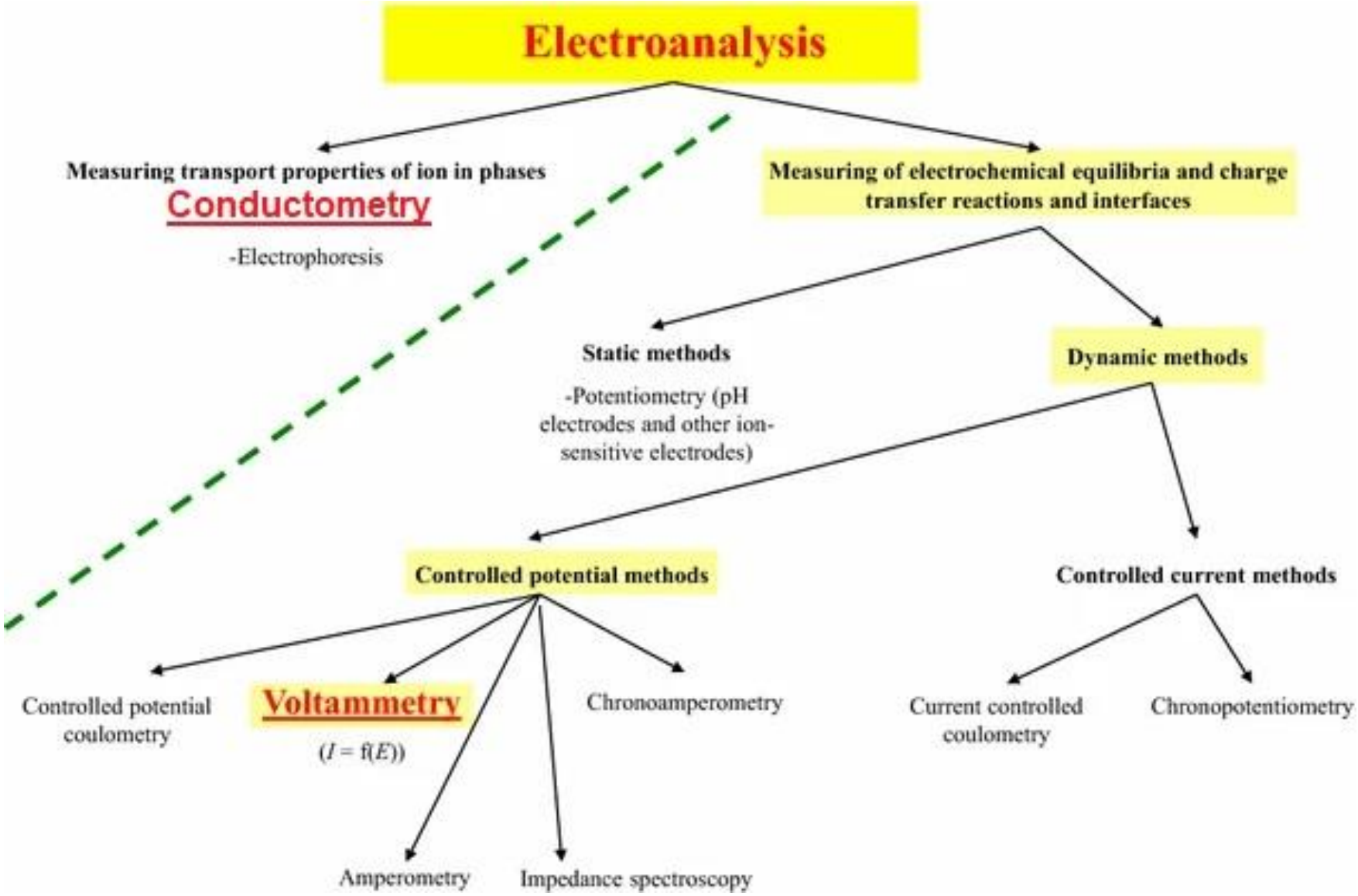
Ministry of higher education and scientific research
AL-Mustaqbal University college
Department of medical physics

Analytical chemistry

Lecture 5

Voltammetric and Conductmetric analysis

By
MSc.Elham Faisal


Electroanalysis
Measuring transport properties of ion in phases
Conductometry
-Electrophoresis
Measuring of electrochemical equilibria and charge transfer reactions and interfaces
Static methods
-Potentiometry (pH electrodes and other ion-sensitive electrodes)
Dynamic methods
Controlled potential methods
Controlled current methods
Controlled potential coulometry
Voltammetry
(I = f(E))
Chronoamperometry
Current controlled coulometry
Chronopotentiometry
Amperometry
Impedance spectroscopy

What are voltammetric techniques?

The term voltammetry is derived from **voltamperometry**, and it expresses that the current is measured as a function of voltage, i.e., electrode potential.

Since any electrochemical cell needs two electrodes, it would be impossible to extract unambiguous analytical information, if both electrodes would determine the magnitude of the flowing current.

Therefore, one electrode is made much smaller than the other, so that the flowing current is limited by this electrode only.

This electrode is called the **working electrode**, and the other (larger) electrode is called the **auxiliary electrode**.

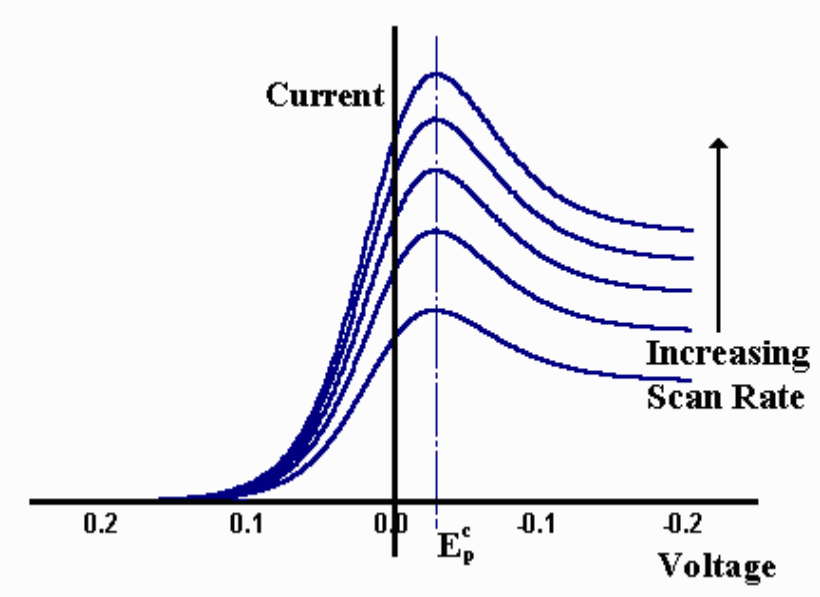
Characteristics

- **Voltammetry** is based upon the measurement of a current that develops in an electrochemical cell under conditions of complete concentration polarization.
- **Potentiometric** measurements are made at currents that approach zero and where polarization is absent.
- **Furthermore,** in voltammetry a minimal consumption of analyte takes place, whereas in electrogravimetry and coulometry essentially all of the analyte is converted to another state
- **Voltammetry** (particularly classical polarography) was an important tool used by chemists for the determination of inorganic ions and certain organic species in aqueous solutions.

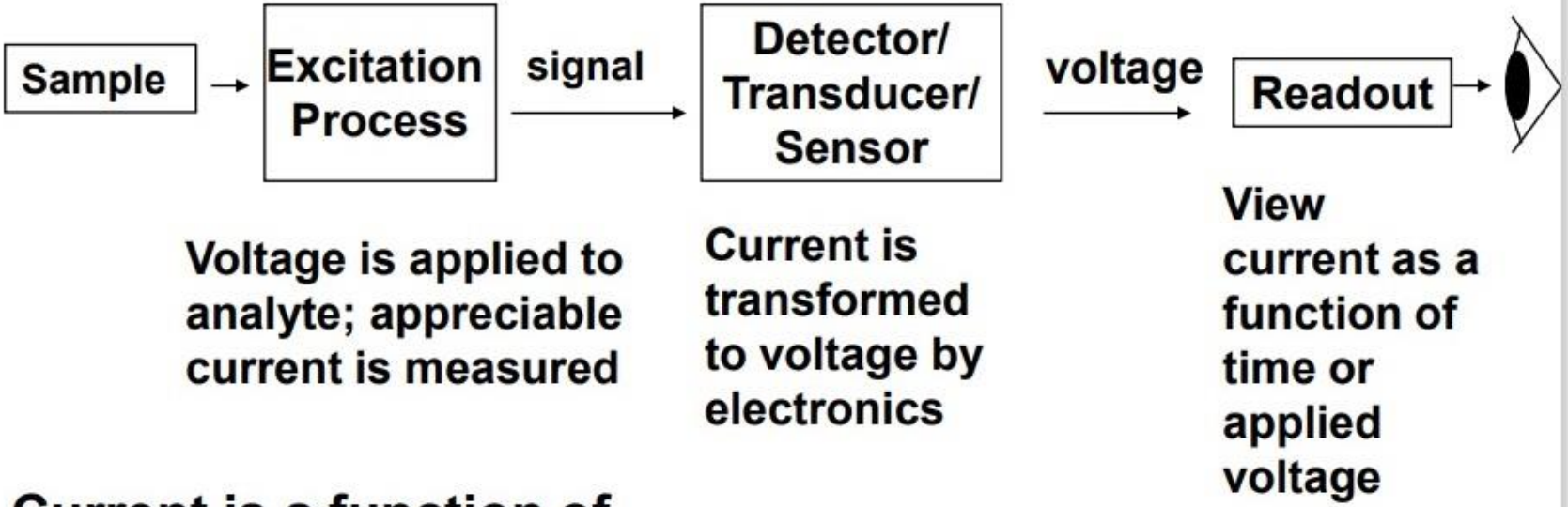
What is the principle of voltammetry?

In voltammetry, information about an analyte is obtained by measuring the current as the potential is varied.The analytical data for a voltammetric experiment comes in the form of

a voltammogram (is a graph that can be drawn after an electrochemical experiment) which plots the current produced by the analyte versus the potential of the working electrode.



Concept



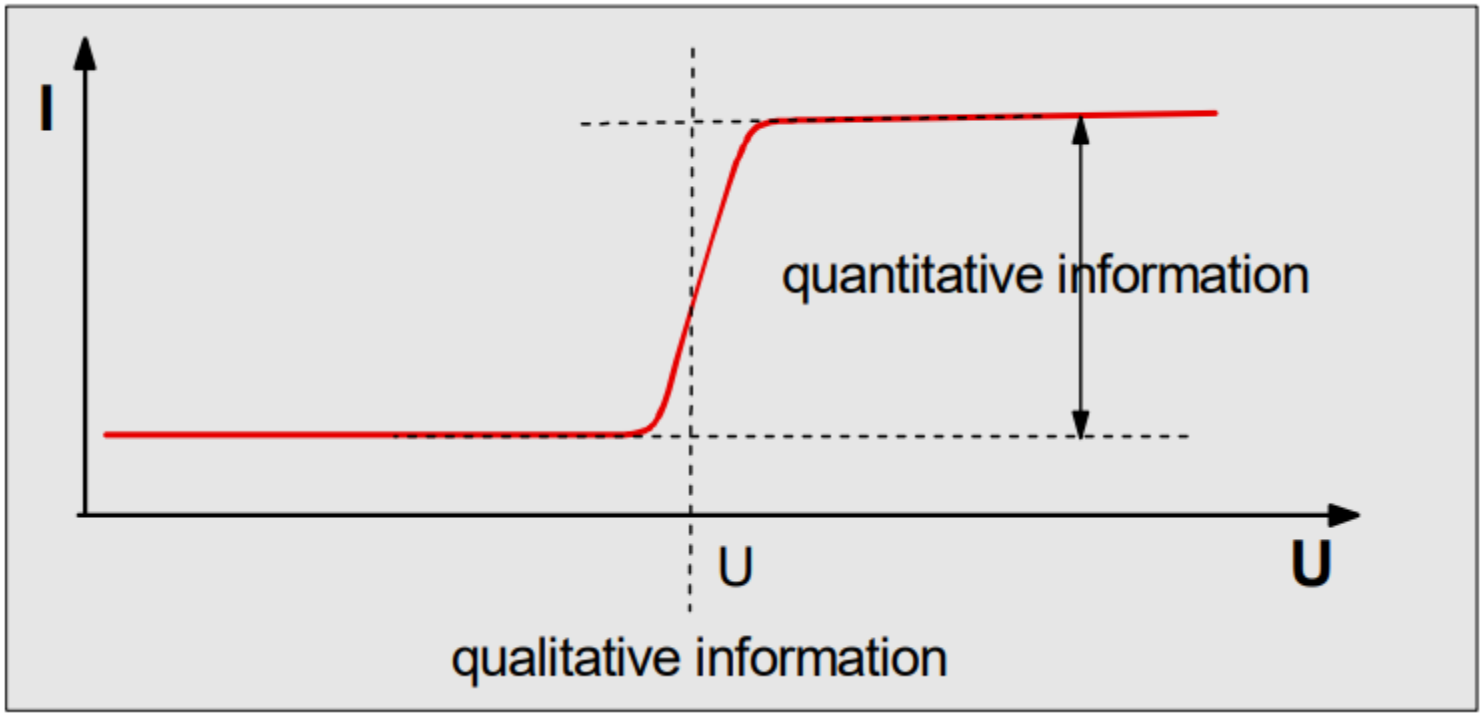
Current is a function of

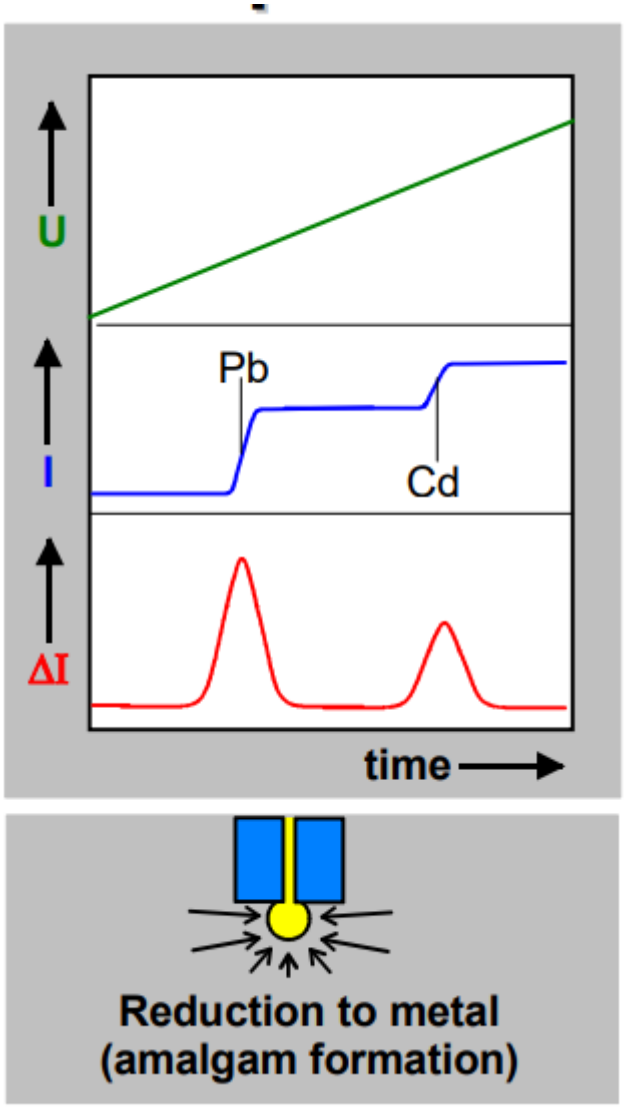
- **analyte concentration**
- **how fast analyte moves to electrode surface**
- **rate of electron transfer to sample**
- **voltage, time...**

Principle of voltammetryre rsulting curve

Voltage ramp applied to electrode Current measured

I = f(U)





potential increased current measured metal ions are reduced and dissolved in mercury.

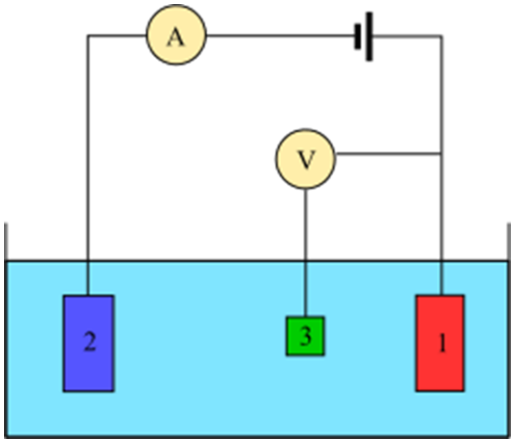
How many electrodes are used in voltammetry?

Three-electrode setup:

(1) working electrode: is the electrode in an electrochemical system on which the reaction of interest is occurring. The working electrode is often used in conjunction with an auxiliary electrode, and a reference electrode in a three electrode system.

(2) 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

(3) reference electrode :is a half cell with a known reduction potential. Its only role is to act as reference in measuring and controlling the working electrode's potential and at no point does it pass any current.



These electrodes, the working, reference, and auxiliary make up the modern three-electrode system.

Types of voltammetry

Voltammetric Techniques:

- Polarography
- Square Wave Voltammetry
- Cyclic Voltammetry
- LSV
- Differential Pulse
- Normal Pulse
- Sampled DC
- Stripping Analysisy

Conductmetric analysis

- Conductometry is defined as determination or measurement of the electrical conductance of an aq. electrolyte solution by means of a conductometer.
- Conductometry is used to analyze ionic species and to monitor a chemical reaction by studying the electrolytic conductivity of the reacting species or the resultant products.
- It has notable applications in analytical chemistry.
- Conductivity measurement can be performed directly by using a conductivity meter or by performing conductometric titration.
- Conductometric analysis of electrolytes is a long-time practice.
- Henry Cavendish and Andreas Baumgartner reported the analysis of mineral waters and salt solutions by using conductometric methods.

PRINCIPLE :-

It is based on the conductance of electrical current by aqueous electrolyte solutions in a manner similar to that of metallic conductors.

The electrical conductance is in accordance with the ohm′s law which states the strength of current passing through a conductor (in this case electrolyte solution.) is directly proportional to the potential difference applied across the electrodes and inversely proportional to the resistance offered by the conductor

$$i=v/R$$

Where:

i= current

v=potential difference

R= resistance (ohms Ω)

CONDUCTOMETRY THEORY :-

In conductometric titration the end point is detected by measuring the change in the electrical conductance of the solution which is being titrated.

Generally the conductometric titrations is based on the conduct of a solution and depends on the concentration and conductive of the ions.

It is also based on the substitutions of one mobility by the ion of another mobility.

Ex:-

Addition of HCl to ammonium hydroxide

$$H^+ \ Cl^- \ + NH_4^+ \ OH^- \ \rightarrow \ NH_4Cl \ + H_2O$$

The high conductivity H ions (350) are replaced by low conductivity NH4 ions (73).

FACTORS AFFECTING CONDUCTANCE :-

1) **Type of current :** Always A.C is used to prevent polarization of electrode in conductivity. As the frequency of current increases, conductance increases.
2) **Type of solute:** Strong electrolytes have higher conductance.
3) **Charge on ions:** As ionic change increases molar conductance increase (SO+2 Cl–)
4) **Size of ions**: As the size of ions increases, conductance decrease
5) **Mobility of ions / Spread of ions**: Absolute velocity of any ion under influence of 1 volt potential per cm is called ionic mobility.
6) **Viscosity:** High viscosity low conductance
7) **Temperature:** High temperature High conductance 1 C rise in temp. cause 2% rise in mobility of ions.

Advantage of conductometric titrations

1. Does not require indicators since change in conductance is measured by conductometer
2. Suitable for coloured solutions
3. Since end point is determined by graphical means accurate results are obtained with minimum error
4. Used for analysis of turbid suspensions, weak acids, weak bases, mix of weak & strong acids

Dis advantage of conductometric titrations

1. Increased level of salts in solution masks the conductivity changes , in such cases it does not give accurate results
2. Application of conductometric titrations to redox systems is limited because, high concentrations of hydronium ions in the solution tends to mask the changes in conductance

Applications

1. Check water pollution in rivers and lakes
2. Alkalinity of fresh water
3. Salinity of sea water (oceanography)
4. Deuterium ion concentration in water- deuterium mixture
5. Food microbiology- for tracing micro organisms
6. Tracing antibiotics
7. Estimate ash content in sugar juices
8. Purity of distilled and de - ionised water can determined
9. Solubility of sparingly soluble salts like AgCl,$BaSo_4$ can be detected
10. Determination of atmospheric so_2,etimation of vanillin in vanilla flavour


Thank You
For Your
Attention