Polarography

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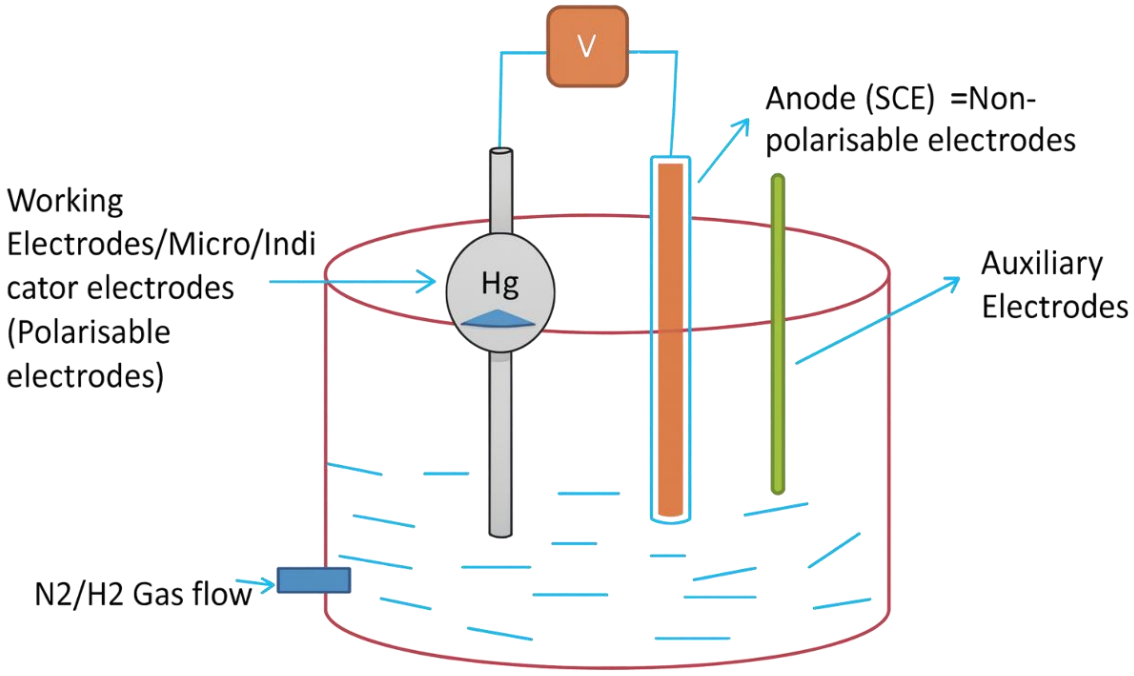
Definition:

- Polarography is an electrochemical method where the current is measured as a function of applied voltage using a dropping mercury electrode (DME) as the working electrode.
- It is especially useful for the quantitative and qualitative analysis of reducible (electroactive) species.

Principle:

- In polarography, a variable voltage is applied between a dropping mercury electrode (DME) and a reference electrode, and the resulting current is measured.
    - The current increases as the analyte is reduced at the DME.
    - A plateau is reached when the reduction is diffusion-controlled—this is called the limiting current or diffusion current (id).
- The **diffusion current** is directly proportional to the **concentration of the analyte**.

Components of Polarographic Instrumentation:



1. Electrochemical Cell

- **Three-electrode system**:
    - **Working Electrode**: Dropping Mercury Electrode (DME)
    - **Reference Electrode**: Saturated Calomel Electrode (SCE) or Ag/AgCl electrode
    - **Auxiliary (Counter) Electrode**: Usually platinum wire

2. Dropping Mercury Electrode (DME)

- A fine capillary delivers mercury drops at regular intervals.
- Each mercury drop serves as a fresh, reproducible surface for reduction or oxidation.
- **Advantages**: Reproducible surface, large cathodic potential window, renewable surface (self-cleaning)

3. Potentiostat/Galvanostat

- Maintains and controls the potential between the working and reference electrodes.
- Measures the resulting current accurately.

4. Voltage Sweep Generator

- Provides a linear sweep of potential over time across the electrochemical cell.
- This can be in the form of a ramp or staircase waveform.

5. Current Measuring Device

- Converts current into a voltage signal (using an I-V converter) and plots current vs. voltage (polarogram).

6. Recorder or Computer Interface

- Records the current-voltage curve (polarogram) either digitally or graphically.

Types of Polarography:

- DC Polarography
- AC Polarography
- Differential Pulse Polarography
- Square Wave Polarography

Polarogram:

- The graphical plot of current (I) vs. applied potential (E).
- A typical polarogram shows a sigmoid (S-shaped) curve with a limiting current plateau indicating the diffusion-controlled region of the reaction.

Functionality

- The applied potential is varied linearly with time.
- The current is measured as a function of applied potential.
- The current response is influenced by the concentration and electrochemical properties of analytes.

Advantages:

- High sensitivity and selectivity for reducible substances.

- Capable of multi-component analysis with proper waveform interpretation.
- Cost-effective and relatively simple instrumentation compared to advanced spectroscopic methods.

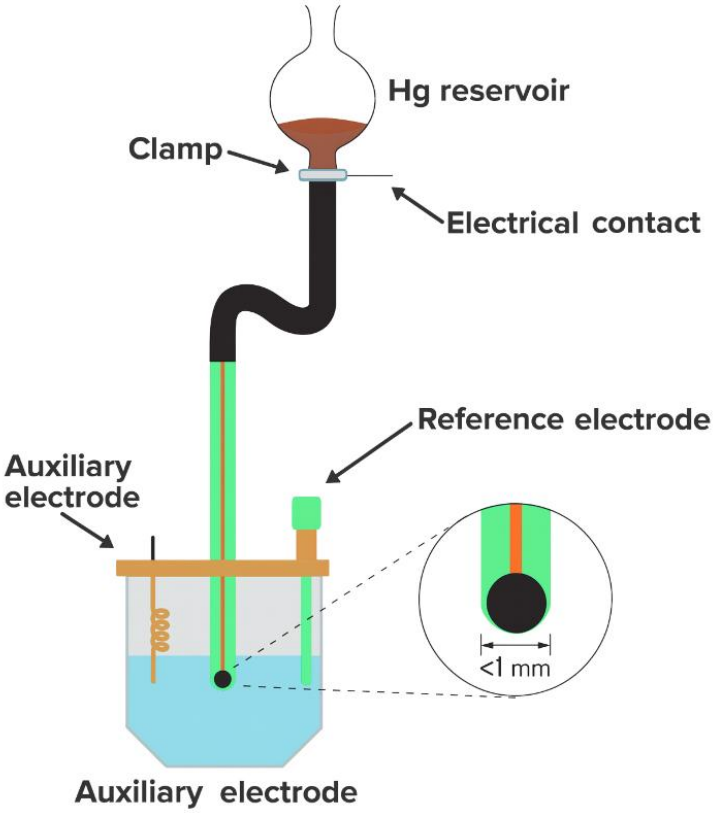
Limitations:

- Requires deaeration of samples.
- Mercury toxicity limits its use and disposal.
- Restricted to analytes with electrochemical activity within mercury's potential window.

Dropping Mercury Electrode (DME)

- The dropping mercury electrode (DME) is the central working electrode in classical polarography.
- It is unique because it continuously renews its surface by forming a new mercury drop at regular intervals.

Construction



1. Capillary Tube

- Fine glass tube (10–50 µm diameter).
- Mounted vertically, connected to a mercury reservoir.

2. Mercury Reservoir

- Stores mercury supply.

- Flow regulated by reservoir height or pressure control.

3. Electrode Holder

- Insulating structure that supports the capillary tube.
- Provides electrical contact to mercury.

4. Electrical Connection

- Conductive wire connects mercury to the potentiostat.

Working

- **Mercury Flow:** Flows through capillary by gravity or controlled pressure.
- **Droplet Formation:** Surface tension allows mercury drop to grow.
- **Droplet Detachment:** Detaches periodically (1–20 drops/sec), exposing a fresh surface.
- **Electrochemical Measurement:** During droplet growth and detachment, redox reactions of analytes occur at the mercury surface.
- **Renewable Surface:** Each droplet provides a new uncontaminated electrode surface.

Advantages:

- Mercury is inert to many pharmaceutical substances.
- Its renewable surface ensures high accuracy and sensitivity, especially for trace-level detection.
- Useful in the determination of heavy metals, vitamins, antibiotics, and drug residues.

Limitations:

- Mercury is toxic and environmentally hazardous.
- The technique is generally limited to substances reducible at the mercury electrode potential.

Applications:

- Commonly used to study redox properties of metal ions, organic molecules, and pharmaceutical compounds.
- Also used in **trace metal analysis**, **kinetic studies**, and **complexation reactions**.

Residual Current

- Residual current in polarography refers to the small current that flows through the electrochemical cell even in the absence of any electroactive species undergoing redox reactions.
- It is an unavoidable background current that exists due to various non-faradaic (non-electrochemical) and minor faradaic processes.

Components of Residual Current:

Residual current consists mainly of two types of background currents:

1. **Capacitive (Charging) Current:**
   - Occurs due to the formation of an electrical double layer at the electrode–solution interface.
   - When a potential is applied, charges accumulate on the electrode surface and attract opposite charges from the electrolyte, forming a capacitor-like layer.
   - This leads to charging/discharging currents as the potential changes with time.
   - These currents do not involve chemical reactions and are purely physical in nature.
2. **Faradaic Background Current:**
   - Due to the trace impurities or oxidation/reduction of species present in very small amounts, such as dissolved oxygen, water electrolysis, or impurities in the solvent/electrolyte.
   - Also includes small residual redox processes involving the mercury electrode itself or minor contaminant reactions.

Characteristics:

- The residual current is generally very small (in the order of microamperes or less).
- It increases slowly with applied potential.
- It is present in all polarographic measurements and must be accounted for to accurately determine the actual current due to the analyte.

Importance:

- It limits the sensitivity of polarographic techniques.
- It needs to be subtracted from the total measured current to isolate the diffusion current (which is the analytical signal).
- Modern polarography instruments and software can automatically correct for residual current by performing blank measurements (without analyte).

Diffusion Current

Diffusion Current

- The diffusion current is the key analytical signal in polarography. It represents the maximum steady-state current that results from the diffusion of the electroactive species to the surface of the dropping mercury electrode.

Origin of Diffusion Current:

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