

## Voltammetric and Conductmetric analysis

- ❖ Electroanalytical methods are a class of techniques in analytical chemistry, which study an analyte by measuring the potential (volts) and/or current (amperes) in an electrochemical cell containing the analyte.
- ❖ The analytical methods can be divided into different groups depending on the parameter measured. A schematic presentation of the methods is shown in Figure 1. The presentation is based on the recommendation of the International Union of Pure and Applied Chemistry.

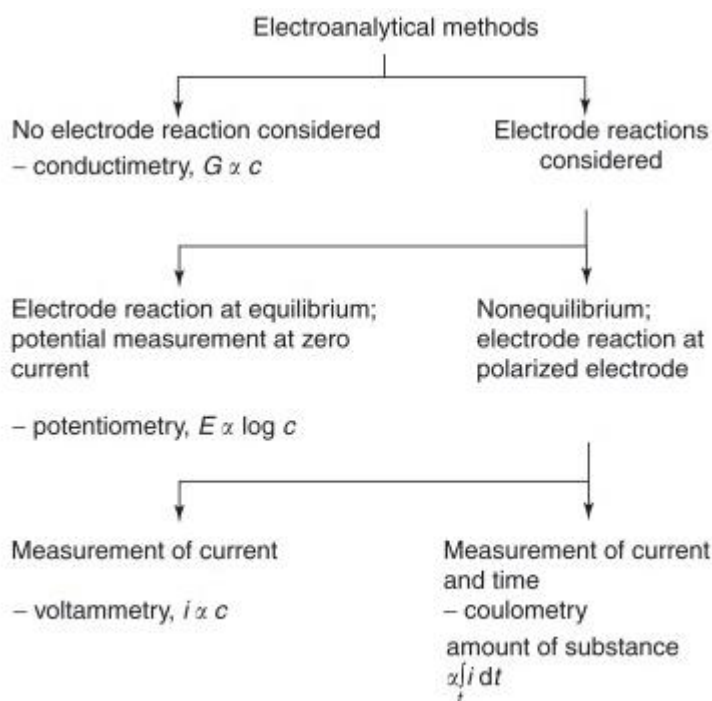


Figure 1. Classification of electroanalytical techniques.

### The three main categories are

- ❖ potentiometry (the difference in electrode potentials is measured),
- ❖ coulometry (the cell's current is measured over time),
- ❖ voltammetry (the cell's current is measured while actively altering the cell's potential).

## 1-Voltammetric analysis:

### Introduction:

- ❖ Analytical chemists routinely use voltammetric techniques for the quantitative determination of a variety of dissolved inorganic and organic substances.
- ❖ The common characteristic of all voltammetric techniques is that they involve the application of a potential (**E**) to an electrode and the monitoring of the resulting current (**i**) flowing through the electrochemical cell.
- ❖ Voltammetry refers to **electrochemical methods** in which a specific voltage profile is applied to a working electrode as a function of time and the current produced by the system is measured.

### Characteristics:

- ❖ 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. This electrode is called the **working electrode**, and the other (larger) electrode is called the **auxiliary electrode**.
- ❖ Therefore, one electrode is made much smaller than the other, so that the flowing current is limited by this electrode only.
- ❖ In voltammetry a minimal consumption of analyte takes place, whereas in electrogravimetry and coulometry essentially all 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.

### Qualitative and quantitative analysis in Voltammetry:

- ❖ Voltammetry is an analytical technique based on the measure of the current flowing through an electrode dipped in a solution containing electro-active compounds, while a potential scanning is imposed upon it.
- ❖ This electrode is called **working electrode** and could be made with several materials.
- ❖ Usually, it has a very little surface in order to assume quickly and accurately the potential imposed by the electrical circuit.
- ❖ The electrode can be solid (gold, platinum or glassy carbon) or formed by a drop of mercury hanging from a tip of a capillary.
- ❖ If the electrode is formed by a drop of mercury rhythmically dropping from a capillary, the analytical technique is called **Polarography**.
- ❖ Voltage ramp applied to electrode Current measured  **$I = f(u)$**  . (Figar 2)

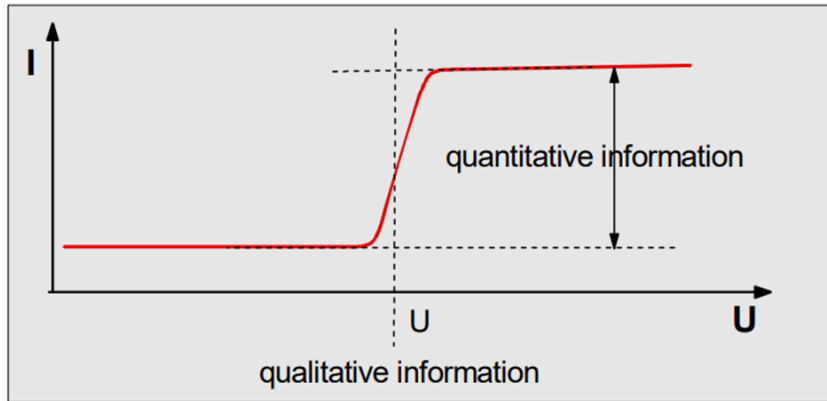


Figure: 2

### General principle of voltammetry:

- ❖ In voltammetry, information about an analyte is obtained by measuring the current as the potential is varied. (**Voltammetry is the study of current as a function of applied potential.**)
- ❖ The potential is varied arbitrarily, either step by step or continuously, and the resulting current value is measured as the dependent variable.
- ❖ These curves  $I = f(E)$  is called voltammograms.
- ❖ 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. (Fig.3)

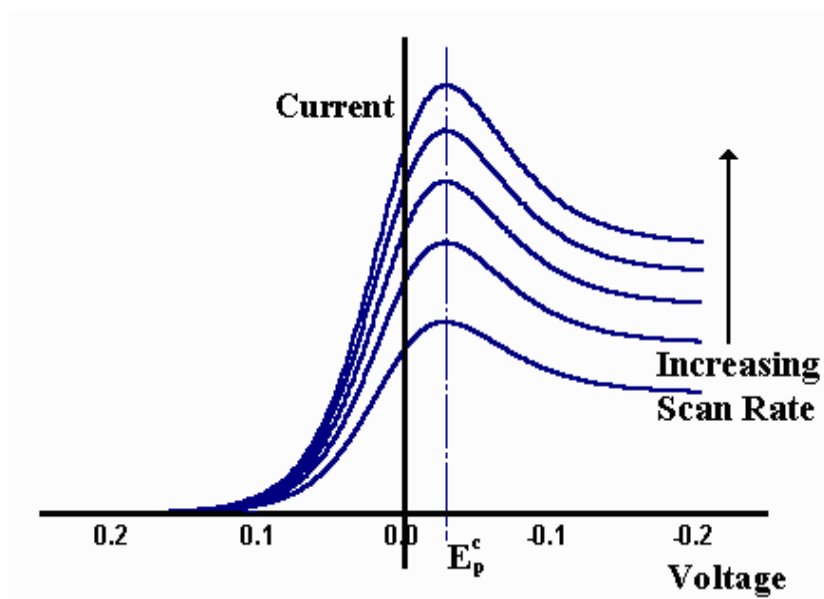


Figure 3

## What Is Cyclic Voltammetry?

- ❖ voltammetry is any experiment where we expose a solution of an analyte to an electrode, change the electrode potential, and observe the current that flows in response.
- ❖ In other words, we make a circuit out of a solution containing a molecule that we are interested in studying (analyte), change the voltage (electrode potential) on one of the electrodes, and see what voltage is required to transfer electrons (cause current to flow) between the electrode and our molecule of interest.
- ❖ Incorporating our analyte into a circuit is as easy as dipping two electrodes into our analyte solution. These two electrodes are connected to a potentiostat, which is an instrument that controls the voltage (potential) of each electrode.
- ❖ The main advantages of cyclic voltammetry over other voltammetric methods is the ease in interpretation of results, as well as how large potential ranges can be examined rapidly.
- ❖ Cyclic voltammetry can be used to determine (or measure) several electrochemical properties about a material, including:
  1. The reversibility of a reaction
  2. The formal reduction potential of a species
  3. Electron transfer kinetics
  4. Energy levels of semiconducting polymers
- ❖ Voltammetry is a sensitive analytic technique that informs us about the thermodynamics and kinetics of electron transfer for a given analyte.(Figar:4)

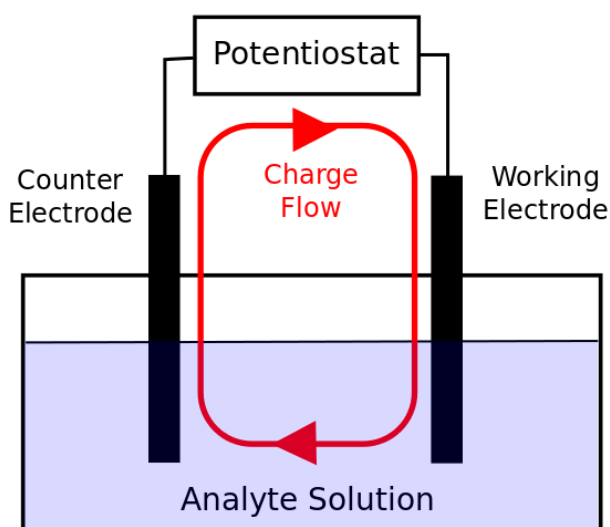


Figure: 4

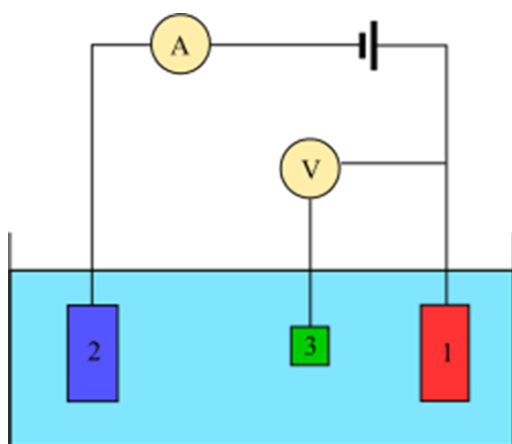
## How many electrodes are used in voltammetry?

### 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.(Figar:5)



### Types of Voltametric Techniques:

- 1- Polarography
- 2- Square Wave Voltammetry
- 3- Cyclic Voltammetry
- 4- LSV
- 5- Differential Pulse
- 6- Normal Pulse
- 7- Sampled DC
- 8- Stripping Analysis

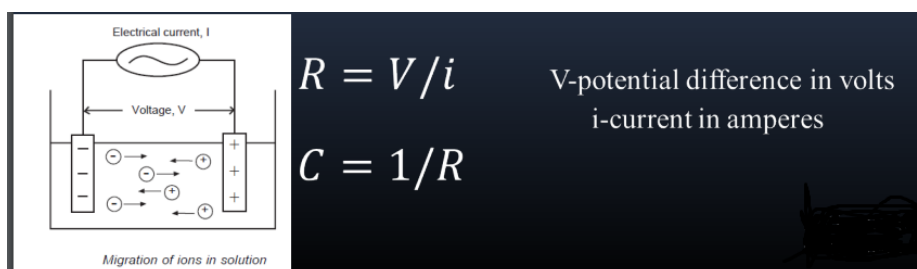
## 2- Conductimetric analysis

### Introduction:

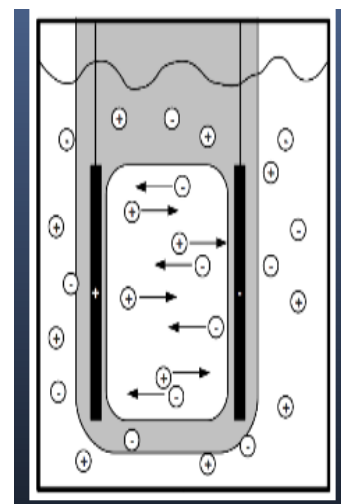
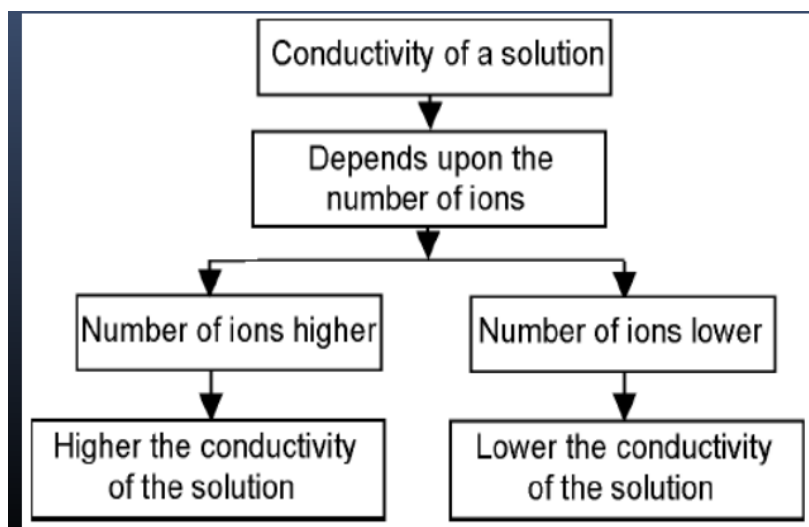
- ❖ Conductometry is defined as determination or measurement of the electrical conductance
- ❖ of an aq. electrolyte solution by means of a conductometer.
- ❖ Conductometric titration is a laboratory method of quantitative analysis used to identify the concentration of a given analyte in a mixture.
- ❖ Conductometric titration involves the continuous addition of a reactant to a reaction mixture and the documentation of the corresponding change in the electrolytic conductivity of the reaction mixture.
- ❖ It can be noted that the electrical conductivity of an electrolytic solution is dependent on the number of free ions in the solution and the charge corresponding to each of these ions.
- ❖ 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.

### 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.



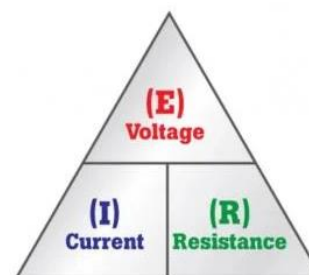
Total conductance of the solution is directly proportional to the sum of the n individual ion contributions .  $G = \sum c_i \Lambda_{m,i}$



### Ohm's law:

Ohm's Law is a formula used to calculate the relationship between voltage, current and resistance in an electrical circuit.

To students of electronics, Ohm's Law ( $E = IR$ ) is as fundamentally important as Einstein's Relativity equation ( $E = mc^2$ ) is to physicists.



(E)

$$E = I \times R.$$

Where: **E = voltage**    **I = current**    **R= resistance**

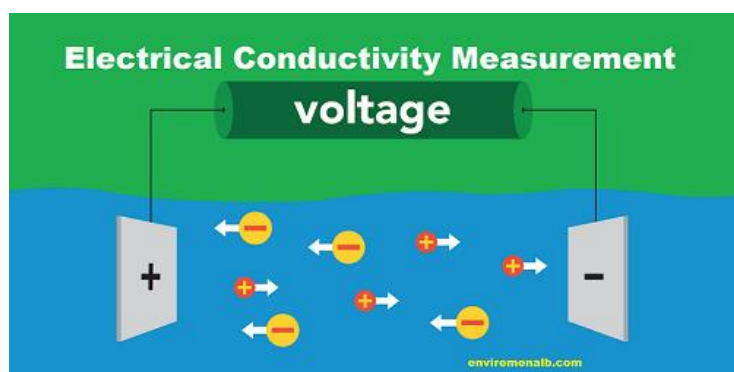
### Conductivity measurements:

**1. Electrodes:** Two parallel platinized Pt. foil electrodes or Pt. black with electrodeposited a porous Pt. film which increases the surface area of the electrodes and further reduces faradaic polarization.

**2. Primary standard solutions:** Primary standard KCl solution ,at 25<sup>0</sup> , 7.419g of KCl in 1000g of solution has a specific conductivity of 0.01286  $\Omega^{-1}/\text{cm}$ .

**3. Conductivity Cell :** Avoid the change of temperature during determination

#### 4. Wheat stone bridge :



#### 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 of ions:** As ionic charge increases molar conductance increase.
  4. **Size of ions:** As the size of ions increases, conductance decrease.
  5. **Viscosity:** High viscosity low conductance.
  6. **Temperature:** High temperature High conductance .
- ✓ **Specific conductivity:-**It is conductivity offered by a substance of 1cm length and 1sq.cm surface area. units are mhos/cm.
  - ✓ **Equivalent conductivity:-**it is conductivity offered by a solution containing equivalent weight of solute in it.

#### Advantage of conductometric titrations

- 1- Does not require indicators since change in conductance is measured by conduct meter.
- 2- Suitable for colored solutions
- 3- Since end point is determined by graphical means accurate results are obtained with minimum error
- 4- Used for analysis turbid suspensions weak acid , weak base , mixed weak and strong acids



## Disadvantage of conductometric titrations

- 1- Increased level of salts in solution makes the conductivity changes in such cases it does not give accurate results.
- 2- Application of conductometric titration to redox systems is limited because high concentration 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 determine.
- 9- Solubility of sparingly solute salts like  $\text{AgCl}$  ,  $\text{BaSO}_4$  ,can be detected.
- 10- Determination of atmospheric  $\text{SO}_2$  estimation of vanillin in vanilla flavor