Polarography

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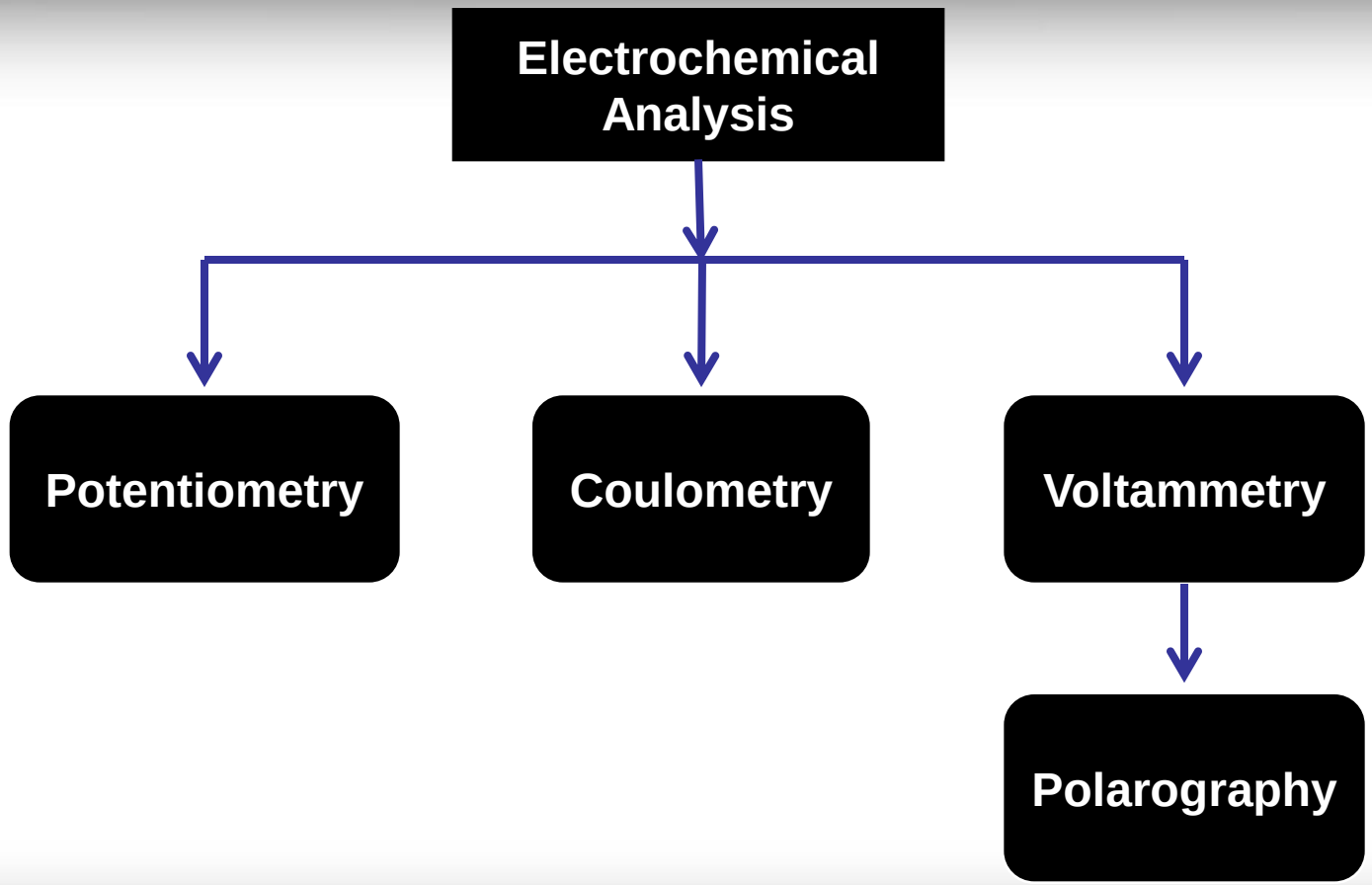
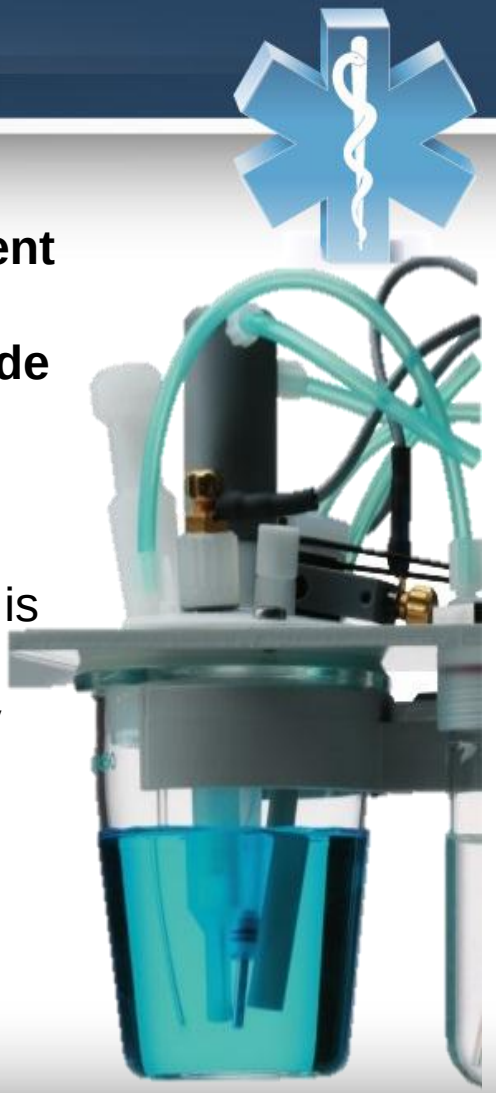
What is Electrochemical analysis?



Polarography

- Is a method of analysis based on the measurement of **current electrolysis** of an electroactive species, at a **given electrode potential**, under controlled conditions.
- It is the branch of voltammetry where the working electrode is a **dropping mercury electrode** (DME) or a **static mercury drop electrode** (SMDE), which are useful for their wide cathodic ranges and renewable surfaces.



Polarography

An electromechanical technique of analyzing solutions that **measures the current flowing between two electrodes in the solution, as well as the gradually increasing applied voltage,** to determine respectively the concentration of a solute and its nature.

Created by: Jaroslav Heyrovsky

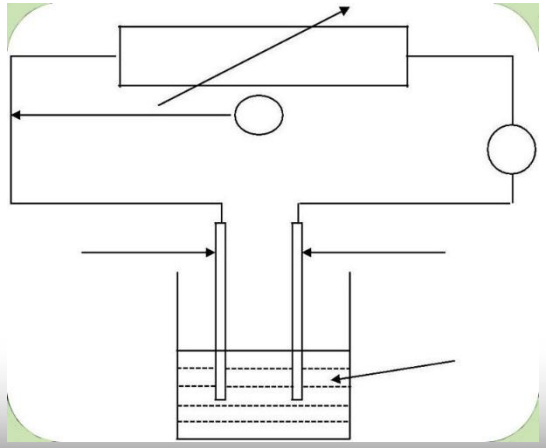
Requirement

In this method, a reference electrode and an indicator electrode are required.

- **Reference electrode-** acts to maintain a constant potential throughout the measurement.
- **Indicator electrode-** assumes the potential impressed upon it from an external source.

Reference electrode

Indicator electrode



Types of mercury electrode

In polarography, mercury is used as a working electrode. The working electrode is often a drop suspended from the end of a capillary tube.

3 examples of electrodes:

1. **HMDE (Hanging mercury drop electrode)-**

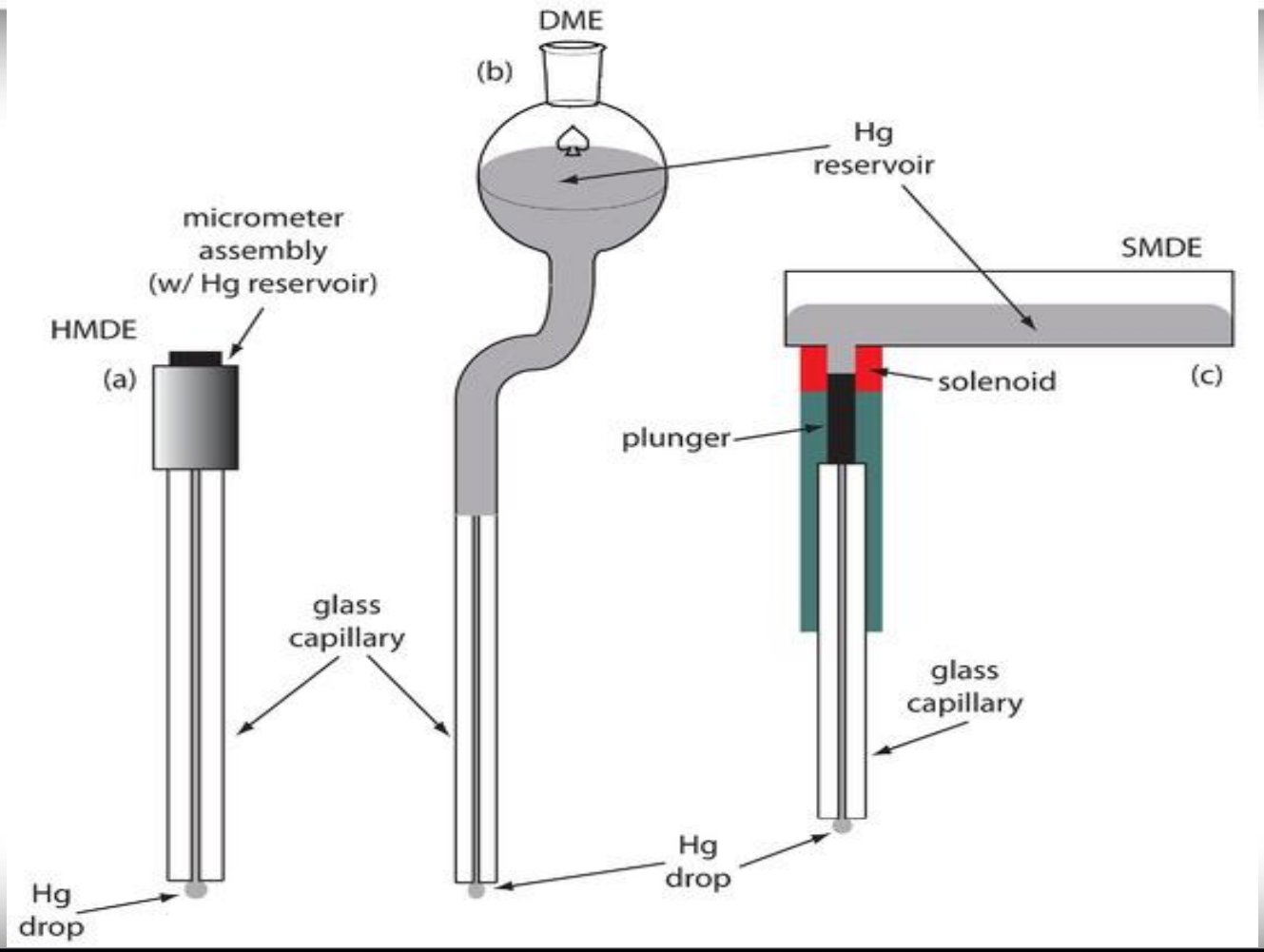
A **micrometer screw** is used to push the mercury from a reservoir through a narrow capillary tube.

2. **DME (Dropping mercury electrode)-**

Mercury drops form the end of the capillary tube as a result of **gravity.** Mercury has a finite lifetime of several seconds. At the end of its lifetime the mercury drop is dislodged and replaced by a new drop.

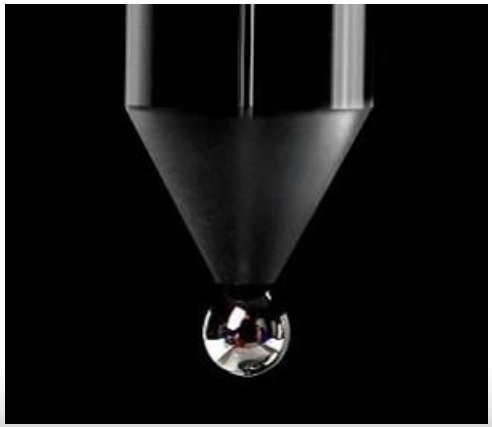
3. **SMDE (Static mercury drop electrode)-**

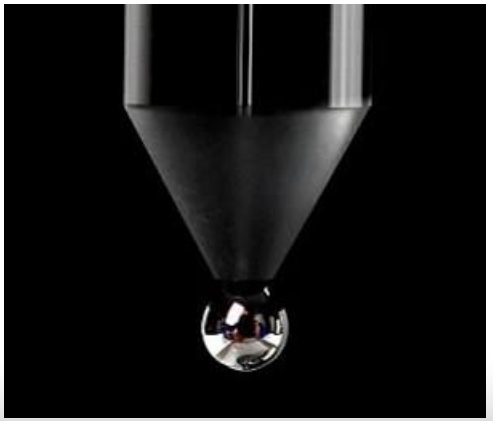
Solenoid driven plunger is used to control the flow of mercury. Activation of the solenoid momentarily lifts the plunger, allowing mercury to flow through the capillary and forming a single, hanging mercury drop.


DME
(b)
Hg
reservoir
micrometer
assembly
(w/ Hg reservoir)
HMDE
(a)
SMDE
solenoid
(c)
plunger
glass
capillary
glass
capillary
Hg
drop
Hg
drop

Mercury

- Mercury as working electrode is useful because:
  - It displays a wide negative potential range.
  - Its surface is readily regenerated by producing a new drop or film.
  - Many metal ions can be reversibly reduced into it.



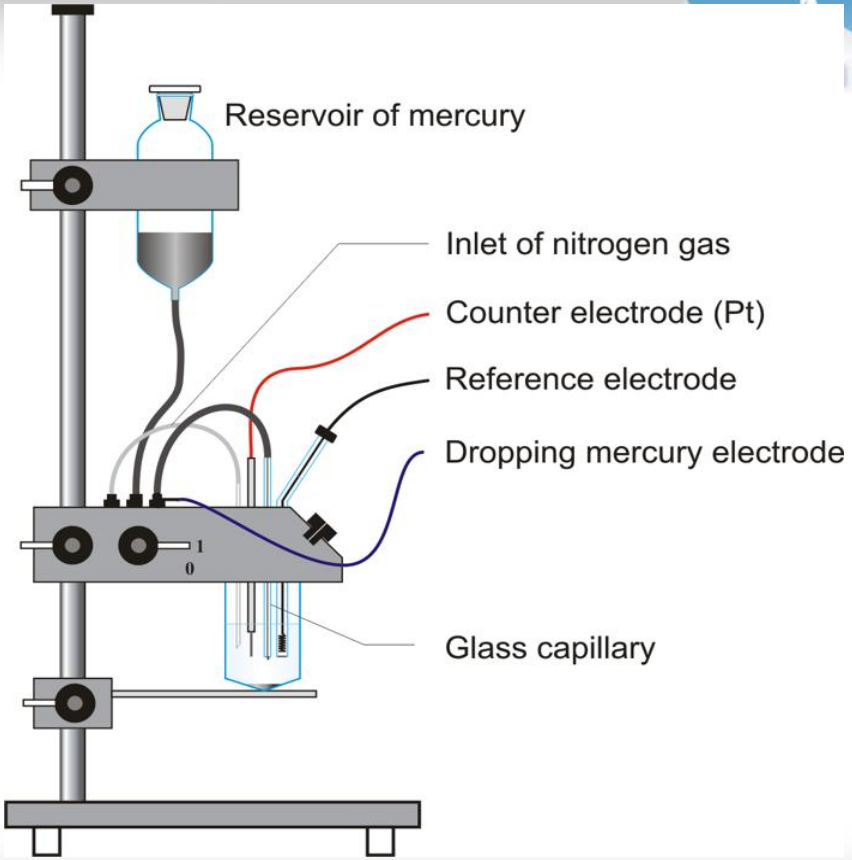


Principle

- Study of solutions or of electrode processes by means of electrolysis with two electrodes, one polarizable and one un-polarizable (de-polarizable).
  - **POLARIZED ELECTRODE**: Dropping Mercury Electrode (DME)
  - **DEPOLARIZED ELECTRODE**: Saturated Calomel Electrode

Principle

Mercury continuously drops from reservoir through a capillary tube into the solution. The optimum interval between drops for most analyses is between **2 and 5 seconds.**



Polarographic data

- Polarographic data obtained from an automatic recording instrument is called a **polarogram**, and the trace is called a **polarographic wave.**

POLAROGRAM

A graph of **current versus potential** in a polarographic analysis.

3 categories:

A. collectively referred to as **residual current.**
B. referred to as **diffusion current** resulting from the reduction of the sample.
C. called the **limiting current.**

- The diffusion current of a known concentration of reference standard are first determined followed by the determination of the diffusion current of the unknown concentration.

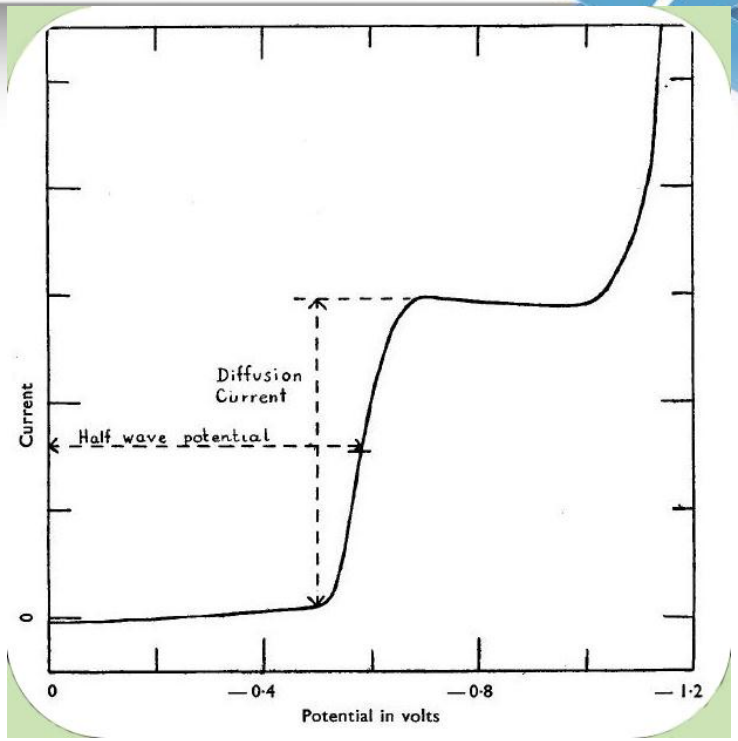
Characteristics of Polarography

- In polarography **the sample to be examined is dissolved in a base solution** containing an excess of a base or supporting electrolyte and is placed in a special electrolytic cell.

- It has a pool of mercury as anode and mercury dropping from a capillary at the rate of one drop every 2 to 4 seconds as cathode.

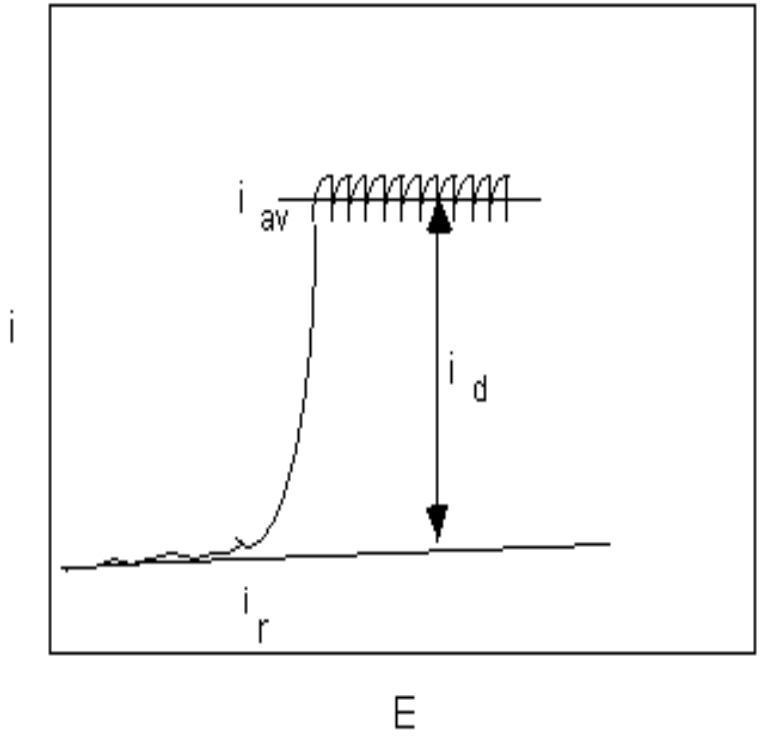
- When a gradually increasing voltage is applied to the cell and the corresponding current is measured on a galvanometer.

- It is possible to determine from the resulting current-voltage curve both the nature and the concentration of the reducible substances in the sample.



Polarogram

- i_r **(residual current)** which is the current obtained when no electrochemical change takes place.
- i_{av} **(average current/limiting current)** is the current obtained by averaging current values throughout the life time of the drop.
- i_d **(diffusion current)** which is the current resulting from the diffusion of electroactive species to the drop surface.



Advantages

1. Simple handling of sample
2. Speed of analysis
3. High sensitivity
4. Comparable or better accuracy
5. Cheaper instrumentation and lower cost of chemicals used
6. Limited used of environmentally unfriendly organic solvents

Applications

- Dissolved oxygen and peroxides
- Trace metals and metal containing drugs
- Antiseptics and insecticides
- Vitamins
- Hormones
- Antibiotics
- Alkaloids
- Blood serum and cancer diagnosis

Any questions