Thermal Analysis techniques

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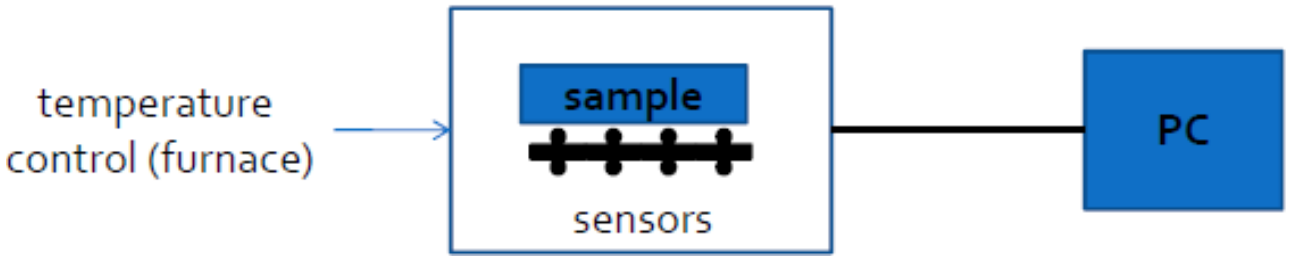
Thermal analysis

- Thermal analysis is a branch of materials science where the properties of materials are studied as they change with temperature.

- Properties are measured as a function of temperature, time, or both
  - Heat flow – direction
  - Mass change – loss / gain
  - Mechanical properties
    - Sheer
    - Strain
    - Dynamic loading
  - Gas evolution

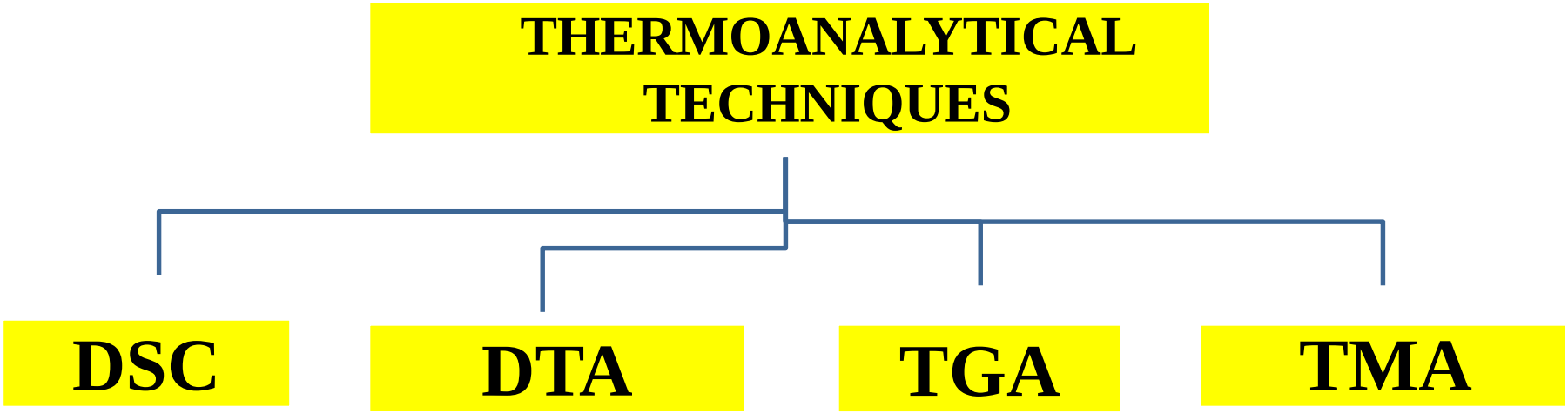
Basic Principles of Thermal Analysis

- Modern instrumentation used for thermal analysis usually consists of the following parts:
  - sample holder/compartment for the sample
  - sensors to detect/measure a property of the sample and the temperature
  - an enclosure within which the experimental parameters (temperature, speed, environment) may be controlled
  - a computer to control data collection and processing



THERMOANALYTICAL TECHNIQUES

Thermal Analysis is the term applied to a group of methods and techniques in which chemical or physical properties of a substance, a mixture of substances or a reaction mixture are measured as function of temperature or time, while the substances are subjected to a controlled temperature programme.



Common Thermal Analysis Methods and the Properties Measured

Method	Abbreviations	Property Measured
Differential scanning calorimeter	DSC	Heat difference
Differential thermal analysis	DTA	Temperature difference
Thermo gravimetric analysis	TGA	Mass
Thermo mechanical analysis	TMA	Dimension

Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter

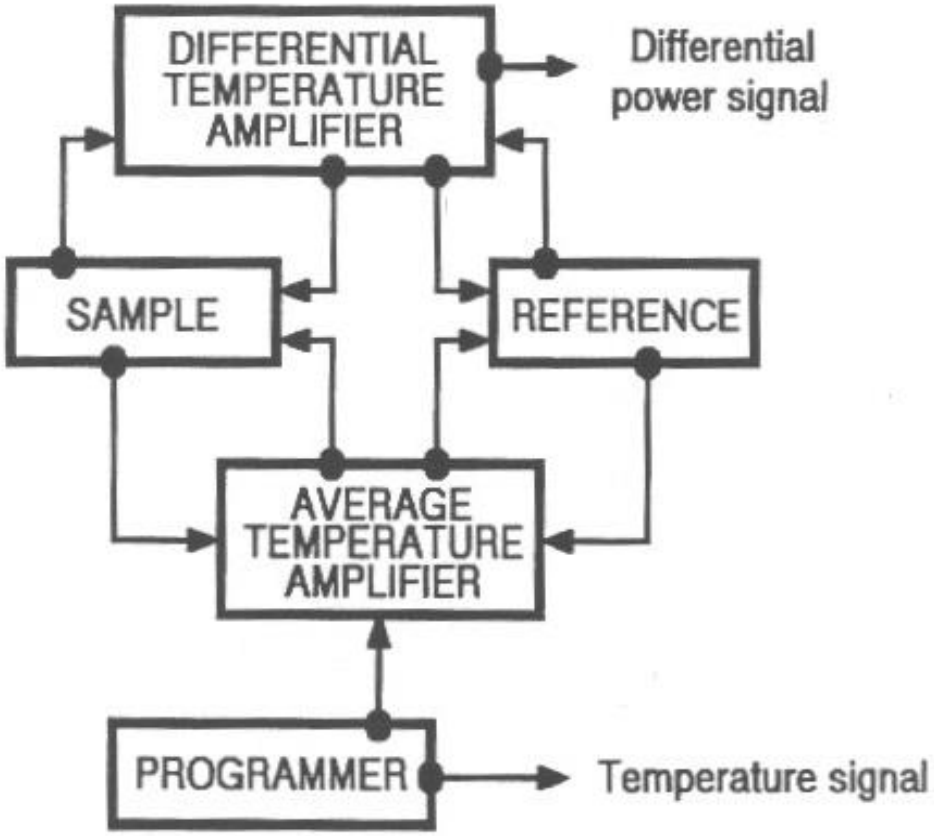
- Differential Scanning Calorimeter (DSC) is one of the most frequently used techniques in the field of thermal characterization of solids and liquids

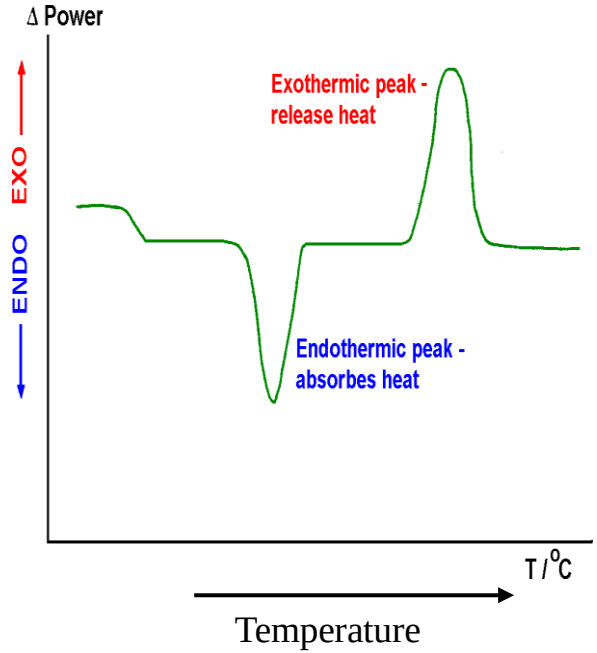
  - melting/crystallization behavior
  - solid-solid reactions
  - polymorphism
  - degree of crystallinity
  - glass transitions
  - cross-linking reactions
  - oxidative stability
  - decomposition behavior
  - purity determination
  - specific heat

Definition

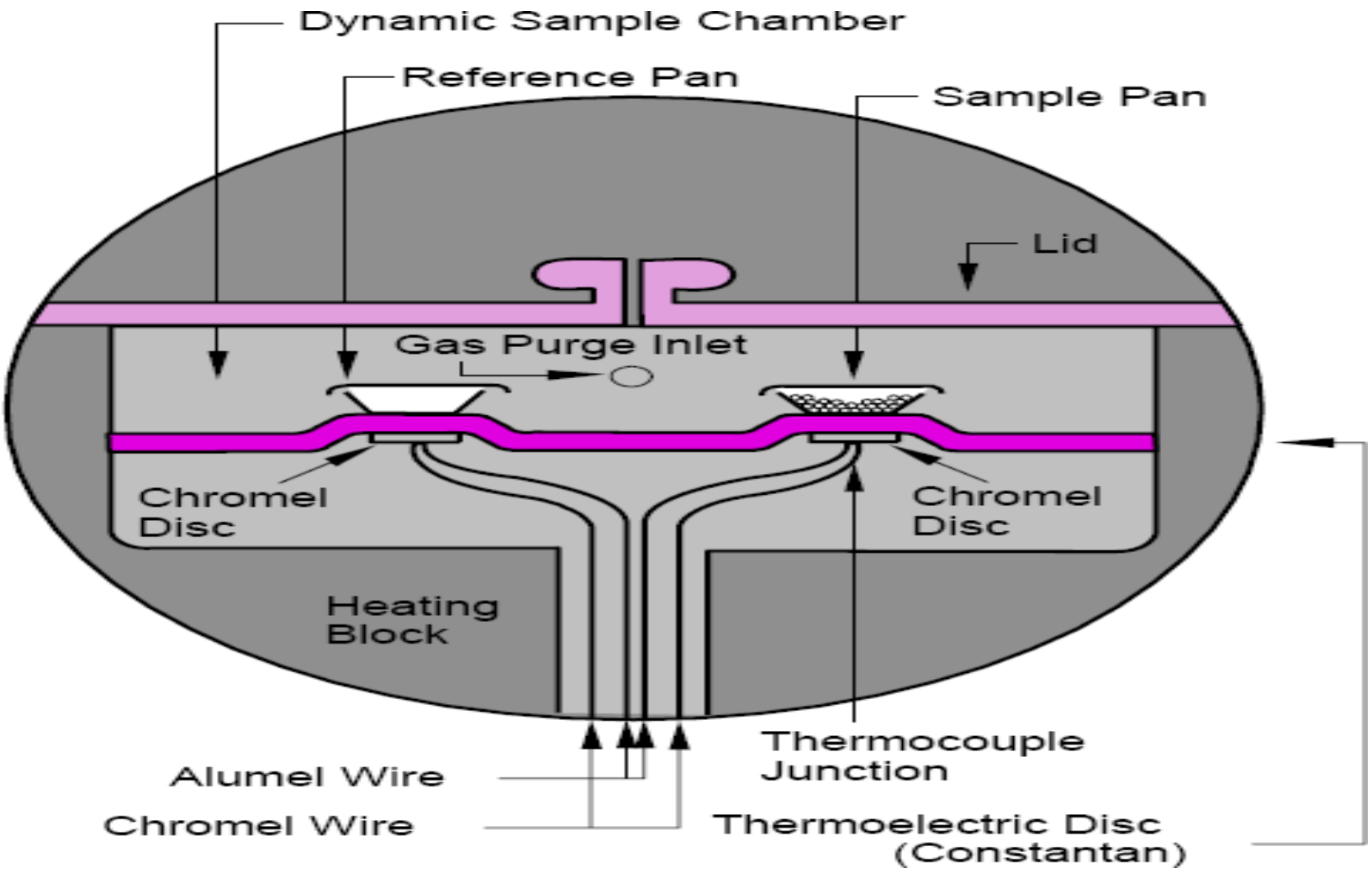
- A **calorimeter** measures the heat into or out of a sample.
- A **differential calorimeter** measures the heat of a sample relative to a reference.
- A **differential scanning calorimeter** does all of the above and heats the sample with a linear temperature ramp.
- **Endothermic** heat flows into the sample.
- **Exothermic** heat flows out of the sample.

Differential Scanning Calorimetry (DSC)





DSC measures differences in the amount of heat required to increase the temperature of a sample and a reference as a function of temperature.

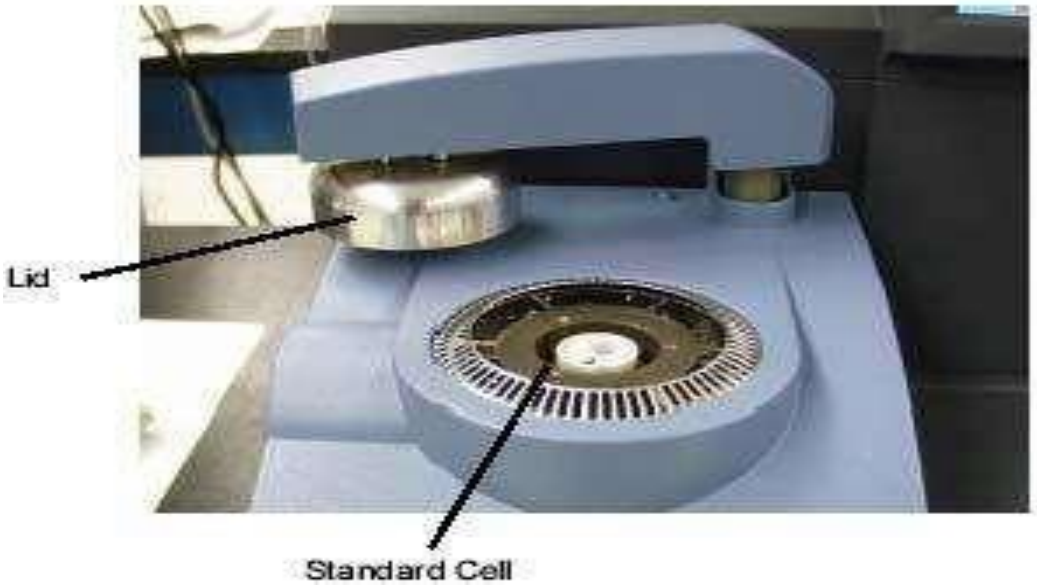

Dynamic Sample Chamber
Reference Pan
Sample Pan
Lid
Gas Purge Inlet
Chromel Disc
Chromel Disc
Heating Block
Thermocouple Junction
Alumel Wire
Chromel Wire
Thermoelectric Disc (Constantan)

Differential Scanning Calorimeter – Principle of Operation

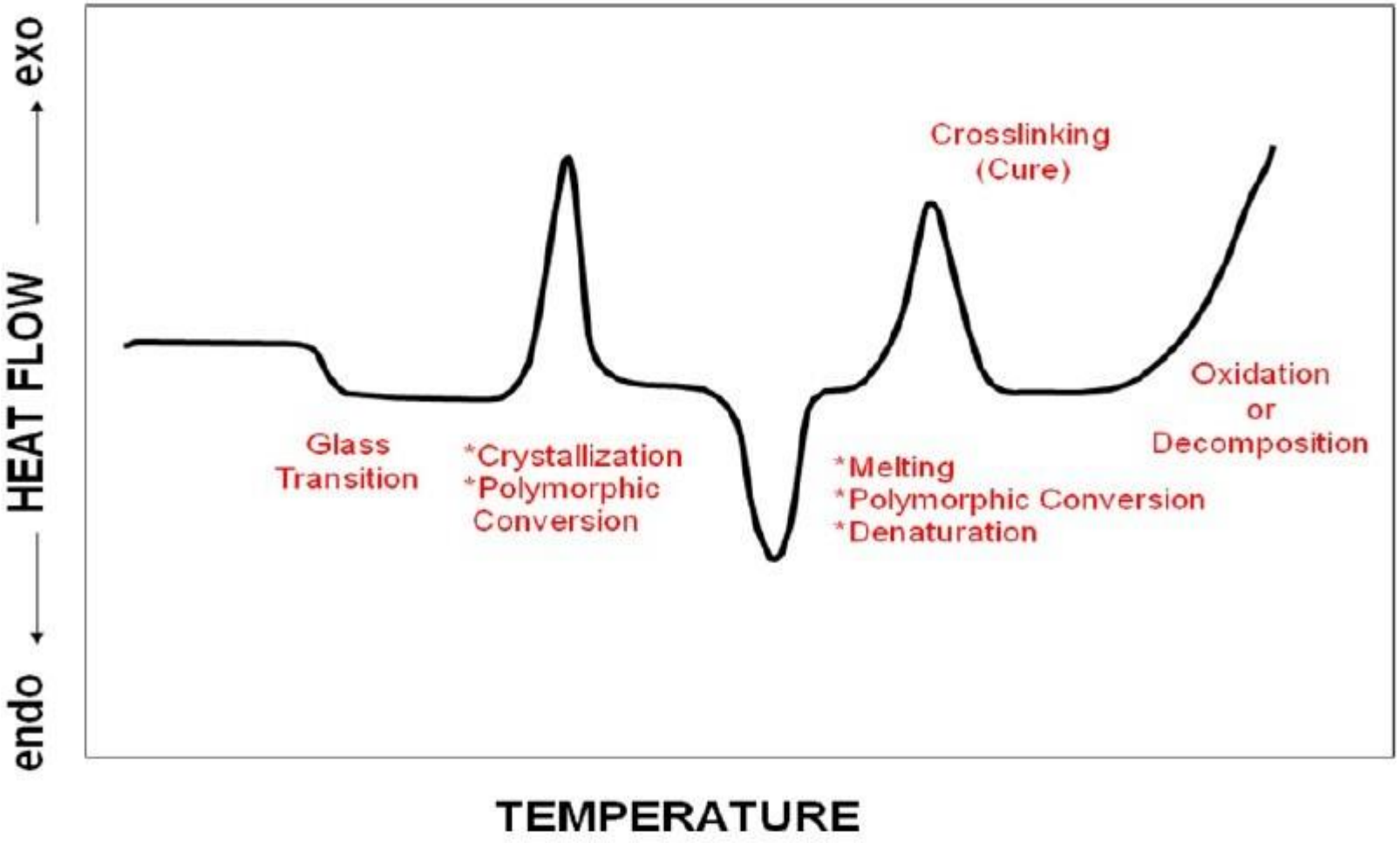
- A sample is placed inside a crucible which is then placed inside the measurement cell (furnace) of the DSC system along with a reference pan which is normally empty (inert gas may be used).
- By applying a controlled temperature program (isothermal, heating or cooling at constant rates), phase changes can be characterized and/or the specific heat of a material can be determined.
- Heat flow quantities are calculated based on calibrated heat flow characteristics of the cell.

Instrument Operation

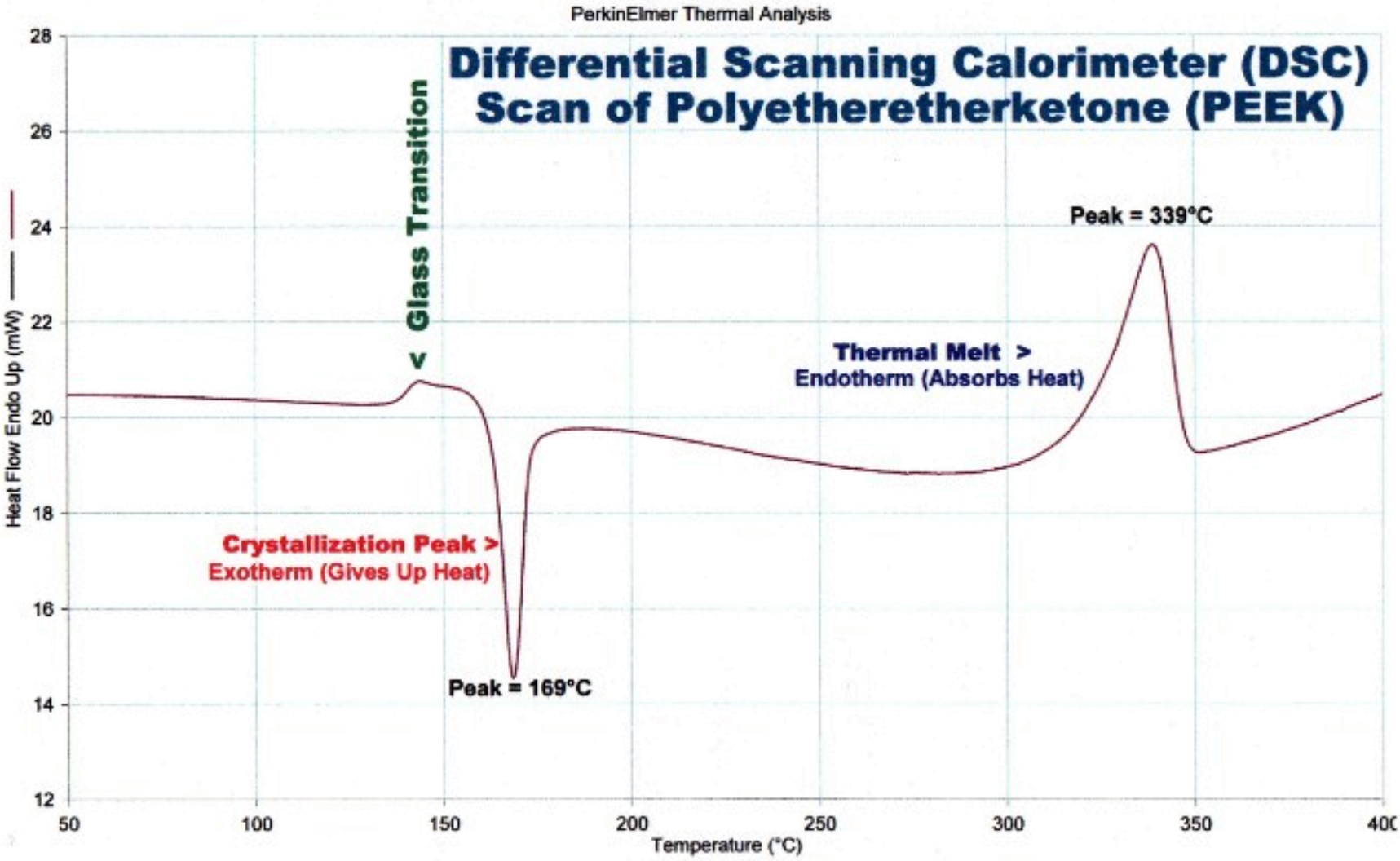
- Powering up the instrument,
- Loading the sample,
- Setting the testing conditions,
- Running a scan and collecting data
- Analyzing the results.



Transitions in a DSC Curve



DSC Data


PerkinElmer Thermal Analysis
Differential Scanning Calorimeter (DSC)
Scan of Polyetheretherketone (PEEK)
Glass Transition
Peak = 339°C
Thermal Melt >
Endotherm (Absorbs Heat)
Crystallization Peak >
Exotherm (Gives Up Heat)
Peak = 169°C
Heat Flow Endo Up (mW)
Temperature (°C)
28
26
24
22
20
18
16
14
12
50
100
150
200
250
300
350

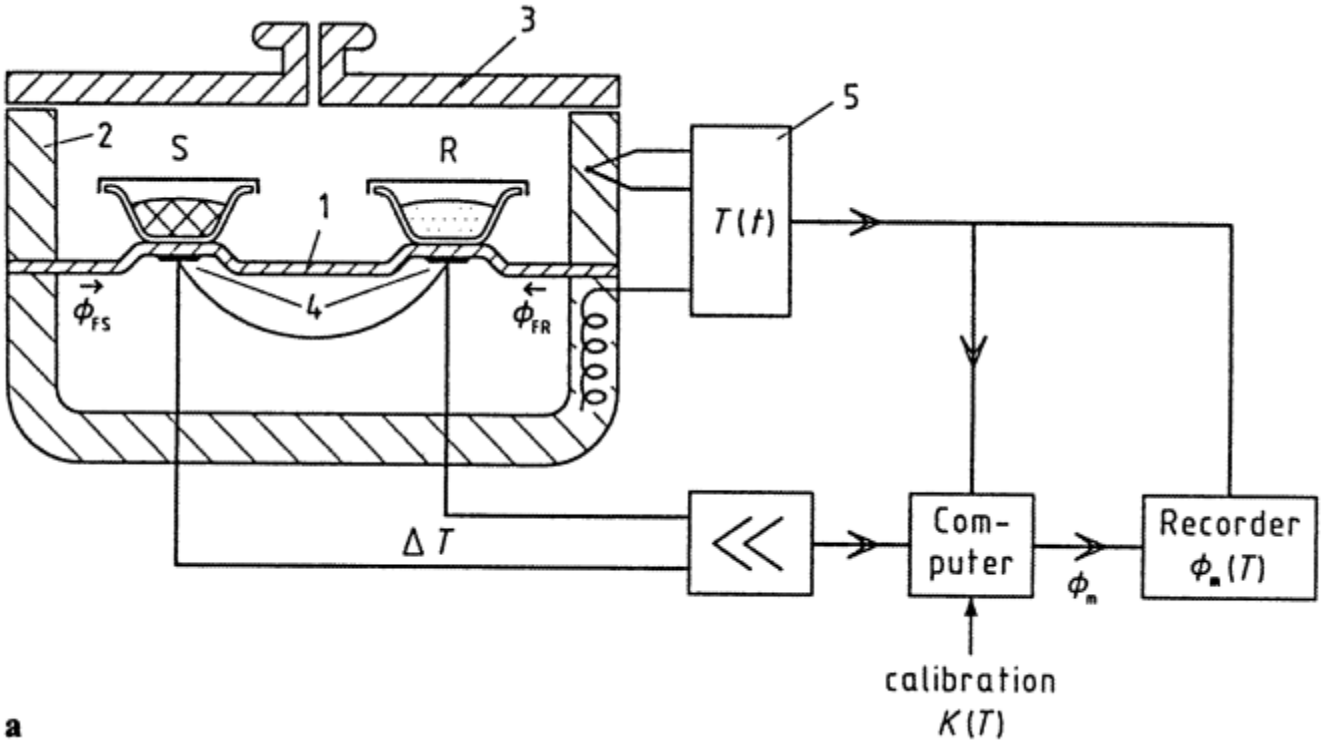
Sample Preparation

- If possible, clean and dry the sample prior to DSC analysis.
- Wear gloves or use forceps when handling your DSC sample.
- DSC samples should be small enough.
- Powder samples or flat solid samples (less than 2 mm tall) work best.
- Sample weight should be between **0.5 and 100 mg.**

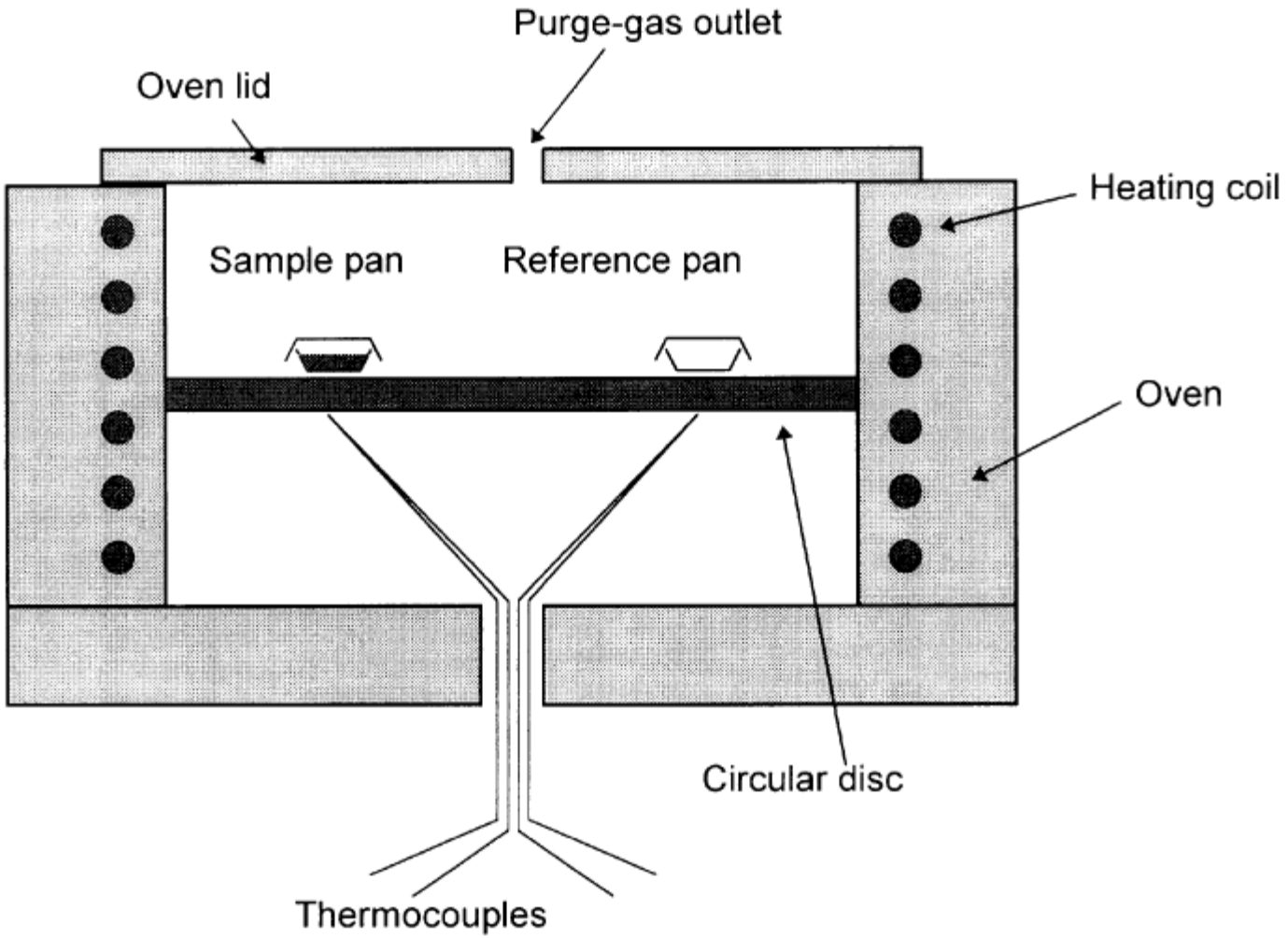
DSC sample preparation procedures

- Weigh sample about 0.5 mg with the analytical balance. Record the weight.
- Use forceps to place sample.
- Use forceps to place the aluminium pan lid on top of the sample.
- Use forceps to load the aluminium pan and sample into the sample encapsulating press .
- Align the sample pan in the encapsulating press, and press down on the handle to
  seal the aluminium pan.
- Use the empty pan as a reference sample.
- Need inert gas like nitrogen to avoid oxidation or decomposition.

Schematics


3
2
S
R
1
4
5
T(t)
$\vec{\phi}_{FS}$
$\vec{\phi}_{FR}$
ΔT
Com-
puter
Recorder
$\phi_m(T)$
ϕ_m
calibration
K(T)
a

Schematics


Purge-gas outlet
Oven lid
Heating coil
Sample pan
Reference pan
Oven
Circular disc
Thermocouples

Applications of DSC

- Identifying the sample
- Measuring Heat Capacity
- Heat of reaction
- Glass transition temp.
- Crystallization Temp.
- Melting
- Evaporation
- Oxidation

DIFFERENTIAL THERMAL ANALYSIS (DTA)

DIFFERENTIAL THERMAL ANALYSIS(DTA)

DTA is a technique in which the difference in temperature between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program.

Differential thermal analysis (DTA)

- DTA involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference.
- This differential temperature is then plotted against time, or against temperature.
- Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference.

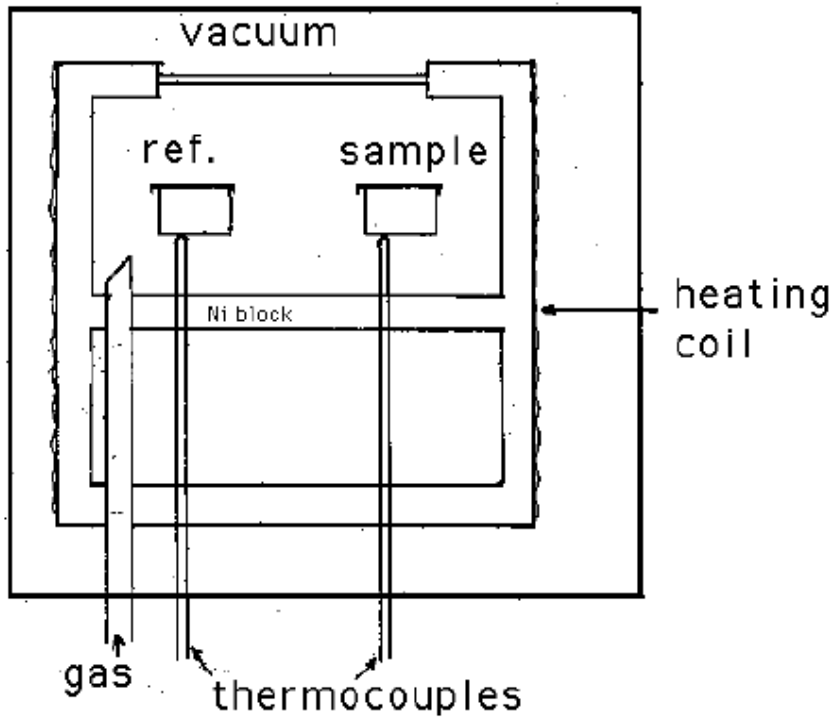


Fig. 1: Schematic illustration of a DTA cell.

Principle

➢It is a technique in which the temperature of the substance under investigation is compared with the temperature of a thermally inert material.

- Initial increase in ΔT is due to the glass transition.
- Tg is the charecteristic temperature at which glassy amorphous polymers become flexible or rubber like.
- When heated to the glass transition temperature, the polymer changes from a glass to a rubber and results in no change in enthalpy.
- The heat capacity of rubber is different from that of glass , which results in the lowering of the baseline. No peak appears during this transition because of the zero enthalpy change.

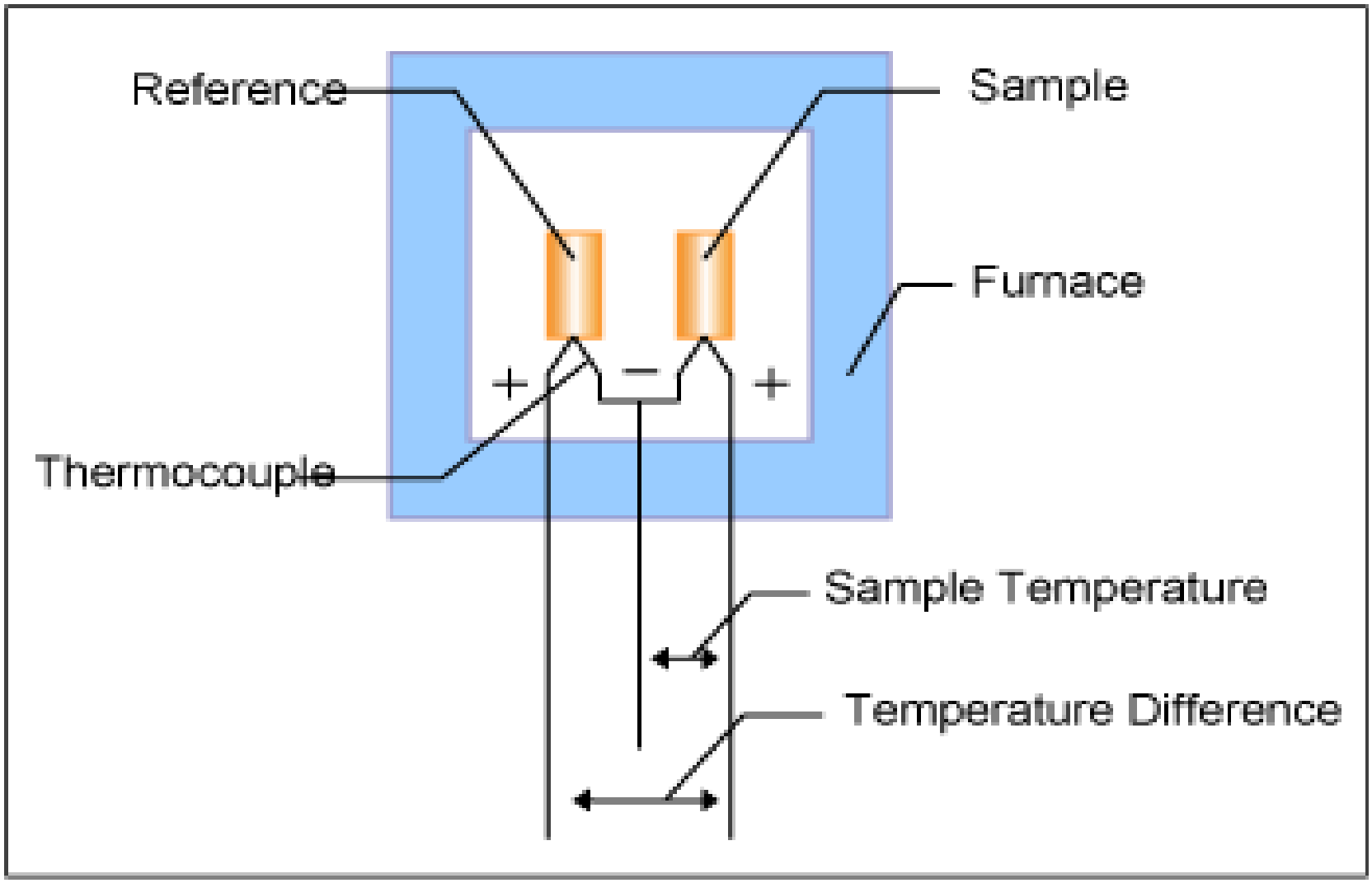


Fig. DTA INSTRUMENTATION

INSTRUMENTATION

- **Sample holder**
- **Sensors**
- **Furnace**
- **Temperature controller**
- **Recording system**

Applications

- **Qualitative and Quantitative Identification of Minerals**
- **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.
- **Measurement of Crystalline:** Measurement of the mass fraction of crystalline material in semi crystalline polymers.
- **Analysis of Biological Materials**

Thermal gravimetric analysis (TGA)

TGA – Principle of Operation

- Thermogravimetry (TG) determines the mass change of a sample as a function of temperature or time.

- A good tool for:
  - quality control and assurance
  - failure analysis of complex polymer mixtures and blends
  - study of a variety of chemical processes accompanied by mass changes

Thermogravimetry (TG)

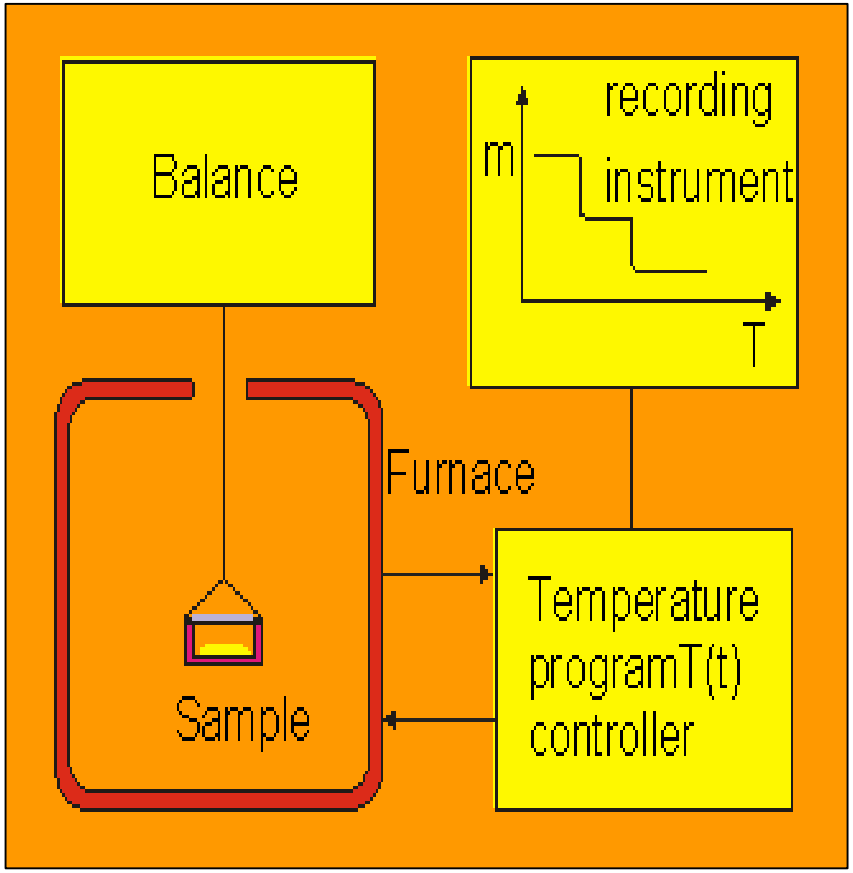
- It is the study of weight changes of a specimen as a function of temperature.
- This technique is useful for transformations involving the absorption or evolution of gases from a specimen consisting of a solid phase.

- **Reactant(s) → Product(s) + Gas** **(a mass loss)**
- **Gas + Reactant(s) → Product(s)** **(a mass gain)**

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

Instrumentation

1. Recording balance
2. Sample holder
3. Furnace
4. Furnace programmer or controller
5. Recording device



1) Recording balance

It is used to record a change in mass of sample/substance.An ideal microbalance must possess following features:

- It should have accuracy and reproducibility and rapid response.
- It should provide electronic signals to record the change in mass using a recorder.
- It should have the capacity of auto-weight/mass adjustment.
- It should be mechanically and electrically stable and user friendly.
- The thermobalance has a clamp which is used to hold the microbalance arm. After the sample has been placed on microbalance, it is left for 10-15 min to stabilize.

2) Sample holder

Available with different size and shape depending upon the weight of sample. Made up of glass, quartz, aluminium, stainless steel etc.

2 TYPES

1)Shallow pan for holding samples which eliminates gas, vapours or volatilematter by diffusion during heating.

2)Deep crucible

3)Furnace

4)Furnace temperature programmer

- These are the controller which can provide gradual rise of temperature at a fixed rate.
- This controlling is done by increasing voltage through the heated element by motor driven variable transformer or by different thermocouples.

INTERPRETATION OF TGA

- This is due to the sequence of physicochemical events that occur under particular conditions over the temperature range
- Ex:1. **calcium carbonate**

  decomposes –single step(800^{o}C–900^{o}C)

  forms calcium oxide (a stable solid) & gas CO_2

  $CaCO3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g)$

- Ex: 2 **ammoniun nitrate**

$NH_4NO_3\ (g) \xrightarrow[(300\ ^{Oc})]{} N2O\ (g) + 2H20\ (g)$

(two volatile prods)

APPLICATIONS

- Determining the purity and thermal stability of both primary and secondary standards.
- Investing the correct drying temperature and the suitability of various weighing forms for gravimetric analysis.
- Determining the composition of alloys and mixtures.

THERMOMECHANICAL ANALYSIS (TMA)

Thermo-Mechanical Analysis (TMA)

- Thermo-mechanical analysis (TMA) provides dimensional properties data for materials.

- Materials tested by thermo-mechanical anlaysis include polymers, composites, laminates, adhesives, coatings, pharmaceuticals, metals, glass, ceramics, fibres and other materials.

Thermo-Mechanical Analysis (TMA)

- Measurement of Dimensional Change
- Coefficient of Linear Thermal Expansion
- Determination of Material Anisotropy
- Softening Temperatures and Glass Transition
- Linear Thermal Expansion

Types of TMA probes and resulting measured properties

TMA Probe Type	Information Obtained
Flat probe/ Light load	Coefficient of Thermal Expansion and Tg
Dilatometer	Coefficient of Thermal Expansion and Tg
Penetration probe/Significant load	Softening (Tg),Melting and creep modulus
Tension accessory	Tg, melting and cure behavior
Parallel plates	Melting, Viscosity and Gelation
Flexure accessory	Softening (Tg) and Melting

**Tg =Glass transition temperature*

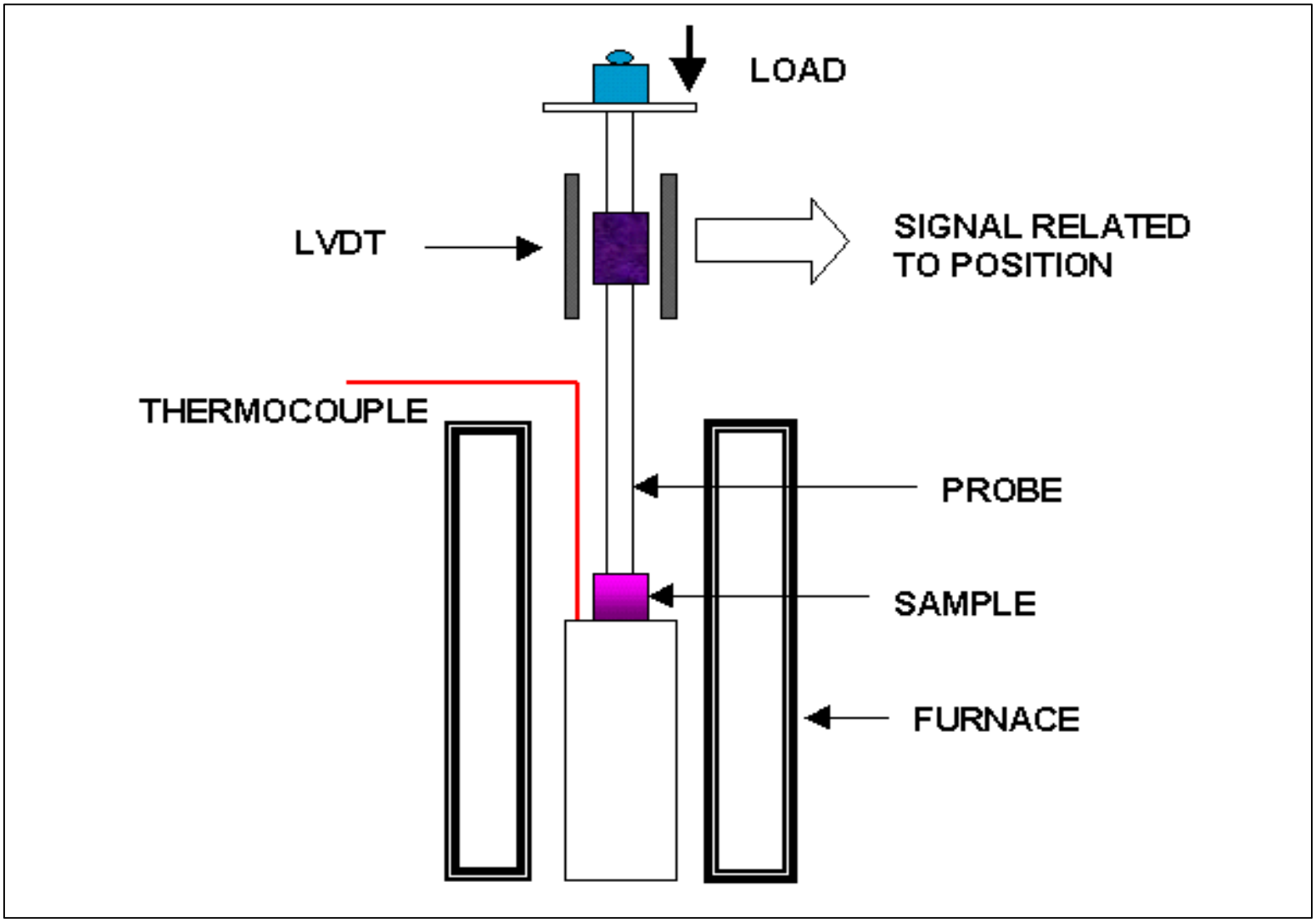
Sample preparation

- The use of TMA in the pharmaceutical industry is limited to polymers.
- In order to examine powdered samples, the sample is packed into a flat DSC pan.
- The dimension of the sample is measured by TMA in millimeters.
- TMA samples should be of 2-6 mm in diameter and 2-10 mm in height.
- Samples for thermal expansion and glass transition measurements should have parallel and flat top and bottom surfaces.
- **NOTE:** To avoid making a mess with molten thermoplastics, you should encapsulate thermoplastic polymer samples in aluminum foil.
- To avoid reactions between molten metals and the quartz probe and stage, you should sandwich your metallic sample between two plates of aluminum oxide.

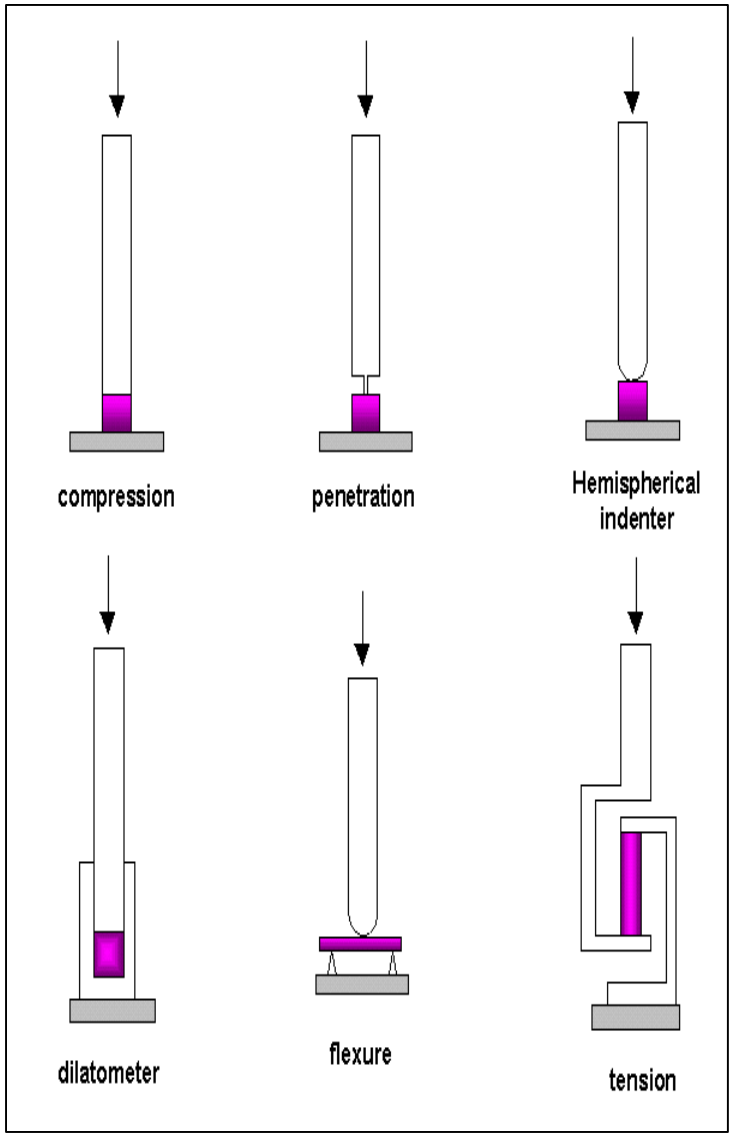
Principle

- A dilatometer is used to determine the linear thermal expansion of a solid as a function of temperature.
- In this a small load acts on the specimen .
- The measured expansion of the specimen can be used to determine the coefficient of linear thermal expansion .
- The 1st heating phase yields information about the actual state of the specimen, including its thermal and mechanical history. When thermoplastics soften, especially above the glass transition, orientations and stresses may relax, as a result of which post crystallization and recrystallization processes may occur.
- To determine the coefficient of expansion as a material characteristic, the material must undergo reversible changes and so forth during a 2nd heating phase that has followed controlled cooling.

Instrumentation



Typical probes



•Where the specimen is large enough, a **macroprobe** with a contact area of approx. 28 mm2 is used.

•For smaller specimens, for example, with an edge length less than 6 mm, a **normal probe** with a contact area of approx. 5 mm2 is suitable.

•**Penetration probes** with a small contact area of just about 0.8 mm2 are suitable for determining the glass transition temperature.

Instrument Operation

- Powering up the instrument,
- Loading the sample,
- Setting the testing conditions,
- Running a scan and collecting data, and Analyzing your results.

Applications

- TMA is used to obtain the melting temperature, softening temperature, coefficient of thermal expansion (CTE) and glass transitions (Tg) of materials.

- Use of the technique on the small scale as a micro-analytical tool to identify the distribution of two materials within a matrix and also on a larger scale to investigate the firing of a ceramic material

TMA Curve of Indium