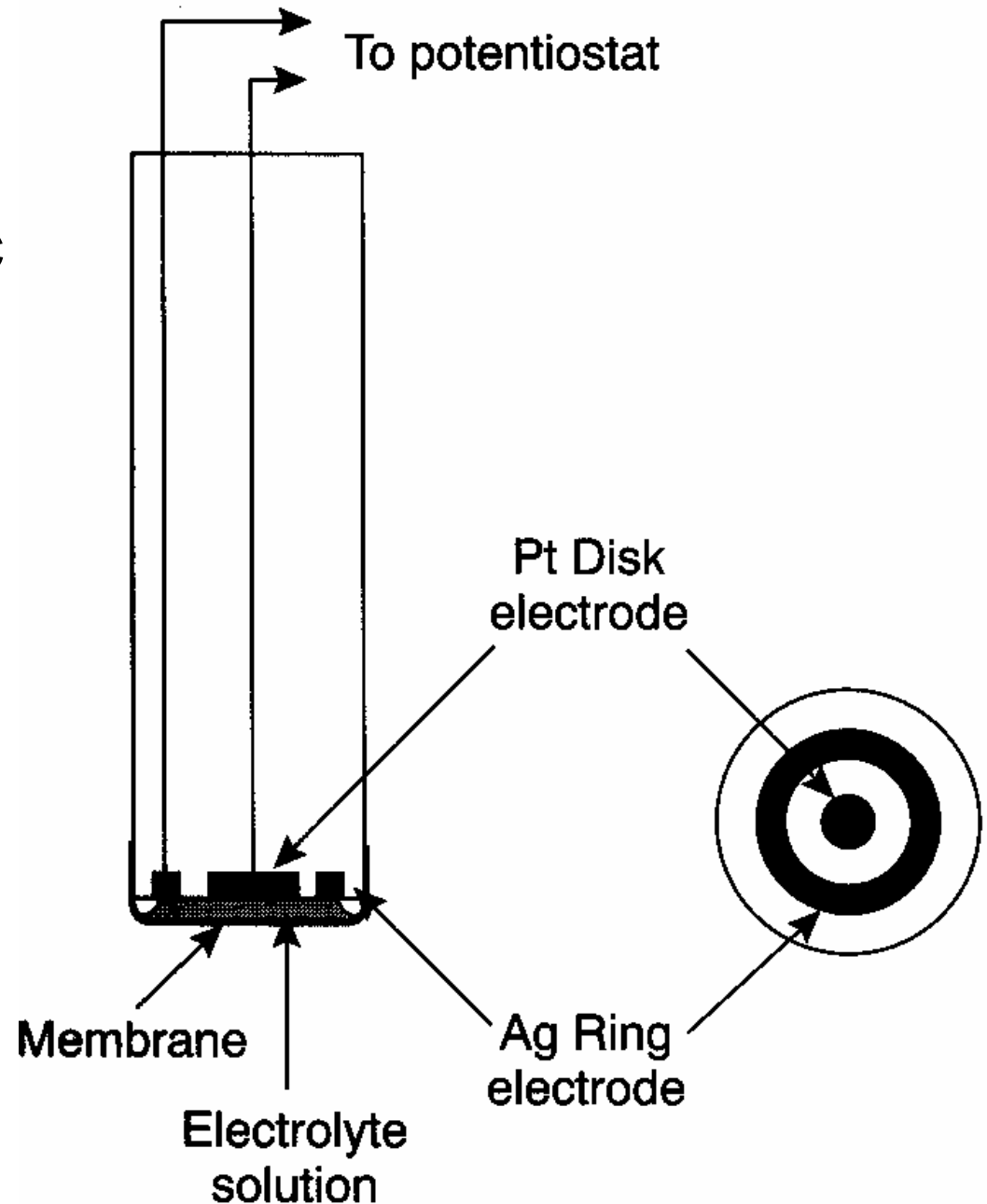
Amperometry

- A constant potential is applied to the working electrode, and current is measured as a function of time.
- Since the potential is not scanned, amperometry does not lead to a voltammogram.
- One important application of amperometry is in the construction of chemical sensors. One of the first amperometric sensors to be developed was for dissolved O_2 in blood
- The design of the amperometric sensor is shown below and is similar to potentiometric membrane electrodes.
- A gas-permeable membrane is stretched across the end of the sensor and is separated from the working and counter electrodes by a thin solution of KCl.
- The working electrode is a Pt disk cathode, and an Ag ring anode is the counter electrode
- Although several gases can diffuse across the membrane (O_2 , N_2 , CO_2), only O_2 is reduced at the cathode



Differential-pulse anodic stripping voltammogram of 25 ppm zinc, cadmium, lead, and copper.

Clark amperometric Sensor for the Determination of Dissolved O_2



Quantitative Analysis

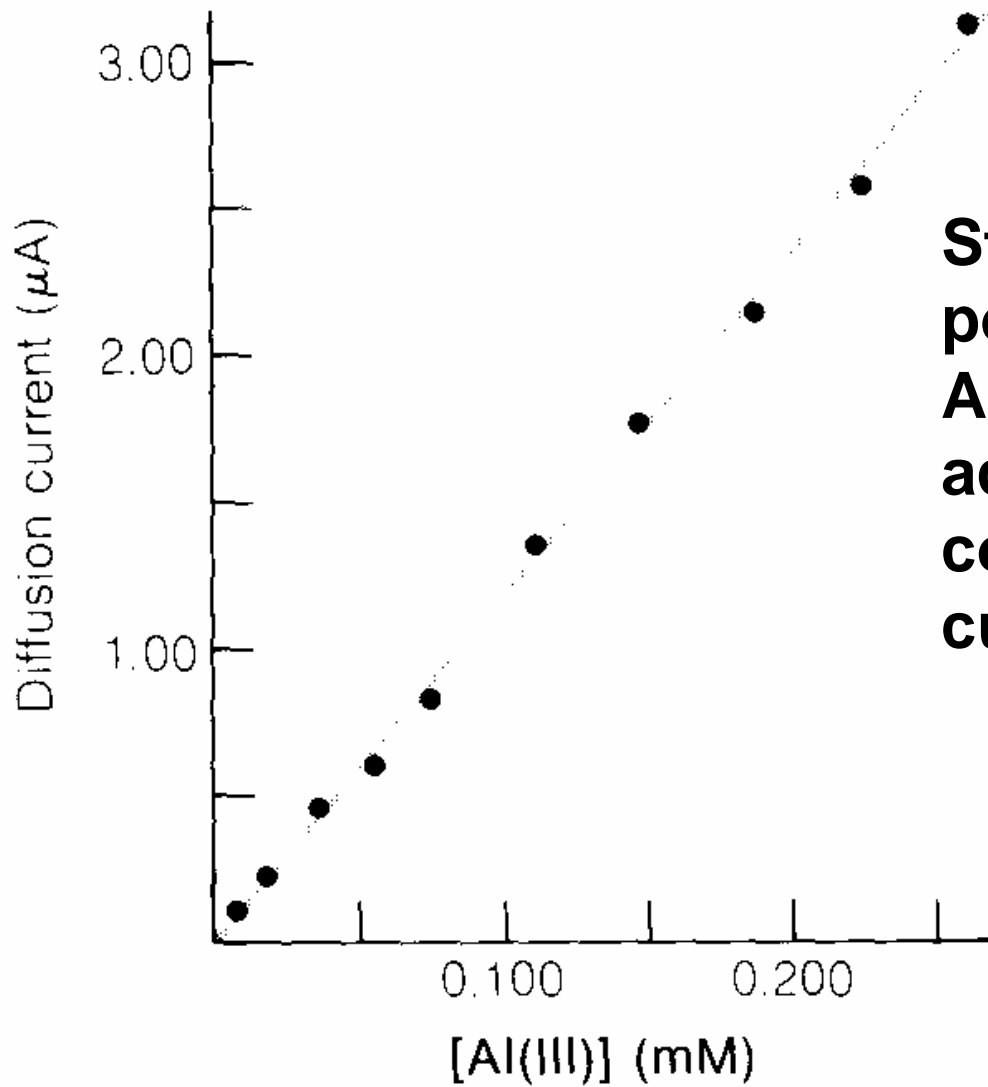
- **The principal use of polarography is in quantitative analysis.**
- **Since the magnitude of the diffusion current is proportional to the concentration of analyte, the height of a polarographic wave tells how much analyte is present.**

One Standard Method

- It is assumed that a linear relationship holds for the concentration and the wave height.
- Assuming that the wave heights for the standard and the analyte were h_1 and h_2 and the concentrations were X_{standard} and X_{analyte} then,
- $H_{\text{standard}} / h_{\text{analyte}} = X_{\text{standard}} / X_{\text{analyte}}$

Standard curves

- The most reliable, but tedious, method of quantitative analysis is to prepare a series of known concentrations of analyte in otherwise identical solutions.
- A polarogram of each solution is recorded, and a graph of the diffusion current versus analyte concentration is prepared.
- Finally, a polarogram of the unknown is recorded, using the same conditions.
- From the measured diffusion current and the standard curve, the concentration of analyte can be determined.
- The figure below shows an example of the linear relationship between diffusion current and concentration.



**Standard curve for
polarographic analysis of
Al(III) in 0.2 M sodium
acetate, pH 4.7. I_d is
corrected for the residual
current**

Example 1

Using a Standard Curve

- Suppose that 5.00 mL of an unknown sample of Al(III) was placed in a 100-mL volumetric flask containing 25.00 mL of 0.8 M sodium acetate (pH 4.7) and 2.4 mM pontachrome violet SW (a maximum suppressor). After dilution to 100 mL, an aliquot of the solution was analyzed by polarography. The height of the polarographic wave was 1.53 μA , and the residual current-measured at the same potential with a similar solution containing no Al(III)-was 0.12 μA . Find the concentration of Al(III) in the unknown.

- **The corrected diffusion current is $1.53 - 0.12 = 1.41 \mu\text{A}$.**
- **In the figure above, $1.41 \mu\text{A}$ corresponds to $[\text{Al(III)}] = 0.126 \text{ mm}$.**
- **Since the unknown was diluted by a factor of 20.0 (from 5.00 mL to 100 mL) for analysis, the original concentration of unknown must have been $(20.0)(0.126) = 2.46 \text{ mm}$.**

Standard addition method

- The standard addition method is most useful when the sample matrix is unknown or difficult to duplicate in synthetic standard solutions.
- This method is faster but usually not as reliable as the method employing a standard curve.
- First, a polarogram of the unknown is recorded. Then, a small volume of concentrated solution containing a known quantity of the analyte is added to the sample.
- *With the assumption that the response is linear*, the increase in diffusion current of this new solution can be used to estimate the amount of unknown in the original solution.
- For greatest accuracy, several standard additions are made.

- The diffusion current of the unknown will be proportional to the concentration of unknown, C_x :
- $I_{d(\text{unknown})} = kC_x$
- *where k is a constant of proportionality.*
- *Let the concentration of standard solution be C_s . When V_s mL of standard solution is added to V_x mL of unknown,*
- *The diffusion current is the sum of diffusion currents due to the unknown and the standard.*

$$I_{d(\text{unknown} + \text{standard})} = kC_x \left(\frac{V_x}{V_x + V_s} \right) + kC_s \left(\frac{V_s}{V_x + V_s} \right)$$

rearrange and solve for C_x

$$C_x = \frac{C_s V_s}{R(V_x + V_s) - V_x}$$

Example 2: Standard Addition Calculation

- **A 25.0-mL sample of Ni^{2+} gave a wave height of $2.36 \mu\text{A}$ (corrected for residual current) in a polarographic analysis.**
- **When 0.500 mL of solution containing 28.7 mM Ni^{2+} was added, the wave height increased to $3.79 \mu\text{A}$. Find the concentration of Ni^{2+} in the unknown.**

- **Using the above Equation we can write:**

$$C_x = \frac{(28.7 \text{ mM})(0.500 \text{ mL})}{\left(\frac{3.79 \mu\text{A}}{2.36 \mu\text{A}}\right)(25.0 + 0.500 \text{ mL}) - 25.0 \text{ mL}} = 0.900 \text{ mM}$$

Example 1

⌘ The concentration of As(III) in water can be determined by differential pulse polarography in 1 M HCl. The initial potential is set to -0.1 V versus the SCE, and is scanned toward more negative potentials at a rate of 5 mV/s. Reduction of As(III) to As(0) occurs at a potential of approximately -0.44 V versus the SCE. The peak currents, corrected for the residual current, for a set of standard solutions are shown in the following table.

[As(III)] (M)	i_p (μA)
1.00×10^{-6}	0.298
3.00×10^{-6}	0.947
6.00×10^{-6}	1.83
9.00×10^{-6}	2.72

What is the concentration of As(III) in a sample of water if the peak current under the same conditions is $1.37 \mu\text{A}$?

SOLUTION

Linear regression gives the equation for the calibration curve as

$$i_p(\mu\text{A}) = 0.0176 + 3.01 \times 10^5[\text{As(III)}]$$

Substituting the sample's peak current into the regression equation gives the concentration of As(III) as 4.49×10^{-6} M.

Example 2

The differential pulse polarographic analysis of mixtures of indium and cadmium in 0.1 M HCl is complicated by the overlap of their respective voltammograms.²⁰ The peak potential for indium is at -0.557 V, and that for cadmium occurs at a potential of -0.597 V. When a 0.800-ppm indium standard is analyzed, the peak current (in arbitrary units) is found to be 200.5 at -0.557 V and 87.5 at -0.597 V. A standard solution of 0.793-ppm cadmium gives peak currents of 58.5 at -0.557 V and 128.5 at -0.597 V. What is the concentration of indium and cadmium in a sample if the peak current is 167.0 at a potential of -0.557 V and 99.5 at a potential of -0.597 V?

SOLUTION

Peak currents in differential pulse polarography are a linear function of the concentration of analyte; thus

$$i_p = k(\text{ppm analyte})$$

where k is a constant that depends on the analyte and the applied potential. To determine the concentrations of indium and cadmium in the sample, we must first find the values of k for each analyte at each potential. For simplicity we will identify the potential of -0.557 V as E_1 , and that for -0.597 V as E_2 . The values of k are

$$k_{\text{In},E_1} = \frac{200.5}{0.800 \text{ ppm}} = 250.6 \text{ ppm}^{-1} \quad k_{\text{In},E_2} = \frac{87.5}{0.800 \text{ ppm}} = 109.4 \text{ ppm}^{-1}$$

$$k_{\text{Cd},E1} = \frac{58.5}{0.793 \text{ ppm}} = 73.8 \text{ ppm}^{-1} \quad k_{\text{Cd},E2} = \frac{128.5}{0.793 \text{ ppm}} = 162.0 \text{ ppm}^{-1}$$

Next, we write simultaneous equations for the current at the two potentials

$$i_{E1} = 250.6 \text{ ppm}^{-1} (\text{ppm In}) + 73.8 \text{ ppm}^{-1} (\text{ppm Cd}) = 167.0$$

$$i_{E2} = 109.4 \text{ ppm}^{-1} (\text{ppm In}) + 162.0 \text{ ppm}^{-1} (\text{ppm Cd}) = 99.5$$

Solving the simultaneous equations, which is left as an exercise, gives the concentration of indium as 0.606 ppm and the concentration of cadmium as 0.205 ppm.

Example 3

• The concentration of copper in a sample of sea water is determined by anodic stripping voltammetry using the method of standard additions. When a 50.0-mL sample is analyzed, the peak current is 0.886 μA . A 5.00- μL spike of 10.0-ppm Cu^{2+} is added, giving a peak current of 2.52 μA . Calculate the parts per million of copper in the sample of sea water.

SOLUTION

Peak currents in anodic stripping voltammetry are a linear function of concentration

$$i_p = k(\text{ppm Cu}^{2+})$$

where k is a constant. Thus, for the sample we write

$$0.886 = k(\text{ppm Cu}^{2+})$$

and for the standard addition

$$2.52 = k \left[\frac{0.0500 \text{ L}}{0.0500 \text{ L} + 5.00 \times 10^{-6} \text{ L}} (\text{ppm Cu}^{2+}) + \frac{5.00 \times 10^{-6} \text{ L}}{0.0500 \text{ L} + 5.00 \times 10^{-6} \text{ L}} (10.0 \text{ ppm}) \right]$$

Solving the first equation for k , substituting into the second equation, and simplifying gives

$$2.52 = 0.8859 + \frac{(8.859 \times 10^{-5})(10.0 \text{ ppm})}{(\text{ppm Cu}^{2+})}$$

Solving gives the concentration of Cu^{2+} as 5.42×10^{-4} ppm, or 0.542 ppb.

Example 4

The following data were obtained from the linear scan hydrodynamic voltammogram of a reversible reduction reaction

Potential (V vs. SCE)	Current (μA)
-0.358	0.37
-0.372	0.95
-0.382	1.71
-0.400	3.48
-0.410	4.20
-0.435	4.97

The limiting current was $5.15 \mu\text{A}$. Show that the reduction reaction is reversible, and determine values for n and $E_{1/2}$.

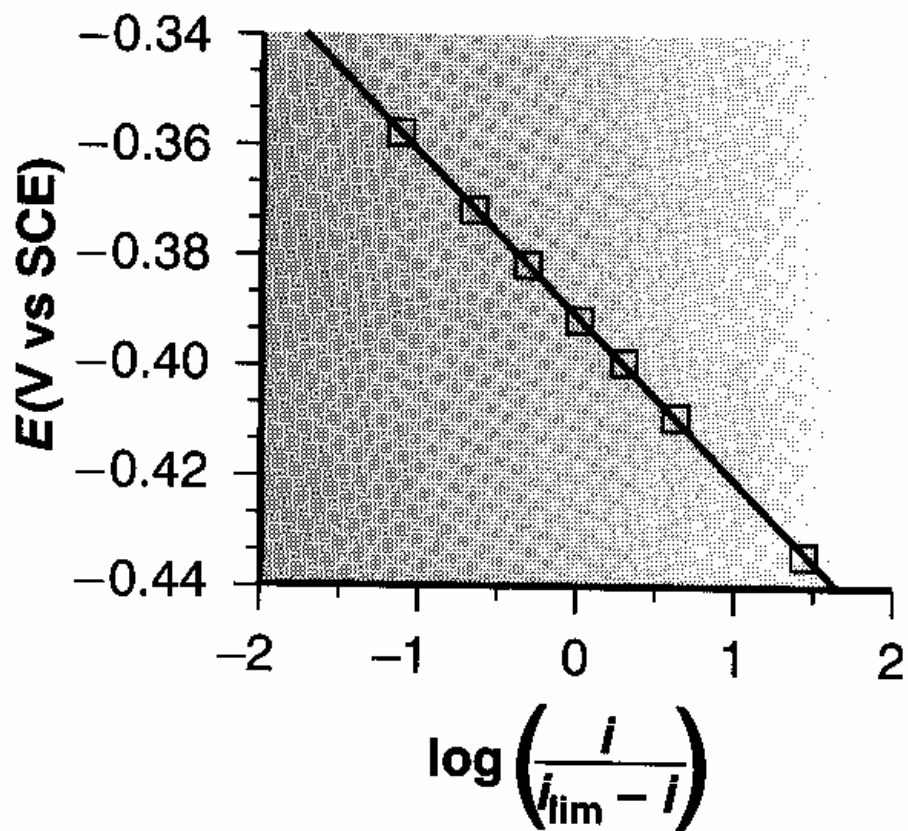


Figure 11.41

Graphical determination of electrochemical reversibility, n , and half-wave potential in linear scan hydrodynamic voltammetry.

If the reaction is reversible, then a plot of E versus $\log(i/i_{\text{lim}} - i)$ will be a straight line with a slope that yields an integer value for n . As shown in Figure 11.41, plotting the data in this manner gives a straight line. Linear regression gives the equation for the straight line as

$$E = -0.391 - 0.02999 \log \frac{i}{i_{\text{lim}} - i}$$

Knowing that

$$\text{Slope} = -0.02999 = -\frac{0.05916}{n}$$

gives a value for n of 1.97, or 2 electrons. Combining equations 11.40 and 11.41 shows that the y -intercept for a plot of E versus $\log(i/i_{\text{lim}} - i)$ is equal to the half-wave potential. Thus, $E_{1/2}$ for the reduction reaction is -0.391 V versus the SCE.