



Dep. of Chem.- Fac. of Science.



South Valley University

Course of:

Instrumental Analysis

for 4th Science students (Zoology & Entomology groups)

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Dr. Ibrahim A. I. Hassan

..... *I. Hassan*

Instrumental Analysis

For University students, (4th level)

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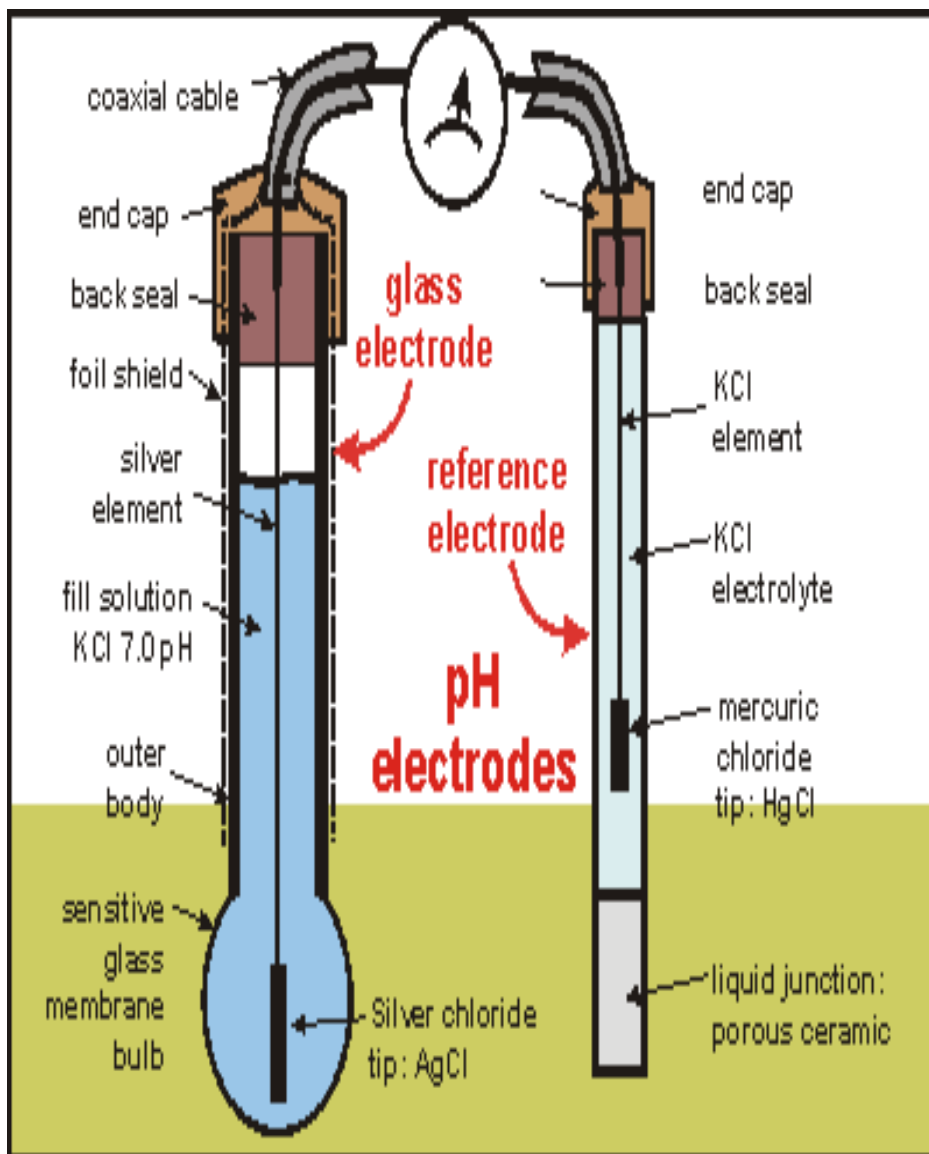
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Chapter I

Potentiometry



Potentiometry

Determines concentrations by measuring the potential (i.e., voltage) of an electrochemical cell (galvanic cell).

Two electrodes are required:

1. Indicator Electrode – potential responds to activity of species of interest.
2. Reference Electrode – chosen so that its potential is independent of solution composition.

Electrode potential

When a metal immersed into its solution; it dissolves acquiring a negative charge.



Accordingly, a potential will arise on the electrode so if it is connected in an external circuit; a current will pass.

Video 1: Potentiometry

<https://youtu.be/xH5noYAOGio>

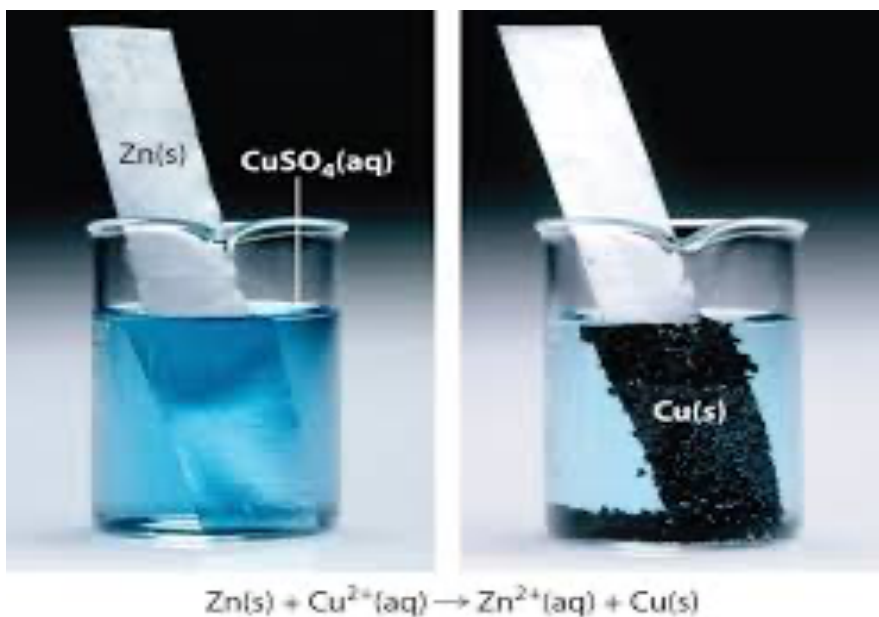


Figure 1: Dissolving of Zn and Dissolving of Cu^{+2}

In these reactions electrons transfer directly from Zinc metal to copper ions without passing through metallic conductor, so it is impossible to obtain electrical energy.

Electrochemical cells

There are two types of electrochemical cells: galvanic ones, which spontaneously produce electrical energy and electrolytic ones that consume electrical energy, in which an external power supply should be used to pass current through the cell to electrolyse the electrolyte content of ions.

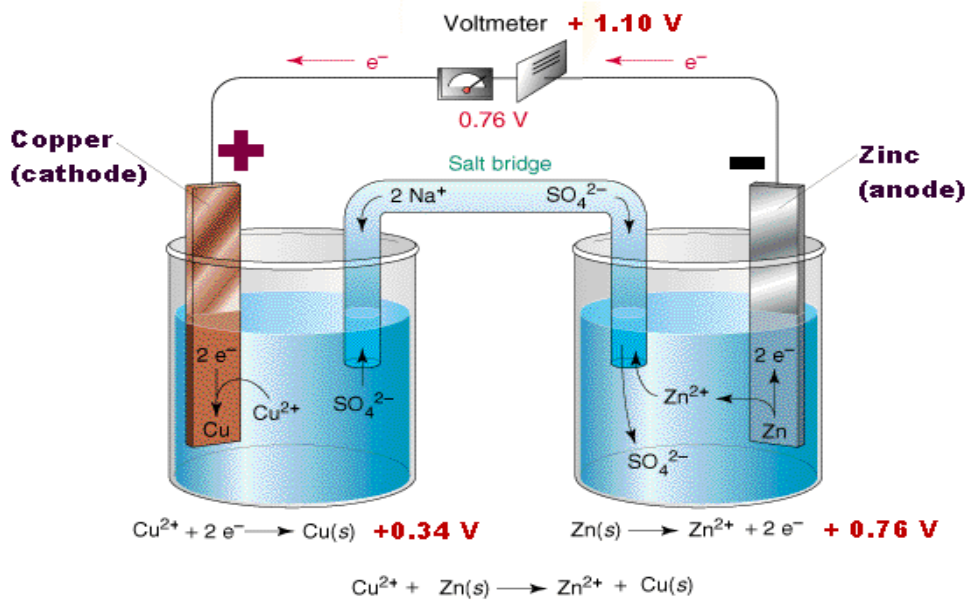


Figure 2.: Galvanic Electrochemical cell (Daniel Cell).

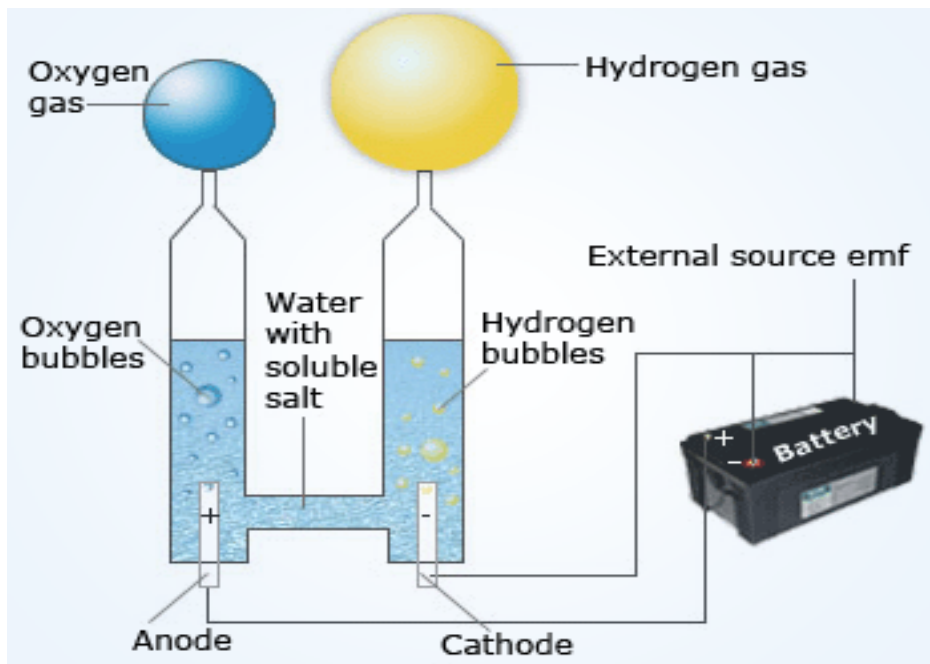


Figure 3.: Electrolytic Electrochemical cell

In Potentiometry, it should be differentiated between two concepts:

- 1) Potentiometric Systems – measure potential of a galvanic cell (produces electricity spontaneously).**
- 2) Voltametric Systems – control potential & usually measure current in an electrolytic cell (consumes power to cause an electrochemical reaction to occur).**

pH measurements

pH Electrode

$$K_w = [H^+] [OH^-] = 10^{-14} \quad \text{pH} = -\log [H^+]$$

$$\text{Neutral Solution} \quad [H^+] = 10^{-7} \text{ M}$$

$$\text{pH} = -\log 10^{-7} = 7$$

$$\text{Strong Base:} \quad [H^+] = K_w / [OH^-] = 10^{-14} / 1 = 10^{-14} \quad \text{pH} = 14$$

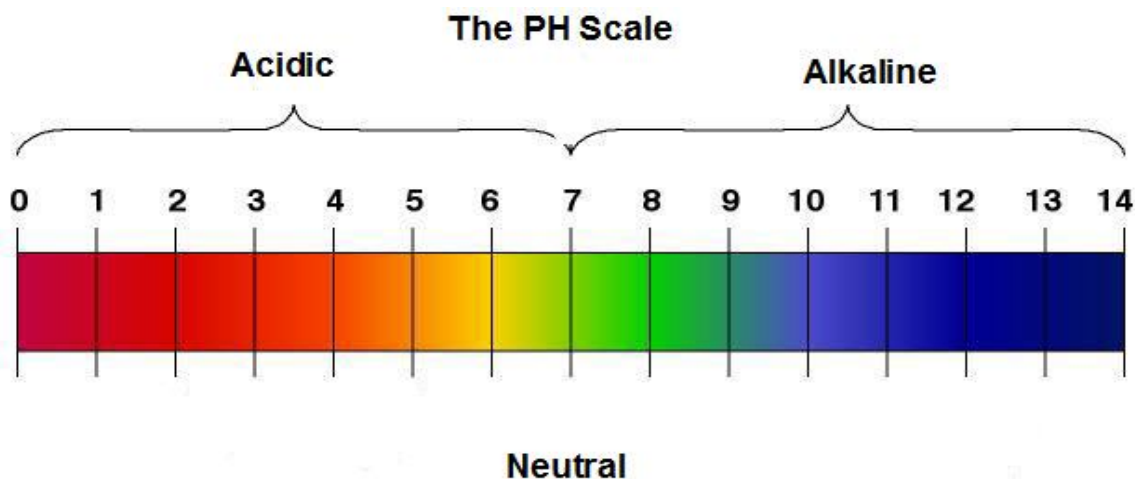


Figure 4.: The pH Scale

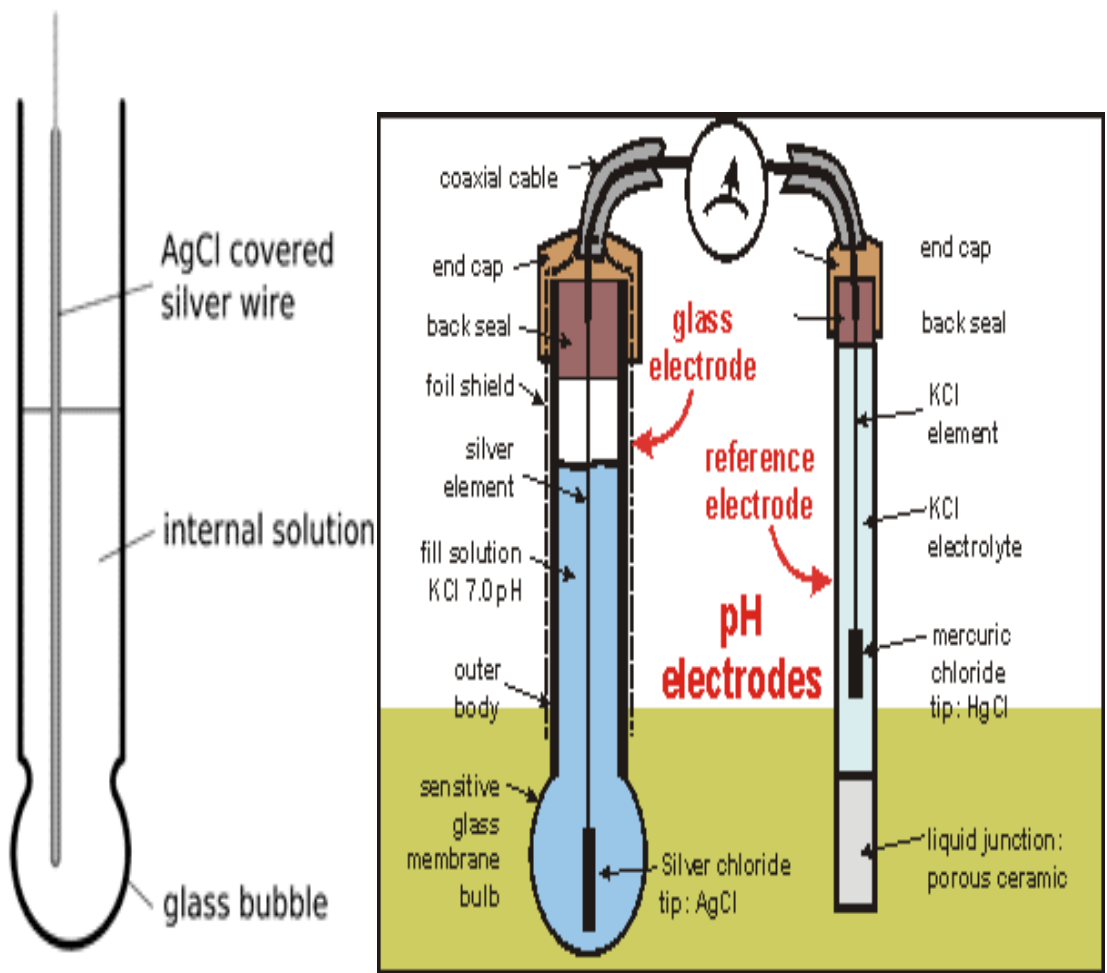


Figure 5.: The pH electrode separated from reference electrode

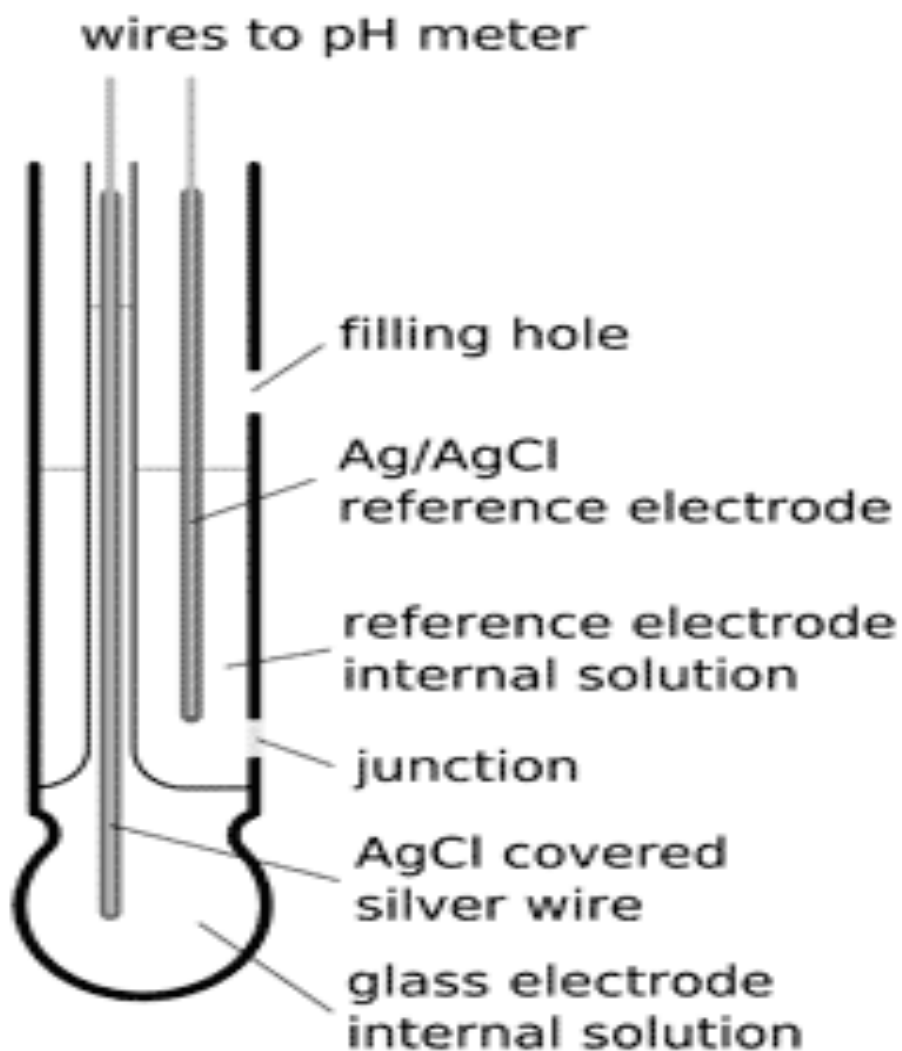


Figure 6.: The pH electrode combined with reference electrode

Video 2: pH electrode1:



<https://youtu.be/4jvremiDpRI>

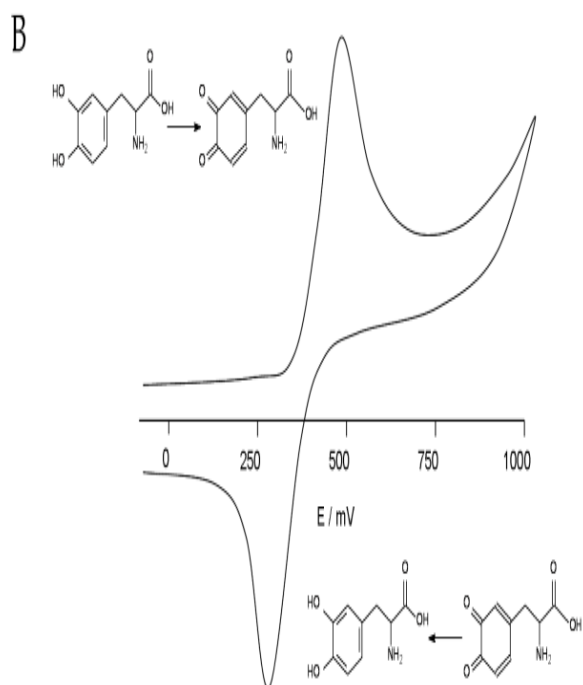
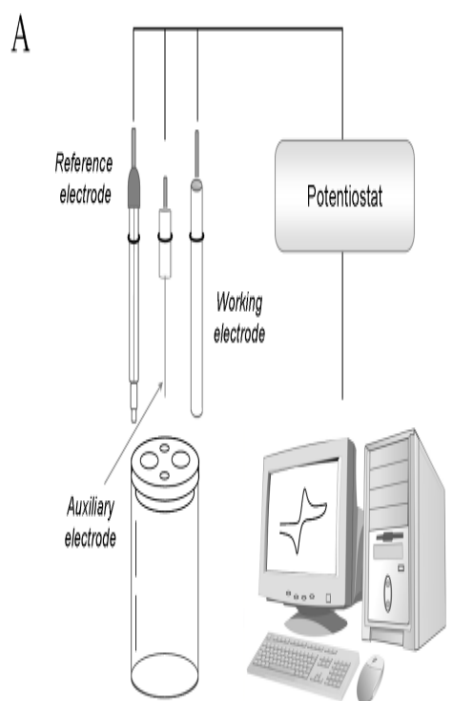
Video 3: pH electrode2



<https://youtu.be/rxWnKKz1YJo>

Chapter II

Voltammetry



Voltammetry

is a name given to a wide range of methods that study the composition of a solution by looking at current–potential relationships. It is essentially an electrolysis on microscale, using a micro working electrode (e.g., a platinum wire).

Voltametric Systems – scanning a potential slowly and the current is measured as a function in the applied potential in an electrolytic cell. The recorded results give a plot of current versus applied potential called **voltammogram**.

- ❑ **Voltammetry techniques measure current as a function of applied potential under conditions that promote polarization of a working electrode.**
- ❑ **Polarography: Invented by J. Heyrovsky (Nobel Prize 1959). Differs from voltammetry in that it employs a dropping mercury electrode (DME) to continuously renew the electrode surface.**
- ❑ **Amperometry: current proportional to analyte concentration is monitored at a fixed potential.**

The Voltametric cell – An electrolytic cell

Consists of three electrodes:

- 1. Micro working electrode:**
- 2. Auxiliary (Counter) electrode.**
- 3. Reference electrode.**

Working electrode including mercury, platinum, gold, silver, and carbon. Because mercury is a liquid, the working electrode is often a drop suspended from the end of a capillary tube.

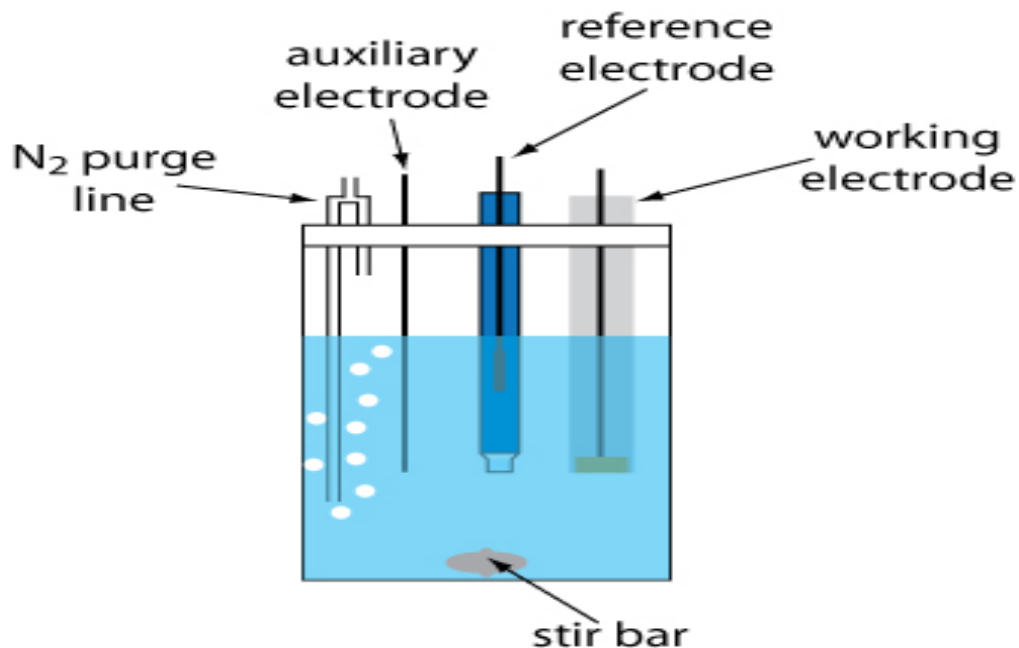


Figure 7.: The Voltametric cell

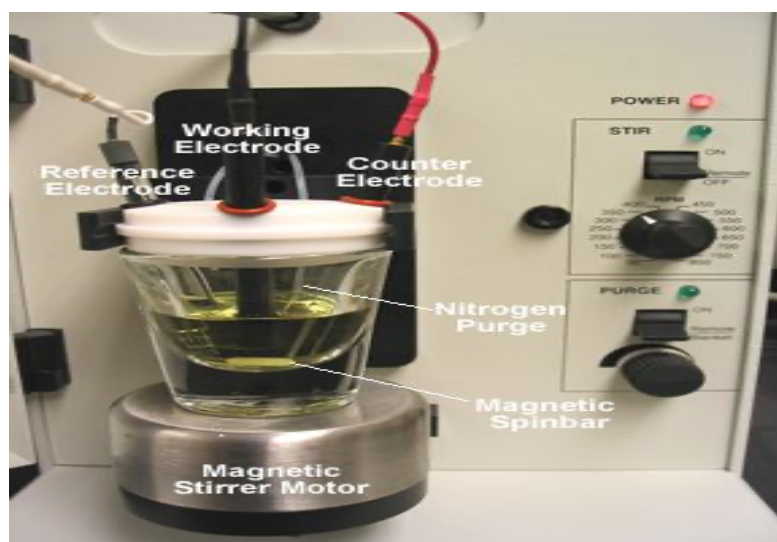


Figure 8.: The Voltametric cell; vital picture.

Voltammetry is one of the techniques which electrochemists employ to investigate electrolysis mechanisms. There are numerous forms of voltammetry:

- 1. Potential step**
- 2. Linear sweep**
- 3. Cyclic voltammetry**

Cyclic Voltammetry

- Cyclic voltammetry (CV) is one of the most widely used electroanalytical methods because of its ability to study and characterize redox systems from macroscopic scales down to nanoelectrodes**
- In CV the potential scans run from the starting potential to the end potential, then reverse from the end potential back to the starting potential.**

The essential elements needed for an electrolysis measurement are:

- 1. The electrode: This is usually made of an inert metal (such as Gold or Platinum)**
- 2. The solvent: This usually has a high dielectric constant (eg water or acetonitrile) to enable the electrolyte to dissolve and aid the passage of current.**
- 3. An electrolyte: is usually added in to allow the current to pass.**
- 4. The reactant: Typically, in low concentration 10^{-3} M**

The waveform, and the resulting I-E curve is shown in Figure 8.

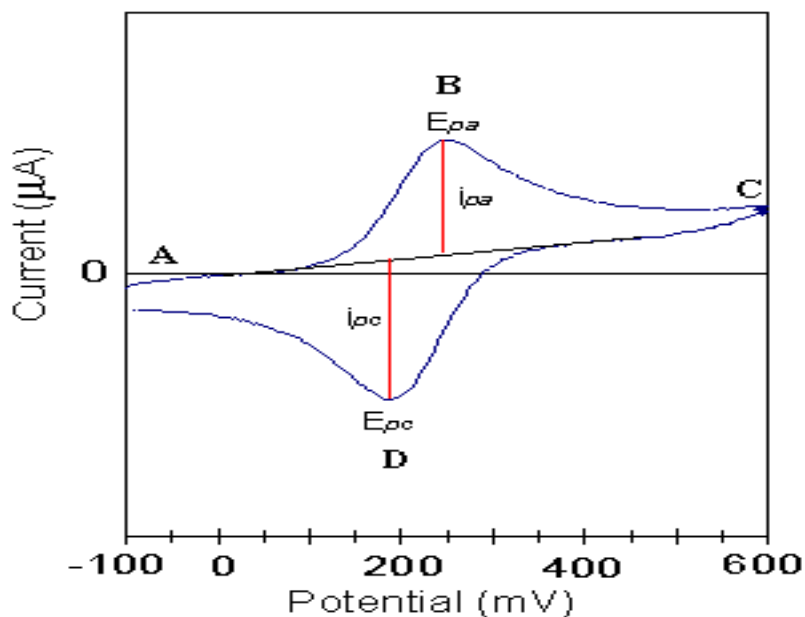


Figure 9.: The Cyclic-Voltammogram

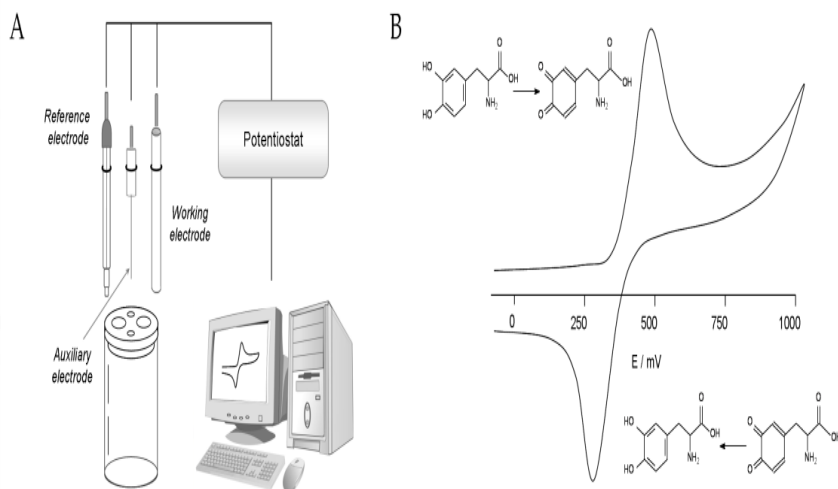


Figure 10.: A: The Cyclic-Voltammetry set. B: Redox reactions shown in Cyclic-Voltammogram.

Advantages of CV

- Can determine mechanisms and kinetics of redox reactions.

Stripping Analysis

Mercury working electrode

1. **Hanging mercury drop electrode (HMDE):** A drop of Hg suspended from the end of a capillary tube extruded by rotating a micrometer screw that pushes the mercury from a reservoir through a narrow capillary tube.
2. **Dropping mercury electrode (DME):** drops form at the end of the capillary tube because of gravity. Unlike the HMDE, the mercury drop of a DME grows continuously.

The Voltametric cell – HDME

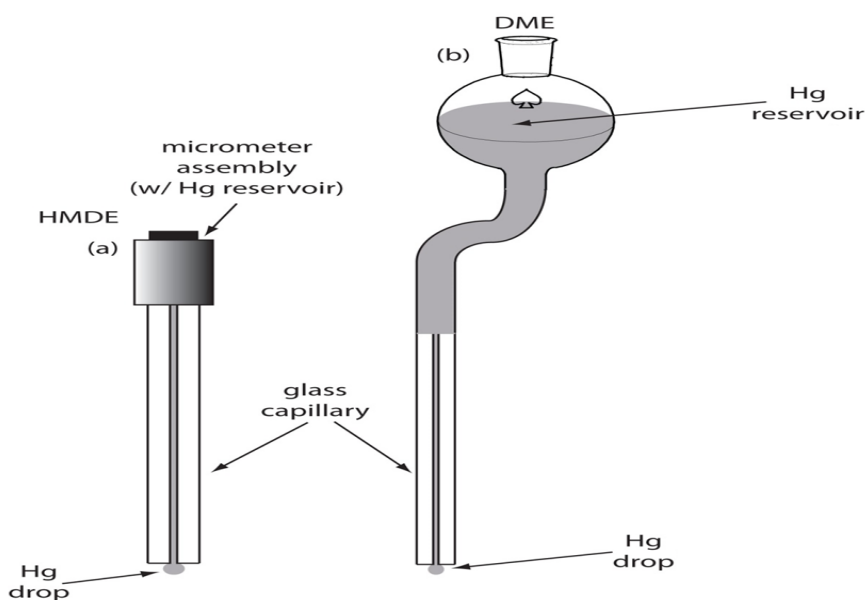


Figure 11.: The HMDE and DME for Stripping Analysis.

Stripping Analysis

- The analyte is electrochemically deposited on the working electrode.
- The polarity of the working electrode is reversed, and the analyte 'stripped' from the electrode.
- During this step, the current is monitored.
- The more easily oxidized substances are removed first.
- The integrated area under each peak is proportional to the amount of that species present.

The Voltametric cell – Stripping Analysis vs HDME

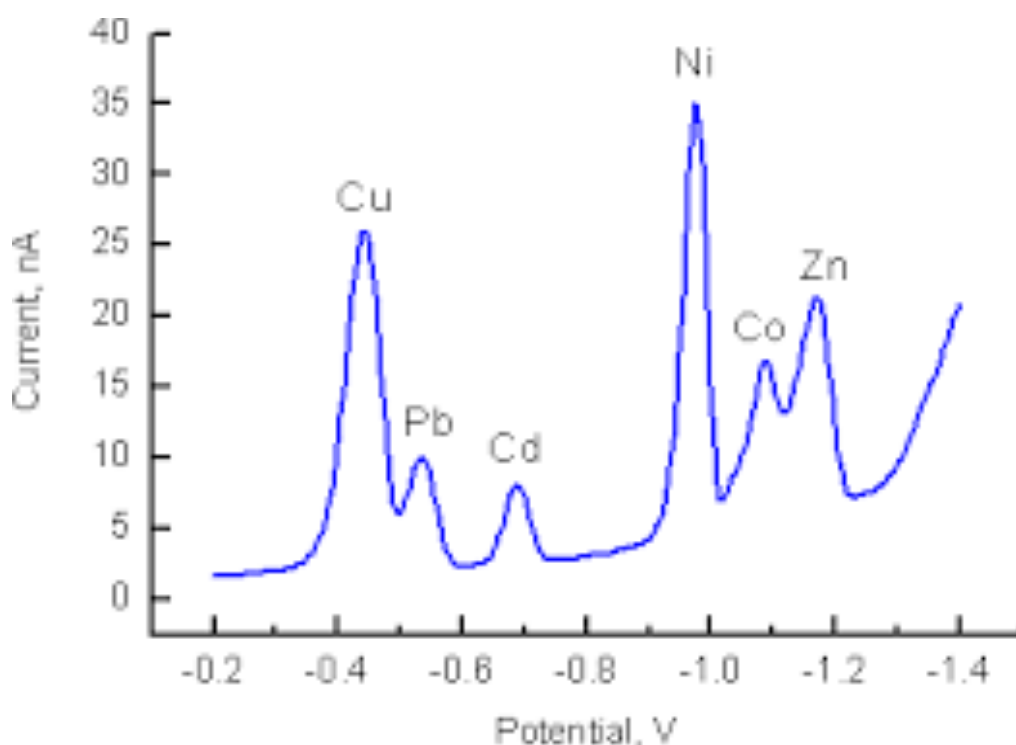


Figure 12: The Voltametric cell – Stripping Analysis vs HDME.

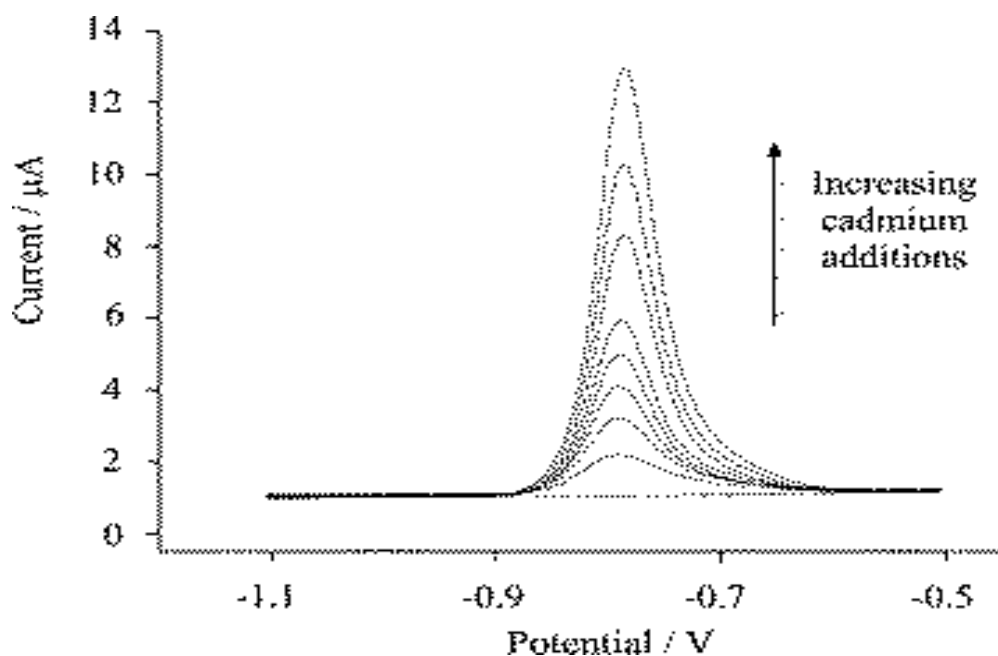


Figure 13.: The Anodic stripping peaks for added Cd^{2+} cell – Stripping Analysis vs HDME.

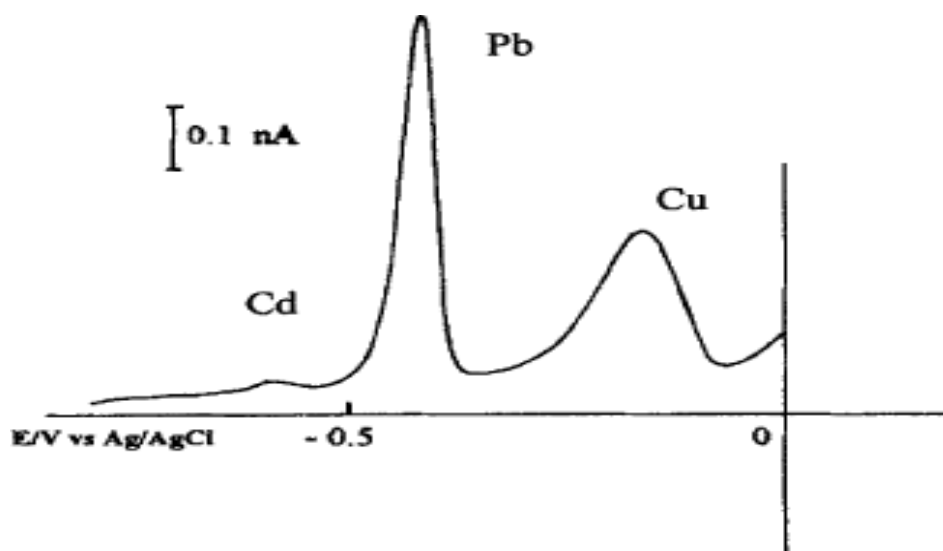


Figure 14.: The Anodic stripping voltammogram recorded at a mercury microelectrode in a pore-water sample acidified at $\text{pH} = 2$. Scan rate 50 mV s^{-1} .

Chapter III

Conductometry



Conductometry

This is a method of analysis based on measuring electrolytic conductance.

Conductance:

Is the ability of the medium to carry the electric current.

Electric current passes through metallic conductors, e.g. wires of iron or copper in the form of electron flow.

While

- **Conduction of electricity through an electrolyte solution involves migration of positively charged species towards the cathode and negatively charged ones towards the anode, i.e. current is carried**

- **by all ions present in solution.**
- **The conductance of the solution is a reciprocal of its resistance and has the units of Ohm^{-1} .**
- **The SI unit of conductivity is S/m (Siemens/meter).**
- **More generally encountered is the traditional unit of $\mu\text{S}/\text{cm}$.**

- **Conductivity is measured by using conductometer.**



Figure 15.: Different versions of conductometer.



Figure 16.: Different versions of conductometer.



Figure 17.: conductometer.

Total conductance of the solution is directly proportional to the sum of the number individual ion contributions.

Video 4: Conductometry



<https://youtu.be/rxWnKKz1YJo>

The magnitude of conductometric titration is based on ohm's law.

$$i = V/R$$

where

i = current in amperes

V = potential difference

R = resistance in ohm's

$$G = 1/R$$

Where **G** is the conductance of the solution.

Factors Affecting Conductivity

1. Nature of ions
2. Concentrations of ions
3. Temperature
4. The size of the electrodes

1. Nature of ions

The velocity by which ions move towards the electrodes carrying the electric current varies according to their nature:

i.e. size, molecular weight, and number of charges.

2. The ions concentration:

- The electrical conductance of a solution is a summation of contribution from all ions present.
- It depends on the number of ions of solution.
- As the number of ions increases, the conductance of the solution increases.

3. Temperature

- The conductance increases by increasing the temperature of the solution.
- An increase of temperature by 1°C is accompanied by 2 % increase in conductance.
- The measurements must be carried out at a constant temperature.

4. The size of the electrodes:

Conductance is directly proportional to the cross-sectional area A of the electrode, and inversely proportional to the length L between the two electrodes.

$$G \propto \frac{A}{L}$$

The conductance of electrolyte solution can be calculated from:

$$G = K \frac{A}{L}$$

Where **G** is the conductivity, **K** is the specific conductivity, **A** is the cross-sectional area of the electrode, **L** the length between the two electrodes.

Specific conductivity: -

- ✓ It is the conductance of a cube of liquid with one centimeter on a side.

$$K = G \frac{L}{A}$$

- ✓ Units are 1/Ohm.cm or Ohm⁻¹cm⁻¹ or siemens/cm.
- ✓ L/A is known by the cell constant, **K**, is a constant value for specific solution.

Equivalent conductivity: -

It is defined as the conductance of one gram equivalent of solute contained between electrodes spaced one centimeter apart.

Instruments used in conductometric determination:

To carry out conductometric measurement it is necessary to measure the resistance of the solution and the conductance is 1/R

The instrument consists of two parts:

1. **Conductance cell: in which the solution to be measured is filled or placed.**

2. Conductivity bridge: to measure the resistance and then converts it to conductivity unit.

1. Conductivity Cell:

Which consists of:

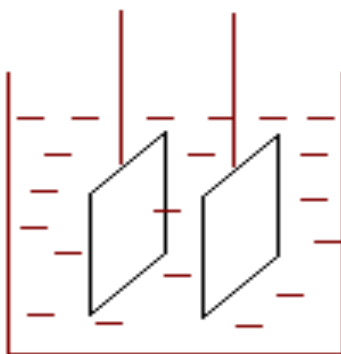


Figure 18.: Basic conductivity cell.

A. Electrodes

Two parallel platinized Platinum foil electrodes or Platinum. black with electrodeposited porous Platinum film which increases the surface area of the electrodes and further reduces faradaic polarization.

B. The cell contains the solution under investigation.

- The solution should be diluted to avoid the faradaic polarization.**
- The temperature should be stable to avoid its effect on conductance measurements.**

2. Wheatstone bridge:

- R_1 , R_2 and R_3 are known.
- R_2 are variable
- V_G is galvanometer employed to indicate an absence of current between D and B, that happened when the voltage between the two points equals zero.
- The conductance cell contains the solution replaces the R_x to be measured.

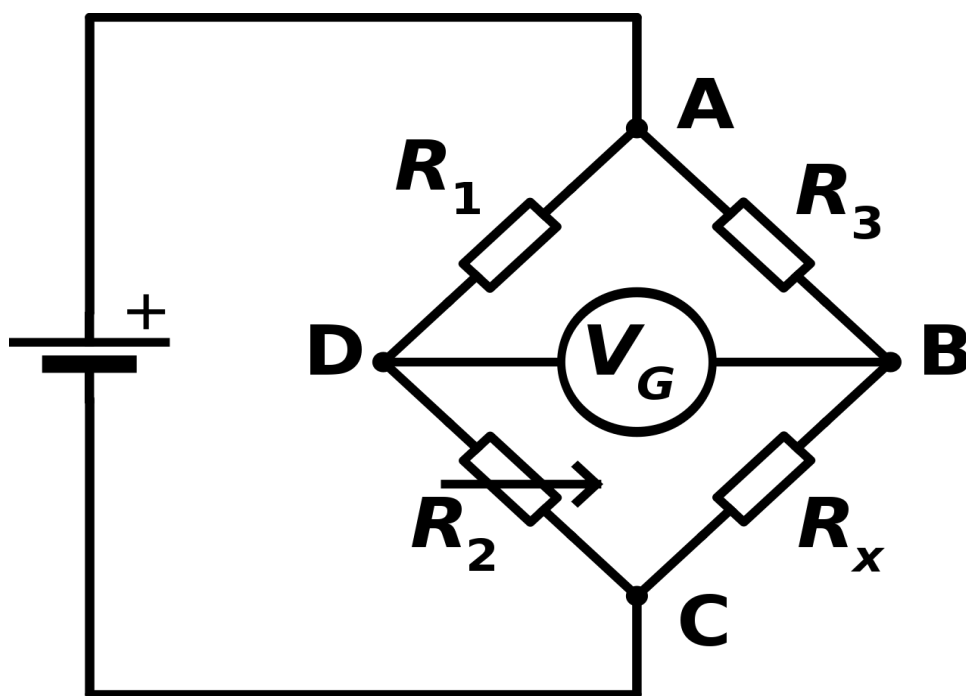


Figure 19.: Wheatstone bridge

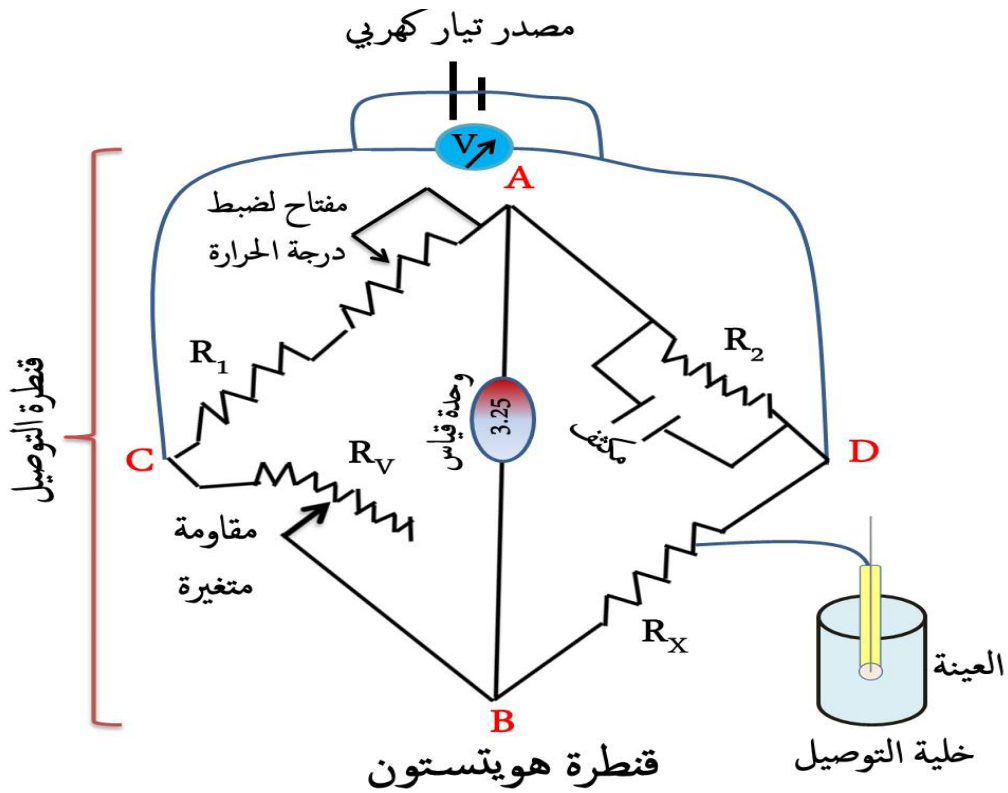


Figure 20.: Wheatstone bridge 2

- When the current at V_G equals zero that means a Balance achieved at which:

$$\frac{R_2}{R_1} = \frac{R_x}{R_3}$$

So,

$$R_x = R_3 \frac{R_2}{R_1}$$

$$G = \frac{1}{R_x}$$

APPLICATIONS OF CONDUCTOMETRY

It can be used for the determination of:-

- **Solubility of sparingly soluble salts**
- **Ionic product of water**
- **Basicity of organic acids**
- **Salinity of sea water**
- **Chemical equilibrium in ionic reactions**

CONDUCTOMETRIC TITRATIONS:

- **The determination of end point of a titration by means of conductivity measurements are known as conductometric titrations.**

Video 5: Conductometric Titration



<https://youtu.be/MopNOn1IRUw>

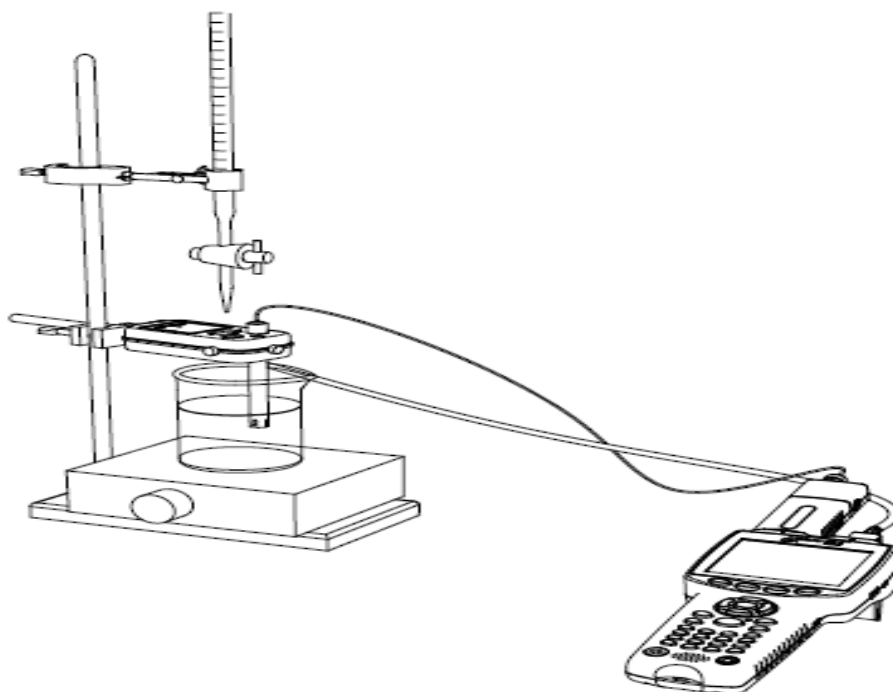


Figure 21.: Conductometric titration set.

Types of conductometric titrations:

- **Acid-base titration**
- **Precipitation titration**
- **Replacement titration**
- **Redox (oxidation-reduction) titration**
- **Complexometric titration**

ACID-BASE TITRATIONS

- Titration of strong acid:

(a) with strong base

e.g. HCl with NaOH

(b) with weak base

e.g. HCl with NH_4OH

(a) HCl vs NaOH

(b) HCl vs NH_4OH

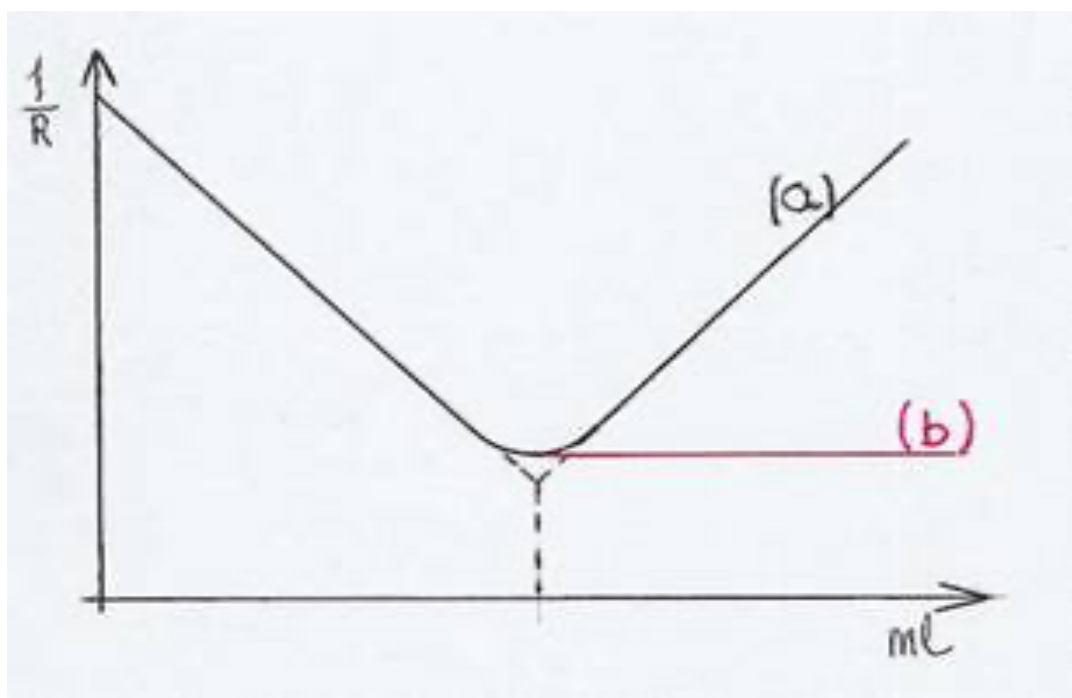
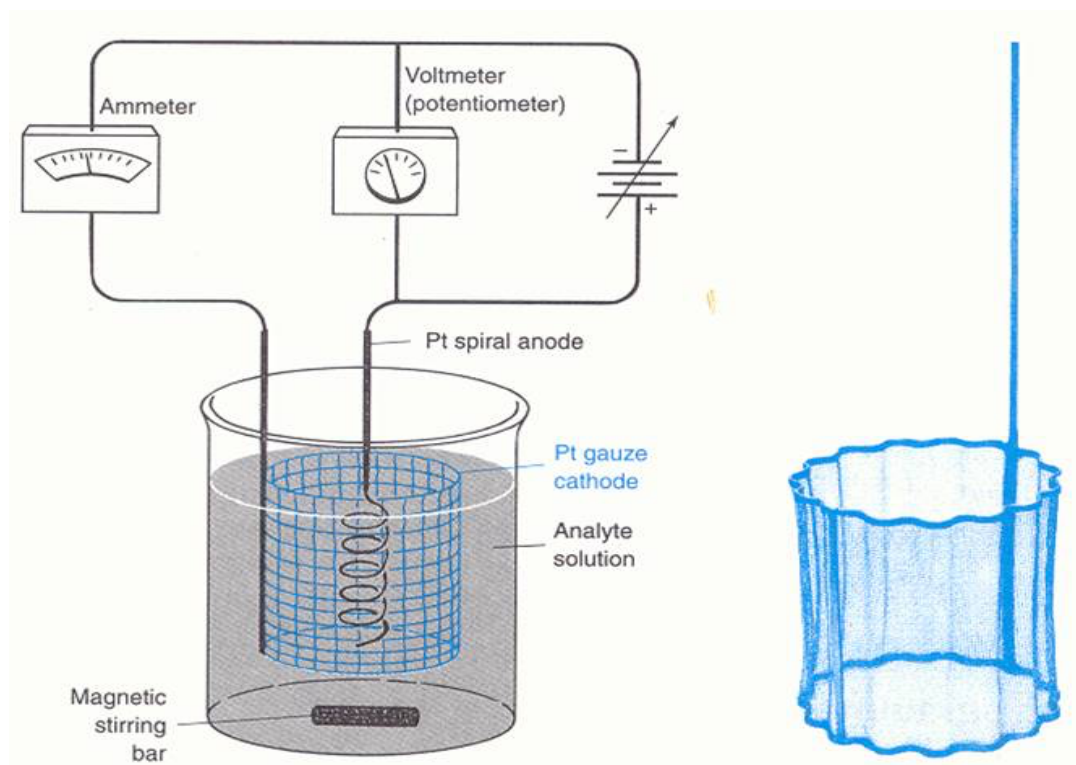


Figure 22.: Conductometric titration curves of (a) HCl vs NaOH
(b) HCl vs NH_4OH

Chapter IV

Electrogravimetry



Electrogravimetry:

is an electroanalytical method used to separate and quantify ions of a substance, usually a metal.

- **In this process, the analyte solution is electrolyzed.**
- **Electrochemical reduction causes the analyte to be deposited on the cathode.**

- **The cathode is weighed before and after the experiment.**
- **The weight difference is used to calculate the amount of analyte in the original solution.**
- **Controlling the potential of the electrode is important to ensure that only the metal being analyzed will be deposited on the electrode.**

- **This method employs two or three electrodes, just as in voltammetry.**
- **Either a constant current or a constant potential is applied to the pre-weighed working electrode.**

- **After the assayed substance has been completely removed from the solution by the electrochemical reaction, the working electrode is removed, rinsed, dried, and weighed.**
- **The increased mass of the electrode due to the presence of the reaction product is used to calculate the initial concentration of the analyte.**

- **If only one component in the solution can react to form a deposit on the electrode, constant-current electrogravimetry is the preferred method.**
- **In constant-potential electrogravimetry, the potential at the working electrode is controlled so that only a single electrochemical reaction can occur.**

- **Electrogravimetry can be conducted with or without a controlled potential.**

When No control:

- **A fixed potential is set, and the electrodeposition is carried out.**
- **The starting potential must be initially high to ensure complete deposition**
- **The deposition will slow down as the reaction proceeds.**

Instrumentation:

- **The apparatus for an analytical electro deposition, without cathode potential control, consists of a suitable cell and direct current supply.**
- **The voltage applied to the cell is controlled by the variable resistance.**

- The voltage is then maintained at about the initial level until the deposition complete.
- A current meter and a voltmeter indicate the approximate current and voltage.

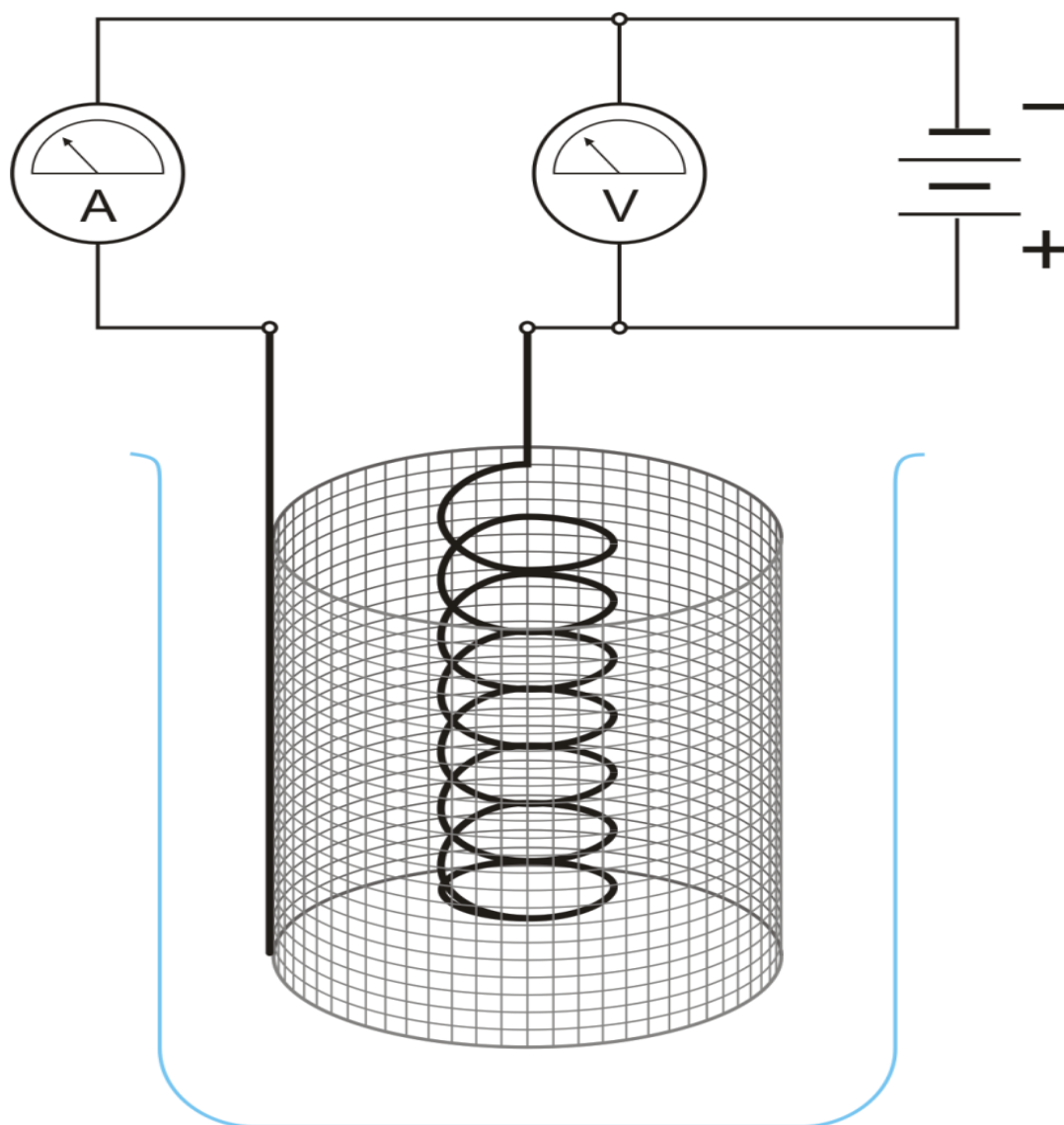


Figure 23.: electrogravimetry measurement set.

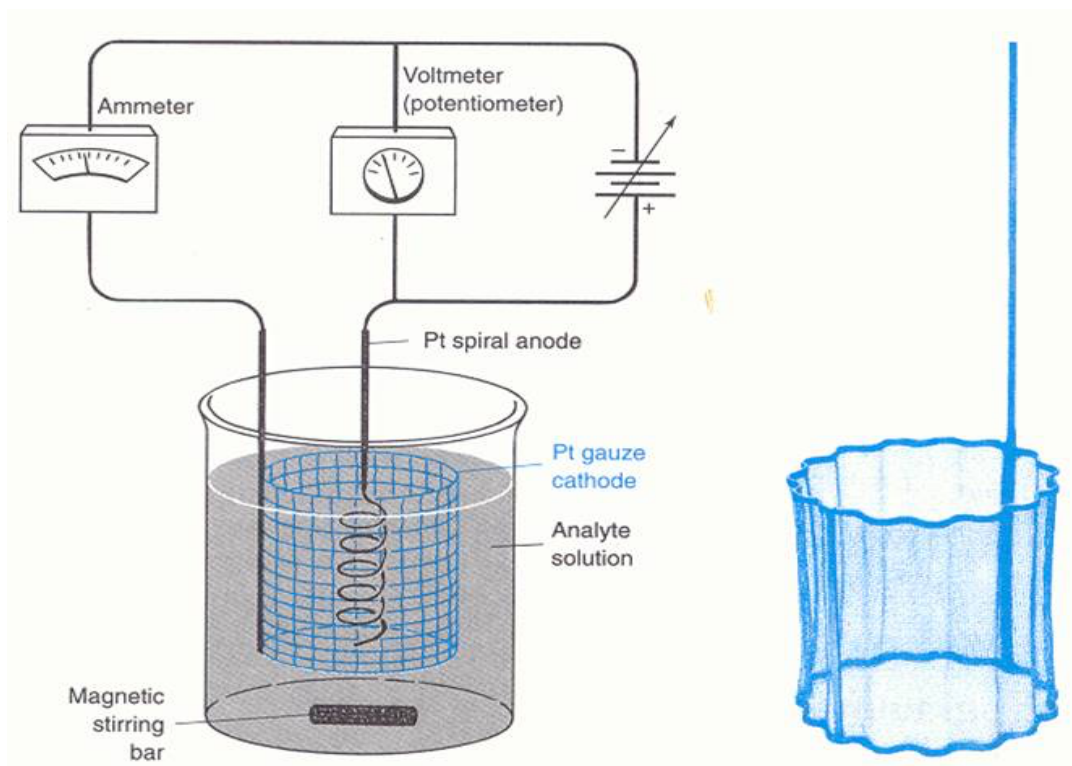


Figure 24.: electrogravimetry measurement set, after separation the precipitate.

Electrogravimetry

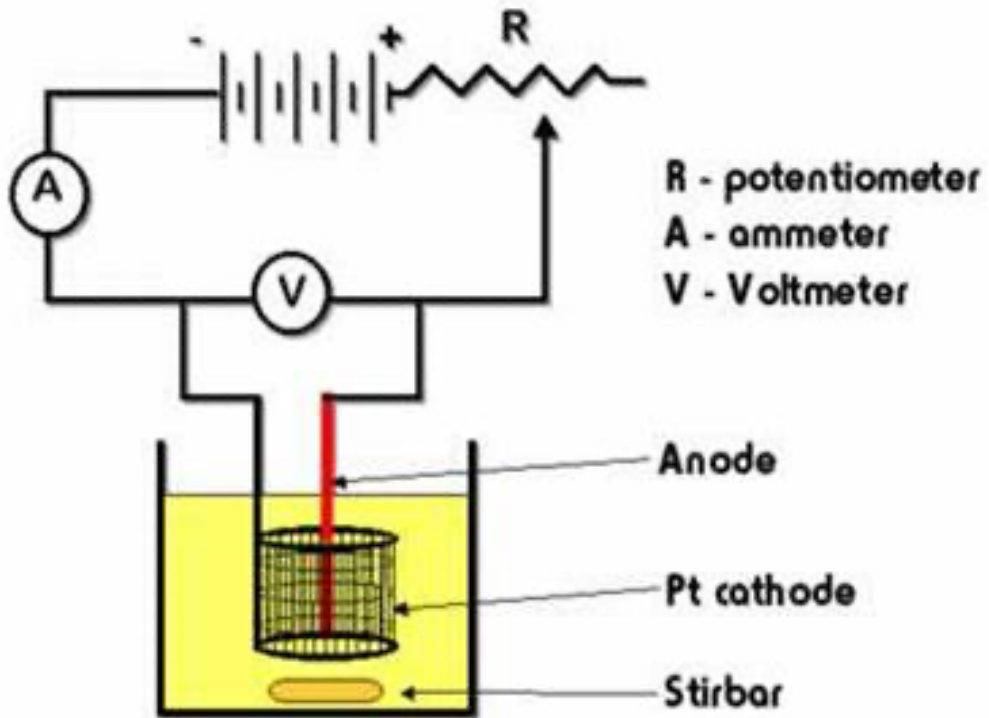


Figure 25.: electrogravimetry measurement apparatus.

Video 6: Electrogravimetry:



<https://youtu.be/BJKAt-eeLRg>

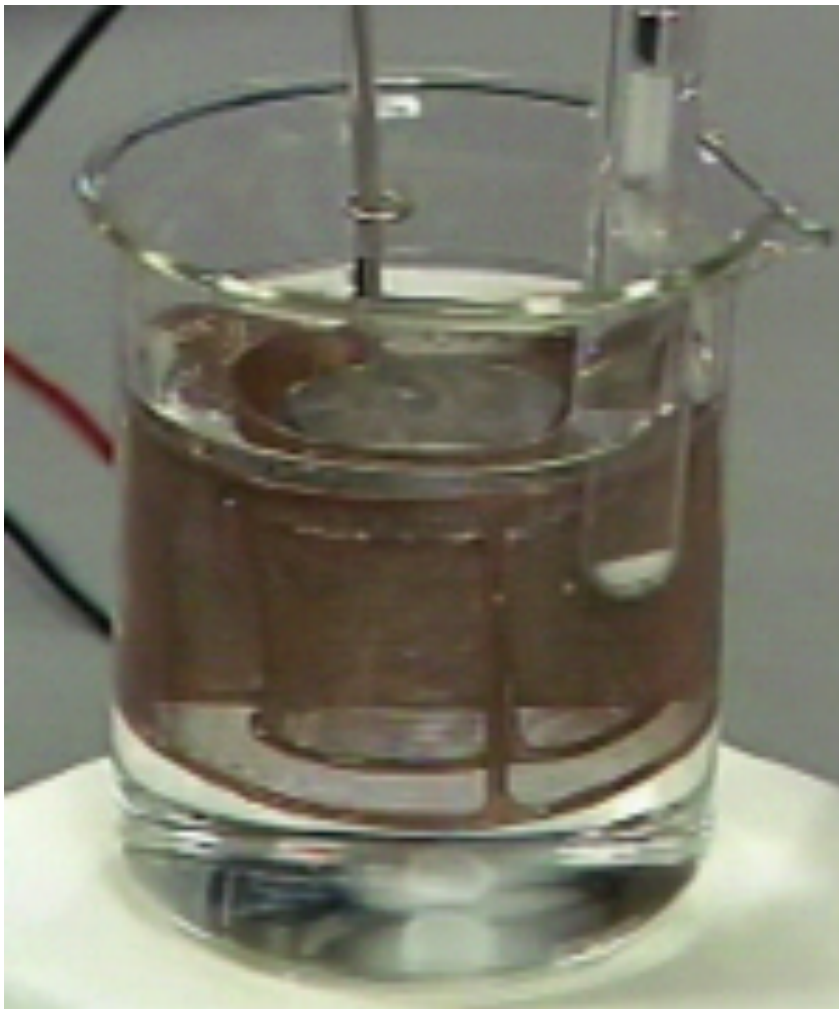


Figure 26.: electrogravimetry measurement set, real picture.

Applications:

- ❑ It is used for the determination of concentration of chemical elements very accurately and precisely in quantitative analysis.**
- ❑ In a mixed solution, the different species are separated by selectively plating on and removing out.**

- ❑ It is used in electrochemical methods for removing interferences.

Co-deposition

- In practice, there may be other electroactive species that interfere by co-deposition with the desired analyte.
- Even the solvent (water) is electroactive, since it decomposes to $\text{H}_2 + \frac{1}{2} \text{O}_2$ at a sufficiently high voltage.
- Although these gases are liberated from the solution, their presence at the electrode surface interferes with deposition of solids.
- Because of these complications, controlling of the electrode potential is an important feature of a successful electrogravimetric analysis.

Examples on electrogravimetry

- ❖ Cu: is deposited from acidic solution using a Pt cathode
- ❖ Ni : is deposited from a basic solution
- ❖ Zn: is deposited from acidic citrate solution
- ❖ Some metals can be deposited as metal complexes e.g., Ag, Cd, Au
- ❖ Some metals are deposited as oxides on the anode e.g.,

Pb^{2+} as PbO_2 and Mn^{2+} as MnO_2

References:

1. **Joseph Wang, “Analytical Electrochemistry”, Third Edition, SBN:9780471678793, Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada, 2006.**
2. **V. S. BAGOTSKY “Fundamentals of Electrochemistry”, Second Edition, Published by John Wiley & Sons, Inc., Hoboken, New Jersey Published simultaneously in Canada, 2006.**