

Principle Paper chromatography separation of mix. A substance is mainly done by flow of solvents on Watman chromatography, filter paper.

Stationary phase is cellulose. and mobile phase is organic solvent which is _____

Types :- Paper partition chromatography.
Absorption paper chromatography.

TGA

(Thermo Gravimetric Analysis).

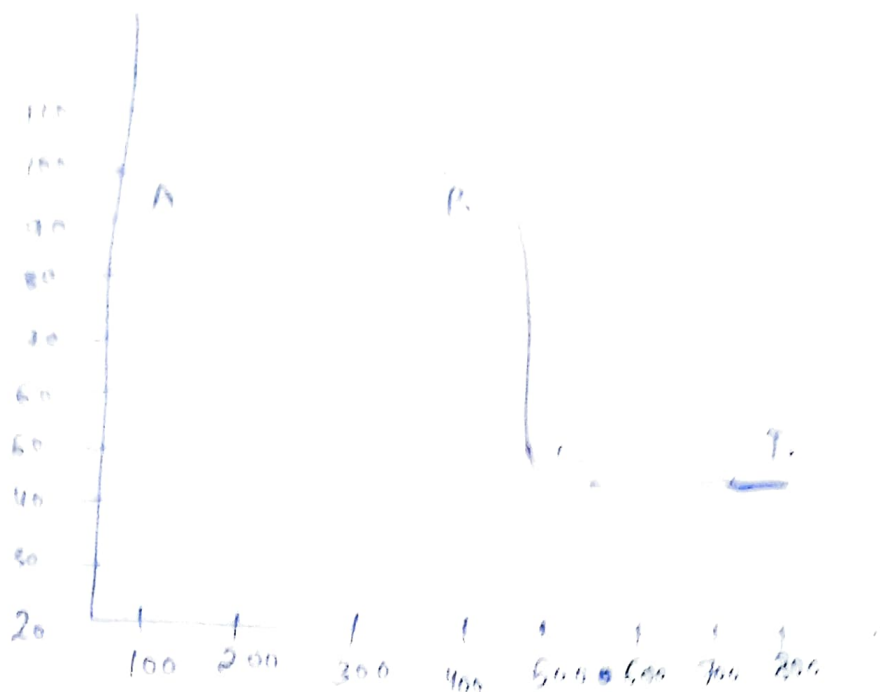
Principle:- In thermogravimetric analysis the sample is heated in a given environment (Air, N_2 , CO_2 , He etc). at controlled rate.

- $\Rightarrow$ The change in the weight of the substance is recorded as a function of temp. or time.
- $\Rightarrow$ The temp. is increased at a constant rate for a known initial weight of the substance and the changes in weights are recorded as a function of temp. at different time interval. temperature is called thermo gravimetric curve or thermogram.

Example:- TGA Curve for $AgNO_3$. (Silver nitrate)

The horizontal portion of the curve indicates that there is no change in weight (AB and CD) and the portion BC indicates that there is weight change.

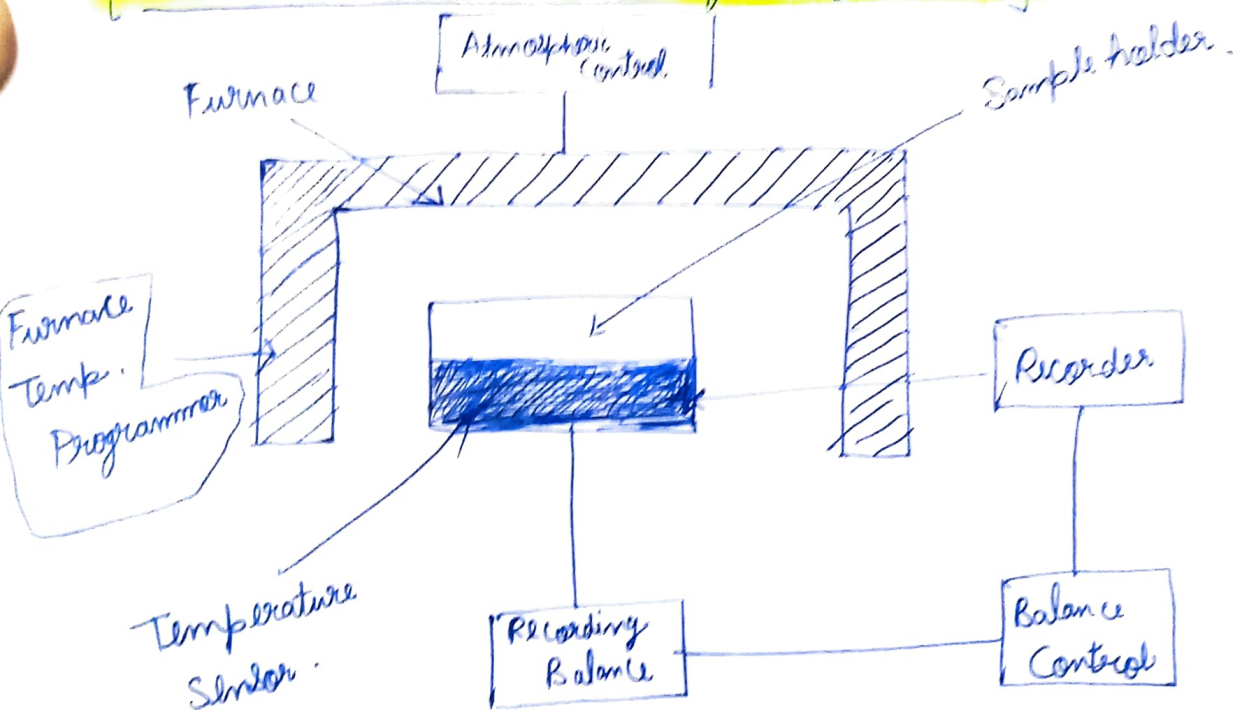
The weight of the substance ($AgNO_3$) remains constant upto a temp. of $473^\circ C$ indicating that $AgNO_3$ is thermally stable upto a temp. of $473^\circ C$.



The diagram indicates the TGA curve for AgNO_3 .



=> [Instrumentation / Block diagram of TGA]



① Sample Holder :- Shape, Size and material of the sample holder (crucible) made of quartz, Platinum, Ceramics, Stainless Steel.

② Recording Balance :- Accuracy, Sensitivity and Capacity
Similar to analytical balance.
Automatic weight adjustment.
Rapid response to weight changes.

③ Furnace and Furnace temp. Controller
→ Choice of the furnace heating element.
→ Depends upon the temp. range being studied.

④ Temperature Sensor :- Common method for measurement of temp. use of a thermocouple. for temp. upto 1100°C . Chromel or Alumel thermocouple.
→ For temp. upto 1750°C - Thermocouples alloys of Platinum or Rhodium are used.
→ For higher temp. tungsten thermocouple.

Application of TGA :-

① A TGA can be used for materials. characterization through analysis of characteristic decomposition patterns.

② It is an especially useful technique for the study of Polymeric materials including thermoplastic thermosets, elastomers etc.

③ TGA is used to study of the kinetics of the reaction rate constant.

④ For studying the sublimation behaviour of various substances.

⑤ From TGA, we can determine the purity and thermal stability of both Primary and Secondary Standard.

Factors affecting of TGA :- The factors which may affect the TGA curves are classified into two main groups :-

- ① Instrumental factors
 - ② Sample characteristics.
- ① Instrumental factors :-

(a) Furnace heating rate :- The temperature at which the compound (or sample) decompose depends upon the heating rate. When the heating rate is high, the decomposition temp. is also high. A heating rate of $3-5^{\circ}\text{C}$ per minute is usually recommended for reliable and reproducible TGA.

(b) Furnace atmosphere :- The atmosphere inside the furnace surrounding the sample has a profound effect on the decomposition temperature of the sample. A pure N_2 gas from a cylinder passed through the furnace, which provides an inert atmosphere.

(c) Particle size of the sample :- The particle size of the sample should be small and uniform. The use of large particle or crystal may result in apparent very rapid weight loss during heating.

Chromatography :- Chrom

Principle :- Chromatography is based on the principle where molecules in mixture applied onto the surface or into the solid and fluid. Stationary phase is separating from each other while moving with the aid of a mobile phase.

Three Components thus form the basis of the Chromatography technique :-

- 1) Stationary Phase :- This Phase is always composed of a solid phase or a layer of a liquid adsorbed on the surface of a solid support.
- 2) Mobile phase :- This Phase is always composed of "liquid" or a 'gaseous component'.
- 3) Separated molecules :- The type of interaction b/w the stationary phase, mobile phase and substances contained in the mixture is the basic component effective on the separation of molecules from each other.

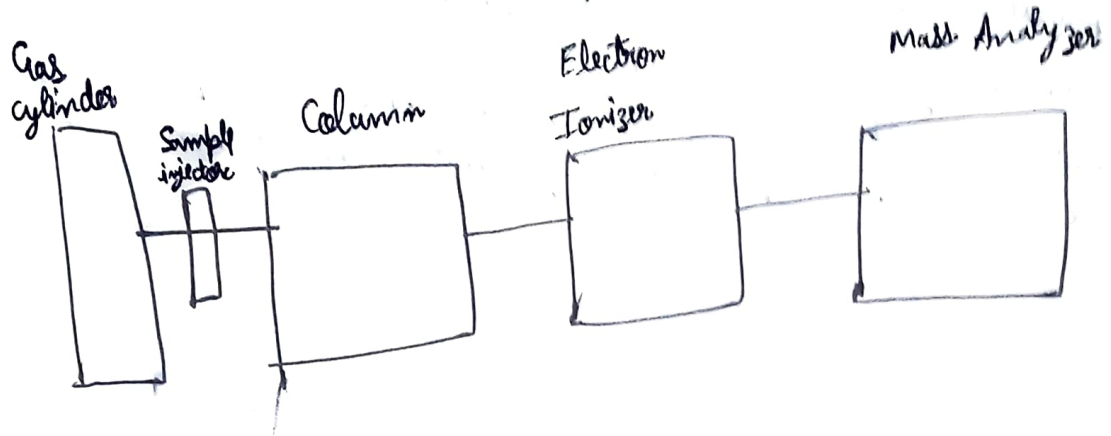
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Types of Chromatography :-

- 1) Substances can be separated on the basis of a variety of methods and the presence of characteristics such as size and shape, total charge, hydrophobic groups present on the surface and binding capacity with the stationary phase.
- 2) This leads to different types of chromatography techniques, each with their own instrumentation and working principle.
- 3) For instance, four separation techniques based on molecular characteristics and interaction type use mechanisms of ion exchange, surface ~~adsorption~~ adsorption, partition and size exclusion.
- 4) other chromatography techniques are based on the stationary bed, including Column, Thin

layer and paper chromatography.

Applications of chromatography.



Polarography

Polarography

In 1922, J. Heyrovsky discovered a technique which is called as Polarography. by which mixture can be analyze quantitatively and qualitatively.

Principle :-

⇒ It is the Gradually increasing potential (voltage) is applied between polarisable and non-polarisable electrode and the corresponding current is recorded.

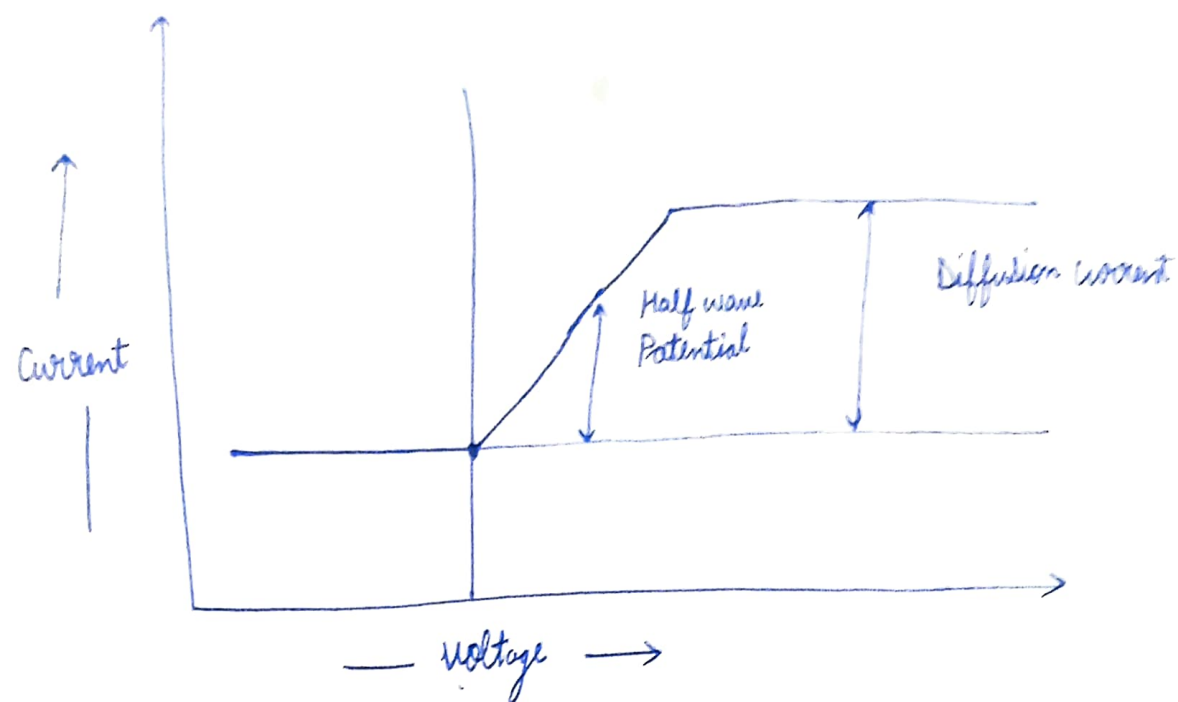
(i) Polarisable electrode :- Dropping Mercury electrode (DME).

(ii) Non-Polarisable electrode :- Saturated Calomel electrode

⇒ A Sigmoid shape current-voltage curve is obtained from which half wave potential as well as diffusion current is calculated.

⇒ Half wave Potential :- It shows the characteristics of ion present in solution. (qualitative analysis).

⇒ Diffusion current :- It shows the Concentration of a particular compound. (quantitative analysis).



Polarographic measurement:-

- => Polarographic measurement is governed by Ilkovic equation.
- => Ilkovic equation is a linear relation is used in polarography relating the diffusion current (i_d), and the concentration of the non-polarisable electrode, i.e. if i_d is known to us we can find out the Concentration of a ~~sub~~ ~~concentration~~ the solution.

Where
$$i_d = 607 n C D \sqrt{\frac{1}{2} m \frac{2}{3} t \frac{1}{6}}$$

i_d = Diffusion current in microamperes.

607 = Constant

n = No. of e^-

D = Diffusion Coefficient.

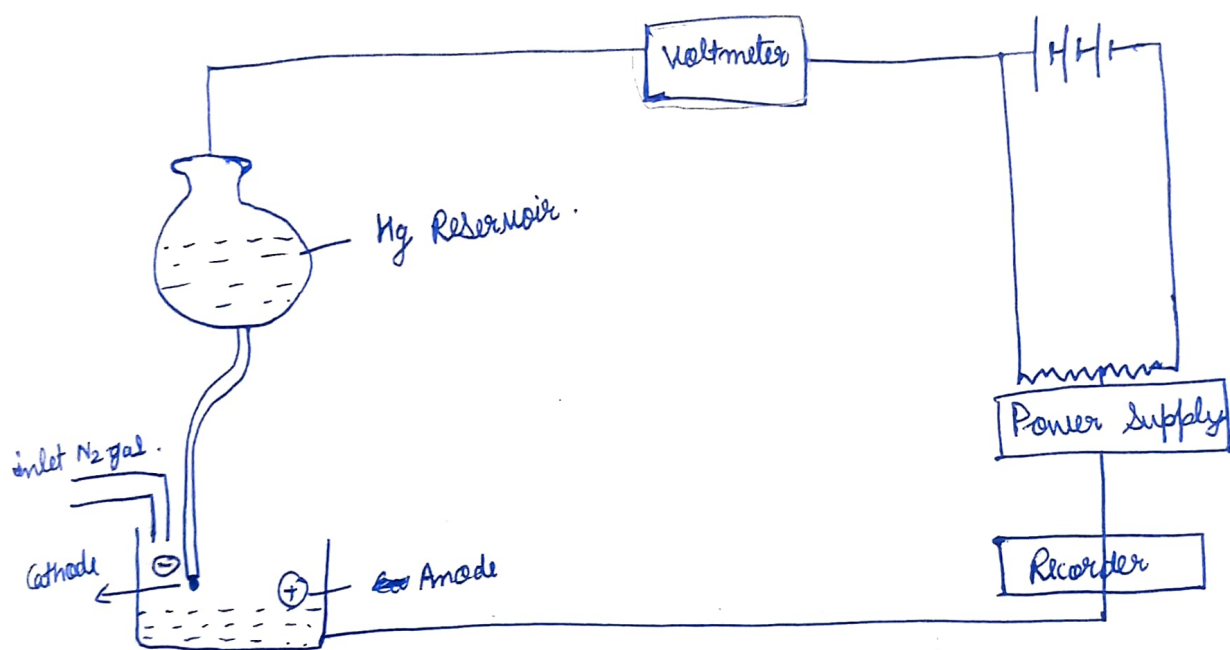
m = Weight of Hg flowing.

t = Drop time in seconds

C = Concentration in mol/L.

Dropping Mercury electrode (DME)

- Dropping mercury electrode is a working electrode arrangement for Polarography.
- In which Mercury continuously drops from a reservoir into a capillary tube into the solution.
- The optimum interval between drops for most analyses is between 1 and 5 s.



Working of Polarography

- 1) Dropping mercury electrode is a polarizable electrode and act as a both anode and Cathode.
- 2) The Pool of mercury acts as Counter electrode i.e. anode if DME is Cathode or Cathode if DME is anode.
- 3) To analyze solution, electrolyte like KCl is added.
- 4) Pure nitrogen gas is pass in solution to expel out oxygen.
- 5) Maximum suppressors are added

- 6> Then, gradually increasing voltage is applied to the polarographic cell and current is recorded.
- 7> Graph is plotted between voltage applied and current.
- 8> The graph is Polarograph and the apparatus is known as Polarogram.

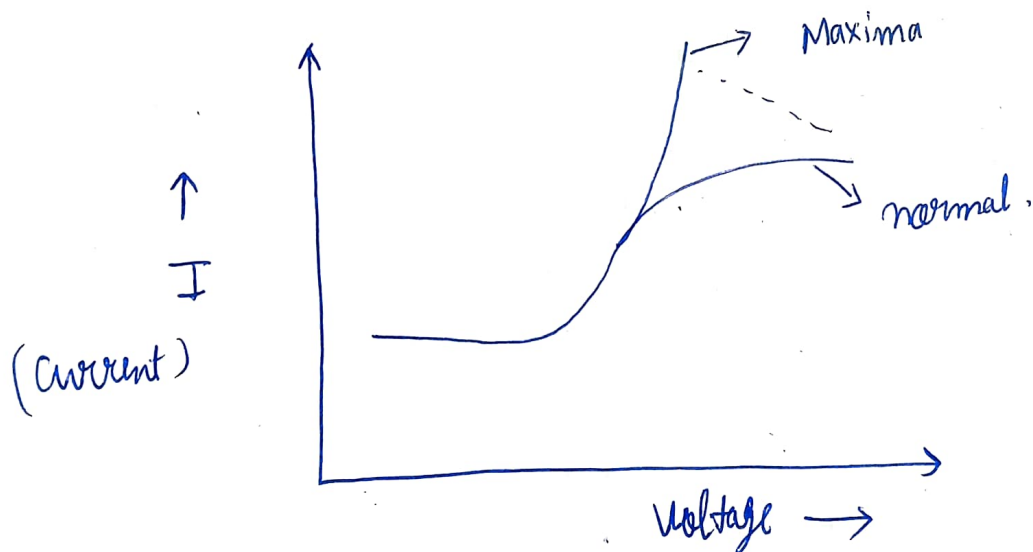
Polarographic maxima:-

When current increase ~~the~~ to cross the limit while increasing voltage that is called Polarographic maxima.

Cause:- This is arise because of the Catalytic discharge of ion.

Effect:- Leads to a error in determining half wave potential and diffusion current.

Elimination:- Maximum suppressors ~~to~~ are added to eliminate the polarographic maxima.



Disadvantages:-

- 1> Capillary is very small and thus can be easily blocked
- 2> Mercury is very toxic
- 3> Surface area of each drop of mercury is never constant.
- 4> It cannot be used at higher positive potential due to oxidation of mercury.

Advantages of Polarography:-

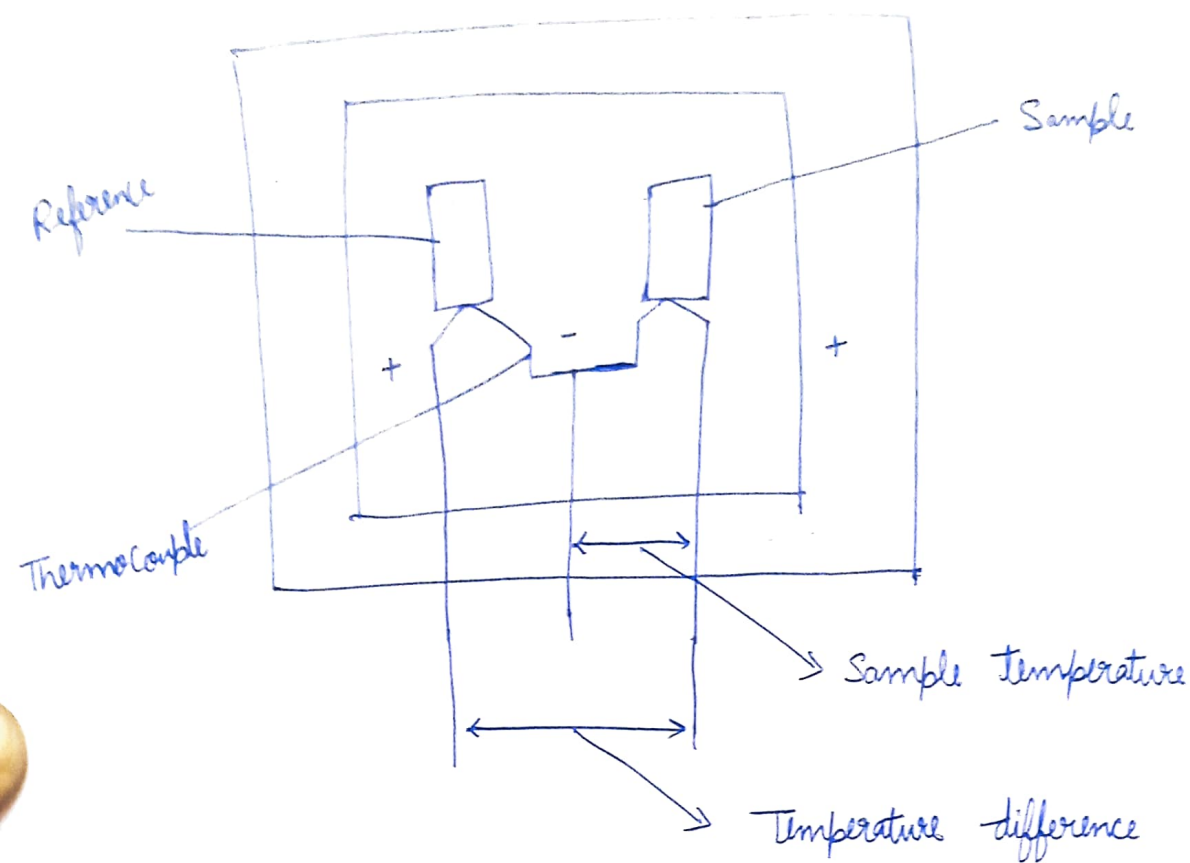
- 1> only small value of sample is required
- 2> Turbid and Colored solution can be analysed.
- 3> Electrode can be renewed and thus eliminate poisoning effect.
- 4> The surface area can be calculated from the weight of the drop.

DTA [Differential Thermal Analysis]

Principle:- A technique in which the difference in temp. between the sample and a reference material is monitored against time or temperature. While the temperature of the sample in a specified atmosphere is programmed.

$$\Delta T = T_R - T_S$$

Instrumentation of DTA / Block Diagram :-

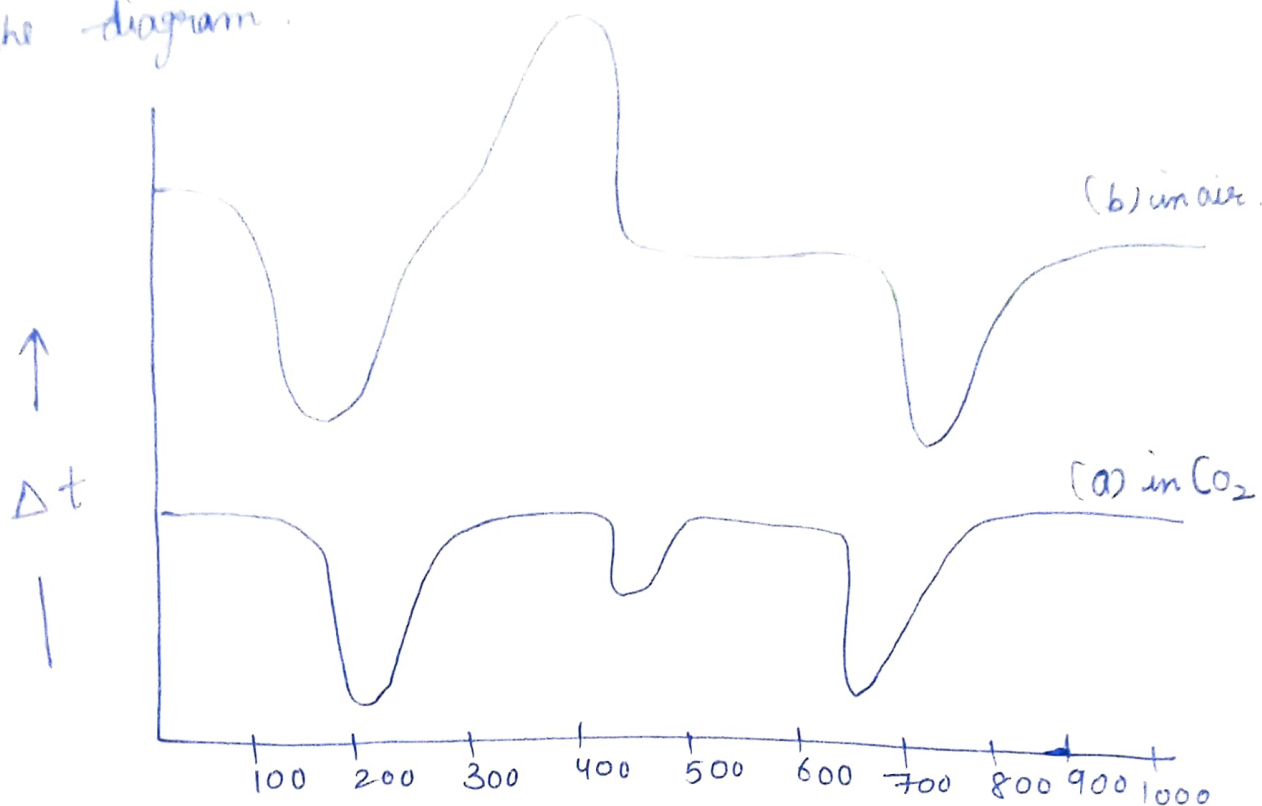


The DTA apparatus consists of the following components:-

- 1) Furnace sample and reference holder with thermocouple assembly.
- 2) Sample holder furnace [To heat sample].
- 3) Furnace atmospheric control system [To maintain a suitable atmosphere in the furnace and sample holder].
- 4) Furnace temperature controller [To increase the furnace temperature steadily].
- 5) Low level DC amplifier.
- 6) Recording device (Recorder).

⇒ DTA curve of calcium oxalate monohydrate:-

⇒ The DTA curve for the decomposition of calcium oxalate monohydrate ($\text{Ca}(\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O})$) is shown in the diagram.



The thermogram shows the decomposition in CO_2 atmosphere and in air atmosphere.

⇒ Applications of DTA:-

→ DTA curves for two substances are not identical. Hence they serve as a fingerprint for various substances.

→ used to study the characteristics of polymeric material.

→ DTA widely used in the pharmaceutical and food industries.

→ DTA may be used in Cement Chemistry, mineralogical research and in ~~an~~ environmental studies.

→ used for the determination of heat of Reaction, specific heat and energy change occurring during melting etc.

⇒ Factors affecting DTA Curve :-

1> Instrumental factors :- → Size and shape of the sample and furnace holder.

→ material from which sample holder is made and its corrosive attack.

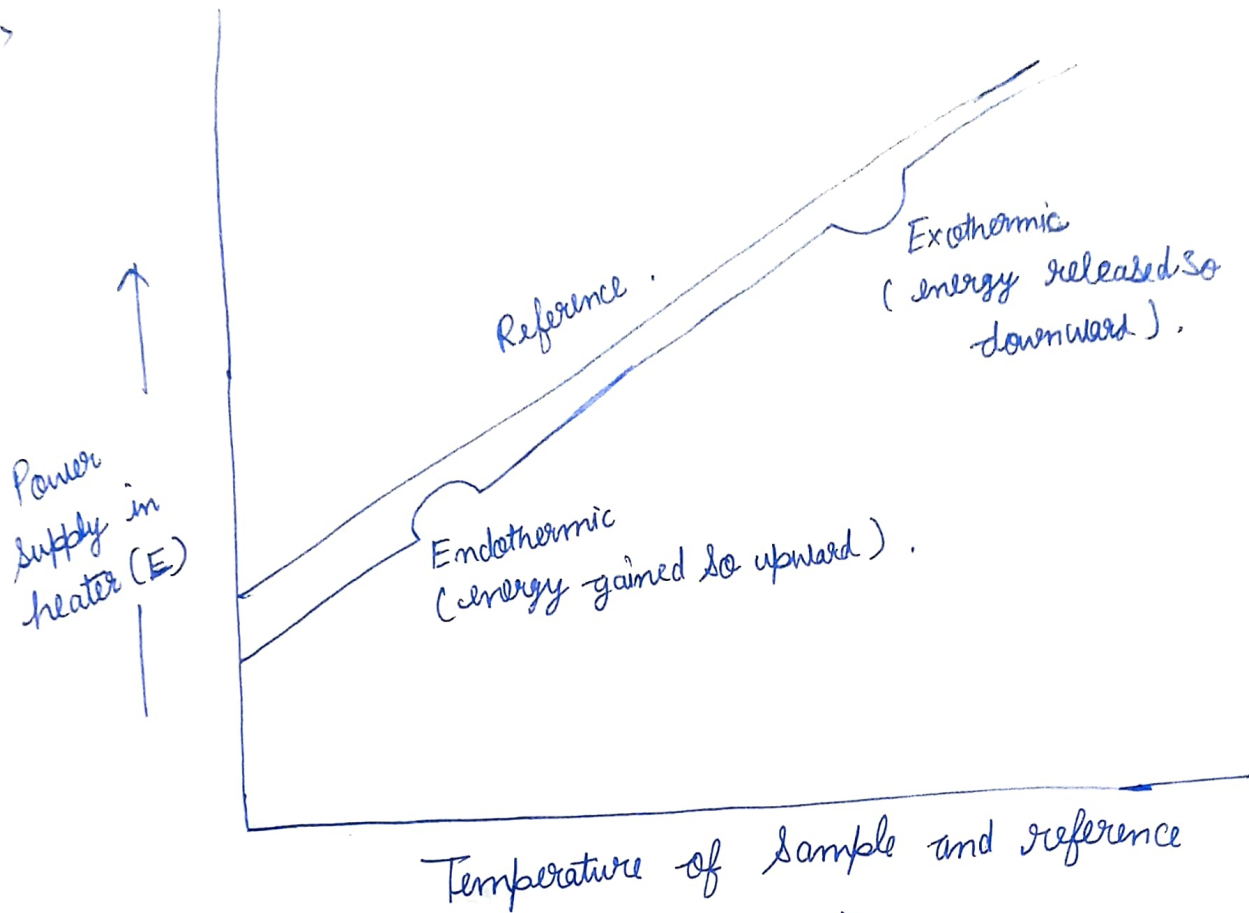
→ Heating Rate (Furnace heating rate)

2> Sample characteristic :- → Amount of sample.

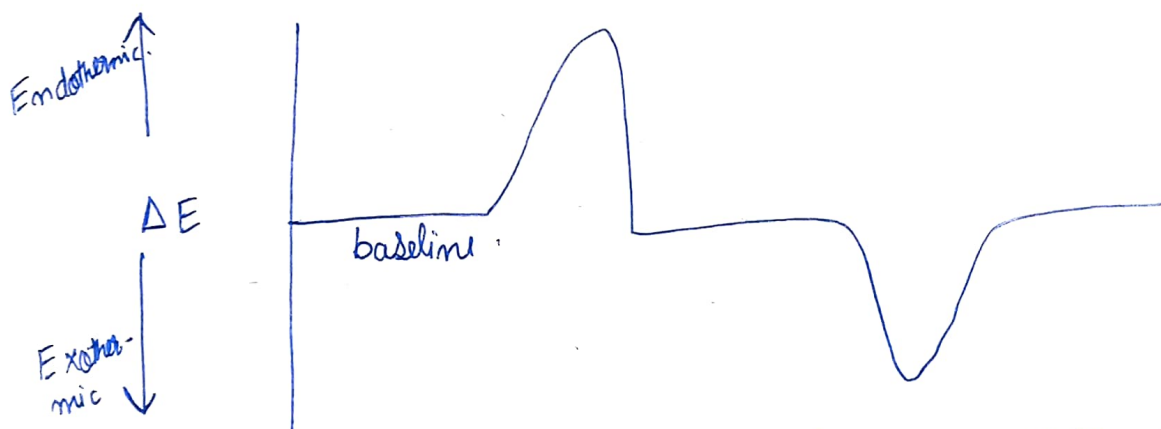
→ Particle size of the sample.

DSC (Differential Scanning Calorimetry) :-

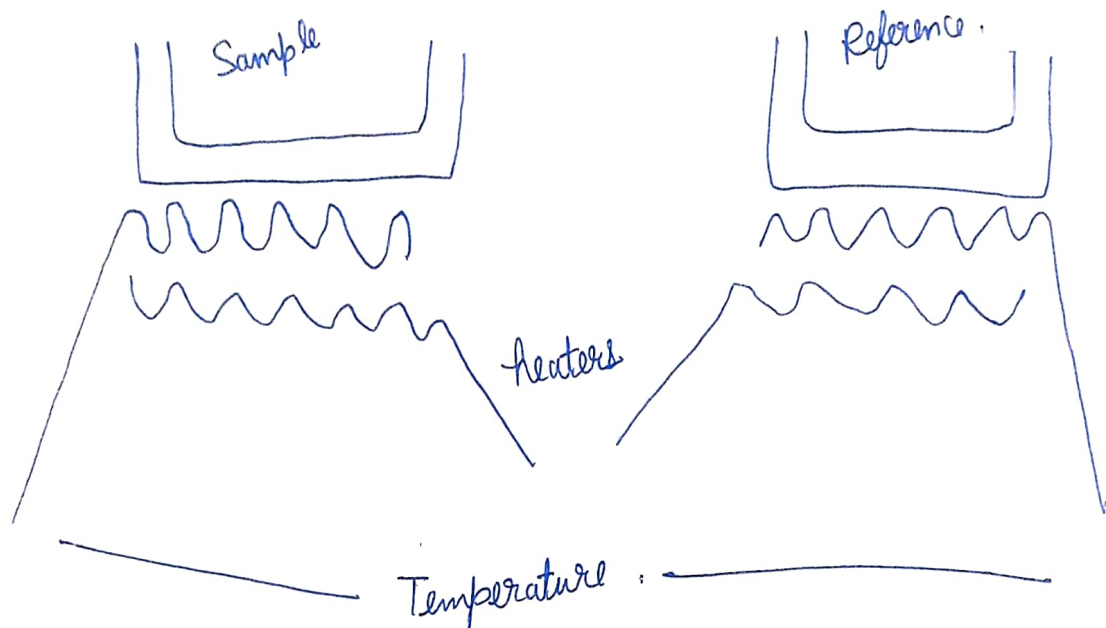
Principle :- Sample and an inert reference are heated separately, with the power supply to the sample heater variable, so that temperature difference can be maintained at zero. Even when endothermic or exothermic change occurs. The difference in power supplied to the two heaters is monitored as the analytical signal (ΔE).



Schematic representation of the variation of Power supply to the sample and reference in DSC.

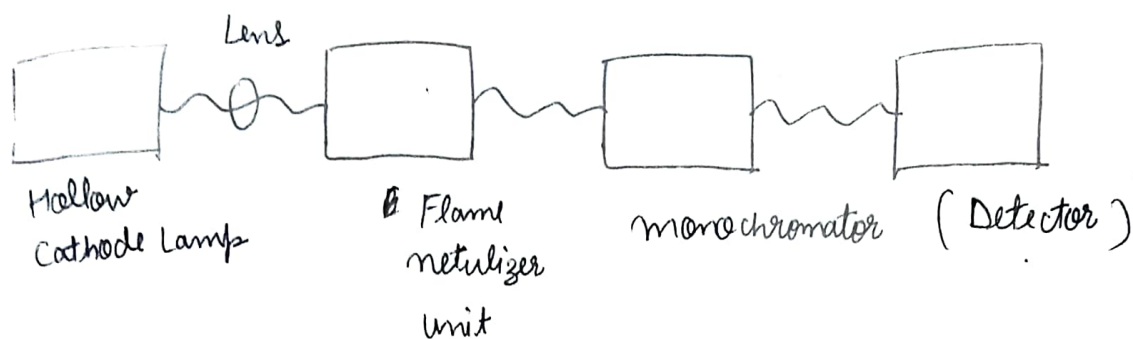


Instrumentation:- Sample and reference crucibles with separate heaters. Thermocouples with feedback to sample heater. So that the power is varied to maintain $\Delta T = 0$. Data output equipment to provide ΔE vs temperature curves. Derivative curves and peak integration. Facility to vary atmosphere of sample.



Application of DSC :-

- ① Differential Scanning Calorimetry can be used to measure a number of characteristics properties of Sample.
- ② Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperature.
- ③ DSC Can also be used to study oxidation as well as other chemical reactions.
- ④ Differential Scanning Calorimetry Can also be used to obtain valuable thermodynamic information about proteins.
- ⑤ DSC is used to ~~scan~~ examining polymeric material to determine their thermal transition ~~ions~~.



Application:-

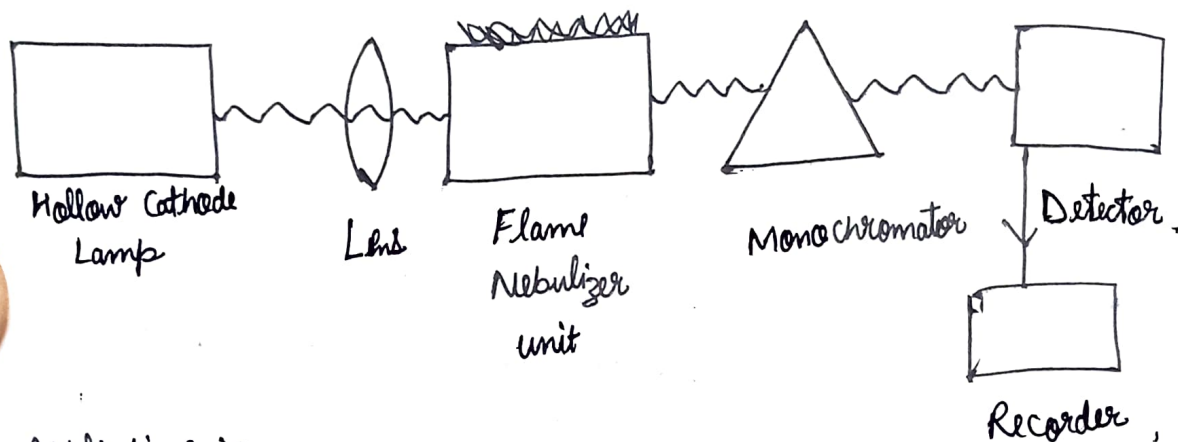
- ① The AAS technique ~~has beco~~ is the most powerful tool of analysis.
- ② The AAS is used in both quantitative and qualitative analysis in the chemical and biological sciences.
- ③ The AAS is used to estimate trace elements in biological fluid like blood, urine, etc.
- ④ The AAS is used to estimate elements in food products like Cu, Ni, Zn.
- ⑤ The AAS is used to estimate elements Zn, Mg in blood.
- ⑥ The AAS is used to estimate elements in soil samples like water, supply ceramics etc.

AAS

Principle:-

AAS stands for Atomic Absorption Spectroscopy. It is used for the study of the study of ^{Absorption} radiant energy, mostly ultraviolet and visible radiations by neutral atoms in the gaseous state.

Instrumentation:-



Applications:-

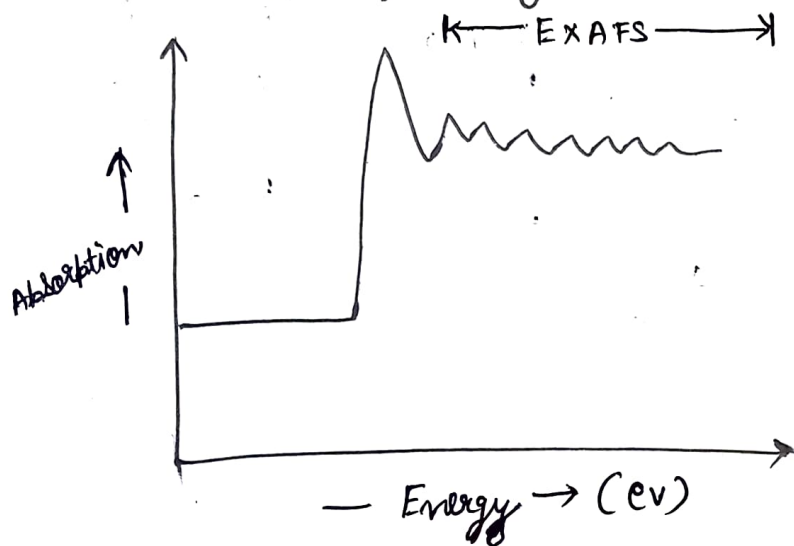
- The AAS technique is used to analyse both qualitative and quantitative analysis.
- The AAS technique is used in Blood to analyse the Mg, Zn, Ca etc.
- The AAS technique is used in food materials to analyse Cu, Zn, Ni etc.
- The AAS technique is used in soil sample to analyse the water supply.
- The AAS technique is used ~~to~~ in biological fluids to analyse like blood and urine.
- The technique is used in Pharmaceutical industries.
- " " " " " Food "

EXAFS Principle:-

EXAFS stands for EX-Ray Extended X-Ray absorption fine structure.

This gives the information about the local environment around a specific absorber atom.

- Distance to neighbouring atom.
- Type of neighbouring atom.
- Number of neighbouring atom.



Applications:-

- 1> It is used to determine the geometrical analysis of amorphous crystalline solids.
- 2> It is used to determine the quantitative analysis of non-crystalline solids.
- 3> It is used in Environmental chemistry to understand the propagation of pollutants.