Chapter-2

Thermal Methods of Analysis

Thermal Methods of Analysis

Thermal methods of analysis is a group of techniques in which a change in physical and/or chemical properties of a substance are measured as a function of temperature, when substance is subjected to a controlled temperature program.

These techniques are used for qualitative and quantitative analysis of various materials like electronic circuit boards, polymers, geological materials etc.

Principle: By measuring the temperature at which physical and chemical changes occur in substance, characteristics and other information related to that compound can be found out.

Thermal Methods of Analysis

Classification of Thermal methods of Analysis

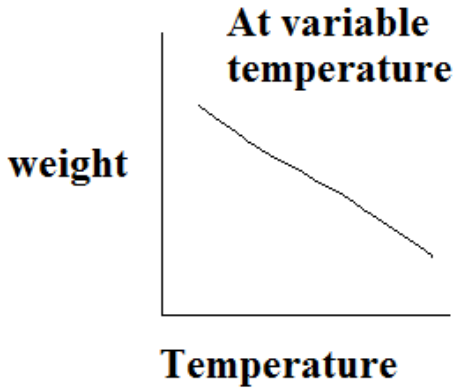
Name	Property studied	Apparatus Used
Thermogravimetric Analysis (TGA)	Change in Weight	Thermo balance
Derivative Thermogravimetric Analysis (DTG)	Rate of change in Weight with respect to temperature	Thermo balance
Differential Thermal Analysis (DTA)	Temperature of transition of reaction	DTA apparatus
Thermometric titration	Change in Temperature	Colorimeter

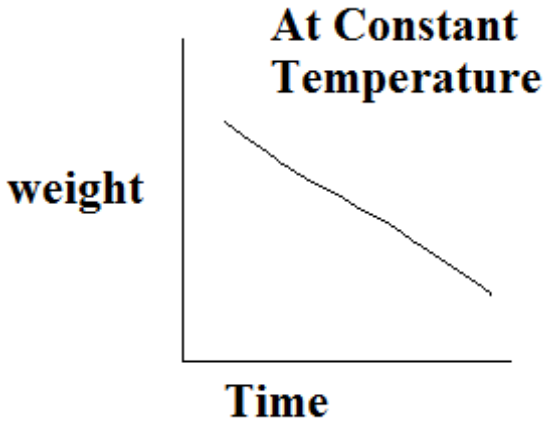
Thermal Methods of Analysis

Thermogravimetric Analysis (TGA)

Principle

The substance under study is heated or cooled at a controlled rate and the weight of the substance is recorded as a function of time or temperature.





At variable temperature weight is plotted against temperature

At constant temperature weight is plotted against time.

Thermal Methods of Analysis

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis gives information on:

1) Changes in sample composition
2) Thermal stability
3) kinetic parameters for chemical reactions in the sample

Physical Changes

Phase transitions
Gas adsorption
Gas desorption
Vaporisation
Sublimation

Chemical Changes

Decomposition
Break down reactions
Gas reactions
Chemisorption (adsorption by means of chemical instead of physical forces)

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Thermogravimetric Analysis (TGA)

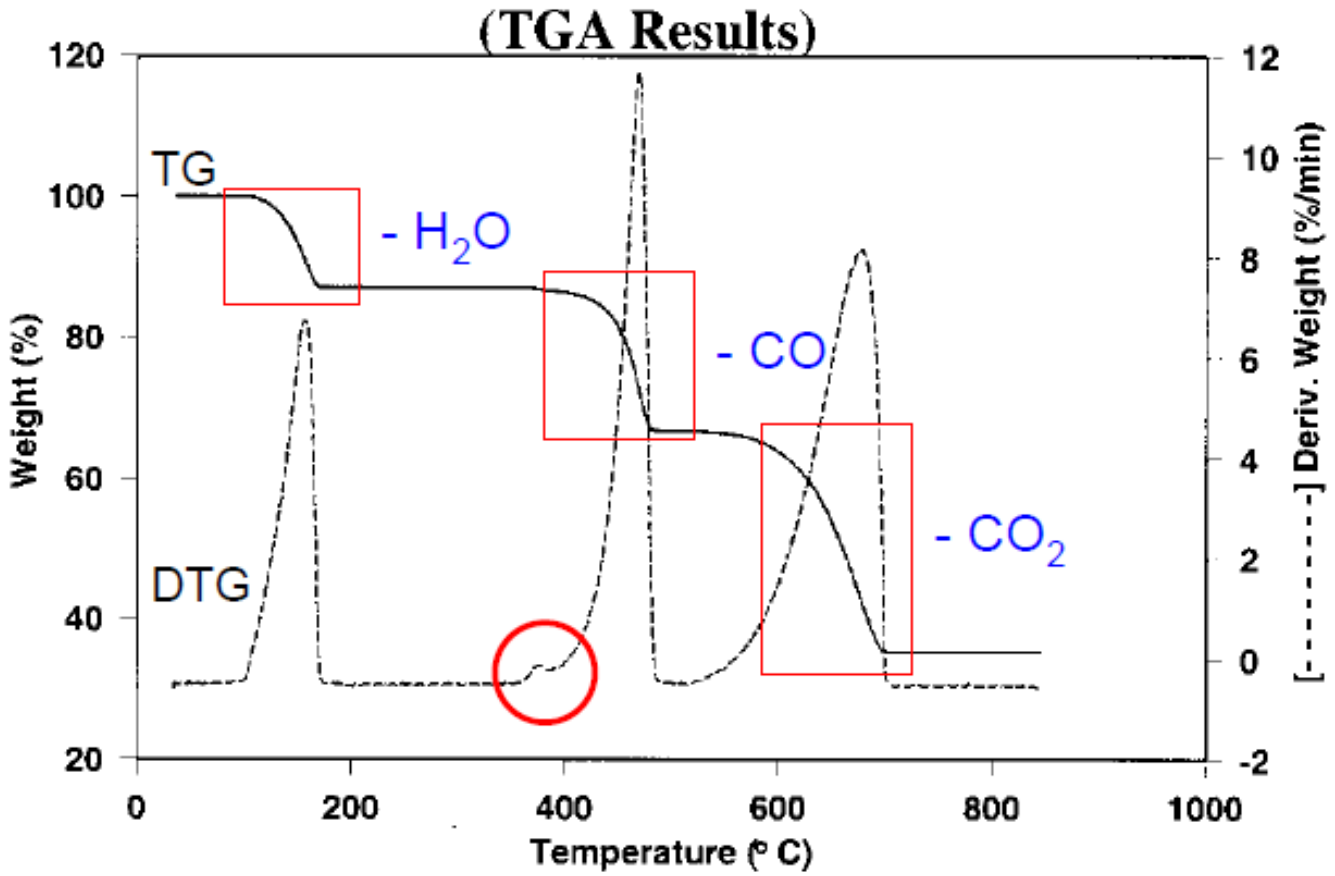
Decomposition of calcium oxalate monohydrate
It exhibits three weight losses with temperature in an inert atmosphere (e.g. N2).

$$CaC_2O_4 \cdot H_2O \xrightarrow{-H_2O} CaC_2O_4 \xrightarrow{-CO} CaCO_3 \xrightarrow{-CO_2} CaO$$

Thermal Methods of Analysis

Thermogravimetric Analysis (TGA)

Ex. Decomposition of calcium oxalat monohydrate



Thermal Methods of Analysis

Types of TGA

1) Isothermal or Static Thermogravimetry

Temperature is kept constant and constant weight is recorded as a function of time.

2) Quasistatic Thermogravimetry

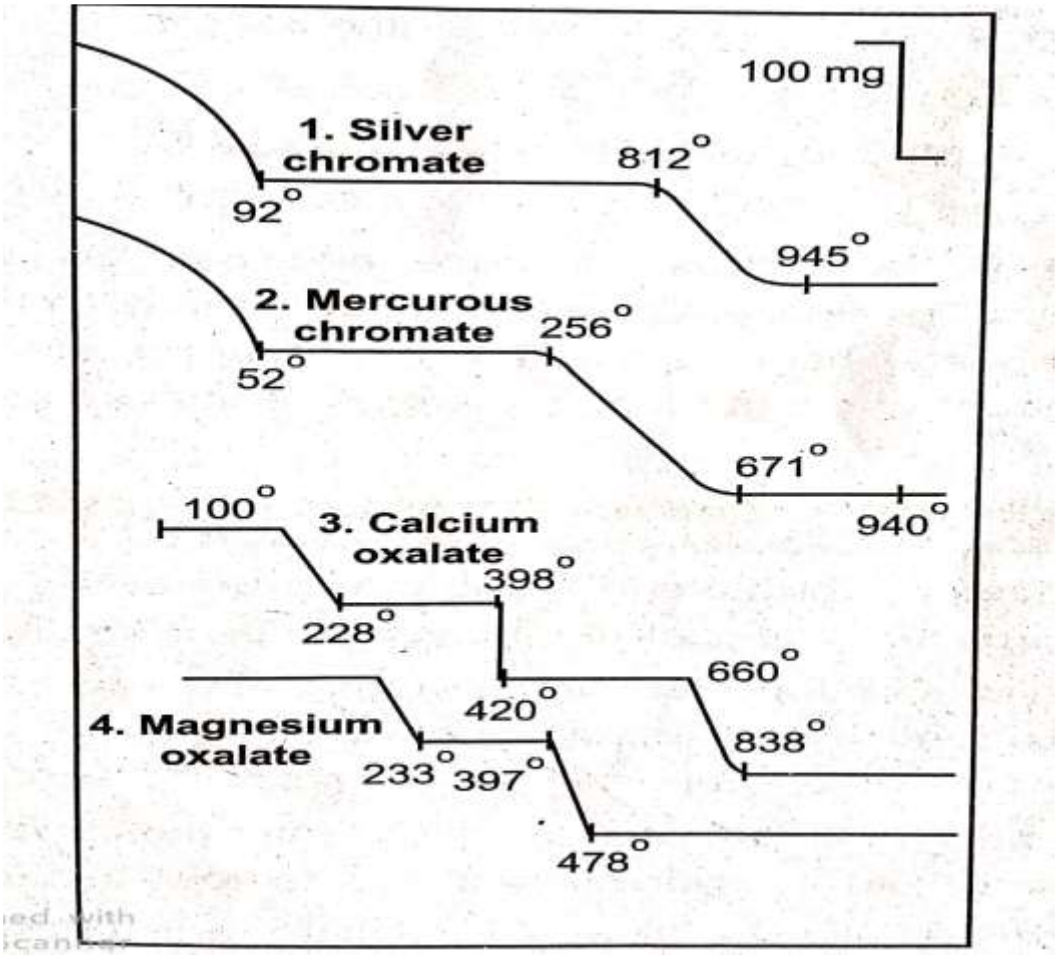
Sample is heated to a constant weight at each series of increasing temperature

3) Dynamic Thermogravimetry

Sample is heated in an environment whose temperature is changes in linear manner

Thermal Methods of Analysis

TGA Curve



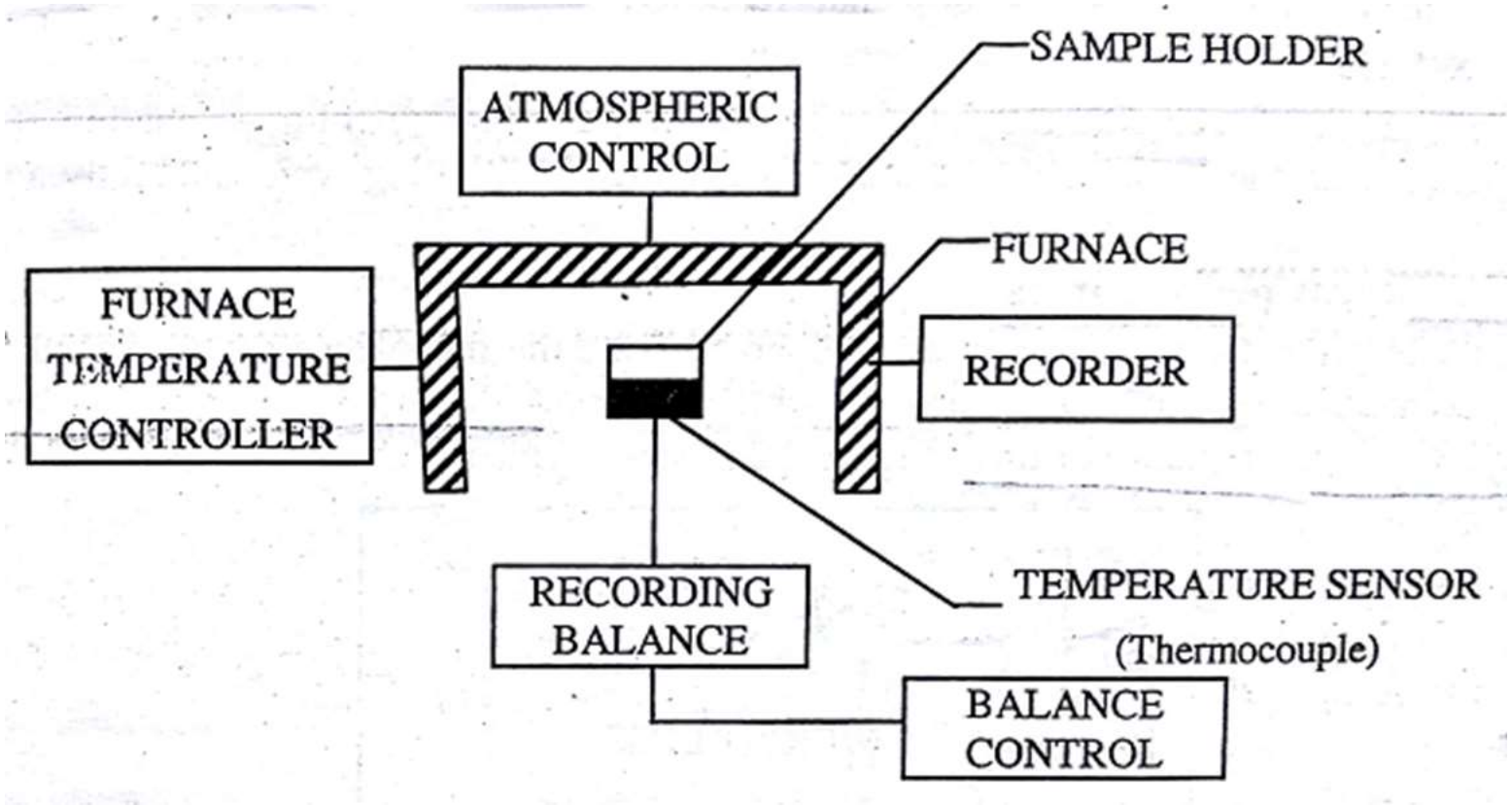
Thermal Methods of Analysis

TGA Curve

(a) $CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O$	100 - 250°C
(b) $CaC_2O_4 \rightarrow CaCO_3 + CO$	400 - 500°C
(c) $CaCO_3 \rightarrow CaO + CO_2$	650-850°C
(d) $MgC_2O_4 \cdot 2H_2O \rightarrow MgC_2O_4 + 2H_2O$	100-250°C
(e) $MgC_2O_4 \rightarrow MgO + CO + CO_2$	400-500°C

Thermal Methods of Analysis

Instrumentation
Thermobalance



Thermal Methods of Analysis

Instrumentation

Thermobalance: The apparatus that simultaneously heat the sample and monitors its weight is called thermobalance

Important features of thermobalance

1) It should be Accurate.
2) It should be sensitive enough to study small changes in weight of sample.
3) The rate of heating should be linear and reproducible.
4) Capable of heating sample up to 1500^0C.
5) It could cover wide range of temperature.
6) Should have high degree of mechanical strength.
7) Should have rapid response to weight change.

Thermal Methods of Analysis

Instrumentation
Components of Thermobalance

1) Sample holder:

The shape, size and material used in the fabrication of the sample holder affect the resolution, shape and size of the DTA peaks.

For better resolution, the size of holders and the amount of sample should be as small as possible.

Sample holder is made up of quartz, Platinum, ceramic or stainless steel.

2) Recording Balance:

It Should be Accurate, Sensitive and reproducible.

It should have high degree of mechanical and electrical stability.

It should not be affected by vibrations.

It should be easy to operate.

Thermal Methods of Analysis

Instrumentation
Components of Thermobalance

3)Furnace and furnace temperature controller:

This depends upon the temperature range in which sample is heated.

4) Temperature sensor/ Thermocouple:

For temperature up to 1100 ^{0}C Chromel or alumel thermocouple is used.

For temperature up to 1750 ^{0}C thermocouples made up of alloy of platinum or rhodium are used is used.

5) Recorder:

i) Time based potentiometric strip chart recorder ii) X-Y recorder

Thermal Methods of Analysis

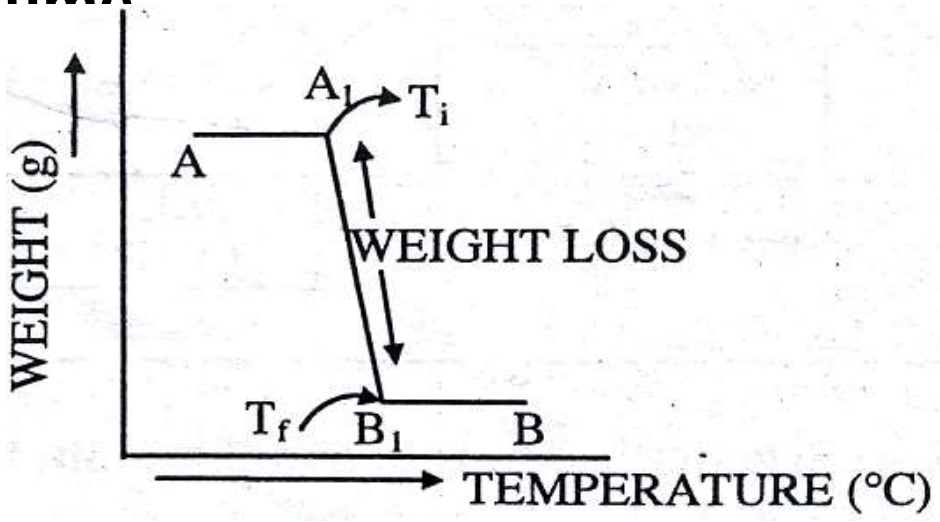
Properties of good Thermobalance

1) Capable of recording continuously the weight change of the sample as a function of temperature or time.
2) Furnace should reach to maximum desired temperature
3) Rate of heating should be linear and reproducible.
4) Temperature should be recorded accurately (+/- 1%)
5) The sample holder must be in hot zone and zone must have uniform temperature.

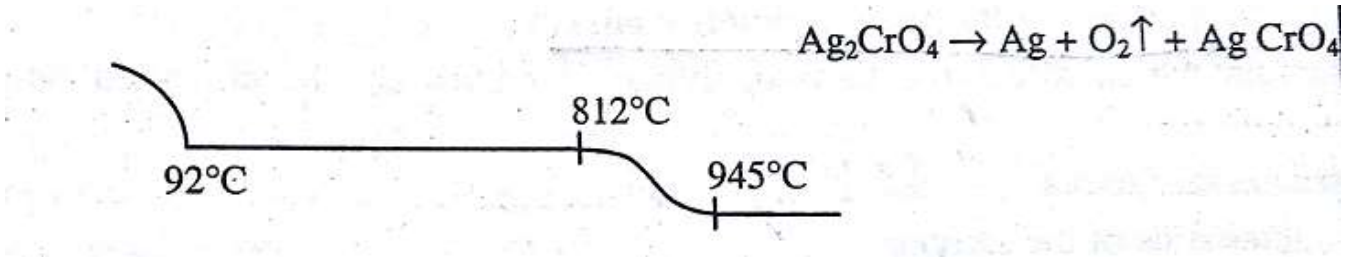
Thermal Methods of Analysis

Thermogravimetric Curve:

Thermogram is a plot of change in weight verses temperature or time



1.Horizontal portion of the plot indicate the temperature range in which there is no weight loss (Portion A to A1)
2.Curved portion indicate the weight loss(Portion A1 to B1)
3.Portion B1 to B shows no weight loss



Thermal Methods of Analysis

Factors affecting Thermogravimetric Curves

a) Instrumental factors

1) Heating rate

If substance is heated at faster rate it decomposes at higher temperature while at slower rate decomposition temperature is less.

Ex. Polystyrene decomposes at 395^0C when heated at 5^0C per minute while at 375^0C when heated at 1^0C per minute

Thermal Methods of Analysis

Factors affecting Thermogravimetric Curves

a) Instrumental factors

2) Furnace atmosphere:

Decomposition of Calcium Carbonate take place at higher temperature when furnace atmosphere is CO_2 gas than N_2 gas

Types of furnace atmosphere:

1) Static air : atmospheric air is used as furnace atmosphere
2) Dynamic air Compressed air is used
3) Inert atmosphere: nitrogen gas is used

Thermal Methods of Analysis

Thermogravimetric Curve:

Factors affecting thermogravimetric Curve :

Other Factors:

1.Particle size of sample: Conditions of precipitation during sample formation.

2. Source of sample

3. Amount of sample

4. Size and shape of crucible

Thermal Methods of Analysis

Applications of Thermogravimetric analysis:

1. Characterisation of material by analysis of decomposition pattern.

2. Study of degradation mechanism and reaction kinetics.

3. Determination of organic and inorganic content in sample.

4. Study of thermal stability of material like polymer

5.Determination of correct drying temperature of precipitates in gravimetry.

6.Study of oxide reactions.

7.It is useful in determination of moisture, ash and volatile matter from different sample.

Thermal Methods of Analysis

Differential Thermal Analysis (DTA)

The material under study (Sample) and an inert reference material are made to undergo identical thermal cycles.

Principle:
Differential thermal analysis (DTA) involves the technique of recording the difference in temperature between a substance and a reference material against either time or temperature.

Thermal Methods of Analysis

Differential Thermal Analysis (DTA)

DTA peaks result from both physical changes and chemical reactions induced by temperature changes in the sample.

Phenomena causing changes in heat / temperature

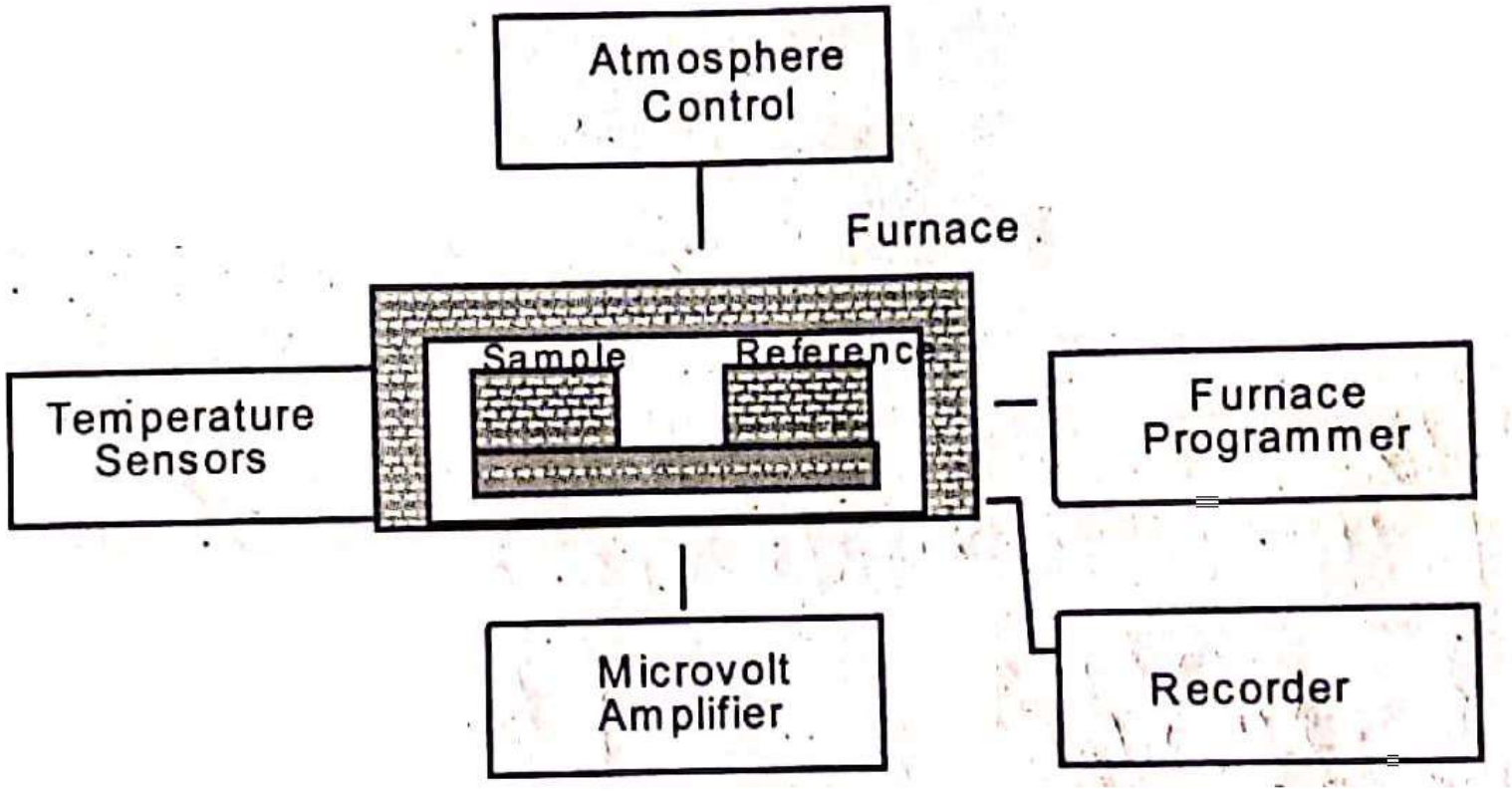
Physical Changes
Adsorption (exothermic)
Desorption (endothermic)
A change in crystal structure
Crystallization (exothermic)
Melting (endothermic)
Vaporization (endothermic)
Sublimation (endothermic)

Chemical Changes
Oxidation (exothermic)
Reduction (endothermic)
Break down reactions (endo – or exothermic)
Chemisorption (exothermic)
Solid state reactions (endo – or exothermic)

Thermal Methods of Analysis

Differential Thermal Analysis (DTA)

Instrumentation



Thermal Methods of Analysis

Differential Thermal Analysis (DTA)

Instrumentation

1. Sample holder:

Metallic material like nickel, stainless steel, platinum and its alloy and non metallic material like silica or glass can be used for fabrication of sample holder.
In DTA two sample holders are required.

2. Furnace:

In DTA tubular furnace is used. It is made up of refractory tubes.

3. Temperature controller and recorder:

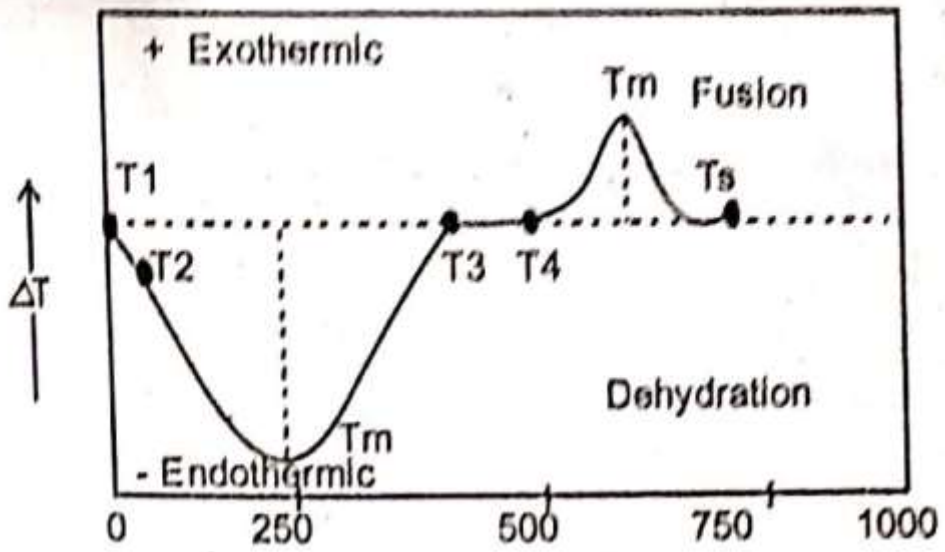
This consist of sensor, control element and heater

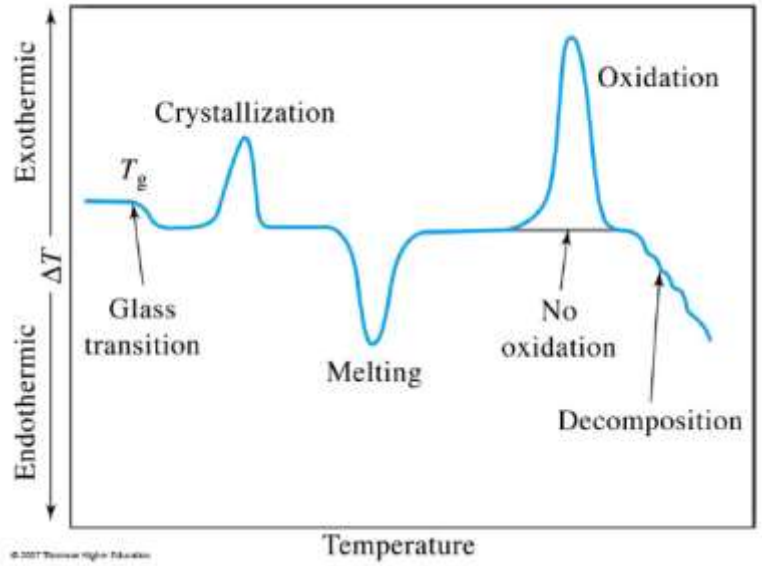
4. Thermocouple: Thermocouple is used as temperature sensor used in DTA.

5. Cooling system: Automatic cooling system is used in DTA

Thermal Methods of Analysis

Differential Thermal Analysis (DTA) : DTA CURVE





Exothermic peaks gives idea about crystallization and fusion process. Endothermic peaks gives idea about dehydration, melting etc.

DTA gives information about every physical and chemical change irrespective of change in weight during these process.

Thermal Methods of Analysis

Differential Thermal Analysis (DTA) : Factors affecting DTA curve

1. Environmental factors:

This technique is very sensitive to the gaseous environment around the sample.

The reaction of gaseous environment with the sample can produce extra peaks in the curve.

For example Oxygen in air can cause an oxidation reaction and give rise to an exothermic peak

2. Instrumental factors

a) Sample holder: The size, shape and the material used for fabrication affect the DTA curve.

For good resolution, the size of sample holders and the amount of sample should be as small as possible.

Thermal Methods of Analysis

Differential Thermal Analysis (DTA) : Factors affecting DTA curve

b) Differential temperature sensing devices:

The heat of transitions are much less as compare to heat of reactions. Therefore differential temperatures in transitions are much smaller. and their pre amplification is essential.

c) Furnace characteristics:

Uniform furnace atmosphere is required for good results. When atmosphere changes base line also changes.

d) Temperature-programmer controller:

As constant heating is required in DTA, selection of temperature- programmer controller is very important.

Thermal Methods of Analysis

Differential Thermal Analysis (DTA) : Factors affecting DTA curve

e) Thermal regime: The rate of heating has a great influence on the DTA curves. Higher the heating rates, higher the peak temperatures and sharper the peaks with greater intensity. Heating rates of 10 to 20 °C per minute are employed.

f) Recorder:

DTA curve is greatly influenced by the type, chart-speed and pen-response of a recorder.

3) Sample characteristics:

Sample characteristics

The weight of sample, degree of crystallinity , particle size affect the nature of DTA curve.

Thermal Methods of Analysis

Differential Thermal Analysis (DTA) : Applications

1) Study of characteristics of polymers
2) Study of decomposition temperature, crystallization point and melting point phase transition temperature and thermal stability of material
3) Quality control of material like ceramic glass, resins etc.
4) Study of metal amine complexes, oxalates, oxides etc.
5) Melting point determined by DTA can be used to check purity of sample.
6) Quantitative analysis of sample is possible by using DTA curve.

Sr.No	TGA	DTA
1.	Weight loss or gain is measured as a function of temperature or time.	Temperature difference between a sample and a reference is measured as a function of temperature.
2	Curve appears as steps involving horizontal and curved portions.	Curve shows upward and downward peaks.
3.	Instrument is thermobalance	Instrument is DTA apparatus
4.	Gives information only for substances which shows a change in mass on heating or cooling.	Used to study any process in which heat is absorbed or liberated.
5.	Upper temperature is 1000^0C	Upper temperature is as high as 1600^0C
6.	Qualitative analysis is done from thermal curve by measuring the loss in mass Δm	Quantitative analysis is done by measuring the peak areas and peak hights.
7.	Data is useful in determining purity and composition of materials, drying and ignition temperatures of materials and knowing the stability temperatures of compounds.	Data obtained is used to determine temperatures of transitions and reactions,specific heats of reactions and melting points of substance.