UNIT – 5 NANOMATERIALS AND INSTRUMENTAL METHODS OF ANALYSIS

Syllabus **08 hours**

Nanomaterials and Instrumental methods of analysis

Nanomaterials: Introduction, size dependent properties (Surface area, Electrical, Optical, Catalytic and Thermal properties). Synthesis of nanomaterials: Top down and bottom up approaches, Synthesis by solgel, hydrothermal and chemical vapour deposition methods. Nanoscale materials: Carbon nanotubes and graphene – properties and applications.

Instrumental methods of analysis: Principle, instrumentation and applications of Colorimetry, Flame Photometry, Potentiometry and Conductometry (mixture of strong acid and a weak acid with a strong base).

Nanomaterials:

Definition

Nanomaterials can be defined as those materials with at least one of the dimensions in the nanometer range, preferably between 1-100 nm. Or one thousand-millionth of a meter (10^{-9}m).

Classification of nanomaterials based on dimensions

Based on reduction in size of materials in different dimensions, nanomaterials are classified as follows.

(i) Zero-dimensional nanomaterials: Here, all dimensions (x, y, z) are at nanoscale, i.e., no dimensions are greater than 100 nm.

Example: Nanospheres and Nanoclusters.

(ii) One-dimensional nanomaterials: Here, two dimensions (x, y) are at nanoscale and the other is outside the nanoscale. This leads to needle shaped nanomaterials.

Example: Nanofibres, nanotubes, nanorods, and nanowires.

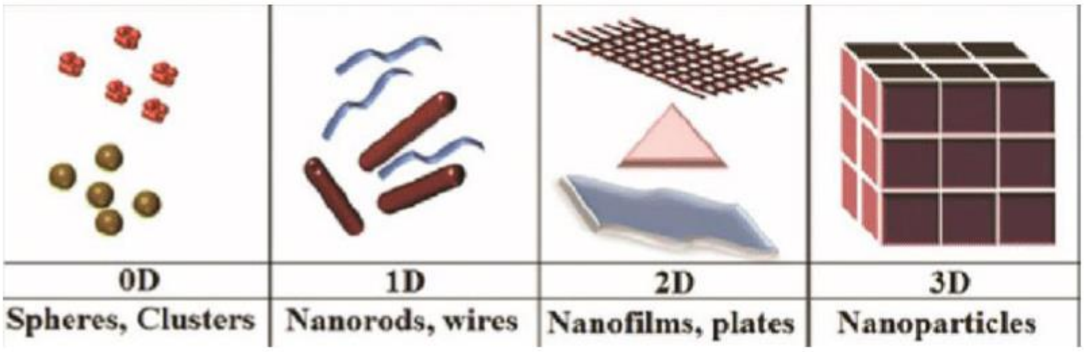


Figure 1: Classification of Nanomaterials

(iii) Two-dimensional nanomaterials: Here, one dimension (x) is at nanoscale and the other two are outside the nanoscale. The 2D nanomaterials exhibit plate like shapes.

Example: nanofilms, nanolayers and nanocoatings with nanometre thickness.

(iv) Three-dimensional materials: These are the nanomaterials that are not confined to the nanoscale in any dimension. These materials have three arbitrary dimensions above 100 nm. The bulk (3D) nanomaterials are composed of a multiple arrangement of nanosize crystals in different orientations.

Example: Bundles of nanowires and nanotubes as well as multinanolayers (polycrystals).

SIZE DEPENDENT PROPERTIES OF NANOMATERIALS

The Size dependant properties make nanomaterials unique and different from other materials. The properties of nanomaterials are very much different from those of bulk materials. Two principal factors cause the properties of nanomaterials to differ significantly from bulk materials are:

(a) Increased relative surface area
(b) Quantum confinement effect

The size dependent properties of nanomaterials are:

a) Surface area
b) Catalytic property
c) Conducting properties

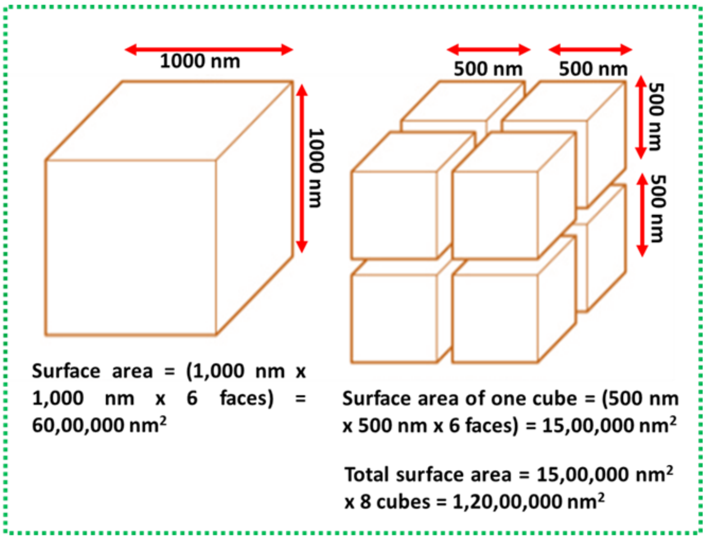
a) Surface area

The physical and chemical properties of the materials depend on its surface area. The bulk material is subdivided into individual nanomaterial, the total volume remaining same but the collective surface area is greatly increased.

Surface area of nanoparticles is very high compared to the bulk material.

Bulk material is divided into individual nanomaterials as a result surface area increases drastically.

For example:



Surface area = (1,000 nm x 1,000 nm x 6 faces) = 60,00,000 nm^2

Surface area of one cube = (500 nm x 500 nm x 6 faces) = 15,00,000 nm^2

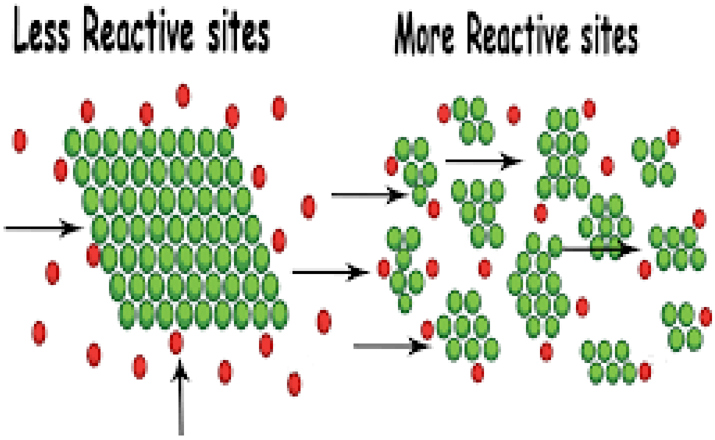
Total surface area = 15,00,000 nm^2 x 8 cubes = 1,20,00,000 nm^2

Surface area of a cube having 1 m^3 is 6 m^2. If this cube is cut into smaller pieces of volume 1 nm^3, there will be 10^{27} small cubes and total surface area will be 6000 km^2. Increase in surface area is because of more number of atoms at the surface of nanomaterials.

b) Catalytic property

– Nanomaterials have significant proportion of atoms existing at the surface. The properties like catalytic activity, gas adsorption and chemical reactivity depends on the surface area of the materials. Therefore, nanomaterials show a specific surface related properties that are not observed in bulk materials.

– Eg: **The catalytic activity of gold**: Bulk gold is catalytically inactive due to less reactive site, whereas the size reduces to nanoscale range, these gold nanoparticles becomes very reactive for selective redox reactions and organic transformations due to more number of reactive site.



In bulk materials active site is very less whereas size reduces to nanoscale reactive site increases drastically due to more surface volume.

Based on the surface area to volume effect, nanoscale materials have:

a) Increased total surface area.

b) Increased number of atoms accessible on the surface.

c) Increased catalytic activity of those large number surface atoms.

d) Different/tunable surface catalytic properties by the change in shape, size and composition.

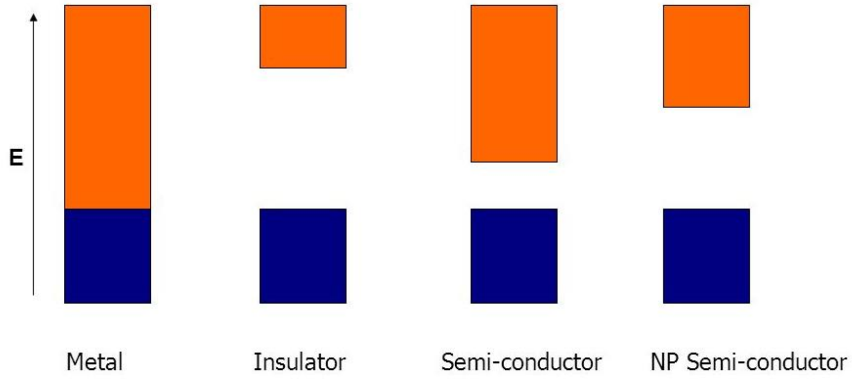
Hence, nanoscale catalysts can increase the rate, selectivity and efficiency of various chemical reactions.

c) Conducting properties

In bulk materials, conduction of electrons is delocalized, that is, electrons can move freely in all directions. When the size is reduced to nanoscale, the quantum effect dominates.

– The electronic bands in bulk material are continuous due to overlapping of orbitals of billions of atoms. The nanoscale materials, very few atoms or molecules are present so the electronic bands become separate leading to widening of the bands and the separation between different electronic stats varies with the size of nanomaterial. Band gap increases with decrease in the size of nanomaterials resulting in low electrical conductivity.

– Due to electron confinement, the energy bands are replaced by discrete energy states which make the conducting materials to behave like either semiconductors or insulators. Therefore nanomaterials are either semiconductors or insulators.



Band gap increases as particle size decreases

Applications of Nanoparticles

a) Silver nanoparticles have good antibacterial properties, and are used in surgical instruments, refrigerators, air-conditioners, water purifiers etc.

b) Gold nanoparticles are used in catalytic synthesis of silicon nano wires, sensors carrying the drugs and in the detection of tumors.

c) ZnO nanoparticles are used in electronics, ultraviolet (UV) light emitters, piezoelectric devices and chemical sensors.

d) $TiO2$ nanoparticles are used as photocatalyst and sunscreen cosmetics (UV blocking pigment).

e) Antimony-Tin-Oxide (ATO), Indium-Tin-Oxide (ITO) nanoparticles are used in car windows, liquid crystal displays and in solar cell preparations.

Synthesis of Nanomaterial's:

Nanomaterials are made by two generalized processes

(i) **Top down:** Start with the big chunk and cut away material to make what you want. It begins with bulk materials that are subsequently reduced into nanomaterials.
Ex: Inert gas condensation, Ion beam technique, Laser ablation, etc

Advantages:

1. Bulk and mass production of nano materials can be prepared by this method

Disadvantages:

1. Method requires expensive apparatus
2. Method causes crystallographic damage and introduce surface defects
3. The nanomaterials will have internal stress
4. The nanomaterials will be generally contaminated
5. The particle sizes may not uniform

(ii) **Bottom -up:** Building what you want by assembling it from small prefabricated units molecules react under chemical or physical circumstances to form nanomaterials. such as atoms and molecules. It begins with atoms and molecules/. These atoms or

Ex: Hydrothermal, Sol-gel method, Co-precipitation and Combustion synthesis

Advantages:

1. Less defects in the Nano particles
2. Good homogenous chemical composition prepared by this method
3. Cost effective and high efficiency.
4. Methods are simple, versatile, and economically viable

Disadvantages:

1. Control the nanoparticle sizes from this method is difficult **6**
2. Agglomeration of particles takes place

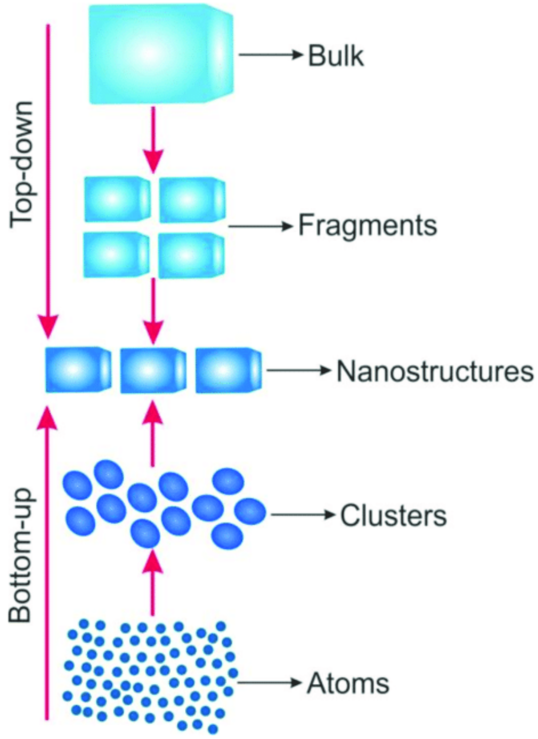


Figure: Schematic of Top down and Bottom up Process.

Synthesis of nanomaterials:

Synthesis of TiO_2 by Sol-Gel Process:

"Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid."

Precursors

TiO_2 nanorods prepared by sol-gel method using anodic aluminium oxide (AAO) as structure directing template.

This process consists of following key steps:

1. Preparation of sol
2. Conversion of sol to gel
3. Aging of a gel
4. Removal of solvent
5. Heat treatment

1. Preparation of sol: First, a sol is prepared by dispersing precursors in a solvent.

The titanium isopropoxide in ethanol and water (first solution) and acetyl acetone $(C_5H_8O_2)_x$ with ethanol [second solution], both solution is mixed with water to obtain a sol.

2. Conversion of sol to gel: Sol is further converted in to a gel by hydrolysis and condensation of precursors.

The AAO membrane is dipped in the sol and an appropriate amount of HCl is added to control hydrolysis and condensation reactions to resulting in a gel.

Hydrolysis and condensation reactions are complex multiple-step processes. They occur sequentially and in parallel forming a gel.

3. Aging of gel: Polycondensation reaction is allowed to continue until the gel transforms into a solid mass, accompanied by contraction of gel network and expulsion of solvent from gel pores.

4. Removal of solvent: The AAO is removed by washing with NaOH solution. The water and other volatile liquids are removed from the gel network. If isolated by thermal evaporation, the resulting gel is termed as xerogel. If the solvent is extracted near super critical conditions, the product is called aerogel.

5. Heat treatment: TiO_2 nanorods are obtained by calcining the as prepared sample at 400 °C for 24 hours.

Advantages of Sol-gel process

– It produces thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.

– It produces thick coating to provide corrosion protection performance.

– It easily shapes materials into complex geometries in a gel state.

– It has low temperature sintering capability, usually 200-600°C.

– It provides a simple, economic and effective method to produce high quality coatings.

Disadvantages of Sol-gel process

– The precursors used are toxic and hazardous to environment.

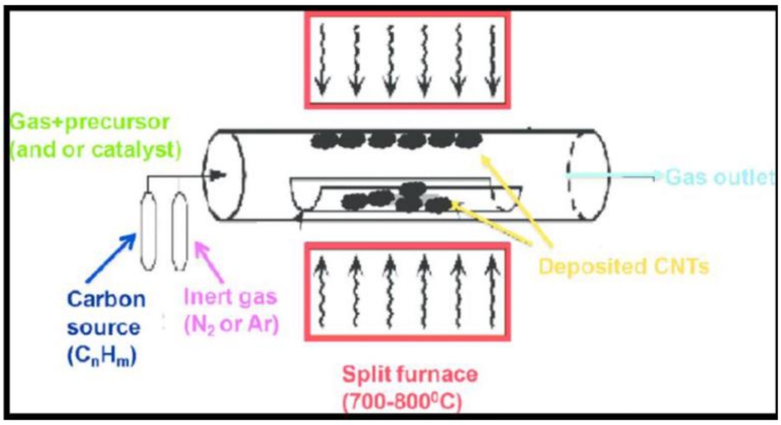
Synthesis of CNTs by Chemical Vapour Deposition (CVD):

Principle:

Chemical vapour deposition (CVD) method involves a transport of reactant gases towards the substrate kept at some temperature where reactants crack into different products which diffuse on the surface and undergo certain chemical reactions at appropriate site nucleate and grow to form desired films, coatings, wires and tubes.

Construction and working:

In CVD process CNTs are synthesized from a gaseous phase by a chemical reaction or decomposition of precursors at high temperature. In this method, precursor (carbon source - C_nH_n) is vaporised and mixed with inert gas like N_2 or Ar and the mixture is fed into a reactor. Reactor is maintained at 700-800^{o}C temperature. As a result, inside the chamber initiate the growth of nanotubes at the sites of the metal catalyst and producing the CNTs, which is deposited over the substrate. The leftovers and by products are passed on to the gas phase, which are easily removable from the reaction chamber (through gas outlet). Reactions are often catalysed by the catalyst (Cobalt, Iron, Nickel and their alloys are the most widely used catalyst) present over the substrate.



Precursor used in CVD process must be very pure and stable at room temperature but with sufficient volatility. It must react with the substrate without any side reaction. Most commonly used precursors are halides carbonyls, organometallics and hydride of metals.

Advantages

a) Versatile- CVD can deposit any element or compound.

b) CVD produces high dense films.

c) Economical in production since many products can be coated at a time.

d) Used for coatings or freestanding structures

e) Fabricates net or near-net complex shapes

f) Self-cleaning—extremely high purity deposits (>99.995% purity)

g) Conforms homogeneously to contours of substrate surface

h) Controllable thickness and morphology

Disadvantages:

Precursors used are volatile, which are usually hazardous and highly toxic. The by-products of these precursors are also very toxic.

Applications

a) CVD can be used for the synthesis of nanotubes and nanowires.

b) CVD can be used for hard coatings and metal films which are used in microelectronics.

c) CVD can also be used for preparing semiconducting devices, dielectrics, energy conversion devices etc.

d) CVD processes are used on a surprisingly wide range of industrial components from aircraft and land gas turbine blades, timing chain pins for the automotive industry, radiant grills for gas cookers and items of chemical plant to resist various attacks by carbon, oxygen and sulphur.

e) Surface modification to prevent or promote adhesion.

f) Photoresist adhesion for semiconductor wafers Silane/substrate adhesion for microarrays (DNA, gene, protein, antibody, tissue).

Hydrothermal Method Synthesis:

1. **Preparation of Precursor Solution**: Dissolve the appropriate precursor salts or compounds in water to form a homogeneous solution. This solution may also contain surfactants, complexing agents, or pH adjusters.
2. **Autoclave Loading**: Transfer the precursor solution into the autoclave. Optionally, seed particles or templates may be added to control nucleation and growth.
3. **Heating and Pressurization**: Seal the autoclave and heat it to the desired temperature. Pressure is generated due to the vaporization of water at elevated temperatures, which increases with temperature.
4. **Reaction Period**: Allow the reaction to proceed for a specified period (usually several hours to days), during which nucleation, growth, and crystallization of the nanomaterials occur.
5. **Cooling and Product Collection**: After the reaction, cool the autoclave slowly to ambient temperature to prevent rapid depressurization and formation of undesired phases. Collect the resulting nanomaterials by filtration, centrifugation, or other separation techniques.

Nanoscale materials:

1. Carbon nanotubes (CNTs):

Properties of Carbon Nanotubes:

1. **Structure**: CNTs are typically cylindrical tubes made of carbon atoms arranged in a hexagonal lattice (like graphene sheets rolled into a tube).
2. **High Strength**: They are extremely strong and stiff, with a tensile strength exceeding that of steel.
3. **Lightweight**: CNTs are very lightweight due to their nanoscale dimensions.
4. **High Electrical Conductivity**: Some types of CNTs exhibit excellent electrical conductivity, comparable to copper.
5. **High Thermal Conductivity**: They also possess high thermal conductivity, making them efficient heat conductors.
6. **Aspect Ratio**: CNTs have a very high aspect ratio (length-to-diameter ratio), which contributes to their mechanical and electrical properties.
7. **Variability**: Depending on their structure (single-walled or multi-walled), CNTs can exhibit different properties suited for various applications.

Applications of Carbon Nanotubes:

1. **Electronics and Optoelectronics**:
    - **Transistors**: CNTs can be used in field-effect transistors (FETs) due to their high electrical conductivity and small size.
    - **Flexible Electronics**: They are suitable for flexible displays, sensors, and electronic textiles due to their flexibility and electrical properties.
    - **Transparent Conductive Films**: Like graphene, CNTs can be used as transparent conductive films in touchscreens and solar cells.
2. **Materials Reinforcement**:
    - **Composites**: CNTs are used to reinforce polymers, ceramics, and metals, enhancing mechanical strength and conductivity.
    - **Structural Materials**: They can be incorporated into structural materials to improve toughness and durability.
3. **Energy Storage and Conversion**:
    - **Batteries**: CNTs improve the performance of lithium-ion batteries by increasing conductivity and stability.
    - **Supercapacitors**: They enable high-energy-density supercapacitors due to their high surface area and conductivity.

4. **Sensors**:
    - **Gas Sensors**: CNT-based sensors can detect gases with high sensitivity and selectivity, useful for environmental monitoring and industrial applications.
    - **Biosensors**: CNTs can be functionalized to detect biomolecules, enhancing biomedical diagnostics.
5. **Medical and Healthcare**:
    - **Drug Delivery**: CNTs can deliver drugs to targeted cells or tissues due to their biocompatibility and ability to penetrate cell membranes.
    - **Imaging**: They are used in imaging techniques for their contrast enhancement properties.
6. **Environmental Applications**:
    - **Water Filtration**: CNT-based filters can remove pollutants and contaminants from water due to their high surface area and nanoscale porosity.
    - **Environmental Remediation**: They are explored for applications in environmental cleanup and remediation technologies.

2 .Graphene:

Properties of Graphene:

1. **Single Layer Structure**: Graphene is a single layer of carbon atoms arranged in a hexagonal lattice, making it a two-dimensional material.
2. **Exceptional Mechanical Strength**: It is incredibly strong—around 200 times stronger than steel—yet lightweight and flexible.
3. **High Electrical Conductivity**: Graphene exhibits excellent electrical conductivity, allowing it to conduct electricity more efficiently than copper.
4. **High Thermal Conductivity**: It has very high thermal conductivity, making it a good conductor of heat.
5. **Transparency**: Graphene is transparent, with around 97.7% of visible light passing through it, making it useful in applications requiring transparency.
6. **High Surface Area**: Its large surface area-to-weight ratio makes it ideal for applications like sensors and energy storage.
7. **Impermeability**: Despite being one atom thick, graphene is impermeable to gases and liquids, which is advantageous in barrier applications.

Applications of Graphene:

1. **Electronics and Optoelectronics**:
    - **Transistors**: Graphene-based transistors could revolutionize electronics due to their high electron mobility.
    - **Flexible Electronics**: Graphene's flexibility and conductivity make it suitable for flexible and wearable electronics.
    - **Touchscreens**: Transparent conductive films made from graphene can replace indium tin oxide (ITO) in touchscreens.

2. **Energy Storage**:
    - **Supercapacitors**: Graphene-based supercapacitors offer high energy density, fast charging times, and long cycle life.
    - **Batteries**: Graphene can improve the performance of lithium-ion batteries by enhancing conductivity and stability.
3. **Composite Materials**:
    - **Structural Composites**: Adding graphene to polymers, metals, and ceramics can enhance strength, conductivity, and durability.
    - **Barrier Materials**: Graphene oxide can create impermeable barriers in coatings and packaging materials.
4. **Sensors**:
    - **Gas Sensors**: Graphene's sensitivity to gas molecules makes it suitable for gas sensors with high selectivity and sensitivity.
    - **Biosensors**: Graphene-based biosensors can detect biomolecules accurately, promising advancements in healthcare diagnostics.
5. **Medical and Environmental Applications**:
    - **Drug Delivery**: Graphene-based materials can deliver drugs more effectively due to their biocompatibility and large surface area.
    - **Water Purification**: Graphene filters can remove contaminants and bacteria from water due to their high permeability and selectivity.

ANALYTICAL TECHNIQUES

Conductometry (Acid Mixture):

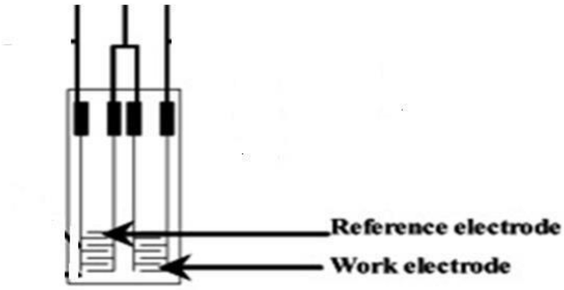
Conductometry is a two electrode devices, measures the electrical conductivity in sample solution between two electrodes.

Principle:

The basic principle of conductometric detection involves a reaction that can change the concentration of ionic species. This reaction leads to changes in electrical conductivity or current flow. In this method, two inert metal electrodes are used. The ions or electrons produces during an electrochemical reaction may change the conductivity or resistivity of the solution.

Working:

The conductivity is result of dissociation of an electrolyte into ions. The migration of the ions is induced by an electrical field. When a potential difference is applied to the electrode, there is an electrical field within the electrolyte, so the positively charged ions move towards cathode and negatively charged ions are move towards anode. Thus, the current in the electrolyte is caused by the ion movement towards the electrodes where the ions are neutralized and isolated as neutral atoms (or molecules). This chemical change is recognized by working electrode and transducers converts this chemical change into electrical signal.



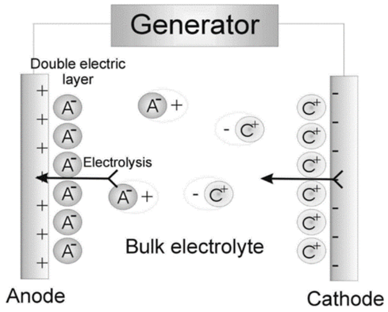
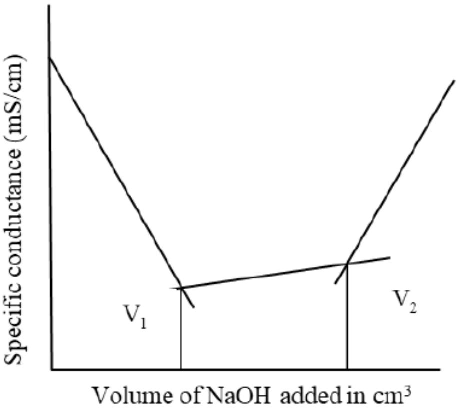


Fig:1.5 Migration of charges in Conductometric Sensors

Procedure: Take 50 cm^3 given acid mixture in a clean beaker. Dip the conductivity cell into it and connect it to the conductivity bridge. Note down the specific conductance of this solution. Add standard sodium hydroxide solution from the burette in increments of 0.5 cm^3 and measure the corresponding specific conductance. Take readings when specific conductance increases significantly (i.e. after the neutralization of weak acid).

Plot a graph of specific conductance versus volume of NaOH. From this graph, find the neutralization points for strong and weak acids and calculate their strength and amount.

Graph:



Calculation:

Volume of NaOH required to neutralize HCl = (V_1) cm^3 (from the graph)
Normally of HCl (N_{HCl}) = [N_{NaOH} x V_1] / V_{mix}
Amount of HCl= N_{HCl} x Equivalent weight of HCl (36.5) = ...g / L = [a]

Volume of NaOH required to neutralize CH_3COOH = (V_2 - V_1) cm^3 (from the graph)
Normality of CH_3COOH, $N_{CH3COOH}$ = [N_{NaOH} x (V_2 - V_1)] /V_{mix}
Amount of CH_3COOH = N x Equivalent weight of CH_3COOH (60) = ... g / L = [b]

Result: Amount of HCl present in given acid mixture is found to be $= \boldsymbol{a/20}$ g

Amount of CH_3COOH in given acid mixture is found to be $= \boldsymbol{b/20}$ g

Applications:

1. Conductivity sensors are used to measure conductivity in aqueous solutions to determine the purity or impurity of a liquid.
2. Conductometric sensors have been fabricated by applying imprinted polymers as receptors for monitoring engine oil quality.
3. Conductometry is used to analyse ionic species and to monitor a chemical reaction by studying the electrolytic conductivity of the reacting species or the resultant products.
4. The conductometric are used determine analyte concentration and enzyme activity.

COLORIMETRY:

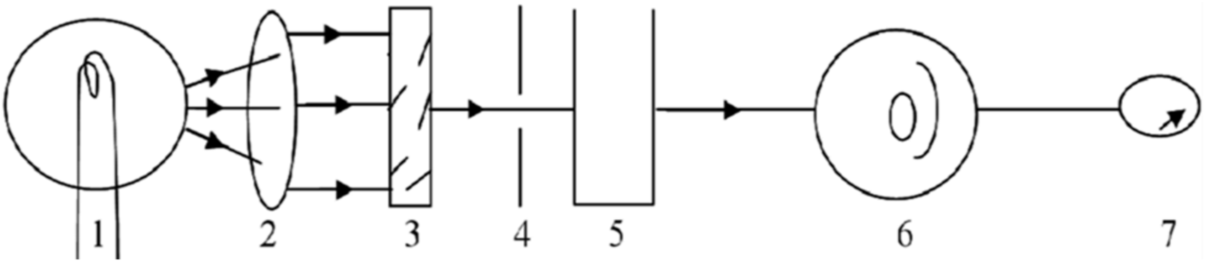
Optical sensors are electronic components designed to detect and convert incident light rays into electrical signals.

Example: Colorimetric Estimation of Copper

Principle: When a sample solution is interacted with a light of suitable wavelength, certain quantity of light is absorbed by the analyte solution and it is observed by a sensor and transducer converts intensity of absorbed light into electrical signal. The change in intensity at certain wavelength within visible (400–800mm) range can be determined using instrument.

Construction and working:

Its basic components include a light source, a wavelength selector, a photodetector and a read-out device. A block diagram of a typical instrumentation system employed colrimetry is shown in Fig.

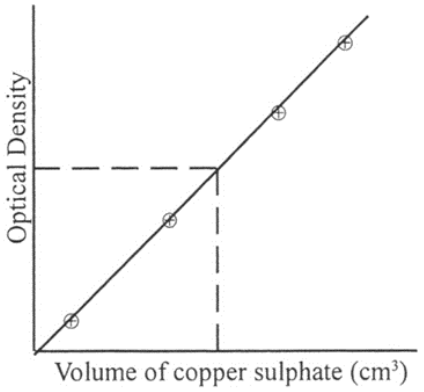


Components of Colorimetric sensors

A monochromatic light is made to pass through analyte solution where certain quantity of light is absorbed and it is a function of concentration of analyte. The change in the intensity of light is detected by photodetector (sensing). The light source generates an intense and stable radiation signal needed to probe an optical property of the molecular recognition element in the sensor. The amount of absorbance is governed by Beer- lamberts law.

Procedure:

Transfer the given copper sulphate solution (stock solution) to a burette and transfer 5, 10, 15, 20 cm^3 of the solution into 50 cm^3 volumetric flasks. Add 2 cm^3 of ammonia solution to each of them and dilute up to the mark with ion exchange water. Stopper the flasks and mix the solutions well. To the test solution given in a 50 cm^3 measuring flask, add 2 cm^3 of ammonia solution then dilute up to the mark with ion exchange water and mix well. Prepare a blank solution by diluting 2 cm^3 of ammonia solution in a 50 cm^3 measuring flask up to the mark with ion exchange water and mix well. After 10 minutes, measure the absorbance of the solutions against blank at 620 nm using a photoelectric colorimeter. Tabulate the readings. Draw a calibration curve by plotting absorbance against volume of copper sulphate solution. Using the calibration curve, find the volume of copper sulphate solution in the test solution and calculate the amount of copper.



Observation and Calculation:

Flask No.	Volume of Copper Sulfate (cm^3)	Concentration of copper sulfate (mg)	Concentration of copper (mg)	Absorbance (optical density)
1.	5	5×8 =	5×2.034 =	
2.	10	10×8 =	10×2.034 =	
3.	15	15×8 =	15×2.034 =	
4.	20	20×8 =	20× 2.034 =	
5.	0	0	0	0.00
6.	Test solution ( )			

Concentration of copper sulfate in stock solution = ...**8**...g / L

Concentration of copper sulfate in stock solution = ...**8**......mg / cm^3

249.68 mg of $CuSO_4 \cdot 5H_2O$ contains 63.54 mg of Cu

∴ ....**8**.....mg of $CuSO_4 \cdot 5H_2O$ contains....**2.034.......** mg of Cu

Applications:

Colorimetric sensors exhibit many applications due to easy fabrication, quick detection, and high sensitivity and selectivity. They find applications in the following,

1. Colorimetric sensors exhibit promising potential application toward the detection of metallic cations, anions, organic dyes, drugs, pesticides
2. Used to detect toxic pollutants
3. Used to estimate concentration of elements
4. Used in food & beverage quality control
5. Used in mineral oils & fuels industry
6. Used in medical & clinical tests

FLAME PHOTOMETRY:

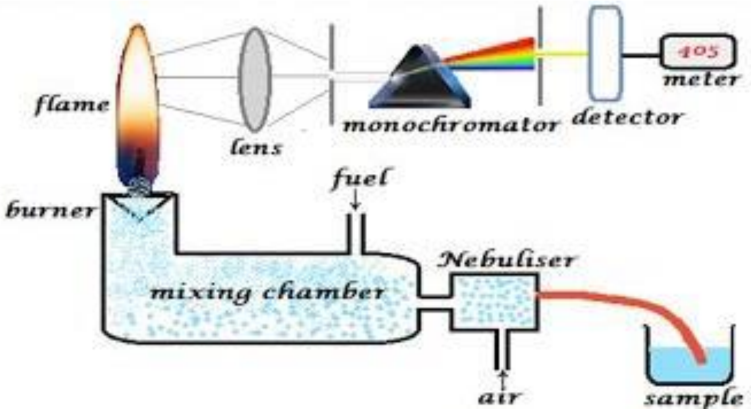
Principle:

Flame Photometry is a simple, rapid method for determining elements, particularly those that can be excited easily like alkali metals. It correlates the emitted radiation with the concentration of elements.

A flame photometer consists of pressure regulator, flow meter for fuel gases, an atomizer, burner, optical system, a filter and a photo sensitive detector and an output display unit/ recorder.

A solution of the sample is nebulised by a flow of gaseous oxidant (air/oxygen), mixed with a gaseous fuel and carried into a flame where atomization occurs. The complex set of processes occurring in the flame can be represented as follows:

Instrumentation:



Flame Photometer

Procedure:

Transfer 2,4,6,8 & 10 cm3of standard sodium salt solution into different 50 cm3volumetric flasks using a burette. Make up all the flasks including unknown with distilled water and shake well.

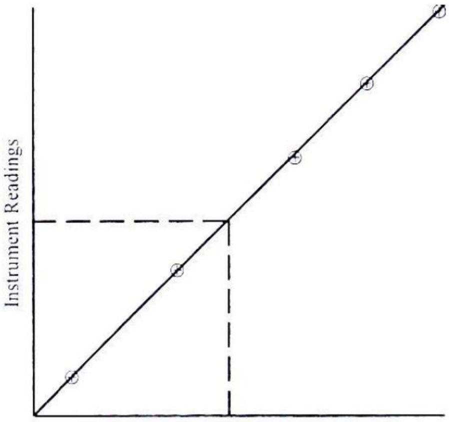
Open the gas supply stop cock & regulate the air pressure so that a blue flame results. Dip the capillary tube in a cell containing distilled water and aspirate the same into the flame. Adjust the instrument reading to zero (control knob). Now aspirate 100 ppm sodium salt solution into the flame and adjust the instrument reading to 100. Ensure steady state conditions by repeating the process.

Repeat the aspirating procedure for all standard sodium solutions and the unknown (given water sample). Distilled water must be sprayed into the flame between trials. Tabulate the readings. Plot a calibration graph with instrument readings on the Y- axis and concentration or volumes of sodium salt solutions on X- axis. The concentration of sodium in the given water sample can be read from the graph.

Calculation:

Flask No.	Volume of Sodium salt solution (cm^3)	Concentration of Sodium (ppm)	Instrument Readings
1.	2		
2.	4		
3.	6		
4.	8		
5.	10		
6.	Test solution ( )		

Model graph:



Volume of sodium salt solution (cm^3)

Results:

1.From graph, volume of sodium salt solution in given test solution = ...cm3

2.Amount of sodium in test solution =.................ppm.

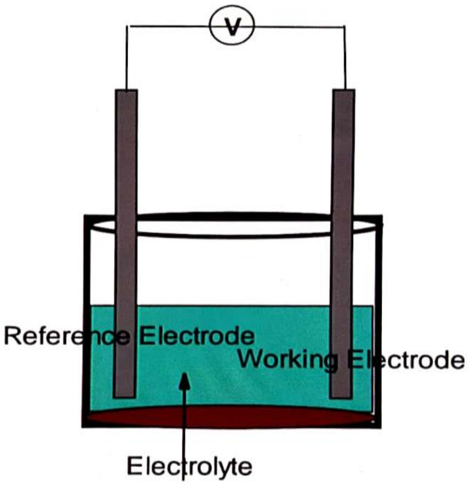
Applications:

Flame photometry is suitable for qualitative and quantitative determination of several cations, especially for metals that are easily excited to higher energy levels at a relatively low flame temperature (Mainly Na, K, Rh, Cs and Ba).

Potentiometry:

Working Principle:

In this sensor change in potential during the chemical interaction between receptor and analyte is measured using combination if an indicator electrode and a reference electrode. Commonly, platinum is used as an inert indicator electrode whereas saturated calomel electrode is used as reference electrode. Indicator electrode is used to measure change in potential due to redox reaction occurring on the surface of the electrode. Using an ion selective electrode as an indicator electrode, concentration of particular ion can be measured with good selectivity. pH glass electrode is an example for this class of electrode. In potentiometric sensor, measurement is taken at zero current.



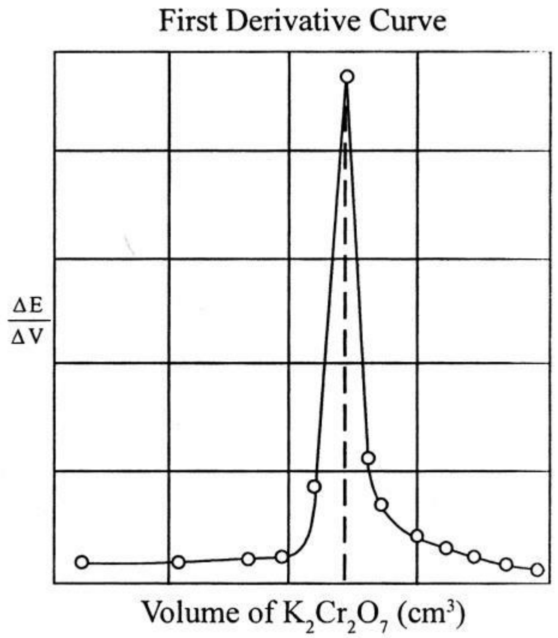
Potentiometric sensor

Procedure:

Pipette out 25 cm3 of the given FAS solution into a clean beaker and add 1 test tube of dil H_2SO_4. Immerse a platinum electrode and a saturated calomel electrode and connect to a pH meter in milli volts (mV) mode. Fill a clean burette with standard $K_2Cr_2O_7$ solution.

Commence the titration by adding large increments (0.5 cm3) of $K_2Cr_2O_7$ solution to FAS solution in the beaker. Stir the solution thoroughly and measure EMF after every addition. At the equivalence point, there is a sudden increase in the EMF. At this stage, add small increments of $K_2Cr_2O_7$ and note EMF values. After equivalence point, there will be a slight increase in EMF on continued addition of $K_2Cr_2O_7$ solution.

A graph of $\Delta E/\Delta V$ (ordinate) against volume of $K_2Cr_2O_7$ (abscissa) is plotted. From the graph volume of $K_2Cr_2O_7$ at equivalence point can be read.



Calculation:

From the graph, volume of $K_2Cr_2O_7$ at equivalence point = (X) cm3.

Normality of $K_2Cr_2O_7$ = a N

$$\text{Normality of FAS} = \frac{\text{Normality of } K_2Cr_2O_7 \times \text{Volume of } K_2Cr_2O_7}{25} = \frac{a \times \mathbf{X}}{25} = \mathbf{b\ N}$$

Weight of FAS / dm^3 = N_{FAS} x Equivalent weight of FAS (392)

= b x 392 = 'c' g

Weight of FAS in 25 cm3 = c/40 g.

Applications of electrochemical sensors:

1. Used in security and defence applications like detection of toxic gases, warfare agents etc.
2. Used in water analysis and environment monitoring
3. Used in diagnostic and health care applications like in situ monitoring of glucose serum uric acid, Ca^{2+}, Fe^{2+}, Acetylcholine etc.
4. Used in the detection of hydrocarbon pollutants
5. Used for pH measurements
6. Used to detect pesticides