Organic Electronics and Analytical Techniques

Organic Electronics: Introduction, Materials for organic electronics-Liquid Crystals-classification, properties and applications. Organic Semiconductors-classification, properties, mechanism of conduction and applications. Organic Semiconductor Material; Organic Light Emitting Diode (OLED)

Sensors: Introduction, working principle and applications of electrochemical sensors.

Analytical Techniques: Introduction, Electrochemical methods of analysis – Conductometry, Potentiometry. Spectrochemical method - Colorimetry.

Organic Electronics

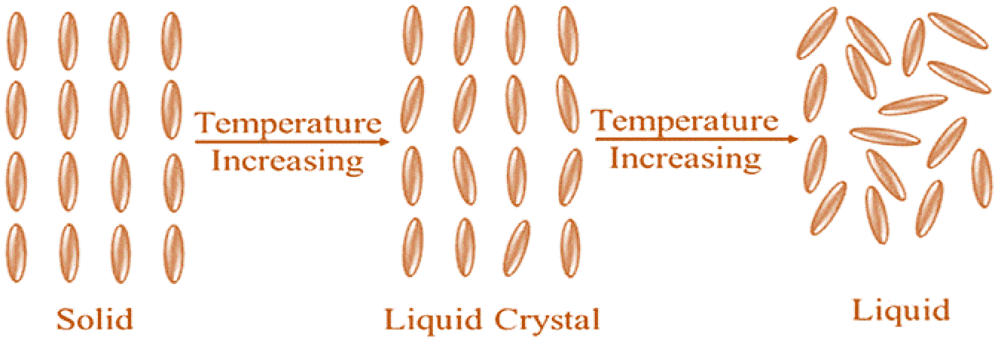
Introduction:

Organic electronics is a field of materials science concerning the design, synthesis, characterization, and application of organic molecules or polymers that show desirable electronic properties such as conductivity. Unlike conventional inorganic conductors and semiconductors, organic electronic materials are constructed from organic (carbon-based) molecules or polymers using synthetic strategies developed in the context of organic chemistry and polymer chemistry.

Organic electronic materials are lighter, more flexible, and less expensive than conventional silicon-based inorganic materials. Organic electronics are more energy-efficient and resource-friendly in production, use, and disposal. Organic electronic materials have an advantage over other semiconducting materials, in that they can be processed in solution under ambient conditions.

Liquid Crystals:

The liquid crystals are a unique state of matter between solid (crystalline) and liquid (isotropic) phases. Liquid crystal is a material which flows like a liquid and shows some properties of solid. The molecular structure of liquid crystal is in between solid crystal and liquid isotropic.



Liquid Crystal Display (LCD) is an flat display screen used in electronic devices such as laptop, computer, TV, cell phones and portable video games. These LCD are very thin displays and it consumes less power than LEDs. In Liquid crystal display (LCD) nematic type of liquid crystal molecular arrangement is used in which molecules are oriented in some degree of alignment.

Liquid Crystals can be classified as follows;

1. Thermotropic liquid crystals

2. Lyotropic liquid crystals

1. Thermotropic liquid crystal

A liquid crystal is said to be thermotropic if molecules orientation is dependent on the temperature. By increasing the temperature, the increase in energy and thereby movement of constituent molecules, will induce phase changes.

Ex:

$$\text{\textit{p}-cholesteryl benzoate (Solid)} \xrightarrow{145°\text{C}} \text{\textit{p}-cholesteryl benzoate (liquid crystal)}$$

Thermotropic liquid crystals can be further classified into the following types:

(a) Nematic liquid crystals

(b) Smectic liquid crystals

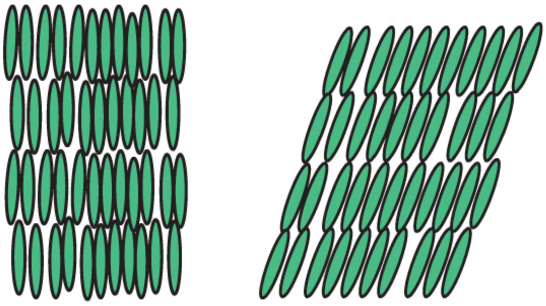
(c) Cholesteric liquid crystals

(d) Discotic liquid crystals

(a) Nematic (or thread-like liquid crystals)

- The molecules move either sideways or up and down. Each molecule can also twist or rotate around its axis giving rise to a twisted nematic.
- Since the molecules are oriented in one direction, they exhibit anisotropy. The molecules are readily aligned in the same direction in the presence of electric and magnetic fields.
- The alignment of molecules is temperature sensitive as the temperature is increased, the degree of orientation of the nematic crystals decreases and they change into isotropic liquids. Ex: p-azoxyphenetole, anisaldazine.

(b) Smectic (or soap-like liquid crystals)



Smectic A

Smectic C

- The molecules are oriented parallel to each other as in the nematic phase but in layers.
- These layers can slide pass each other because the force between the layers is weak.
- They are denoted by letters A, B, C, etc.

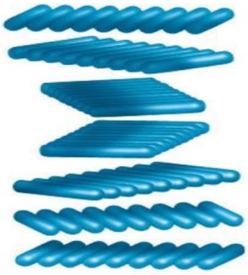
  Some common types of smectic liquid crystals are given below.

  i. **Smectic A**: The molecules are aligned perpendicular to the layer planes.

  ii. **Smectic C**: The arrangement of molecules is similar to smectic A except that the molecules are slightly tilted. They have high viscosity and are not suitable for devices.

(c) Cholesteric liquid crystals

- This type of mesophase is formed by derivatives of cholesterol such as cholesteryl esters. Ex: Cholesteryl benzoate.
- Like the nematic phase, the molecules are also parallel to each other but arranged in layers.
- The molecules in successive layers are slightly twisted or rotated with respect to the layers above and below so as to form a continuous helical or spiral pattern.

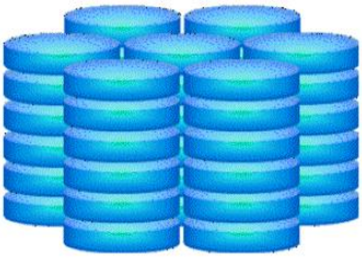


Cholesteric phase

(d) Discotic liquid crystals

- Molecules are arranged in a column arrangement with disc like structure.
- These are referred to as columnar phases.
- Applications are: in photovoltaic devices, organic light emitting diodes (OLED), and molecular wires.

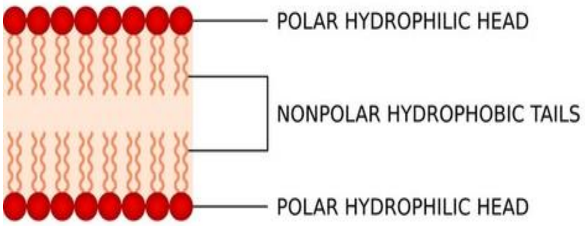
  Ex: anthraquinone



Discotic Phase
(Columnar Phase)

2. Lyotropic liquid crystals

- Lyotropic liquid crystals result when fat-loving and water-loving chemical compounds known as amphiphiles dissolve into a solution that behaves both like a liquid and a solid crystal.



- The hydrophilic end of chemical substance is attracted towards water, whereas the hydrophobic end is water repellent and attracted towards non-polar solvents.
- At low concentrations, these molecules are randomly oriented but as the concentration increases, the molecules start arranging themselves.
- Cell membranes and cell walls are examples of lyotropic liquid crystals. Soaps and detergents form lyotropic crystals when they combine with water.

Properties of liquid crystals:

- They exhibit optical anisotropy which is defined as the difference between refractive index parallel to the director and refractive index perpendicular to the director. These two properties are important for the electro-optic effects in liquid crystals.
- The intermolecular forces are weak and can be perturbed by an applied electric field.
- Because the molecules are polar, they interact with an electric field, which causes them to change their orientation slightly.
- Liquid Crystal can flow like a liquid, due to loss of positional order.
- Liquid crystal is optically birefringent, due to its orientation order.

Applications of liquid crystals:

- Liquid crystals have a wide range of applications in various fields, including electronics, optics, displays, sensors, and medicine.
- Liquid Crystal Displays (LCDs): The liquid crystal layer in LCDs allows for the display of images and text through the use of electrical currents that control the orientation of the crystals.
- Sensors: Liquid crystal sensors are used in various applications such as temperature sensing, humidity sensing, and chemical sensing.
- Optical Devices: Liquid crystals are used in various optical devices such as variable optical attenuators, phase shifters, and tuneable filters. These devices are used in optical communication systems, spectroscopy, and imaging.
- Medicine: Liquid crystals have been used in drug delivery systems, where the drug is encapsulated in the liquid crystal matrix and delivered to specific target cells.

Organic Semiconductors

Introduction:

Inorganic semiconductors are either elementary, binary, or ternary compounds which are held together by covalent bonds. The most dominant material by a wide margin is silicon, a covalently bound group-IV semiconductor. Besides these inorganic semiconductors, organic semiconductors have been investigated for about a century. These materials have entirely different properties to their inorganic counterparts: they are formed of organic molecules which are bound by the van der Waals interaction. Therefore, organic semiconductors are characterized by a typically much lower electron or hole mobility than inorganic semiconductors.

The first actual application of organic semiconductors was for photoconductive coatings on the drums of copier machines and laser printers. However, in the last few years other applications have increased the interest in organic semiconductors once more: the demonstration of efficient organic light-emitting diodes (OLEDs) and organic solar cells (OSCs), both shown that organic semiconductors are very useful for these optoelectronic devices.

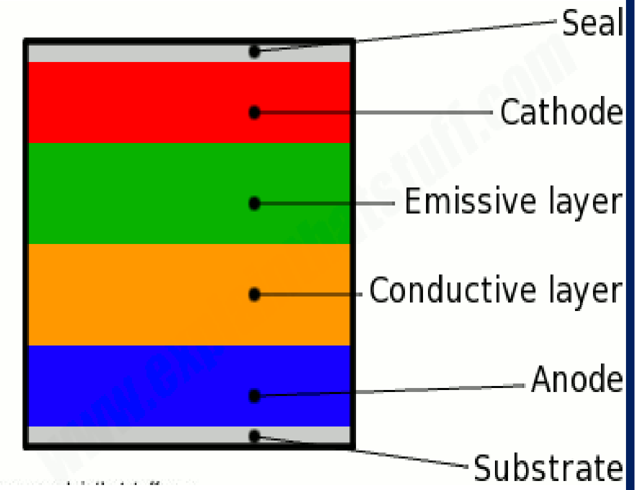
Organic Light Emitting Diodes (OLED's):

An OLED is simply an LED where the light is produced ("emitted") by organic molecules. OLEDs are thin film devices consisting of a stack of organic layers sandwiched between two electrodes. OLEDs operate by converting electrical current into light via an organic emitter". The basic OLED cell structure consists of a stack of thin organic layers sandwiched between a conducting anode and a conducting cathode.

Principle:

OLEDs work in a similar way to conventional diodes and LEDs, but instead of using layers of n-type and p-type semiconductors, they use organic molecules to produce their electrons and holes. A simple OLED is made up of six different layers. On the top and bottom there are layers of protective glass or plastic. The top layer is called the seal and the bottom layer the substrate. In between those layers, there's a negative terminal (cathode) and a positive terminal (anode). Finally, in between the anode and cathode are two layers made from organic molecules called the emissive layer (where the light is produced, which is next to the cathode) and the conductive layer (next to the anode).

Working:



When the electricity supplied, the cathode receives electrons from the power source and the anode loses them. This makes the emissive layer negatively charged (similar to the n-type layer in a junction diode), while the conductive layer is becoming positively charged (similar to p-type material). Positive holes are much more mobile than negative electrons so they jump across the boundary from the conductive layer to the emissive layer. When a hole (a lack of electron) meets an electron, the two things cancel out and release a brief burst of energy in the form of a particle of light- a photon, in other words. This process is called recombination, and because it's happening many times a second the OLED produces continuous light for as long as the current keeps flowing.

Properties of OLED:

- Thinness and flexibility: OLEDs are very thin and flexible, which makes them suitable for use in curved or flexible displays.
- High contrast: OLEDs have a high contrast ratio, which means that they can produce deep blacks and bright ewhites, resulting in images with vivid and rich colours.
- Fast response time: OLEDs have a fast response time, which means that they can switch on and off quickly, resulting in smooth and seamless motion in video content.
- Wide viewing angle: OLEDs have a wide viewing angle, which means that the image quality is maintained even when viewed from different angles.
- Energy efficiency: OLEDs are energy efficient, as they do not require a backlight like traditional LCD displays, resulting in lower power consumption.
- Self-emissive: OLEDs are self-emissive, which means that they do not require a separate light source, resulting in a thinner display.

Applications of OLED:

- Organic Light Emitting Diodes (OLEDs) have a wide range of applications due to their unique properties, including high contrast, energy efficiency, thinness, and flexibility. Like,
- Televisions and displays: OLED displays are used in televisions, monitors, smartphones, and other electronic devices.
- Lighting: OLEDs can also be used as a source of lighting in various applications, including automotive lighting, street lighting, and architectural lighting.
- Wearable devices: The thin and flexible nature of OLEDs makes them suitable for use in wearable devices, such as smartwatches and fitness trackers.
- Automotive: OLEDs can be used in automotive applications, such as dashboard displays, interior lighting, and taillights.
- Medical: OLEDs can be used in medical applications, such as in surgical lighting and medical imaging. They offer bright and highly accurate lighting options that can help improve medical procedures and diagnosis.

Sensors

Sensor is an object that detects signals from its surrounding environment and converts it to meaningful or quantifiable information. Eyes, ears, and nose are all different types of sensors that help you navigate your surroundings on a day-to-day basis by detecting and processing light, sound, and smell/taste.

Electrochemical Sensors:

Electrochemical reactions take place at electrode-electrolyte interfaces and provide a switch for electricity to flow between two phases of different conductivity, i.e. the electrode (electrons or holes are the charge carriers) and solid or liquid electrolyte (ions are the main charge carriers).

Working:

Electrochemical sensors are made up of three essential components: a receptor that binds the sample, the sample or analyte, and a transducer to convert the reaction into a measurable electrical signal. In the case of electrochemical sensors, the electrode acts as the transducer. An electrode surface is used as the site of the reaction. The electrode will either oxidize or reduce the analyte of interest. The current that is produced from the reaction is monitored and used to calculate important data such as concentrations from the sample

The fundamental concept in the detection of analytes by electrochemical sensors involves the measurement of electric current generated by chemical reactions in the electrochemical system.

- Electrochemical sensor's working mechanism involves the interaction of the target analyte material with the electrode surface and bringing the desired change as a consequence to a redox reaction, which generates an electrical signal that can be transformed to explore the nature of the analyte species.
- The reactions which occur at the interface of the surface of an electrode between the recognition element, and the target/binding analyte generate an electrical double layer and thus this potential is measured after transforming these chemical reactions into this measurable electrochemical signal by a recognition element, and a transducer of the sensor.

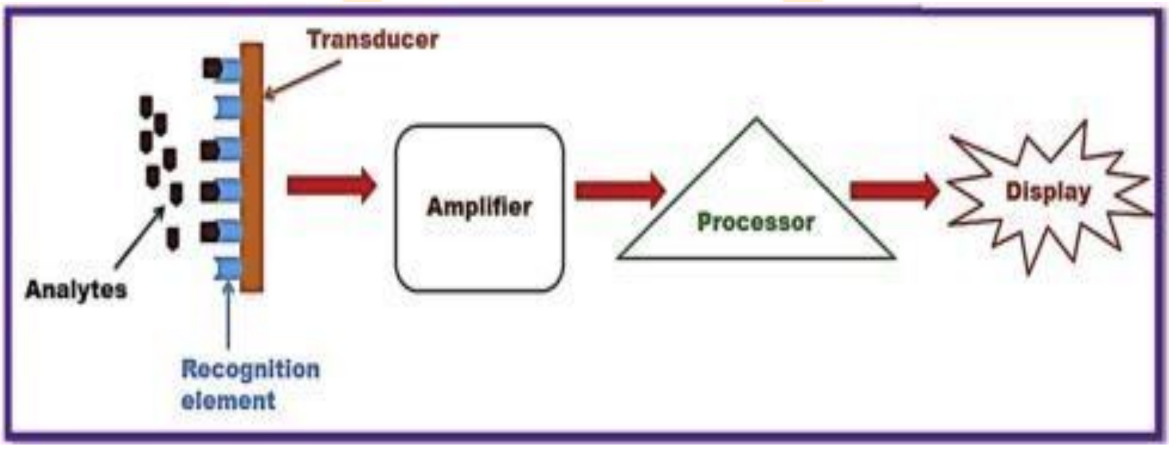


Figure 2. Electrochemical Sensor

Application Electrochemical sensors:

- Detection of important molecules or biomarkers that are used for the diagnosis of diseases and disorders.
- They are used for the monitoring toxic levels of different substances in food quality and environmental control.
- The biosensor application areas of these sensors extend to medical and biomedical applications, process control, bioreactors, quality control, agriculture, bacterial and viral diagnosis, industrial wastewater control.

Analytical Techniques

Analytical techniques are the techniques involved in the study of separation, identification and quantification of chemical components of materials. Qualitative analysis and quantitative analysis are the analytical techniques used to determine the identity of chemical species and amount or concentration of species present in the sample respectively.

Instrumental methods use simple or advanced instrument to measure physical quantities of analyte by relating concentration with light absorption, fluorescence, conductivity or potential. Some of the important instrumental methods of analysis are discussed below.

1. Conductometric Sensor

Principle:

According to Ohm's law, current (i) flowing in a conductor is directly proportional to emf (E) and inversely proportional to resistance (R).

Therefore, $i = \frac{E}{R}$

The reciprocal of resistance is conductance. It is expressed in ohm^{-1}, mho or Siemen. The resistance of a homogeneous material of uniform cross section with an area of 'a'sq.cm and length 'l' cm is given by,

$$R = \frac{\rho \times l}{a}$$, ρ is specific resistance

The reciprocal of specific resistance is specific conductance.

Specific conductance:

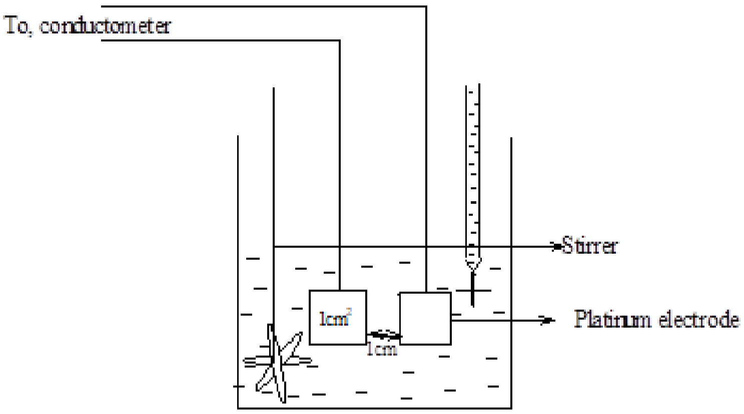
Specific conductance is the conductance of a solution present between 2 parallel electrodes of area $1cm^2$ which are kept 1cm apart.

$$K = \frac{1}{R} \times \frac{l}{a} \qquad \left[\frac{l}{a} = \text{cell constant}\right]$$

The specific conductance of an electrolytic solution at any temperature depends on ions present and hence varies with ionic concentration. On dilution, specific conductance decreases as no of ions per ml also decrease.

Instrumentation:

It consists of two platinum electrodes of unit area of cross-section placed unit distance apart. The electrodes are dipped in electrolyte solution taken in a beaker. It is connected to a conductance measuring device. The titrant is added from the burette and the solution is stirred. The conductance is measured after the addition of the titrant at intervals of 0.5ml.



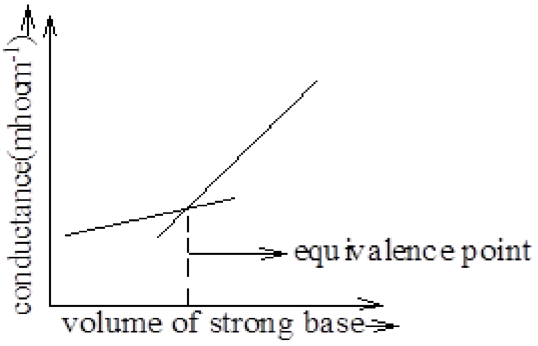
Application of conductometry in the estimation of a weak acid:

Specific conductance is the conductance of a solution present between 2 parallel electrodes of area 1cm^2 which are kept 1cm apart.

$$K = \frac{1}{R} \times \frac{l}{a} \qquad \left[\frac{l}{a} = \text{cell constant}\right]$$

Conductivity cell is dipped in the beaker containing given weak acid and one test tube of water is added such that the conductivity cell is completely immersed. Conductivity cell is connected to a conductivity meter and initial conductance is measured. Now standard NaOH solution is added from a burette in increments of 0.5 ml to the beaker containing acid and after each addition the solution is mixed thoroughly and the conductance is noted. Continued the titration till the conductance initially decreases then gradually increases and then rises sharply. The conductance of the acid will be initially less since acetic aided acid is a weak electrolyte. When NaOH is added to the acid, the salt formed is highly ionized because of this conductance increases.

After the neutralization point, further addition of NaOH increases the fast moving OH$^-$ ions. Hence the conductance increases sharply. Plotted a graph of conductance on Y – axis versus volume of NaOH on X – axis. The point of intersection of the lines gives the volume of sodium hydroxide needed to neutralize the acid.



Calculations

Volume of NaOH (in ml)	Conductance (Siemens Or ohm $^{-1}$)
0.0	
0.5	
1.0	

Volume of acid taken = 25 ml

Normality of sodium hydroxide solution, N NaOH = 0.5 N

Estimation of Weak acid (Acetic acid)

Vol. of NaOH required to neutralise Acetic acid = V_1 = ml

Normality of CH_3COOH = N_{NaOH} x V_1

25

=----------------N

Therefore weight of weak acid/litre = $N_{CH3COOH}$ x Eq.wt of weak acid

= x

Result: Amount of weak acid in the given solution = --------- g/litre

2. Potentiometric Sensor

Principle: Redox titrations can be carried out potentiometrically using platinum calomel electrode combination in a manner similar to acid-base neutralizations. For the reaction,

Reduced form → Oxidised form + n e-

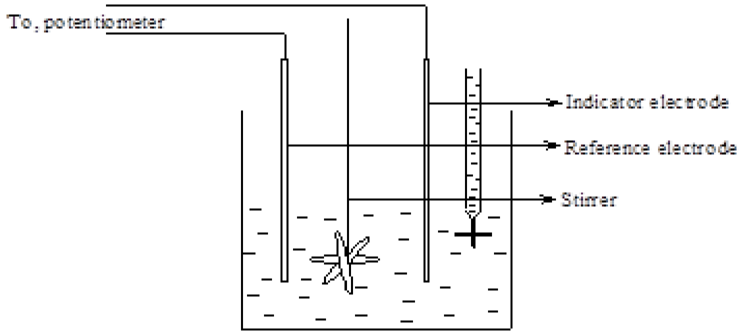
The potential is given by;

$$E = E^{o} + \frac{0.0591}{n} \log \frac{[Oxidized form]}{[Reduced form]}$$

$$E = E^{o} + \frac{0.0591}{n} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

Where E° is the standard potential of the system. The potential of the system is controlled by the ratio of concentration of the oxidized and reduced form of the species present. As the reactions proceed the ratio increases and reaches to a highest value at the end point.

Instrumentation:



Potentiometer consists of a reference electrode (Saturated Calomel Electrode), an indicator electrode, and a potential measuring device. The indicator electrode responds to the changes in concentration of analyte. An emf is measured at each time when titrant is added in the increments of 0.5 ml to a known volume of analyte taken in the beaker. At equivalence point, emf increases rapidly and a few readings are taken beyond the end point.

Application of potentiometry in the estimation of iron

Redox titrations can be carried out potentiometrically using platinum calomel electrode combination in a manner similar to acid-base neutralizations. For the reaction,

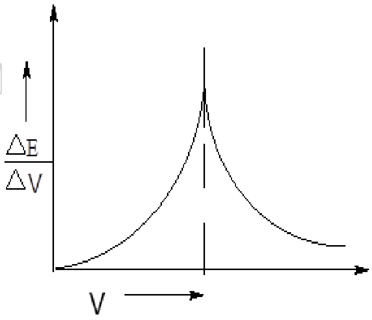
Reduced form → Oxidised form + n e-

The potential is given by;

$$E = E^{o} + \frac{0.0591}{n}\log\frac{[Oxidizedform]}{[Reducedform]}$$

$$E = E^{o} + \frac{0.0591}{n}\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

- Mohr's salt is treated with 2 test of dil H_2SO_4.
- The calomel and platinum electrodes are dipped and connected to a potentiometer and the initial potential is measured.
- The burette is filled with standard potassium dichromate solution, 0.5 ml of which is added to the beaker, stirred well and the potential is measured.
- Potential is continuously measured by adding 0.5 ml increments of dichromate solution at a time.
- Initially the emf increases slowly and at the equivalence point there will be a sudden jump in the emf. At least 5-6 readings are recorded after equivalence point.
- The end point is determined by plotting $\Delta E/\Delta V$ versus volume of potassium dichromate.
- The volume of potassium dichromate corresponding to the peak of the curve indicates the end point.
- From this the concentration and finally the amount of FAS, in turn amount of iron per litre is determined.



Observations and Calculation:

Volume of Mohr's salt pipetted out V_{Fe} = 25 ml

Normality of $K_2Cr_2O_7$, $N_{K2Cr2O7}$ = 0.5 N

Vol. of $K_2Cr_2O_7$ in ml	Emf (mv)	ΔE	ΔV	ΔE/ΔV
0.0				
0.5			0.5	
1.0			0.5	

Volume of $K_2Cr_2O_7$ required for the reaction = ……………. (V_{eq}) ml (from graph)

Normality of Iron solution, N_{Fe} =

$$\frac{N_{K2Cr2O7} \times V_{K2Cr2O7}}{V_{Fe}}$$

=-------------------------N

Amount of iron per litre = N_{Fe} **x** At. wt. of Fe

= **x** 55.85

= ------------------- g

3. Colorimetry

Principle: Colorimetry is concerned with the determination of the concentration of a light absorbing substance by measurement of relative absorption of light with respect to a known concentration of the same substance.

<u>Beer- Lambert’s law:</u>

“When a monochromatic light passes through a transparent light-absorbing medium the intensities of the transmitted light decreases exponentially as the concentration and thickness of the light absorbing substance increases arithmetically”.

$$I_t = I_o e^{-\text{€} ct}$$

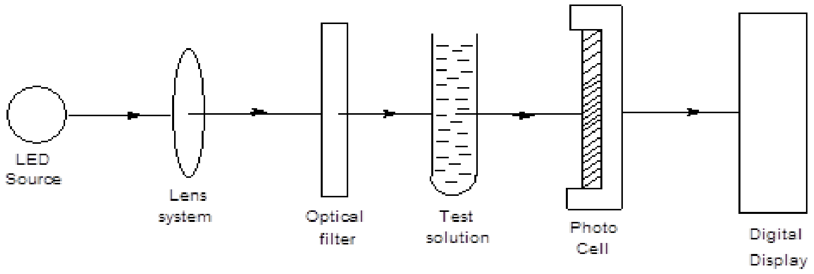
Where I_o is the intensity of incident light, I_t is the intensity of transmitted light, € is molar absorptivity, c is the concentration of the solution & t is the thickness of the medium. .

$$\log \frac{Io}{It} = \text{€}\, ct \quad \text{It is called Beer- Lambert's law.}$$

$$\text{Or} \quad \underline{\mathbf{A = \text{€}\, ct}} \qquad \text{Where } \log \frac{Io}{It} = A$$

If the path length of the cell is kept constant then absorbance A is proportional to the concentration c.

Instrumentation:



The essential parts of a photoelectric colorimeter are

a) Light Source: Tungsten bulb or LED is used as a light source
b) Collimating lens: (Lens is used to make parallel beam) narrow beam of light
c) Filter: It is a device which is used to produce monochromatic light with the desired wavelength range where in the solution gives the maximum absorbance.
d) Sample cell: It is made up of glass
e) Photocell: Converts the emitted light into electrical signal

Application of colorimetric sensor in the estimation of copper

Beer- Lambert's law:

"When a monochromatic light passes through a transparent light-absorbing medium the intensities of the transmitted light decreases exponentially as the concentration and thickness of the light absorbing substance increases arithmetically".

$$A = € ct$$

If the path length of the cell is kept constant then absorbance A is proportional to the concentration c.

- When a copper sulphate containing cupric ions treated with ammonia solution, a soluble complex, with characteristic deep blue colour is formed.

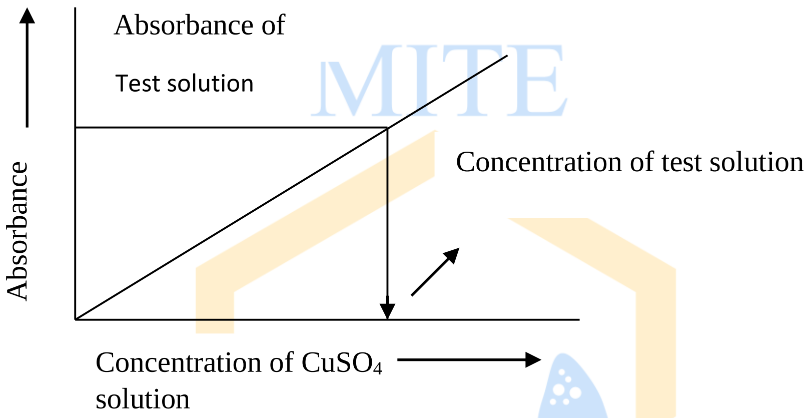
$$Cu^{2+}_{(aq)} + 4\ NH_{3(aq)} \longrightarrow \left[Cu\ (NH_3)_4\right]^{2+}_{(aq)}$$

light blue solution.

Deep blue complex

- The absorbance of this solution is measured at 620nm, since the complex shows maximum absorbance at this wavelength. A series of standard solutions are prepared by using brass solution in different 50ml standard flask.
- Place the given copper sulphate solution (stock solution) in a burette and transfer 2, 4, 6, 8 and 10 ml of the solution into separate labelled 50 cm^3 volumetric flasks

- Add 5 cm^3 of ammonia (1:1) solution to each of them and make up to the mark with distilled water. Stopper the flasks and mix the solutions well.
- To the test solution taken in a 50 cm^3 volumetric flask add 5cm^3 of ammonia solution and make up to the mark and mix well.
- Measured the absorbance of each standard solutions and test solution after adjusting the blank solution reading to zero at 620nm using a colorimeter.
- A calibration curve is drawn by plotting absorbance against volume of $CuSO_4$ solution. Using the calibration curve concentration of copper in the test solution and hence the amount of copper in the solution is calculated



Volume of copper in the test sample (from graph) V = ------------ml

Therefore, weight of copper in the test solution = V x W

= ……x 2.037

= --------mg

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