Analisi Termica

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Introduzione storica all’analisi termica

- Si pensa che sia una tecnica moderna, ma niente di più falso, anzi già anticamente la riconoscibilità di alcune sostanze passava attraverso il trattamento termico: metodi per il riconoscimento dell’oro, dell’argento e dello stagno.
- Lo sviluppo della termodinamica nel 19mo secolo grazie agli studi di Carnot, Gibbs ed Helmoltz, ha contribuito enormemente e definitivamente all’affermazione e diffusione delle tecniche analitiche
- Il primo esperimento termoanalitico è databile 1887 e fu eseguito da Le Chatelier, ponendo una termocoppia in un’argilla sottoposta a riscaldamento fino a 1000°C
- Roberts-Austen è colui che per primo nel 1899 pose attenzione all’aspetto differenziale, rispetto ad un inerte, della misura della temperatura della sostanza in esame e registrò la curva DTA del ferro
- Boersma nel 1955 sviluppò la calorimetria a flusso di calore e nel 1964 Watson sviluppo la calorimetria a compensazione di potenza

Analisi termiche

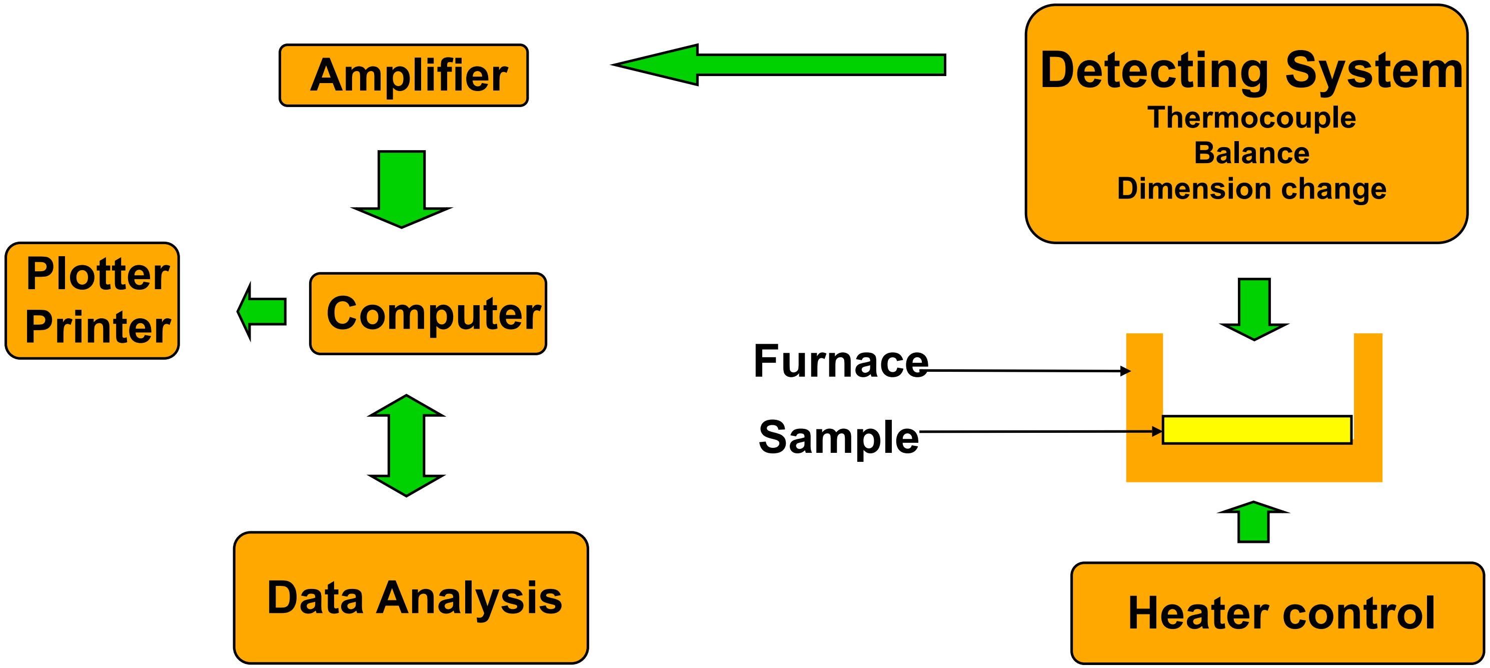
Tutte le attività di misura di proprietà chimico-fisiche e meccaniche dei materiali in funzione del tempo e della temperatura

Technique (abbreviation)	Measured Parameter	Instrument
Differential Thermal Analysis (DTA)	ΔT	DTA Apparatus
Differential Scanning Calorimetry (DSC)	dH/dt	DSC Calorimeter
Thermogravimetry (TG)	mass	Thermobalance
Thermomechanical Analysis (TMA)	dl/l	Dilatometer
Dynamic Mechanical Thermal Analysis (DMTA)	Storage and loss moduli	DMA Apparatus

Methods of Thermal Analysis

- **Calorimetric Effects**
  - **DSC D**ifferential **S**canning **C**alorimeter
  - **DTA D**ifferential **T**hermal **A**nalyser
- **Changes in Mass**
  - **TGA T**hermo **G**ravimetric Analyser
  - **TG/DTA T**hermo **G**ravimetric/ **D**ifferential **T**hermal **A**nalyser
- **Dimension Change**
  - **TMA T**hermo **M**echanical **A**nalyser
  - **TMA/SS T**hermo **M**echanical **A**nalyser/**S**tress **S**train
- **Viscoelastic Properties**
  - **DMA D**ynamic **M**echanical **A**nalyser
  - **DMTA D**ynamic **M**echanical **T**hermal **A**nalyser
  - **DMS D**ynamic **M**echanical **S**pectrometer
- **Other Techniques and Combined Techniques**
  - **EGA E**volved **G**as **A**nalyser
  - **TG/MS T**hermo **G**ravimetry/ **M**ass **S**pectroscopy
  - **TG/GC/MS T**hermo **G**ravimetry/**G**as **C**hromatography/**M**ass **S**pectroscopy

Fundamental Thermal Analysis

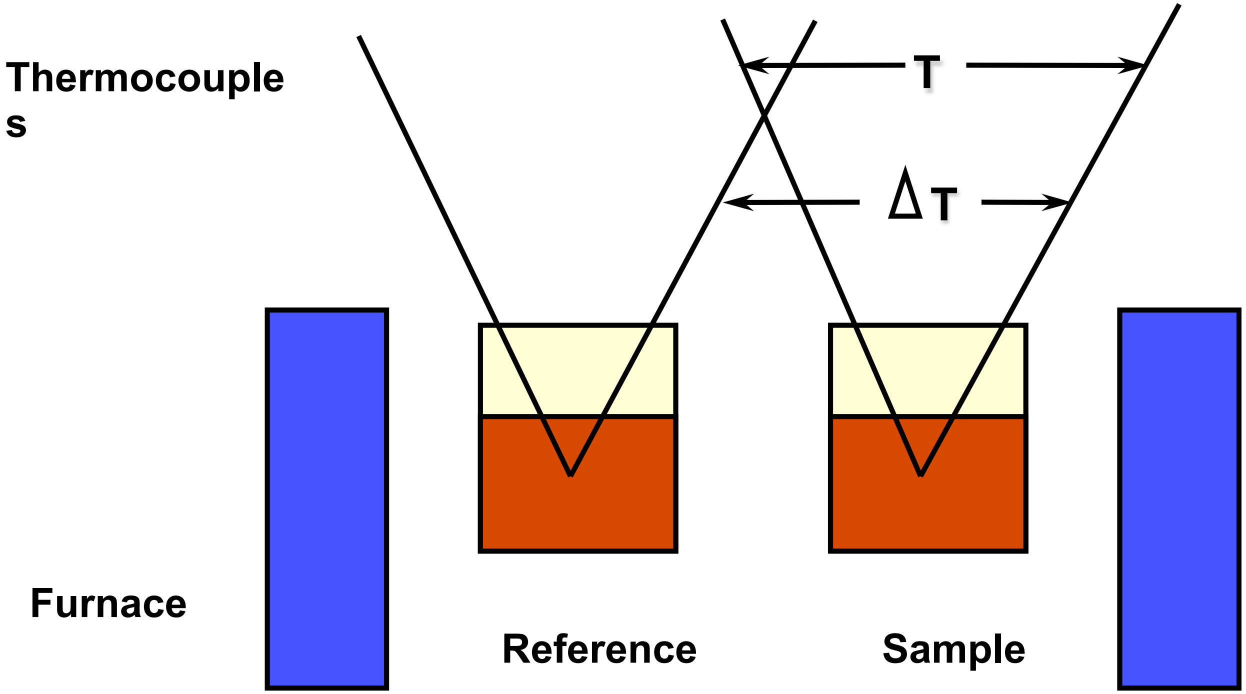


Differential Thermal Analysis

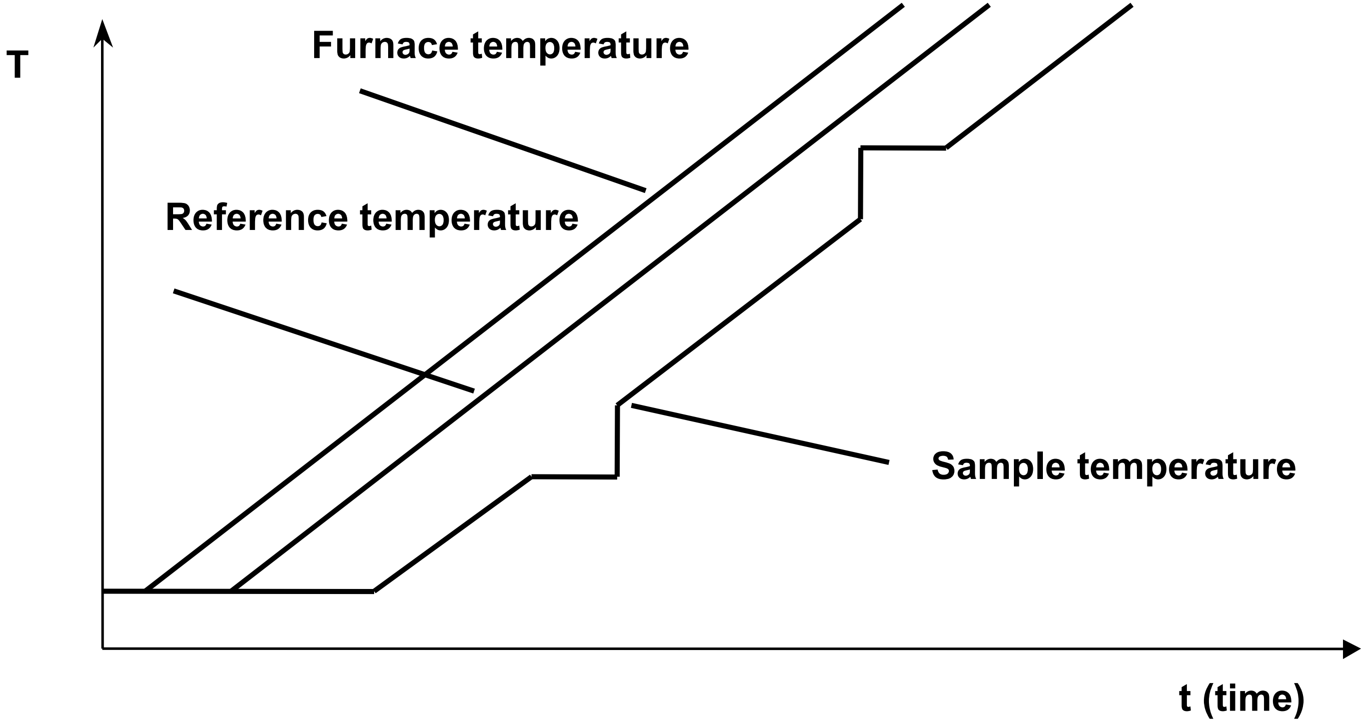
Differential Thermal Analysis (DTA) is a technique in which the Temperature of a sample is measured against a thermally inert substance, while both are subjected to a controlled temperature program.

The data are acquired as a function of Sample (T_s), Reference (T_r) or Furnace (T_c) Temperature

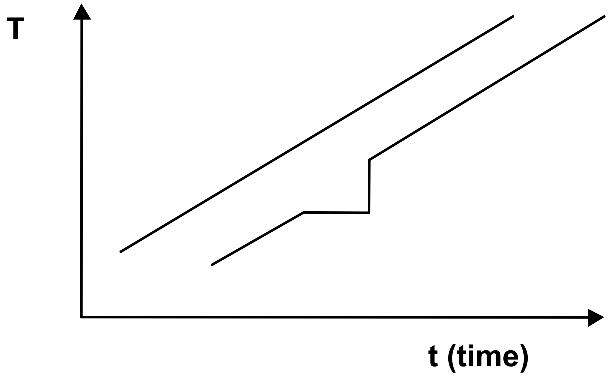
Differential Thermal Analyser



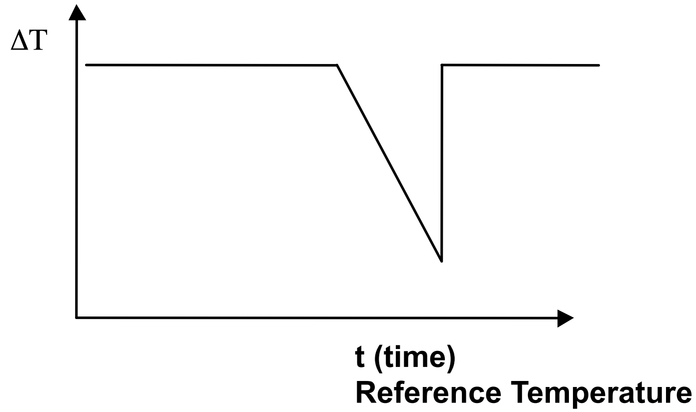
Differential Thermal Analyser

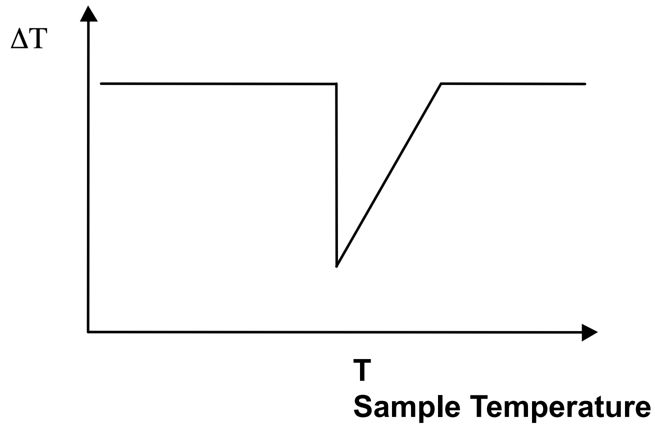


Differential Thermal Analyser

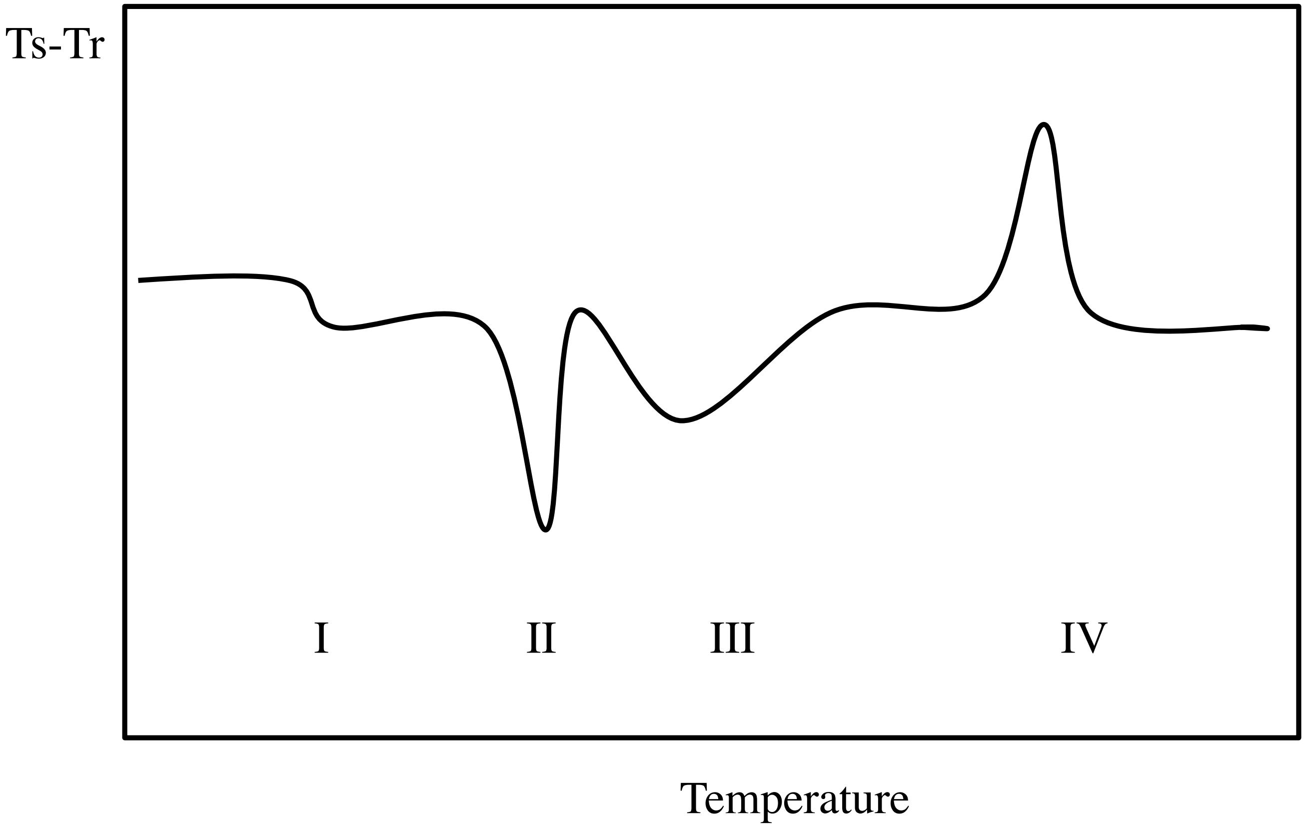


Endothermal effect





Generalized DTA curve



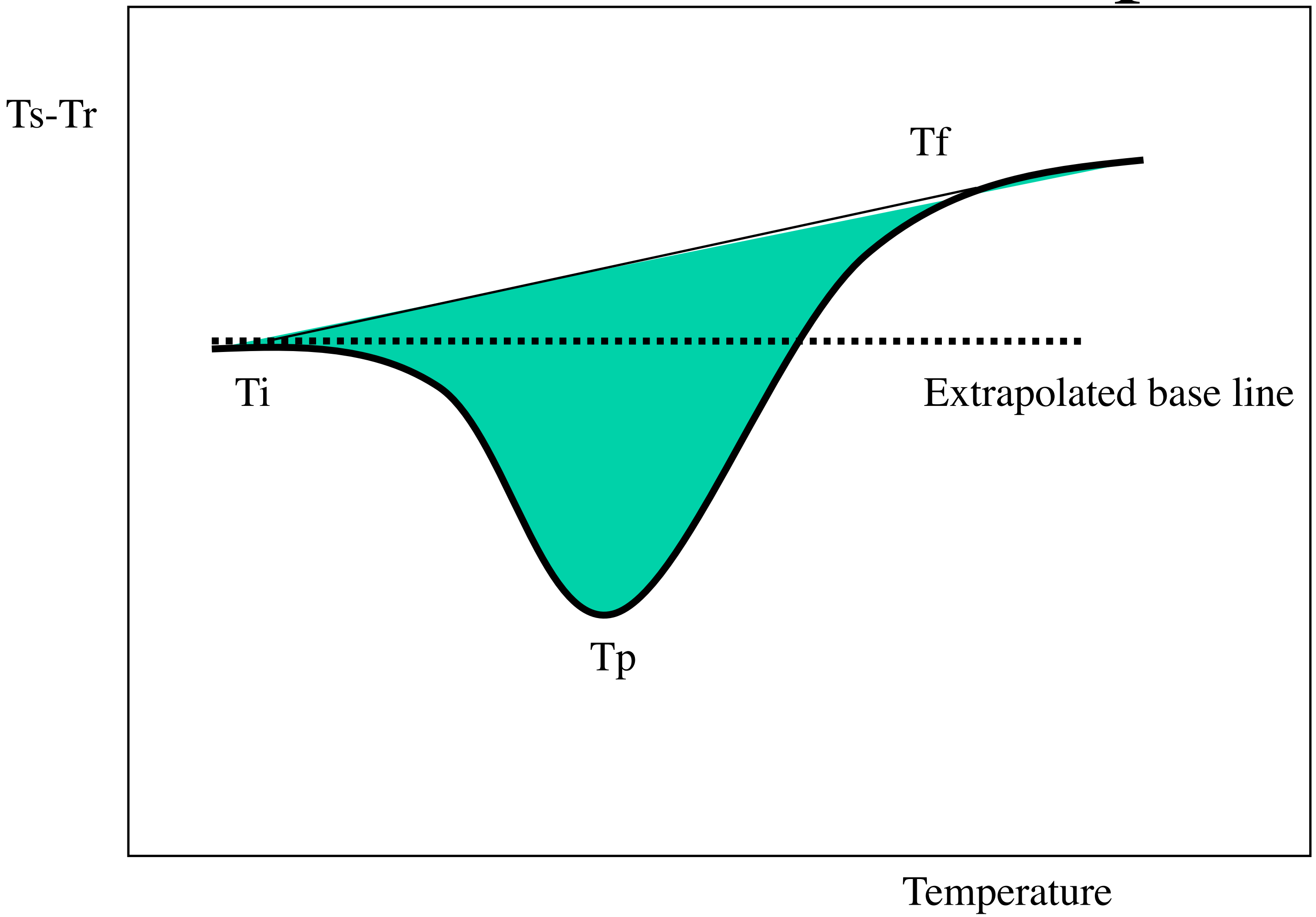
I: Second-order Transition

II: Endothermic peak caused by a fusion

III: Endothermic peak caused by a decomposition or dissociation reaction

IV: Exothermic peak caused by a crystalline phase change

Generalized DTA peak



ΔH m = KA

m=mass

K= calibration coefficient

A= curve peak area

Quantitative aspects: calibration

The calibration constant is related to the geometry and thermal conductivity of the sample holder and is usually determined with compounds having well known heats of transition (experimentally determined by old-fashioned calorimeter).
It must be taken into account that many disadvantages affects the calibration:

- Relative low accuracy and precision (90-95%)
- Inaccuracies in determining peak areas due to the baseline change during the transition or reaction
- The need for calibrating over the entire temperature range of interest, because K is a function of Temperature

Standards used for calibration

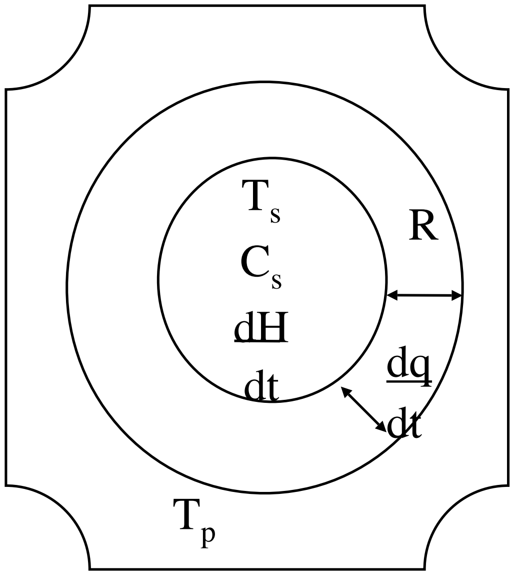
Substance (99.999%)	T (°C)	ΔH (J/g)
Indium	156.6	28.47
Tin	231.9	60.61
Lead	327.5	22.99
Zinc	419.4	115.79
K_2SO_4	583	45.98
Aluminum	660.2	398.1
K_2CrO_4	665	54.34
Silver	960.8	110.6

Theoretical aspects of DTA

$$\frac{m(\Delta H)}{gk} = \int_{t1}^{t2} \Delta T dt$$

It neglects the temperature gradients and considers the peak area to be independent of the specific heat of the sample

A more general theory takes into account a schematic diagram of a thermal analysis cell



$$\frac{dH}{dt} = C_s\left(\frac{dT_s}{dt}\right) - \left(\frac{dq}{dt}\right) \qquad \frac{dH}{dt} = C_r\left(\frac{dT_r}{dt}\right) - \left(\frac{dq}{dt}\right) = 0$$

$$\frac{dq}{dt} = \frac{T_P - T_s}{R} \qquad \frac{dq}{dt} = \frac{T_P - T_r}{R}$$

$$R\left(\frac{dH}{dt}\right) = (T_s - T_r) + R(C_s - C_r)\left(\frac{dT_r}{dt}\right) + RC_s d\frac{T_s - T_r}{dt}$$

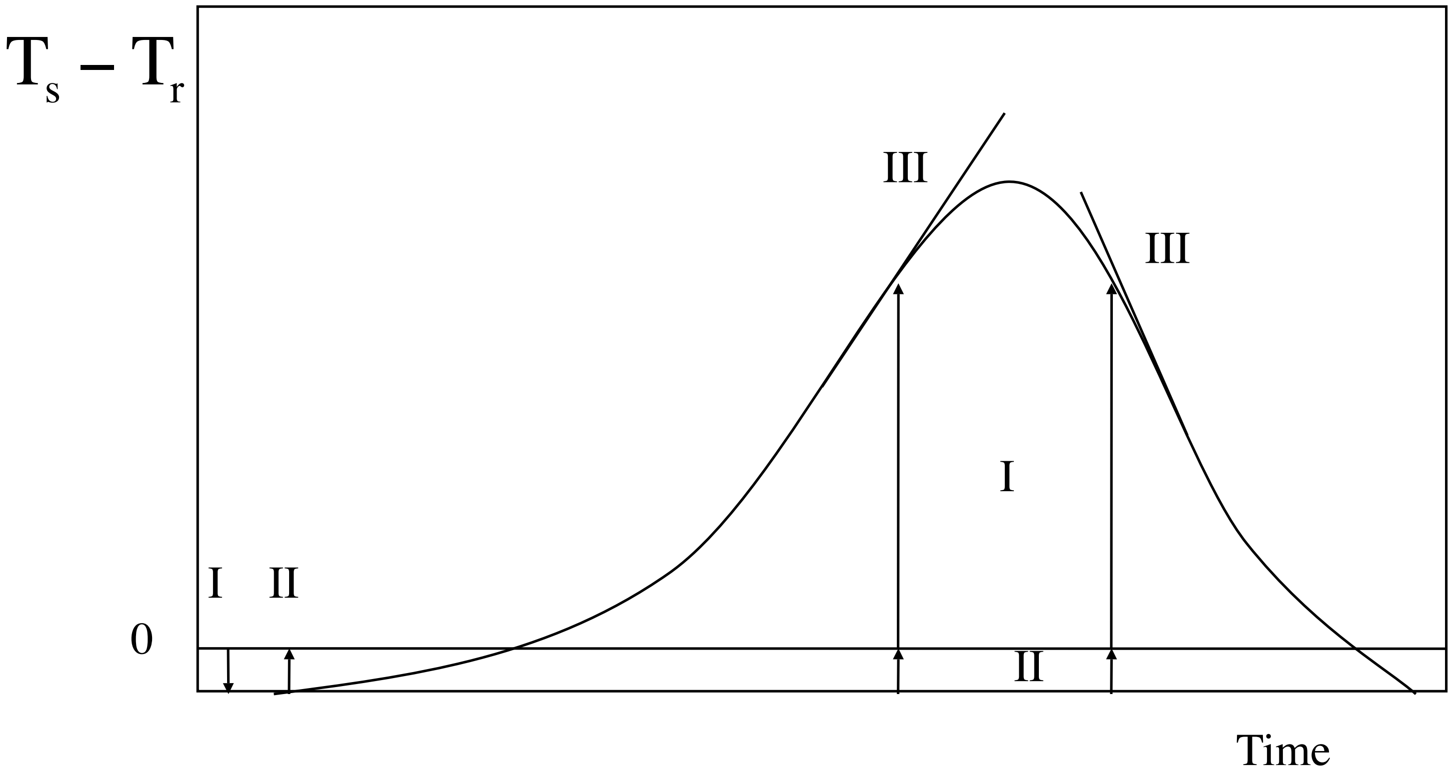
Theoretical aspects of DTA

$$R\left(\frac{dH}{dt}\right) = I + II + III$$

$$R\left(\frac{dH}{dt}\right) = (T_s - T_r) + R(C_s - C_r)\left(\frac{dT_r}{dt}\right) + RC_s d\frac{T_s - T_r}{dt}$$

I II III

$$R\left(\frac{dH}{dt}\right) = I + II - III$$

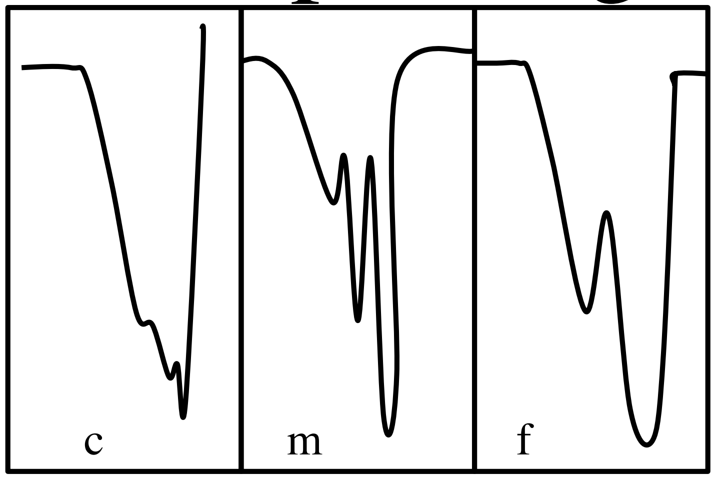


Factors affecting the DTA curve

- Particle size and packing
- Thermal conductivity
- Heat capacity
- Packing density
- Swelling or shrinkage
- Amount
- Degree of crystallinity
- Furnace atmosphere
- Sample-holder material and geometry
- Heating rate
- Thermocouple location in sample

Sample-particle size and packing

- The mass and particle size are source of errors when two or more thermal phenomenon occur in a small range of Temperature

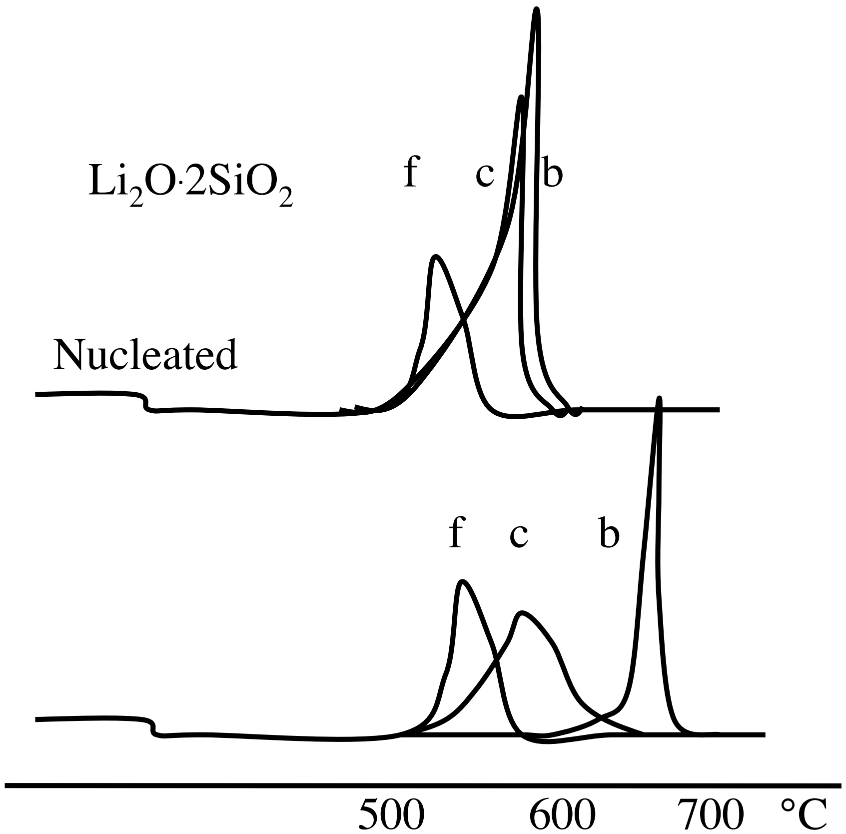


Dehydration of $CuSO_4 \cdot 5H_2O$

$CuSO_4 \cdot 5H_2O \text{-->} CuSO_4 \cdot 3H_2O + 2H_2O$

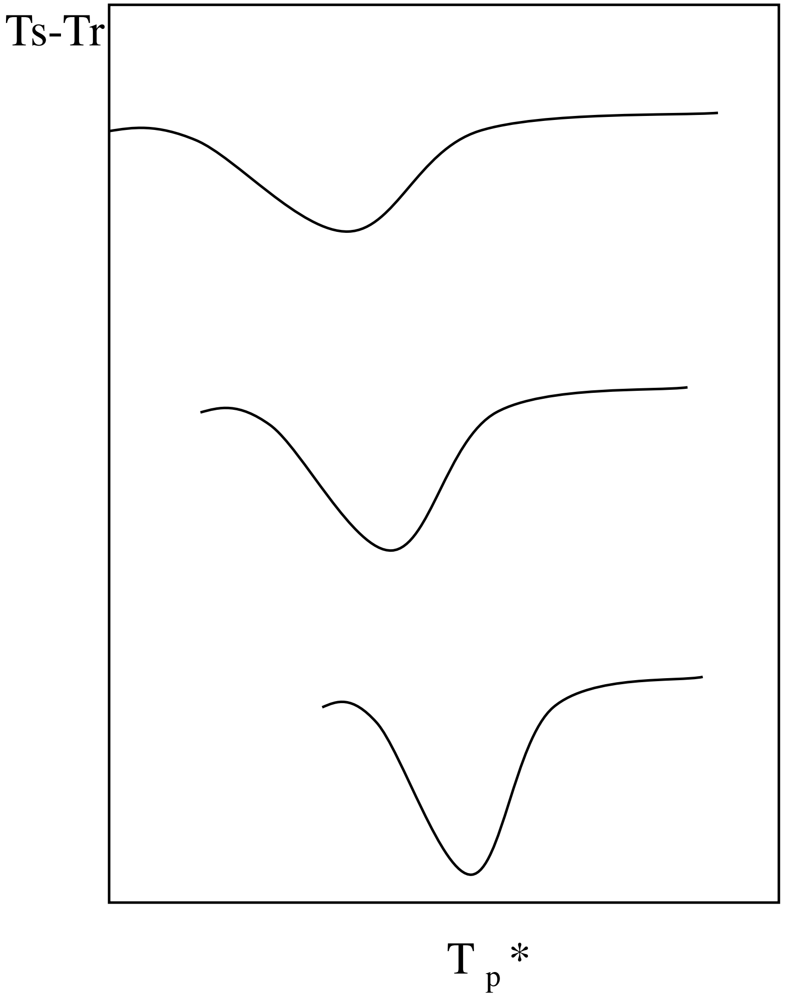
$CuSO_4 \cdot 3H_2O \text{-->} CuSO_4 \cdot H_2O + 2H_2O$

$CuSO_4 \cdot H_2O \text{-->} CuSO_4 + H_2O$



- The peak shape and Tp is allowed to change with the particle size when a thermal phenomenon dependent on surface amount occurs

Heating rate



β=5°C/min

β=10 °C/min

β=20 °C/min

$$\frac{d\left[\ln\left(\beta/\Delta T_p^2\right)\right]}{d\left(1/\Delta T_p\right)} = -\frac{E_{att}}{R}$$

$$\Delta T_p = \left(\frac{dH}{dt}\right)_{\max} \frac{m}{gk}$$

The peak temperature is the point at which the differential heat input equals the rate of heat absorption

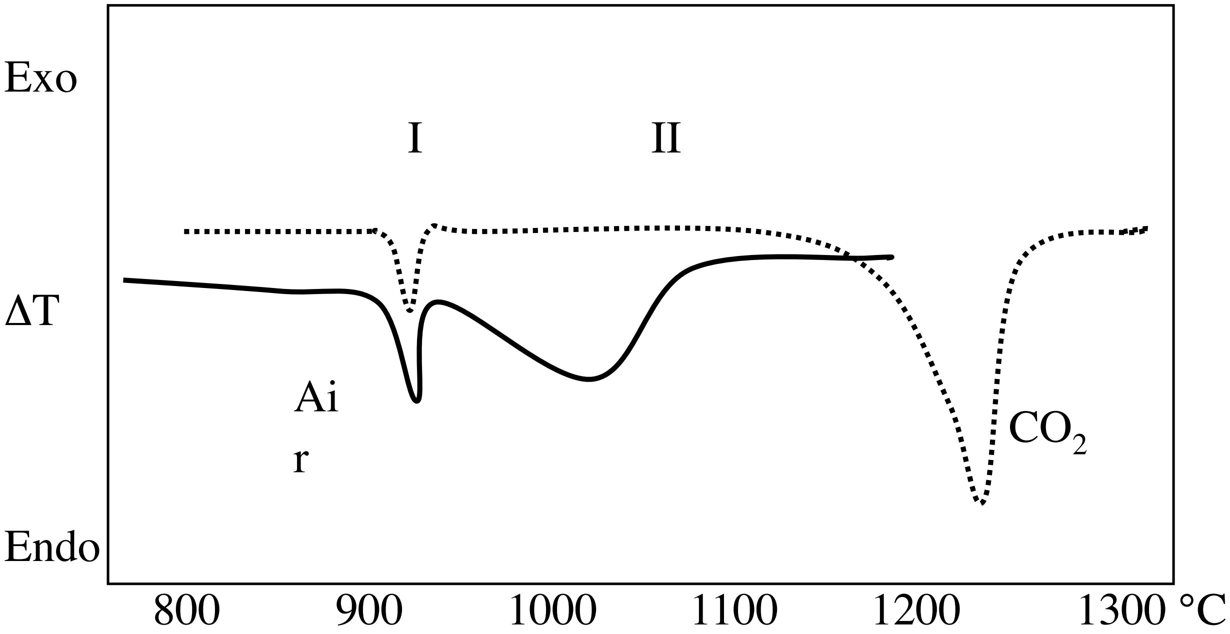
Furnace atmosphere

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$

$$\ln p = -\frac{\Delta H}{RT} + C$$

$$\frac{d\ln k_p}{dT} = \frac{\Delta H}{RT^2}$$

$$\mathrm{A_{solid}} \leftrightarrow \mathrm{B_{solid}} + \mathrm{C_{gas}}$$

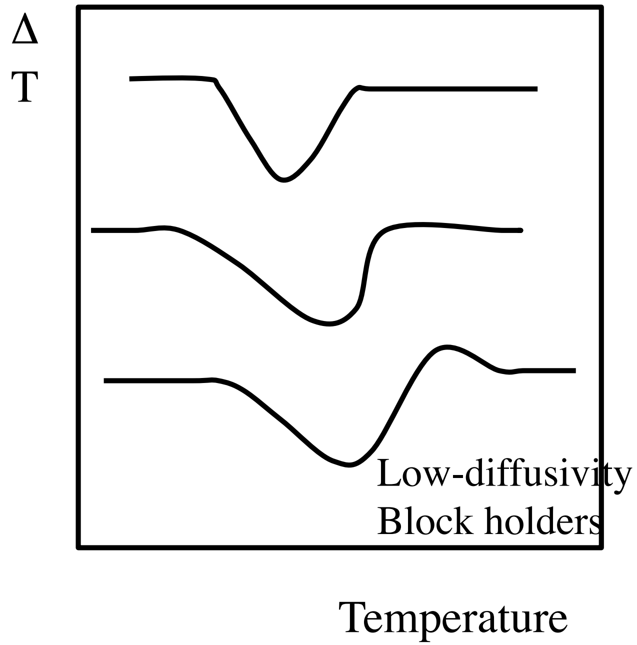


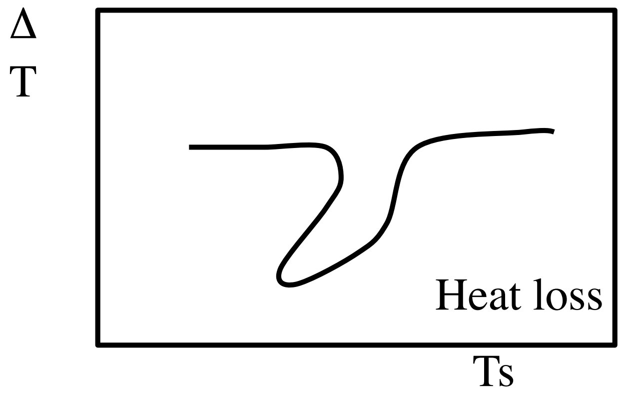
I $SrCO_{3\ rhombic}$ <---> $SrCO_{3\ hexagonal}$

II $SrCO_3$ <--->$SrO + CO_2$

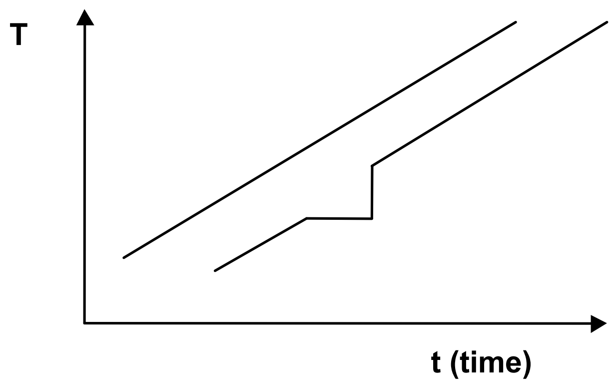
Sample Holders

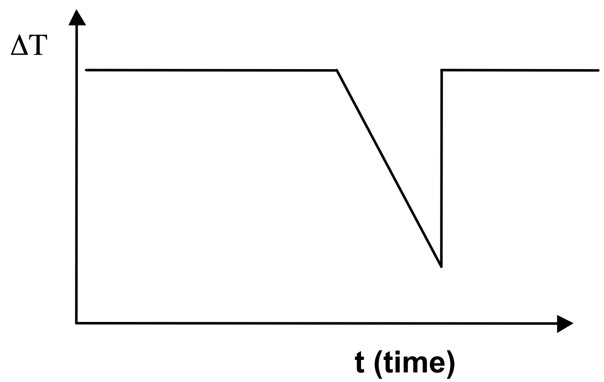
- Since the shape of a DTA curve is affested by the transfer of heat from the source to the sample and by the rate of internal generation or absorption of heat, the material and geometry of sample holders as well as the size of thermocouple wires play a key role in the experiment.
- Low diffusivity or high thermal capacities and heat leakage of electric wires are a great source of errors.



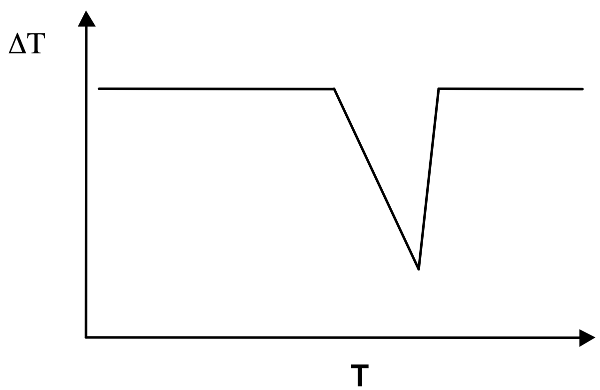


Thermocouple location

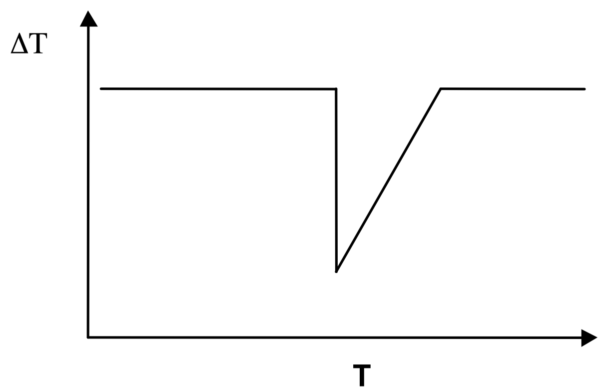




Reference Temperature



Sample Surface Temperature



Sample Core Temperature

Key Operational Parameters

- Large sample size are useful for detecting low-level transitions, non-homogeneous materials. Curve peaks are broad and it had better to use slow heating rate. Low resolution and temperature accuracy.
- Small sample size increases resolution. Peaks are sharp and let fast heating rate be used.
- Fast heating rate increases sensitivity, but decreases resolution and temperature accuracy.
- Atmosphere can react with sample and generally dynamic is preferred over static

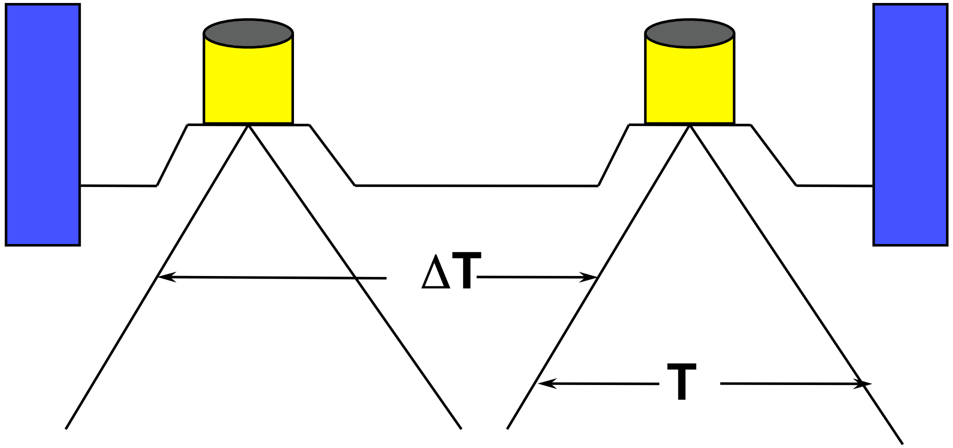
Summary

Parameter	**Maximum resolution**	**Maximum sensitivity**
Sample size	small	large
Heating rate	slow	fast
Sample holder	block	isolated container
Surface/volume	large	small
Atmosphere	high k (He, H2)	low k (vacuum)

Differential Scanning Calorimetry

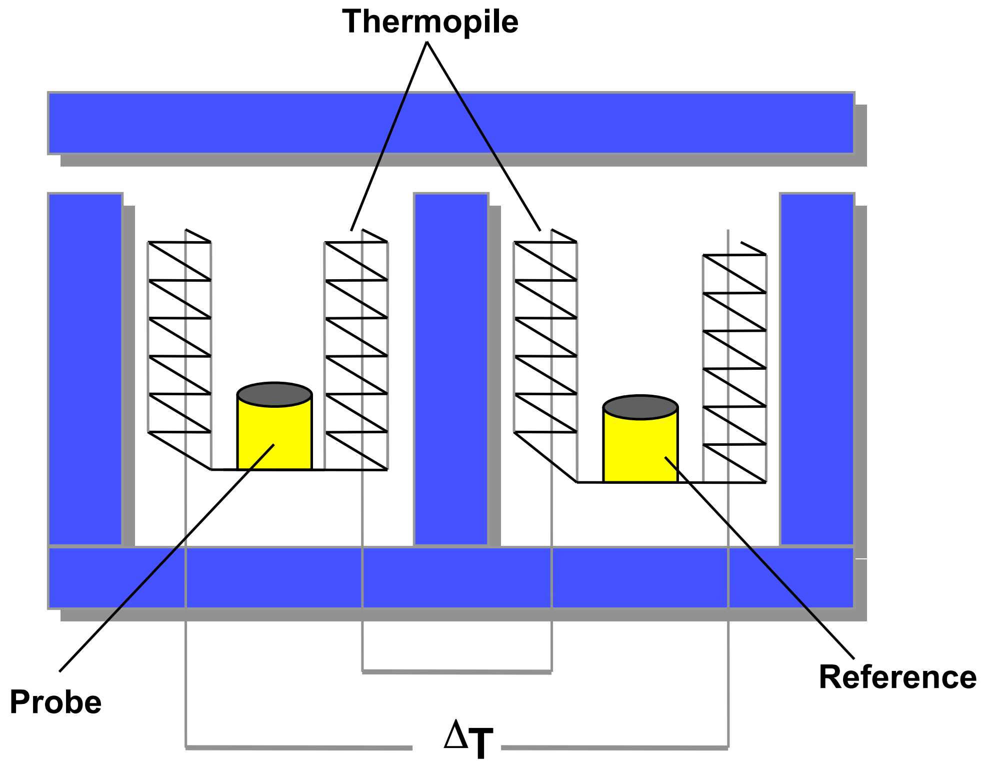
DSC measures the *Heat Flow* Into and Out of a Sample as a Function of Temperature, while the Sample is Subjected a Controlled Temperature Program

Differential Scanning Calorimeter



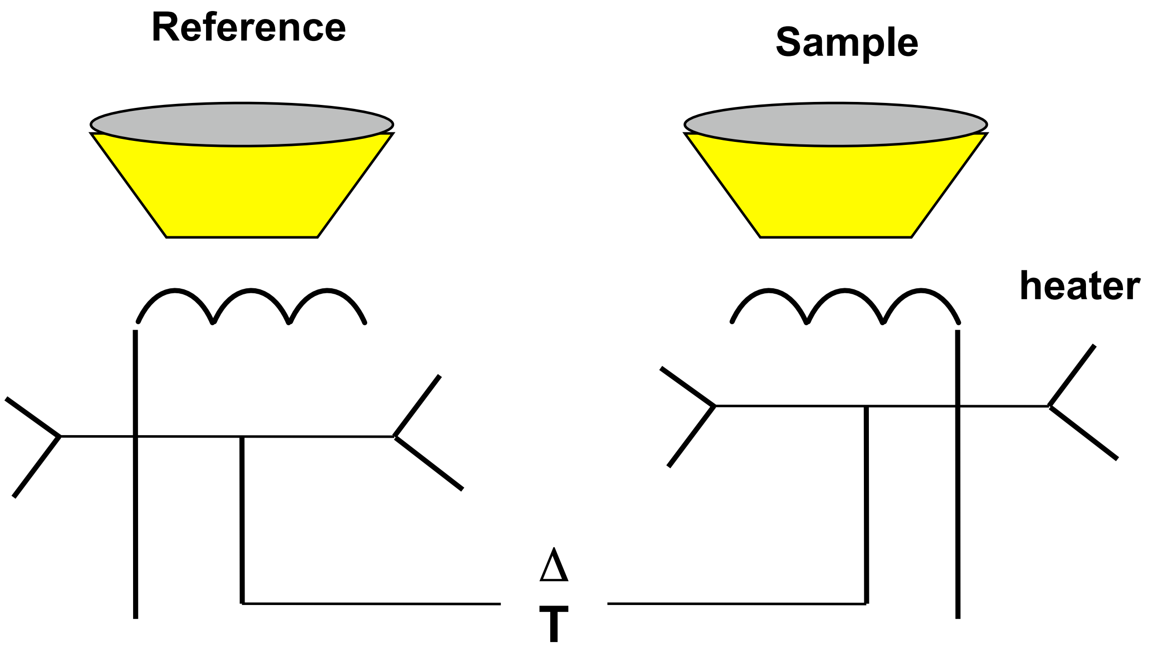
Heat-Flux System

Differential Scanning Calorimeter



Heat-Flux System

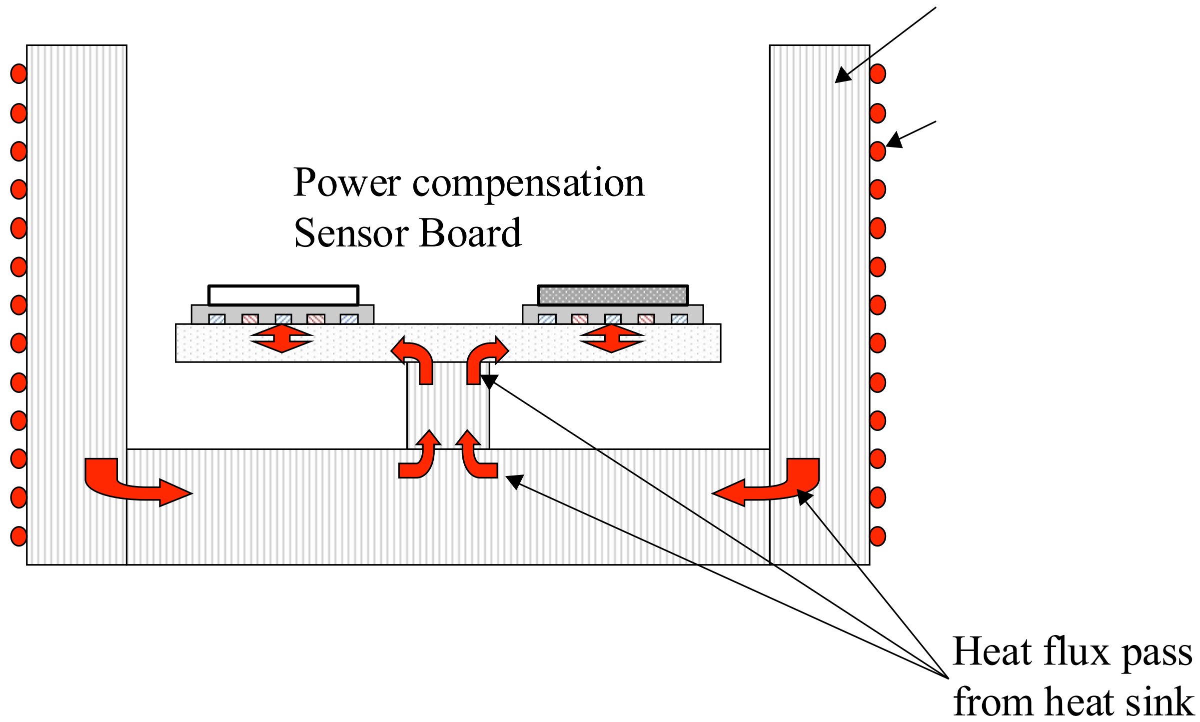
Differential Scanning Calorimeter

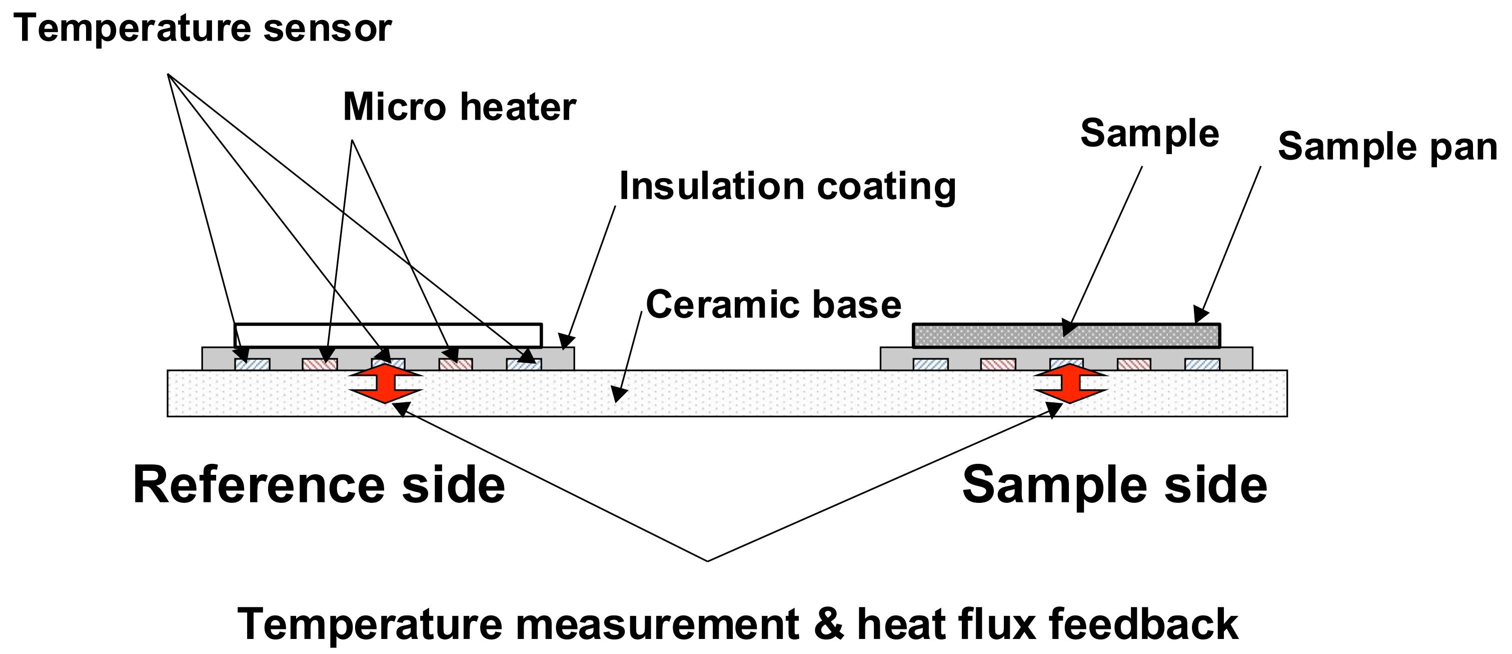


Power Compensation DSC

Power Compensation DSC

- **Have Serious Problems with Water Condensation**
- **Extremely Long Stabilisation Times in the Low Temperature Range**
- **Very Difficult Temperature Calibration**
- **Does Not Measure Real Sample Temperature**
- **Unable to Measure Isothermal Crystallization**
- **Baseline Correction and Temperature Calibration MUST be done for EACH set of Experiment Parameters**


Power compensation
Sensor Board
Heat flux pass
from heat sink


Temperature sensor
Micro heater
Insulation coating
Ceramic base
Sample
Sample pan
Reference side
Sample side
Temperature measurement & heat flux feedback

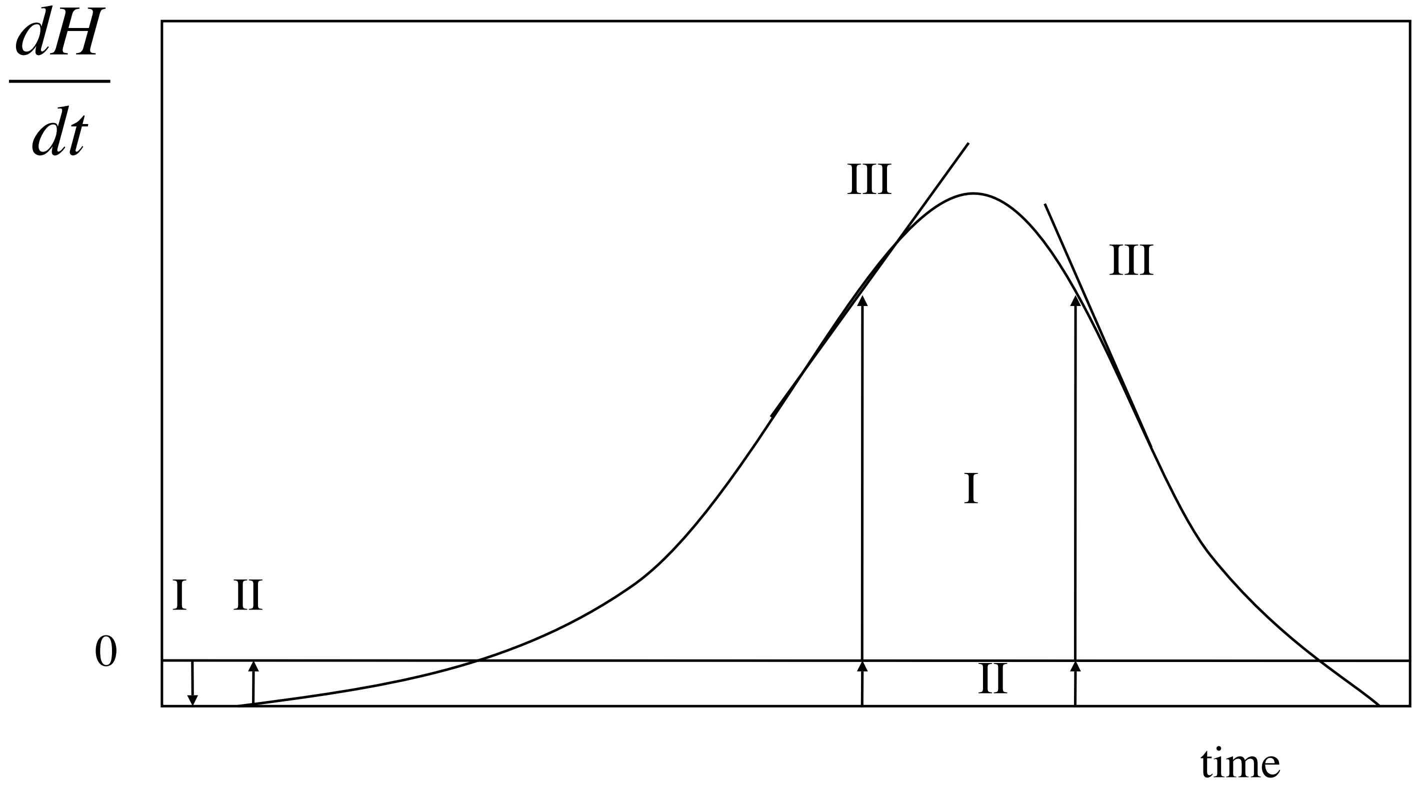
Theoretical aspects of DSC

$$\frac{dH}{dt} = I + II + III$$

$$\frac{dH}{dt} = \frac{dq}{dt} - \left(C_s - C_r\right)\left(\frac{dT_{\text{sink}}}{dt}\right) + RC_s\frac{d^2q}{dt^2}$$

I II III

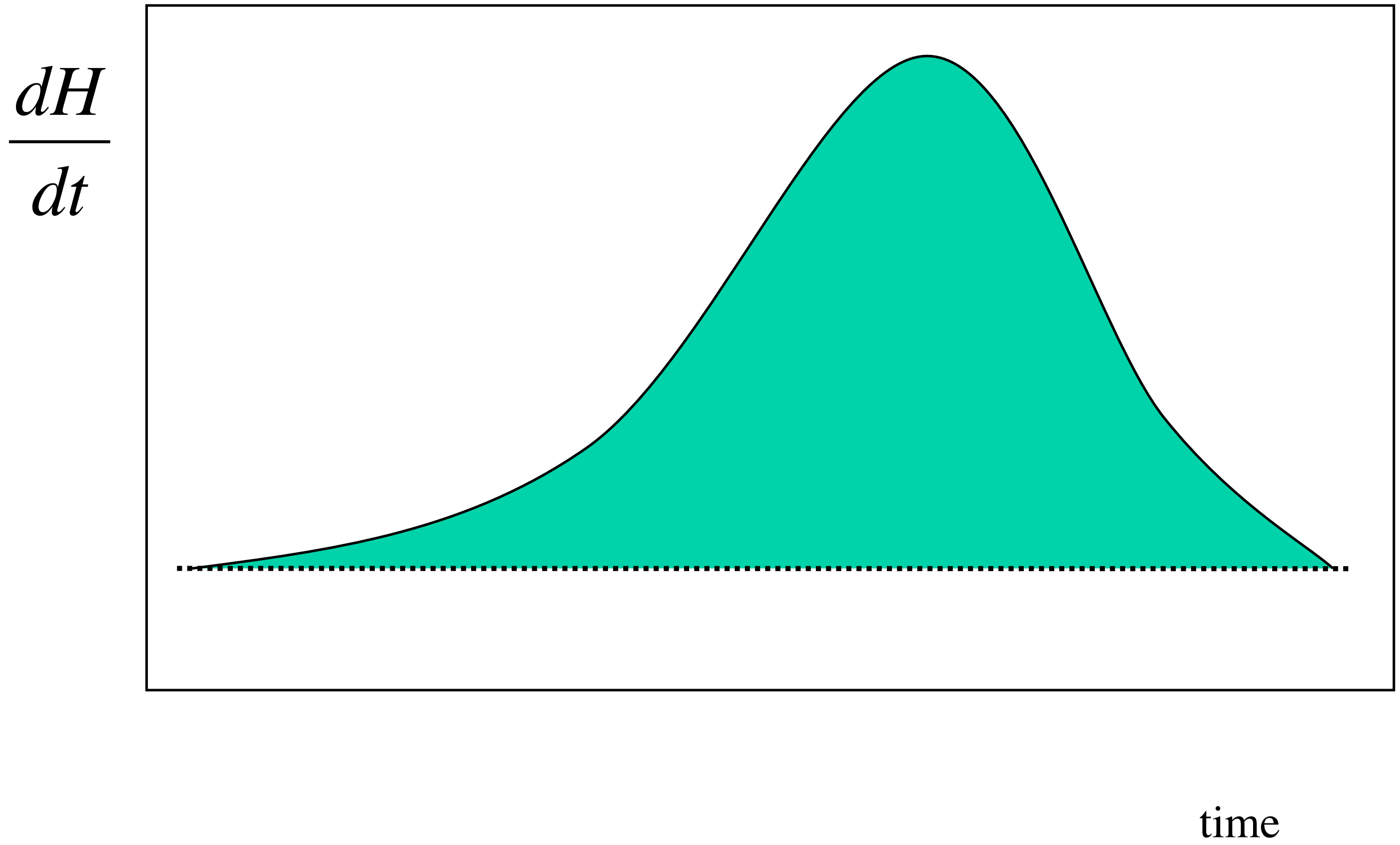
$$\frac{dH}{dt} = I + II - III$$



Theoretical aspects of DSC

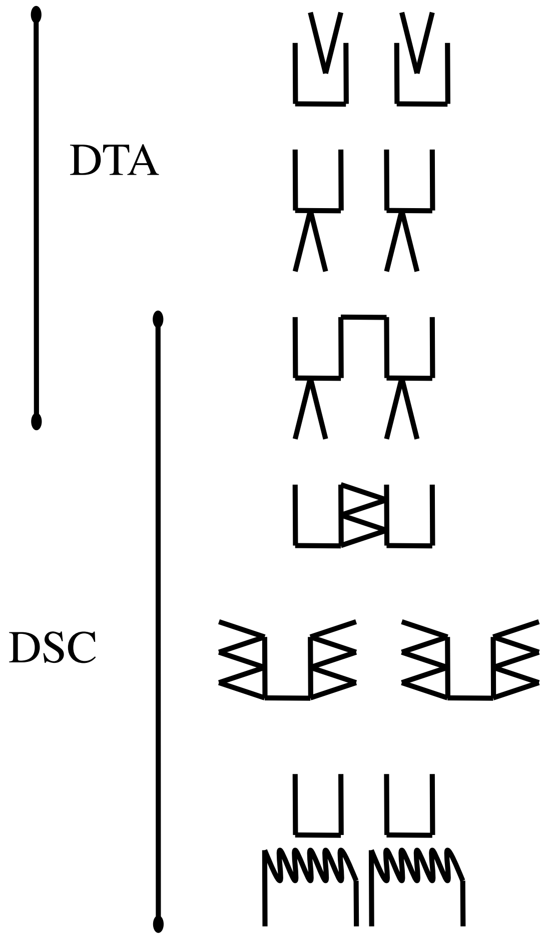
Area = ΔH m/K but K is not dependent on temperature

$$\Delta H = \int_{T1}^{T2} \frac{dH}{dt} dt = \int_{T1}^{T2} cp dT$$



Differences Between DTA and DSC

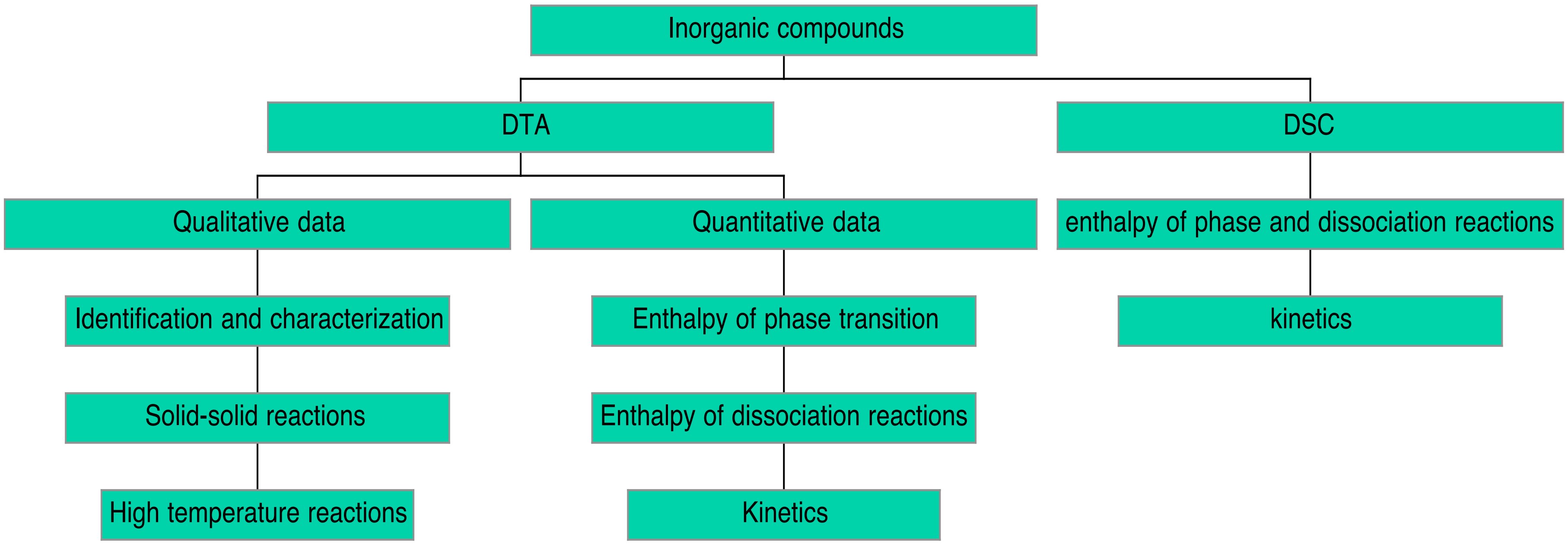
The term Differential Scanning calorimetry has become a source of confusion in the field of thermal analysis, because there are several totally different type of instruments with the same name.

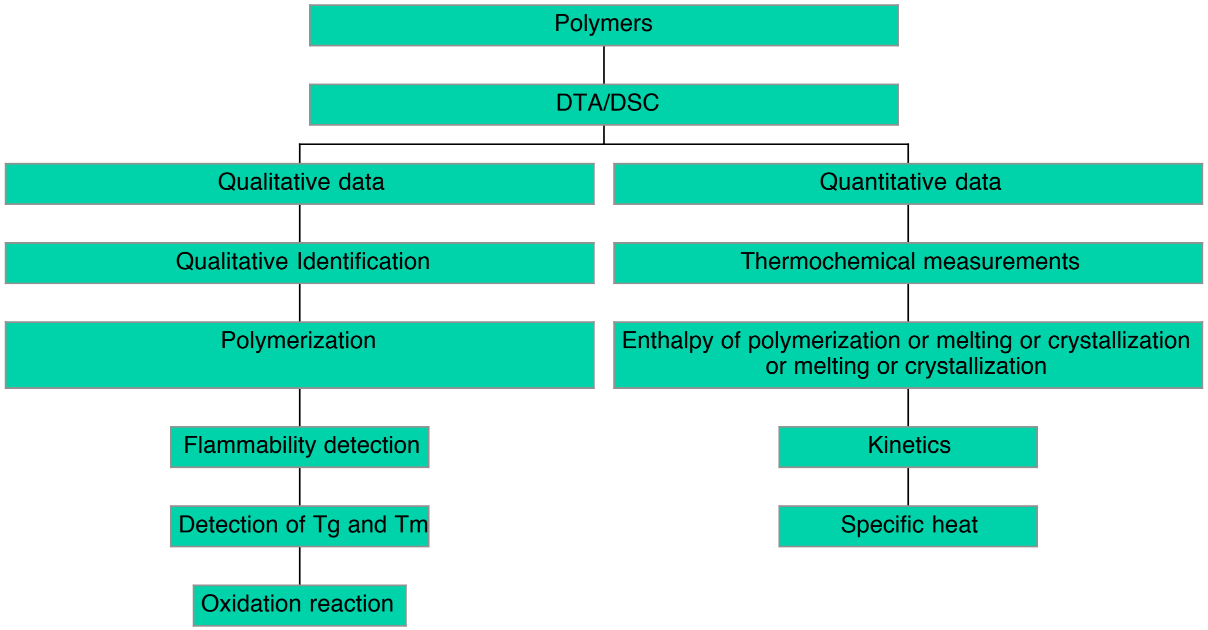


DTA	T_s-T_r=ΔT
Quantitative DTA	T_s-T_r=ΔT
Heat-flux DSC or Boersma-type DTA	T_s-T_r=ΔT
Heat-flux DSC	dq/dt
Heat-flux DSC or Calvet type DSC	dq_s/dt- dq_r/dt=d (Δq)/dt

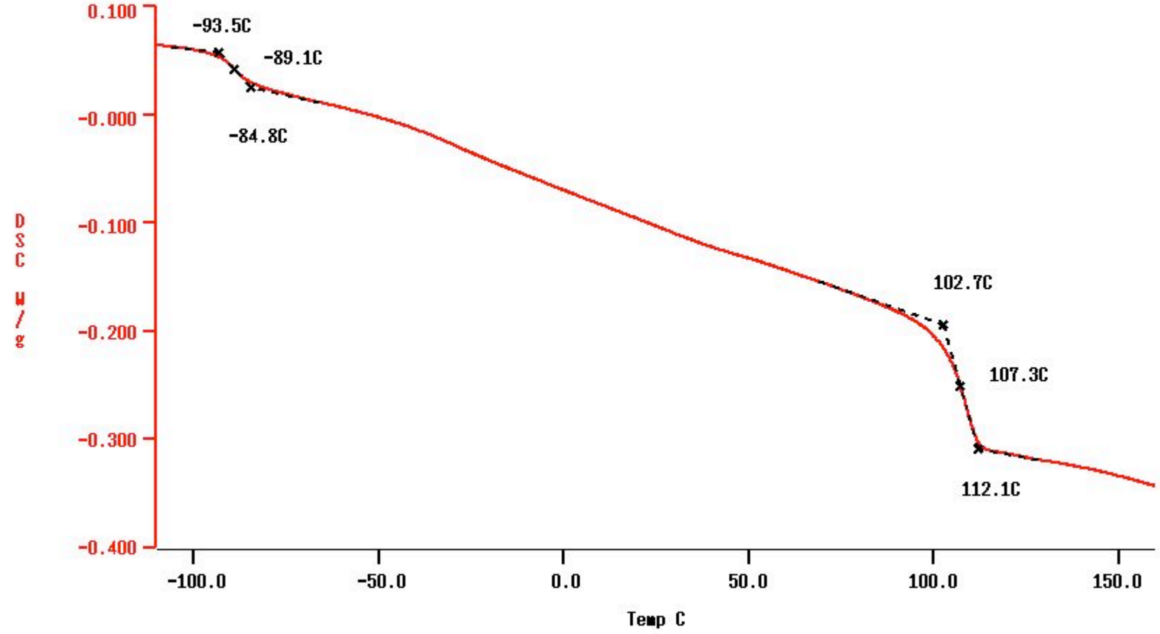
DTA/DSC

- Characteristic Temperature of a Transition
- Time for a Transition
- Semi-Quantitative Determination of the Amount of Calorimetric Effects
- Purity
- Phase Diagrams
- Identification of Components in Mixtures
- Burning Behavior
- Safety Inspections

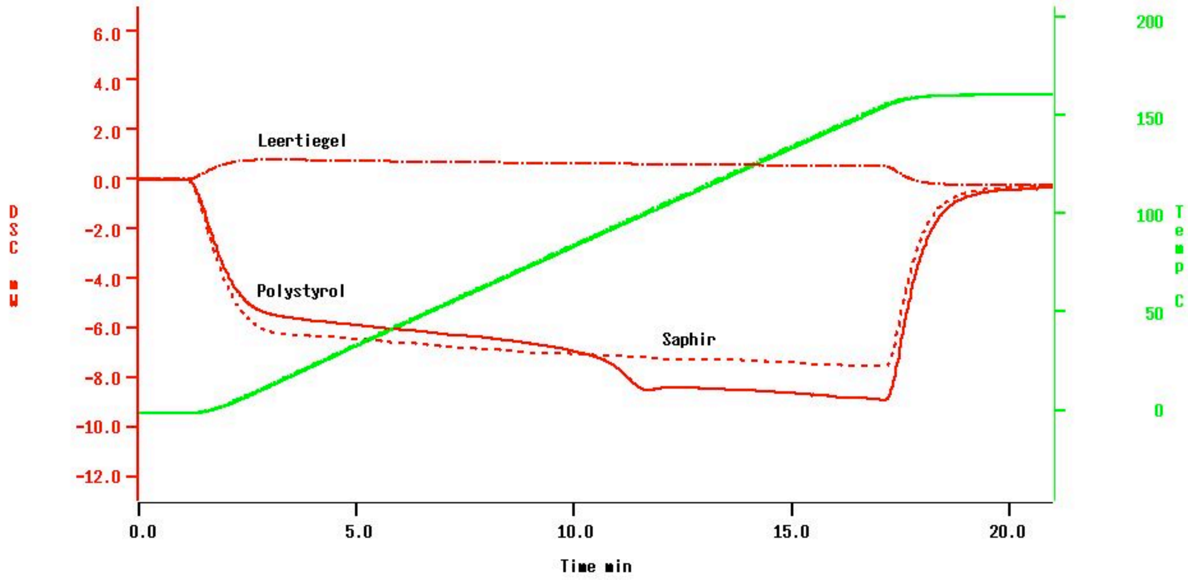

Inorganic compounds
DTA
DSC
Qualitative data
Quantitative data
enthalpy of phase and dissociation reactions
Identification and characterization
Enthalpy of phase transition
kinetics
Solid-solid reactions
Enthalpy of dissociation reactions
High temperature reactions
Kinetics

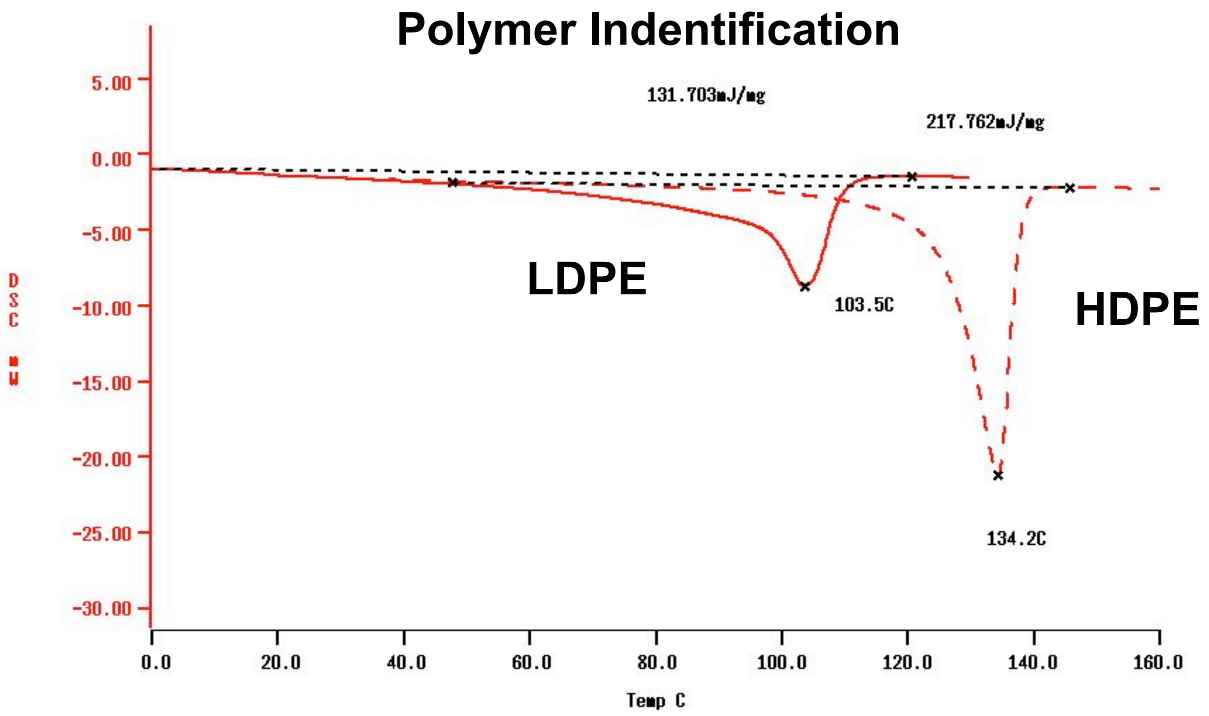

Polymers
DTA/DSC
Qualitative data
Quantitative data
Qualitative Identification
Thermochemical measurements
Polymerization
Enthalpy of polymerization or melting or crystallization
or melting or crystallization
Flammability detection
Kinetics
Detection of Tg and Tm
Specific heat
Oxidation reaction

Measurement of Styrol-Butadiene



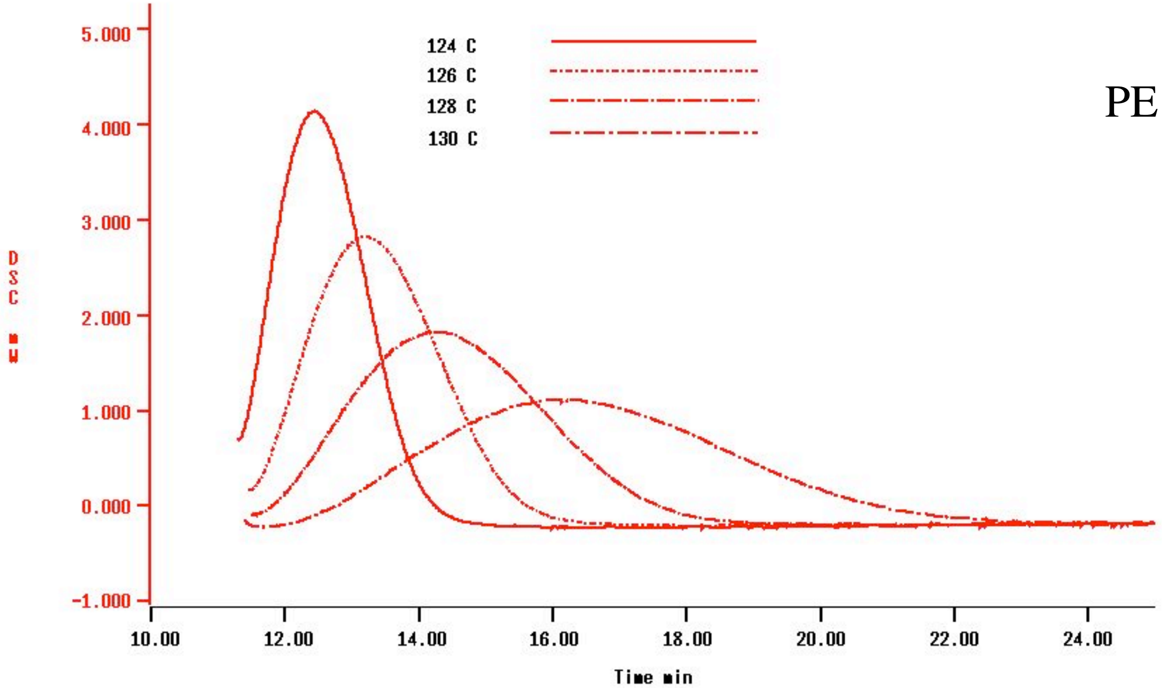
Heat Capacity Measurement



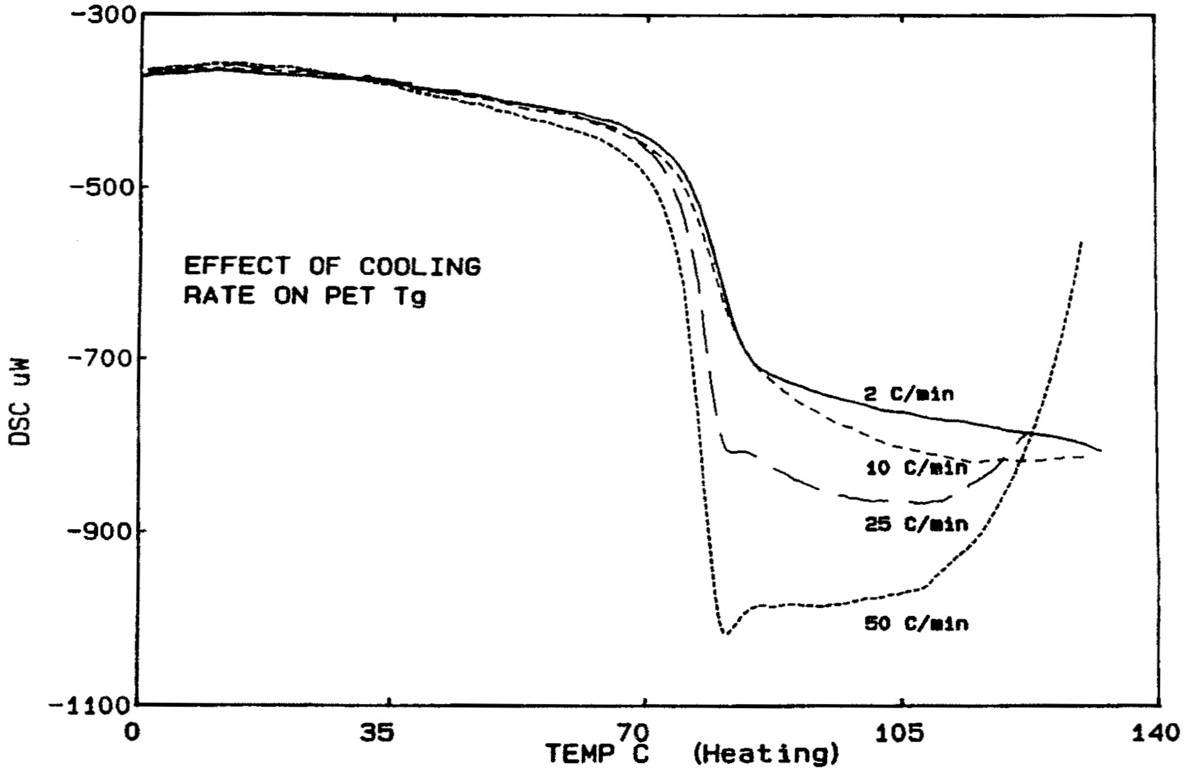


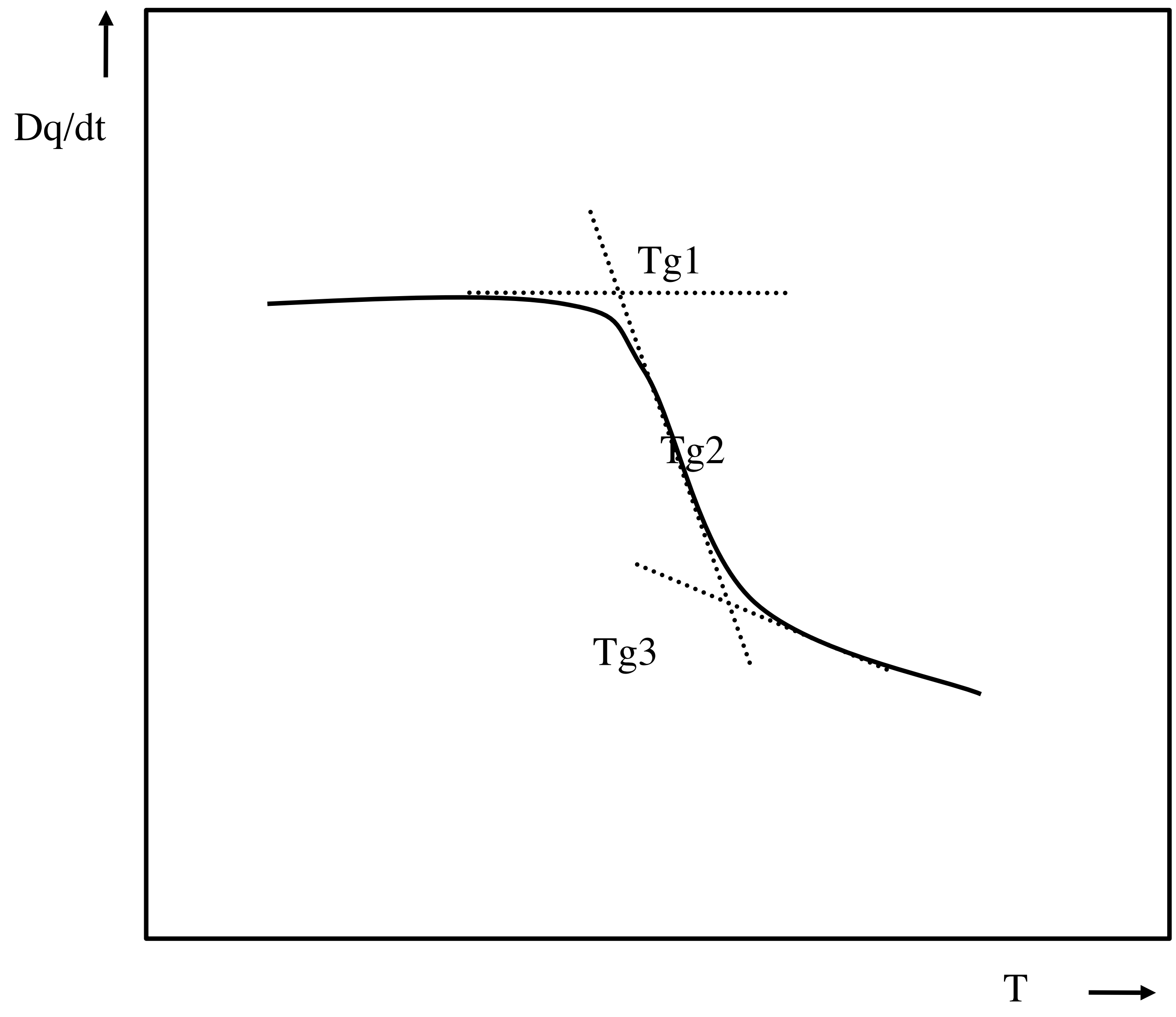
Polymer Indentification
131.703mJ/mg
217.762mJ/mg
5.00
0.00
-5.00
-10.00
-15.00
-20.00
-25.00
-30.00
DSC mW
LDPE
103.5C
HDPE
134.2C
0.0
20.0
40.0
60.0
80.0
100.0
120.0
140.0
160.0
Temp C

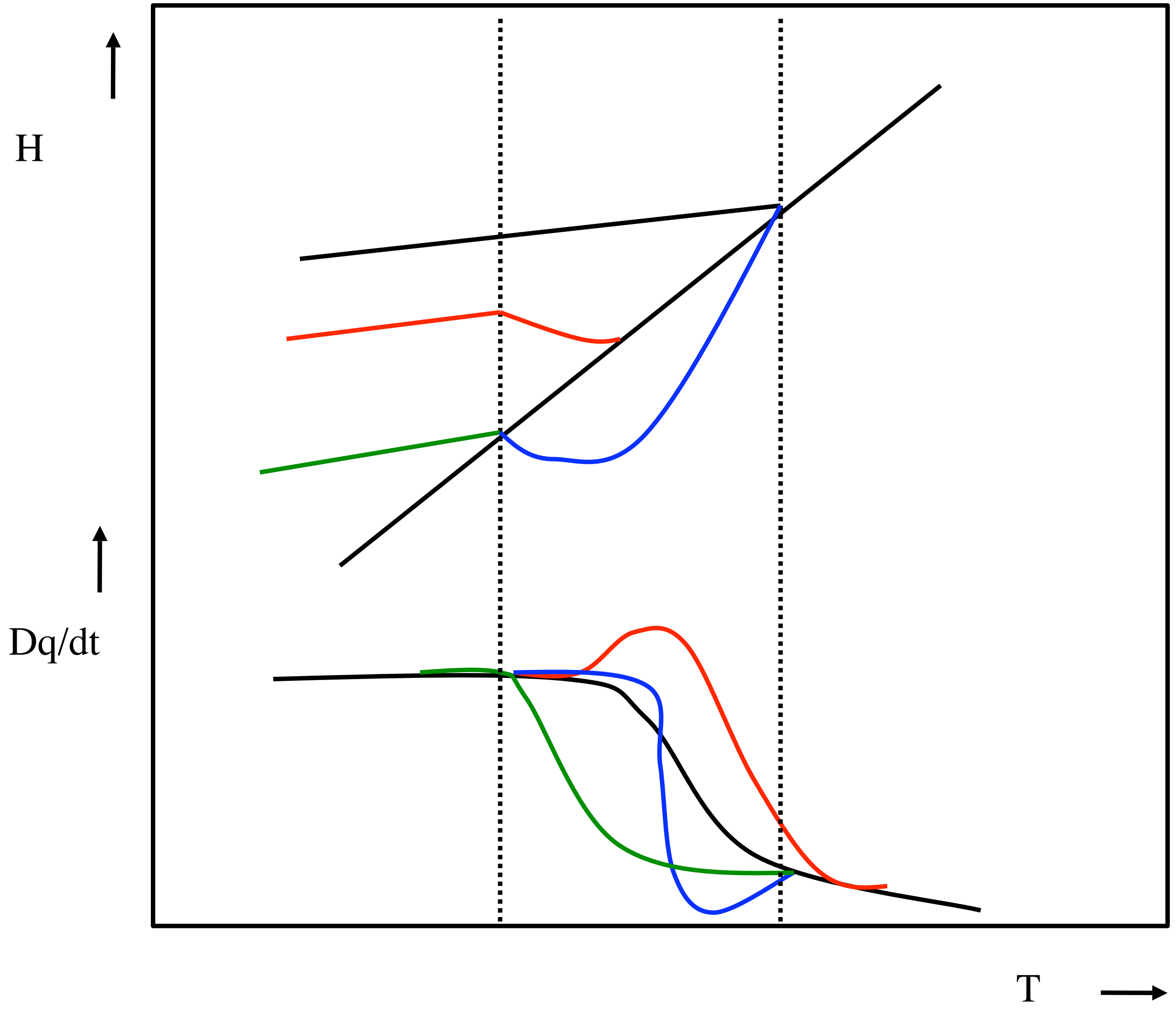
Isothermal Crystallization



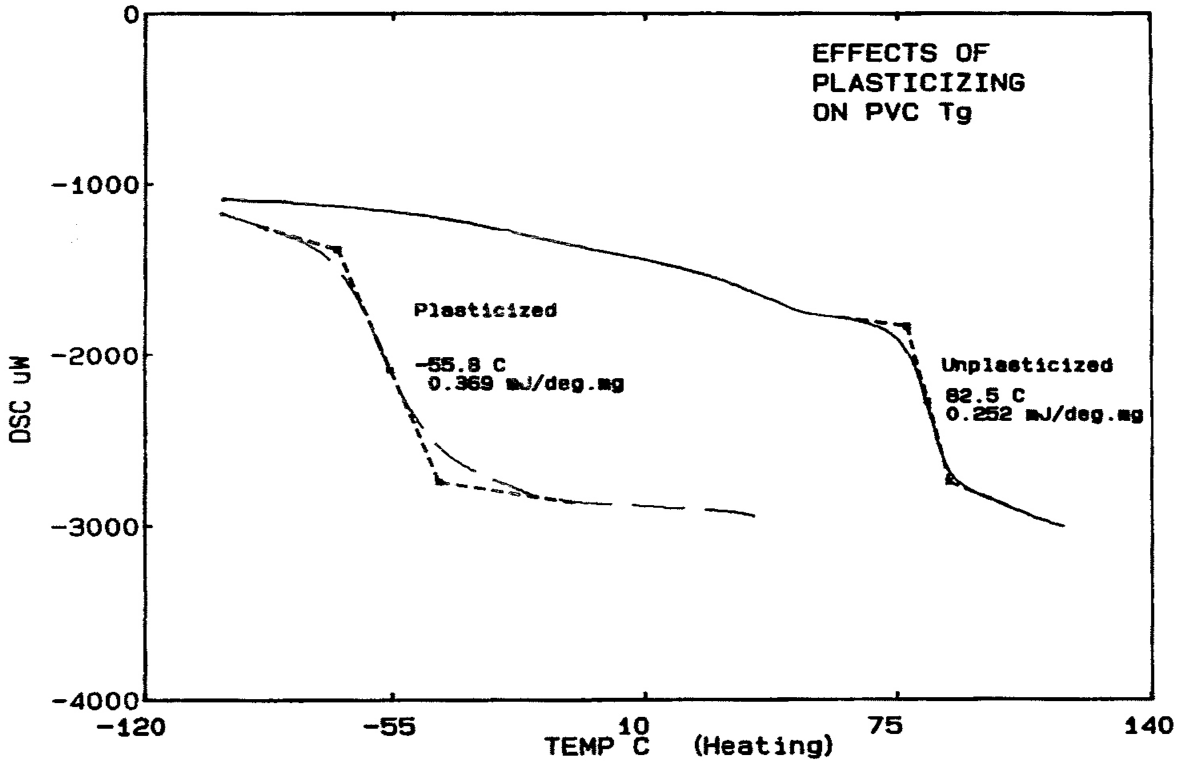
PE


-300
-500
-700
-900
-1100
DSC uW
EFFECT OF COOLING
RATE ON PET Tg
2 C/min
10 C/min
25 C/min
50 C/min
0
35
70
105
140
TEMP C (Heating)


Dq/dt
Tg1
Tg2
Tg3
T



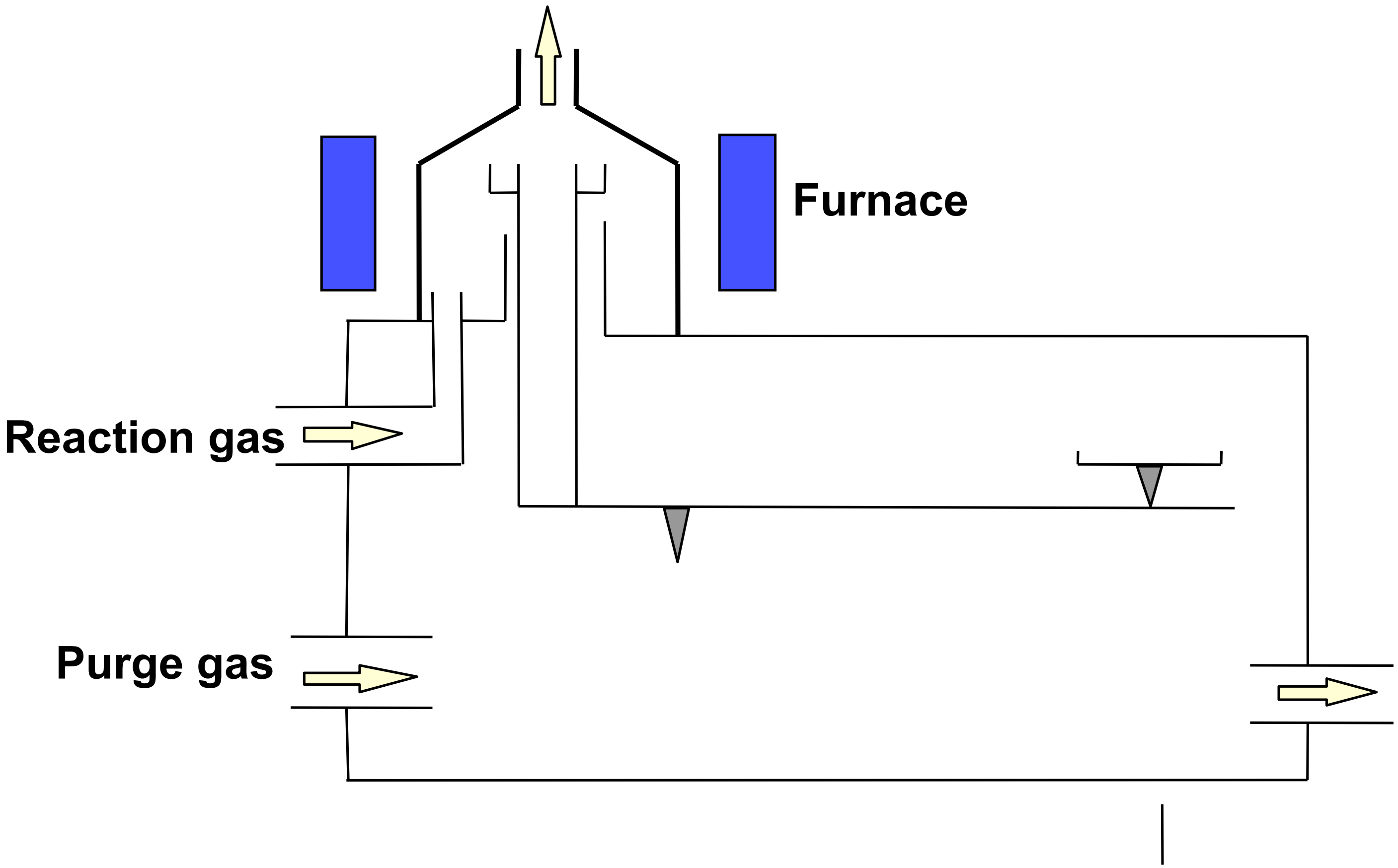
H
Dq/dt
T


EFFECTS OF
PLASTICIZING
ON PVC Tg
Plasticized
-55.8 C
0.369 mJ/deg.mg
Unplasticized
82.5 C
0.252 mJ/deg.mg
DSC uW
0
-1000
-2000
-3000
-4000
-120
-55
10
75
140
TEMP C (Heating)

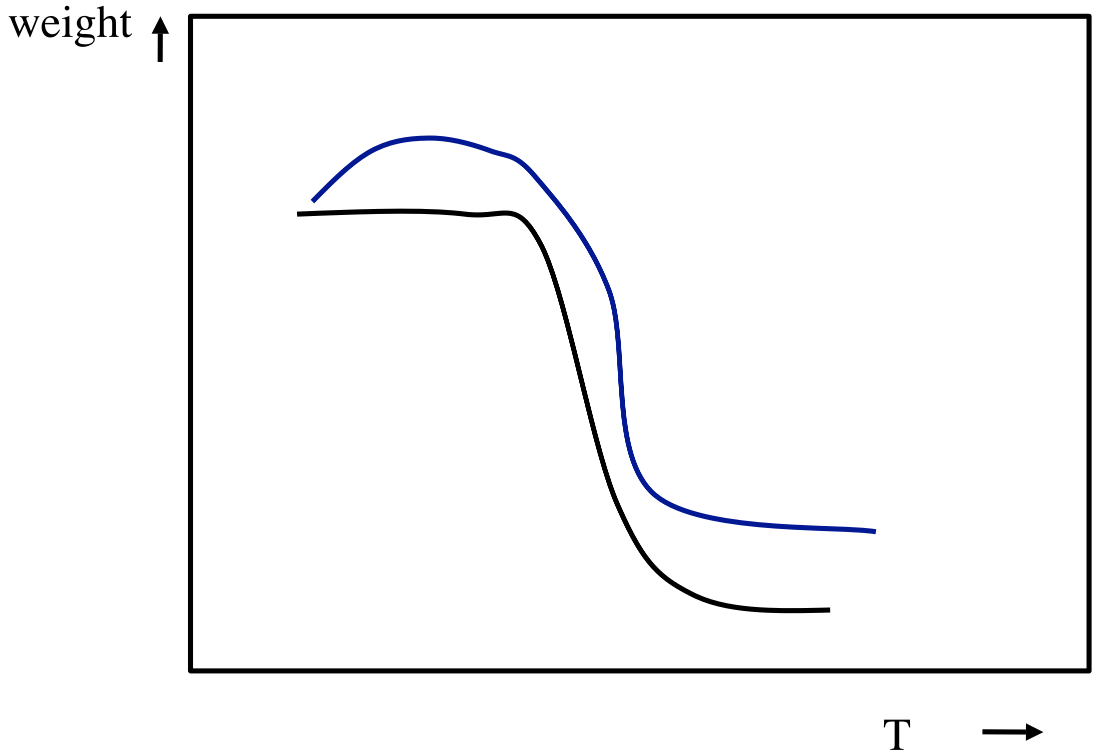
Thermogravimetric Analysis (TGA)

TGA measures the Mass Loss and the Rate of Mass Loss of a Material as a Function of Temperature

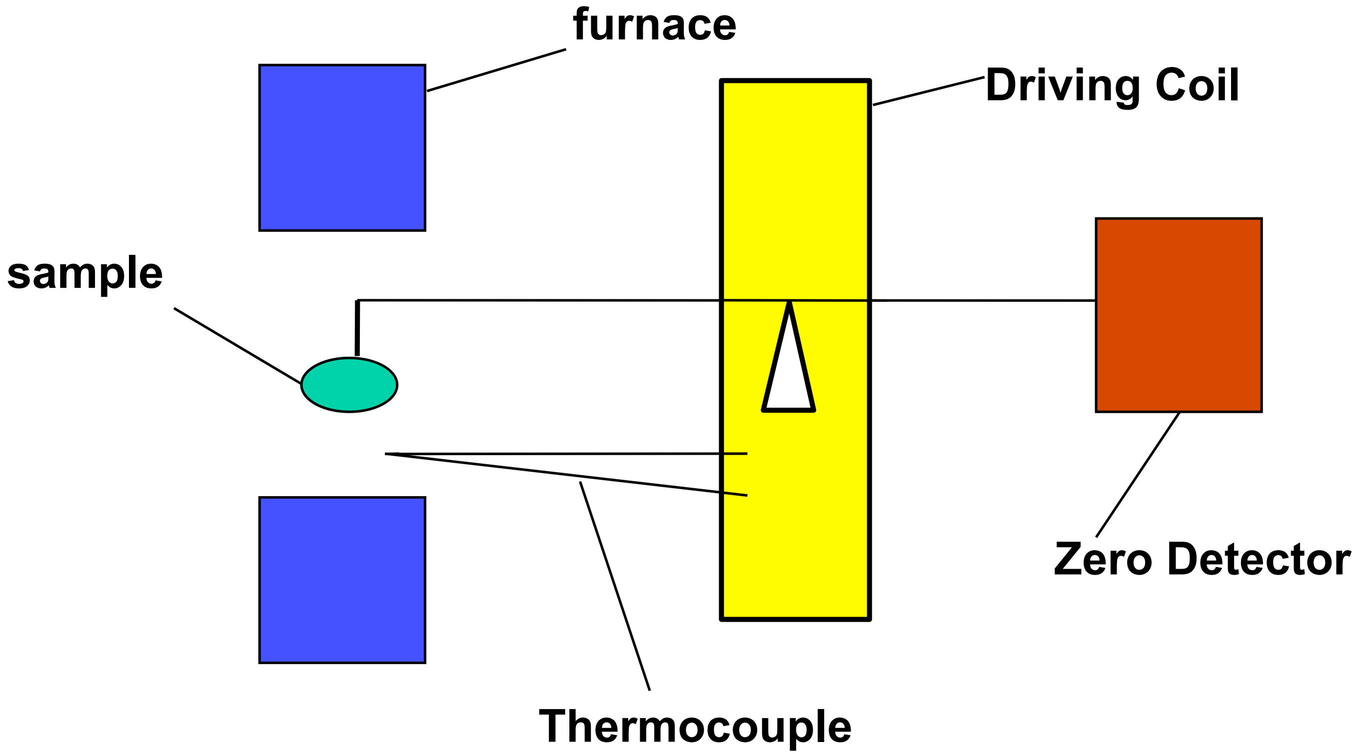
Thermogravimetric Analyser



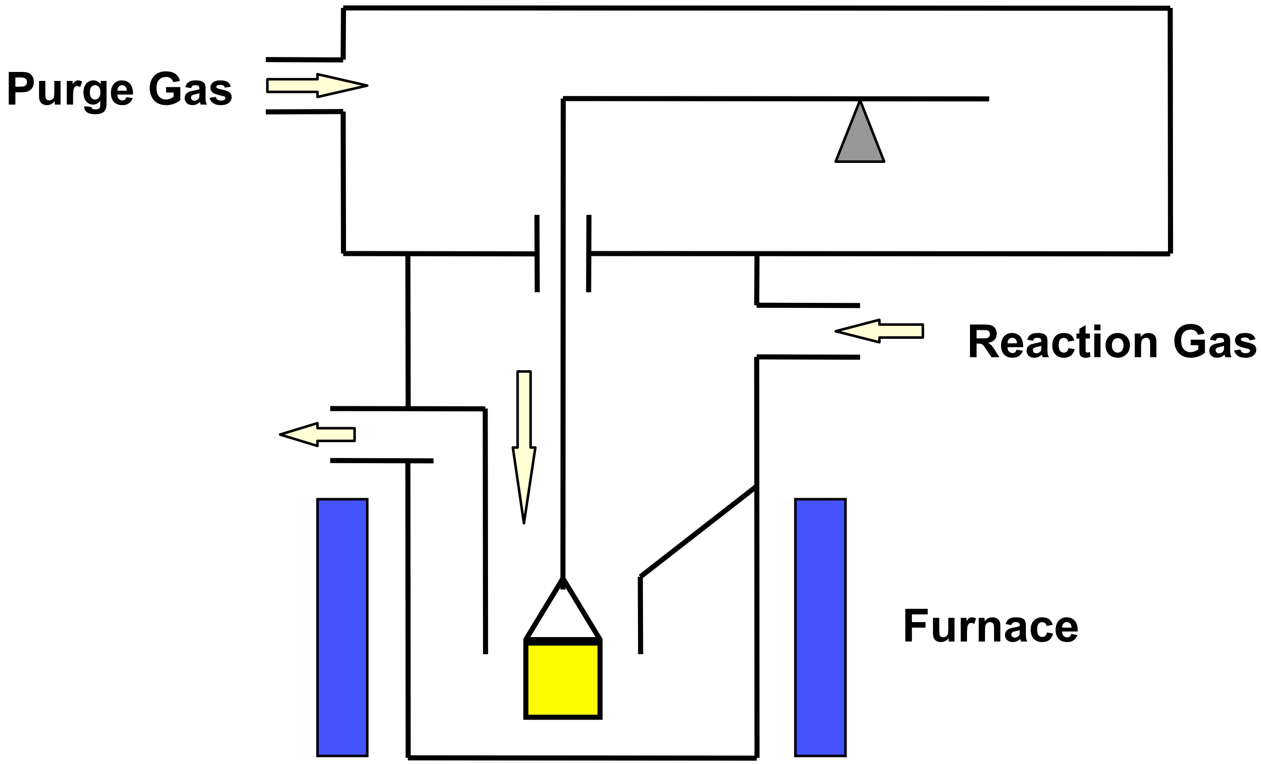
Buoyancy effects



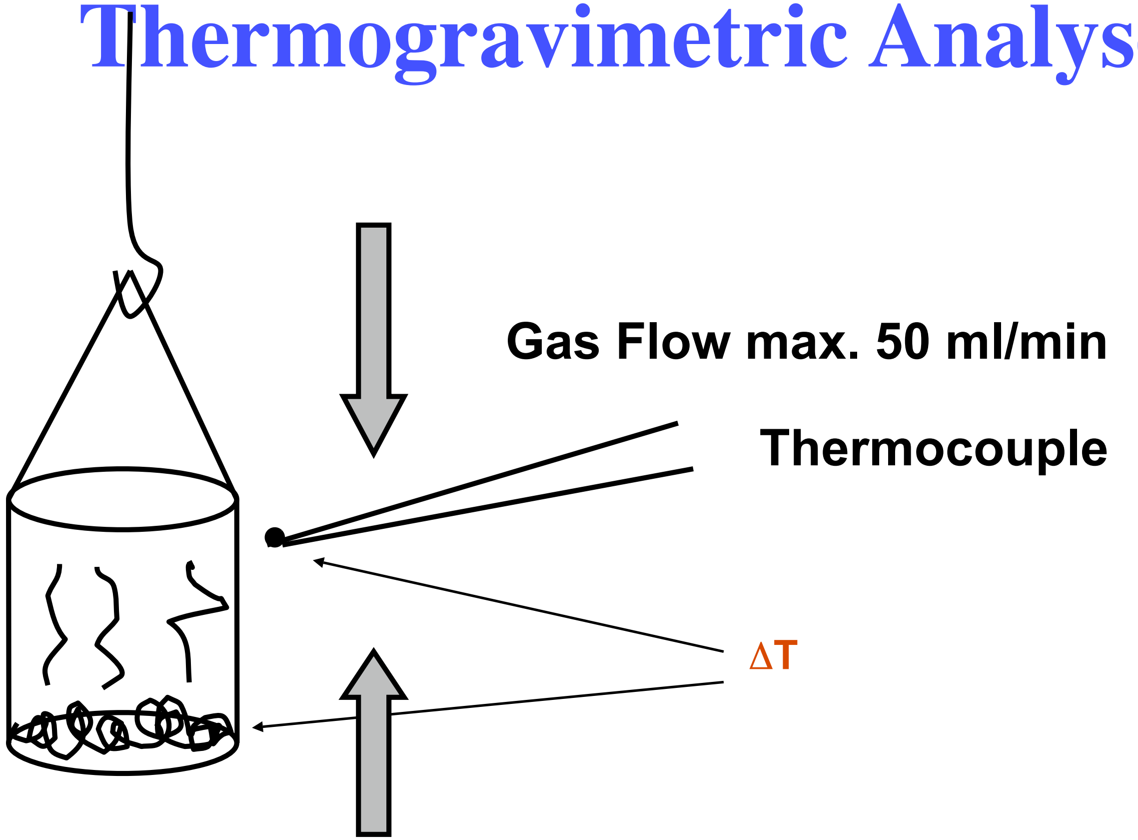
Thermogravimetric Analyser



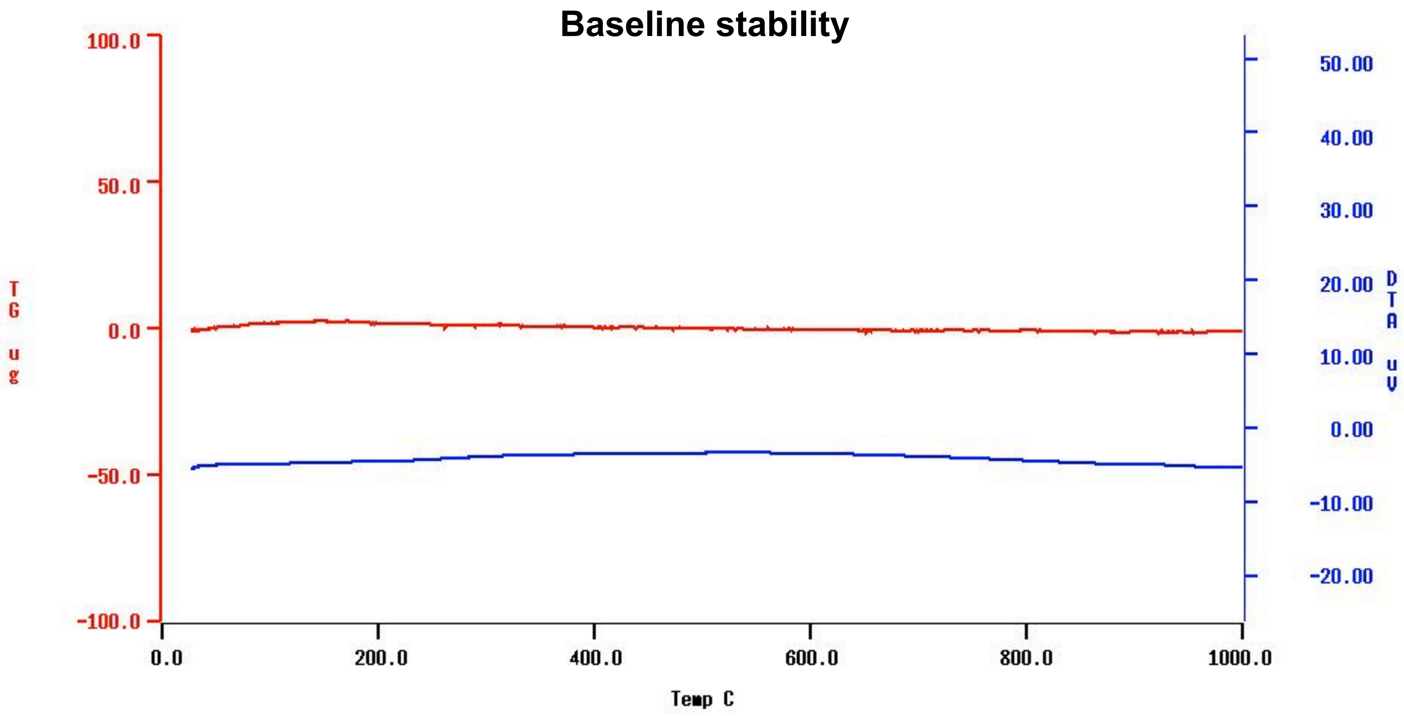
Thermogravimetric Analyser



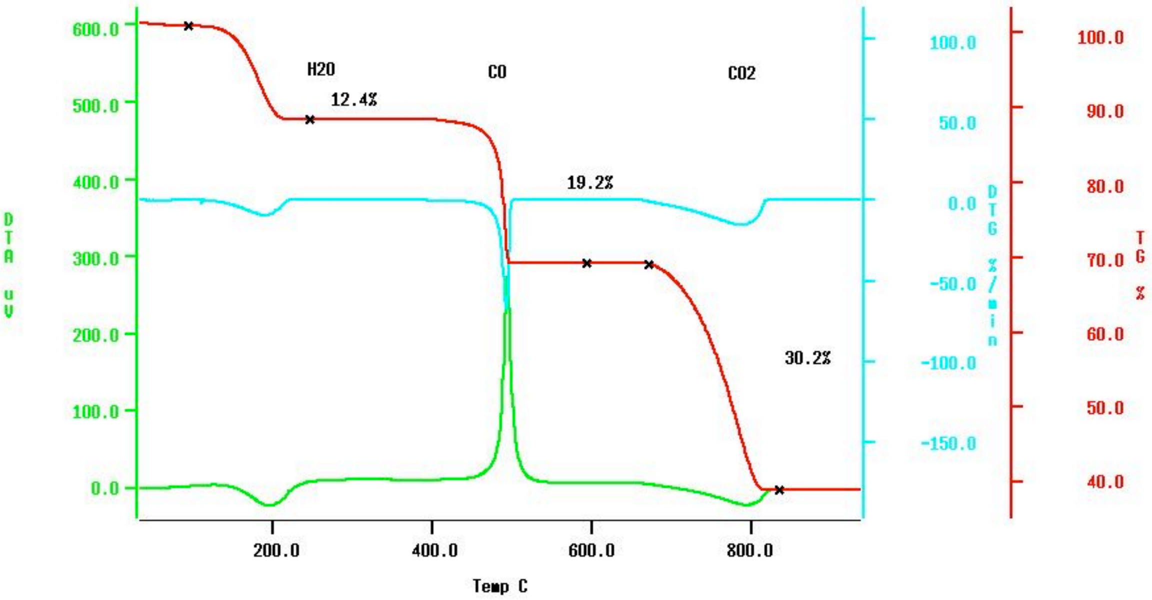
Thermogravimetric Analyser



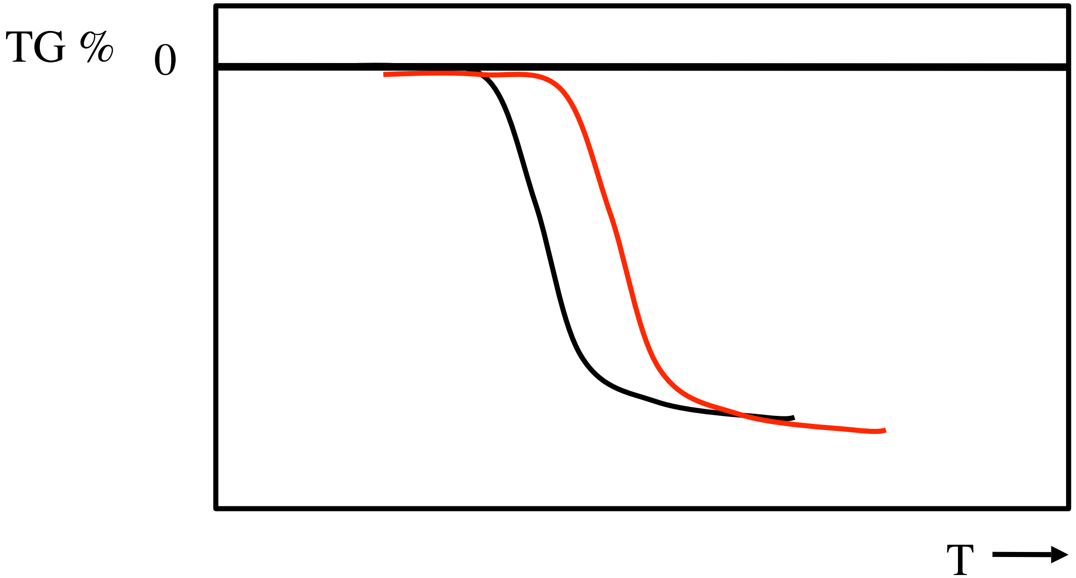
Thermogravimetric Analyser

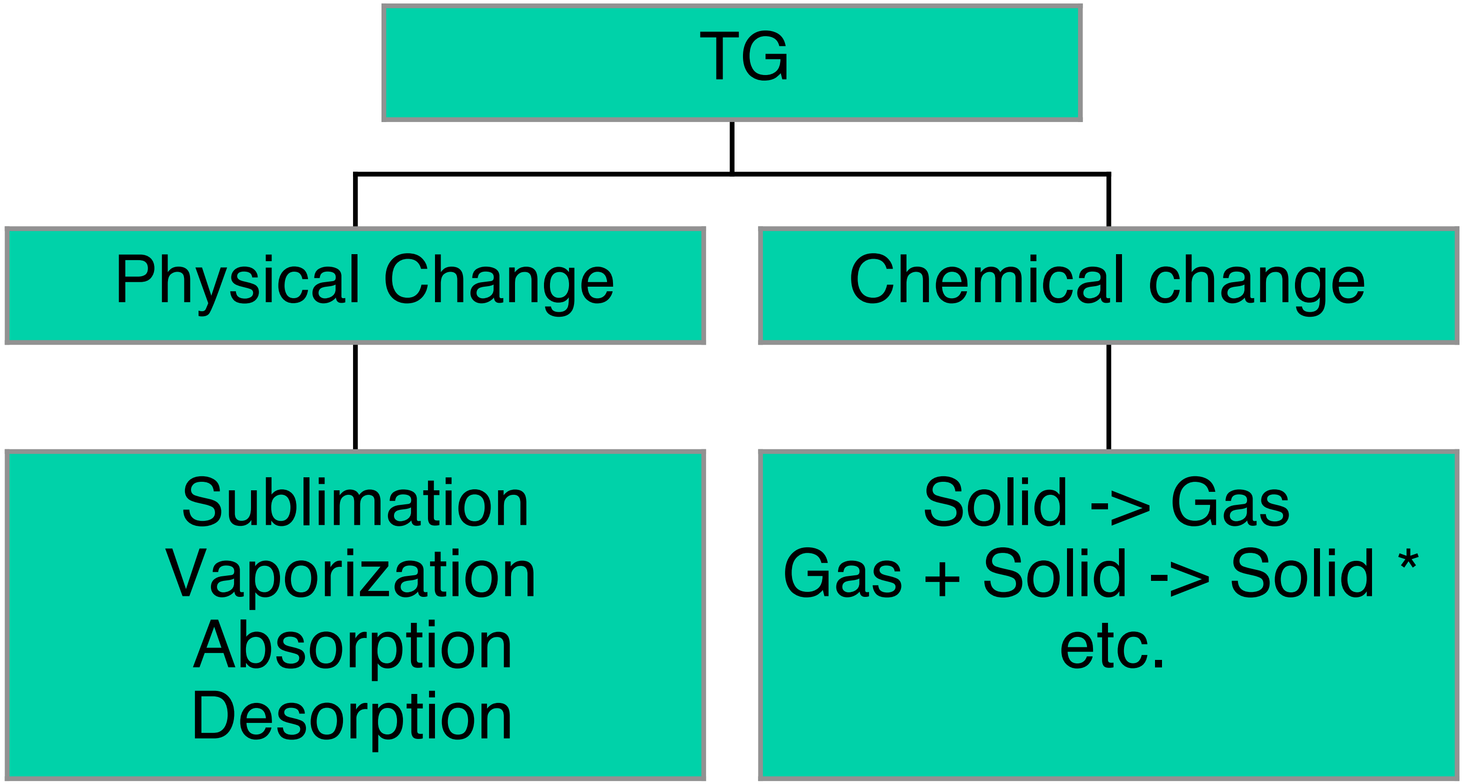


Thermogravimetric Analyser

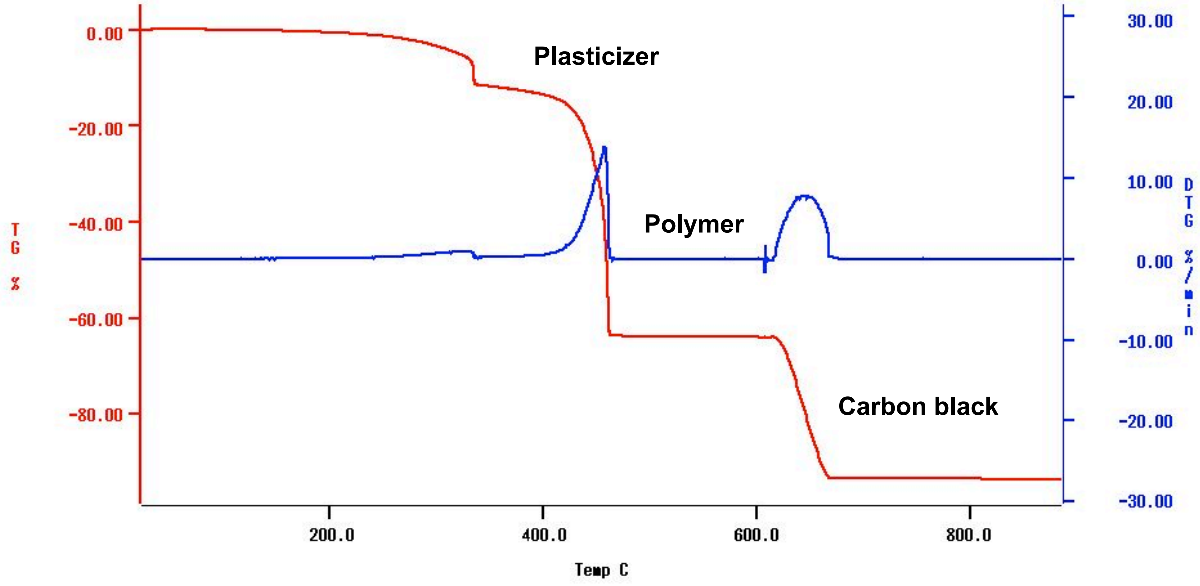


Heating rate and sample mass effects




TG
Physical Change
Chemical change
Sublimation
Vaporization
Absorption
Desorption
Solid -> Gas
Gas + Solid -> Solid *
etc.

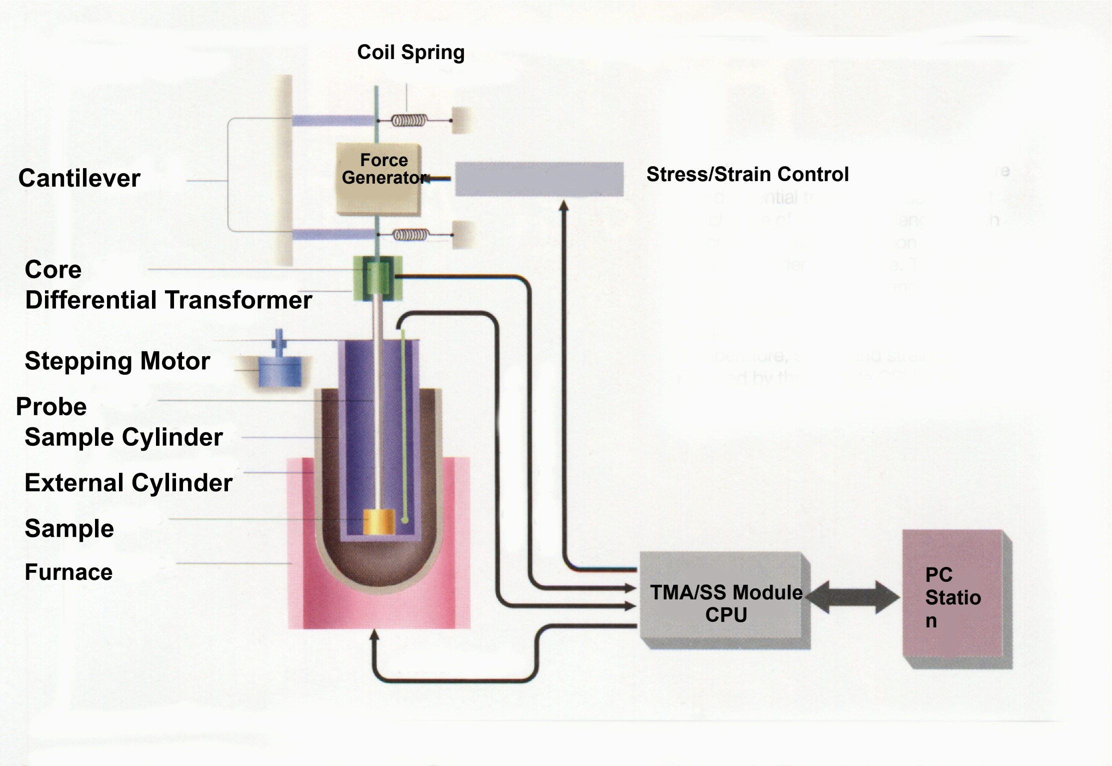
TG/DTA-Applications



Thermomechanical Analysis (TMA)

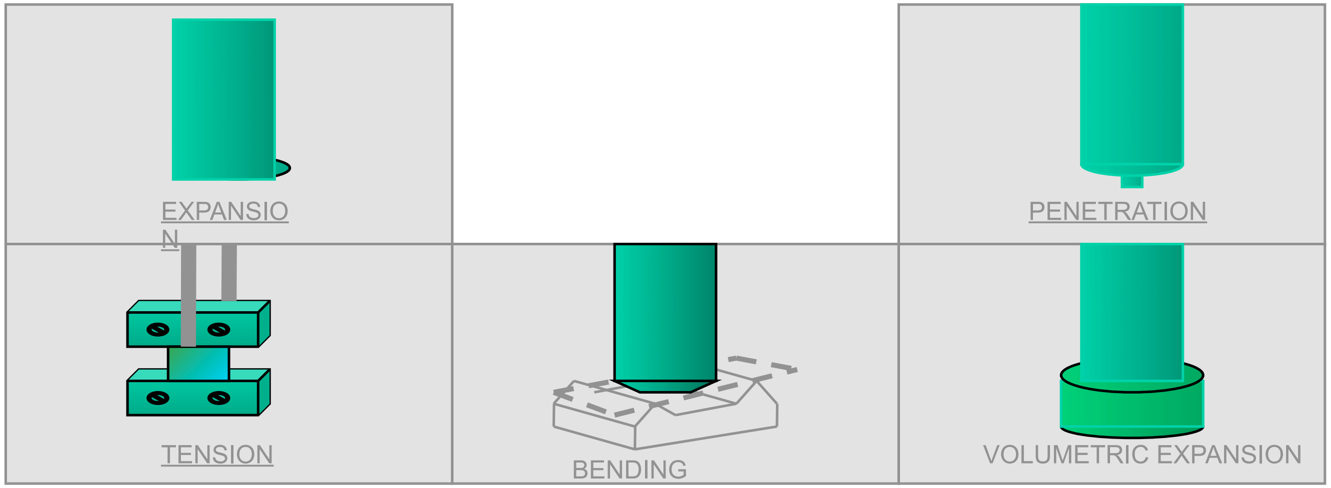
TMA Monitors Linear or Volumetric Changes in a Sample's Dimensions as a Function of Temperature, Time or Applied Force Loading.

Thermomechanical Analysis



Thermomechanical Analysis

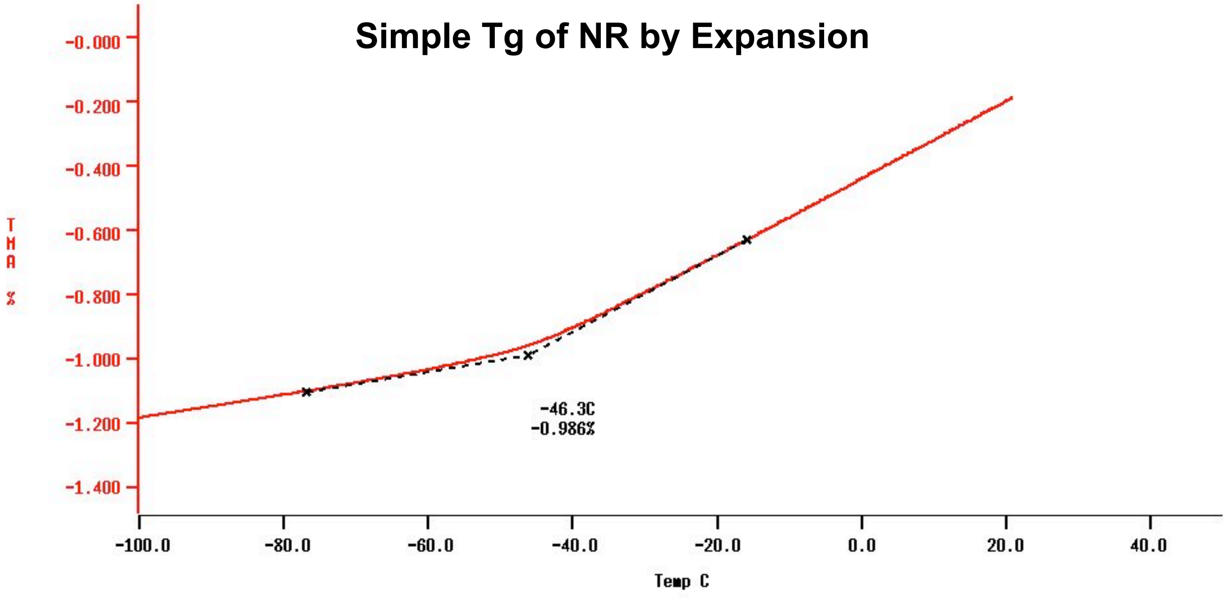
Probe Types



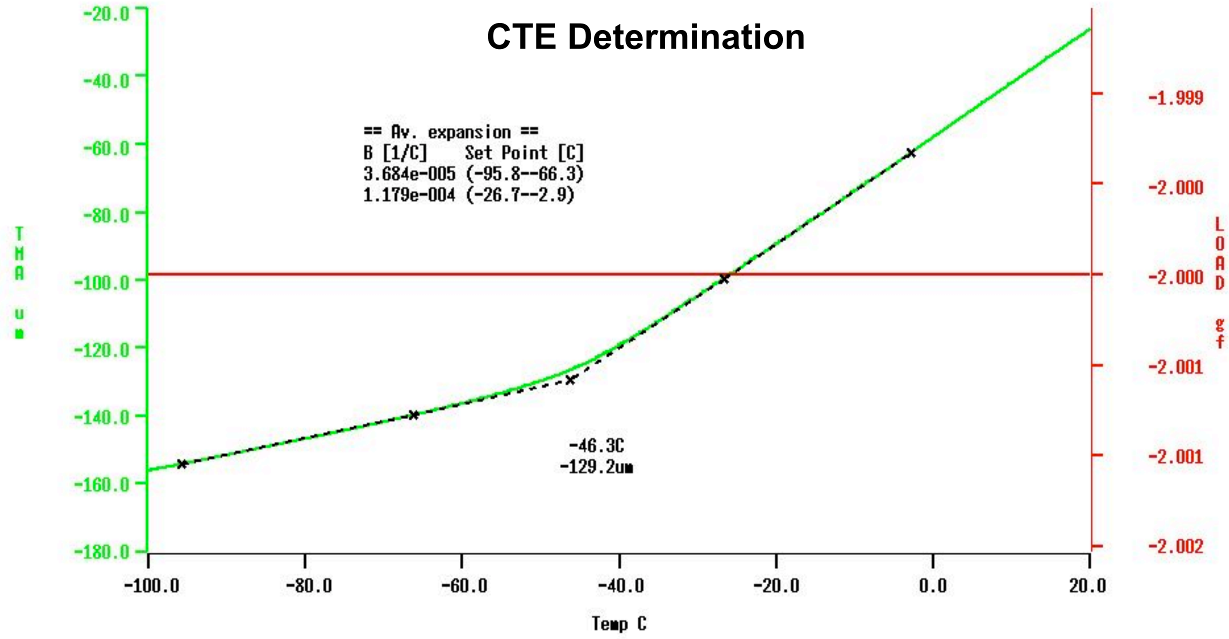
Thermo Mechanical Analyser

- **Wide linear measurement range +/- 5 mm**
- **High Sensitivity - 0.02 μm**
- **High Forces - Up to 600 g**
- **Stress-Strain Measurement**
- **Creep and Stress Relaxation**
- **Can be used as a Small DMA**

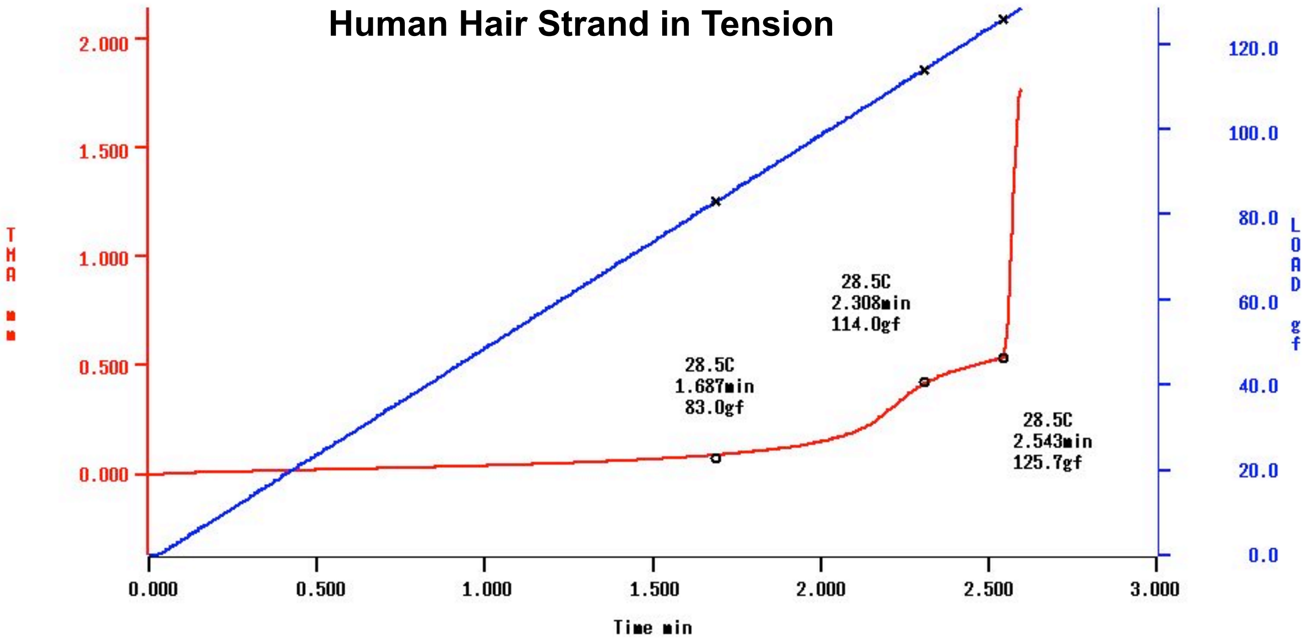
TMA Applications



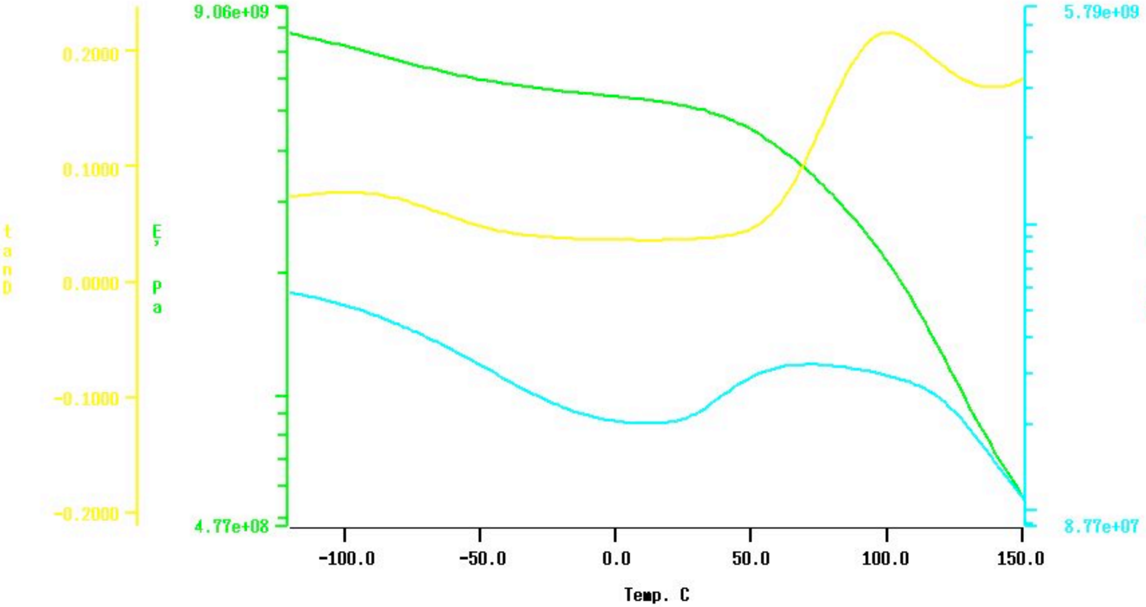
TMA Applications



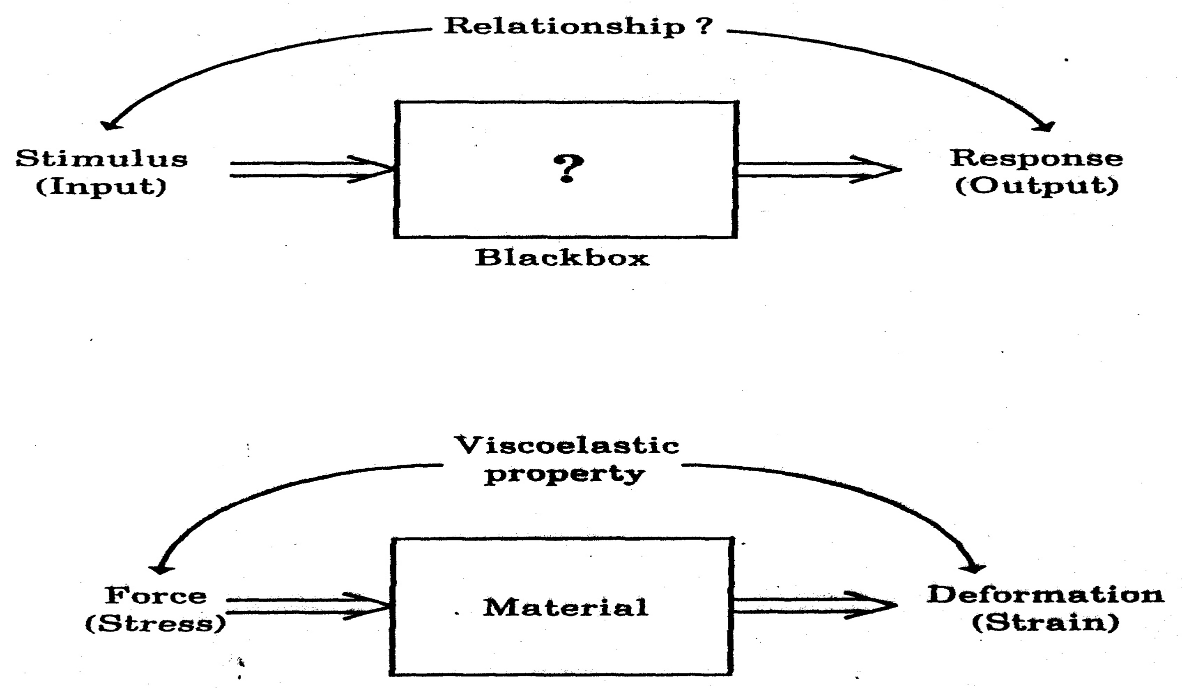
TMA Applications



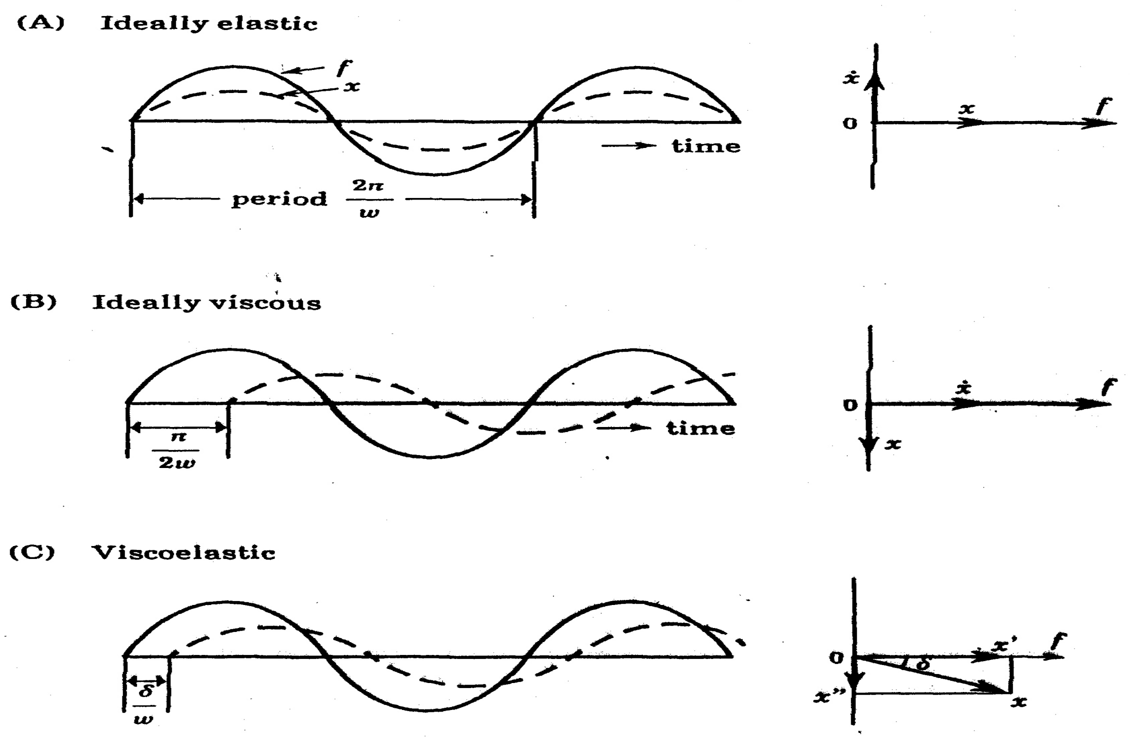
TMA Applications



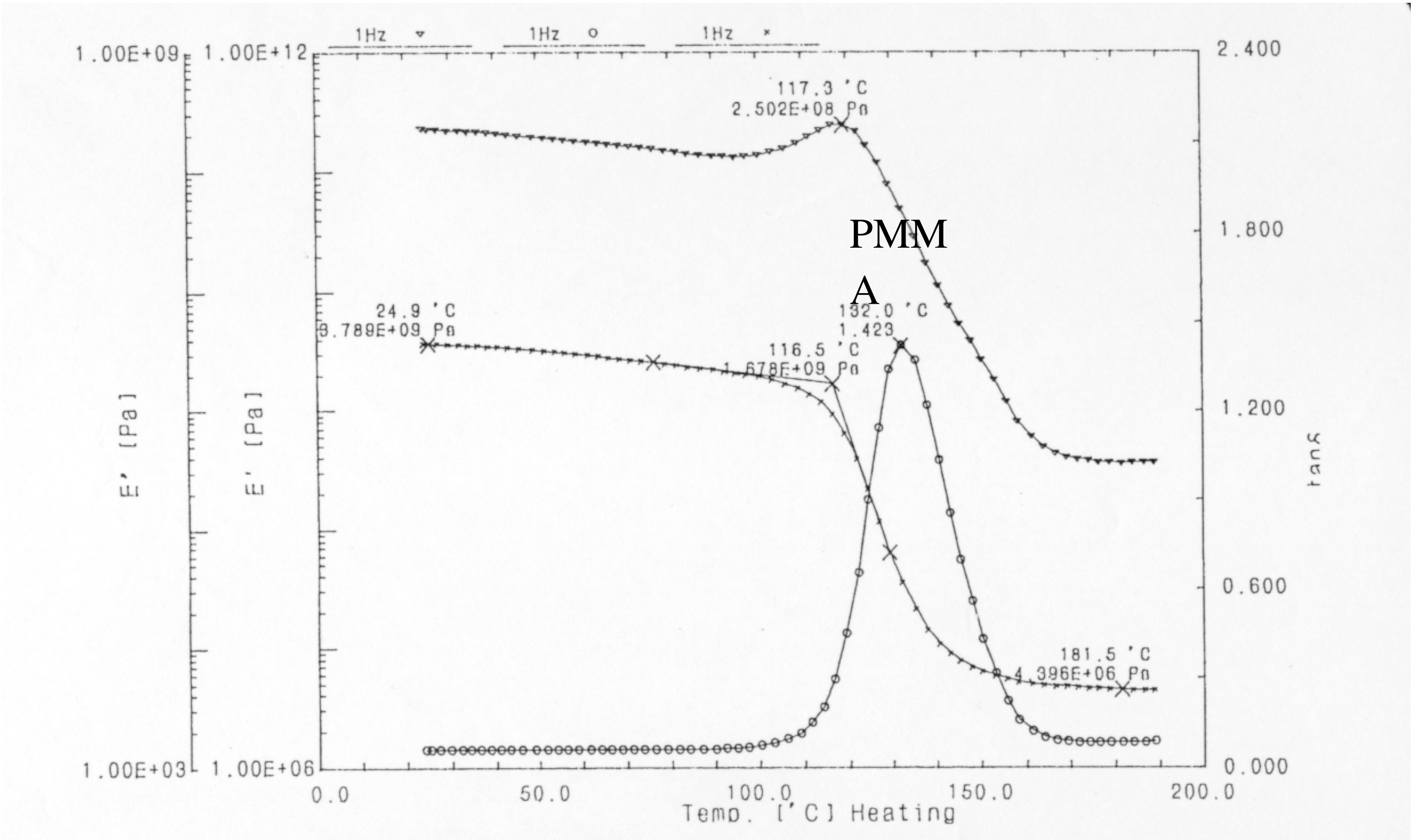
Analisi Dinamico Meccanica



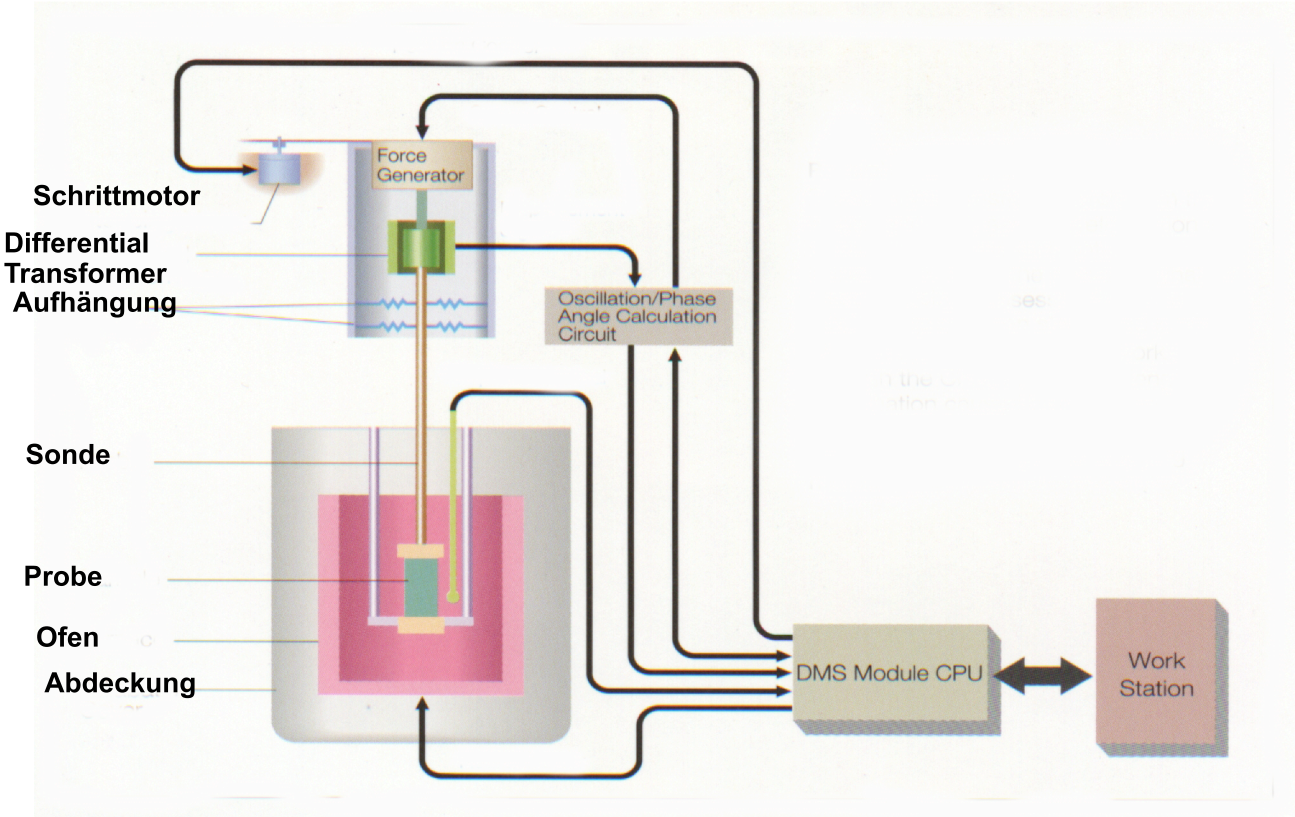
Analisi Dinamico Meccanica



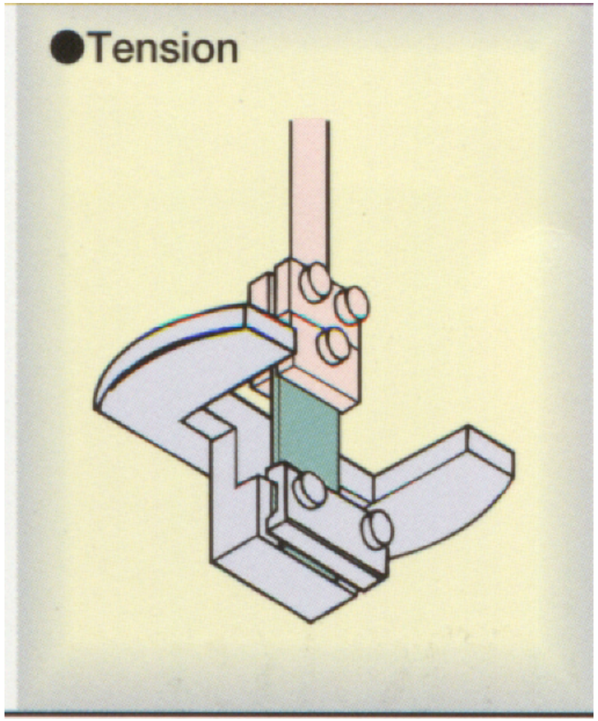
Analisi Dinamico Meccanica



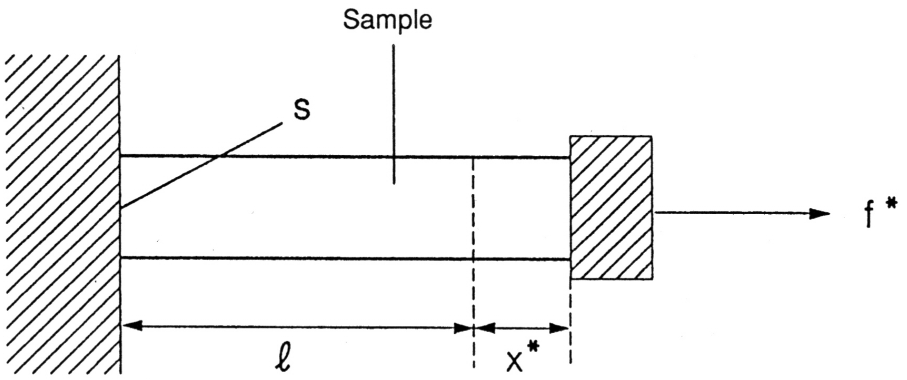
Analisi Dinamico Meccanica



Analisi Dinamico Meccanica



Analisi Dinamico Meccanica

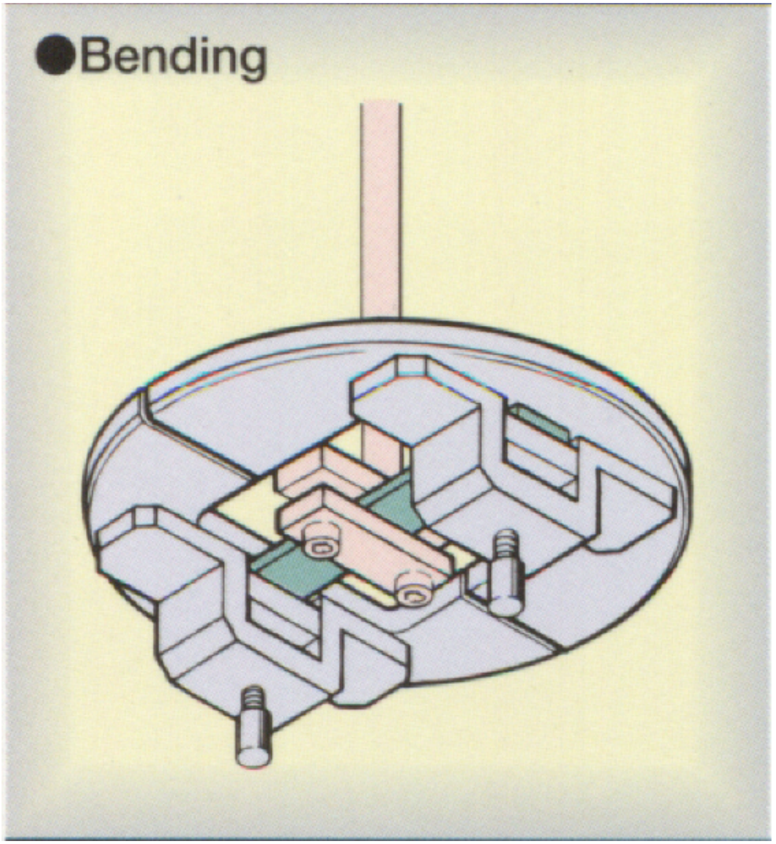


$$\frac{f^*}{x^*} = \frac{s}{\ell} E^*$$

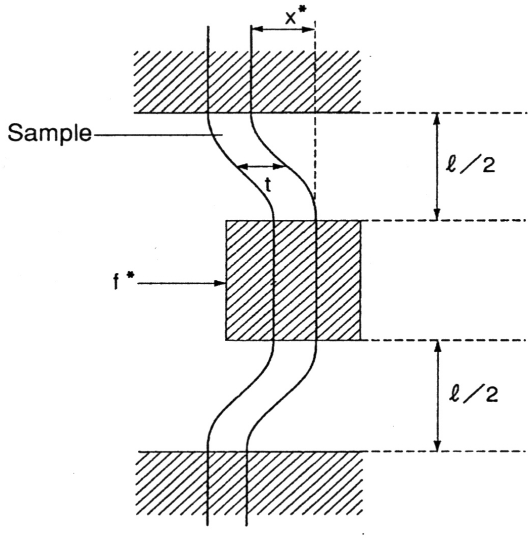
s Cross Section

ℓ Length

Analisi Dinamico Meccanica



Analisi Dinamico Meccanica

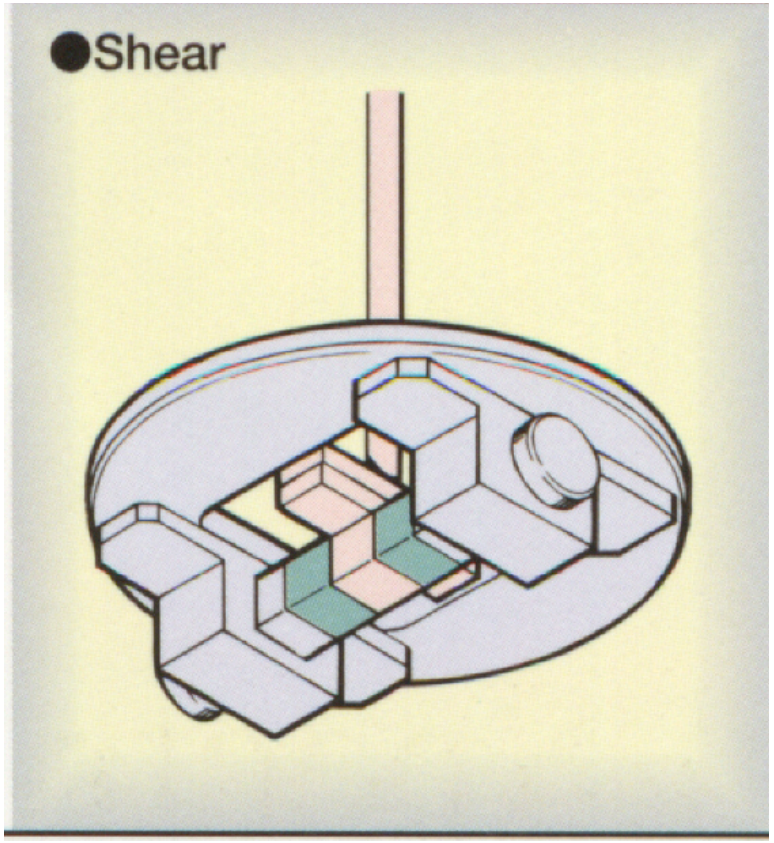


$$\frac{f^*}{x^*} = \frac{16t^3w}{\ell^3} E^*$$

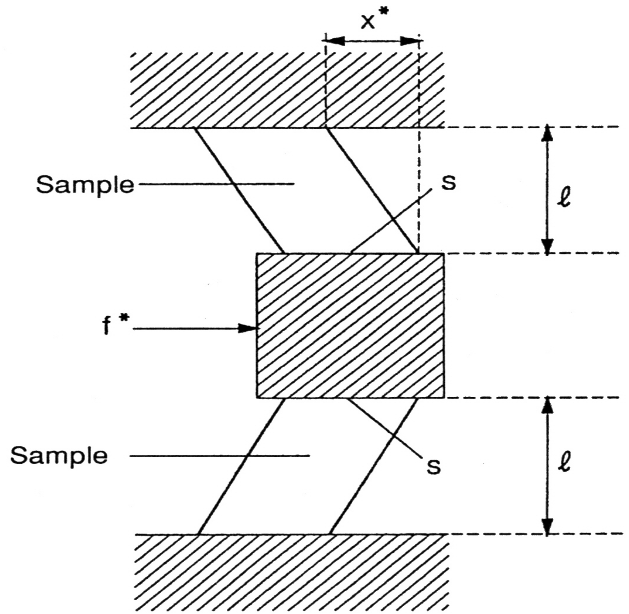
t Thickness
w Width
ℓ Effective Length

f*/x*=4t³wE*/ l³

Analisi Dinamico Meccanica



Analisi Dinamico Meccanica

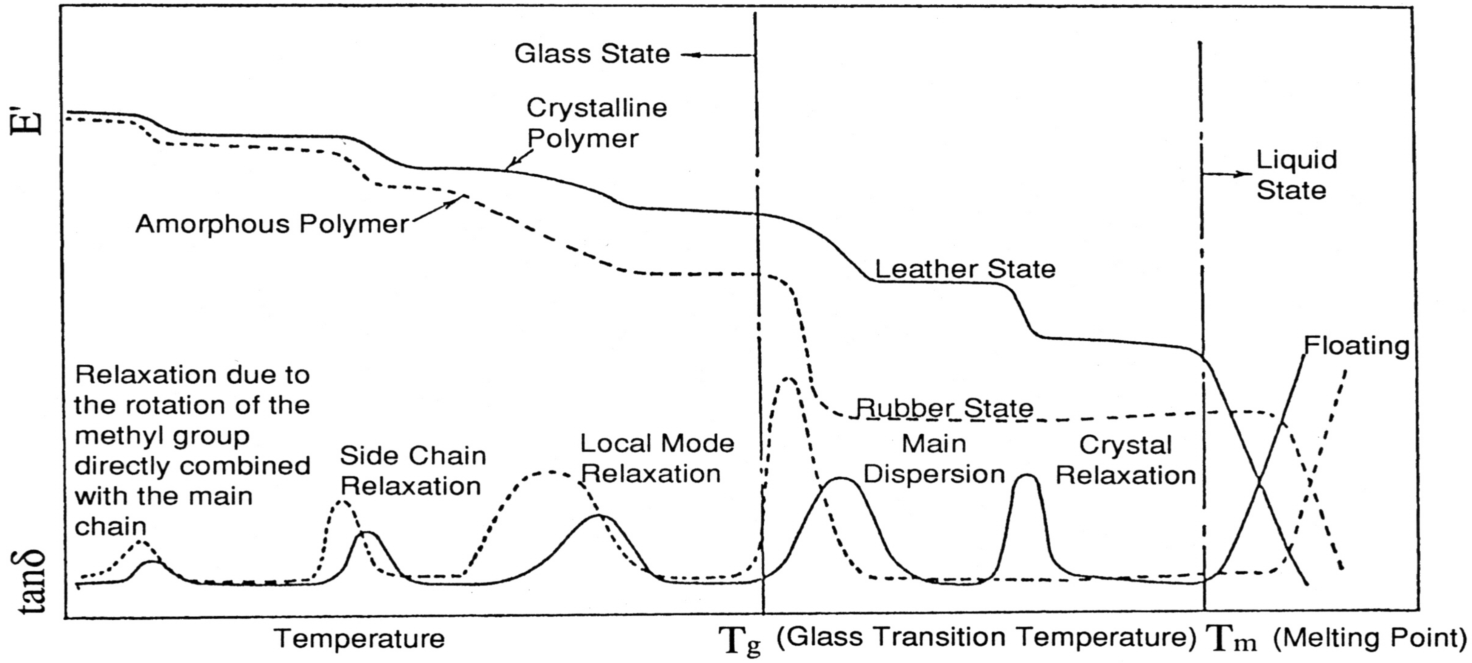


$$\frac{f^*}{x^*} = \frac{2s}{\ell} G^*$$

s Cross Section

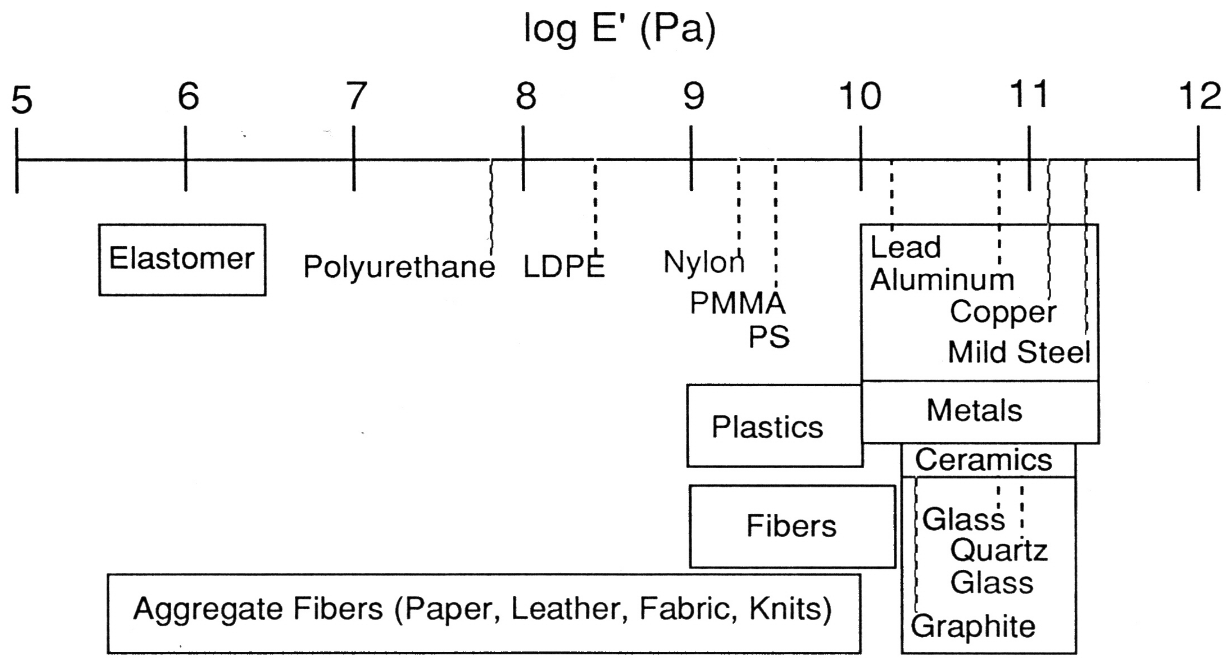
ℓ Length

Analisi Dinamico Meccanica



Temperature Dispersion Curve for Amorphous and Crystalline Polymers

Analisi Dinamico Meccanica



Viscoelastic Spectra for Various Materials

DSC-DTA Thermal analysis- Netsch

Seiko: TMA Exstar 6000 (Attualmente Perkin-Elmer Diamond)

Seiko: DMS Exstar 6000 (Attualmente Perkin-Elmer Diamond)

Setaram: DSC 92

Setaram: TG-DTA/DSC HT
Capacità: 20g-5 mg Risoluzione 0.4 μm (20-1600°C)

DSC 2010 TA Instruments

STA 409 (444) Netzsch
Intervallo di temperatura: RT-1600 °C
Peso campione: 10-300 mg
Sensibilita' temperatura: 0,1 °C
Sensibilita' peso campione: 0,1 mg2)

DIL 402 Netzsch
Intervallo di temperatura/ RT -1600 °C
Dimensioni campione: diametro: 3-14 mm; lunghezza: 25-50 mm (nominali)Sensibilita' temperatura: 0,1 °C
Sensibilita' dimenasionale: 10 micron3)

TG-MS
Setaram: TG-DTA/DSC HT
Capacità: 20g-5 mg Risoluzione 0.4 μm

Spettrometro: QMD1000 Carlo Erba (a quadrupolo)

Laboratorio di Polimeri e Compositi

Mettler DSC 30
Intervallo di temperatura: -150°C/ 600 °C
Velocità riscaldamento 0.5-50°C/min
Peso campione: circa 5-60 mg
Sensibilita' temperatura: 0,1 °C
Sensibilita' peso campione: 0,1 mg

DSC TA 2920 (DSC modulato)
Intervallo di temperatura/ -150°C/ °CVelocità riscaldamento/raffreddamento 0.2-20°C/min
Peso campione: 1-20 mg
Sensibilita' temperatura: 0,1 °

Termograviemtrical Mettler TG50
Intervallo di temperatura : 30-800°C
Velocità riscaldamento : 0.2-100°C/min
Sensibilita' temperatura: 0,1 °C
Sensibilita': 1 X 10-6 g (1 microgrammi)