VOLTAMMETRY

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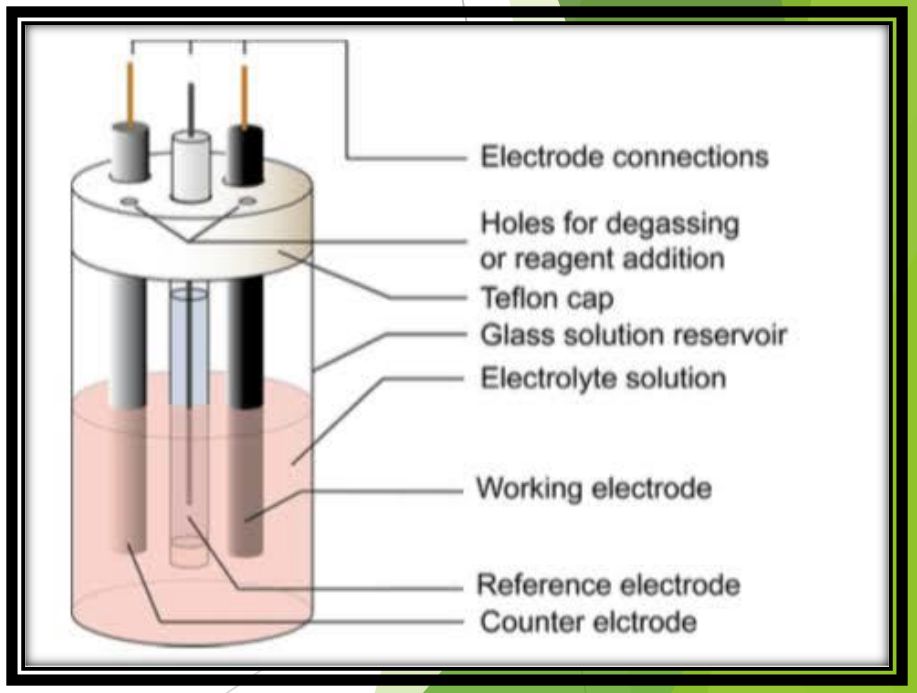
- Applications

VOLTAMMETRY

Voltammetry is a term coined in 1940 by **H. A. Laitinen** & **I. M. Kolthoff**

Voltammetry is an electrochemical method in which information about an analyte is obtained by current.

- This technique uses an instrument called a potentiostat, invented by **Archie Hickling.**
- Commonly uses 3 electrodes :
  1. Working electrode (WE)
  2. Auxiliary electrode (AE)
  3. Reference electrode (RE)



ELECTRODES :-

1. WORKING ELECTRODE (WE)

- The electrode in an electrochemical system on which the reaction of interest is occurring….
- Depending on whether the reaction on the electrode is a reduction or an oxidation, the working electrode is called cathodic or anodic, respectively.

Different Types of Working Electrodes :-

1. **Glassy Carbon**
2. **Mercury**
3. **Platinum**
4. **Gold**

- **Among this , Platinum is likely the favorite,due to demonstrating good electrochemical inertness and ease of fabrication into many forms.**

2. AUXILIARY ELECTRODE (AE)

- Also called the **counter electrode**.
- Auxiliary electrode is an electrode used in a three electrode electrochemical cell for voltammetric analysis or other reactions in which an electric current is expected to flow.
- Functions as a cathode whenever the working electrode is operating as an anode and vice versa
- The purpose of the auxiliary electrode is **to provide a pathway for current to flow in the electrochemical cell without passing significant current through the reference electrode**.
- Auxiliary electrodes are fabricated from electrochemically inert materials such as
  - **Gold**
  - **Platinum**
  - **Carbon**

- **Platinum** is a good choice of material for a counter electrode **mostly due to its inertness**

3. REFERENCE ELECTRODE (RE) :-

A reference electrode refers to an electrode that has an established electrode potential.

- In an electrochemical cell, the reference electrode can be used as a half cell.
- The most commonly used reference electrode is calomel electrode.
- It consists of a mercury and mercury-chloride molecules.

Application :-

1. **Used in pH sensing, corrosion monitoring, environmental sensing and blood gas analysis**
2. **The accurate sensing hybridization using the BioFET is therefore critically dependent on having a highly stable gate potential imposed through a reference electrode.**

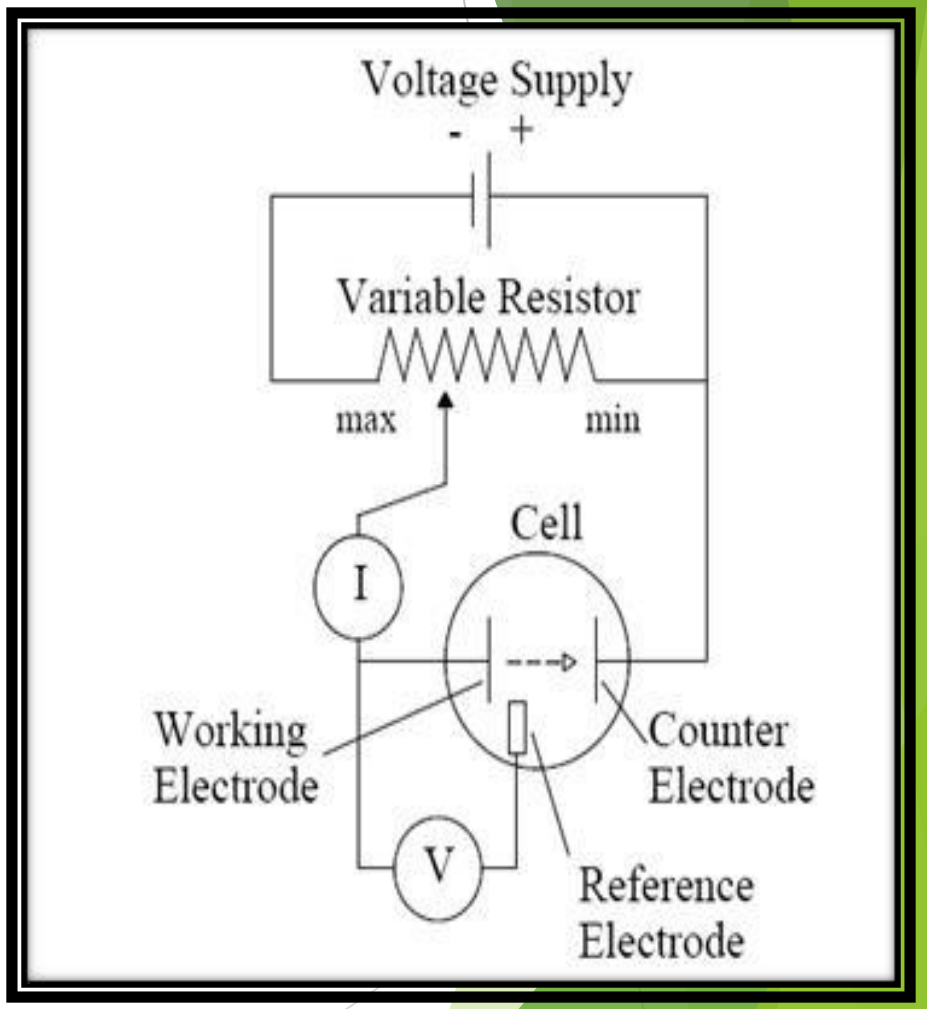
INSTRUMENTATION

Three electrodes in solution containing analyte :-

1. **Working electrode** : microelectrode whose potential is varied with time

2. **Reference electrode** : potential remains constant (Ag/AgCl electrode or calomel)

3. **Counter electrode** : Hg or Pt that completes circuit, conducts e- from signal source through solution to the working electrodeSupporting electrolyte: excess of nonreactive electrolyte (alkali metal) to conduct current

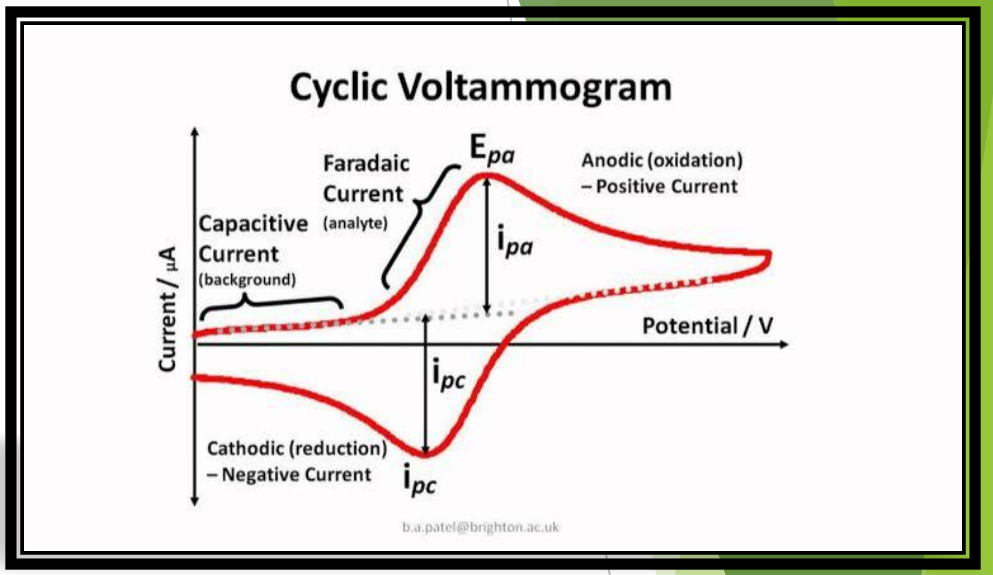


TYPES OF VOLTAMMETRY

1. Cyclic voltammetry.
2. Linear sweep voltammetry
3. Squarewave voltammetry (SWV)
4. Differential pulse voltammetry (DPV)
5. Stripping voltammetry
   - Anodic
   - Cathodic
   - Adsorptive

1. CYCLIC VOLTAMMETRY

- A voltammetric method that can be used to determine diffusion coefficients and half cell reduction potentials.
- Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution or of a molecule that is adsorbed onto the electrode.

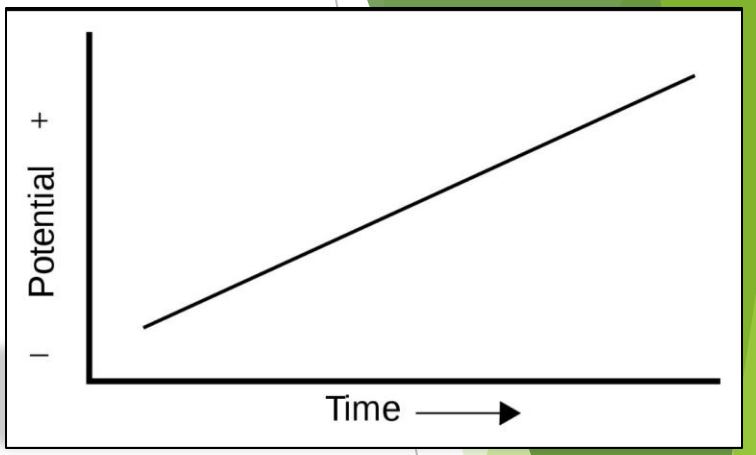


Applications :-

1. Used to study a variety of redox processes, to determine the stability of reaction products, the presence of intermediates in redox reactions, electron transfer kinetics, and the reversibility of a reaction.
2. Determine the electron stoichiometry of a system, the diffusion coefficient of an analyte, and the formal reduction potential of an analyte, which can be used as an identification tool.
3. In cellular biology it is used to measure the concentrations in living organisms. In organometallic chemistry, it is used to evaluate redox mechanisms.

2. LINEAR SWEEP VOLTAMMETRY

- It is a voltammetric method where the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in time.
- Oxidation or reduction of species is registered as a peak or trough in the current signal at the potential at which the species begins to be oxidized or reduced.

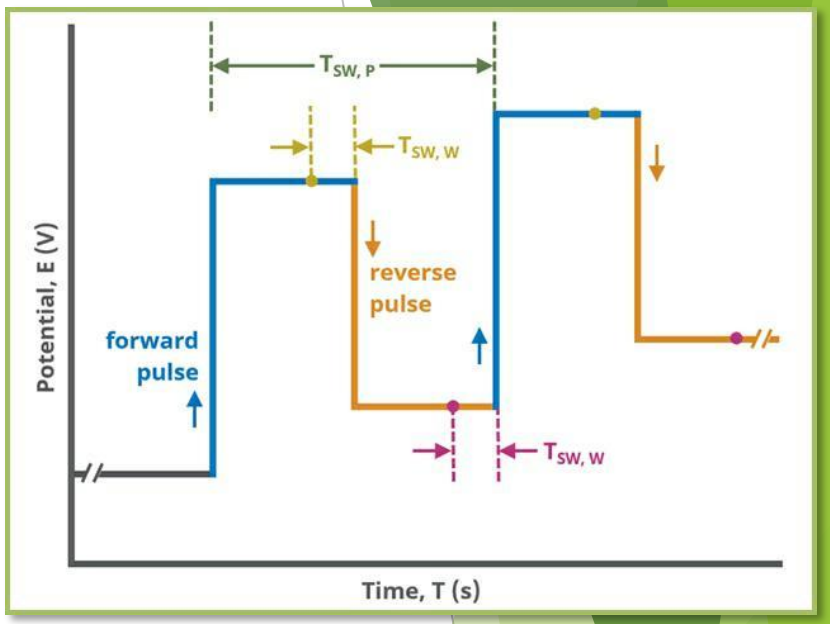


Applications :-

1. Linear voltammetry was used to examine direct methane production via a biocathode. Since the production of methane from CO2 is an irreversible reaction, cyclic voltammetry did not present any distinct advantage over linear sweep voltammetry. This group found that the biocathode produced higher current densities than a plain carbon cathode and that methane can be produced from a direct electric current without the need of hydrogen gas.

3. SQUAREWAVE VOLTAMMETRY (SWV)

- **Squarewave voltammetry** is a form of linear potential sweep voltammetry that uses a combined square wave and staircase potential applied to a stationary electrode.



Applications :-

1. SWV analysis has been used recently in the development of a voltammetric catechol sensor, in the analysis of a large number of pharmaceuticals, and in the development and construction of a 2,4,6-TNT and 2,4-DNT sensor.
2. It is coupled with other analytical techniques, including but not limited to thin-layer chromatography (TLC) and high-pressure liquid chromatography

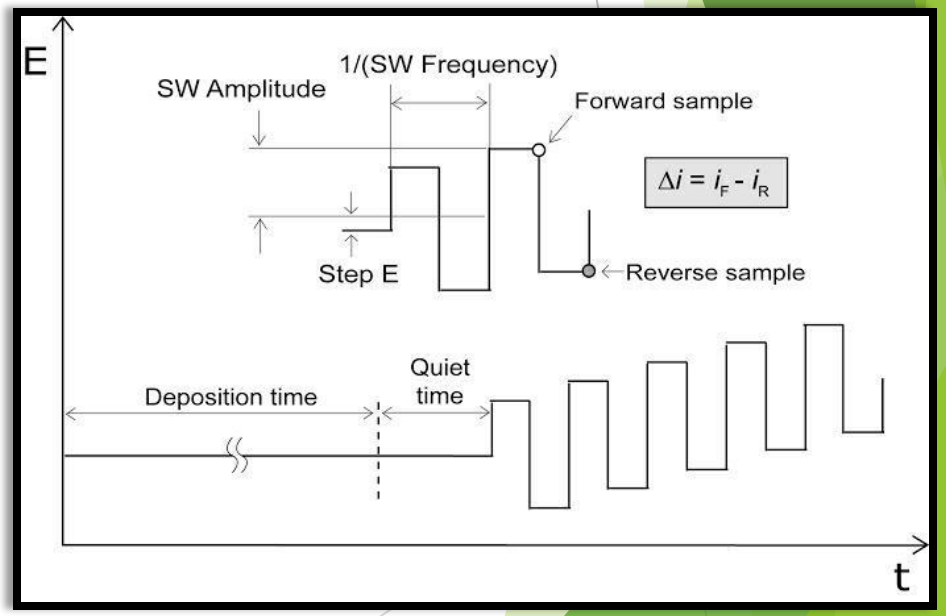
4. DIFFERENTIAL PULSE VOLTAMMETRY (DPV)

- **It** is a voltammetry method used to make electrochemical measurements and a derivative of linear sweep voltammetry or staircase voltammetry, with a series of regular voltage pulses superimposed on the potential linear sweep or stairsteps.
- The current is measured immediately before each potential change, and the current difference is plotted as a function of potential..
- By contrast, in normal pulse voltammetry the current resulting from a series of ever larger potential pulses is compared with the current at a constant 'baseline' voltage.

Applications :-

These measurements can be used to study the redox properties of extremely small amounts of chemicals because of the following two features:

1) in these measurements, the effect of the charging current can be minimized, so high sensitivity is achieved.
2) only faradaic current is extracted, so electrode reactions can be analyzed more precisely.

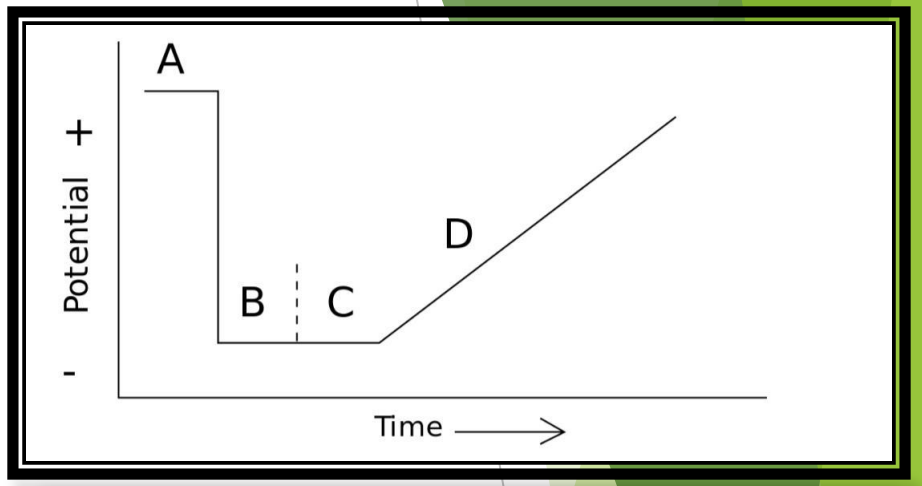


5. STRIPPING VOLTAMMETRY :-

* Stripping analysis is an analytical technique that involves

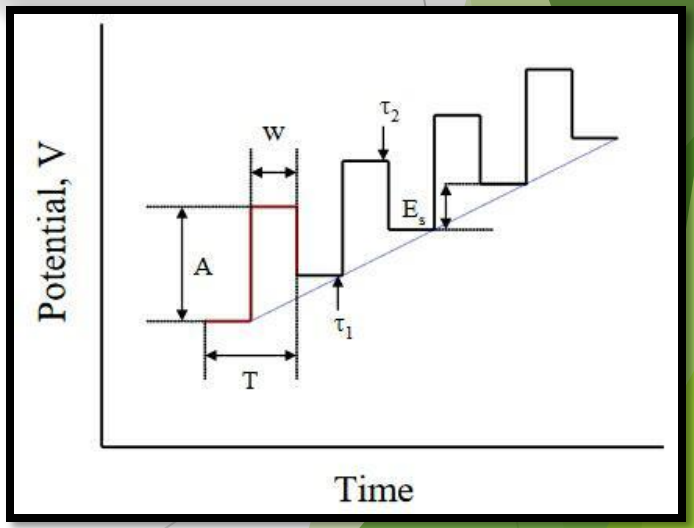
(i) preconcentration of a metal phase onto a solid electrode surface or into Hg (liquid) at negative potentials and

(ii) selective oxidation of each metal phase species during an anodic potential sweep.



Stripping voltammetry consist of three types :-

1. Anodic stripping voltammetry .
2. Cathodic stripping voltammetry .
3. Adsorptive stripping voltammetry .



TYPES OF STRIPPING VOLTAMMETRY :-

1. **Anodic stripping voltammetry** is a voltammetric method for quantitative determination of specific ionic species. The analyte of interest is electroplated on the working electrode during a deposition step, and oxidized from the electrode during the stripping step. The current is measured during the stripping step. The oxidation of species is registered as a peak in the current signal at the potential at which the species begins to be oxidized. It is widely used for testing drinking water quality, surface water and sewage or waste water – water that leaves the treatment plant before being discharged into surface water.

2. **Cathodic stripping voltammetry** is similar to the trace analysis method anodic stripping voltammetry, except that for the plating step, the potential is held at an oxidizing potential, and the oxidized species are stripped from the electrode by sweeping the potential negatively. This technique is used for ionic species that form insoluble salts and will deposit on or near the anodic, working electrode during deposition. The stripping step can be either linear, staircase, squarewave, or pulse.

3. **Adsorptive stripping voltammetry** is similar to anodic and cathodic stripping voltammetry except that the preconcentration step is not controlled by electrolysis. The preconcentration step in adsorptive stripping voltammetry is accomplished by adsorption on the working electrode surface, or by reactions with chemically modified electrodes.

APPLICATIONS OF VOLTAMMETRY

- **Voltammetric sensors ;-**

The voltammetric cells and are better referred to as sensors. These sensors can be employed for the analysis of various organic and inorganic analytes in various matrices.

- **The oxygen Electrode :-**

The determination of dissolved oxygen in a variety of aqueous environments, such as sea water, blood, sewage, effluents from chemical plants, and soils is of tremendous importance to industry, biomedical and environmental research, and clinical medicine.

- Determination of Metal ion concentration in water to sub parts per billion level.
- Wastewater analysis.
- Pharmacueticals analysis.
- Environmental studies.
- Plating analysis.
- Biochemical /Biological analysis.
- Handles high Salt concentration better than chromatographic instrumentation.
- Extremely low detection limits.
- Can detect a wide range of species

THANK YOU