Electrochemical methods of analysis

Presented By;-

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Specialization:- Pharmaceutical Chemistry

Electrochemical methods of analysis

Electrochemical methods of analysis are analytical techniques that involve the measurement of electrical properties such as potential, current, or charge in a chemical system.

These methods are widely used in pharmaceutical, environmental, clinical, and industrial analysis.

Electrochemical methods

1. **Conductometry**
2. **Potentiometry**
3. **Voltammetry / polarography / amperometry**

1. Conductometry

Introduction

Introduction

Conductometry is an **electrochemical method of analysis** that involves the measurement of the electrical conductivity of a solution. It is primarily **used** to monitor chemical reactions, especially **titrations**, by observing changes in conductivity due to the formation or removal of ions.

Electrical conductivity (κ) is the ability of a solution to conduct electric current.

It depends on:

- ☐ Nature and concentration of ions
- ☐ Temperature
- ☐ Viscosity of the medium

Conductivity cell

A **conductivity cell** is a device used to measure the electrical conductivity of a solution, which reflects its ability to conduct electric current. Conductivity arises due to the presence of **ions** in the solution, and this measurement is widely used in pharmaceutical analysis, water quality testing, and chemical laboratories.

Components of a Conductivity Cell:

- **Electrodes** – Usually made of **platinum**, coated with platinum black to reduce polarizatic
- **Glass or Plastic Body** – Insulating body that holds the electrodes in position.
- **Leads** – Wires to connect the electrodes to a **conductivity meter**.
- **Fixed Electrode Distance** – Important for consistent **cell constant (K)**.

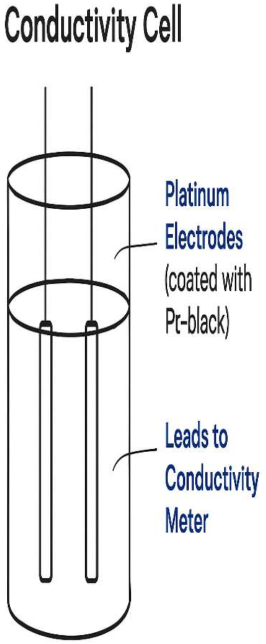
Working Principle:

- An **alternating current (AC)** is passed through the electrodes.
- The **ionic species** in the solution conduct electricity.
- The **conductance (G)** is measured, and using the **cell constant (K)**, the **conductivity (κ** calculated:

$$\kappa = K \times G$$

Where:

κ = conductivity (S/cm) / K` = cell constant (cm^{-1}) / G = conductance (S or mho)



Conductometric Titrations

Titration of Hydrochloric Acid (HCl) with Sodium Hydroxide (NaOH)

(*Strong Acid vs. Strong Base using Conductometry*)

Link:- https://pharmrecord.com/bp108p/

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Applications Of Conductometry

S. No.	Application	Description
1	**Conductometric Titrations**	Used to determine endpoints in acid-base, precipitation, and redox titrations.
2	**Purity Testing of Water**	Measures ionic impurities in distilled or purified water.
3	**Determination of Total Dissolved Solids (TDS)**	Estimates ionic content in pharmaceutical and environmental samples.
4	**Electrolyte Concentration Monitoring**	Analyzes concentration of ions like Na$^+$, K$^+$, Cl$^-$ in electrolyte solutions.
5	**Dissociation Constant of Weak Electrolytes**	Determines KaK_a of weak acids and bases by measuring conductivity.
6	**Monitoring Industrial Processes**	Controls the ionic content in chemical, food, and pharma industries.
7	**Pharmaceutical Formulation Analysis**	Assesses ionic strength and conductance of injectable drugs or IV fluids.
8	**Studying Solubility of Salts**	Evaluates solubility by measuring the ionic conductivity of saturated solutions.

2. Potentiometry

Potentiometry

Definition of Potentiometry:-Potentiometry is an electroanalytical method in which the potential (voltage) of an electrochemical cell is measured **without drawing any significant current**. It is **used** to determine the **concentration of an ion** in solution.

Electrochemical Cell in Potentiometry

An **electrochemical cell** used in potentiometry consists of:

1. **Reference Electrode** – has a constant and known potential.

   Examples: Standard Hydrogen Electrode (SHE), Silver-Silver Chloride Electrode, Calomel Electrode.
2. **Indicator Electrode** – develops a potential that depends on the **concentration of the analyte** (the ion being measured).

   Examples: Glass electrode (for pH), metal electrodes (for redox systems).
3. **Salt Bridge** or porous junction – allows ionic conduction and completes the circuit without mixing the solutions.

I. Reference Electrode

1. Standard Hydrogen Electrode (SHE)

Introduction:

- The **Standard Hydrogen Electrode (SHE)** is a **reference electrode** used to measure the **electrode potentials** of other electrodes.
- It is assigned a **potential of 0.00 V** at all temperatures by convention.
- SHE is also called the **Normal Hydrogen Electrode (NHE)**

Working Principle

The SHE is based on the **reversible redox reaction** between **hydrogen ions (H^+)** and **hydrogen gas (H_2)**:

$$2H^+ + 2e^- \rightleftharpoons H_2(g)$$

When connected to another electrode:

- If the other electrode has a **higher reduction potential**, SHE acts as **anode** (oxidation of H_2 occurs).
- If the other electrode has a **lower reduction potential**, SHE acts as **cathode** (reduction of H^+ occurs).

3. Construction

The SHE consists of the following parts:-

1.Platinum electrode

- A **platinum foil or wire** is coated with **platinum black** (a finely divided form of platinum) to increase surface area for reaction.
- Acts as an **inert conductor** for electron transfer.

2.Hydrogen gas inlet

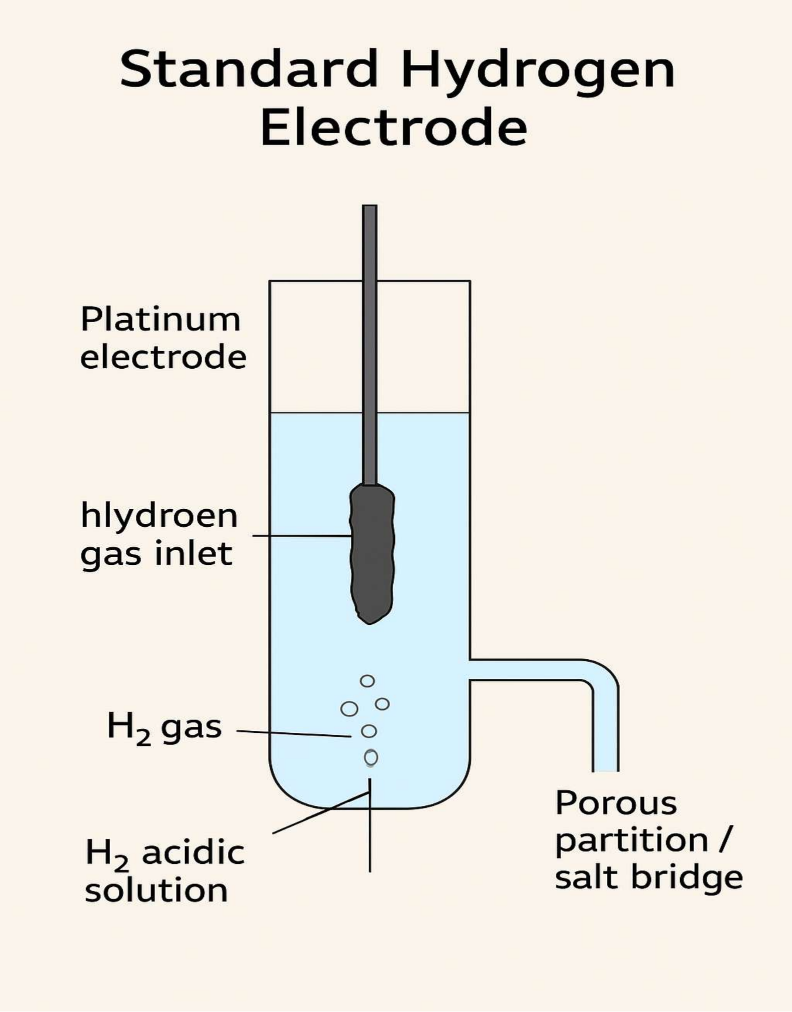
- **Pure hydrogen gas (H_2)** is **bubbled continuously** over the platinum surface.
- The pressure of hydrogen gas is **maintained at 1 atmosphere**.

3.Electrolyte solution

- The electrode is immersed in an **acidic solution containing H^+ ions**, usually **1 M HCl** or **1 M H^+** concentration.

4.Porous partition / salt bridge

- Connects the SHE to another half-cell to complete the circuit and allow ionic conduction without mixing solutions.



2. Silver-Silver Chloride Electrode (Ag/AgCl Electrode)

1. Introduction

- The **Silver–Silver Chloride Electrode (Ag/AgCl)** is a **secondary reference electrode** commonly used in potentiometric and electrochemical measurements.
- It is **simple, stable, and reproducible**.
- Its potential depends on the **chloride ion concentration** of the solution in which it is immersed.
- It is often used as an alternative to the **Standard Hydrogen Electrode (SHE)** because it is easier to maintain and non-hazardous.

2. Working Principle

The electrode works based on the **reversible redox reaction** between **solid silver** and **silver chloride** in the presence of chloride ions.

Electrode reaction:

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

3. Construction

The Ag/AgCl electrode consists of:-

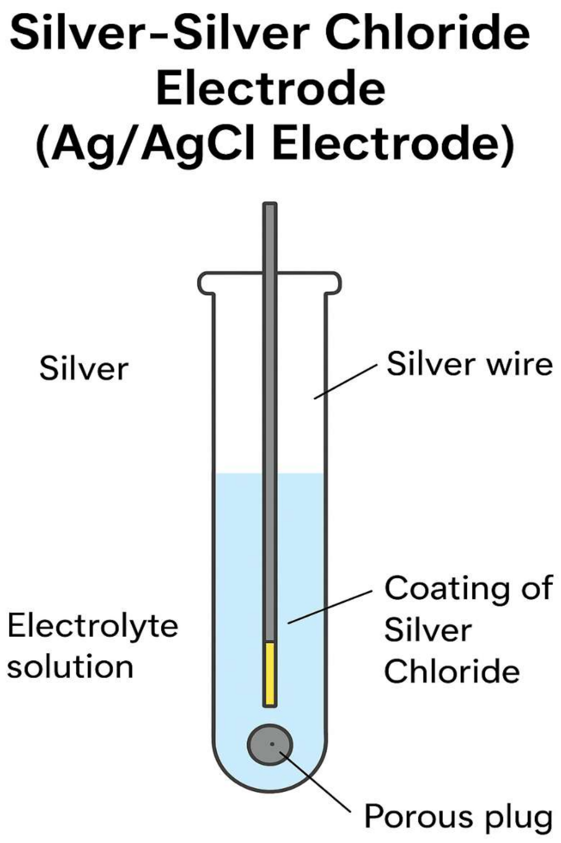
I. **Silver wire (Ag)** — acts as the base metal.

II. **Coating of Silver Chloride (AgCl)** — formed on the silver surface by dipping it in **chlorine solution** or by **electrolytic chlorination**.

III. **Electrolyte solution** — generally a **saturated solution of KCl** (potassium chloride) or 1 M KCl.

IV. **Porous plug or salt bridge** — allows ionic contact with the test solution without mixing directly.

V. **Glass tube** — holds the electrolyte and electrode assembly.



3. Calomel Electrode

1. Introduction

- The **Calomel Electrode** is a **secondary reference electrode** widely used in electrochemical measurements.
- It consists of **mercury (Hg)** and **mercurous chloride (Hg_2Cl_2, called calomel)** in contact with a **potassium chloride (KCl) solution**.
- It provides a **stable and reproducible potential** and is often used in **potentiometric titrations** and **pH measurements**.

2. Working Principle

The working is based on the **redox reaction** between **mercury (Hg)** and **mercurous chloride (Hg_2Cl_2)** in the presence of **chloride ions (Cl^-)**.

Electrode reaction:

$$Hg_2Cl_2(s) + 2e^- \leftrightarrow 2Hg(l) + 2Cl^- (aq)$$

3. Construction

The **Calomel Electrode** consists of:

I. **Glass tube** — Holds all the components.

II. **Mercury (Hg)** — Present at the bottom of the tube, acts as the conducting phase.

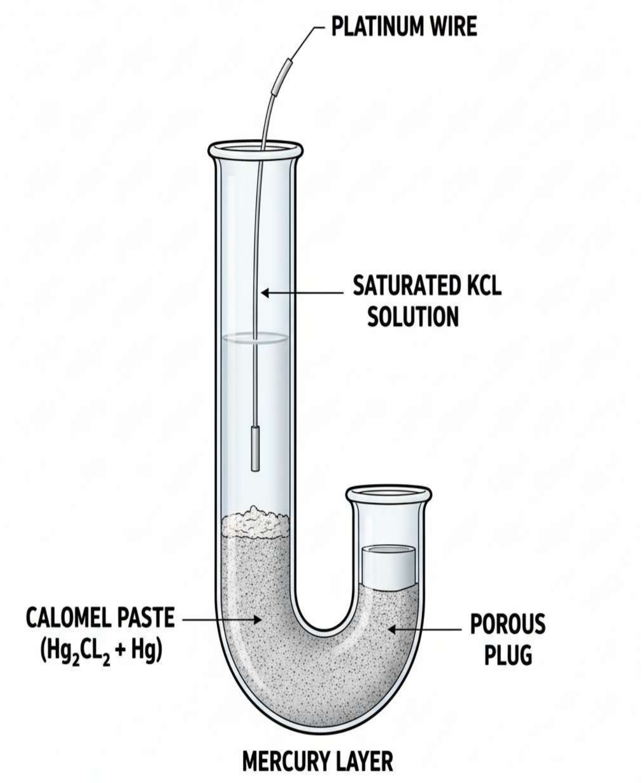
III. **Calomel paste (Hg_2Cl_2)** — A layer of **mercurous chloride** is placed over mercury; it maintains equilibrium between Hg and Cl^- ions.

IV. **Electrolyte solution** — Filled with **KCl solution** (can be **saturated**, **1 M**, or **0.1 M** depending on desired potential).

V. **Porous plug or side arm** — Connects the electrode to the test solution (completes the circuit).

VI. **Platinum wire** — Used as a terminal for external electrical connection.

Calomel Electrode



II. Indicator Electrode

Indicator Electrode

Introduction

- Indicator electrodes are electrodes whose potential changes with the concentration of specific ions present in the solution.
- They are used in **potentiometric titrations** to determine the **end point** or to **measure ion concentration**.
- The potential developed depends on the **activity of ions** that the electrode can respond to.

Indicator electrodes are mainly of two types:

1. **Metal electrodes**
2. **Membrane electrodes (Glass electrode)**

1. Metal Electrodes

(a) Metal Electrode of the First Kind

- Made of a pure metal dipped into a solution containing its own ions.

Example:-**$Cu \mid Cu^{2+}$, $Zn \mid Zn^{2+}$, $Ag \mid Ag^{+}$**

Working:
The electrode establishes an equilibrium between the metal and its ions:

$$M \rightleftharpoons Mn + ne^-$$

The potential developed depends on the **concentration of metal ions (M^{n+})** in solution.

(b) Metal Electrode of the Second Kind

- Consists of a metal coated with a **sparingly soluble salt** of that metal and dipped in a solution containing the **anion** of that salt.

Example:-**$Ag \mid AgCl \mid Cl^-$, $Hg \mid Hg_2Cl_2 \mid Cl^-$**

Working:
The electrode potential depends on the **anion concentration** (like Cl^-).

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

2. Glass Electrode

Introduction

The **glass electrode** is the most common **membrane electrode**, mainly used to measure **pH (hydrogen ion concentration)**.

It consists of:

I. A **thin glass bulb** filled with **internal solution of constant pH (usually HCl)**.

II. An **internal reference electrode** (Ag/AgCl).

III. The **outer surface** of the glass bulb is in contact with the test solution.

Working

- The potential develops across the **glass membrane** due to **H^+ ion exchange** between the internal and external solutions.
- This potential depends on the **H^+ ion concentration (pH)** of the test solution.
- According to the Nernst equation:

$$E = E0 - 0.0591 \times pH$$

Hence, the electrode potential decreases linearly as pH increases.

Methods to Determine End Point of Potentiometric Titration

S.No.	Method	Description / How It Is Used
1	**Graphical Method (E vs Volume Curve)**	A graph of electrode potential (E) vs volume of titrant added is plotted. The end point is located at the point of sharp change in potential or at the inflection point of the curve.
2	**First Derivative Method ($\Delta E/\Delta V$ vs Volume)**	The first derivative of the titration curve is plotted. The peak (maximum point) corresponds to the end point. It gives more precise detection than the direct curve.
3	**Second Derivative Method ($\Delta^2 E/\Delta V^2$ vs Volume)**	The second derivative curve is plotted. The end point occurs where the curve crosses zero (changes sign). This method gives a very accurate end point, especially for weak acids/bases.
4	**Double Indicator (Differential) Method**	Two electrodes are used—one acts as an indicator and the other as a reference. The difference in potential between them is measured. The point of sudden potential difference indicates the end point.
5	**Automatic (Digital) Method**	Modern potentiometers or pH meters with microprocessors automatically detect the end point based on sudden potential change and display it digitally.

Applications of Potentiometric Titration

S.No	Application Area	How It Is Used
1	**Acid–Base Titrations**	Used to determine the concentration of acids or bases by measuring the change in potential (voltage) as titrant is added — no visual indicator required.
2	**Redox Titrations**	Used to find the concentration of oxidizing or reducing agents by measuring potential changes between two redox couples (e.g., Fe^{2+} vs $KMnO_4$).
3	**Precipitation Titrations**	Applied to determine ions that form precipitates (e.g., Cl^- titrated with $AgNO_3$) by detecting the sharp change in electrode potential at the end point.
4	**Complexometric Titrations**	Used for estimation of metal ions (like Ca^{2+}, Mg^{2+}, Zn^{2+}) with EDTA; the potential changes indicate completion of complex formation.
5	**Pharmaceutical Analysis**	Used to determine purity and strength of drugs (e.g., vitamin C, aspirin) without using colored indicators.
6	**Water Analysis**	Determines hardness of water by titration with EDTA and measures potential to locate the end point.
7	**Environmental Analysis**	Measures pollutants such as sulphite, nitrite, or chlorine content in water through redox potentiometric titrations.
8	**Determination of Mixtures**	Used to find the composition of acid mixtures or base mixtures by identifying multiple potential jumps (end points).

3.Polarography

Polarography

Introduction

- ✓ **Polarography** is an **Electroanalytical technique** based on the measurement of current as a function of applied potential at a **dropping mercury electrode (DME)**.
- ✓ It was **introduced by Jaroslav Heyrovský** in **1922**, who received the **Nobel Prize in Chemistry (1959)** for this invention.

Principle

The principle of polarography is based on the **measurement of current–voltage (I–E) relationship** during the electrolysis of a solution containing reducible or oxidizable species at a **dropping mercury electrode (DME)** or other working electrodes.

When a gradually increasing potential is applied to the working electrode:

- ❑ Initially, **no current flows** (before reduction potential).
- ❑ As the potential reaches the **reduction potential of the analyte**, current increases.
- ❑ Finally, a **limiting diffusion current** (plateau) is reached, which depends on the concentration of the electroactive species.

Ilkovic Equation

The **Ilkovic Equation** is a fundamental relationship in **polarography**, which describes the **diffusion current** obtained at a **dropping mercury electrode (DME)** during electrochemical reduction or oxidation.

Ilkovic Equation:-

$$i_d = 607\, n\, D^{1/2}\, m^{2/3}\, t^{1/6}\, C$$

Where:-

Symbol	Meaning
i/d	Diffusion current (µA)
n	Number of electrons involved in electrode reaction
D	Diffusion coefficient (cm²/s)
m	Rate of mercury flow (mg/s)
t	Drop time (s)
C	Concentration of electroactive species (mM)

1. Dropping Mercury Electrode (DME)

Introduction:

- The **Dropping Mercury Electrode (DME)** is the **working electrode** used in **polarography**.
- It was introduced by **Jaroslav Heyrovský**, the inventor of the polarograph.
- The electrode consists of a **fine capillary tube** through which **mercury drops** fall periodically into the test solution.
- Each drop acts as a **smooth, and reproducible electrode surface**, ideal for accurate electrochemical measurements.

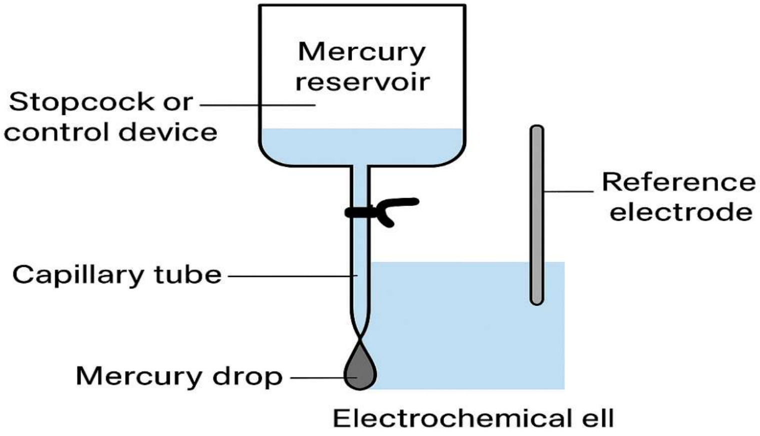
Working Principle:-

- A **slowly varying potential** is applied between the **DME (cathode)** and a **reference electrode (anode)**.
- When the potential reaches the **reduction potential** of the analyte, ions are **reduced at the surface** of the mercury drop.
- The resulting **current increases** until the drop detaches and a new drop forms.
- This process repeats, producing a **periodic current** that is recorded as a **polarogram** (current vs potential graph).

Construction:

Component	Description
Mercury reservoir	Contains pure mercury used to form the drops.
Capillary tube	A fine glass tube (internal diameter ≈ 0.05–0.1 mm) through which mercury flows drop by drop.
Stopcock or control device	Regulates the rate of mercury flow and drop time.
Electrochemical cell	The DME dips into the test solution containing the analyte and electrolyte.
Reference electrode	Usually a Calomel or Ag/AgCl electrode to complete the circuit.

Dropping Mercury Electrode (DME)



2. Rotating Platinum Electrode (RPE)

Introduction:

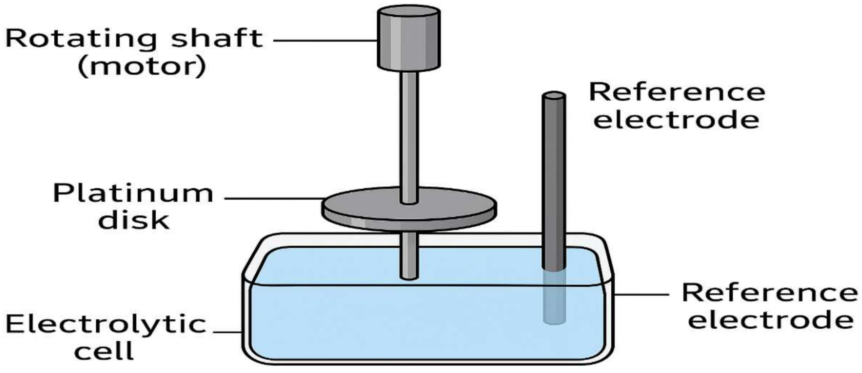
- The **Rotating Platinum Electrode (RPE)** is a **modified working electrode** used in **polarography** and **voltammetry**.
- Unlike the **Dropping Mercury Electrode (DME)**, it provides a **solid, stationary surface** (platinum) that **rotates** at a constant speed.
- Rotation ensures **uniform mass transport** of ions toward the electrode surface by creating a **steady hydrodynamic flow**, giving a **steady-state current**.

Working Principle:

- When a **potential** is applied between the **RPE** (working electrode) and the **reference electrode**, electroactive species near the electrode are **oxidized or reduced**.
- As the electrode **rotates**, it continuously **refreshes the diffusion layer** near its surface by convection.
- This creates a **steady diffusion current** that depends on the **rotation rate** and **concentration of the analyte**.
- This current–potential relationship forms the **polarogram**, similar to that obtained with a DME but **more stable and reproducible**

Construction:

Component	Description
Platinum disk	Small circular piece of platinum acts as the electrode surface.
Rotating shaft (motor)	Holds the platinum disk and rotates it at a controlled speed (usually 500–3000 rpm).
Insulating sheath	Surrounds the shaft, leaving only the flat platinum disk exposed to the solution.
Reference electrode	Calomel or Ag/AgCl electrode completes the electrochemical cell.
Electrolytic cell	Contains the analyte solution and supporting electrolyte.



Rotating Platinum Elctrode

Applications of Polarography

S.No	Area	Application
1	**Quantitative analysis**	Determination of metal ions (e.g., Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+})
2	**Pharmaceutical analysis**	Estimation of drugs like vitamins (e.g., Vitamin C), antibiotics, sulfa drugs
3	**Environmental analysis**	Detection of heavy metals in water, wastewater analysis
4	**Biochemical analysis**	Study of enzyme-catalyzed redox reactions
5	**Kinetic studies**	Determination of reaction mechanisms and rate constants
6	**Trace element detection**	Determination of very low concentrations (ppm or ppb) of metals

THANK YOU

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