Differential Thermal Analysis (DTA):

- **Differential thermal analysis (DTA),** in analytical chemistry, a technique for identifying and quantitatively analyzing the chemical composition of substances by observing the thermal behavior of a sample as it is heated.

- The technique is based on the fact that as a substance is heated, it undergoes reactions and phase changes that involve absorption or emission of heat.

Differential Thermal Analysis (DTA):

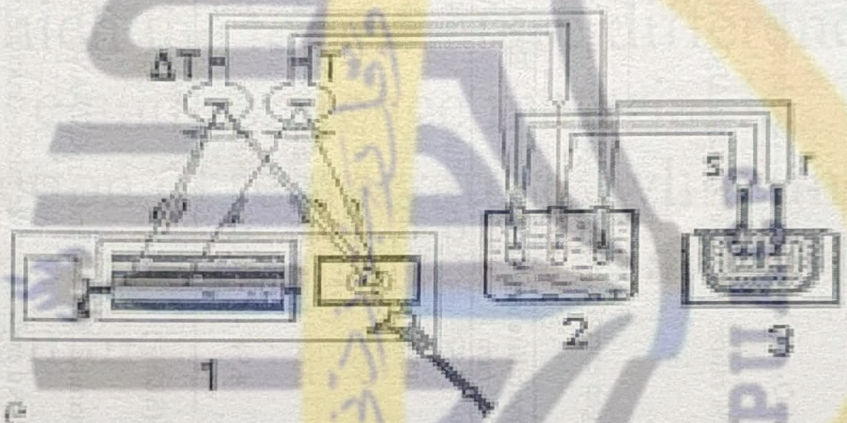
History of Differential Thermal Analysis

Roots of DSC:

heating curves
and twin calorimetry:
middle 19th century

Development:

continuous temperature
measurement and recording:
LeChatelier 1887
time - ΔT recording:
Roberts-Austen 1899
classical DTA setup
Kurnakov and Saladin 1904



Kurnakov DTA:

1. photographic T-ΔT recording
2. reference ice bath
3. DTA furnace

Principle:

- A Technique in which the temperature difference between a substance and reference material is measured as a function of temperature, while the substance and reference are subjected to a controlled temperature programme.

- The Difference in temperature is called as Differential temp(Δt) is plotted against temp. or a function of time.

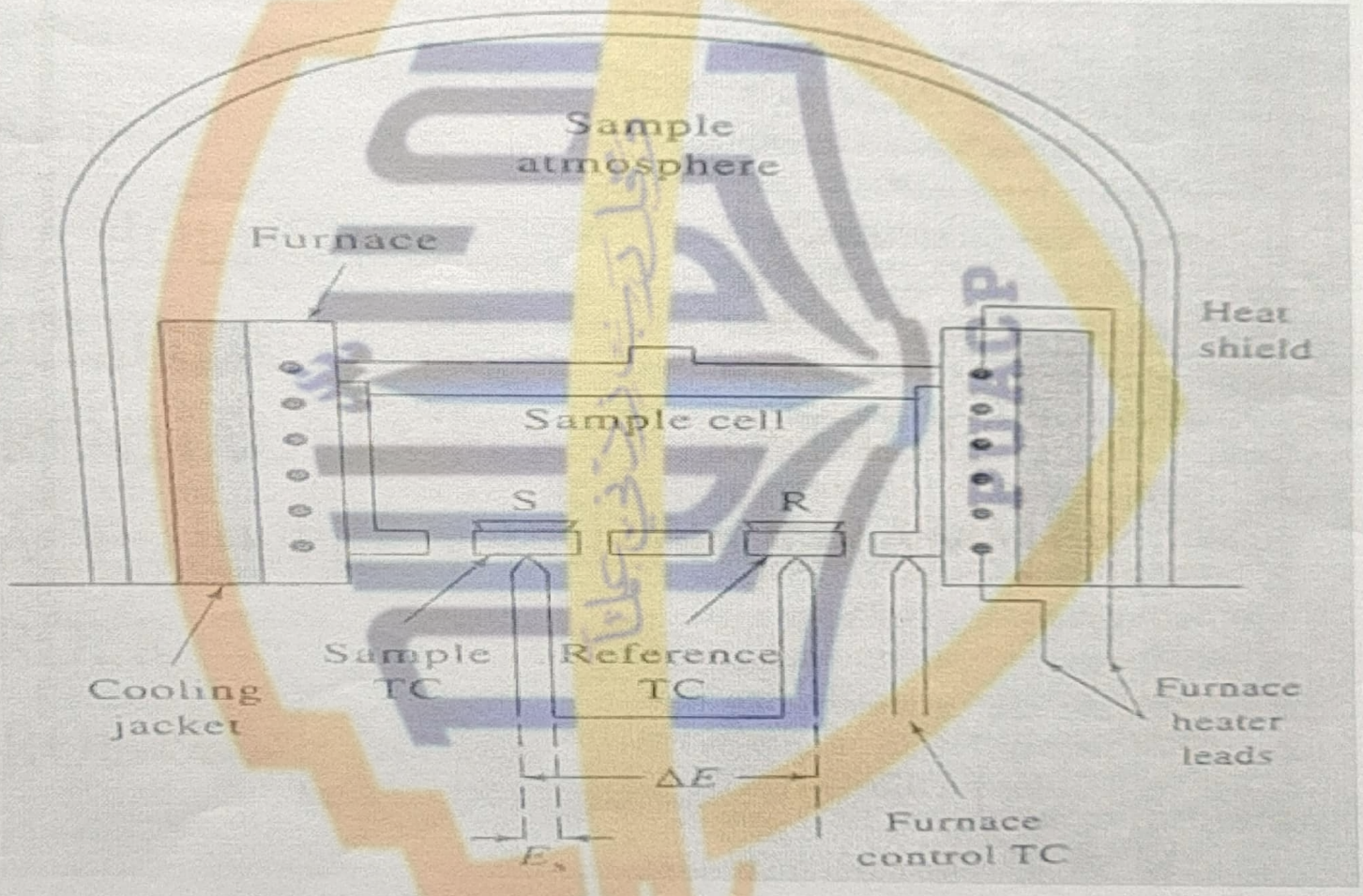
Principle:

- Physical changes usually result in Endothermic peak, whereas chemical reactions those of an oxidative nature are exothermic.

- Endothermic reaction (absorption of energy) includes vaporization, sublimation, and absorption & gives downward peak.

- Exothermic reaction (liberation of energy) includes oxidation, polymerization, and catalytic reaction & gives upward peak

Instrumentation:



Instrumentation:

1. FURNACE
2. SAMPLE HOLDER
3. DC AMPLIFIER
4. DIFFERENTIAL TEMPERATURE DETECTOR
5. FURNACE TEMPERATURE PROGRAMMER
6. RECORDER
7. CONTROL EQUIPMENT

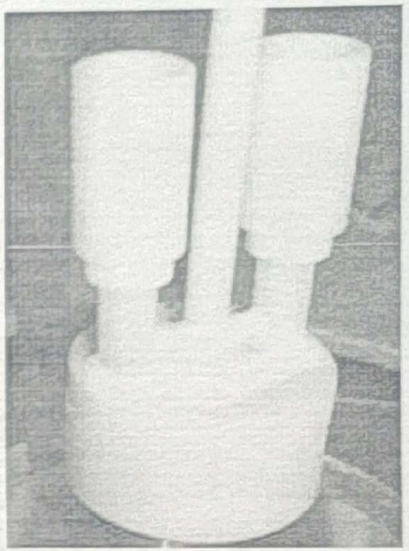
1.Furnace:

- In DTA apparatus ,one always prefers a tubular furnace.

- This is constructed with an appropriate material (wire or ribbon) wound on a refractory tube.

- These are fairly inexpensive . Generally , the choice of the resistance material as well that of refractory is decided from the internal maximum temperature of operation and gaseous environments.

2.Sample holders:



- Both metallic as well as non-metallic are employed for the fabrication of sample holders.
- Metallic materials generally include nickel , stainless steel , platinum and its alloys.
- Non-metallic material generally includes glass , vitreous silica or sintered alumina.
- Metallic holders give rise to sharp exotherms and flat endotherms . On the other hand non-metallic holders yield relatively sharp endotherms and flat exotherms.

3.DC Amplifier:

- It is used for amplification of signals obtained from (T)c.

- It is gain and low noise circuit.

4.Differential temperature detector:

- In order to control temperature , the three basic elements are required.

  - These are sensor , control element and heater.

ON-OFF CONTROL – In this device , if the sensor-signal indicates the temperature has become greater than the set point , the heater is immediately cut off.

Not used in DTA

4.Differential temperature detector:

- PROPORTIONAL CONTROL- In on-off controllers there occurs fluctuations of temperature around the set value. These can be minimized if the heat input to the system is progressively reduced as the temperature approaches the desired value .

- Such a controller that anticipates the approach to the set value is known as proportional controller.

5.Furnace temperature programmer/Sensors:

- It provides smooth heating or cooling at a linear rate by changing the voltage through heating component. Modern DTA instruments incorporate electronic temp controller in which the signal from thermocouple in furnace is compared electically against ref.potential which can be programmed to corresponds to a variety of heating modes & heating rates.

6.Recorder:

- In thermo analytical studies , the signal obtained from the sensors can be recorded in which the signal trace is produced on paper or film , heating stylus , electric writing or optical beam.

- There are two types of recording devices similar to the TG-

  DEFLECTION TYPE

  NULL-POINT TYPE

7.Control Equipment:

- For some type of samples the atmosphere must be controlled to suppress and undesirable reaction such as oxidation by flowing an inert gas.

Working of DTA:

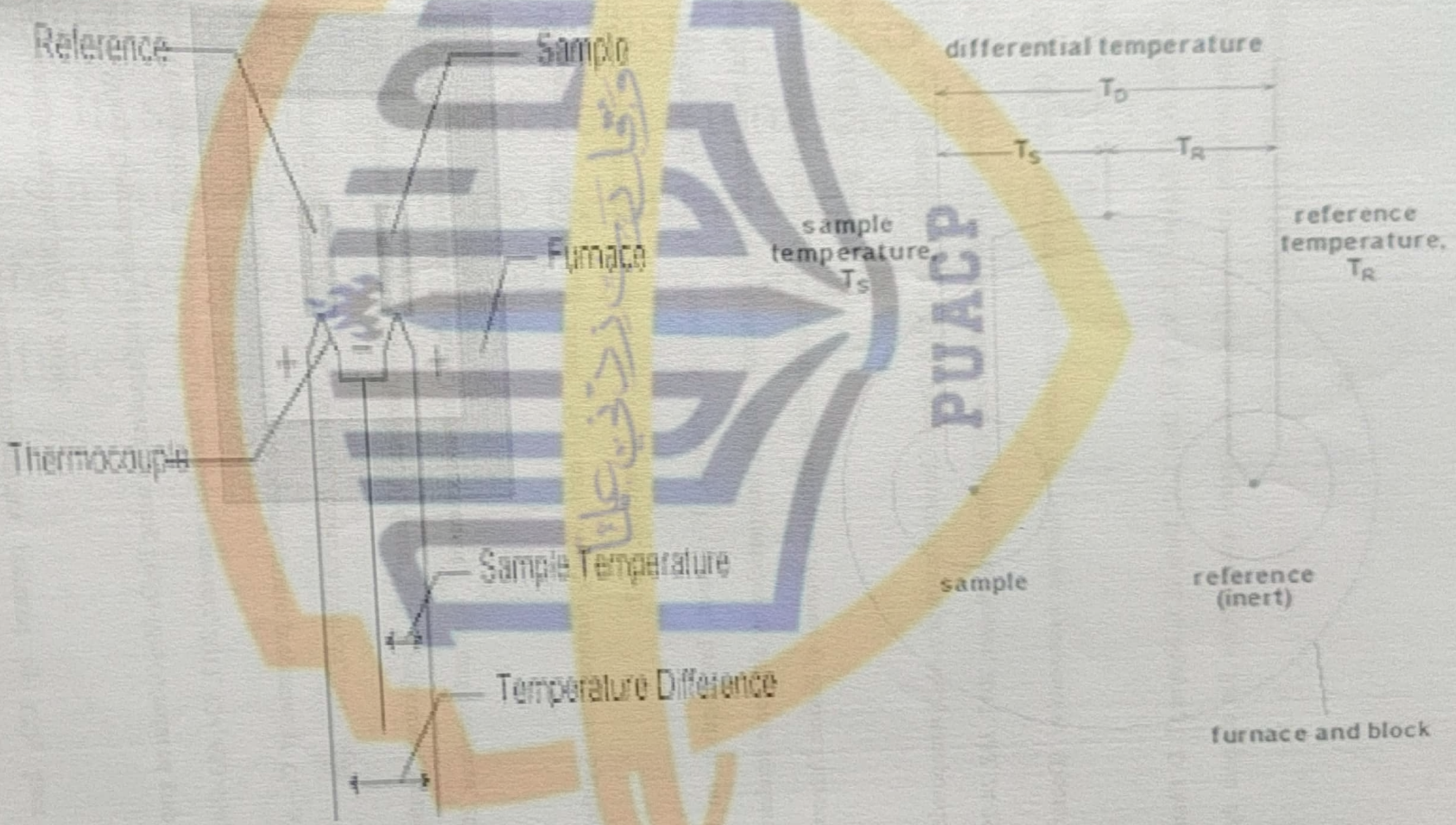
- The sample and reference standard are placed in the furnace on flat , highly thermally conductive pans and the thermocouples are physically attached to the pans directly under the sample .

- This procedure avoids or reduces any thermal lag resulting from the time required for the heat to transfer to the sample and reference materials then to the thermocouples.

Working of DTA:

- The thermocouple are connected in opposition.
- In a similar manner any change in state that involves a latent heat of transition will cause the temperature of the sample to lag or lead that of the reference standard and identify the change of state and the temperature at which it occurred.

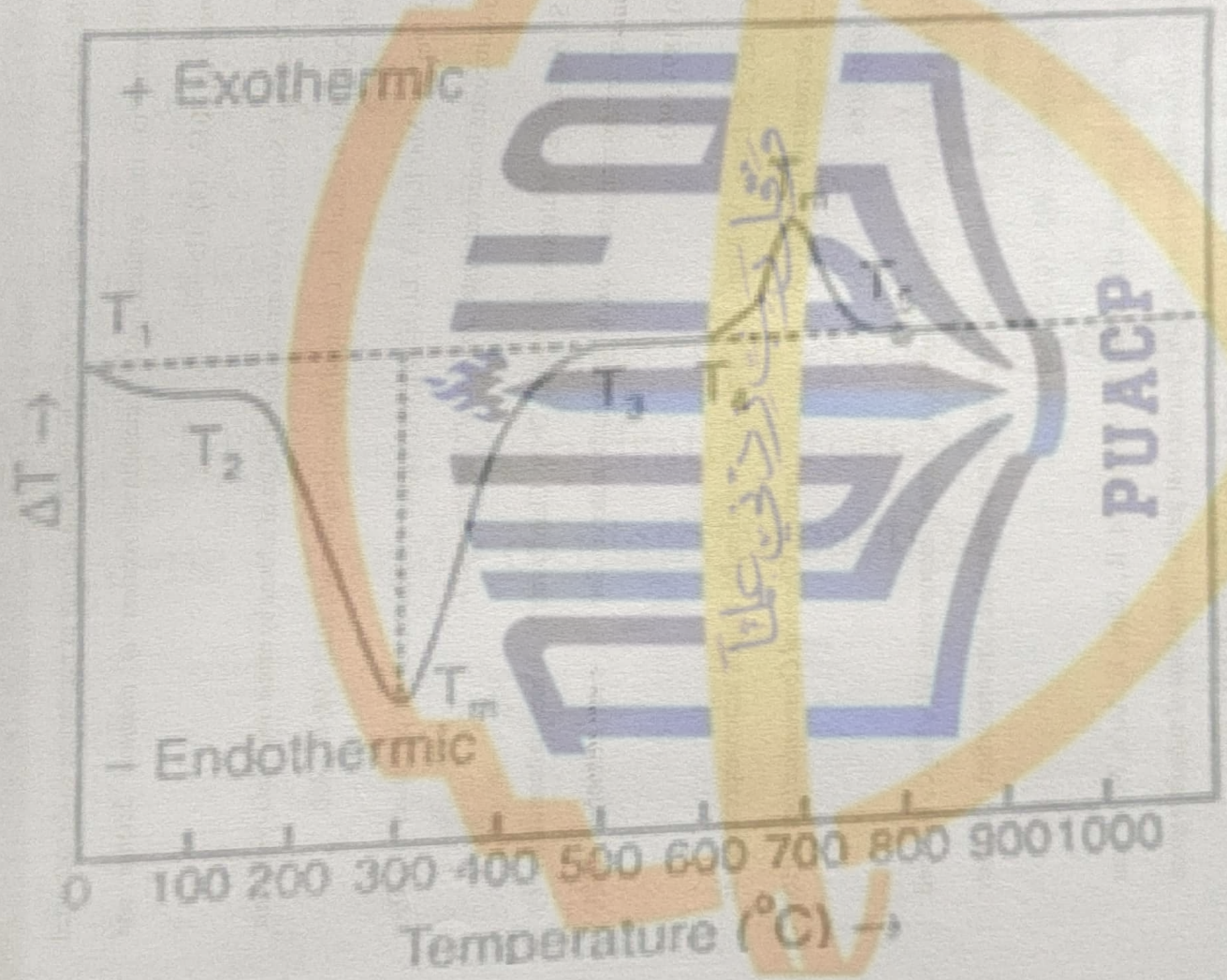
Working of DTA:



Thermogram:

- A differential thermogram consists of a record of the difference in sample and reference temperature (ΔT) plotted as a function of time t , sample temperature (Ts) , reference temperature (Tr) or furnace temperature (Tf).

Thermogram:

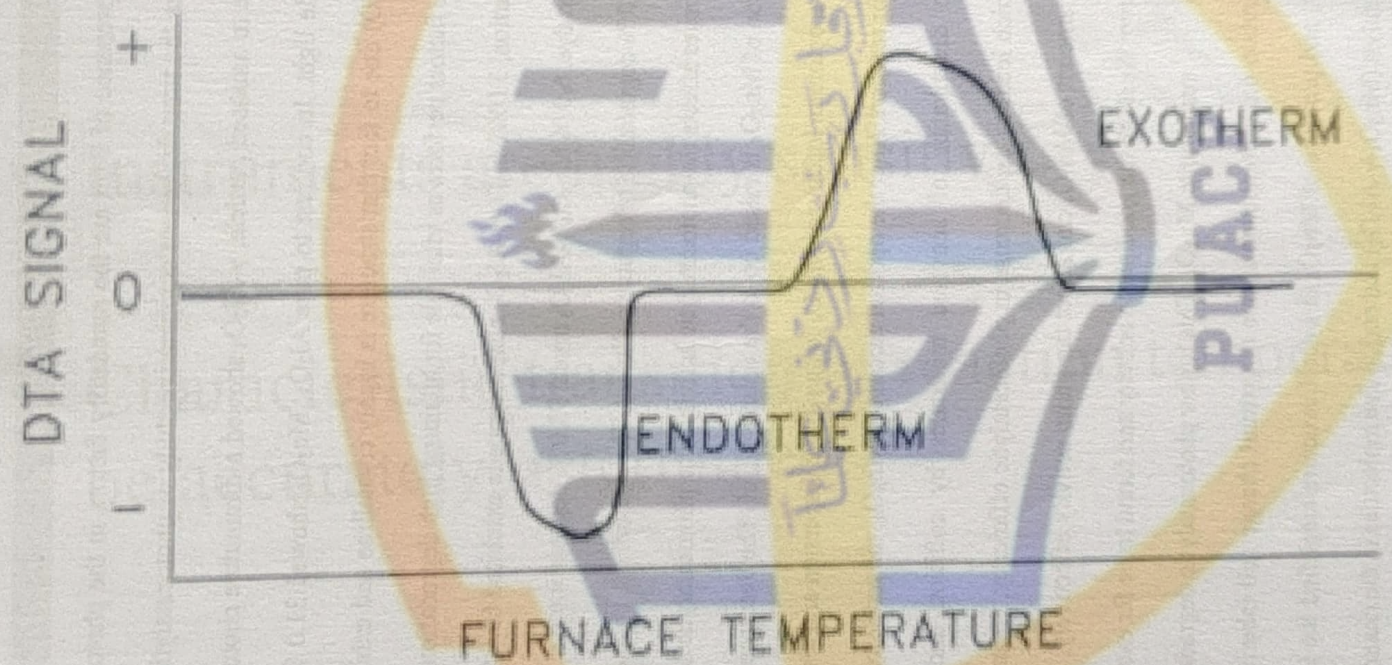


Thermogram:

In most of the cases physical changes give rise to endothermic curves whereas chemical reaction gives rise to exothermic .

- Sharp endothermic-change in crystallinity or fusion
- Broad endothermic-dehydration reaction.
- Exothermic – mostly oxidative reaction.

Thermogram:



Advantages of DTA:

- Instruments can be used at very high temperatures.
- Instruments are highly sensitive.
- Characteristic transition or reaction temperatures can be accurately determined.

Limitations of DTA:

- ΔT determined by DTA is not so accurate (2-3 ℃).
- Small change in ΔT cannot be determined and quantified.
- Due to heat variation between sample and reference makes, it less sensitive.

Applications:

- Qualitative and Quantitative Identification of Minerals: detection of any minerals in a sample.

- Polymeric Materials: DTA useful for the characterization of polymeric materials in the light of identification of thermo physical , thermo chemical, thermo mechanical and thermo elastic changes or transitions.

Applications:

- Measurement of Crystalline: measurement of the mass fraction of crystalline material

- Analysis of Biological Materials: DTA curves are used to date bone remains or to study archaeological materials

Derivative Differential thermal analysis:

- A method based on the use of the two temperatures of the inflection determined on a single derivative differential thermal analysis (DDTA) curve and of the temperature of the extremum determined on the differential thermal analysis (DTA) curve is proposed for computing the activation energy and the order of reaction of a chemical process.

- The obtained formulae do not contain the heating rate. If the conversion degree corresponding to the three temperatures required by the formulae are known, the third kinetic parameter, *A*, may be also computed. The formulae are fitted to the reaction order model.

Differential Thermal Analysis (DTA)

- **Principle:**

The basic principle involved in DTA is the temperature difference (ΔT) between the test sample and an inert reference sample under controlled and identical conditions of heating or cooling is recorded continuously as a function of temperature or time, thus the heat absorbed or emitted by a chemical system is determined.

Differential Thermal Analysis (DTA)

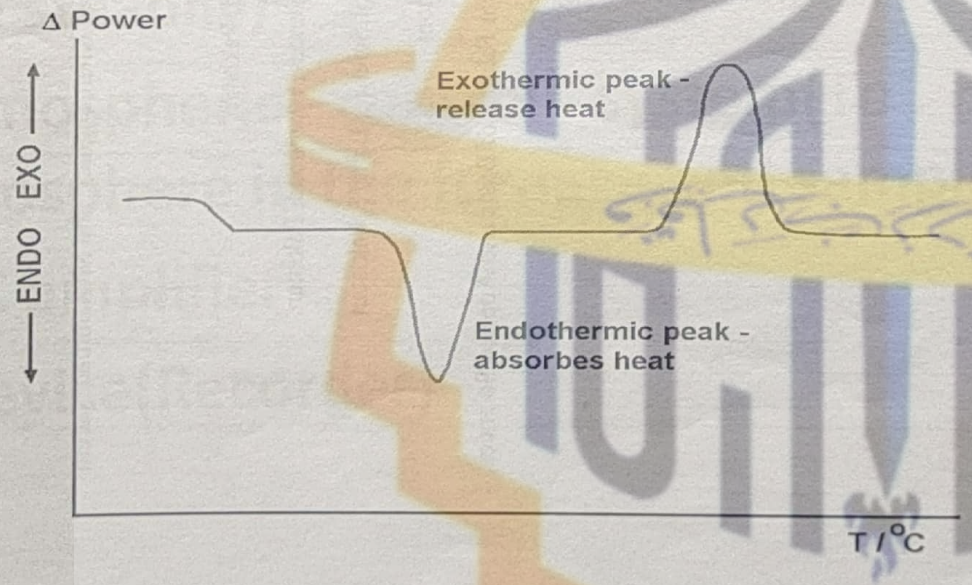
- If any reaction takes place in the sample, then the temperature difference will occur between the sample and the reference material.
- In an endothermic change (such as melting or dehydration of the sample) the temperature of the sample is lower than that of the reference material
  (i.e) $\Delta T = -$ ve (for endothermic process)
- In an exothermic change or process the sample temperature is higher than that of the reference material.
- (i.e) $\Delta T = +$ ve (exothermic process)

The shape and the size of the peak give information about the nature of the test sample.

(1)Sharp endothermic peaks indicate phase changes (such as melting, fusion etc.) transition from one crystalline form to another crystalline form.

(2) Broad endothermic peaks are obtained from dehydration reactions

(3)Chemical reactions like oxidative reactions are exothermic reactions.

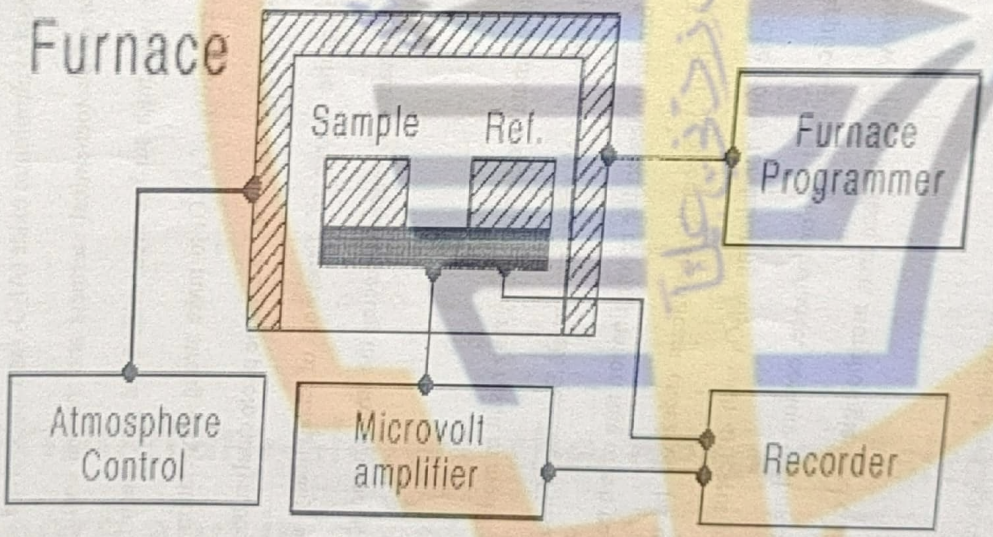


Instrumentation for DTA/Block Diagram

The DTA apparatus consists of the following components

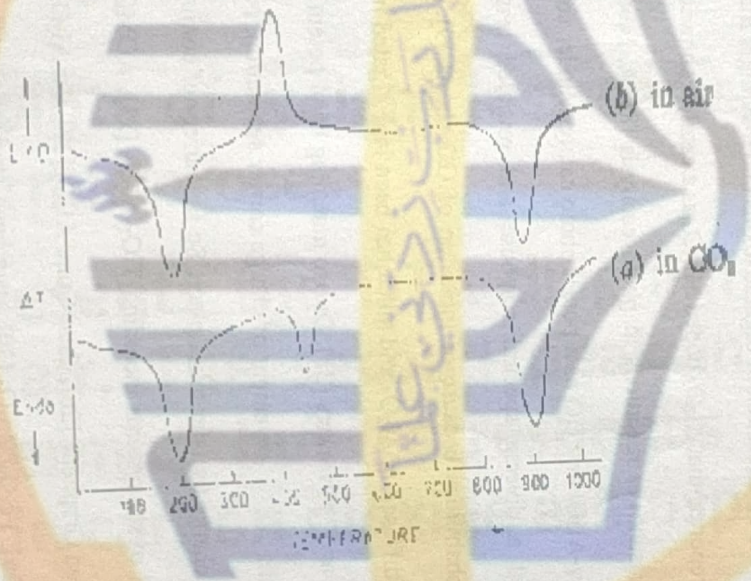
- Furnace sample and reference holder with thermocouple assembly.
- Sample holder furnace(To heat the sample)
- Furnace temperature controller(to increase the furnace temperature steadily)
- Furnace atmospheric control system(To maintain a suitable atmosphere in the furnace and sample holder)
- Low level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

- Differential temperature sensor (to measure the temperature difference between the sample and reference material) the sample and reference holder are kept inside the furnace and the temperature of the furnace and sample holder is controlled by using furnace controller.



DTA of calcium oxalate monohydrate

- The DTA curve for the decomposition of calcium oxalate monohydrate ($CaC_2O_4.H_2O$) is shown in the diagram.



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

DTA of calcium oxalate monohydrate

- The thermogram of calcium oxalate monohydrate has three peaks corresponding to the successive elimination of H_2O, CO and CO_2.
- These three points of weight loss corresponds to the three endothermic process.
- Curve (b) represents the DTA diagram for the same compound in air. The second peak in this curve is sharply exothermic, but corresponds to the same weight loss as in carbon dioxide atmosphere.
- This peak represents the exothermic burning of carbon monoxide in air at the temperature of the furnace.

Factors affecting the DTA Curve

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)

Sample characteristics:

- Amount of the sample(sample weight)
- Particle size of the sample

Applications of DTA

- DTA curves for two substances are not identical. Hence they serve as finger prints for various substances.
- Used to study the characteristic of polymeric material.
- This technique is used for testing the purity of the drug sample and also to test the quality control of number of substances like cement, soil, glass,etc.
- Used for the determination of heat of reaction, specific heat and energy change occurring during melting etc.
- Trend in ligand stability (thermal stability of the ligands) gives the information about the ligands in the coordination sphere.