Thermal Methods of Analysis
Theory, General Techniques and Applications

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1- General introduction and theory:

Thermal analysis (TA) is a group of physical techniques in which the chemical or physical properties of a substance, a mixture of substances or a reaction mixture are measured as a function of temperature or time, while the substances are subjected to a controlled temperature programmed heating or cooling rate.

The program may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant at different time spam. The graphical results obtained are called the thermogram.

These methods are usually applied to solids, liquids and gels to characterize the materials for quality control.

■ **The advantages of TA over other analytical techniques can be summarized as follows:**

(1) The samples can be studied over a wide temperature range using various temperature programs.

(2) Almost any physical from of sample (solid, liquid or gel) can be accommodated using a variety of sample vessels.

(3) A small amount of sample (0.1 µg – 10 mg) is required.

(4) The atmosphere of the sample can be standardized.

(5) The time required to complete an experiment ranges from several minutes to hours.

2-Thermal analysis techniques

The general components of TA apparatus are; a physical property sensor, a controlled temperature programmed furnace and a recording device (x-y recorder or a micro-computer).

According to the measured property, the following table is a list of the main thermal analysis methods:

Name of Method	Symbol	Property Measured
Thermogravimetry	TG	Mass
Derivative Thermogravimetry	DTG	First derivative of mass change
Differential Thermal Analysis	DTA	Differential temperature
Differential Scanning Calorimetry	DSC	Enthalpy
Thermomechanical Analysis	TMA	Mechanical properties
Dynamic Mechanical Analysis	DMA	Visco-elastic properties
Dynamic Load Thermomechnaical Analysis	DLTMA	Mechanical properties
Thermodilatometry	-	Dimensions
Evolved Gas Detection	EGD	Evolved gas detection-thermal conductivity
Evolved Gas Analysis	EGA	Identity and amount of gas/gases evolved
Dielectric Thermal Analysis	DETA	Dielectric constant
Thermoluminescence	TL	Light emission

1: Thermogravimetric Analysis (TGA)

- **Thermogravimetric analysis is the study of the changes in weight of a sample as a function of temperature. The technique is useful strictly for transformations involving the absorption or evolution of gases from a specimen.**

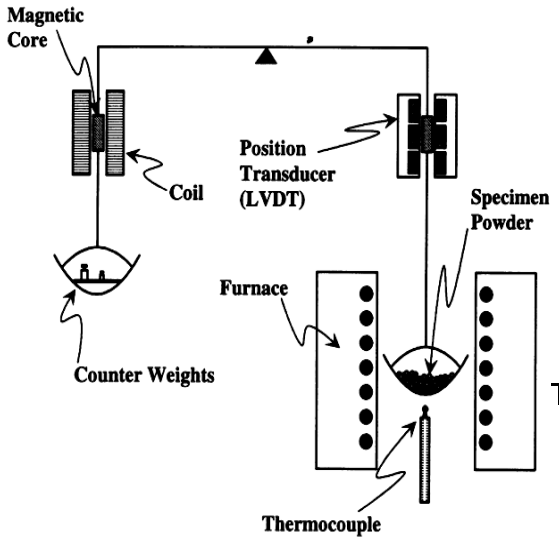
Suitable samples for TGA are solids that undergo one of the two general of reactions:

Reactant(s) → Product(s) + Gas (a mass loss)

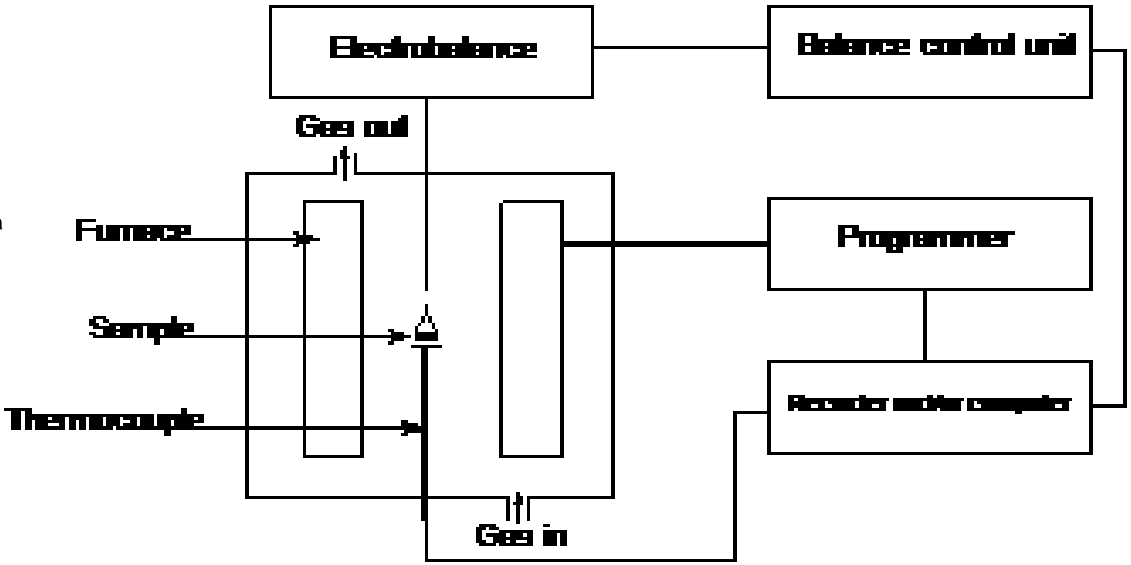
Gas + Reactant(s) → Product(s) (a mass gain)

- **A plot of the changes of the mass versus temperature, is called TGA thermogram.**
- **It permits studying of the thermal stabilities, rate of reactions, reaction processes, and sample composition.**
- **Measurements of changes in sample mass with the temperature are made using thermobalance. The balance should be in a suitably enclosed system so that the atmosphere can be controlled.**

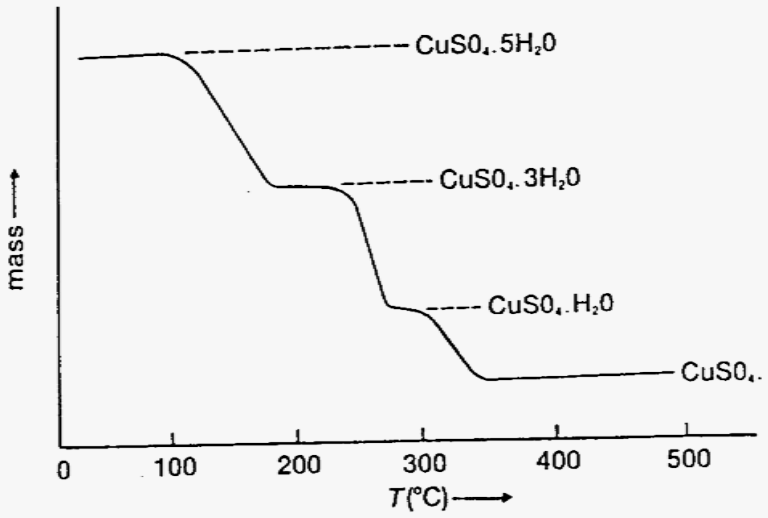
- **Thermogravimetric instrument should include several basic components to provide the flexibility necessary for the production of useful analytical data:**
  - **A microbalance,**
  - **A heating device,**
  - **A unit for temperature measurement and control,**
  - **A means for automatically recording the mass and temperature changes,**
  - **A system to control the atmosphere around the sample.**

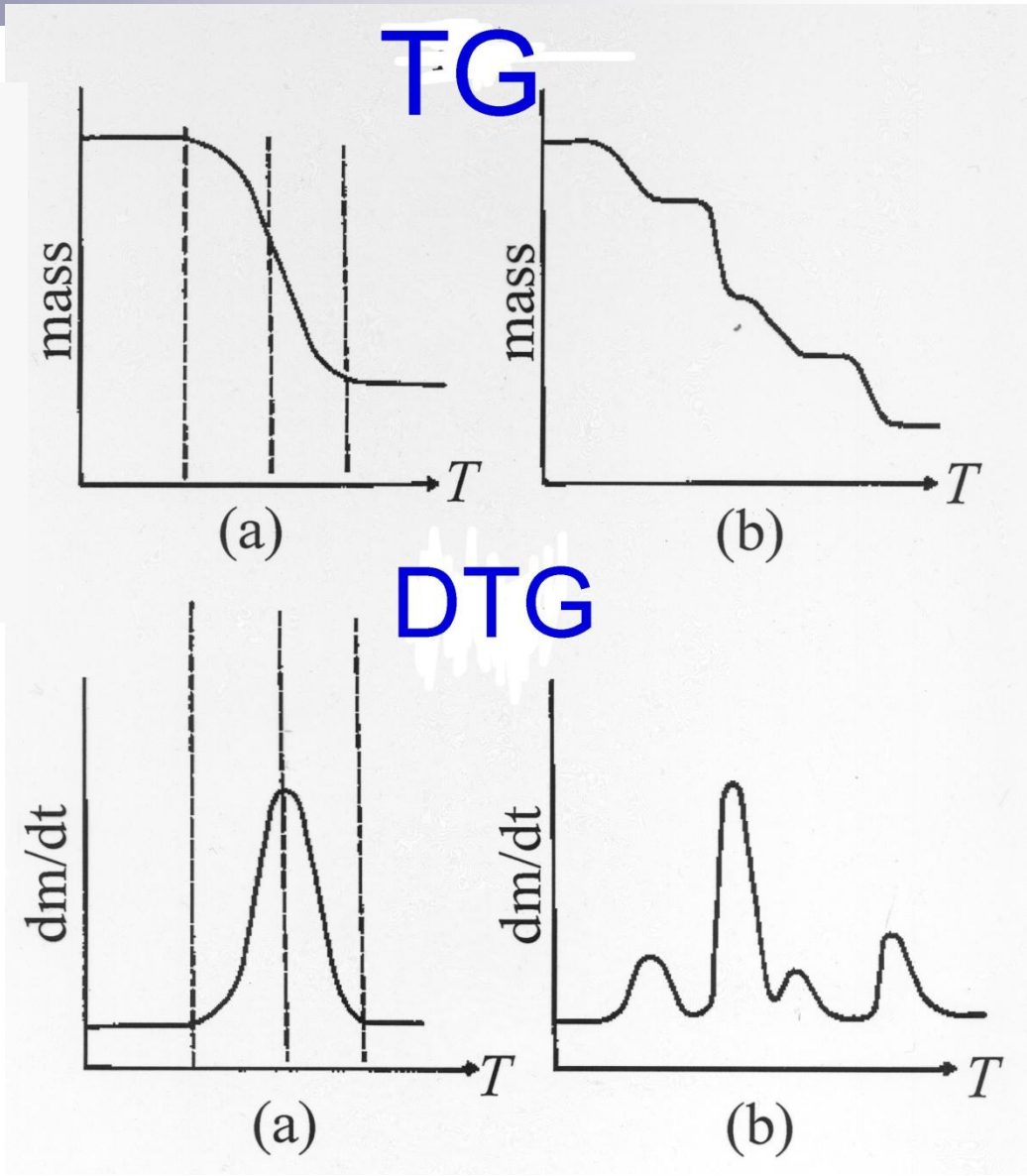


Thermobalance



TGA technique



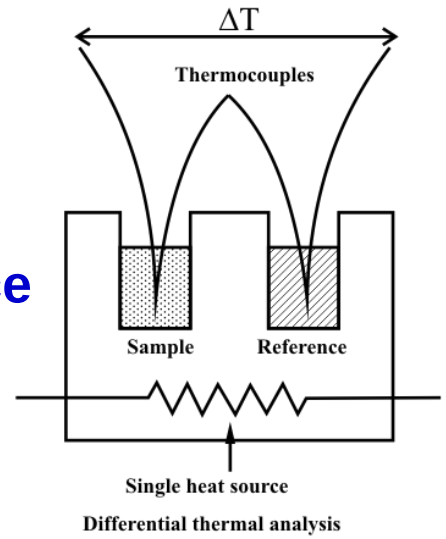


TG thermogram for the dehydration of CuSO4·5H2O It shows three dehydration in three steps, reflecting different types of water molecules.

TGA thermogram

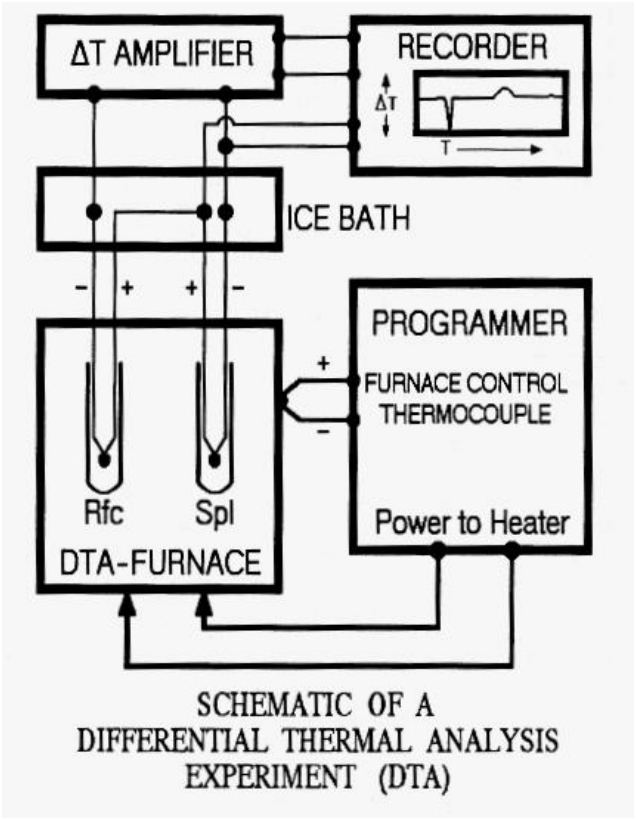
Differential Thermal Analysis (DTA)

- **DTA measures temperature difference between a sample and an inert reference, Δ T, (usually Al_2O_3) while the heat flow to the reference and the sample remains the same.**



(c)

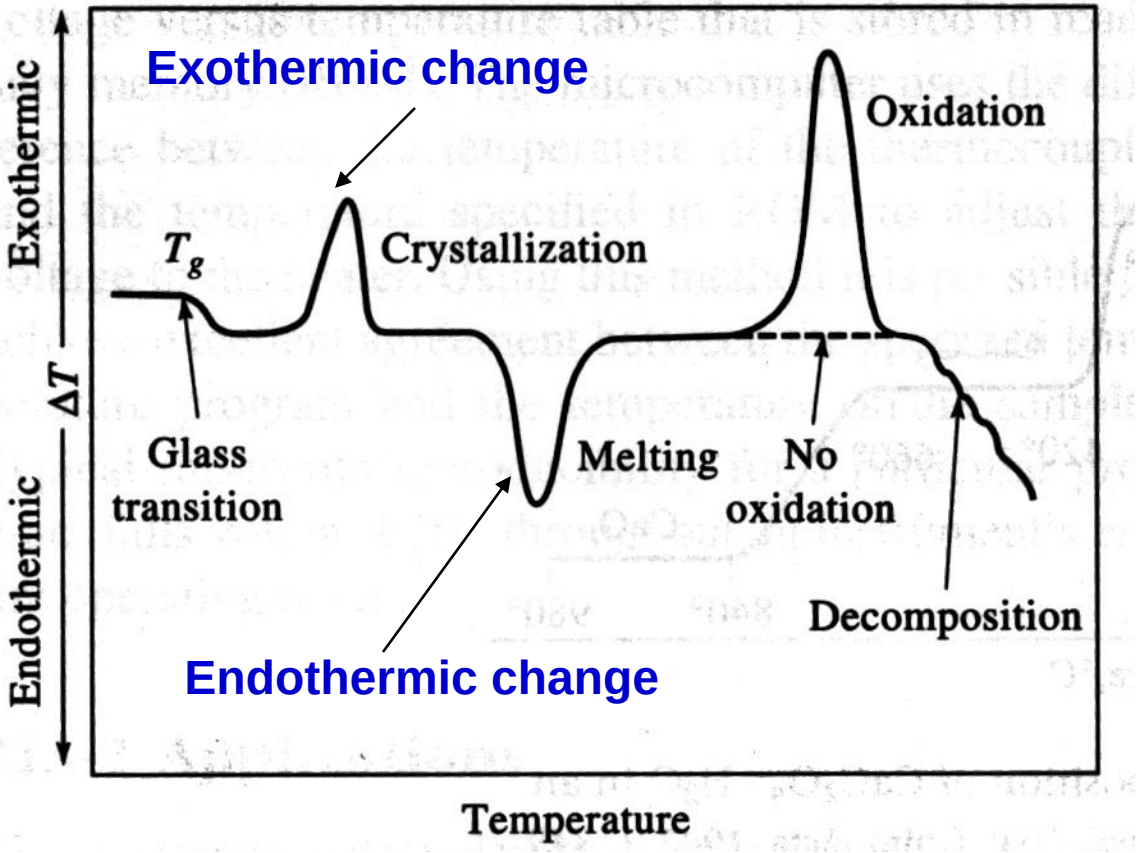
Heating furnace



SCHEMATIC OF A DIFFERENTIAL THERMAL ANALYSIS EXPERIMENT (DTA)

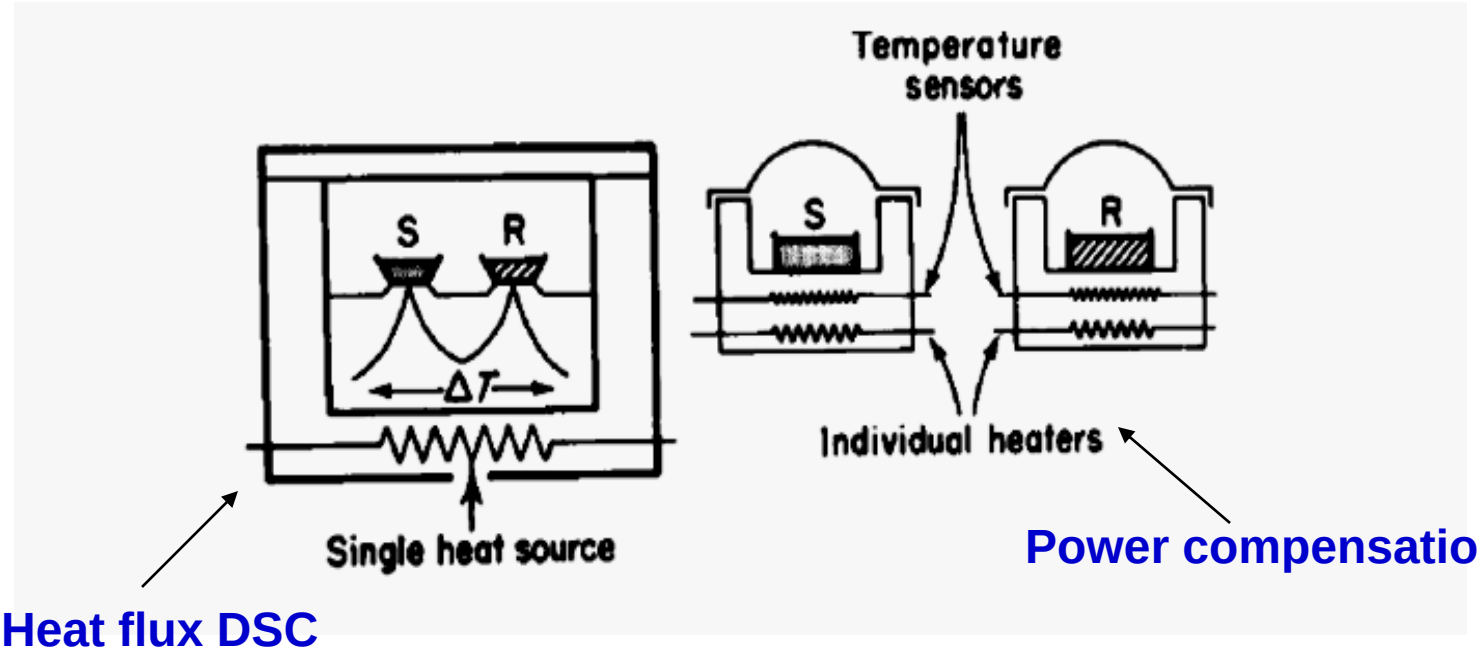
DTA Thermogram

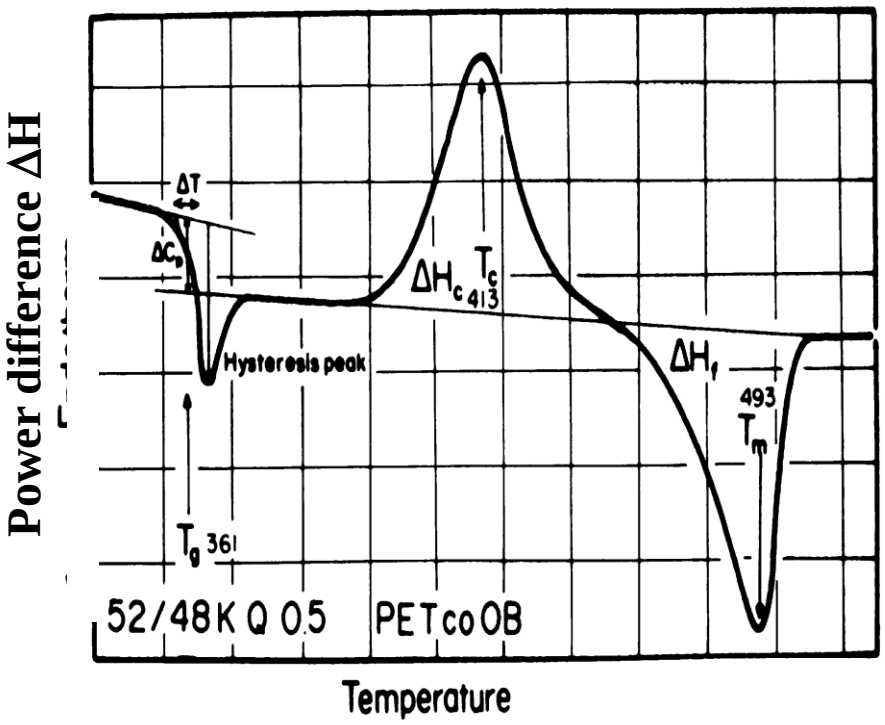
- In Exothermic changes, as crystallization, the sample temperature increases than the reference.
- In endothermic changes, as melting, the sample temperature decreases than the reference.



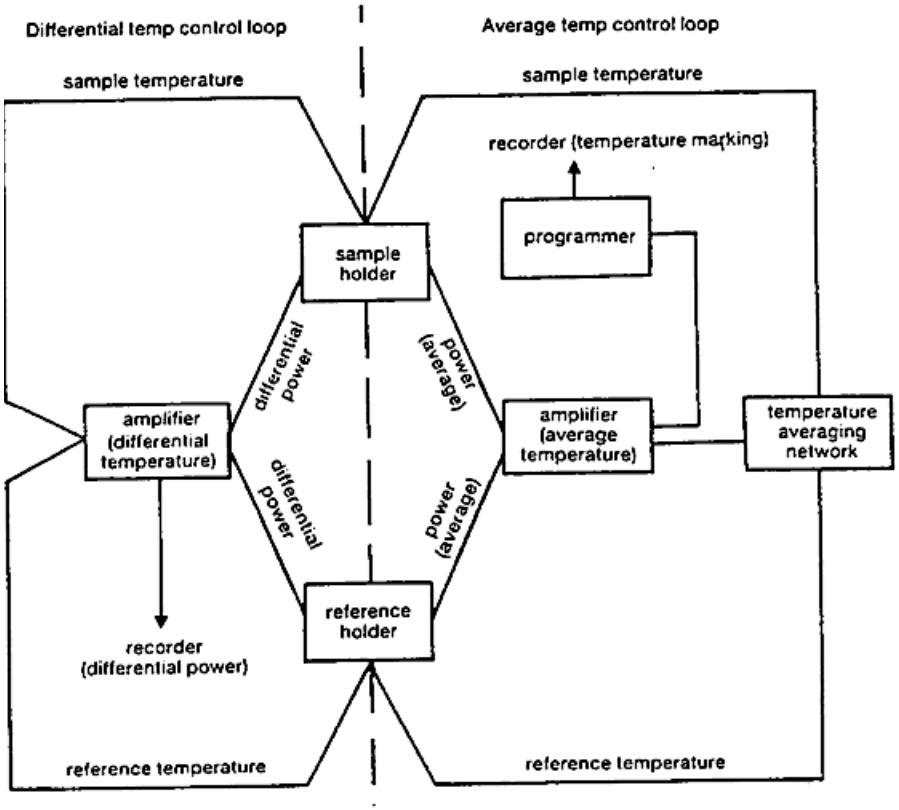
Differential Scanning Calorimetry (DSC)

- DSC measures differences in the amount of heat (ΔH) required to increase the temperature of a sample and a reference as a function of temperature.
- DSC can be used to study heats of reaction, kinetics, heat capacities, phase transitions, thermal stabilities, sample composition and purity and phase diagrams.





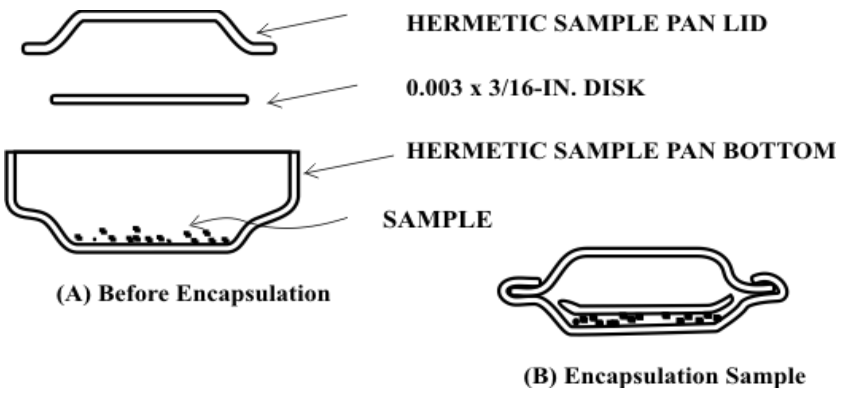
DSC trace of poly(ethylene terephthalate-co-p-oxbenzoate



DSC circuit

Common notes:

- Sample in TA measurements is usually contained in aluminium sample pans (crucible) which can be sealed by cold-welding for holding volatile samples
- For T >500 °C ; quartz, alumina (Al_2O_3), gold or graphite pans are used.
- The reference material in most DTA or DSC applications is simply an empty sample pan.
- Purging of gas into the TGA, DTA and DSC sample holder is possible, e.g. by N_2, O_2, etc.



Variables affecting sensitivity of TA techniques

- **1. The sample**

  The chemical description of the sample together with its source, purity and pre-treatments, the particle size may alter the shape of the TA curve, especially where a surface reaction is involved.

- **2. The crucible**

  The material of the sample holder or crucible should be stated. Sample holders should not interact with the sample during the course of the experiment.

- **3. The heating rate (dT/dt)**

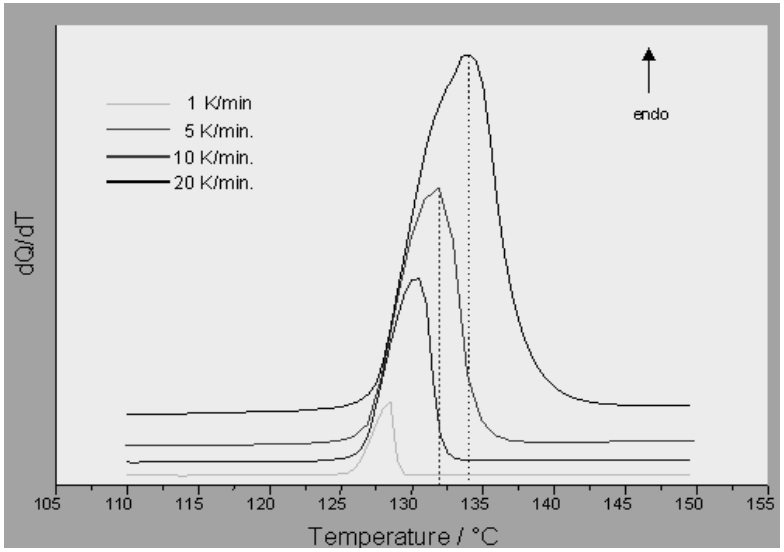
  Experiments may be carried out at slow to very high rates. The 'normal' rate is about 10 K min^{-1}. In order to approach equilibrium conditions most closely, we should use a very small heating rate.

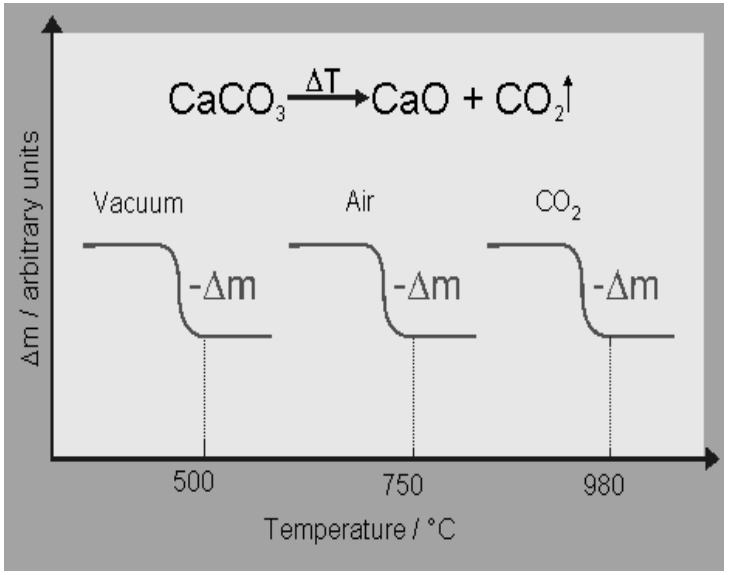
- **4. The atmosphere**

  The atmosphere surrounding the sample and its products may greatly affect the measurements. There may be a reaction between the sample and the atmosphere.

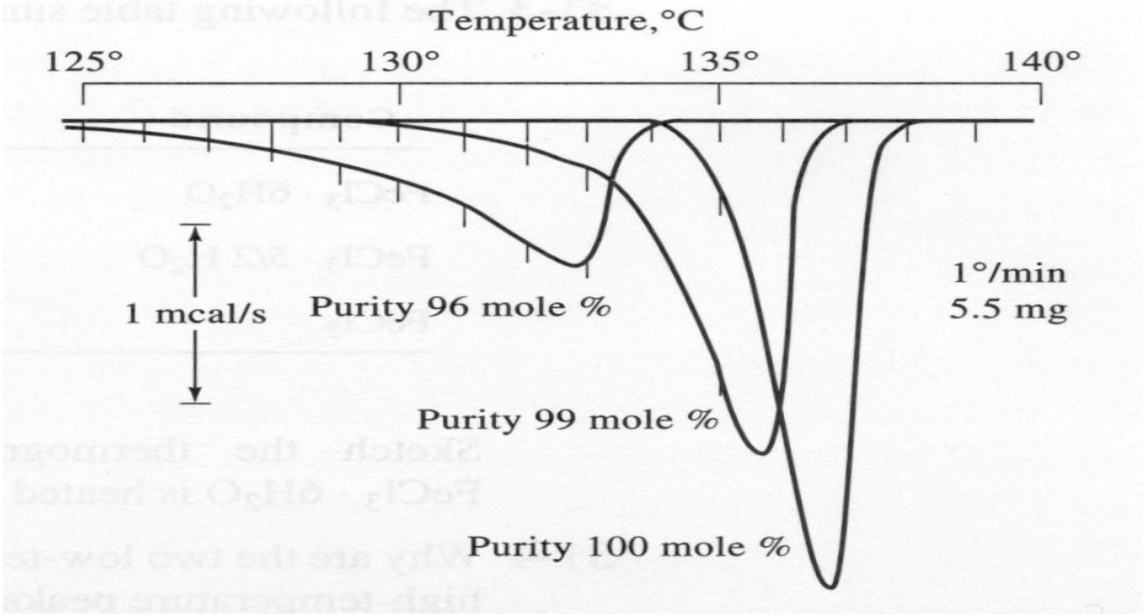
- **5. The mass of the sample**

- **The physical properties, amount and the packing of the sample can affect the results obtained. Small samples are preferable and the average is about 10 mg. Powdered samples or thin films may react more readily than large crystals or lumps.**





- **Measurement of the melting point of Di-tert.-biphenyle at different heating rates.**



- **Thermal decomposition temperatures for $CaCO_3$ in different gas atmospheres.**

- **Effect of changing of purity of pharmaceutical products, e.g. phenacetin on DSC thermogram**

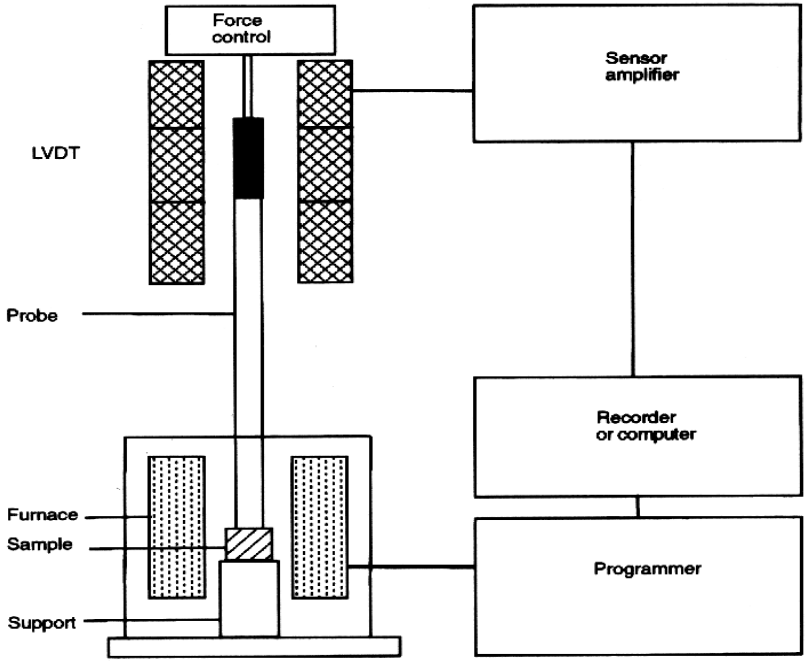
Thermomechanical Analysis (TMA)

Thermomechanical Analysis (TMA) is the study of the relationships between the sample's length (or volume) and its temperature under constant load.

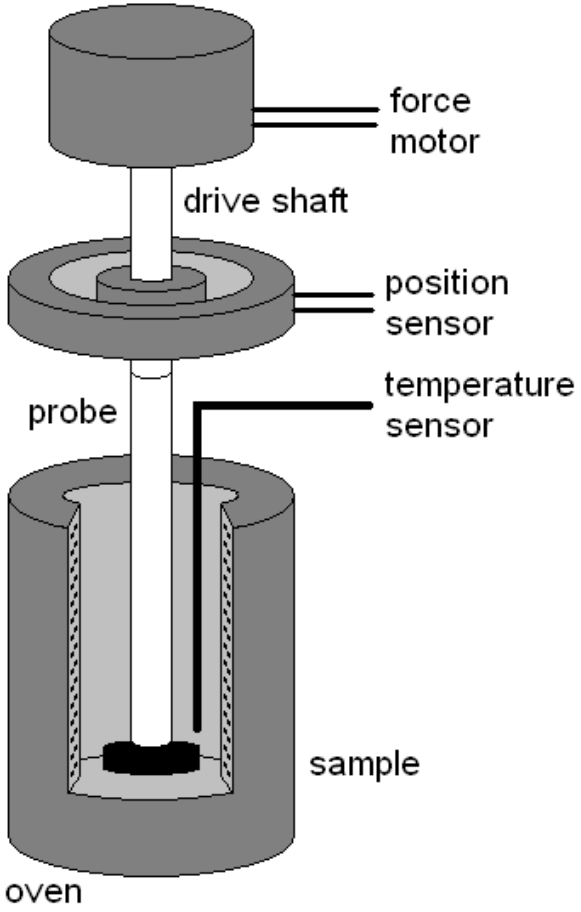
It can be used to study:

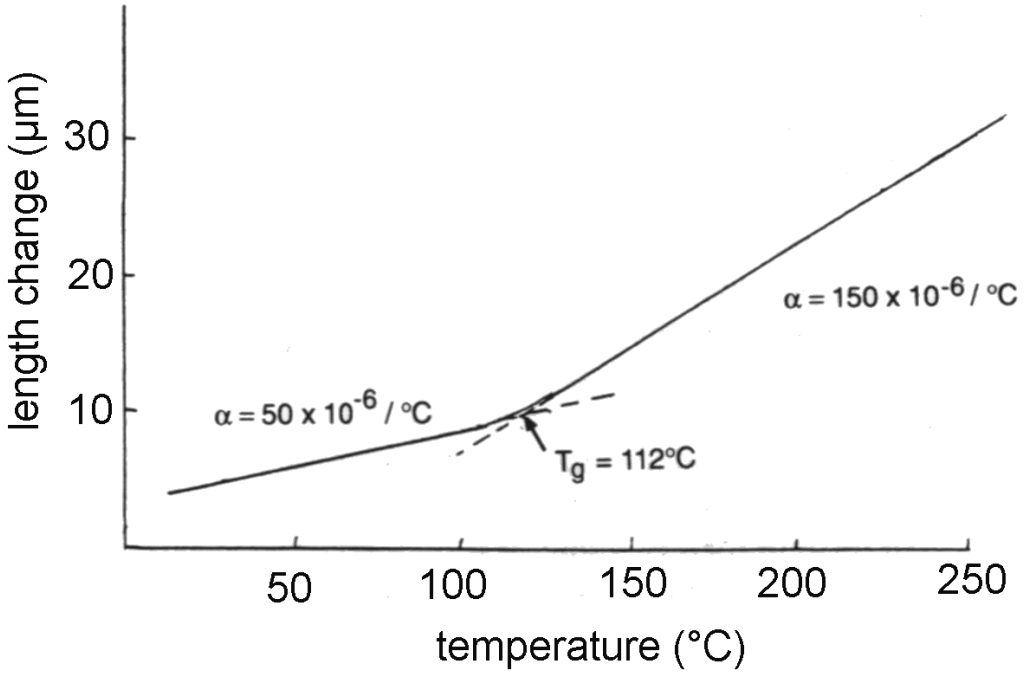
- **mechanical response of sample vs. temperature, as;**

1) expansion coefficient.
2) tension properties, shrinkage & expansion under stress.
3) dilatometry, volumetric expansion.
4) fiber properties, tensile response.
5) softening or penetration under load.
6) Yields soften points, modulus changes, phase transitions & creep properties.



TMA thermogram



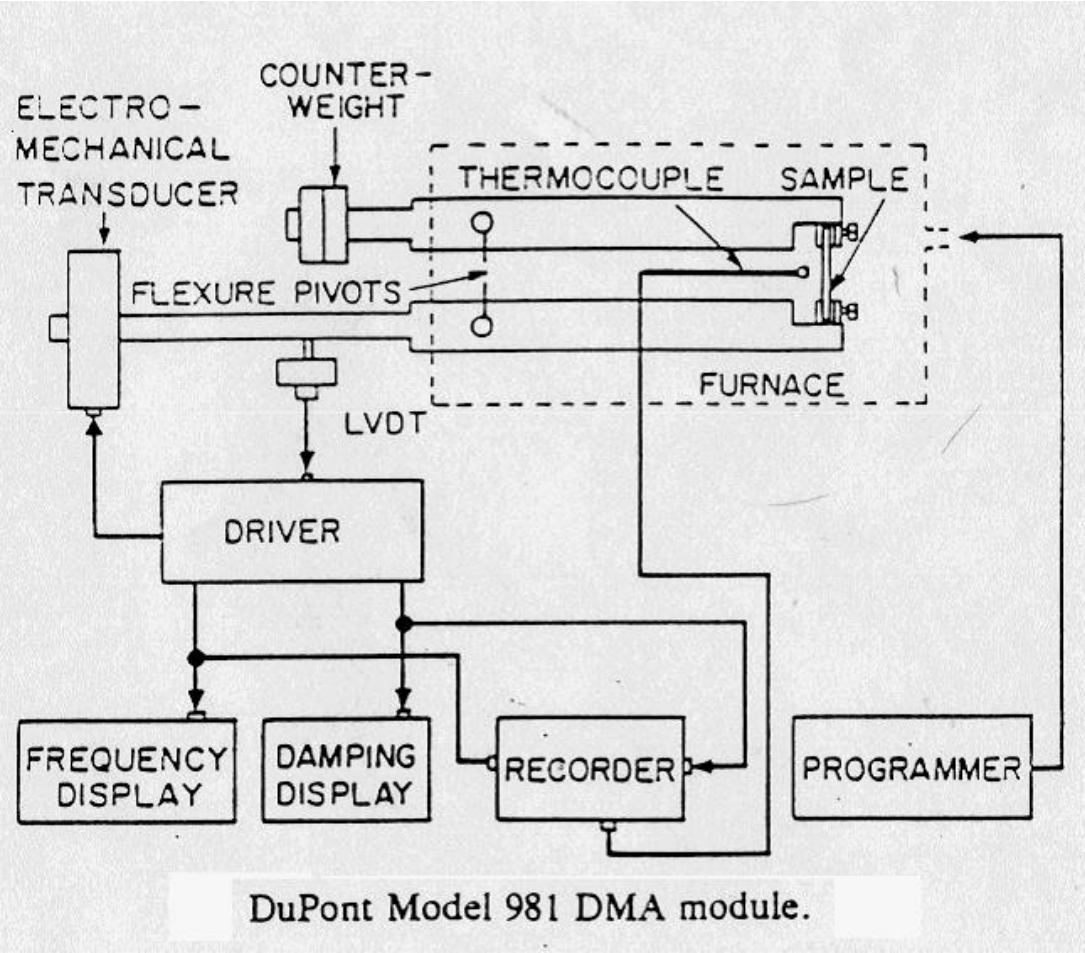


Instrumentation

Thermal expansion coefficient (α) is a useful engineering quantity:
$\alpha = (dL/dt)/Lo$

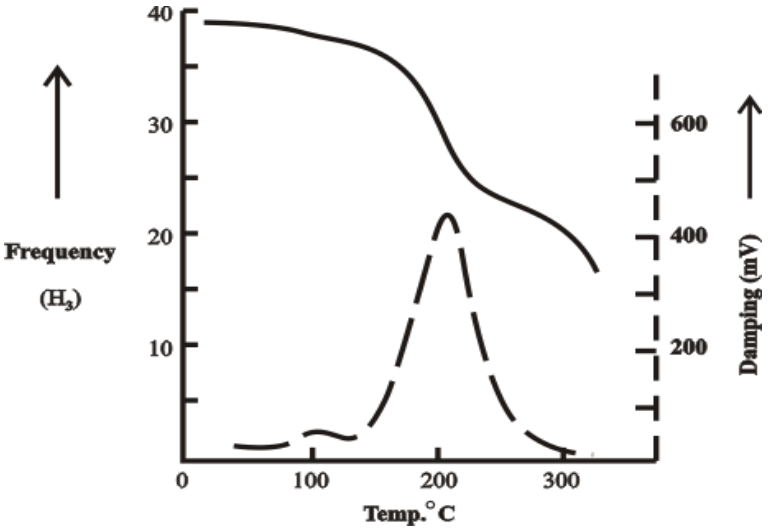
dynamic Mechanical Analysis (DMA)

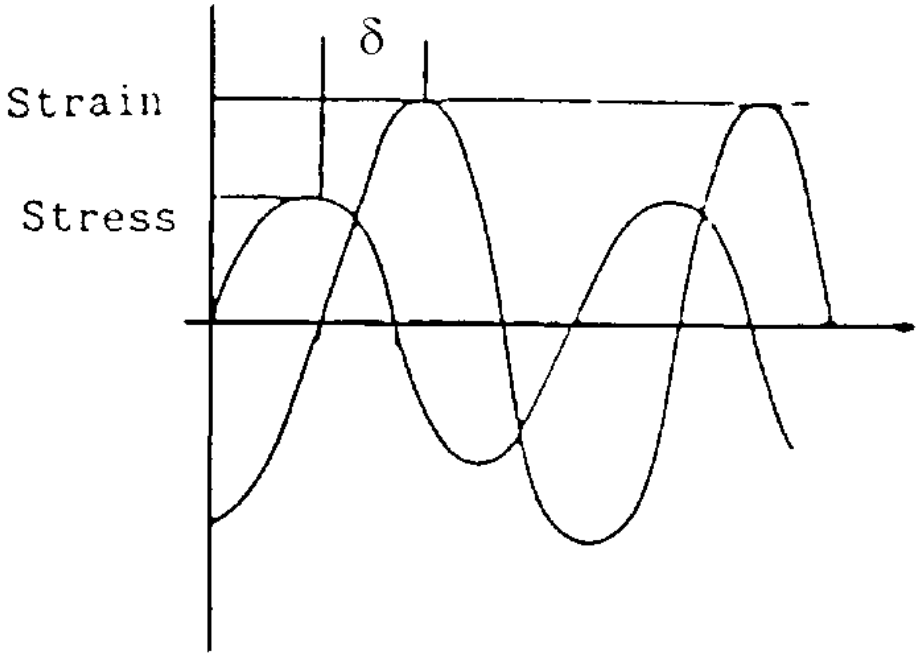
Dynamic mechanical Analysis (DMA) is the study of the relationships between the sample's dimensions (length or volume) and its temperature under constant oscillating load, i. e. under stress or strian. Stress is the force per unit area. Strain is the change of dimension to the original one.



DuPont Model 981 DMA module.

In DMA, the sample properties as elastic modulus and tensile strength are measured. Modulus is the ratio of stress to strain.





- **DMA thermogram of graphite / epoxy composite**

- **Stress and strain wave**

Applications TA

TA often gives information impossible to be obtained by other analytical methods. Often, for complex materials, as polymer composites for development requirements and control incoming of raw material of end use quality.

Generally, the important applications of thermal analysis can be summarized as following:

1) Polymer industries and product reliability, include;

- **Heat capacity and liquid crystal transitions.**
- **Cures and purity of polymers.**
- **The glass transition.**
- **Expansion coefficient and creep studies.**
- **Dynamic properties including viscoelastic measurements, elastic, loss and shear modulus.**

2) Chemical reactions

- Reaction kinetics and the desorption and adsorption behavior of minerals are measured.

3) Pharmaceuticals industry

- Characterization and specification of active and inactive ingredients.
- polymorphic modifications by annealing and purity are studied.
- Solvent detection and quantification of additives.
- Expansion and decomposition of the polymers used to encapsulate the drugs.

4) Ceramic / Glass / Building Materials

- Binder burnout and dehydration of ceramic materials. Decomposition behavior of inorganic building materials.

5) Food industry

- Provide rapid solutions to production and shelf-life of food stuffs.
- Characterization of fat and butter crystallinity.
- Quality control of fat and phase behaviour in frozen systems.
- Denaturation of vegetable and egg proteins.
- Gelatinization of starch.

6) Cosmetics

Develop and analysis quality of cosmetics such as lipstick and nil polish.
The degree of purity of the active ingredients.
Curing of adhesives and powder paints.
Study the penetration behavior of fluids, pastes and powders.

7) Metals and alloys

Measuring of the melting, crystallization, glass transition, secondary phase transition, and specific heat. The influence of corrosion, oxidation or reduction as well as magnetic transitions and thermostability can also be determined.