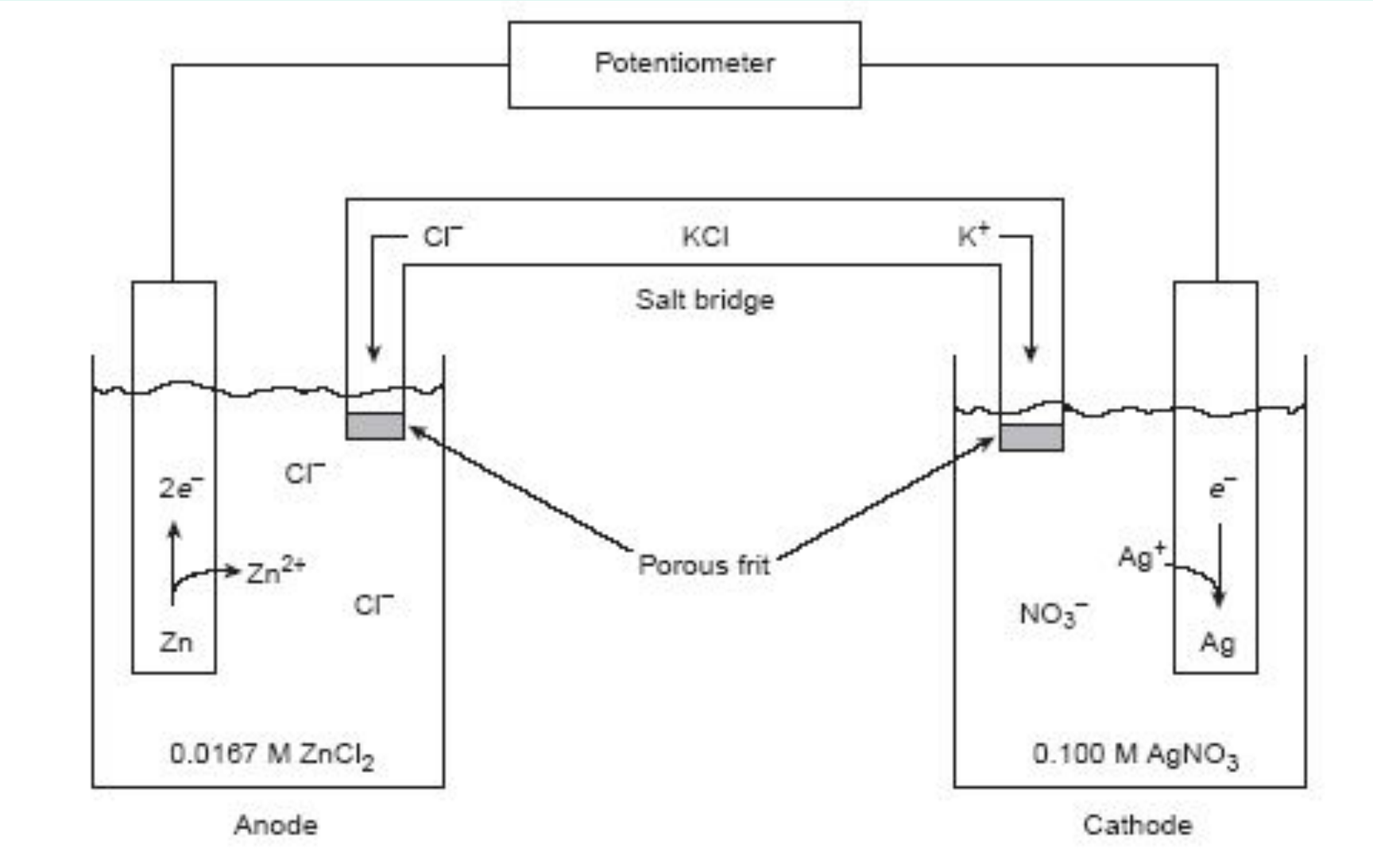
Electroanalytical Chemistry

Electroanalytical Chemistry:

Electroanalytical Chemistry encompasses a group of quantitative analytical methods that are based upon the electrical properties of a analyte solution when it is part of an electrochemical cell.

Electrochemical cell



Potential and Concentration:

The Nernst equation indicates the relationship between the activity of species in solution and the potential (E) produced by a half-cell involving those species.

$$ox + ne^- \longrightarrow red$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[red]}{[ox]} = E^\circ + \frac{RT}{nF} \ln \frac{[ox]}{[red]}$$

The potential of a electrochemical cell is given as:

$$a\ ox_1 + b\ red_2 \longrightarrow c\ red_1 + d\ ox_2, \qquad K_{equil}$$

Ecell = Ec – Ea

$$E_{cell} = E_1^\circ - E_2^\circ + \frac{RT}{nF} \ln \frac{[ox_1]^a\ [red_2]^b}{[ox_2]^d\ [red_1]^c}$$

The simplest division is between:

- bulk methods, which measure properties of the whole solution (Conductometric methods)
- Interfacial methods, in which the signal is a function of phenomena occurring at the interface between an electrode and the solution in contact with the electrode.

Interfacial Electrochemical Methods

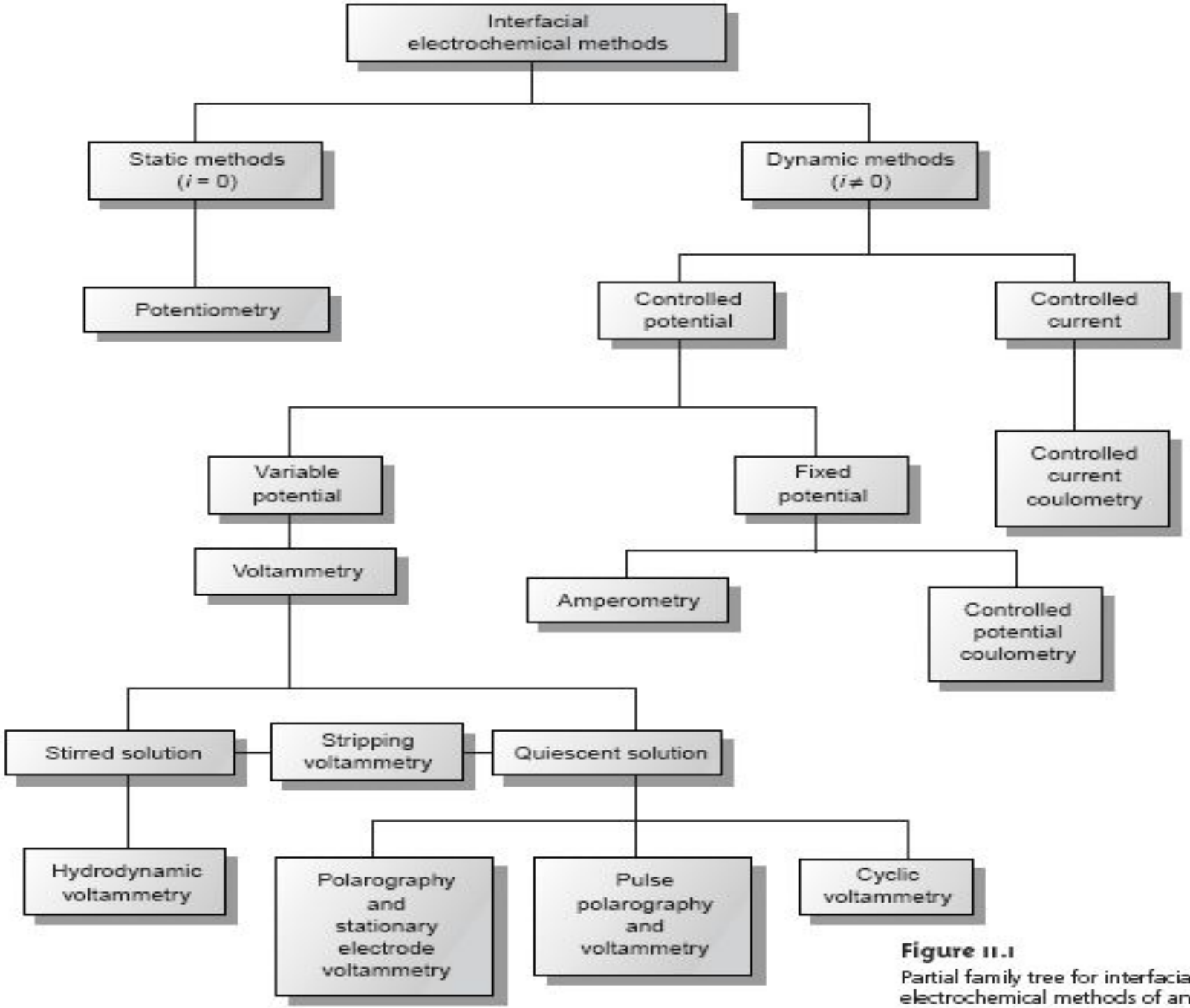


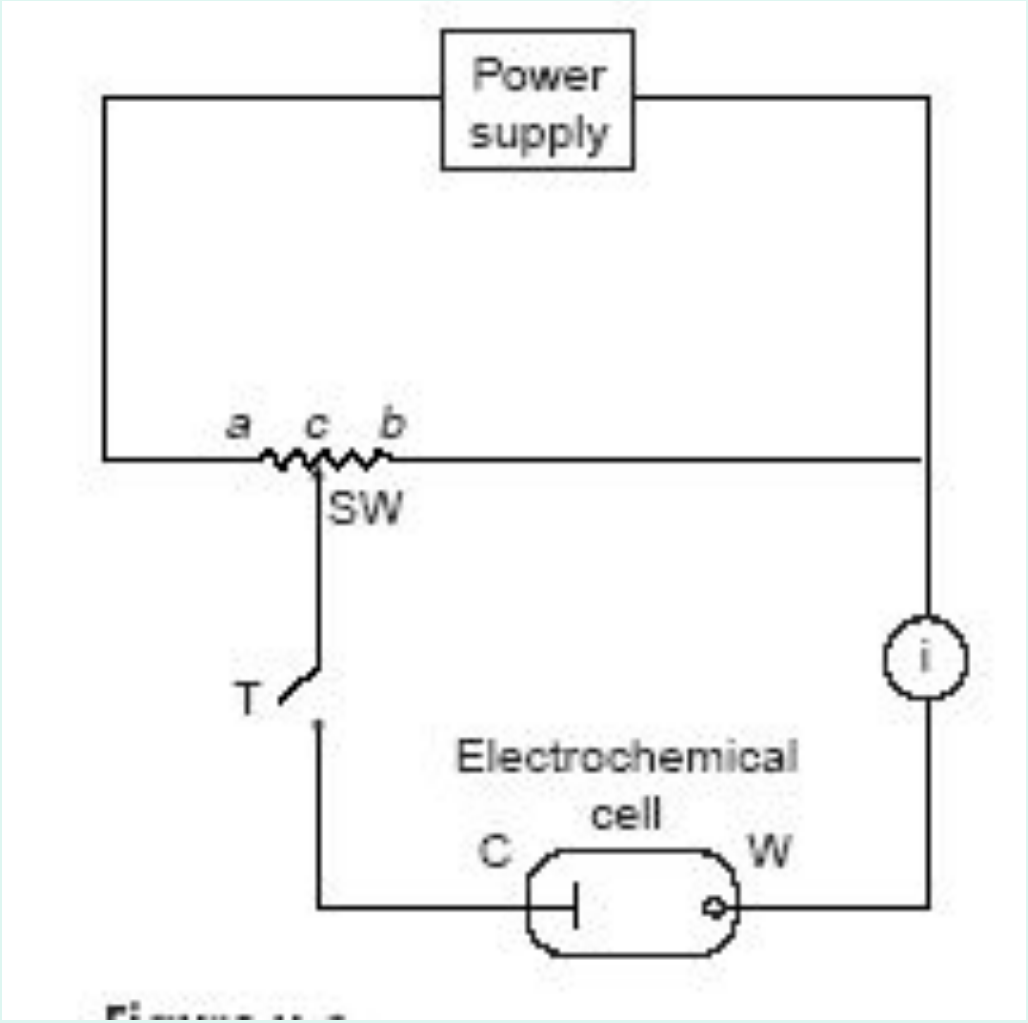
Figure 11.1
Partial family tree for interfacial electrochemical methods of analysis.

Ohm's law

- The statement that the current moving through a circuit is proportional to the applied potential and inversely proportional to the circuit's resistance:

$$E = iR$$

potentiostat

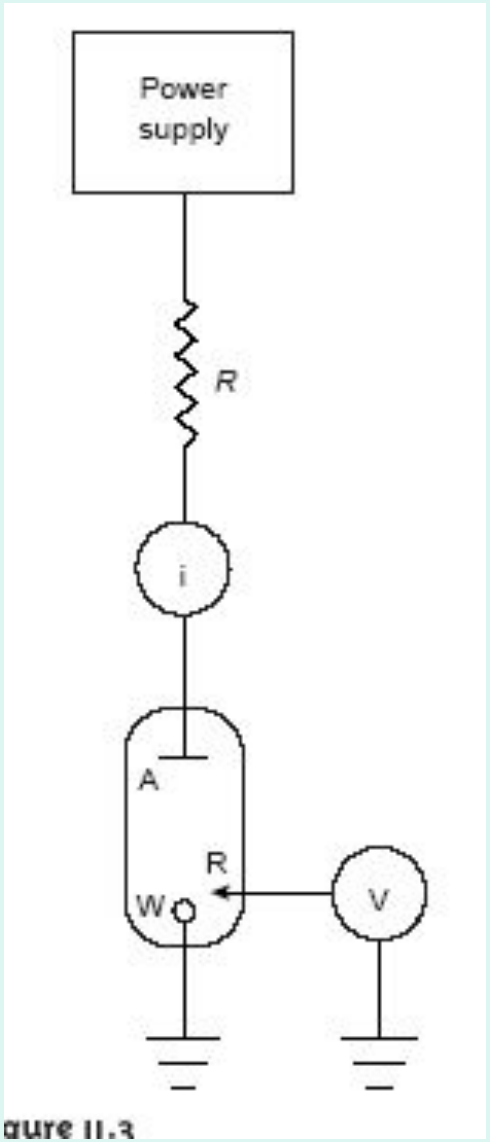


potentiostat
A device used to control the potential in an electrochemical cell.

Three principal sources for the analytical signal:

1. Potential
2. Current
3. charge

Galvanostat



gure II.3

galvanostat

A device used to control the current in an electrochemical cell.

Three main Electroanalytical methods are:

- Potentiometry
- Voltammetry
- Coulometry

Potentiometry

The electrochemical technique called potentiometry measures the potential developed by a cell consisting of an indicator electrode and a reference electrode.

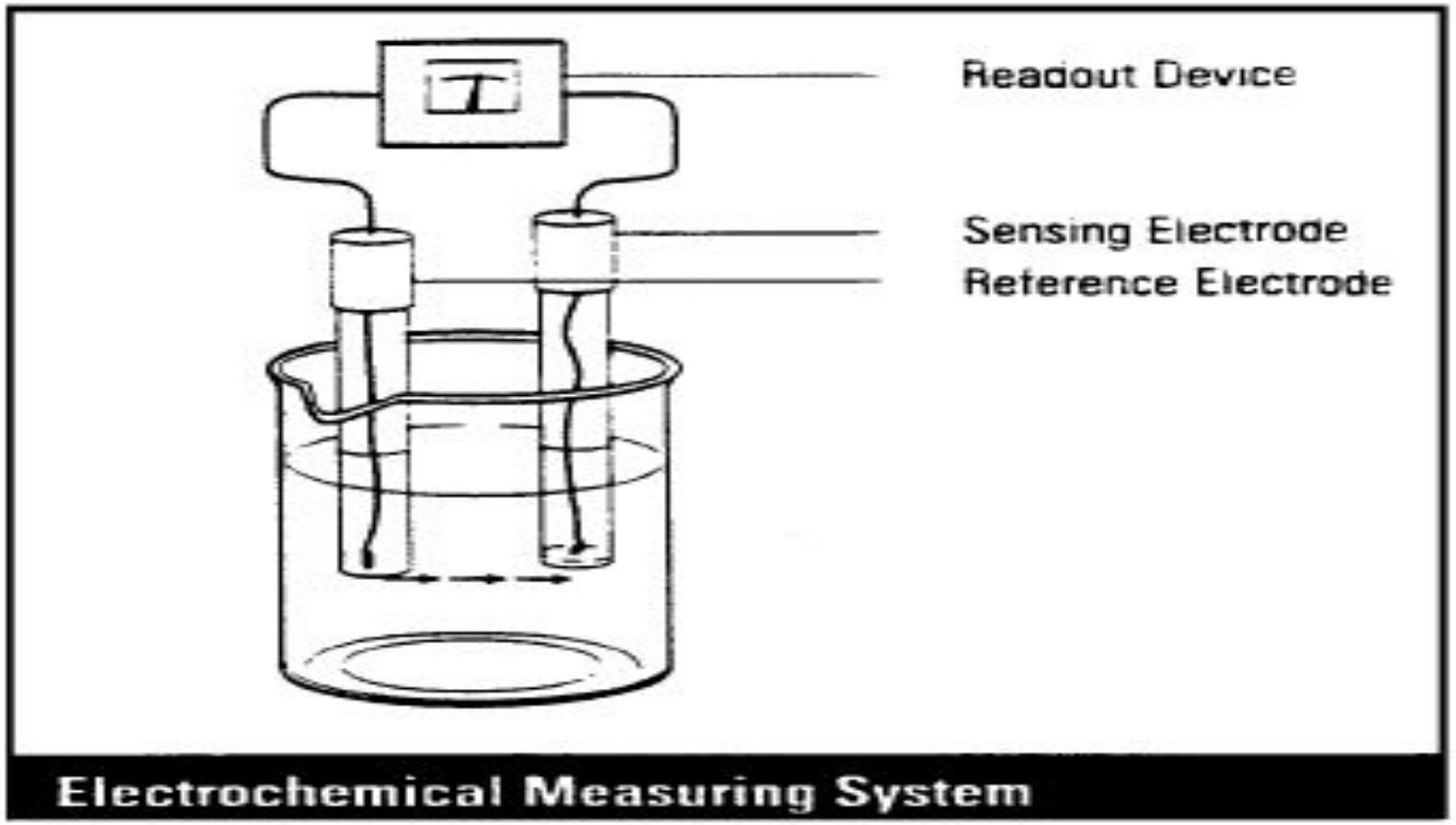
$$E(total) = E(indicator) - E(reference)$$

Accurate determination of the potential developed by a cell requires a negligible current flow during measurement.

Potentiometer:

A device for measuring the potential of an electrochemical cell without drawing a current or altering the cell's composition.

Electrochemical measuring System:



Electrodes in Potentiometry:

1- Reference Electrodes:

- The Saturated Calomel Electrode (SCE)
- The Silver/Silver Chloride Electrode

2-Indicator Electrodes:

- Metallic Electrodes
- Membrane Electrodes

Calomel Electrode (SCE)

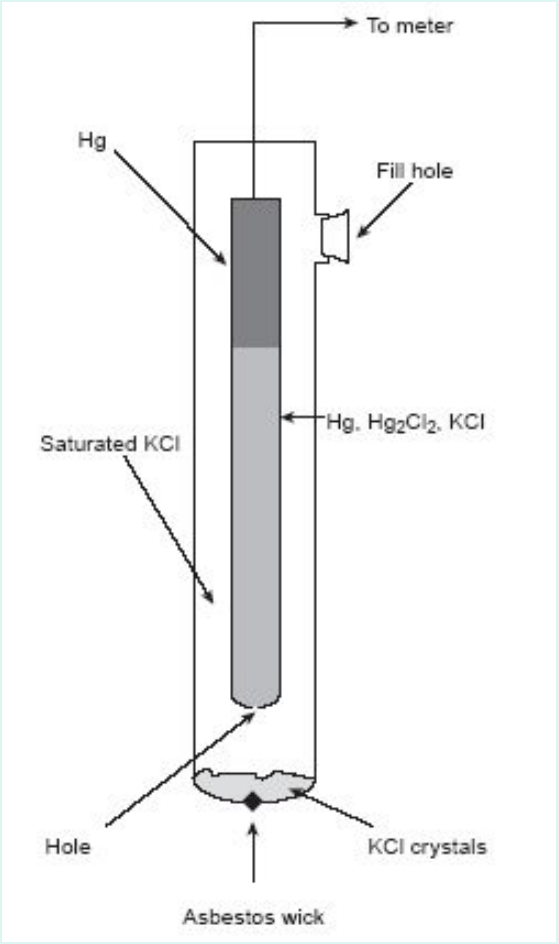
$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(\ell) + 2Cl^-(aq)$$

The Nernst equation for the calomel electrode is

$$E = E^\circ_{Hg_2Cl_2/Hg} - \frac{0.05916}{2}\log[Cl^-]^2 = +0.2682 - \frac{0.05916}{2}\log[Cl^-]^2$$

$$Hg(\ell) \mid Hg_2Cl_2 \text{ (sat'd)}, KCl\ (aq, \text{ sat'd}) \parallel$$

potential at 25 °C of +0.2444 V.



Silver / Silver chloride electrode

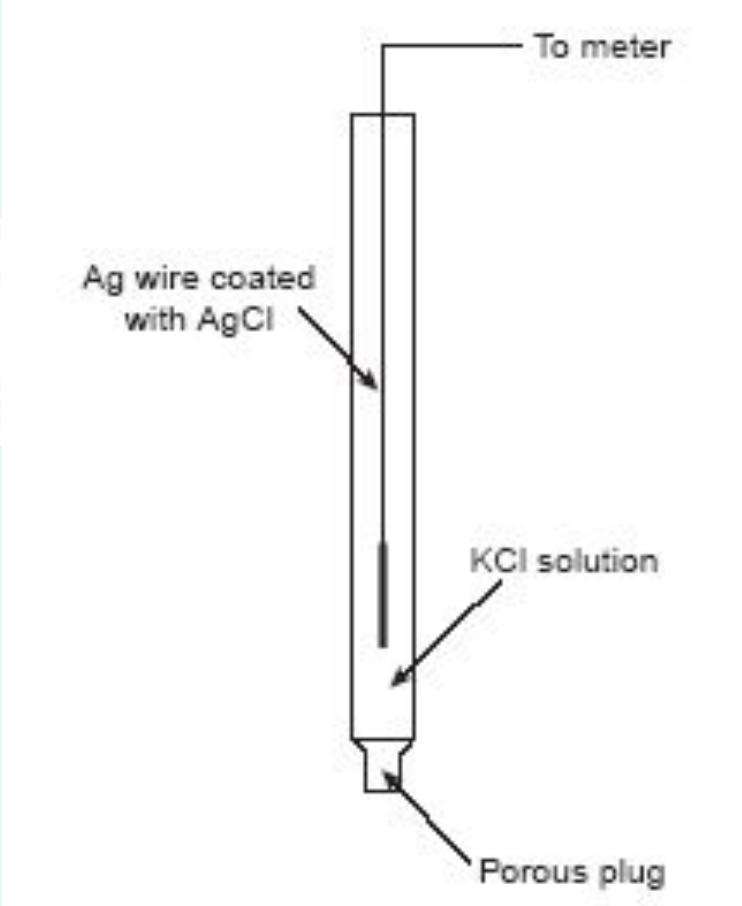
$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$$

$$E + E^0_{AgCl/Ag} - 0.05916 \log [Cl^-] = +0.2223 - 0.05916 \log [Cl^-]$$

$Ag(s) \mid AgCl$ (sat'd), KCl (x M) ||

ration of KCl

potential of +0.197 V at 25 °C.



Metallic indicator electrodes:

1- First kind

2- Second kind

3- Redox electrode

electrode of the first kind
A metallic electrode whose potential is a function of the concentration of M^{n+} in an M^{n+}/M redox half-reaction.

electrode of the second kind
A metallic electrode whose potential is a function of the concentration of X in an MX_n/M redox half-reaction.

redox electrode
An inert electrode that serves as a source or sink for electrons for a redox half-reaction.

Electrode of the First kind

$$\text{SCE} \,||\, \text{Cu}^{2+}\,(\text{unk}) \,|\, \text{Cu}(s)$$

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} = +0.3419 - \frac{0.05916}{2}\log\frac{1}{[\text{Cu}^{2+}]} - +0.2444$$

$$E_{\text{cell}} = K - \frac{0.05916}{n}\log\frac{1}{[\text{M}^{n+}]} = K + \frac{0.05916}{n}\log[\text{M}^{n+}]$$

Electrode of the Second kind

$$\text{REF} \,\|\, \text{AgI (sat'd)}, \text{I}^- \text{(unk)} \mid \text{Ag}(s)$$

$$E_{\text{cell}} = K - 0.05916 \log [\text{I}^-]$$

$$E = E^\circ_{\text{Ag}^+/\text{Ag}} - 0.05916 \log \frac{1}{[\text{Ag}^+]} = +0.7996 - 0.05916 \log \frac{1}{[\text{Ag}^+]}$$

If the solution is saturated with AgI, then the solubility reaction

$$\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq)$$

determines the concentration of Ag^+; thus

$$[\text{Ag}^+] = \frac{K_{\text{sp,AgI}}}{[\text{I}^-]}$$

where $K_{\text{sp,AgI}}$ is the solubility product for AgI. Substituting equation 11.5 into 1

$$E = +0.7996 - 0.05916 \log \frac{[\text{I}^-]}{K_{\text{sp,AgI}}}$$

Redox Electrode

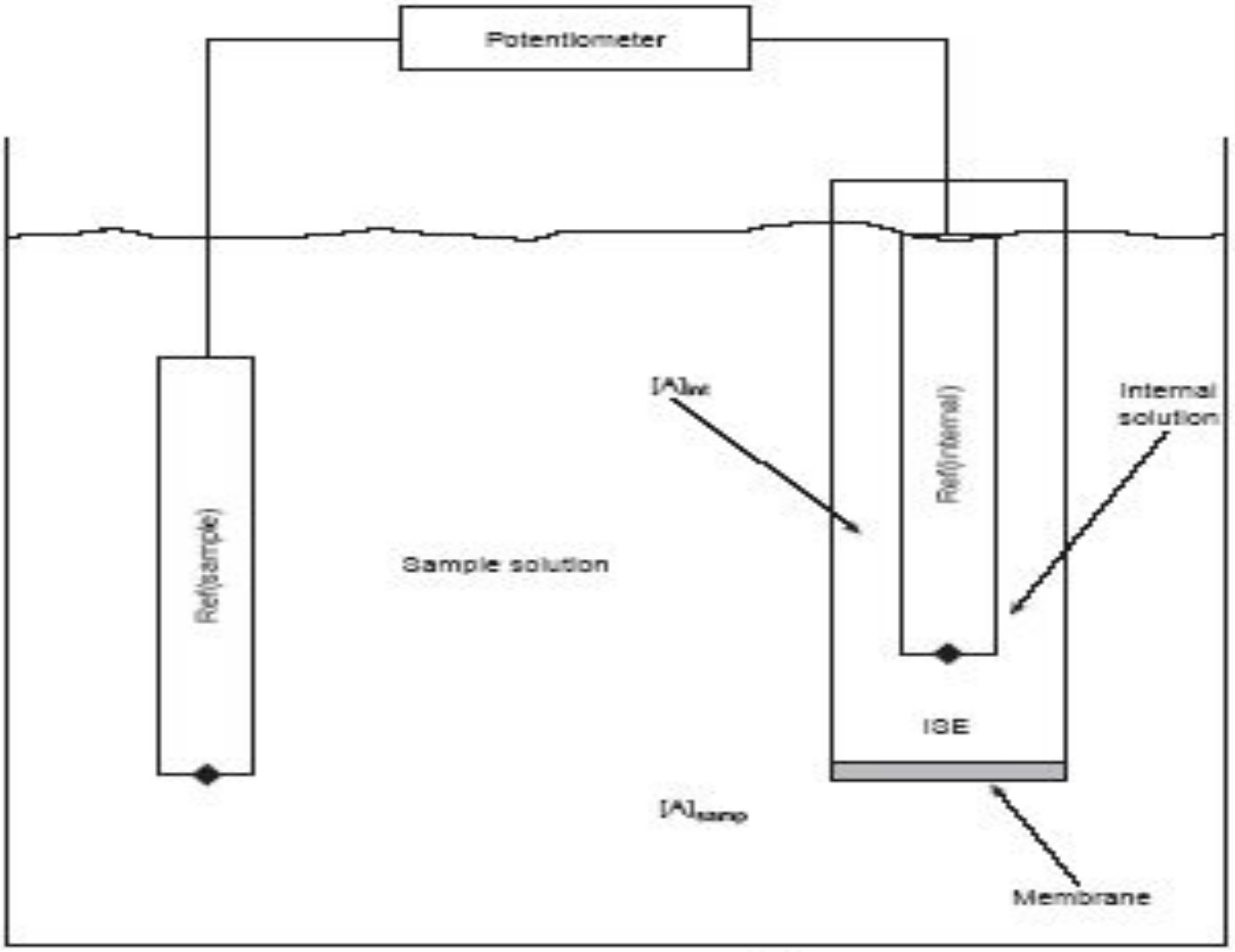
$$Fe^{3+} + e^- = Fe^{2+}$$

$$E = E^\circ - 0.059\,\text{V} \log_{10} \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Membrane Electrodes (Ion Selective Electrodes or *ISE*) :

Membrane electrodes are a class of electrodes that respond selectively to ions by the development of a potential difference across a membrane that separates the analyte solution from a reference solution.

Ion Selective Electrode



$$E_{mem} = E_{asym} - \frac{RT}{zF} \ln \frac{[A]_{int}}{[A]_{samp}} \qquad 11.7$$

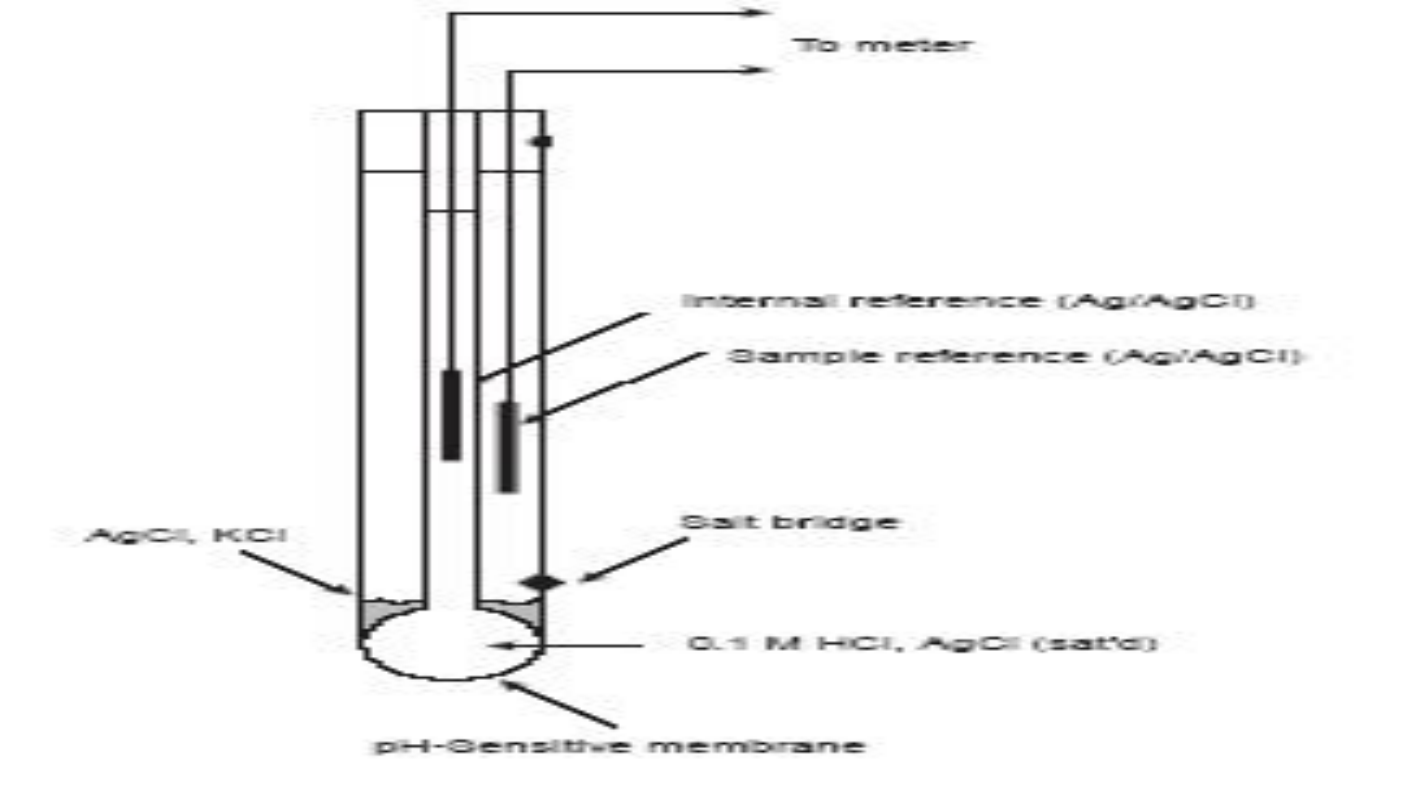
Types of Ion – Selective Membrane Electrodes:

- Glass Ion Selective electrodes
- Crystalline Solid-State Electrodes
- Liquid Membrane ISEs

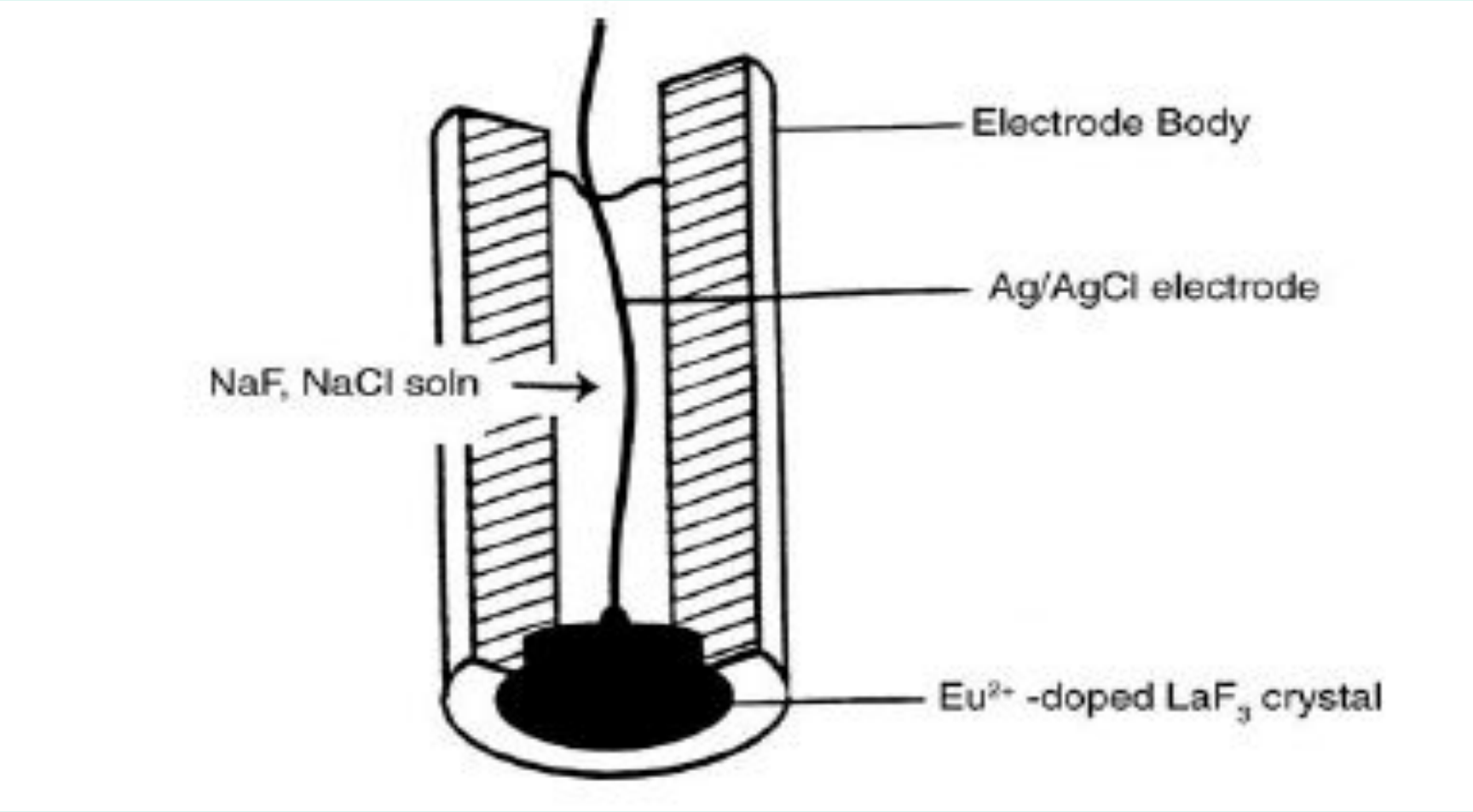
Glass ion selective electrodes

$$H^+(aq) + G^-\text{–}Na^+(s) \rightleftharpoons G^-\text{–}H^+(s) + Na^+(aq)$$

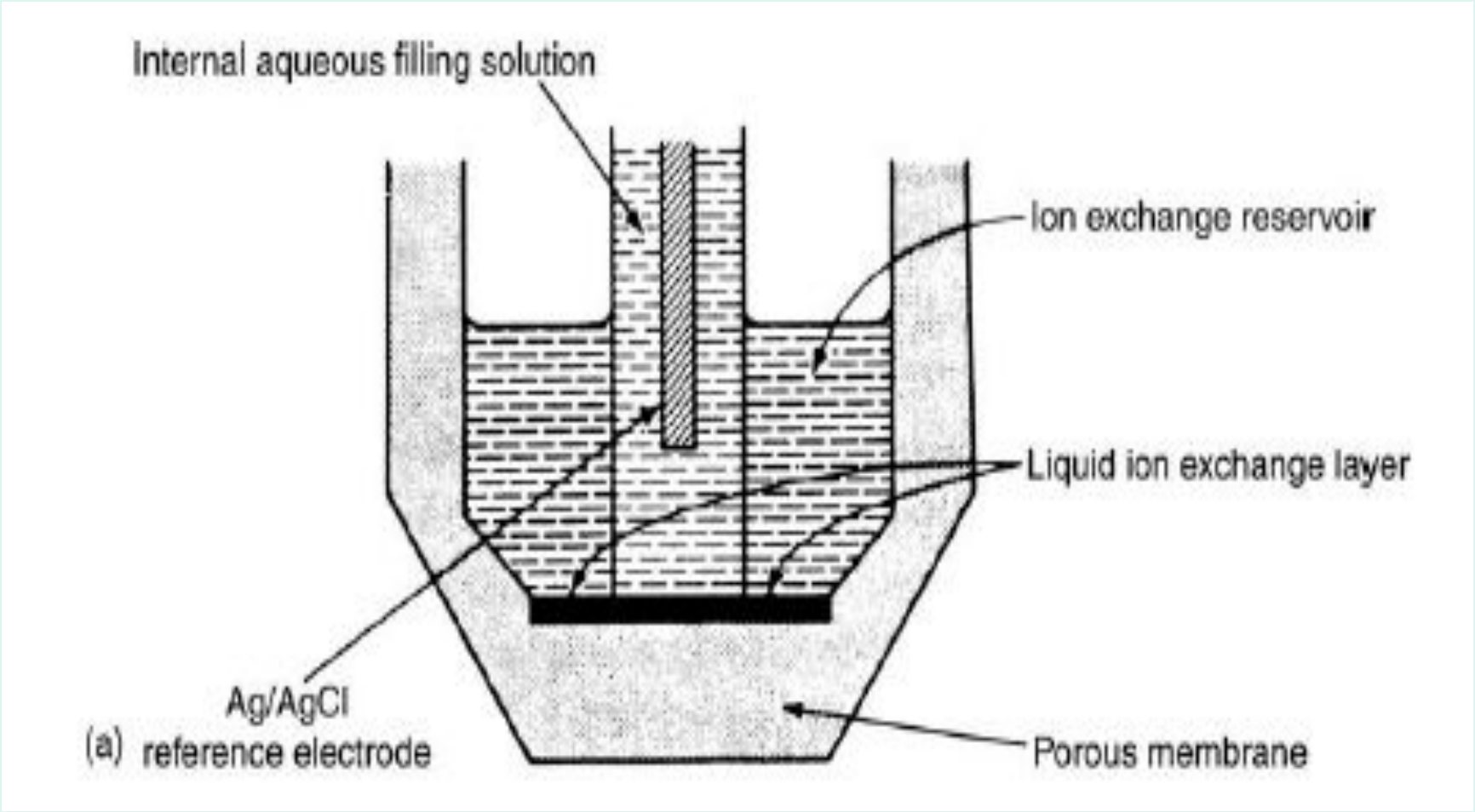
$$E_{cell} = K + 0.05916 \log [H^+]$$



Crystalline Solid-State Electrodes (Flouride Ion Selective Electrode):



Liquid Membrane ISEs:



The ion-exchanger may be a cation exchanger, an anion exchanger, or a neutral complexing agent.

Analytical applications of Potentiometry:

A) Direct Potetiometry

B) Potentiometric Titrations

A) Direct Potetiometry

- 1- Direct Determination
- 2- Calibration Curve
- 3- Standard addition Method

Direct Determination

Measurement of Ag+ Ion Concentration:

E(cell) = E(Ag+) - E(SCE)

$$E(\text{Ag}) = E^0(\text{Ag}) - \frac{RT}{nF}\ln\frac{1}{[\text{Ag}^+]}$$

$$E(\text{cell}) = E^0(\text{Ag}) - (0.05916)\log\frac{1}{[\text{Ag}^+]} - E(\text{SCE})$$

$$E(\text{cell}) = 0.799 - (0.05916)\log\frac{1}{[\text{Ag}^+]} - 0.244$$

$$\log[\text{Ag}^+] = \frac{0.400 - 0.555}{0.05916} = -\frac{0.155}{0.05916}$$
$$\log[\text{Ag}^+] = -2.62$$

$$\text{The concentration of } \text{Ag}^+ = \text{antilog}(-2.62) = 2.4 \times 10^{-3}\,\text{M}$$

2- Calibration Curve

3- Standard addition Method

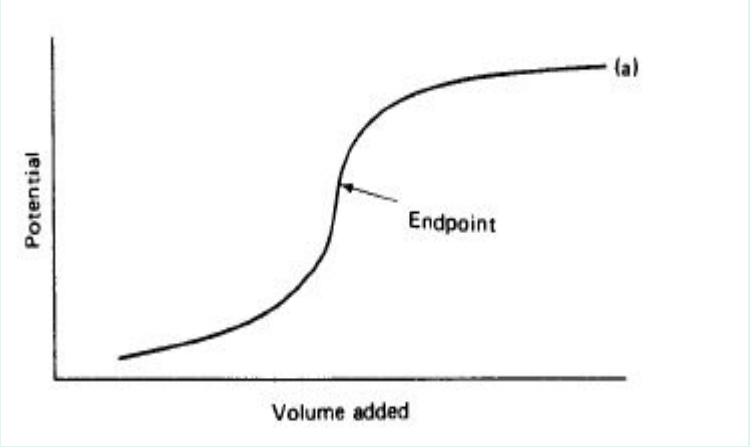
LIKE AAS ANALYTICAL METHODS

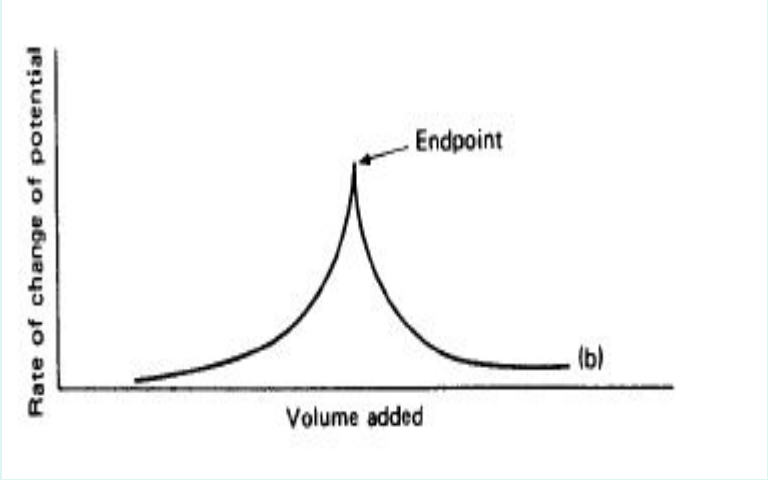
B) Potentiometric Titrations

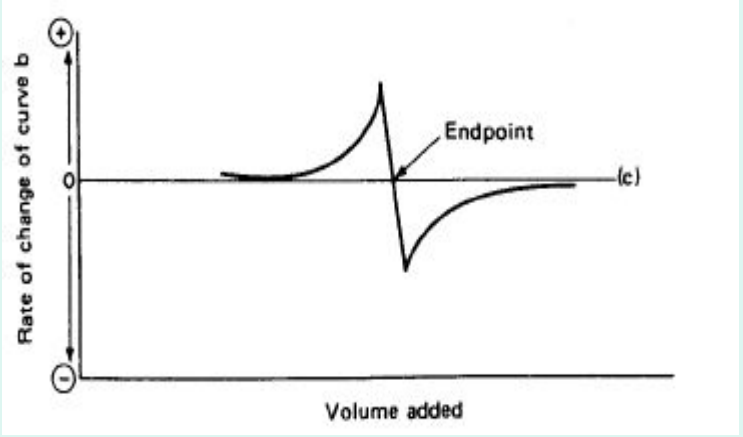
Potentiometry is a useful way to determine the endpoint in many titrations. For example, the concentration of Ag+ ion in solution can be used to determine the equivalence point in the titration of Ag+ with Cl^- . In this titration the following reaction takes place:

$$Ag^+ + Cl^- \rightleftharpoons AgCl(s) \text{ (precipitation)}$$

Potentiometric Titration Curves:







Voltammetry:

- Determination of the concentrations of trace metals in a variety of Clinical, Environmental, food, steels and other alloys, gasoline, gunpowder, residues, and pharmaceuticals matrices.
- Quantitative analysis of organics, particularly in the pharmaceutical industry

Voltammetry

Voltametry comprises a group of electroanalytical methods in which information about the analyte is derived from the measurement of current as a function of applied potential under conditions that encourage polarization of an indicator or working microelectrode.

Controlling and Measuring Current and Potential:

Voltammetric measurements are made in an electrochemical cell:

- **indicator electrode**

The electrode whose potential is a function of the analyte's concentration (also known as the working electrode).

- **counter electrode**

The second electrode in a two-electrode cell that completes the circuit.

- **reference electrode**

An electrode whose potential remains constant and against which other potentials can be measured.

Typical cell for Voltammetry:

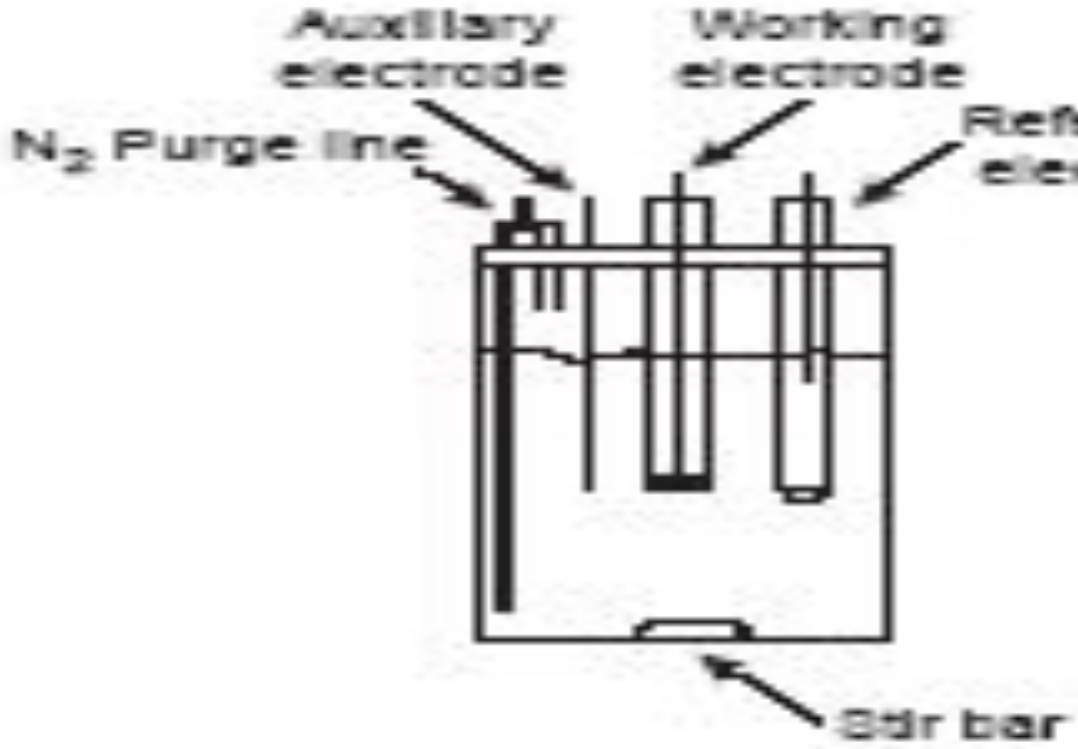


Figure II.28
Typical electrochemical cell for use in voltammetry.

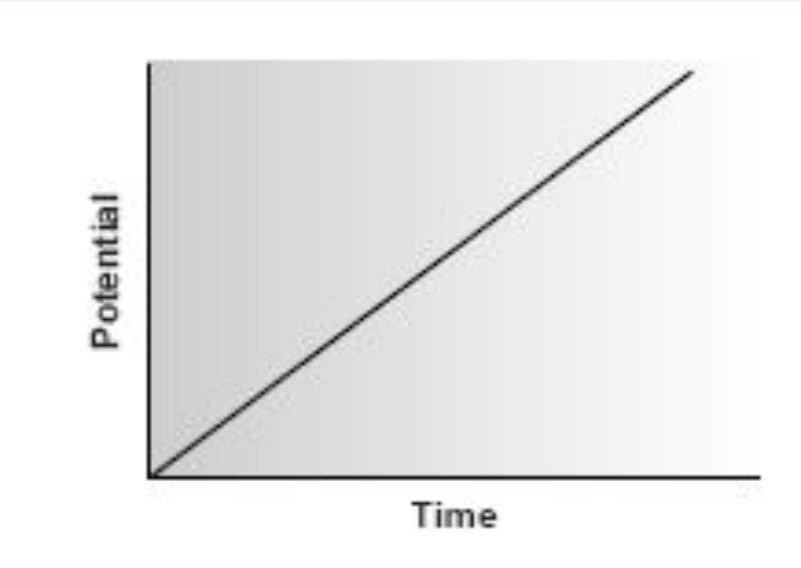
Voltammetric Techniques:

- Polarography (NPP, DPP)
- Cyclic Voltammetry
- Normal pulse voltammetry (NPV)
- Differential pulse Voltammetry (DPV)
- Staircase Voltammetry
- Square Wave Voltammetry (SWV)
- Stripping Voltammetry

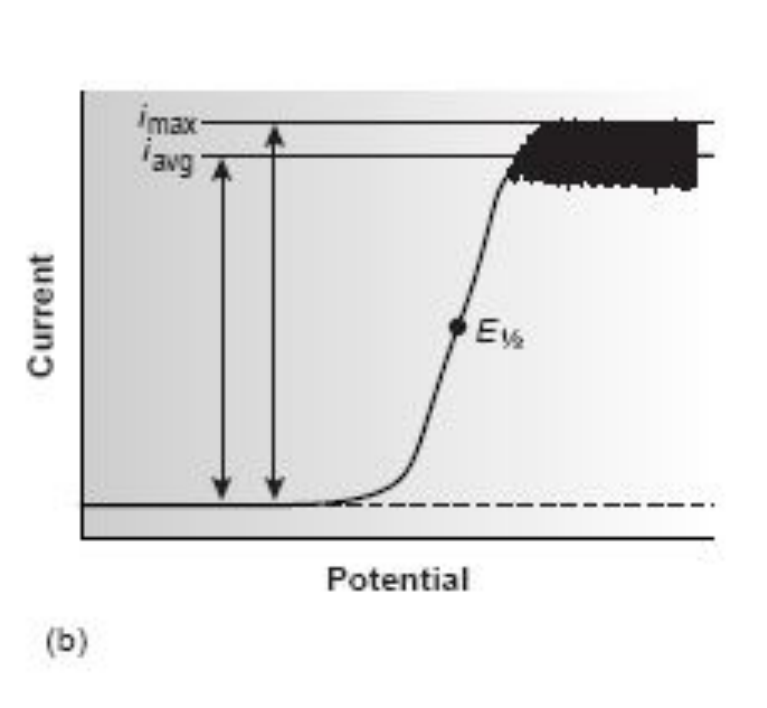
Polarography(Voltammetry with Dropping Mercury Electrode):

the Ilikovic equation

$$i_{max} = 706nD^{1/2}m^{2/3}t^{1/6}C_A$$



Potential excitation signal



Polarogram

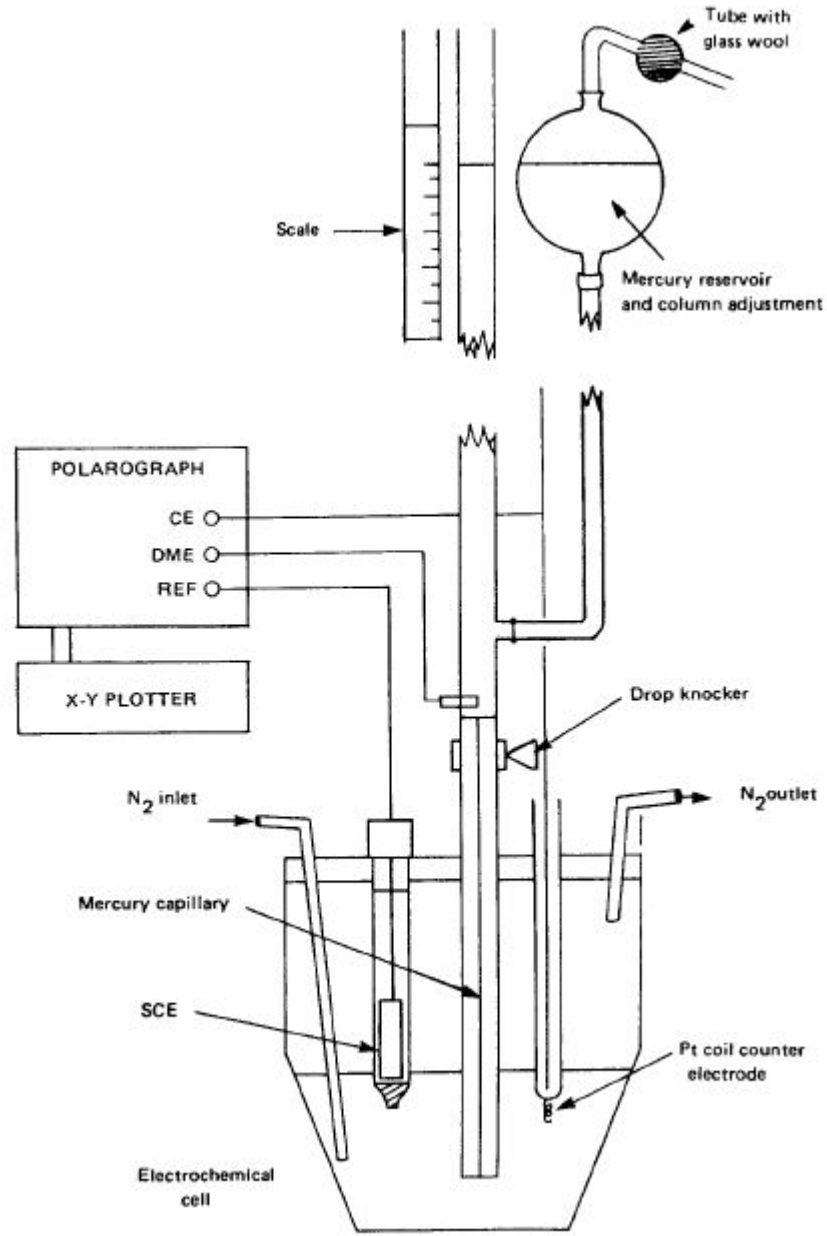


Figure 15.26 Modern polarographic cell and three-electrode circuit.

Polarographic Cell and three electrode circuit

Different types of Hg electrodes:

1- hanging mercury drop electrode

An electrode in which a drop of Hg is suspended from a capillary tube.

2- dropping mercury electrode

An electrode in which successive drops of Hg form at the end of a capillary tube as a result of gravity, with each drop providing a fresh electrode surface.

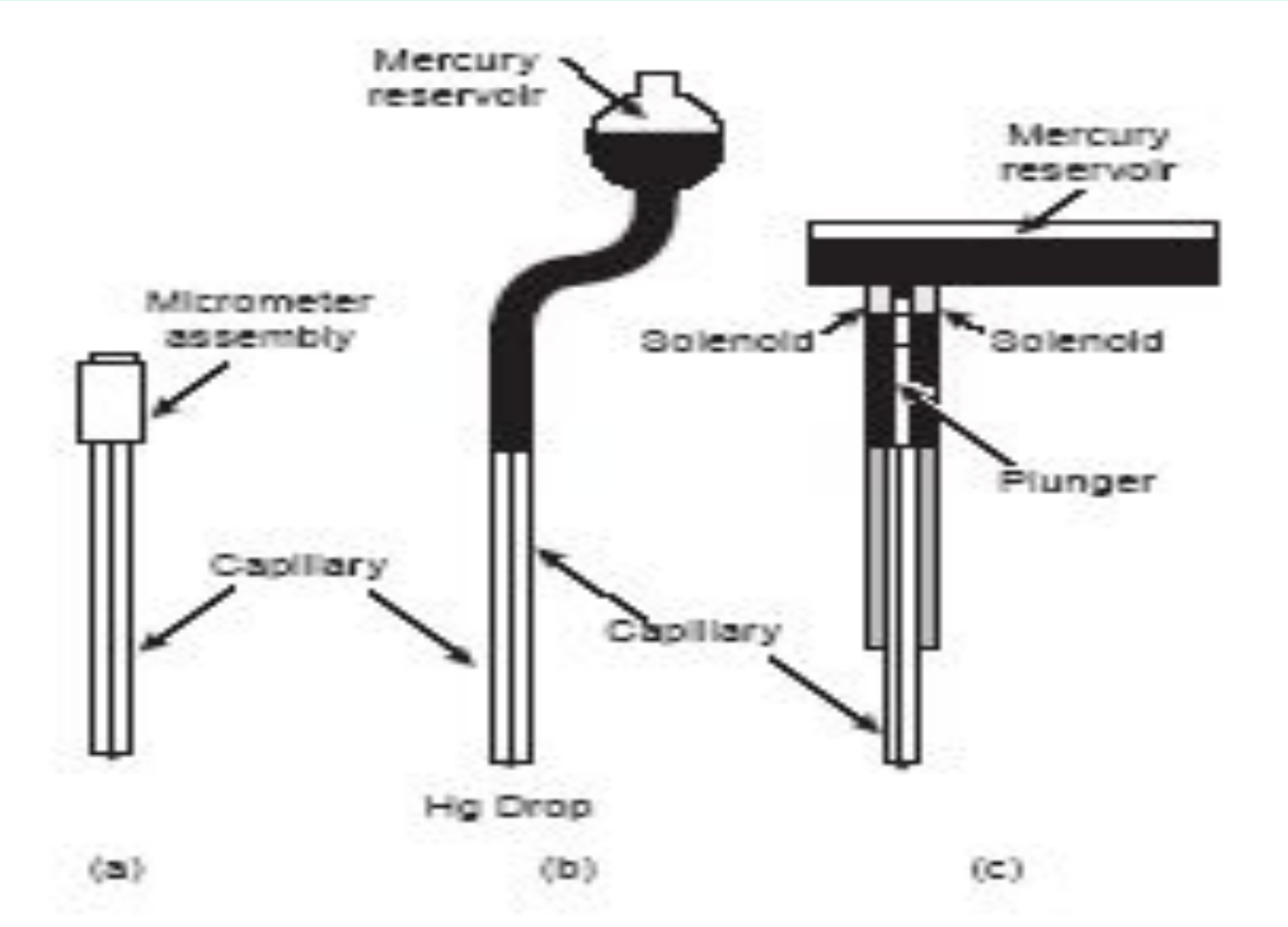
3- static mercury drop electrode

An electrode in which successive drops of Hg form at the end of a capillary tube as the result of a mechanical plunger, with each drop providing a fresh electrode surface.

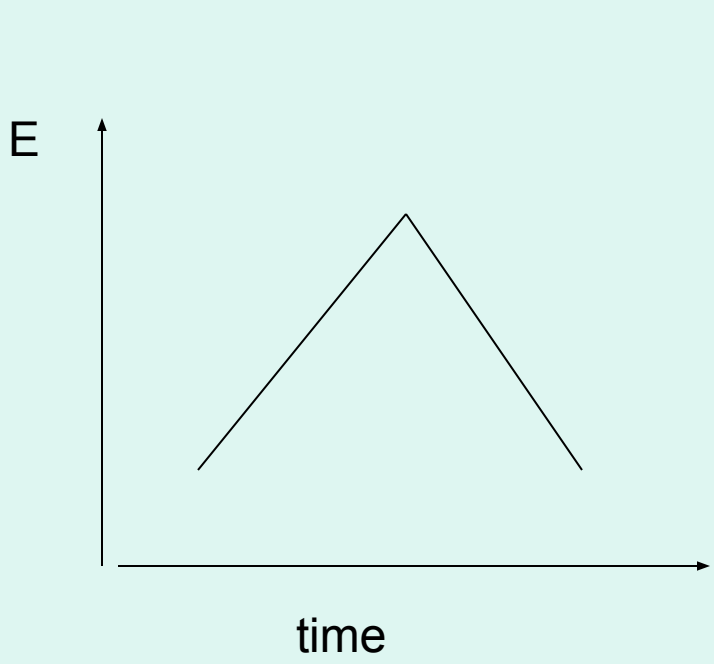
4- amalgam

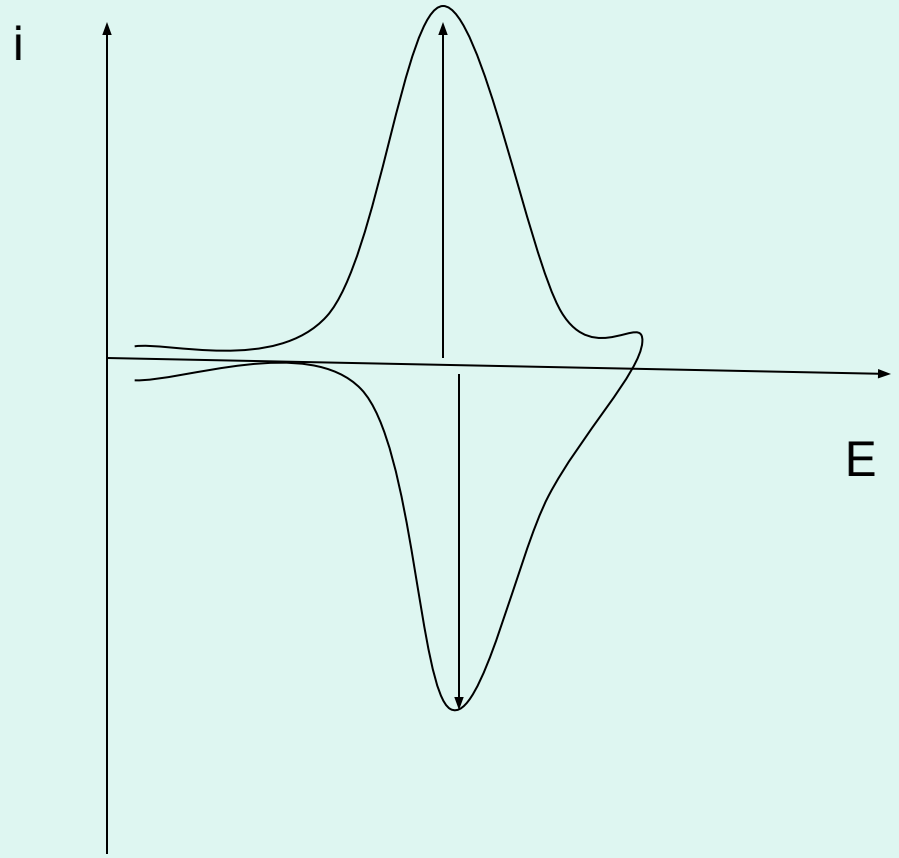
A metallic solution of mercury with another metal.

Hg electrodes

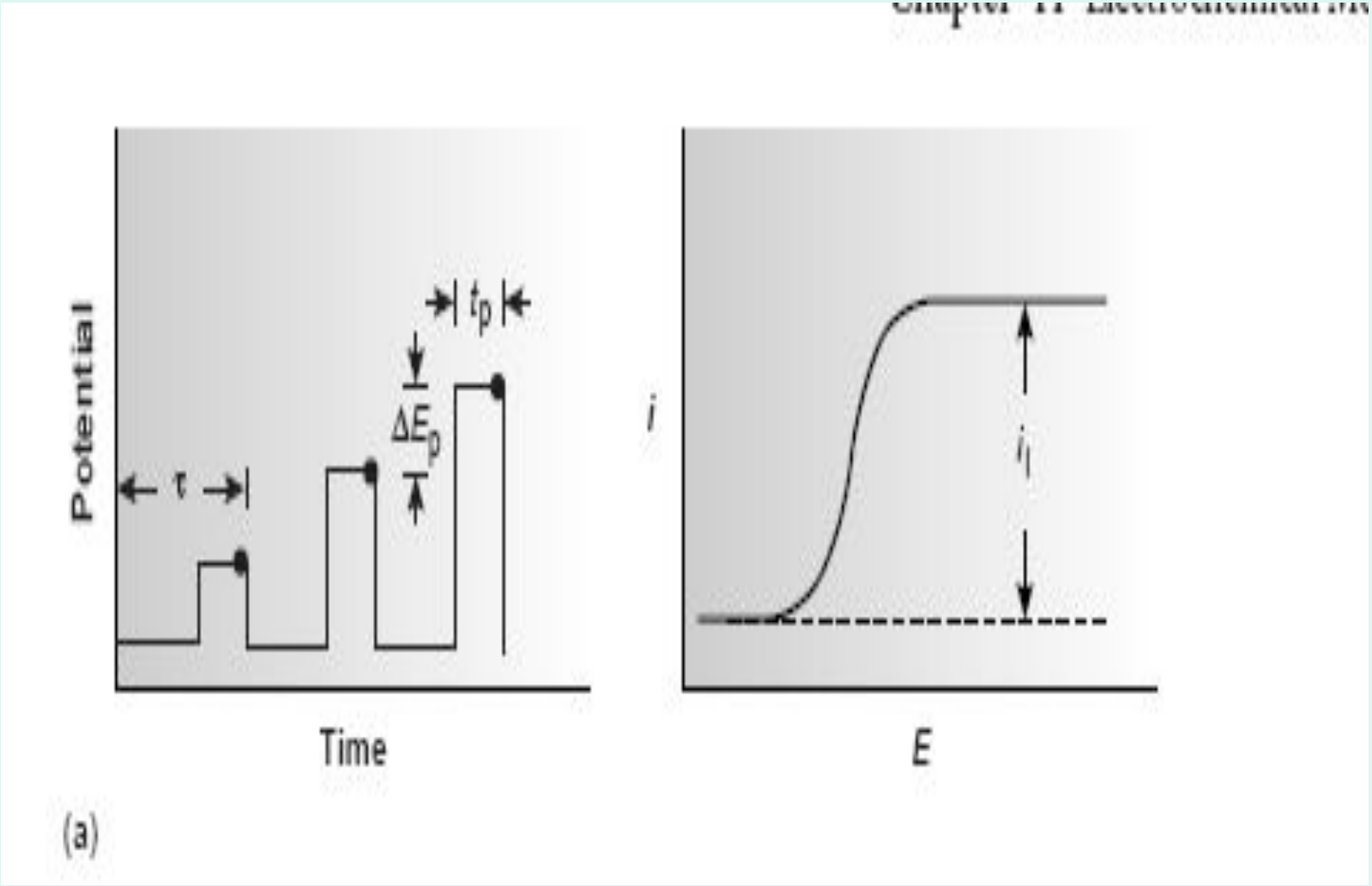


Cyclic voltammetry:

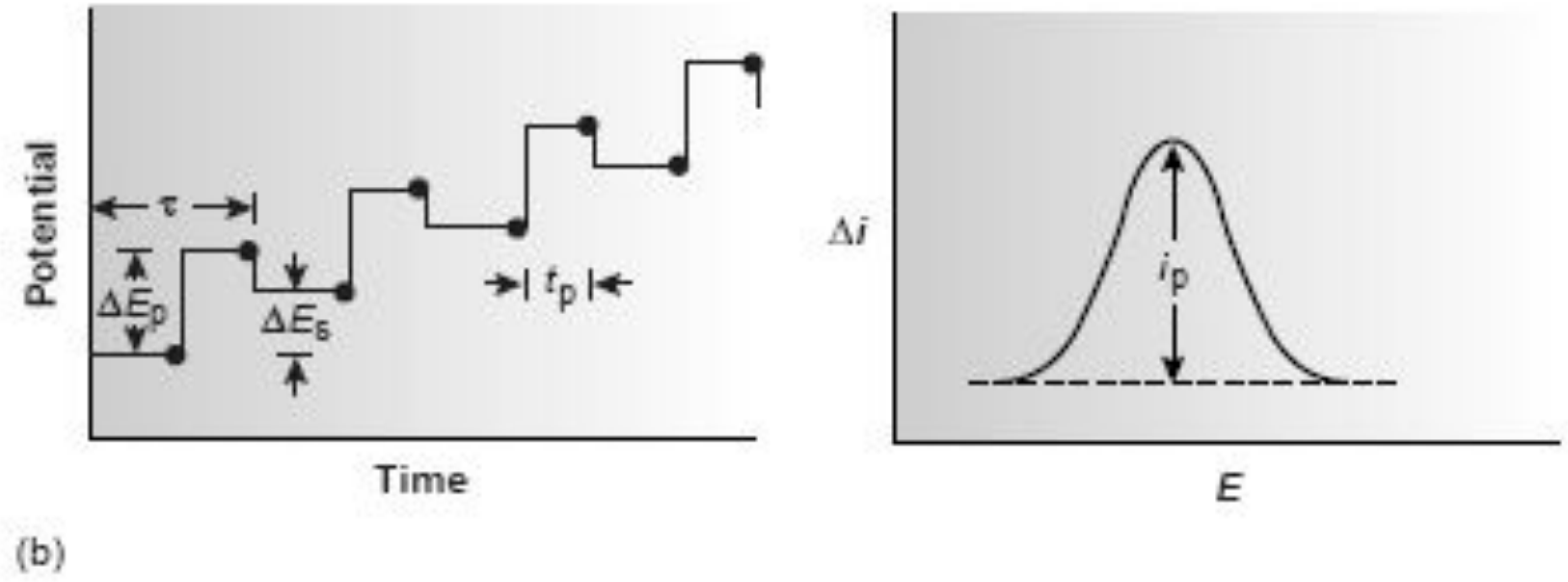




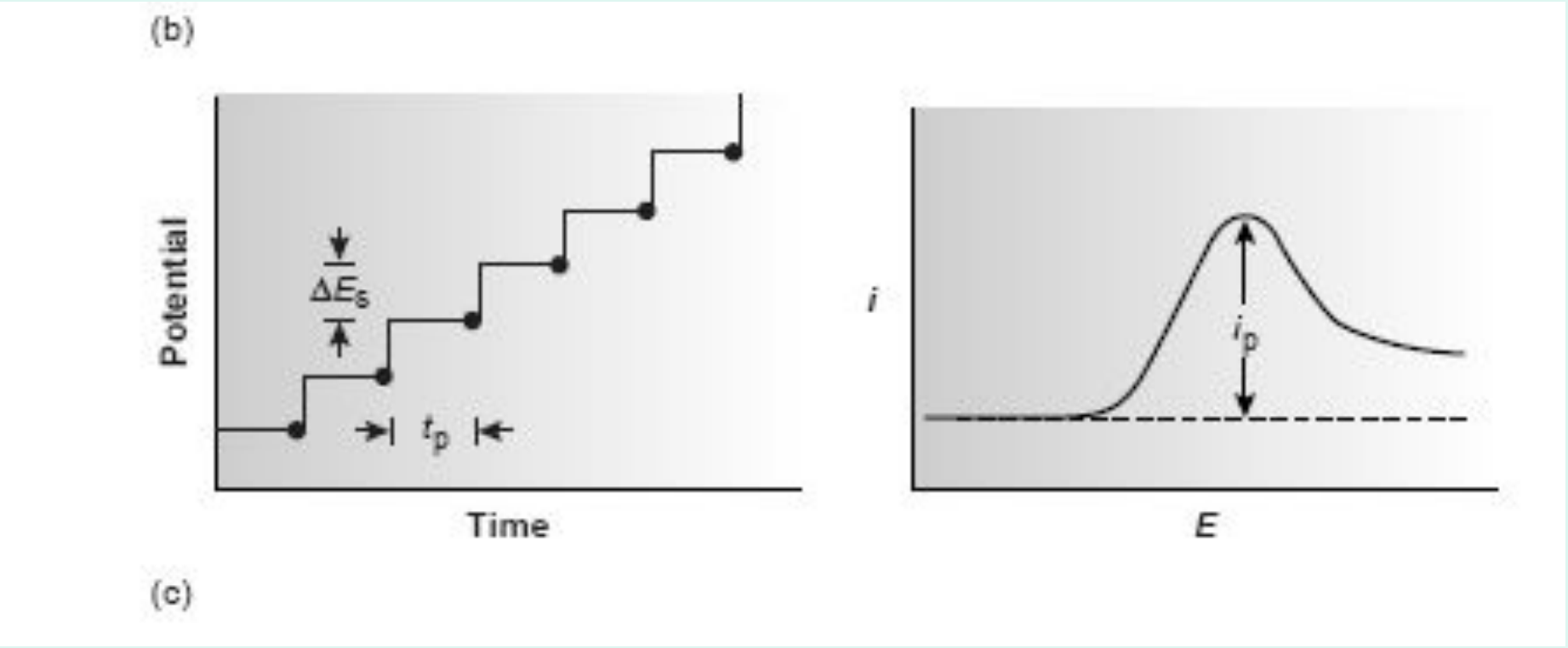
Normal pulse voltammetry:



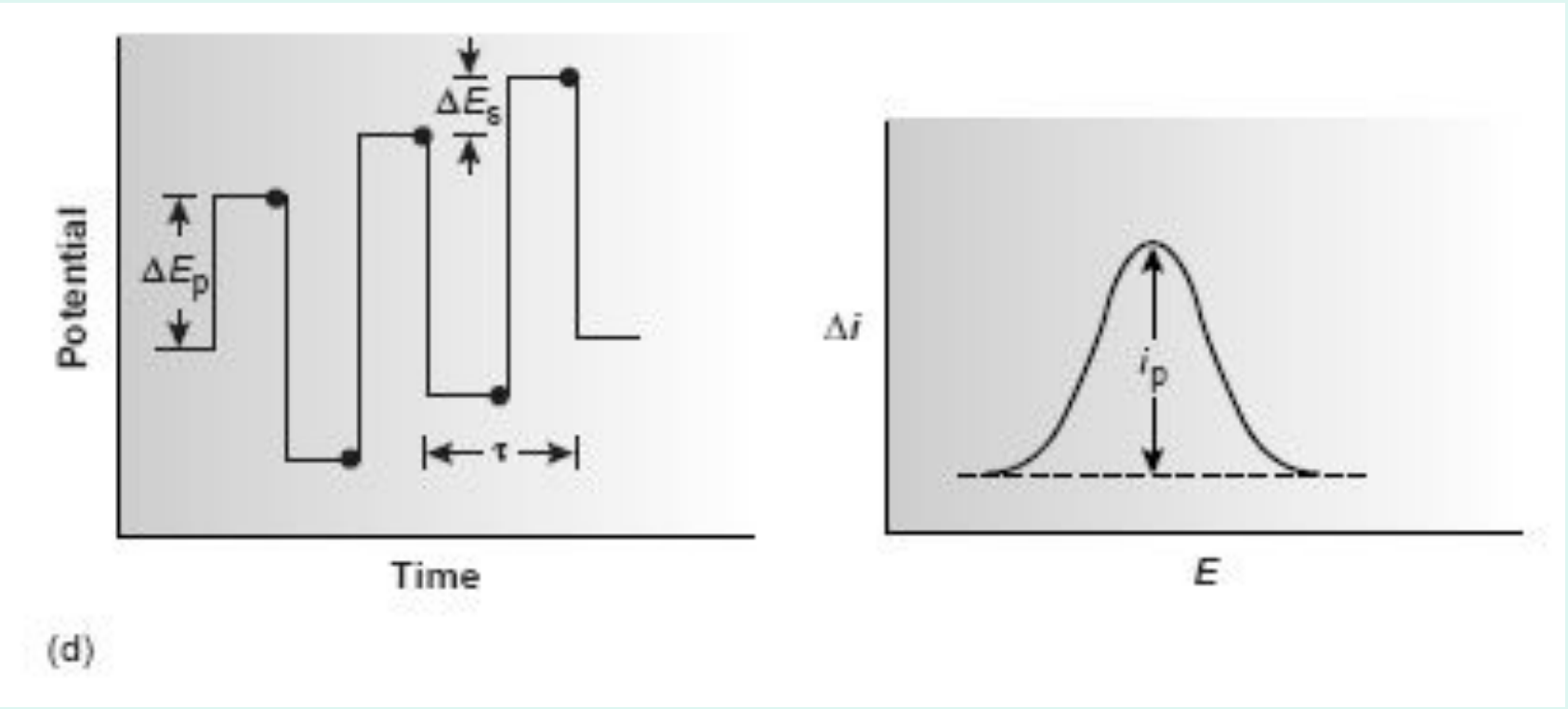
Differential pulse Voltammetry:



Staircase Voltammetry:



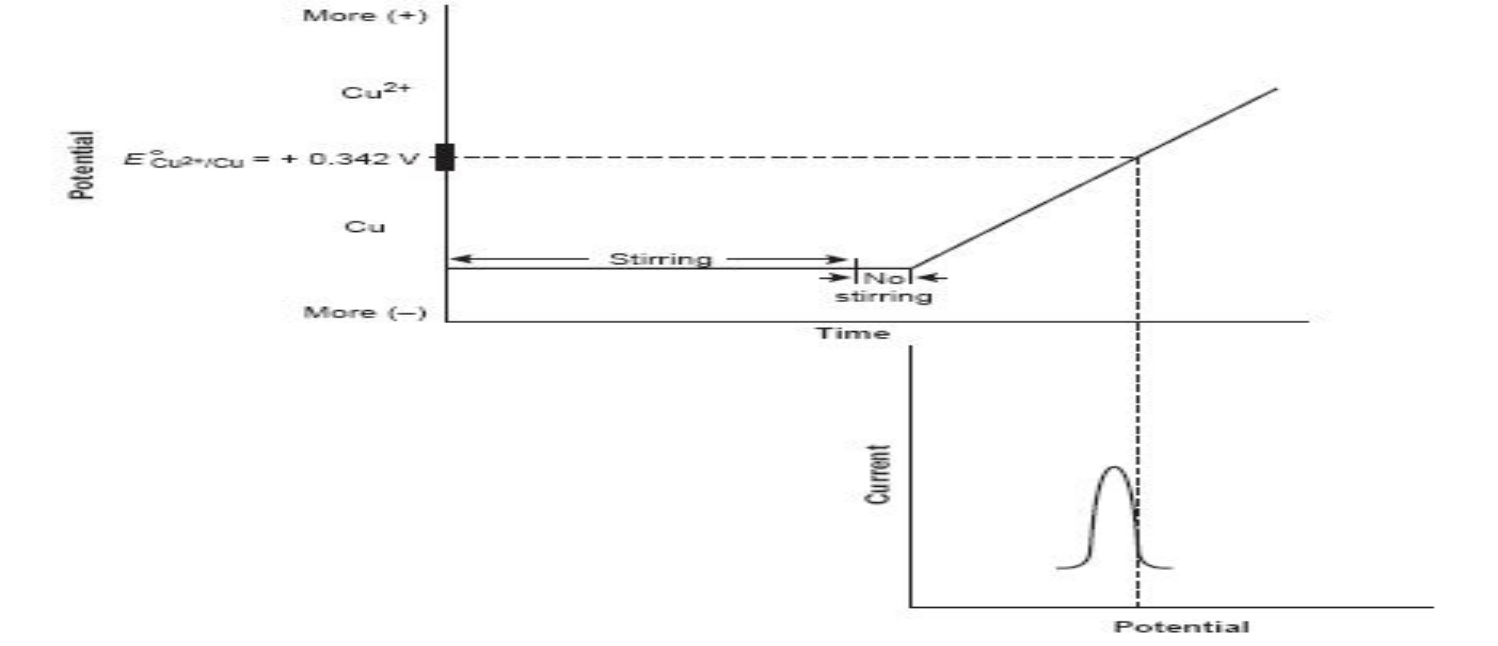
Square Wave Voltammetry:



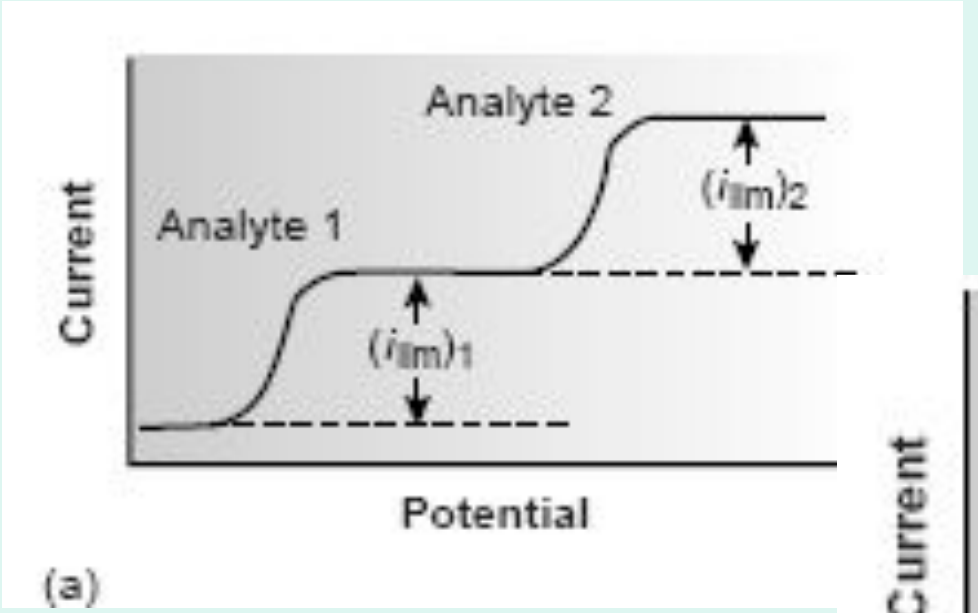
Stripping Voltammetry:

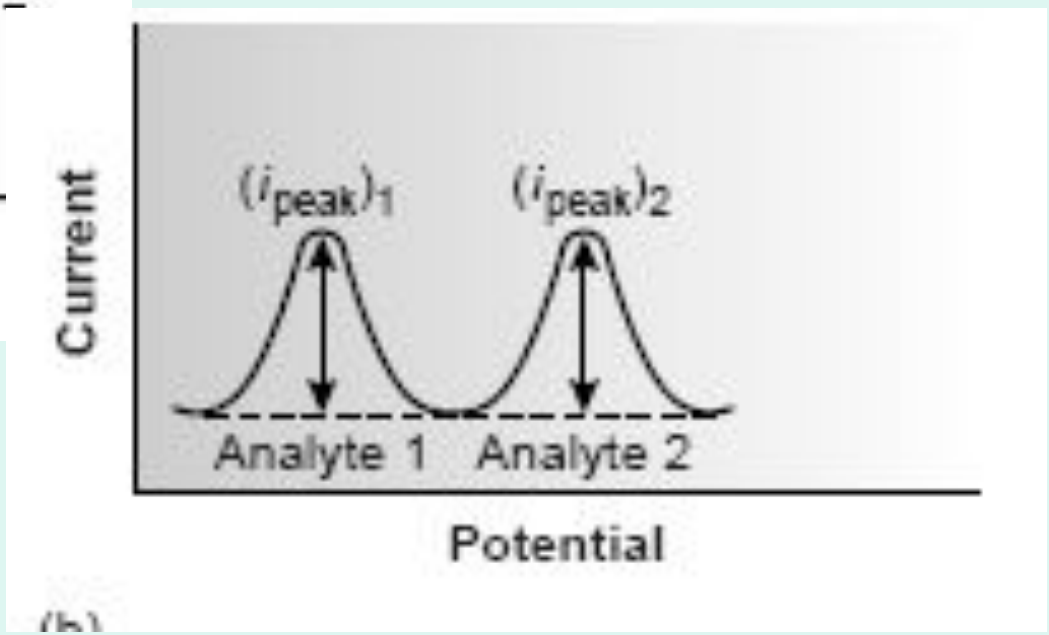
This method is composed of three related techniques:

anodic, cathodic, and adsorptive stripping voltammetry.



Simultaneous Determination:

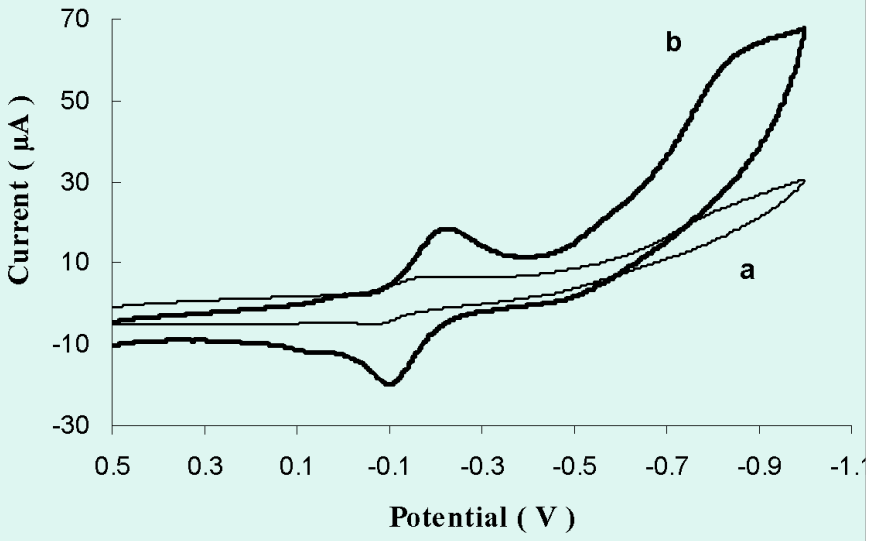


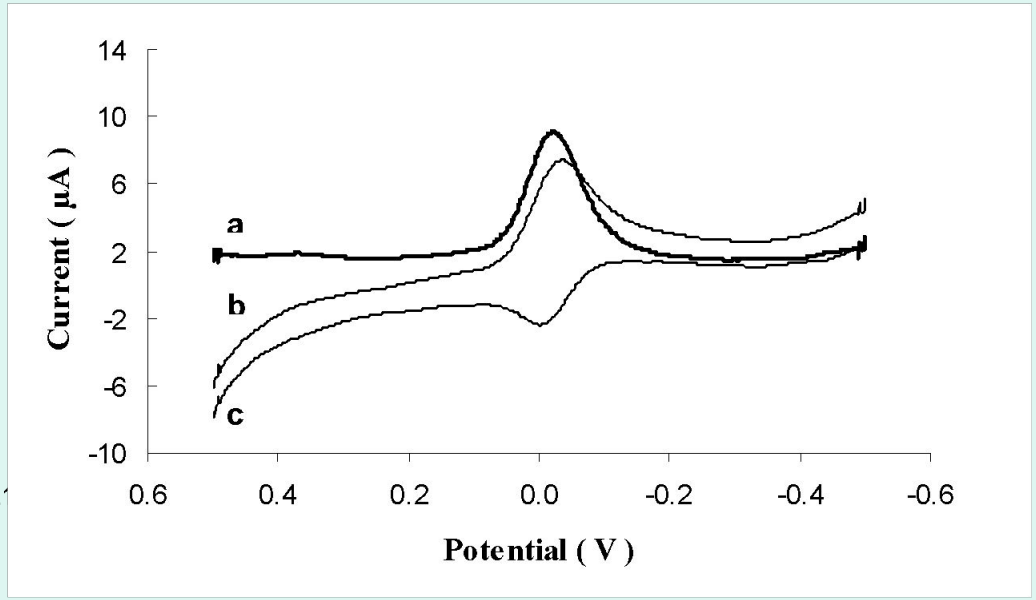


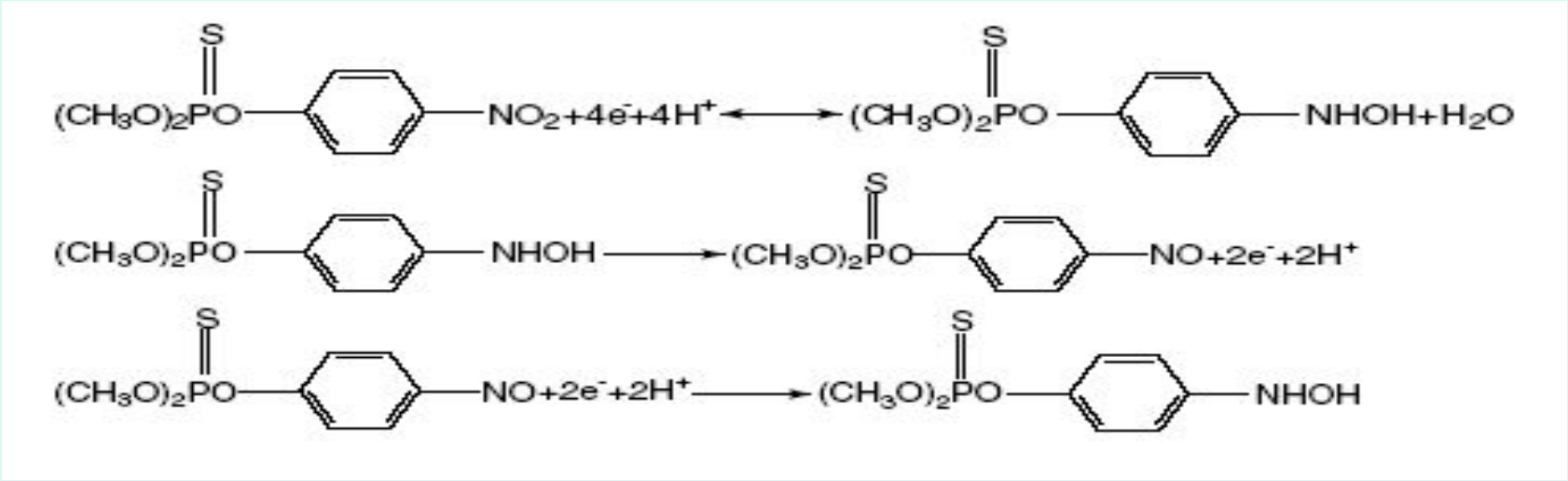
Analytical methods of Voltammetry:

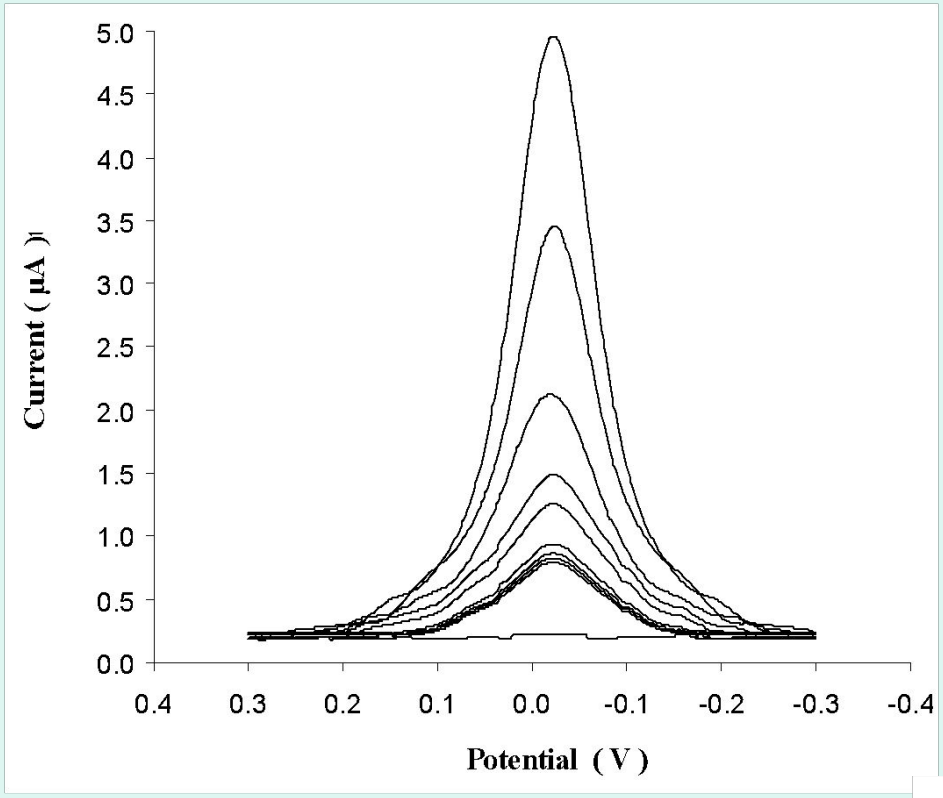
- Calibration Curve
- Standard addition Method

Cyclic and Square Wave Voltammograms:



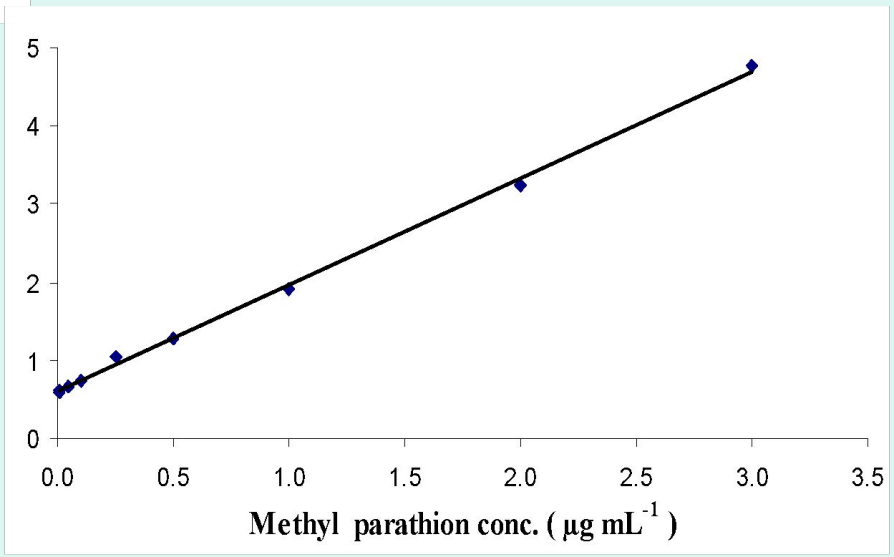


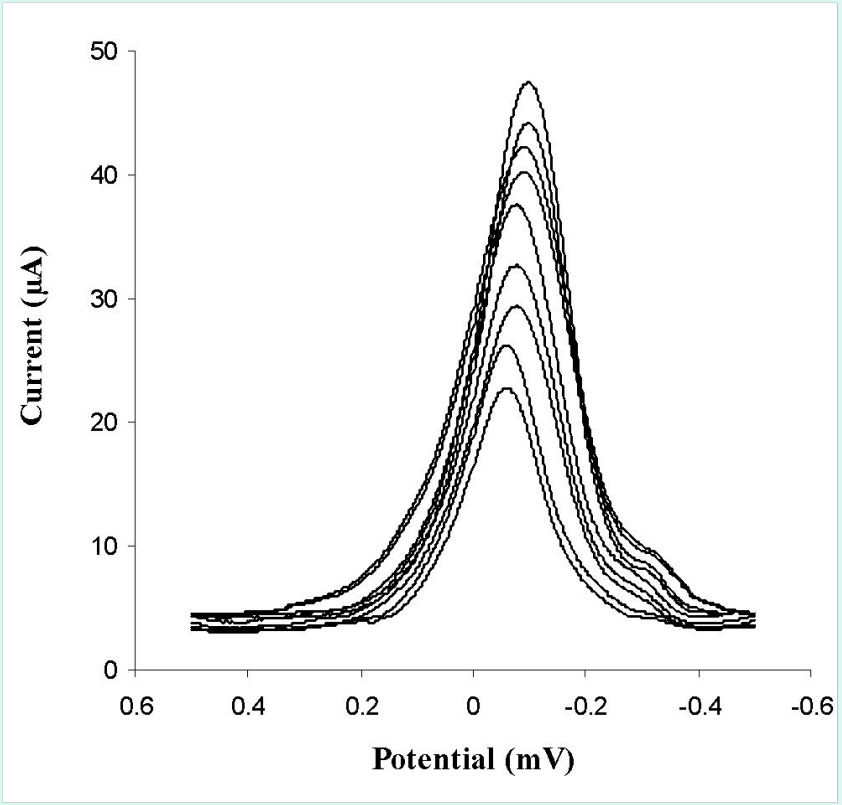




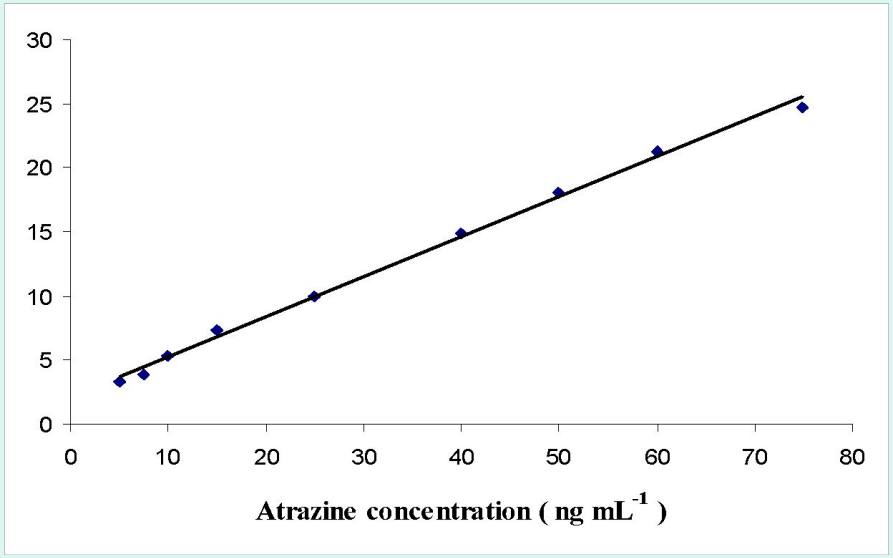
Voltammograms of Standard solutions of Methyl parathion

Calibration curve for Standard solutions of Methyl parathion





Voltammograms of Standard solutions of Atrazine



Calibration curve for Standard solutions of Atrazine

Evaluation:

- **Scale of Operation:**

  Voltammetry is routinely used to analyze samples at the parts-per-million (ppm) level and, in some cases, can be used to detect analytes at the parts-per-billion (ppb) or parts-per-trillion level.

- **Accuracy and Precisoin:**

  The accuracy of a voltammetric analysis often is limited by the ability to correct for residual currents, ppm level, accuracies of ±1–3%. Under most experimental conditions, precisions of ±1–3% .

Evaluation

- **Precision** is generally limited by the uncertainty in measuring the limiting or peak current. Under most experimental conditions, precisions of ±1–3% . One exception is the analysis of ultratrace analytes in complex matrices by stripping voltammetry,(precisions as poor as ±25%).
- **Sensitivity** In many voltammetric experiments, sensitivity can be improved by adjusting the experimental conditions.
- **Selectivity** Selectivity in voltammetry is determined by the difference between half-wave potentials or peak potentials, with minimum differences of ±0.2–0.3 V required for a linear potential scan, and ±0.04–0.05 V for differential pulse voltammetry.

Evaluation

- **Time, Cost and Equipment:** Commercial instrumentation for voltammetry ranges from less than $1000 for simple instruments to as much as $20,000 for more sophisticated instruments. In general, less expensive instrumentation is limited to linear potential scans, and the more expensive instruments allow for more complex potential-excitation signals using potential pulses.
- Except for stripping voltammetry, which uses long deposition times, voltammetric analyses are relatively rapid.

Application

- **Clinical Samples:** voltammetry and stripping voltammetry have been used to determine the concentration of trace metals in a variety of matrices, including blood, urine, and tissue samples. The determination of lead in blood is of considerable interest due to concerns about lead poisoning.

- Besides environmental and clinical samples, voltammetry and stripping voltammetry have been used for the analysis of trace metals in other samples, including food, steels and other alloys, gasoline, gunpowder residues, and pharmaceuticals.
- Voltammetry is also an important tool for the quantitative analysis of organics, particularly in the pharmaceutical industry, in which it is used to determine the concentration of drugs and vitamins in formulations.

General advantages of the electroanalytical methods:

1- Electroanalytical methods are often specific for a particular oxidation form of an element.

2- Instrumentation in these methods are relatively inexpensive.

3- They provide information about activities rather than concentrations of chemical species.