CHAPTER 3
THERMAL ANALYSIS

3.1 INTRODUCTION

Thermal analysis refers to a group of techniques developed and used, in which any physical property of the given system is continuously measured as a function of temperature. Thermal analysis is employed in virtually every area of modern science and technology. The basic information that these varieties of techniques can provide includes crystallinity, specific heat, expansion and information on various physical and chemical transformations that can take place on the sample under inspection. These are analytical techniques for studying the purity, decomposition, and phase transformation etc. of a compound with respect to change in temperature. In thermal analysis generally we are plotting mass of a substance with respect to change in temperature.

Thermal analysis can be classified broadly into two.

(1) Thermo gravimetric analysis (TGA)
(2) Differential thermal analysis (DTA)

3.2 THERMO GRAVIMETRIC ANALYSIS (TGA)

This is the simplest of the thermal analysis wherein, one measures, the weight changes that occur as a result of programmed heating of the substance. In TGA valuable information such as phase transformation, decomposition, dehydration etc. can be studied. In TGA mass of a substance is plotted and recorded against temperature. This analysis requires that the test instrument be able to accurately measure mass, temperature, and temperature change.

Instrumentation: TGA apparatus is highly sophisticated equipment with the following components,

(1) **Furnace**: The furnace is connected to a power source. The temperature of the furnace can be controlled by the microprocessors. The sample under investigation is kept inside the furnace in a crucible.
(2) **Environmental protection system**: This facilitates the handling and working of the furnace and protects the operator from high temperature thermal radiations. The insulating mechanism acts as a shield (providing inert atmosphere).

(3) **Temperature sensor and thermo balance:** The ... the furnace can be analyzed for any mass change with the temperature sensor and thermo balance.

(4) **Recorder:** The final result or thermogram can be taken out from the recorder. The data from thermobalance and sensor is amplified and send to the recorder by the machine for further processing and printout.

Working of TGA: The sample under analysis is placed in a crucible or shallow dish that is attached to an automatic thermobalance. It is continuously heated linearly from room temperature to a temperature as high as 1200°C. Heating is effected by a power source controlled by microprocessor attached to the furnace.

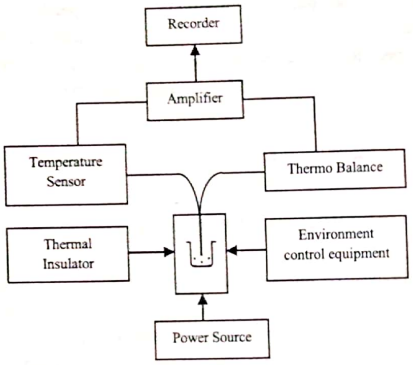


Fig. TG Apparatus

The change in mass of the sample is converted in to an electrical signal and recorded. In a thermogram temperature is plotted in the X- axis with corresponding mass in Y-axis. The thermogram is a graphical representation of mass (m) against temperature (T).

The TGA curve gives qualitative and quantitative information about a particular substance under analysis. A typical TGA curve consists of two portions.

1. A horizontal portion (A) representing the region where there is no change in mass of the compound. This region of the graph gives valuable information about the thermal stability of the material. This information is very important to the engineer because it reveals the temperature range in which substances like polymers, packing materials, alloys and building materials may be safely used.

considerable change in mass of the compound. The change in mass may be due to dehydration, decomposition, dissociation etc.

3. From a TGA curve, we can determine the weight loss at a particular temperature. This can be illustrated by the following case study.

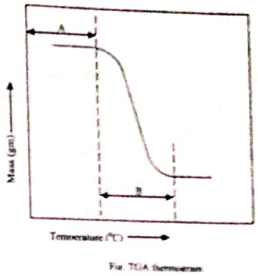


Fig. TGA thermogram

Decomposition of hydrated calcium oxalate

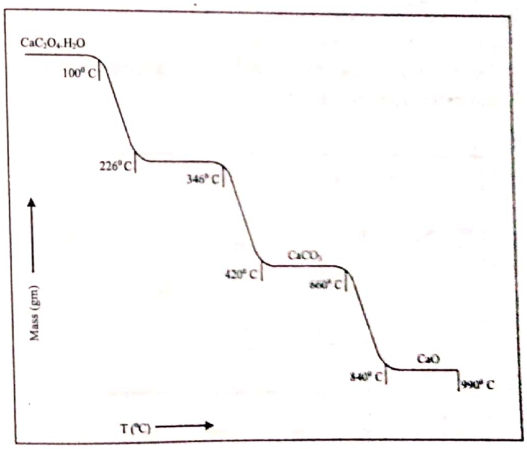


Figure 3.3 Thermogram of $CaC_2O_4.H_2O$

The thermogram for the decomposition of pure calcium oxalate ($CaC_2O_4.H_2O$) obtained by increasing the temperature at a rate of 5°C/min is shown in the figure. Various reactions taking place during heating are,

$$CaC_2O_4.H_2O \xrightarrow{100-250^0C} CaC_2O_4 + H_2O$$

$$2CaC_2O_4 \xrightarrow{400-500^0C} 2CaCO_3 + 2CO$$

$$CaCO_3 \xrightarrow{650-850^0C} CaO + CO_2$$

$CaC_2O_4.H_2O$ is thermally stable up to 100°C and water evaporates slightly above 100°C to form anhydrous calcium oxalate. (CaC_2O_4). The horizontal portion between 226-346°C indicates that anhydrous salt is thermally stable in this range. At slightly above 346°C, the anhydrous calcium oxalate decomposes to give calcium carbonate. This process is completed at about 420°C. Calcium carbonate is stable up to 660°C. Above 660°C it decomposes to CaO and CO_2. This process is completed at 840°C and above this the horizontal portion represents the stable CaO.

Study of the thermal stability of polymers

The following figure gives the TG curves of some polymers. The curves clearly indicate that PVC is the least thermally stable and PTFE is the most thermally stable. PTFE do not lose weight below 500°C and then decomposes abruptly around 600°C. The other polymers are decomposed around 450°C. PMMA decomposes more slowly than the others as indicated by slope of TG curve.

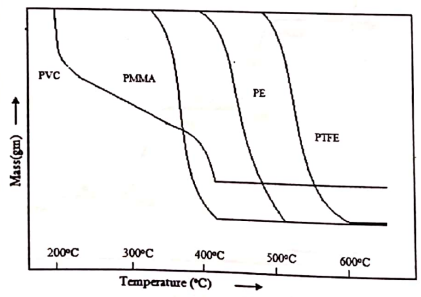


Fig.3.4 TG Curve of some polymers: PVC = Polyvinyl chloride; PMMA = Polymethylmethacrylate, PE = Poly ethylene; and PTFE = Polytetrafluoroethylene

Applications of TGA

1. Qualitative analysis

It is concerned with investigation of the type of chemical substances present in the sample with the help of TGA curve (thermogram). It is used for

(1) To identify a particular polymer in a polymeric mix.
(2) To establish the purity of a compound.
(3) To study the decomposition behavior of compound (organic and inorganic).
(4) Stability of substances at elevated temperatures.

2. Quantitative analysis

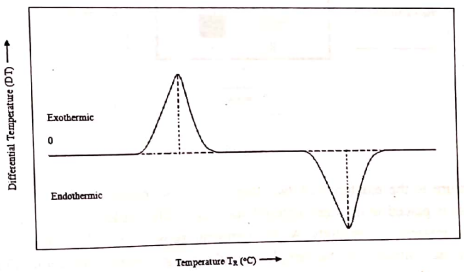
TGA can be used for estimating the quantity of a particular substance present in a mixture of various compounds. For example,

(1) To find out the quantity of filler present in a polymeric mix.
(2) To study the extent of adulteration in food stuffs.
(3) The percentage of particular metal present in an alloy or mixture of salts.

Limitations of TGA

(1) TGA's scope is limited to the study of dehydration, decomposition, oxidation etc.
(2) Fusion reaction cannot be investigated.
(3) Glass transition temperature cannot be studied.
(4) Crystalline transitions where there is no mass change cannot be investigated.

3.3 DIFFERENTIAL THERMAL ANALYSIS (DTA)



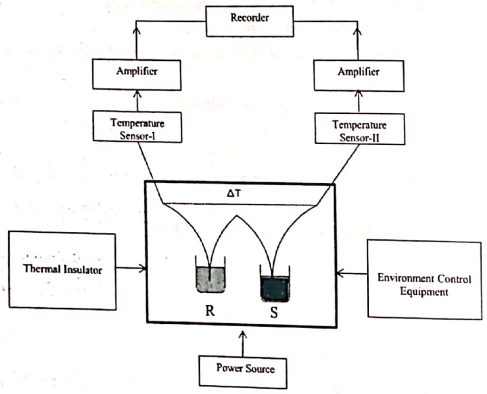
Differential thermal analysis (DTA) is a thermo analytic technique. In DTA, the material under study and an inert reference are made to undergo identical thermal cycles, while

recording any temperature difference between sample and reference. This differential temperature is then plotted against temperature (DTA curve) changes in the sample. Either exothermic or endothermic changes can be detected relative to the inert reference. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample.

Instrumentation:

DTA instrument is similar to the one for TGA. It consists of,

1. A sample holder, sample containers and a ceramic or metallic block- furnace.
2. A temperature programmer, comprising of thermocouples.
3. Recorder.

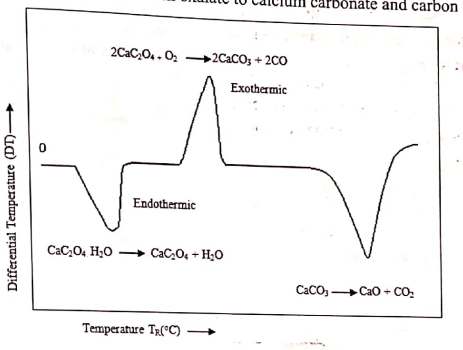


DTA Apparatus

The key feature is the existence of two thermocouples connected to a voltmeter. One thermocouple is placed in an inert material such as Al_2O_3, while the other is placed in a sample of the material under study. As the temperature is increased, there will be a brief deflection of the voltmeter if the sample is undergoing a phase transition. This occurs because the input of heat will raise the temperature of the inert substance, but it will be incorporated as latent heat in the material changing phase. The thermogram obtained is a plot of ΔT versus reference temperature T_R. It is known as differential thermogram.

Decomposition of hydrated calcium oxalate

The thermogram contains two minima representing endothermic regions .The first minima indicates the dehydration of $CaC_2O_4.H_2O$. The middle maxima indicate the decomposition of anhydrous calcium oxalate to calcium carbonate and carbon monoxide.



DTA thermogram of decomposition of $CaC_2O_4.H_2O$

In general

1. For exothermic changes like oxidation, crystallization, adsorption etc. the peak appear above zero in the differential thermogram (maxima).
2. For endothermic changes like vapouraisation, sublimation, desorption, fusion etc., the peaks appear below zero in the differential thermogram (minima).

Study and characterization of polymers

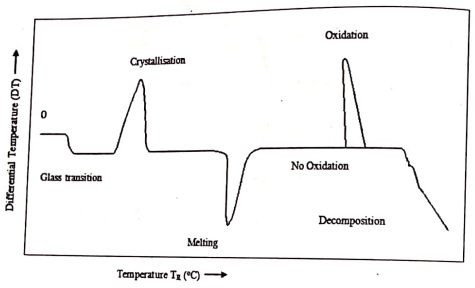
DTA has been widely used for the study and characterization of polymers. The following curve illustrates various transitions and changes during heating of a polymer.

Applications of DTA

DTA curve can be used as a finger print for the identification and other purposes.

(1) In phase transition studies.
(2) For the determination of specific heat and heat of reaction.
(3) Decomposition of polymers and compounds.

(4) Glass transition temperature.
(5) Crystallization behavior.
(6) In the analysis of clay and identification of clays.
(7) The DTA technique is widely used for identifying minerals and mineral mixtures.
(8) DTA is widely used in the pharmaceutical and food industries.
(9) DTA may be used in cement chemistry- in Quality control applications.



DTA thermogram of Polymer

IMPORTANT QUESTIONS

1. Define TGA and explain the instrumentation of TGA. Explain the features of a TGA curve. Write the applications of TGA in qualitative and quantitative analysis.(K.U2014)
2. Explain the differential thermal analysis and its applications with an example.
3. Discuss the basic principle of thermogravimetric analysis with instrumentation, graphical interpretation and applications. (KU 2008, June)
4. Explain the principle involved in themogravimetric analysis using one example. (KU 2008, June)
5. Describe briefly thermogravimetric analysis. (KU 2006June; KU 2009Jan; KU 2011, may)
6. Briefly explain the differential thermal analysis. (KU 2007, June)
1. Explain the principle involved in thermogravimetric analysis using one example. (KU 2008, June)

CHAPTER 4
CHROMATOGRAPHY

4.1 INTRODUCTION

Chromatography is a technique of separation and purification of the components of a mixture by their differing affinities for two phases (states) of matter with which they come in contact. In 1903, Mikhail Tswett used the term chromatography to describe the separation of plant pigments by percolating a petroleum ether extract through a glass column packed with calcium carbonate. The various pigments migrated through the column at different rates and produced different colored zones. His column developed bands of colors, and he named this separation technique chromatography, which in Greek means "written in color". This method is very useful when the components of a mixture have almost the same physical and chemical properties and hence cannot be separated by other methods. Chromatographic method of separation is based on the selective distribution of components in a mixture between a fixed (stationary) and a moving (mobile) phase. The stationary phase can be a solid or liquid; while the mobile phase is a liquid or gas. When the stationary phase is a solid, the selective distribution is based on adsorption; and when it is a liquid, the basis of selective distribution is partition.

4.2 CLASSIFICATION OF CHROMATOGRAPHIC METHODS

Chromatographic methods can be classified based on the types of mobile and stationary phase and mechanism of separation. It can be broadly classified into adsorption and partition chromatography. In adsorption chromatography, the stationary phase is a solid and the mobile phase may be a liquid or gas. If the stationary phase is a solid and mobile phase is a liquid, it is called liquid-solid chromatography or LSC (note: the mobile phase is named first). When the mobile phase is a gas it is called gas-solid chromatography or GSC. When the stationary phase is taken as a column, it is known as column chromatography. When the solid adsorbent is used as a thin layer coated on a glass plate, it is called thin layer chromatography or TLC. In partition chromatography, the stationary phase is a liquid, held in an inert solid support and the mobile phase may be a liquid or gas. In liquid-liquid chromatography (LLC), the separation involves, predominantly a simple partitioning between the immiscible liquid phase, one stationary and the other mobile. The conventional LLC has been improved into a modern, efficient

method called high performance (pressure) liquid chromatography or HPLC. The variou chomatographic techniques can be classified as shown figure 4.1.

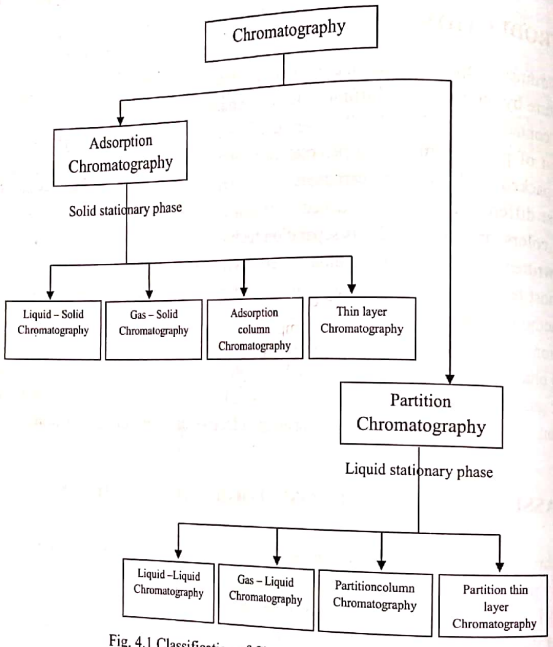


Fig. 4.1 Classification of Chromatographic techniques

4.3 HIGH PERFORMANCE (PRESSURE) LIQUID CHROMATOGRAPHY (HPLC)

High-performance liquid chromatography (HPLC; formerly referred to as high-pressure liquid chromatography), is a technique in analytic chemistry used to separate the components in a mixture, to identify each component, and to quantify each component. It relies on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material. Each component in the sample interacts slightly differently with the adsorbent material, causing different flow rates for

the different components and leading to the separation of the components as they flow out the column. The principle is much the same as in GLC, where the stationary phase is a solid (adsorption) or a liquid supported by a solid (partition) and the mobile phase is a liquid. The solid phase usually employed is silica, alumina, calcium carbonate, magnesia, calcium phosphate, etc. The mobile phase may be a single liquid or a mixture of liquids which is pumped into the column at a high pressure of the order 400-1000 atmosphere at a flow rate of 0.1 to 10 ml /minute. The most common liquids used in mobile phases are benzene, cyclohexane, carbontetrachloride, carbon disulphide, acetic acid, ethyl acetate or their suitable mixture.

Instrumentation

An HPLC instrument is highly sensitive analytical equipment with the following essential components.

1. **Reservoirs:** Are used to store the different solvents (mobile phase)
2. **Pressure pump:** The role of the pump is to force a liquid (called the mobile phase) through the instrument at a specific flow rate. The pumps can be of three different types such as a) reciprocating, b) displacement c) pneumatic or constant pressure type.

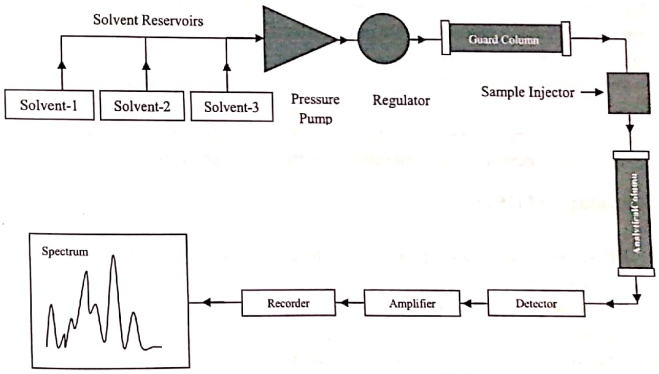


Fig.4.2 Schematic Representation of HPLC instrument

3. **Sample injector:** The injector serves to introduce the liquid sample into the flow stream of the mobile phase. Typical sample volumes are 5- to 20-microliters (μL). The injector must also be able to withstand the high pressures of the liquid system.
4. **Regulator:** The regulator can control the flow rate of the mobile phase.

5. **Guard column (pre- column)**: The guard column can act like a filter and can remove the particulate matter and contaminants from the mobile phase. The guard column increases the life of the analytical column.
6. **Analytical column**: Is considered as the "heart of the chromatograph". Basically, these are long, narrow, smooth stainless steel column having a length of 10-30 cm. These columns have an inside diameter of around 4-10cm with small particles inside 3-10 µm.
7. **Detectors**: The detector can see (detect) the individual molecules that come out (elute) from the column. HPLC detectors are of two types.

a) Bulk property detector: This can respond to mobile phase bulk properties like refractive index, dielectric constant or density, which is modulated by the presence of solutes.

b) Solute property detector: These can respond to properties of the solutes such as UV absorbance, fluorescence or the diffusion current that is not possessed by the mobile phase.

Working/ procedure

The schematic of an HPLC instrument is shown above. The sample injector brings the sample mixture into the mobile phase stream which carries it into the column. The pumps deliver the desired flow and composition of the mobile phase through the column. The detector generates a signal proportional to the amount of sample component emerging from the column, hence allowing for quantitative analysis of the sample components. During the chromatographic experiment, a pump can deliver a constant mobile phase composition (isocratic) or multiple solvent composition (gradient).

Advantages of HPLC

1. HPLC is an automated process that takes only a few minutes to produce high resolution results.
2. Highly sensitive and accurate.
3. High speed of separation.
4. Separation can be done at ambient temperature.
5. It enables determination of compounds present even in trace concentrations.
6. Automation of the analytical procedure and data handling.
7. Wide choice of stationary and mobile phases.

Applications

1. Quantitative/qualitative analyses of amino acids, nucleic acids, proteins etc.
2. Monitoring environmental samples.
3. Measuring levels of hazardous compounds such as pesticides and insecticides.
4. Forensic analysis
5. Quality and process control.
6. Biomedical research.
7. Clinical testing.

4.4 GAS CHROMATOGRAPHY

Gas Chromatography is used for the separation and analysis of gaseous mixture and volatile organic compounds. This is a process by which a mixture is separated in to its constituents by a moving gaseous phase passing over a stationary sorbent. The stationary phase may be either liquid or solid. Gas chromatography is classified into two.

1. Gas-solid chromatography (GSC) - in which the separation takes place by adsorption between a mobile gas phase and an active solid phase.
2. Gas-liquid chromatography (GLC) – in which the separation takes place by partitioning a sample between a mobile phase and a thin layer of non-volatile liquid coated on an inert support.

Gas chromatography technique was originally developed in 1941 by A. J. P. Martin and R. L. M. Synge for which they were awarded the Nobel Prize in 1952. Today this technique is the most important and extensively used analytical tool for the determination of the number of components in a mixture, the presence of impurities in a substance and identification of a compound.

Theory of gas chromatography

The sample mixture is introduced into the moving carrier-gas (such as N_2, Ar, H_2, He etc.). The mixture is then swept along through the thermostated GLC or GSC column. During the passage of mixture through the column, the components of the mixture distribute themselves between the two phases. Some components are adsorbed or absorbed by the stationary phase better than others, and hence, they are retained for a longer time in the column. Thus, each component of the mixture is carried along the column at different rates and finally emerges from the column at different time. In other words, time for passage through the column is characteristic for each component. As the component leaves the column, it is detected by instrumental means. The apparatus employed is called gas chromatograph.

Instrumentation

A gas chromatograph consists of

1. **Carrier-gas:** A supply of gas (such as N_2, Ar, H_2, He etc.) from a high pressure cylinder having a pressure regulator and flow meter.
2. **A sample injection system**: Usually, the sample is introduced by means of a micro-syringe into a flash vaporizer port located at the head of the column. The injection port is heated to a temperature which will ensure rapid vaporization but not thermal degradation of solute.
3. **Separation column:** The actual separation of sample components takes place in this column. Separation column is made from a variety of materials including glass, copper, stainless steel, teflon, etc. Generally the column length in GSC is around 0.2-2 m and in GLC around 3-300m. Packed columns contain uniform, finely divided and densely packed materials or solid support coated with a thin layer (0.05-1 μm) of the stationary liquid phase.
4. **Detector:** These are situated at the exit side of the separation column to detect the signals. The main functions of the detector are to sense and measure small quantities of the separated components present in the carrier gas stream leaving the column. The detectors most widely used are

a) **Thermal conductivity detector (TCD) or Katharometer**– Is a non-destructive universally accepted concentration sensitive bulk property detector. It works on the principle that the presence of analyte molecules in a gas stream will produce changes in thermal conductivity. The sensing element here is an electric element (made of fine platinum, gold, tungsten or a semiconducting thermistor) whose temperature at constant electrical power depends upon the thermal conductivity of the surrounding gas. The main advantages of thermal conductivity detector (TCD) are 1) It is simple to use 2) It has a large linear dynamic range 3) It gives response to both inorganic and organic compounds 4) It is non-destructive. But the main disadvantage is that the sensitivity is low.

b) **Flame ionization detector (FID)** –It works on the principle that when the effluent from the column is mixed with hydrogen and burnt in air, the flame produced can ionize solute molecules. The ions thus produced are collected at the electrodes and the resulting current is measured. The flame ionization detectors (FID) are the most widely used detectors in gas chromatography because of its stability, high sensitivity, fast response, low noise and wide range of linear response.

c) **Electron capture detector (ECD):** In this detector, a beta-ray source is used to generate electrons by ionization of the carrier gas flowing through the detector. These

electrons migrate to anode under fixed potential and give rise to a steady baseline current. When an electron capturing gas (i.e. elute molecules) emerges from the column and reacts with an electron, the result is the replacement of an electron by a negative ion of much greater mass with a corresponding reduction in current flow. The response of the ECD is related to the electron affinity of the elute molecules. It is used in the trace analysis of pesticides, herbicides, drugs, biologically active compounds etc.

5. **Recorder**: Almost all detectors give small and weak electrical signals. Hence it is necessary to pass these signals through an amplifier before going to the recorder. The recorder is a mobile recording pen activated by the signal and recording chart sheet moving at a pre-selected speed. The amplified signals drive the pen on the moving strip of the paper and trace out a chromatogram containing a series of Gaussian (i.e. bell shaped) peaks.
6. **A thermostat compartment:** To provide constant temperature to the column and detector.

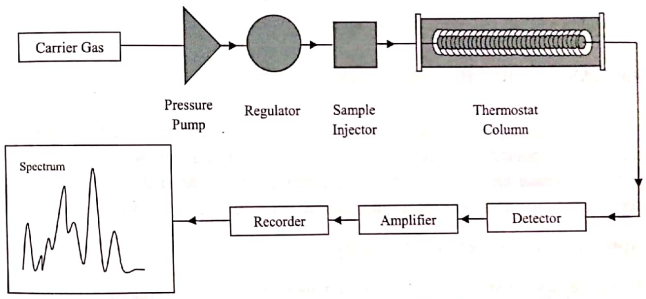


Figure 4.3 Schematic representation of Gas chromatograph

Procedure

The sample mixture is injected into the moving carrier gas stream from where it is taken in the vapor form into a thermostated chromatographic column (GLC or GSC). During their journey through the column, the components in the mixture get distributed between the two phases (mobile and stationary phases). The rate of distribution depends on the extent of partition or adsorption. In this way, the different components are carried

at different rates and hence they emerge out from the column at different rates. The time taken by each component to pass through the column is the characteristic property which helps in identifying the component. They are then detected by a detector, in which the recorder gives a peak for each component. The size and location of the peak are an indication of the nature of the component.

4.5 GAS- LIQUID CHROMATOGRAPHY (GLC)

It is a partition chromatography in which a thin film of a high boiling liquid such as paraffin or polyethylene glycol coated on an inert solid like keisulghur or celite is used as the stationary phase. A mixture of the vapourised sample and an inert carrier gas like nitrogen, hydrogen or argon is used as the mobile phase. As the mixture of gases passes through the column, partition occurs between gas mixtures and the stationary phase. Since the partition coefficient of individual gases in the mixture is different, they are carried along the column at different rates. The components which leave the column pass through the detector and recorder. The detector produces an electric signal and the recorder converts the signal to a trace on a paper. This results in a chromatogram containing a series of Gaussian (i.e. bell shaped) peaks.

4.6 GAS- SOLID CHROMATOGRAPHY (GLC)

In gas solid chromatography, the separation is based on the selective absorption of different components of a gaseous mixture. A solid of large surface area is used as the stationary phase and a gas is the mobile phase. This method is largely used for the separation of isomers like cresols, dichlorobenzenes, toluidines and xylenes.

Applications of gas chromatography

1. The separation of thermally stable and volatile organic and inorganic compounds.
2. Industries for process monitoring.
3. Determining specific surface areas in adsorption studies.
4. Drugs and pharmaceuticals – for quality control, analysis and monitoring.
5. Environmental studies- air samples can be very complex mixtures due to pollution. Gas chromatography is easily adapted to the separation and analysis of such mixtures.
6. Clinical chemistry- blood, urine and other biological fluids can be analyzed for proteins, carbohydrates, fatty acids, steroids etc..
7. Petroleum industry- for the determination and separation of many components in petroleum products.

8. In food industry- for the analysis of fruit juices, beverages, dairy products, decomposition products, contaminants, adulterants, etc.

Table 4.1 Comparison between GSC and GLC

No	Point of difference	GSC	GLC
1	Stationary phase	Solid	Liquid
2	Mobile phase	Gas	Gas
3	Basis of separation	Adsorption	Partition between phases
4	Packing of the column	Fine graded powder	Liquid coated on an inert support or thin layer.
5.	Length of the column	0.7 to 2 m	3-300 m
6.	Thermal stability of stationary phase	Good thermal stability	Only a few stable over 300°C
7.	Reaction on the column	Packing may catalyse to produce some chemical change.	Vary rarely with stationary liquid, but may occur due to interaction with solid support
8.	Usefulness	Limited applications due to surface catalysis	Vast applicability
9.	Applications	Useful in the separation of permanent gases and low boiling substances.	All volatile materials, except permanent gases

Advantages of gas chromatography

1. Versatility: Gas chromatography is easily adapted for the analysis of volatile solids, high boiling liquids or samples of permanent gases.
2. Convenience: It is easy to train non-technical personnel to carry out routine separations because of relatively straight forward procedure of gas chromatography.
3. Analysis time: It requires only few minutes to complete the analysis.
4. High separating power
5. Sensitivity: The sample size used is the order of 1 μL or less. Because of this high sensitivity, gas chromatography finds extensive applications.
6. Automation: It can be used for automatic monitoring of various chemical processes in which samples may be periodically taken and injected into a column for separation and detection.
7. High relative precision and easy recording of data

Disadvantages of gas chromatography

1. Gas chromatography requires that the samples must be volatile and thermally stable below 400°C.
2. Most commonly used detectors are non-selective
3. Secondary data are not reliable for qualitative analysis.

Retention time

Figure 4.4 is a typical chromatogram for a sample containing a single analyte. Retention time (t_r) can be defined as the time taken by the solute between the sample injection point to reach the detector. It is a unique characteristic of the solute and can be used for identification purposes. The solute may be identified by comparing its retention time with that of standard reference under identical conditions. In other words, the retention time of a solute is the elapsed time between the injection point and the peak maximum of the solute. The small peak on the left is for a species that is not retained by the column. Such a species may be added to as an aid in peak identification.

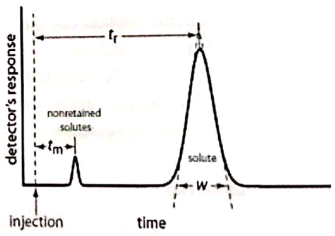


Fig.4.4 A typical chromatogram showing retention time

The time 't_m' for the unretained sample to reach the detector is called dead time. The rate of migration of the unretained species is the same as the rate of motion of the mobile phase. The volume of mobile phase that passes through the column between injection point and the peak maximum is called the retention volume. If the mobile phase is incompressible, as in the case of liquid chromatography, the retention volume will be the product of flow rate and retention time. Mathematically retention time (t_r) can be written as, shown in the following equation.

$$t_r = \frac{\text{Length of the column (L)}}{\text{Liner flow rate of solute migration (V)}}$$

Factors affecting Retention time

1. **Polarity:** The more polar a molecule, the higher will be its boiling point. Naturally this will cause a higher retention time as it will take longer time for the compound to be reach the detector.
2. **Column temperature:** Very high column temperature result in very short retention times due to the fact that all components mainly stay in the gas phase and interact little with the stationary phase.
3. **Flow rate of the carrier gas:** A high flow rte reduces retention times, as well as causing poor separation. Again, this is because the component molecules have little time to interact with stationary phase as they are quickly pushed through the column.
4. **Column length:** A longer column generally increases retention times but improves separation.
5. **Volatility of the component:** Volatile components travel through a column faster than non-volatile components. The volatility is related to the boiling point and to the size of the molecules. This means that smaller molecules have shorter retention times than the larger molecules.

Applications of Retention time

1. In the qualitative analysis of compounds.
2. In the quantitative estimation of a compound in a mixture.
3. To predict the column efficiency
4. To calculate the flow rate

4.7 COLUMN CHROMATOGRAPHY

When a column of solid is used as the adsorbent, it is called adsorption column chromatography. On the other hand, when the solid column is acting only as a support to the liquid adsorbent, it is called partition column chromatography.

The common adsorbent used in column chromatography are silica, calcium carbonate, calcium phophate, magnesia, starch etc. selection of the solvent is based on the nature of components in the mixture. Adsorption depends upon the nature of both the solvent and the adsorbent.

The rate of separation of the mixture depends up on the activity of the adsorbent and the polarity of the solvent. If the activity of the adsorbent is very high and the polarity of the solvent is low, then the separation is very slow with good separation. On

the other hand, if the activity of the adsorbent is low and the polarity of the solvent is high, the separation is rapid and gives poor separation.

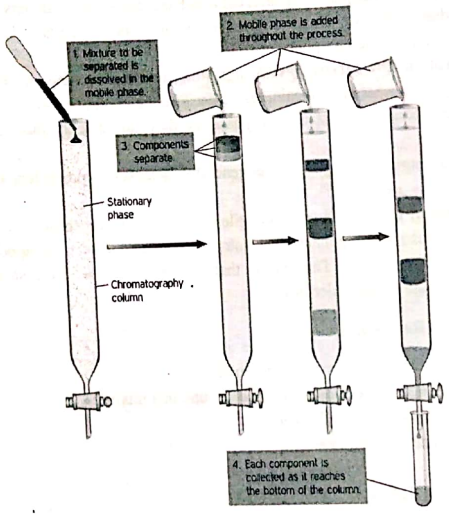


Figure 4.5 Column Chromatography

Procedure

A proper adsorbent is selected and made slurry with a suitable liquid and placed in a tube which is plugged at the bottom with glass wool or porous disc. The mixture which is to be separated is dissolved in a suitable solvent and introduced at the top of the column and is allowed to pass through the column. The components are adsorbed at different regions depending on their ability for adsorption. The component with greater adsorption power will be adsorbed at the top and the one with lower adsorption power will be adsorbed at the bottom. The banded column of adsorbed constituents is called chromatogram.In order to separate or estimate the various constituents, the chromatogram after development is pushed out of the glass tube and various zones are cut with a knife at the boundaries.

The colored components are dissolved in suitable solvents, which on evaporation give the pure components. The different components in the chromatogram can be adsorbed and collected separately by adding more solvent at the top and this process is known as ***elution.*** The process of dissolving out of the components from the adsorbent is called elution and the solvent is called elutent or eluent. The different fractions are collected separately. Distillation or evaporation of the solvent from the different fractions gives the pure components.

Solvents Used: Selection of a solvent depend on the dissolving power and boiling point (60-85°C) of the solvent. For most purposes light petroleum with a boiling point of around 85°C is recommended. The other solvents used are benzene, cyclohexane, chloroform, carbon tetra chloride, carbon disulphide, ethyl alcohol, acetic acid and ethyl acetate. Basically a solvent has to perform three important functions:

1. They dissolve the mixture of various components. Usually non polar solvents like benzene and petroleum ether are used, so the adsorption takes place more readily.
2. They are passes in to the column for the development of chromatogram. The solvent used for this purpose is known as developers. The developer is generally a solvent in which the components of the mixture are not highly soluble.
3. They are also used for removing the various constituents of the mixture from the chromatogram after it is properly developed, and are called elutent.

Applications

1. Quantitative separation of two or more components in a mixture
2. Purification of substances from their contaminants
3. Identification of products
4. Concentration of solutes from their dilute solutions

4.8 THIN LAYER CHROMATOGRAPHY

Thin-layer chromatography (TLC) is a very commonly used technique in synthetic chemistry for identifying compounds, determining their purity and following the progress of a reaction. It also permits the optimization of the solvent system for a given separation problem. In comparison with column chromatography, it only requires small quantities of the compound and is much faster as well.

Thin layer chromatography is another type adsorption chromatography, which involves separation of substances of a mixture over a thin layer of adsorbent. This technique is

based on the principle of adsorption as well as partition chromatography. TLC involves the following steps.

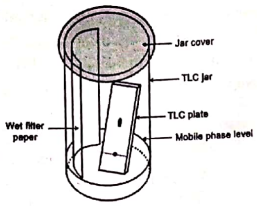


Figure 4.6 Thin Layer Chromatography

1. **Preparation of the plate:** A thin layer plate is prepared by coating a layer of sorbent (e.g. silica gel, cellulose powder or alumina) on an inert rigid backing material such as a glass plate, aluminum foil or plastic foil.
2. **Sample application:** Sample application is the most critical part of TLC. A horizontal line is drawn approximately 2.0-2.5 cm from the bottom of the plate. Sample spot of the solution is applied on this line using a syringe or micropipette (usually1,2 or 5µL).
3. **Development of Plates:** The chromatogram is developed using ascending technique in which the plate is immersed in the developing solvent to a depth of 0.5 cm. Development is allowed to proceed, until the solvent front has travelled the required distance (usually 10-15 cm). The plate is then removed from the chamber and the solvent front reached is marked using a pointer. The plate is then allowed to dry in an oven or fume cupboard.
4. **Locating and identification of solutes on the plate:** The positions of separated solutes can be located by various methods. Colored substances can be identified directly, where as colorless substances may be detected by spraying the plate with an appropriate reagent that produces colored spots in the regions which they occupy. UV lights can also be used for locating the solutes.

Retention Factor Rf

After the separation is complete, individual compounds appear as spots separated vertically. Each spot has a retention factor (Rf). It can be defined as the ratio of distance travelled by the sample spot to the distance travelled by the solvent front. Mathematically it can be expressed as

$$R_f = \frac{\text{Distance travelled by the sample spot}}{\text{Distance travelled by the solvent front}}$$

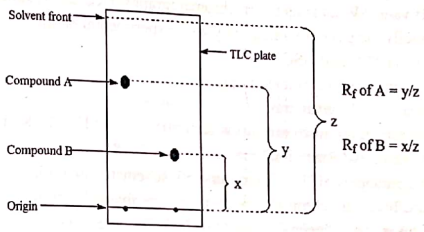


Fig. 4.7. Calculation of Rf Values

The Rf value can be used to identify the compounds due to the uniqueness of each compound in a particular solvent.

Applications of TLC

1. To check the purity of a sample.
2. For monitoring the progress of a chemical reaction.
3. Identification of a compound.
4. To determine the appropriate solvent for a column-chromatographic separation
5. To monitor a column-chromatographic separation

Advantages of TLC

1. It can be used for the separation of minute quantities of components.
2. Sharp and sensitive separation is possible.
3. Separation speed is high.
4. Wide range of stationary phase possible.

IMPORTANT QUESTIONS

1. Explain the principle, instrumentation and applications of HPLC.
2. Explain the principle, instrumentation and applications of gas chromatography.
3. What is meant by chromatography?
4. Outline the principle and applications of gas chromatography (KTU June 2016)

5. What is meant by
   I. Chromatogram.
   II. Retention time. (KU.2009, Jan)
6. What is Rf value? What is its use in chromatography?(KU.2007, June)
7. Explain briefly the gas chromatography with experimental details.
8. Write notes on TLC and GSC
9. Briefly explain column chromatography
10. What is meant by chromatogram?
11. Explain the principles, instrumentation & applications of HPLC (KTU Dec.2017)
12. Explain Rf value and Retention time. (KTU July 2018)
13. Explain the principles of HPLC. Explain with schematic diagram (KTU May2018)
14. Explain briefly the gas chromatography with experimental determination.
15. Make a comparison between GSC and GLC. (KTU June 2019)
16. Discuss the terms i) Carrier gas ii) columns iii) stationary phase and iv) detectors (KTU June 2019)

CHAPTER 5

NANOMATERIALS

5.1 INTRODUCTION

Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanoscience and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. The concept of nanotechnology was first given by renowned physicist Richard Feynman (Nobel Prize winner) in 1959 with his talk "Thers's plenty of Room at the bottom". It is already having a significant commercial impact, which will definitely increase in the future. Nanoscience is a new discipline concerned with the unique properties associated with nanomaterials, which are assemblies of atoms or molecules on a nanoscale. 'Nano' refers a scale of size in the metric system. A nanometer is 10^{-9} meter, a dimension in the world of atoms and molecules. Nanoscience and technology are emerging areas of technological importance with profound impact on a variety of physical science, engineering, biology and medical fields. Nanoscience involves the study of materials at atomic, molecular and macromolecular level where the properties of materials differ significantly from those bulk materials. Nanotechnology involves designing and producing objects at nanoscale size (~1 to 100 nm). Nanomaterials are one of the main products of nanotechnology as nanoparticles, nanotubes, nanorods etc. Nanoparticles are defined as substances where at least one dimension is less than approximately 100 nanometers. In other words, materials having at least one dimension in the nanoscale are called nanomaterials. Nanomaterials are of interest because at this scale, unique optical, magnetic, electrical, and other properties emerge. Nano carbons such as fullerenes and carbon nanotubes are excellent examples of nanomaterials.

Characterization

Materials reduced to nanometer scale show unique characteristics. For instance, opaque substances become transparent (copper), stable materials turn combustible (aluminum) and insoluble materials become soluble (gold). Therefore, materials on nanoscale find wide applications in the field of medicine, electronics and in all fields of engineering.

5.2 CLASSIFICATION OF NANOMATERIALS

Nanomaterials can be classified based on the dimensions or the nature of the materials in to different types as shown below.

Classification of nanomaterials based on dimensions: The classification of nanomaterials based on the number of dimensions are shown in Fig.5.1. According to Seigel, nanomaterials are classified as: Zero –dimensional (0D), one–dimensional (1D), two–dimensional (2D) and three–dimensional (3D) nanomaterials.

1. Zero –dimensional nanomaterials: Here, all dimensions (x,y,z) are at nanoscale, i.e., no dimensions are greater than 100 nm. It includes nanospheres and nanoclusters.
2. One–dimensional nanomaterials: Here, two dimensions (x,y,) are at nanoscale and the other is outside the nanoscale. This leads to needle shaped nanomaterials. It includes nanofibers, nanotubes, nanorods, and nanowires.
3. 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. It includes nanofilms, nanolayers, and nanocoating with nanometric thickness.
4. Three–dimensional nanomaterials: These are nanomaterials that are not confined to the nanoscale in any dimensions. 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. It includes dispersions of nanoprticles, bundles of nanowires and nanotubes as well as multinanolayers in which 0D, 1D and 2D structural elements are in close contact with each other and form interfaces.

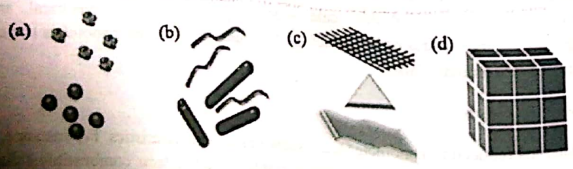
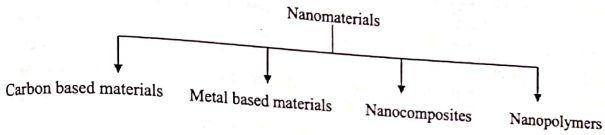


Fig.5.1 Classification of nanomaterials (a) 0D spheres and clusters, (b) 1D fibers,wires and rods, (c) 2D films, plates and networks (d) (3D) nanomaterials

Classification based on materials

Based on the nature of materials, nanomaterials are broadly classified in to four as

1. Carbon based materials
2. Nanocomposites
3. Metal based materials
4. Nano polymers



1. **Carbon based nanomaterials:** These are composed of carbon, taking the form of hollow spheres, ellipsoids or tubes. The spherical and ellipsoidal forms are referred to as fullerenes, while cylindrical forms are called carbon nanotubes. Spherical fullerenes are called Bucky balls. They consist of clusters of C_{60}, C_{70}, C_{80} etc. A carbon nanotube is a structure which seems to be formed by rolling a sheet of graphite in to the shape of a cylindrical tube. Properties and potential applications are discussed seperately in this chapter.
2. **Metal based nanomaterials:** Metal nanoparticles such as silver, gold, copper, and iron are widely used in catalysis, electronics, various sensors, photonics, imaging and environmental cleanup. Scientists have found that metal nanoparticles contain many unexpected benefits in both medical and technology fields.
3. **Nanopolymers / Dendrimers:** Dendrimers are repetitively branched molecules. The name comes from the Greek word 'Dendron' (tree). These are nanosized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can perform specific chemical functions. Dendrimers are used in molecular recognition, nanosensing , light harvesting and opto-electrochemical devises. Polymeric nanoparticles prepared from polymers are considered as potential drug delivery devices due to recent applications in drug targeting to particular organs and tissues. These nanoparticles are also used as DNA in gene therapy and delivery of proteins, peptides and genes through oral route administration. Dendrimers are one kind of polymeric nanoparticles constructed by the successive addition of layers of branching groups. The properties of dendrimers are dominated by the functional groups on the molecular surface. These are used in various applications such as a) detecting agents (dyes) b) pharmaceutically active compounds (drug delivery) c) targeting components

and d) as imaging agents. Example: Poly(amidoamine) or (PAMAM) dendrimer.

4. **Nanocomposites:** The definition of nanocomposite material has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale. The general class of nanocomposite organic/inorganic materials is a fast growing area of research. The properties of nanocomposite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. Therefore, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes and ionics, nano-wires, sensors and other systems.

5.3 PROPERTIES OF NANOMATERIALS

Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most micro structured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them: (i) large fraction of surface atoms, (ii) high surface energy, (iii) spatial confinement and (iv) reduced imperfections, which do not exist in the corresponding bulk materials.

1. **Physical properties:** Crystal structure of nanoparticles is same as bulk structure with different lattice parameters. The inter-atomic spacing decreases with size and this is due to long range electrostatic forces and the short range core-core repulsion. The melting point of nanoparticles decreases with size.
2. **Chemical properties:** A large fraction of the atoms are located at the surface of the nanomaterial which increase its reactivity and catalytic activity. The large surface area to volume ratio, the variations in geometry and the electronic structure of nano particles have a strong effect on their catalytic properties.
3. **Electrical properties:** The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic properties of the materials. Nanoparticles made of semiconducting materials like Germanium, Silicon and Cadmium are not semiconductor. Nanoclusters of different sizes will have different electronic structures and different energy level separations. So they show diverse electronic properties which depends on its size.

4. **Magnetic properties:** The magnetic moment of nanoparticles is very less compared with its bulk size. Actually, it should be possible that non-ferromagnetic bulk exhibit ferromagnetic-like behavior when prepared in nano range. Bulk Gold and Pt are non-magnetic, but at the nano size they are magnetic.
5. **Optical properties:** One of the most fascinating and useful aspects of nanomaterial is their optical properties. The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photo catalysis, photo electrochemistry and biomedicine.

5.4 PREPARATION OF NANOMATERIALS

Synthesis of nanomaterials with strict control over size, shape, and crystalline structure has become very important for the applications of nanotechnology in numerous fields including catalysis, medicine, and electronics. Synthesis methods for nanoparticles are typically grouped into two categories: "top-down" and "bottom-up" approach. The first involves the division of a massive solid into smaller and smaller portions, successively reaching to nanometer size. This approach may involve milling or attrition. The second, "bottom-up", method of nanoparticle fabrication involves the condensation of atoms or molecular entities in a gas phase or in solution to form the material in the nanometer range.

Top-down approach

The term top-down refers to reducing size of material by crushing/milling/cutting/ scaling- down by means of an external agency. This is similar to making of a small statue from a big rock or a big stone. In top down approach nanomaterials are synthesized by breaking down of bulk solids in to nanosizes. It is the predominant process in semiconductor manufacturing. Different kinds of techniques are used for scaling down bulk materials.

1. Ball milling 2. Plasma arcing 3. Laser sputtering 4. Vapor deposition
5. Nanolithography

Among all top-down approaches, ball milling has been widely used for the preparation of various nanomaterials. In this technique, bulk materials are broken in to nano-size

particles. The precursors or source materials (such as metal oxides) are crushed using high energy ball mills.

Advantages

1. High production rate 2. Wide range of techniques for crushing down the size.
3. Formation of nanoparticles can be externally controlled. 4. It is slow process.

Disadvantages

1. Formation of variable nano-size particles.
2. Surface dislocations.
3. Formation of aggregates or clusters.
4. Non-homogeneity of chemical compositions.
5. Difficulty in controlling the morphology of nanomaterials.

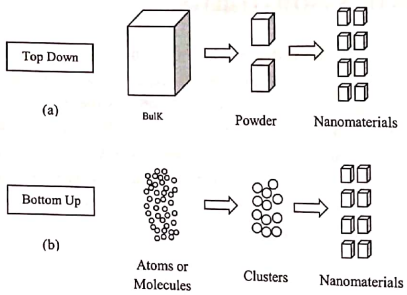


Fig. 5.2 Schematic of the basic approaches for the synthesis of nanomaterials (a)Top down and (b)Bottom up approach

Bottom- up approach

In bottom up approach, nanomaterials are synthesized by assembling the atoms/ molecules together. The techniques used are by chemical processes. It is to be noted that nature utilizes the bottom up approach to build complex systems. For example, formation of DNA by cells using enzymes by taking constituent molecules and binding them together. The bottom up approach has the following distinct advantages over the top down approach.

1. No material is wasted; as destructive processes are not involved.

2. Carbon nanotubes and silicone nanowires can be obtained using the bottom-up approach. 3. Very small geometries can be realized.

Following are common bottom–up methods for the synthesis of nanomaterials.

1. Sol-gel method 3. Hydrothermal method/ solvochemical method
2. Chemical precipitation method 4. Colloidal method

Table.5.1 Difference between Top-down and Bottom-up processes

No	Top-down method Physical method/ hard method	Bottom –up method Chemical method/ soft method
1	In top-down method, a bulk material is taken and machined to modify in to the desired shape and product.	The bottom –up method is used to build something from basic materials.
2	The ball milling is a technique where crystalline structures are broken down to nanocrystalline structures.	The self-assembly of nanomaterials, sol-gel method is some of the well-known methods in bottom up approach.
3	More expensive technique	Less expensive
4	Difficulty in controlling size and shape of nanomaterials.	Easy in controlling size and shape of nanomaterials.
5	Formation of nanoparticles can be externally controlled.	Chemical reactors create conditions for special growth.
6	There is material wastage during top-down approach	No material is wasted; as destructive processes are not involved.

Hydrolysis

Nanoparticles of metal oxides can be prepared by the hydrolysis of their alkoxide solution under controlled conditions. Commercially important nanoparticles of silica (SiO_2), titania (TiO_2), alumina (Al_2O_3) are prepared by this method. Hydrolysis occurs by the attack of oxygen contained in the water on the silicon atom. During hydrolysis, addition of water results in the replacement of [OR] group with [OH-] group. Hydrolysis occurs by the attack of oxygen on silicon atoms in silica gel. Hydrolysis can be accelerated by adding catalysts such as HCl, NH_3 etc. Hydrolysis continues until all alkoxy groups are replaced by hydroxyl groups. Subsequent condensation of silanol group (Si-OH) produces siloxane bonds (Si-O-Si), alcohol and water. For example, nano

TiO_2 can be prepared by the hydrolysis of alcoholic titanium isopropoxide. The resultant suspension obtained is peptized at a temperature of 60-70°C for a period of 20 hours. In the presence of water alkoxides gets hydrolyzed and subsequently polymerized to a three dimensional network of TiO_2.

$$Ti(OR)_4 + 4\,H_2O \rightarrow Ti(OH)_4 + 4ROH \text{ (Hydrolysis method)}$$

Where, " R" is ethyl, propyl, butyl etc.

$$Ti(OH)_4 \xrightarrow{heat} TiO_2\,x\,H_2O + (2-x)H_2O$$

The precipitate obtained is washed dried and annealed to produce nano TiO_2

Reduction Process

Nanoparticles of gold and silver can be prepared by the reduction of their respective solutions using reducing agents. In this method there is no control over the size of particles. The method can be divided in to two types.

1. **Reduction using reducing agents:** In this type of reduction, reducing agents such as sodium borohydride, ascorbic acid, glucose etc. are used along with a protective agent. For example,

$$MCl_x + x\,NaB(C_2H_5)_3\,H \longrightarrow M + X\,NaCl + B(C_2H_5)_3 + \frac{1}{2}xH_2$$

Nanoparticles of Molybdenum (Mo with dimensions in the range of 1-5 nm) can be prepared by reducing Molybdenum chloride in toluene with $NaB(C_2H_5)_3H$ as reducing agent at room temperature.

$$MoCl_3 + 3\,NaB(C_2H_5)_3\,H \longrightarrow Mo + 3\,NaCl + 3B(C_2H_5)_3 + \frac{3}{2}H_2$$

2. **Electro reduction**: For example, copper nanoparticles can be prepared by this method. The electro reduction process chamber consists of copper plating bath containing homogeneously acidified $CuSO_4$ solution. The nanoparticles formed as spongy layers of ball structures at the cathode. The spongy layers of copper can be easily separated to give fine particles.

Nanoparticles of Pt can be prepared by the reduction of H_2PtCl_6 dissolved in water with the help of hydrogen plasma generated just above the aqueous solution. The average particle size of around 2 nm can be prepared by this method.

Silver nanoparticles of uniform size and morphology have been prepared at room temperature using ascorbic acid as reducing agent and sodium polyacrylate as a protective agent in aqueous solution.

Hydrothermal Synthesis

Hydrothermal synthesis is typically carried out in a pressurized vessel called an autoclave with the reaction in aqueous solution. The temperature in the autoclave can be raised above the boiling point of water, reaching the pressure of vapor saturation. Hydrothermal synthesis is widely used for the preparation of metal oxide nanoparticles which can easily be obtained through hydrothermal treatment of peptized precipitates of a metal precursor with water. The hydrothermal method can be useful to control grain size, particle morphology, crystalline phase and surface chemistry through regulation of the solution composition, reaction temperature, pressure, solvent properties, additives and ageing time. The method can be used to prepare thermodynamically stable states including new materials that cannot be formed from other synthetic routes.

Sol-Gel Process or Chemical Solution Deposition

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 and consists of the chemical transformation of a sol in to a gel state and successive gelation and solvent removal. Sol-gel processes are wet-chemical technique for the preparation of metal oxides or hybrid polymers. The sol is a name of a colloidal solution made of solid particles few hundred nm in diameter, suspended in a liquid phase.

The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds, which by hydrolysis and polycondensation reactions to form the sol. The rates of hydrolysis and poly condensation reactions are governed by temperature, pH, molar ratio, concentration of catalysts etc.

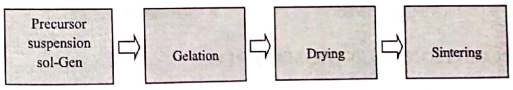


Fig.5.3. Schematic of Sol –Gel process

The sol - consisting in a suspension of the precursors – is transformed to a gel consisting of a liquid and a solid phase. The chemical reactions that occur during a sol-gel process are hydrolysis, poly-condensation, and gelation. Hydrolysis of metallic alkoxides or metal salts can give a sol at a suitable temperature and pH. The impurities present in the sol can be purified by converting it into a gel by changing the pH or other factors. The

purified gel on drying give solid nanoparticles. For example aluminium oxide alkoxide nanoparticles are obtained by hydrolysis of aluminum alkoxide by sol gel technique. Various steps involved are:

1. Formation of stable sol solution
2. Gelation via a polycondensation or polyesterification reaction
3. Gel ageing into a solid mass.
4. Drying of the gel to remove liquid phases. This can lead to fundamental changes in the structure of the gel.
5. Dehydration at temperatures as high as 8000°C
6. Densification and decomposition of the gels at high temperatures.

Sol-Gel process advantages

The main benefits of sol–gel processing are

1. The high purity and uniform nanostructure.
2. Low processing temperatures.
3. The process is cheap and is of low cost
4. Homogeneity of the final product up to atomic scale
5. The ability to control the porosity for producing high surface area materials

Applications of Sol-Gel process

1. Solar collectors and cells
2. Anti-reflecting coating
3. Optical switching
4. Fuel cells
5. Non-volatile memory
6. Refractory ceramics

5.5 APPLICATIONS OF NANOMATERIALS

Nanomaterials are materials possessing grain sizes of the order of a billionth of a meter. They manifest extremely fascinating and useful properties, which can be exploited for a variety of structural and nonstructural applications. Nanochemistry has applications ranging from engineering to medicine.

Electronics

a. Today's solar cells utilize only 40% of solar energy. Nanotechnology could help to increase the efficiency of light conversion using nanostructures.
b. The efficiency of internal combustion engine is about 30-40%. Nanotechnology could

improve combustion by designing catalysts with maximized surface area.
c. The use of batteries with higher energy content is possible with nanomaterials.

Tissue Engineering: This may replace today's conventional treatment like organ transplants/artificial implants. Advanced forms in tissue engineering may lead to life extension. It can repair damaged tissue.

Biomaterials: Food quality monitoring and identification of bacteria using bio-sensors are classical examples of the application of nanotechnology. Nanocomposite coating can act as antimicrobial agents.

Longer-Lasting Medical Implants: Medical implants with nanomaterials are hard, wear-resistant, corrosion-resistant and biocompatible. These materials are porous and can withstand up to 100 times their weight. This can reduce implant replacements and reduction in surgical expenses.

Better Insulation Materials: Nanocrystalline materials synthesized by the sol-gel technique result in foam like structures called "aerogels." By using aerogels for insulation, heating and cooling bills are drastically reduced, thereby saving power and reducing the attendant environmental pollution. They are also being used as materials for "smart" windows, which darken when the sun is too bright (as in changeable lenses in prescription spectacles and sunglasses) and they lighten themselves, when the sun is not shining too brightly.

Tougher and Harder Cutting Tools: Cutting tools made of nanocrystalline materials are much harder, much more wear-resistant, and last longer than their conventional counterparts. They also enable the manufacturer to machine out various materials much faster, thereby increasing productivity and significantly reducing manufacturing costs.

Elimination of Pollutants: Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power next generation equipment to prevent environmental pollution arising from burning gasoline and coal.

High Energy Density Batteries: Nanocrystalline materials synthesized by sol-gel techniques are ideal for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than their conventional counterparts.

High-Power Magnets: Magnets made of nanomaterials possess very unusual magnetic properties. Typical applications for these magnets include quieter submarines, automobile

alternators, power generators, motors for ships, ultra-sensitive analytical instruments, and magnetic resonance imaging (MRI) in medical diagnostics.

High-Sensitivity Sensors: Sensors made out of nanocrystalline materials are extremely sensitive to the change in their environment. Typical applications for sensors made out of nanocrystalline materials are smoke detectors, ice detectors on aircraft wings, automobile engine performance sensors etc.

Automobiles with Greater fuel efficiency: Currently, automobile engines waste considerable amounts of gasoline, thereby contributing to environmental pollution. Also, automobiles waste significant amounts of energy by losing the thermal energy generated by the engine. The engine modified with nanomaterials can retain heat much more efficiently and result in complete and efficient combustion of the fuel.

Aerospace Components with Enhanced Performance Characteristics: By making the components out of nanomaterials strength and life of aircraft increases considerably. They can operate at higher temperatures, and fly faster and more efficiently (for the same amount of aviation fuel). In spacecrafts, nanomaterials can operate at much higher temperatures.

Longer-Lasting Satellites: Nanomaterials can increase the life of satellites by enhancing life and performance characteristics.

Medicine and Health: Nanotechnology will provide new tools for medicine. It could radically change the method of surgery. It will make it possible to do molecular-scale surgery to replace defective cells, repair and rearrange cells. Since disease is the result of physical disorder, misarranged molecules and cells, medicine at this level should be able to cure most diseases. Mutations in DNA could be repaired and cancer cells, toxic chemicals and viruses could be destroyed through the use of medical nanodevices. There are numerous other potential applications of nanoscience to biology.

a. Rapid, efficient genome sequencing, revolutionizing diagnostics and therapeutics.
b. Effective and less expensive healthcare using remote devices.
c. New formulations and routes for drug delivery that enormously broaden their therapeutic potential by effecting delivery of new types of medicine to previously inaccessible sites in the body.
d. More durable, rejection-resistant artificial tissues and organs.
e. Sensor systems that detect emerging disease in the body, which will shift the focus of patient care from disease treatment to early detection and prevention.

5.6 FULLERENES

Fullerene is an allotrope of carbon. The most common fullerene molecule is having a molecular formula C_{60}. It was discovered by H.W.Kroto and R.Smalley at Rice University, USA in 1985. It is popularly known as Buckminster fullerene in honor of the American architect Buckminster Fuller, who designed geodesic dome structure based on hexagons and pentagons. The shape of C_{60} resembles that of such domes designed by Fuller.

Preparation: Fullerenes are prepared by vaporizing a graphite rod in a helium atmosphere. Mixture of fullerenes like C_{60}, C_{70} etc, are formed which are separated by solvent extraction. Pure C_{60} is isolated from this mixture by column chromatography.

Structure: The C_{60} molecule has a truncated icosahedron structure. An icosahedron is a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. A carbon atom is present at each vertex of this structure. The molecule is aromatic and has several resonance structures. The valencies of each carbon atom are satisfied by two single and one double bond. C_{60} is also known as buckyball as it is a spherical cluster of carbon atoms arranged in series of 5- and 6- member rings to form a soccer ball shape. In the solid state, C_{60} form a normal face-centered cubic lattice just as is observed for cubic-close packing of spheres. Usually the carbon atoms in fullerenes are in the sp^2 hybridized state.

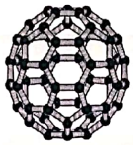


Fig.5.4 The structure of C_{60}: "Buckminsterfullerene"

Properties of Fullerenes

1) Fullerene is a black powdery material.
2) It forms deep magenta solution, when dissolved in benzene.
3) It is very tough and thermally stable (it can be sublimed at 600° C under vacuum).
4) It exists as a discrete molecule, unlike the other two allotropes of carbon (viz. diamond and graphite).

5) It can be compressed to lose 30% of its volume without destroying its carbon cage structure.

Potential applications of fullerenes:

1) It is suitable for use as a lubricant due to its spherical structure. The Bucky balls would act as molecular ball bearings.
2) It can be used as superconductor when doped with alkali metals (e.g., $C_{60}K_x$)
3) It can also be used as soft ferromagnet (e.g., TDAE C_{60}).
4) Other possible areas of uses are:
   (i) Electronic and Microelectronic devices (ii) Non-linear optical devices

5.7 CARBON NANOTUBES

The discovery of carbon nanotubes (CNT) in 1991 opened up a new era in materials science. These incredible structures have an array of fascinating electronic, magnetic and mechanical properties. CNT are at least 100 times stronger than steel, but only one-sixth as heavy, so nanotube fibers could strengthen almost any material. Nanotubes can conduct heat and electricity far better than copper. CNT are already being used in polymers to control or enhance conductivity and are added to anti-static packaging. A carbon nanotube is a tube-shaped material, made of carbon, having a diameter measuring on the nanometer scale.

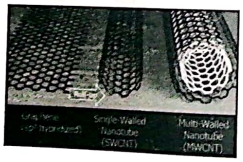


Fig. 5.5 Carbon nanotubes

A carbon nanotube is a structure which seems to be formed by rolling a sheet of graphite in to the shape of a cylindrical tube. Nanotubes are categorized as single-walled nanotubes (SWNT) and multiwalled nanotubes (MWNT). Single- walled nanotubes have a diameter close to 1 nm, with a tube length that can be many millions of times longer. The structure of a SWNT can be conceptualized by wrapping a one- atom- thick

layer of graphite called graphene in to a seemless cylinder. Multi-walled carbon nanotubes consits of multiple concentric nanotube cylinders.

Properties of carbon nanotubes

1. Carbon nanotubes are very strong.
2. Their tensile strength is 100 times greater than that of steel of the same diameter.
3. Young'smodulus is about 5 times higher than that of steel.
4. They have high thermal conductivity –more than 10 times that of silver.
5. They conduct electricity better than metals.
6. Electrons travelling through a carbon nanotube behave like a wave in a smooth channel. This movement of electrons within a nanotube is called " ballistic transport".
7. They are of light weight and density about one fourth of steel.
8. They are sticky due to Vander Waal's force of attraction.

Applications of Carbon Nanotubes

Carbon nanotubes are used for a wide range of existing and emerging applications . Some of the important applications of carbon nanotubes are outlined herewith.

1. SWNTs are used in solar panels due to their strong UV absorption characteristics.
2. MWNTs are used in Lithium Ion batteries to enhance their life cycle.
3. CNTs can be used as multifunctional coating material.
4. CNTs are used as reinforcing materials in a wide range of aerospace and automotive applications.
5. CNTs are used for applications in energy storage devises.
6. CNTs are used in various types of Biochemical sensors.
7. They act as molecular size test tubes or capsules for drug delivery.
8. Depending on their size, they act as electrical conductors or semiconductors.
9. They are used as tips for analysis of DNA and proteins by atomic force microscopy.

5.8 SCANNING ELECTRON MICROSCOPE (SEM)

Surface Characterization Techniques

Nanoparticles have vast medical, environmental and engineering applications. The properties of nanoparticles are dependent on size and structure. Hence it is important to understand the structure of nanoparticles as it enables us to correlate the physicochemical properties of nanomaterials with their chemical, ecological or biological responses.

Characterization of nanoparticles helps in understanding the physical and chemical properties of nanoparticles. It also helps in determining the structure at atomic and microscopic level. Bulk properties like shape, size, phase, electronic structure and crystallinity and surface properties like arrangement of surface atoms, surface area, and surface composition are determined by various characterization techniques.

To study the structure of nanoparticles they are observed using electrons, photons, scanning probes, ions, atoms etc. The commonly used techniques are Brunauer-Emmet-Teller (BET) surface area analysis, Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Powder X-ray diffraction (XRD), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Low Energy Electron Diffraction (LEED), Ultraviolet-Visible Spectroscopy, Nuclear Magnetic Resonance Spectroscopy (NMR) etc. A brief description of SEM is given below.

Scanning Electron Microscope (SEM)

The word microscope is derived from the Greek word *micros* (small) and *skopeo* (look at). In 1935 German Physicist Max Knoll, introduced the concept of a scanning electron microscope. He proposed that an image can be produced by scanning the surface of sample with a finely focused electron beam. Another German Physicist Manfred von Ardenne explained the principles of the technique and elaborated upon beam-specimen interactions. He went on to produce the earliest scanning electron microscope in 1930s.

Just like any microscope, the primary function of the scanning electron microscope (SEM) is to enlarge small features of objects otherwise invisible to human sight. It does that by way of using electron beam rather than light which is used to form images in optical microscopes. The images are obtained by scanning an electron beam of high energy on the sample surface in a raster pattern, hence the name scanning electron microscope. By virtue of its smaller wave length, electrons are able to resolve finer features / details of materials to a much greater extent compared with optical light. A Modern SEM can magnify objects up to one million times their original size and can resolve features smaller than 1 nm in dimension. Similarly, electron beam interaction with specimen emits X-rays with unique energy that can be detected to determine the composition of material under examination. The SEM is, therefore, a tool used for material characterization that provides information about the surface or near surface, composition, and defects in bulk materials. It allows scientists to observe surfaces at submicron and nano-level to elaborate material properties. It has emerged as one of the

most powerful and versatile instruments equally valuable to materials and life scientists working in wide ranging industries.

Instrumentation of SEM

A schematic representation of an SEM is shown in the Fig.5.6 with all essential components and features.

1. **Electron gun:** Located at the top of the column where free electrons are generated by thermionic emission from a tungsten filament at ~2700K. The filament is inside the Wehnelt which controls the number of electrons leaving the gun. Electrons are primarily accelerated towards an anode that is adjustable from ~~200~~ an anode that is adjustable from 200V to 30 kV.
2. **Condensing Lens**: All the electrons are negatively charged and hence the electrons in a beam will repel each other. This will increase the beam diameter and will adversely affect the resolution of the image. Hence electrical coils are used to squeeze the beam to a diameter of 5 nm or less. These are called condensing lens coils.

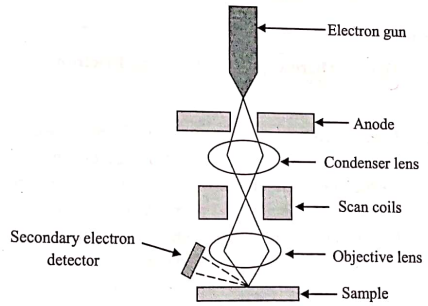


Fig.5.6 Scanning Electron Microscope

3. **Deflection coils**: There are many differences between the SEM and optical microscopes, in terms of the techniques used. An electron beam is not used in the same way as light in optical microscope. In light microscope, the entire sample (or the region of interest) is illuminated simultaneously. In SEM, only one tiny spot is 'illuminated' with the beam. Then the beam is moved in small steps

(usually in nm) by a process called 'rastering'. This is similar to moving electron beam in a cathode ray tube (CRT). By applying suitable electric field, the beam can be made to 'walk' in the X and Y direction. The entire sample is analyzed by scanning the electron beam. Hence the instrument is called scanning electron microscope. The coils used for moving the electron beam are called deflection coils.

4. **Objective Lens:** After the deflection coil, there is another electromagnetic lens called objective lens which can focus the electron beam down to the sample.
5. **Sample Chamber:** After passing through the objective lens, the electron beam passes in to the sample chamber. This chamber holds the sample under vacuum to eliminate interference of unwanted particles.
6. **Detectors:** Finally there are detectors. These are used to produce magnified images, and collect other data. They will detect various signals given off by the sample as it is struck by electrons from the beam scanning over it. These signals include secondary electrons, back scattered electrons and X-rays among others. The display monitor can be used for the display of images.

Table 5.2 Comparison between Optical and Scanning Electron Microscope (SEM)

Parameter	Optical Microscope	Scanning Electron Microscope
Illumination Source	Light source	Electrons from an electron gun
Type of Lens	Glass	Electromagnetic lens
Magnification method	By the movement of lens	Changing the current through the lens
Sample viewing	Eye piece (Ocular)	Monitor or Camera
Use of vacuum	No vacuum required	Entire path from gun to camera under vacuum

Applications:

1. In morphological and topographical analysis of materials.
2. In materials science for research, quality control and failure analysis.
3. In Semiconductor inspection
4. In microchip design and production.
5. Criminal and other forensic investigations utilize SEMs to uncover evidence.
6. In biological sciences, SEMs are used to study bacteria and viruses.
7. In Geological studies for weathering processes and morphology of the samples.

8. In medical science to compare blood and tissue samples.
9. In assessing the length of nanowires.

Advantages of SEM

1. It gives detailed 3dimensional topographical imaging and information.
2. Modern SEMs allow for the generation of data in digital form.
3. Works very fast
4. Most SEM samples require minimal preparation actions.

Disadvantages of SEM

1. SEMs are very expensive.
2. Special training is required to operate SEM
3. Preparation of samples can result in artifacts.
4. Limited to solid samples.
5. Small risk of radiation exposure.

IMPORTANT QUESTIONS

1. Explain briefly the classification of nanomaterials with examples.
2. Write note on the applications of nanomaterials (K.U)
3. How nanomaterials differ from bulk materials in their physical properties.
4. Relate the structure of fullerenes and CNTs.
5. What are the advantages of SEM?
6. What are the important applications of SEM.
7. Draw the instrumentation of SEM with important components.
8. Briefly describe SEM with advantages and applications.
9. Write a note on biological nanomaterials (KTU June 2016)
10. Write a note on structure and applications of fullerene (KTU June 2016)
11. Briefly outline the chemical synthesis of nanoparticles (KTU 2017 December)
12. Discuss the classification of nanomaterials (KTU 2017 December)
13. Give any two applications of carbon nanotubes (KTU 2018 April)
14. Describe any two methods for the preparation of nanomaterials (KTU 2018 April)
15. Brief out fullerenes. Give two properties (KTU July 2018)
16. What are CNTs? How they are classified? List two applications. (KTU July2018)
17. Explain the classification of nanomaterials based on dimensions with examples.
18. Discuss chemical method for the preparation of nanomaterials.(KTU July2018)
19. What are carbon nanotubes? (KTU June 2019)