

Module-5

INSTRUMENTAL METHODS AND NANOMATERIALS

INSTRUMENTAL METHODS OF ANALYSIS

Chemical analysis involves

- Identification of elements of a compound in a mixture called qualitative analysis.
- Determination of amount of element or substance present in the sample called quantitative analysis.

Quantitative analysis involves

- Titrimetry, where the substance to be analyzed is made to react with a standard solution of appropriate reagent.
- Gravimetry, where the substance to be analyzed is precipitated by the addition of reagent and precipitate is collected and weighed.
- Instrumental analysis, where the substance to be analyzed is converted into an electrical signal, that is measured using a suitable device.

Advantages of Instrumental methods of analysis:

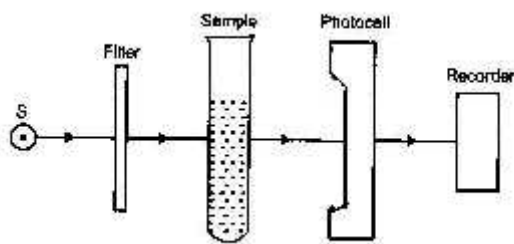
- It is faster than chemical methods.
- Requires only small quantity of sample.
- Easy when a large number of samples have to be analyzed.
- Accurate results are obtained.

COLORIMETRY

Photometric Colorimeter :

Instrumentation:

The essential parts of photoelectric colorimeter are a light source, a light filter, a container for the solution, a photocell to receive the transmitted light and some means for measuring the response of the photocell. The simple block diagram is shown below.



The function of the filter is to isolate any desired spectral region by filtering off the undesired radiations. Optical filters consist of either thin films of gelatin containing different dyes or of colored glass.

Principle; Electromagnetic radiation is a form of energy, travels in space at high velocity. Based on the wavelengths, electromagnetic radiations are divided into γ -rays, X-rays, UV rays, visible rays, infra red rays, micro waves and radio waves. These radiations when passed through matter, get absorbed and bring about various changes.

Therefore, when radiations like UV, IR and visible are passed through the sample, a part of it is absorbed, resulting in decrease in intensity of radiation. The wavelength of the radiation absorbed is a characteristic of that substance and quantity of radiation absorbed is a function of its concentration. Hence this principle is used to identify and quantify a substance. The Beer-Lambert law relates the light absorbed with the chemical analysis.

LAMBERT'S LAW:

It relates incident, absorbed and transmitted light. "When a monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to intensity of light."

BEER'S LAW:

It states that "the intensity of the transmitted light decreases exponentially as the concentration of the medium increases arithmetically."

Then, $I_t = I_0 e^{-kc}$, Where, c = molar concentration of sample solution.

Combining equations for Beer's law and Lambert's law, equation for Beer-Lambert's law is obtained and is written as,

$$I_t = I_0 e^{-kct} \quad \text{Or,} \quad I_t = I_0 10^{-ct}$$

Where k is molar absorption coefficient, a constant for a given substance at a given wavelength.

The unit is $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$. The above equation can be written as

$$\log \left(\frac{I_0}{I_t} \right) = \Sigma ct. \text{ is called Beer - Lambert's law.}$$

The term $\frac{I_0}{I_t}$ is called Optical Density or Absorbance A .

$$\frac{I_t}{I_0} = \text{Transmittance, } T$$

Therefore relation between A , T and E is given by,

$$A = c t$$

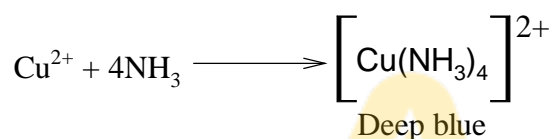
$$= \log \left(\frac{I_0}{I_t} \right) = \log \left(\frac{1}{T} \right) = -\log T$$

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

Application of colorimetry:

1) Estimation of unknown volume:

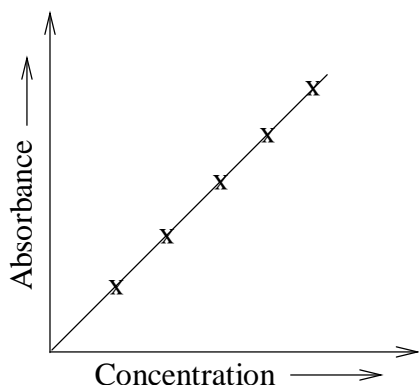
When Cu^{2+} ions are treated with ammonia solution, a deep blue colored cuprammonium complex is obtained. The absorbance is measured at 620nm (max) since the complex shows maximum absorbance at this wavelength. When absorbance of known solutions is plotted against concentration, a straight line is obtained. From this, unknown solution concentration can be obtained by measuring the absorbance of that solution.



PROCEDURE:

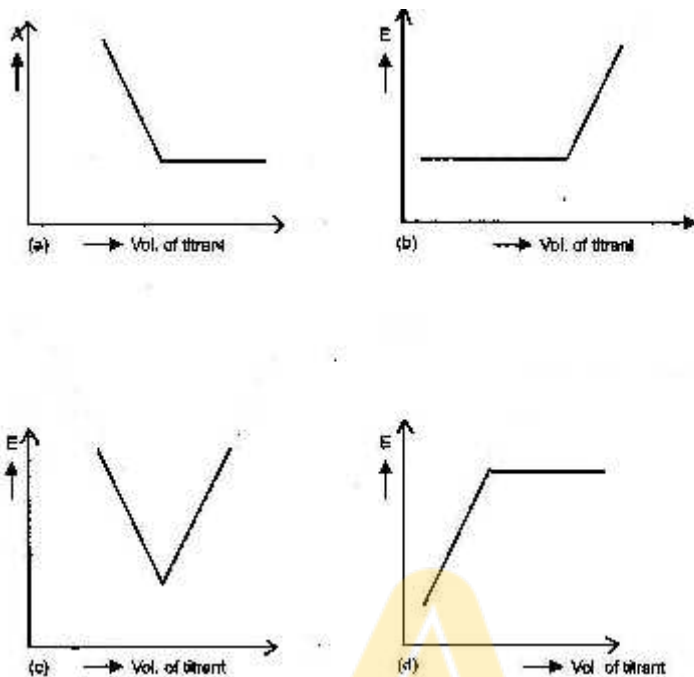
5, 10, 15, 20 and 25ml of standard Copper sulphate solution is taken in separate standard flasks. 5ml of ammonia is added to each of these flasks and made up to the mark using distilled water. The flasks are stoppered and shaken well for uniform concentration. To the given test solution, 5ml of ammonia is added and made up to the mark with distilled water, stoppered and shaken well. A blank solution is also prepared taking 5ml of ammonia, making up to the mark using distilled water and shaken well. The absorbance of solutions against blank is measured at 620nm using colorimeter. A calibration curve is drawn by plotting concentration of Cu (mg/cm^3) against absorbance. From this, concentration of Cu in test solution can be determined.

The method is used to estimate Copper in brass, Mn in steel, glucose in fluids etc.



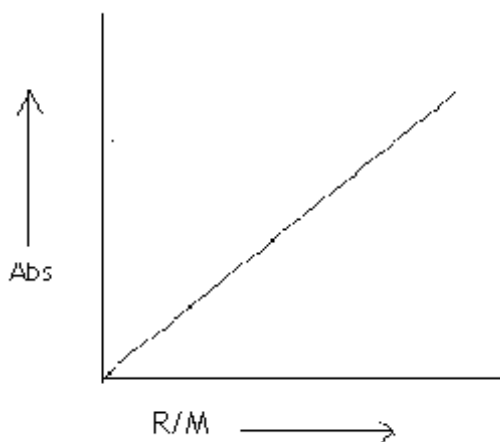
- 2) **Photometric titrations:** In locating the equivalence point in a titration where one of the species (either the reactant, titrant or the product) has an absorbance proportional to its concentration. In such a case the plot of absorbance versus volume of the titrant added will consist of two straight lines intersecting at the equivalence point.

Some typical plots are given below



- (a) Reactant absorbs, titrant does not
- (b) Titrant absorbs, reactant does not
- (c) Both absorb
- (d) Reactant and titrant do not absorb, but product absorbs

3) **Determination of composition of a colored complex:** Here absorbance is measured for a series of solutions which contain varying amounts of one of the constituents either the metal (M) or the reagent (R) with a constant amount of the other. A plot of absorbance versus mole ratio (R/M) gives a straight line with the absorbance increasing as the mole ratio till all the metal ions are completely complexed. Addition of excess of reagent does not produce further increase in absorbance.



Advantages of colorimetry:

- 1) Gives more accurate results at low concentration than corresponding titrimetric and gravimetric procedure.
- 2) Method is simple and rapid.

POTENTIOMETRIC TITRATION:

The concentration of ionic solution can be determined by measuring emf by the method of potentiometric titration.

PRINCIPLE:

The potential of an electrode is given by Nernst equation,

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

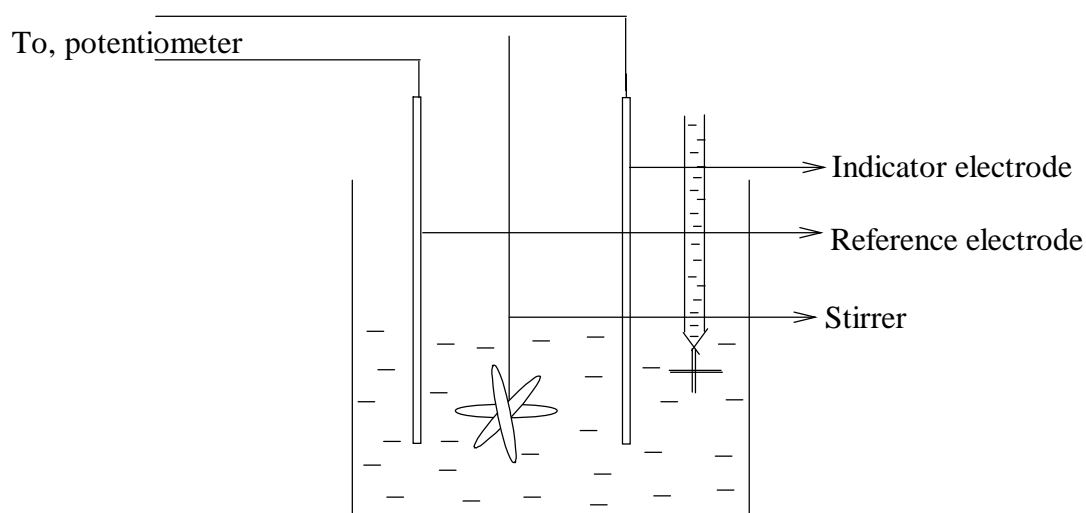
i.e. the potential of an electrode depends on concentration of ion to which it is reversible. This method can be used in the determination of end points of acid-base titrations, red-ox titrations etc.

When a known volume of analyte is titrated with a standard solution, neutralization or red-ox reaction takes place. During the course of titration, concentration of product will be continuously altered. If a metal electrode, reversible with respect to corresponding ions is placed in the solution, the potential will vary throughout the titration, which can be determined using a suitable device. Initially, the change in potential is very small. At the equivalence point, when the amount of titrant added is equivalent to the amount of analyte present, there will be a sharp rise in potential. Beyond the equivalence point, there will be no significant change in potential. By plotting a graph of change in potential against the volume of titrant added, the equivalence point can be determined.

INSTRUMENTATION:

Potentiometer consists of a reference electrode, an indicator electrode, and a potential measuring device. The indicator electrode responds to the changes in concentration of analyte. A reference electrode like saturated calomel electrode is also used. A known volume of analyte is taken in the beaker and its potential is determined. The titrant is added in increments of 1ml and emf is measured each time.

At equivalence point, emf increases rapidly. At this point, titrant is added in small increments of 0.1ml. a few readings are taken beyond the end point. Thus the changes in potential at different volumes of titrant are recorded.



ADVANTAGES:

- ✓ Potentiometric titrations can be carried out in colored solutions where indicators cannot be used.
- ✓ The prior knowledge of relative strengths of acids and bases to select a proper indicator is necessary in normal titrations, whereas such knowledge is not required in potentiometric titrations.
- ✓ By potentiometry, it is possible to determine the end point in titrations of very weak acids or very weak bases.

Based on the nature of chemical reactions, potentiometric titrations are classified as

- ❖ Neutralization titrations
- ❖ Redox titrations
- ❖ Precipitation titrations

1. Neutralization (Acid – Base) titrations:

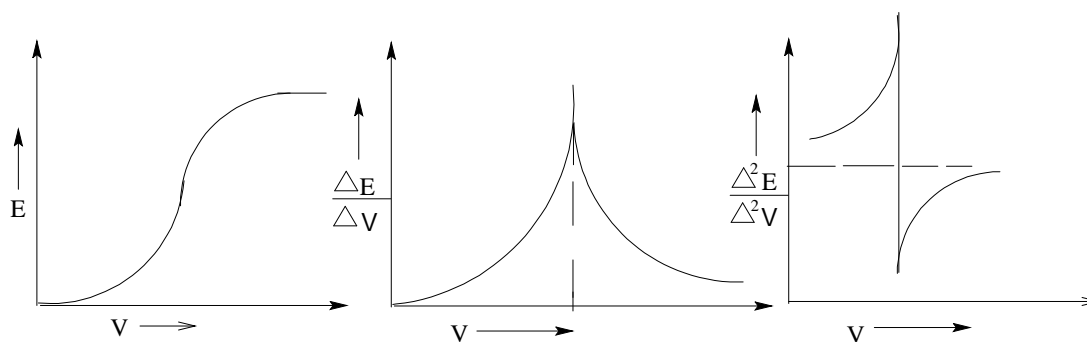
If a solution of HCl is titrated against NaOH, an electrode whose potential depends on H^+ ion concentration (glass electrode) is placed in HCl and coupled with a reference electrode to form a galvanic cell. The emf of the cell is measured potentiometrically, and is given by

$$E_{\text{cell}} = E_{\text{ref}} - 0.0591 \log[H^+]$$

$$= E_{\text{ref}} + 0.0591 \text{ pH}$$

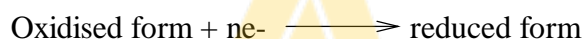
As the titration proceeds, H^+ ion concentration goes on decreasing (pH increases) and hence emf of the cell increases. Initially, emf increases slowly & then rapidly at the neutralization point. After the neutralization point, there is no significant change in emf. A graph of change in emf against volume of titrant is plotted and equivalence point is determined. The end point in acid-base titrations can also be found by direct measurement of pH of solution after each addition of a

base to acid, using pH meter. The equivalence point is found by plotting a graph of emf against volume of a base, also by plotting E/V or E^2/V^2 against volume as follows.



2. Redox titrations:

These are also carried out potentiometrically using an inert metal electrode like platinum. It is immersed in a solution containing both oxidized and reduced forms of same species.



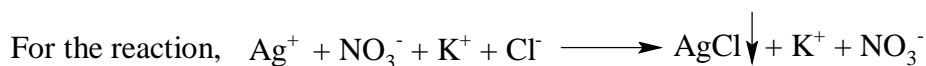
$$E = E^\circ + \frac{0.0591}{n} \log \frac{[\text{oxidised state}]}{[\text{reduced state}]}$$

The potential of the indicator electrode is controlled by ratio of oxidized and reduced forms. During oxidation or reduction, the ratio of concentration and hence the potential near the end point changes rapidly and can be readily detected. Thus titrations involving redox reactions can be followed potentiometrically, since at the equivalence point there will be a sudden change of potential. Platinum electrode is used as indicator electrode and saturated calomel electrode as reference electrode. Generally, oxidizing agent is taken in the burette.

3. Precipitation titrations:

Consider a titration of AgNO_3 Vs standard KCl , where Ag^+ ions are precipitated as AgCl . Using a silver electrode as indicator electrode & calomel as reference electrode, the potential can be measured as,

$$E = E^\circ + 0.0591 \log [\text{Ag}^+]$$



As KCl is added, Ag^+ ions are precipitated as AgCl . i.e., concentration of Ag^+ ions decreases during the process. The potential of Ag^+/Ag goes on decreasing continuously on addition of KCl . At the end point, Ag^+ ion concentration is very small. Hence change in electrode potential is maximum. On continued addition of KCl , the concentration of Ag^+ ion remains almost same. Beyond the end point therefore, it causes a small change in electrode potential.

The potentiometric curves obtained are similar as obtained in acid base titration as described earlier.

CONDUCTOMETRIC TITRATION:

Principle:

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

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

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,

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

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.

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

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.

Equivalent conductance is defined as the conductance of a solution containing one gram equivalent weight of the electrolyte. It is denoted as Λ . Molar conductance is defined as the conductance of a solution containing one mole of an electrolyte. It is denoted as μ .

Measurement of conductivity:

The measurements are made based on the principle of wheatstone bridge.

To measure the conductance of a solution, it is placed in a cell carrying a pair of platinum electrodes which are firmly fixed in position. The platinum electrodes are generally electroplated with platinum black.

The measurements are done by connecting the conductance B till a null point is obtained as detected by the detector. The balancing length AD and DB are measured.

Then, $R/R_{\text{soln}} = AD/DB$

Therefore $R_{\text{soln}} = (DB/AD) \times R$

The observed conductance of the solution $C_{\text{obs}} = 1/R_{\text{soln}}$

The specific conductivity $K = C(1/a)$

For a given conductivity cell (l/a) is called its constant and given in cm^{-1} or m^{-1}

Specific conductance = observed conductance \times cell constant

Cell constant is evaluated by the calibration method.

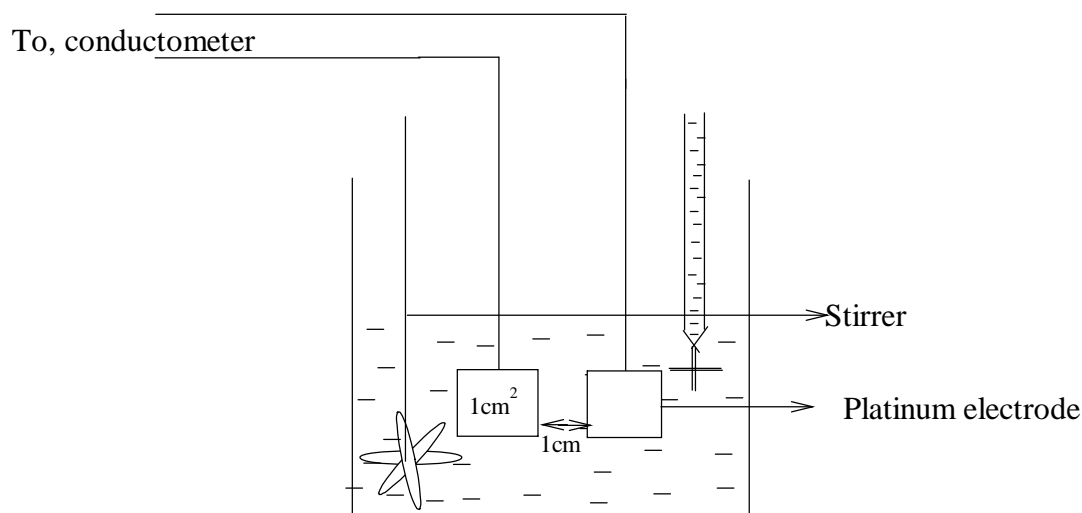


ADVANTAGES:

- ✓ Mixture of acids can be titrated accurately.
- ✓ When visual or potentiometric methods fail due to solubility or hydrolysis, in such cases conductometric methods hold good.
- ✓ Accurate results are obtained in dilute as well as more concentrated solutions.
- ✓ The method can be employed for colored solutions also.
- ✓ Very weak acids which can't be titrated potentiometrically, can be titrated by conductometric method.

INSTRUMENTATION:

Conductometer consists of 2 platinum electrodes and a conductance measuring device. The 2 electrodes have unit area of cross section and are placed unit distance apart. The solution to be estimated is taken in a beaker. The system responds readily to changes in concentration of analyte.

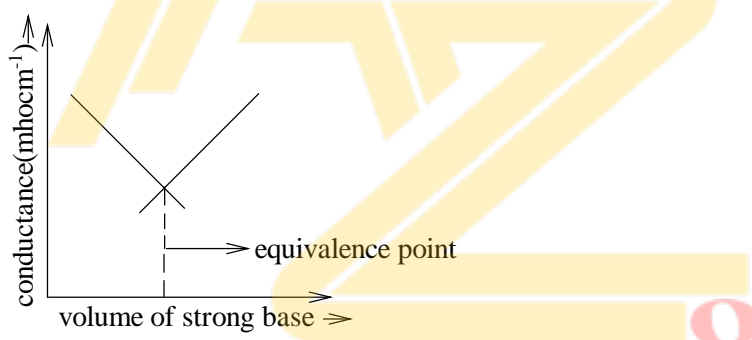


APPLICATIONS:

a) Acid- base titrations:

1. Titration of strong acid with a strong base: eg: HCl Vs. NaOH

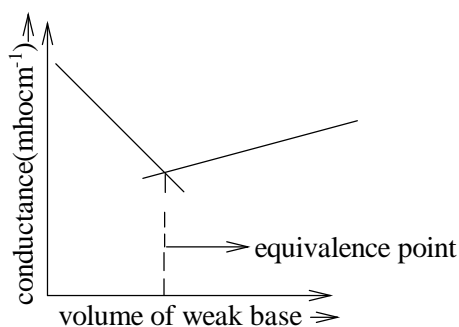
When strong acid is titrated with a strong base, conductance first falls since highly mobile H^+ ions are replaced by Na^+ of base. After the equivalence point, conductance rapidly increases with further addition of base due to increase in concentration of OH^- ions. The graph obtained on plotting conductance versus volume of base is as follows.



Two straight lines are obtained. The point of intersection is the end point.

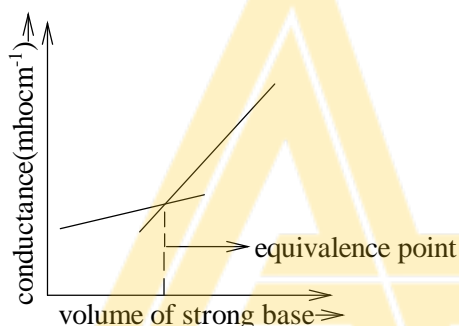
2. Titration of strong acid with a weak base: eg: H_2SO_4 Vs. NH_4OH

Here conductance first falls due to replacement of highly mobile H^+ ions by NH_4^+ of weak base. After the equivalence point, conductance is almost same as the excess of weak base added is not ionized. The plot of conductance versus volume of weak base is as follows. The point of intersection is the neutralization point.



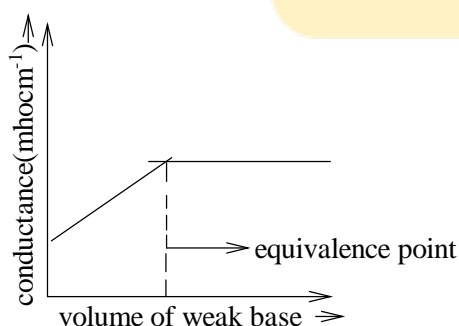
3. Titration of weak acid with a strong base: eg: CH_3COOH Vs. NaOH

The conductance of weak acid is initially low, due to poor dissociation. When a strong base is added, the salt is formed, gets ionized and conductance increases slowly. On complete neutralization, further addition of base increases no of OH^- ions, and conductance increases sharply. The plot of conductance versus volume of strong base is as follows.



4. Titration of weak acid with a weak base: eg: CH_3COOH Vs. NH_4OH

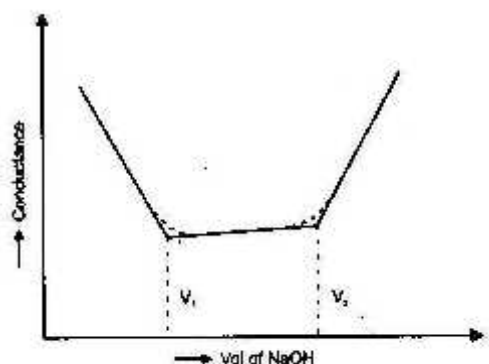
Initially, conductance increases slowly since the salt formed is ionized. After the equivalence point, conductance is almost constant, since NH_4OH added in excess, is not ionized. The plot is as follows.



5) Titration of Mixture of a strong acid and a weak acid with a strong base

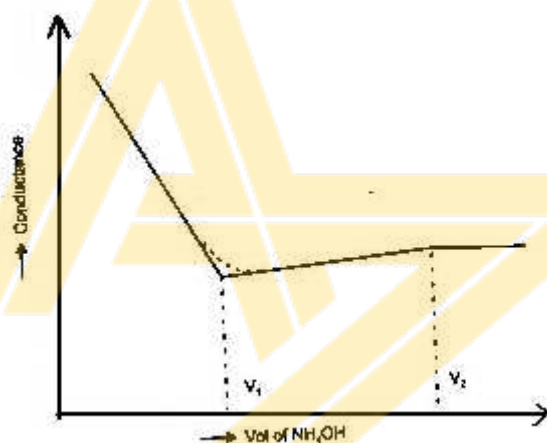
(Eg $\text{HCl} + \text{CH}_3\text{COOH}$)

Upon adding a strong base to a mixture of a strong acid and a weak acid, the conductance falls until the strong acid is neutralized completely, due to the removal of H^+ ions. The weak acid remains undissociated in the presence of strong acid. Once the strong acid is completely neutralized, the weak acid begins to dissociate and gets neutralized. This results in the increase in conductance of the solution as the weak acid is consumed and converted into its salt. When the neutralization of the second acid is complete, there is steep increase in conductance due to the ions furnished by the strong base.



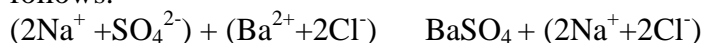
6) Mixture of strong acid and weak acid with a weak base:

The first and second part of the titration curve is same as previous. After both acids are neutralized further addition of weak base hardly increases the conductance as the dissociation of the excess weak base is suppressed by the presence of common ions. The first point of intersection gives the amount of base consumed by strong acid and the difference between first and second is the amount of base consumed by the weak acid.

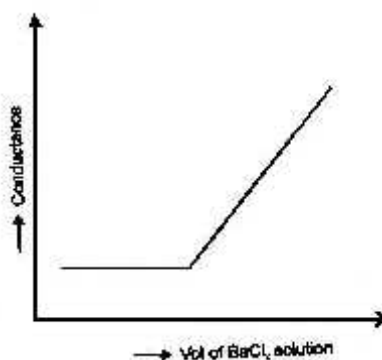


b) Precipitation titrations:

During the titration of sodium sulphate and barium chloride, the reaction taking place is as follows.



The net change taking place is a sulphate ion is substituted with two chloride ions in the solution during titration. Since the conductance of two chloride ions are almost equal to the conductance of sulphate ion, the conductance of the solution remains almost constant till the end point. After the end point addition of excess of BaCl_2 solution furnishes more of ions increasing the conductance of the solution sharply.



Advantages:

- 1) Very weak acids can be titrated conductometrically in aqueous solutions.
- 2) Mixture of acids can be titrated accurately.
- 3) The method is as accurate in dilute solutions as in more concentrated solutions.
- 4) Can be employed with colored solutions.

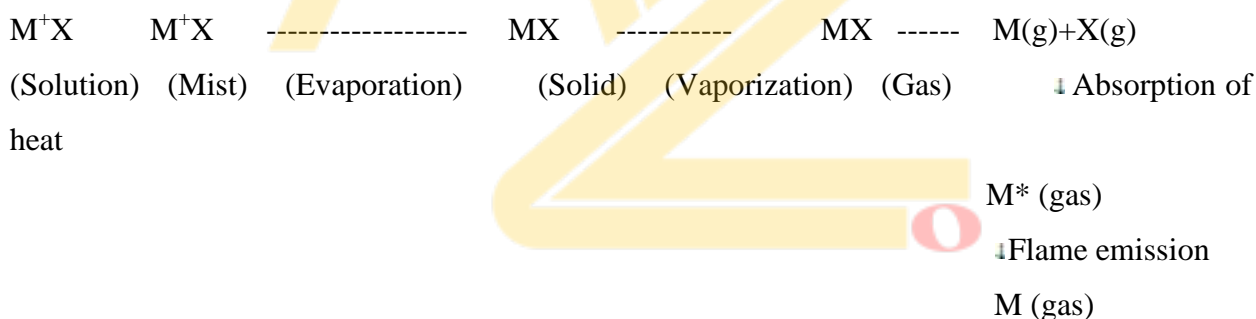
Limitations:

- 1) Can be employed only when there is appreciable change in conductance during titration.
- 2) Redox titrations cannot be carried out.

Flame photometry:

When a solution containing sample element or ion is aspirated into the flame, the solvent gets evaporated leaving behind the salt in the flame. The salt then gets evaporated into vapours of the salt which further undergo dissociation to the constituent atoms. Some of the metal atoms formed in the flame may absorb heat energy from the flame and get electronically excited to their higher energy level. Being unstable at the excited level the atoms fall back to their ground state by emitting the energy difference between the excited and ground state in the form of light radiation. The intensity of the light radiation emitted is proportional to the no of atoms in the excited state, which in turn is proportional to the no of atoms in the flame or concentration of the solution fed into the flame. Thus concentration of the solution is related to intensity of the emitted radiation. By measuring the intensity of the emitted radiation, the concentration can be determined.

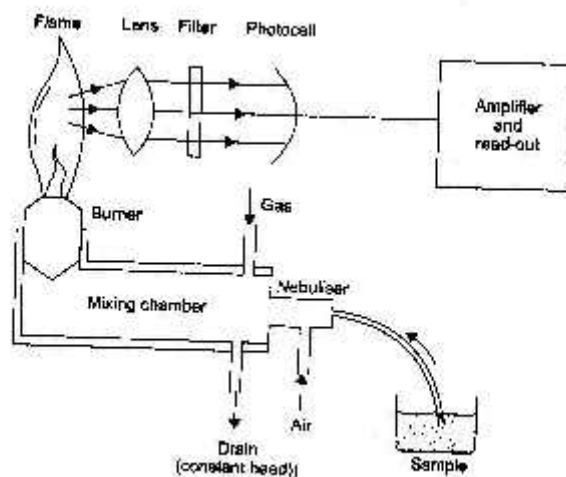
The sequence of changes taking place at the flame is



The intensity of the emitted radiation measured as detector response is related to the concentration by an expression $E = k c$

Where E is the detector response, k is a constant, ϕ is the efficiency of atomic excitation and c is the concentration of the solution.

The quantitative analysis by flame photometry can be carried out by the calibration curve method. For this purpose a series of standard solutions of the analyte metal are taken aspirated into the flame and the emission of each solution is measured in a flame photometer. Then the calibration curve is obtained by plotting the emission intensity against the concentration of the standard solutions. From the calibration curve the concentration of the sample solution can be determined.



Instrumentation:

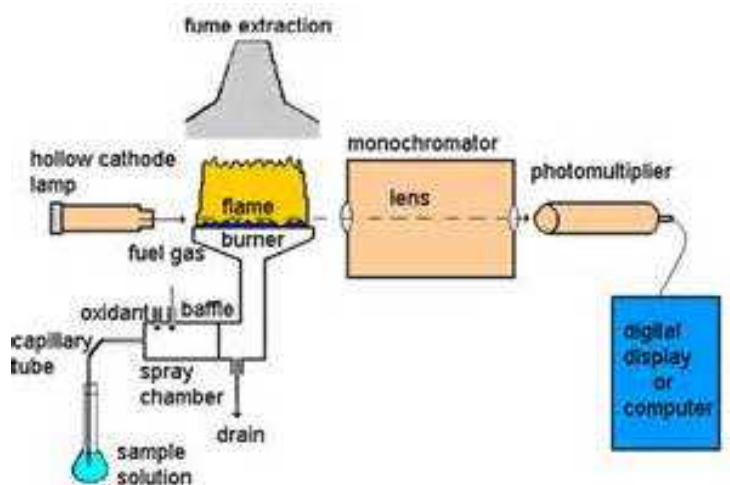
A Simple flame photometer consists of an atomizer, mixing chamber, burner, filter, detector and a readout device. Pressurized air is passed into the atomizer and this produces suction which draws the solution of the sample into the atomizer. Inside the atomizer it mixes with the air stream as a fine mist and passes into the mixing chamber. In the mixing chamber it mixes with fuel gas and then passes into the burner where the mixture is burnt. The radiation from the resulting flame passes through a lens and finally through filters which permits only the radiation characteristic of the element under investigation to pass through the detector. The output from the detector is read on a suitable readout system.

Atomic absorption spectroscopy is a technique which studies absorption of electromagnetic radiations in relationship to molecular structure. It is a technique for measuring the concentration of various elements in the sample through their absorption of light. It is a relatively simple and reliable technique which uses absorption of optical radiation by free atoms for determining the contents of different elements.

Principle:

Atomic absorption spectroscopy is based on the principle that when a beam of electromagnetic radiation is passed through a substance, the radiation may either be absorbed or transmitted depending upon the wavelength of the radiation. The absorption of radiation would bring about an increase in the energy of the molecule. The energy gained by the molecule is directly proportional to the wavelength of radiation. The increase in the energy of the molecule leads to the electronic excitations where electrons jump to higher energy levels. A particular wavelength that a given molecule can absorb depends upon the changes in vibrational, or rotational or electronic states.

In the atomic absorption spectrometer, the source of radiation in the spectrometer is the tungsten filament emitting white light or hydrogen discharge lamp. The radiation from the source is directed by some device (for example in this case a mirror) on the sample. The radiation then passes through an analyser (the grating in this case), which selects the frequency reaching the detector at any given time. The signal from the detector passes then to a recorder which is attached to the analyser so as to produce a trace of the absorbance of varying frequencies



Monochromator

The main purpose of the monochromator is to isolate a single atomic resonance line (wavelength) from the lines emitted by the Hollow cathode lamp and transmit it to the detector. I

Photomultiplier

tube

(PMT)

This is the detector. The PMT determines the intensity of photons of the analytical line exiting the monochromator. Before an analyte is aspirated, a signal is generated by the PMT as a measurement of the light flowing from the HCL. When the sample is aspirated in the flame, some of this light is absorbed by "excited" atoms now present in the flame. This causes a decrease in PMT signal which is proportional to the amount of analyte. This decrease in light intensity by the atoms is referred to as atomic absorption. The signal from the PMT is converted to digital format by a transducer for read-out. not only selects the specific analytical line, but excludes all other interfering lines in that region.

Samples

The samples and standards are often prepared in duplicate with acid to match the analyte's chemical matrix as closely as Possible.

Autosampler

With the autosampling accessory, tedious and time-consuming operations can be avoided. The autosampler is a computer-controlled, multi-purpose system. It automates standard and sample introduction for instrument calibration and analysis, and is a fully automated analytical workstation.

Atomic absorption spectrophotometry detects trace metal content and concentration in aqueous solution. This is useful for:

- Groundwater sampling
- Evaluation of bore water samples
- Determination of the amount of contamination from mines
- Evaluation of specific elements in food or pharmaceuticals
- Evaluation of specific elements in petrochemicals
- Use in medicine for biological monitoring
- Use in evaluating nanomaterials
- Use in pathology

Agriculture – analyzing soil and plants for minerals necessary for growth

Chemical – analyzing raw chemicals as well as fine chemicals

Environmental Study – determination of heavy metals in water, soil, and air

Food Industry – quality assurance and testing for contamination

Forensic's – substance identification

Mining – testing the concentration of valuable substances in potential mining areas

Nuclear Energy – monitoring potentially hazardous elements in water and waste output

Petrochemical – analyzing products for metals and other substances that can have adverse affects such as oil and gas

Pharmaceutical – many applications from quality control to detecting impurities in drugs

NANO MATERIALS

1. Introduction:

Today, everyone uses the term ‘nano’ for anything which is small. But in chemistry, a nano material refers to a material with at least one of its dimension in nano scale. Typically, size of a nano material varies from a nanometer to hundred nanometers.

- 1 nanometer = 10^{-9} meter. One nanometer is approximately the length equivalent to ten hydrogen or five silicon atoms aligned in a line.
- Nanomaterials are usually considered to be materials with at least one external dimension less than 100 nanometers. They may be in the form of particles, tubes, rods or fibres. The nanomaterials and bulk materials of the same composition have different physico-chemical properties.

2. Definitions

- a. Particle: A particle is defined as a small object that behaves as a whole unit in terms of its transport and properties.
- b. Nanomaterial: A nanomaterial is defined as that having at least one of its dimensions between 1 and 100 nm.
- c. Nanoscience: Nanoscience primarily deals with synthesis, characterization, exploration and engineering of nanostructured materials.
- d. Nanotechnology: Nanotechnology is defined as the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometer scale.

3. Size dependent properties of nanomaterials

- Materials in the micrometer scale exhibit physical properties almost same as that of bulk form. However, materials in the micrometer scale exhibit physical properties distinctively different from the bulk.

- Properties of any bulk material are independent of its size. Properties of a bulk material can be altered only by altering their structure and composition.

Ex: melting point of gold remains same whether the size of gold is 1 gram or 1 kg. A piece of gold is golden in colour however big or small it is.

- But in nanoscale range, a material with same structure and composition will show different properties when the size of material is slightly varied.
- A colloid of gold nanoparticles is no longer “golden” but ruby red in colour. Only the materials in the nano size range exhibit these size dependent properties, because a transition from atoms or molecules to bulk form takes place in this size range.
- Matter at the nanoscale no longer follows Newtonian physics but rather governed by quantum mechanics.

Nano materials exhibit several size dependent properties.

4. Nanomaterial - synthesis and processing

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the ‘bottom up’ or the ‘top down’ approaches (Fig. 5) to synthesize nanomaterials, i.e. either to assemble atoms together or to dis-assemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms. This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering up to medicine.

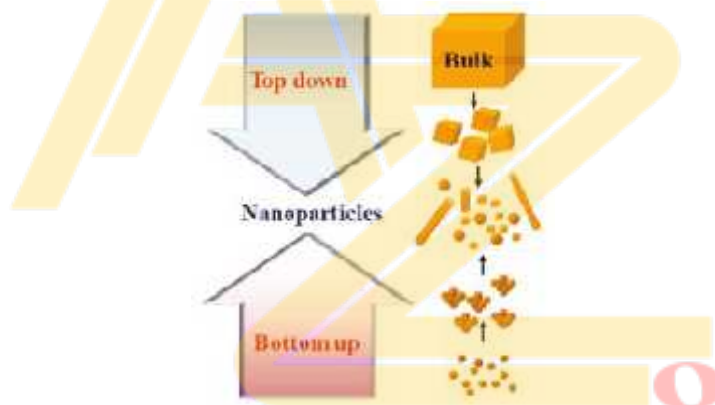


Figure.3 Schematic illustration of the preparative methods of nanoparticles.

5. Wet Chemical Synthesis of Nanomaterials

In principle we can classify the wet chemical synthesis of nanomaterials into two broad groups:

1. The top down method: where single crystals are etched in an aqueous solution for producing nanomaterials, For example, the synthesis of porous silicon by electrochemical etching.
2. The bottom up method: consisting of sol-gel method, precipitation etc. where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.

i. Sol-gel process

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (**sol**) and gelation of the sol to form a network in a continuous liquid phase (**gel**). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid

from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as Si (OEt)₄ (tetraethyl orthosilicate, or TEOS). The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides M(OR)_z can be described as follows:



Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.

1. Formation of different stable solutions of the alkoxide or solvated metal precursor.
2. Gelation resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation reaction that results in a dramatic increase in the viscosity of the solution.
3. Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.
4. Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv) the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed a xerogel. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an aerogel.
5. Dehydration, during which surface- bound M-OH groups are removed, thereby stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 800°C.
6. Densification and decomposition of the gels at high temperatures (T>800°C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

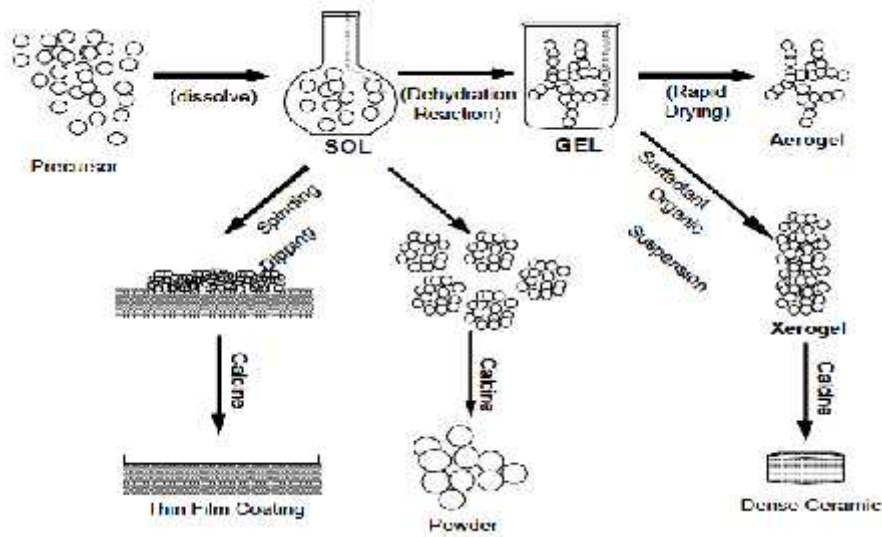


Figure 4. Schematic representation of sol-gel process of synthesis of nanomaterials.

ii. Precipitation process

This method relies on the precipitation of nanometer-sized particles within a continuous fluid solvent. An inorganic metal salt, such as chloride, nitrate, sulphate, etc., is dissolved in water. Metal cations exist in the solution in the form of metal hydrate species, for example, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ or $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. These hydrates are added with basic solutions, such as NaOH or NH_4OH .

The precipitated hydrolysed species is filtered, washed, dried and calcined in order to obtain a final nanomaterial product. Several other precipitation agents such as oxalate, carbonate, etc. can also be used.

Advantages:

- The method is relatively simple and widely used for production of single and multi-components oxide nanopowders using optimized reactions and reaction conditions.
- Subsequent processing of colloids can include additional colloidal precipitation on particle surfaces to produce a core-shell nanoparticle structure, deposition on substrates.

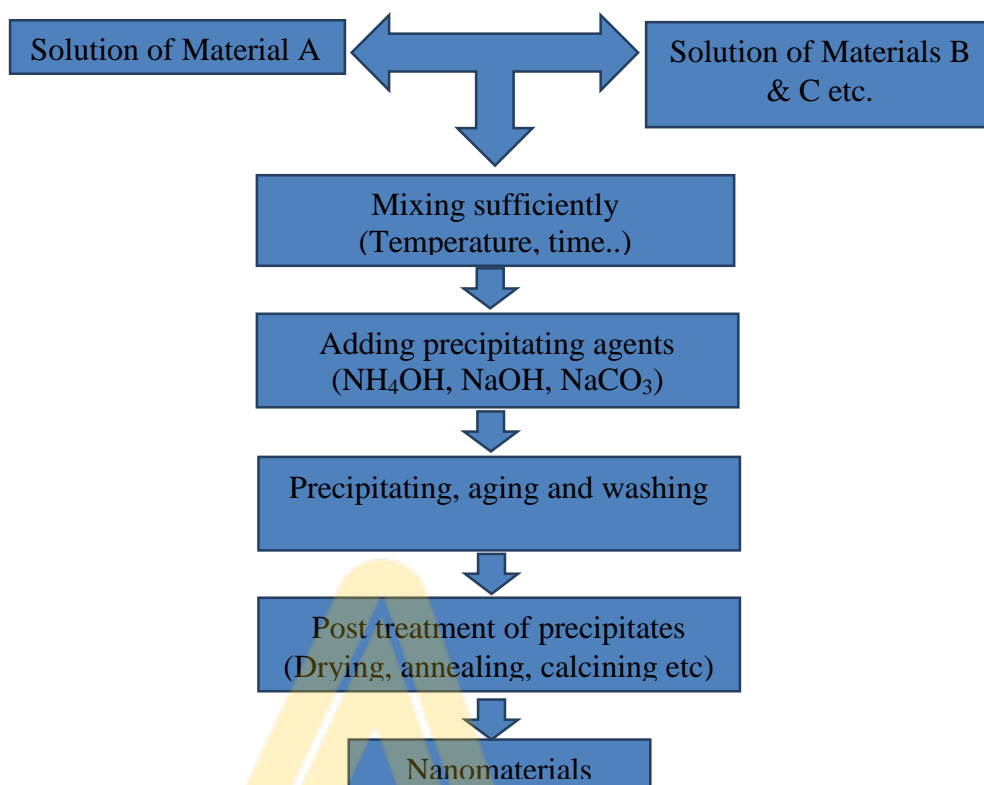


Figure 5. Procedures of chemical precipitation synthesis of nanomaterials

To obtain cleaner, larger particles, an aging process, from few hours to one or two days, is often required before collecting the precipitates. The precipitates-mainly metal hydroxides and metal complexes are then collected by filtration or centrifugation. To obtain high purity nanomaterials, distilled water, absolute ethanol, or other solvents are used several times to rinse out impurities.

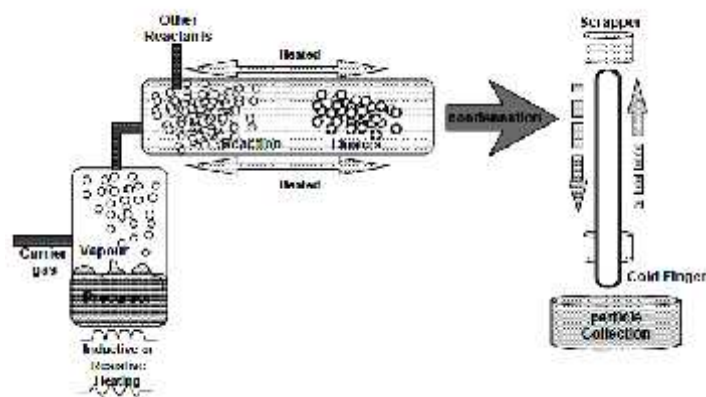
Chemical Vapour Condensation (CVC)

As shown schematically in Figure, the evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapour Condensation or the CVC process.

In this method a mixture of gas reactants are delivered into a reaction chamber. Inside the chamber the chemical reactions among the gas molecules are induced by an input of energy such as resistant heating laser or plasma. The products are formed in the vapour state and on condensation, deposits nanoparticles. The by-products of the reaction are exhausted.

CVC enables us to obtain:

1. Mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and
2. Coated nanoparticles, i.e., n-ZrO₂ coated with n-Al₂O₃ or vice versa, by supplying a second precursor at a second stage of the reactor. In this case nanoparticles which have been formed by homogeneous nucleation are coated by heterogeneous nucleation in a second stage of the reactor.



Advantages:

- Very flexible, can produce wide range of materials.
- Precursors can be solid, liquid or gas under ambient conditions; but delivered to reactor as vapour.
- Allows formation of doped or multi-component nanoparticles by use of multiple precursors.

6. Nanoscale Materials

a. Fullerenes

Fullerenes are nanosized allotropes of carbon, having a cage like structure. They are represented as C_{60} or C_{70} depending on the number of carbon atoms present in the cage. Fullerenes are made by heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by the condensation of carbon vapour consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes containing even number of carbon atoms upto 350 or above.

C_{60} molecule has a shape like soccer ball and is called **Buckminsterfullerene**. It contains 20 six-membered rings and 12 five-membered rings. All carbon atoms are equal and are sp^2 hybridised. The delocalized electrons in molecular orbitals, give aromatic character to the molecule. The fullerenes are soluble in organic solvents such as benzene, toluene and chloroform.

Applications:

- In optics, the fullerenes were proposed to use for the electro-photographical imaging, optical filters and nonlinear optical materials.
- In electronics they are used as molecular switchers, diodes, transistors, resistors for lithography, solar cell elements, magneto-optical recorders, photo electronic devices.
- In military sphere, the fullerenes are used as the optical and microwave absorption coatings to prevent the aircraft and missiles from radar detection.
- Fullerenes are chemically reactive and can be added to polymers and elastomers to create new copolymers with specific physical and mechanical properties.

b. Carbon Nanotubes (CNTs)

Carbon nanotubes are 1D quantum cylinders, whose diameter is in nano-range and length is in micro-range. CNTs are members of fullerene structural family. CNTs are single sheets of graphene, rolled into cylinders. They are categorized as single walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

CNTs are generally produced by three main techniques: arc discharge, laser ablation and chemical vapour deposition.

Properties:

- High electrical conductivity.
- High thermal conductivity.
- High mechanical strength, which results from the covalent sp^2 bonds formed between the individual carbon atoms.

- High thermal stability.
- Enhanced chemical reactivity, compared with a graphene sheet, as a direct result of the curvature of the CNTs.

Applications:

- Energy storage.
- Biomedical applications.
- CNT based fibres and fabrics.
- CNT based ceramics.
- In molecular electronics; CNT based non-volatile RAM, CNT based transistors.

Graphene

Graphene is an allotrope of carbon that exists as a two-dimensional planar sheet.

Properties of graphene

- The electronic mobility of graphene is very high .
- Graphene is one of the strongest materials ever discovered with a tensile strength of 1.3×10^{11} Pa.
- Graphene is highly flexible and elastic in nature.
- Graphene has high electrical & Thermal conductivity.
-

Applications of graphene

- ❖ Graphene could be used in sensors in various fields including bio-sensors, DNA sensors and gas sensors etc.
- ❖ Graphene can be incorporated into both the anode or the cathode in various battery systems to increase the efficiency of the battery and improve the charge/discharge cycle rate.
- ❖ Graphene is an ideal material for use in electron emission displays as it exhibits a high aspect ratio.
- ❖ graphene is being incorporated into many materials to make the existing material stronger and more lightweight.
- ❖ Graphene can be incorporated into polymeric materials to form graphene-polymer composite materials.
- ❖ Graphene can be used in functional inks for electronic, heat resistant and anti-corrosion purposes.