100 Years
1920-2020
University of Lucknow | Centenary Year
लखनऊ विश्वविद्यालय | शताब्दी वर्ष

THERMAL METHODS OF ANALYSIS

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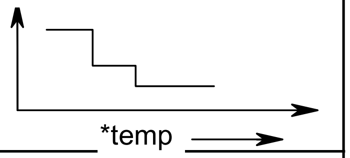
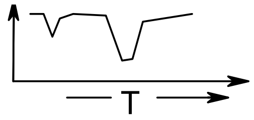
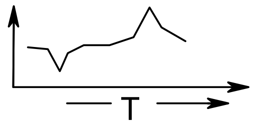
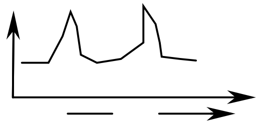
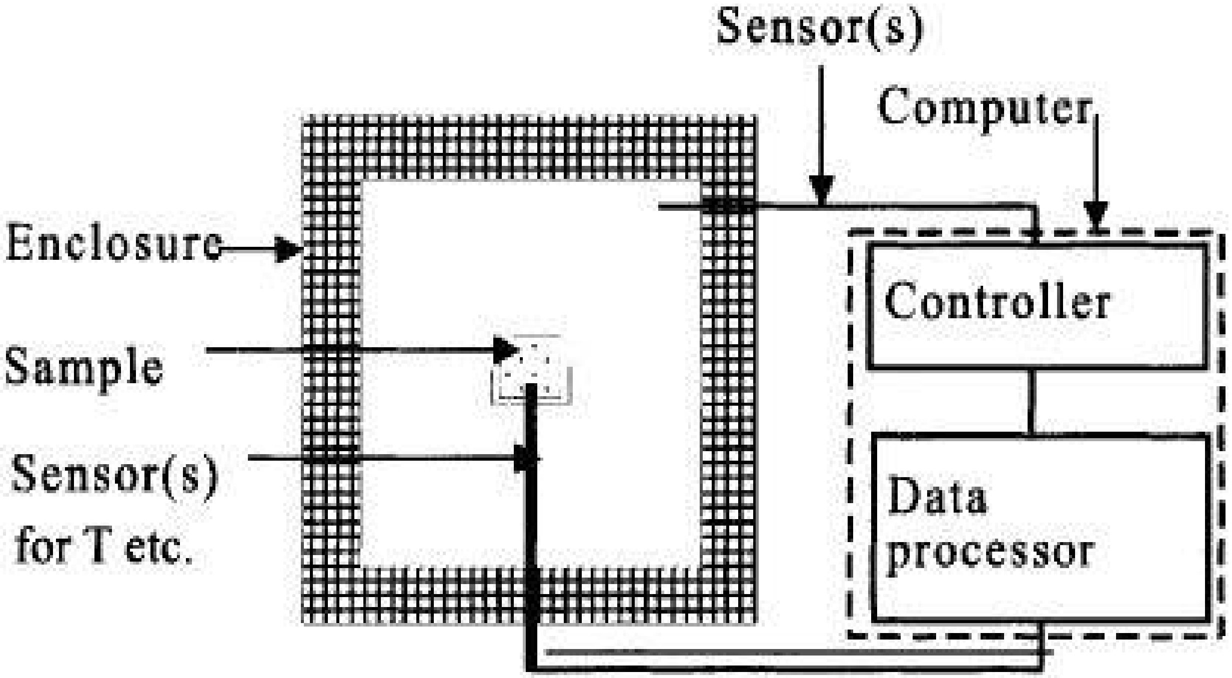
Techniques in which some physical parameters of the system are determined and recorded as a function of temperature.

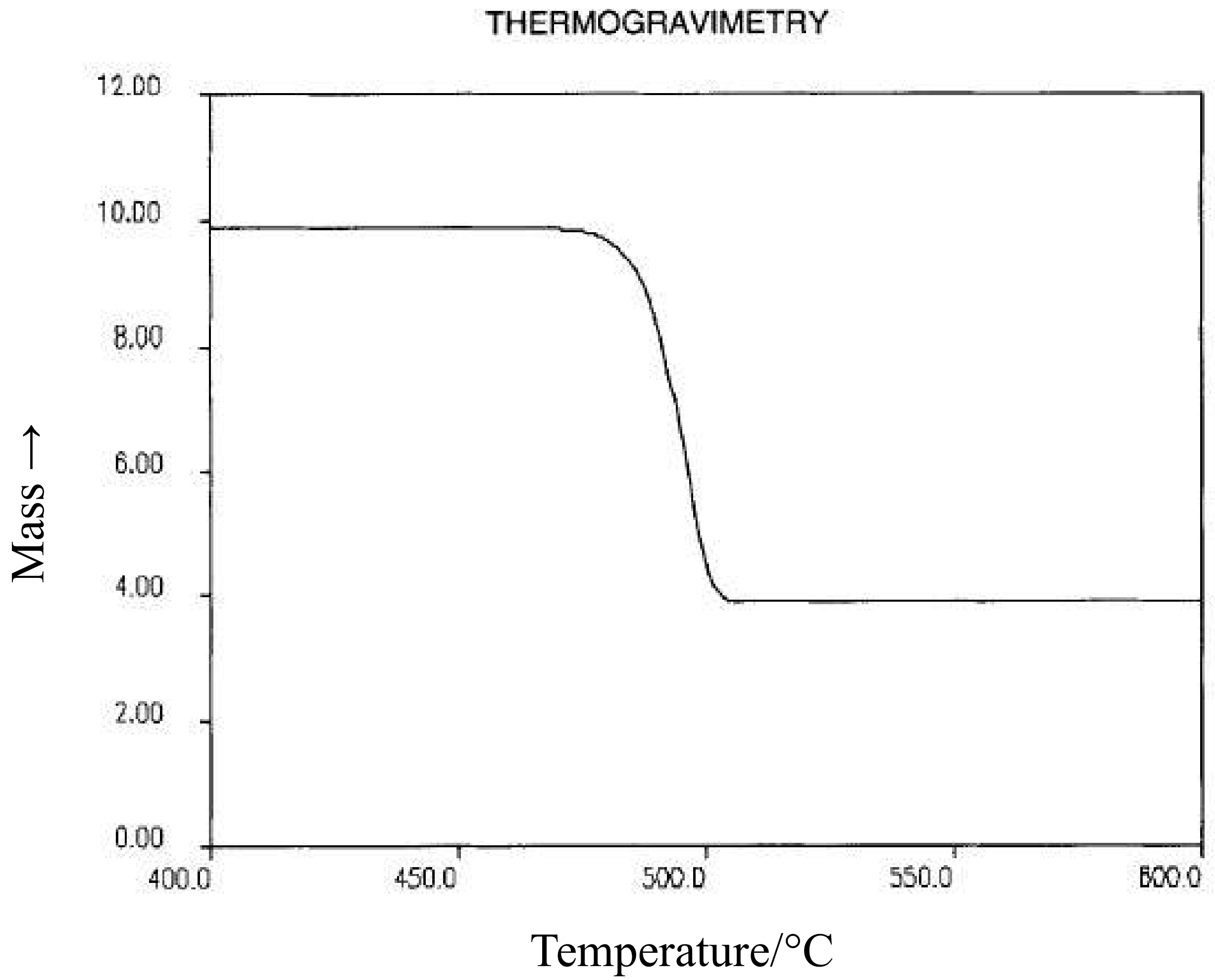
These methods find wide use for quality control and research applications on industrial products, such as polymers, pharmaceuticals, clays and minerals, Metals and alloys.

Some Thermal Analysis Techniques

TECHNIQUE	**ABBREVIATION**	**PROPERTY**	**NATURE OF PLOT**
Thermogravimetry	TG	Mass	
Derivative thermogravimetry	DTG	*dm/dt*	
Differential Thermal Analysis	DTA	T_s–T_r (Δ T)	
Differential Scanning Calorimetry	DSC	Heat flow, *dH/dt*	
Evolved Gas Analysis	EGA	Gases evolved	

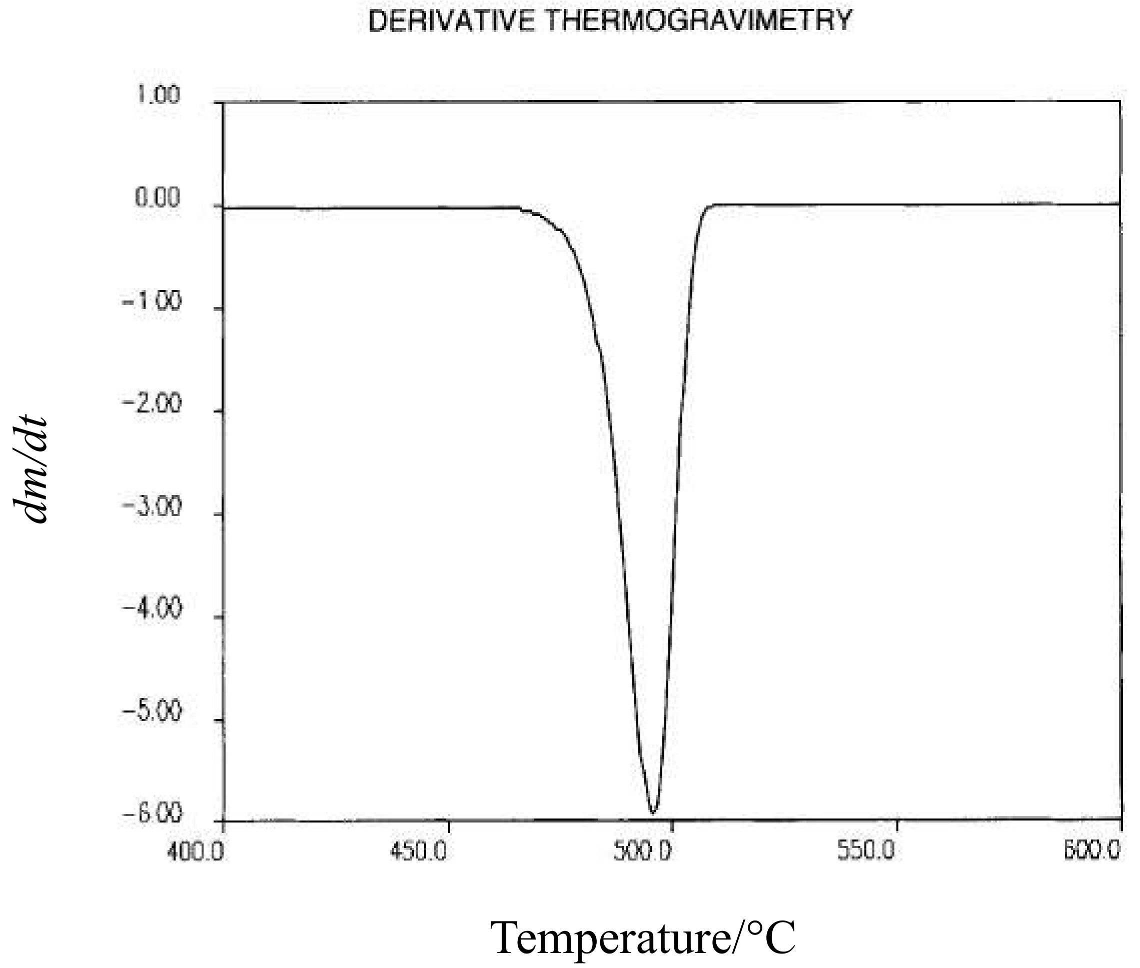


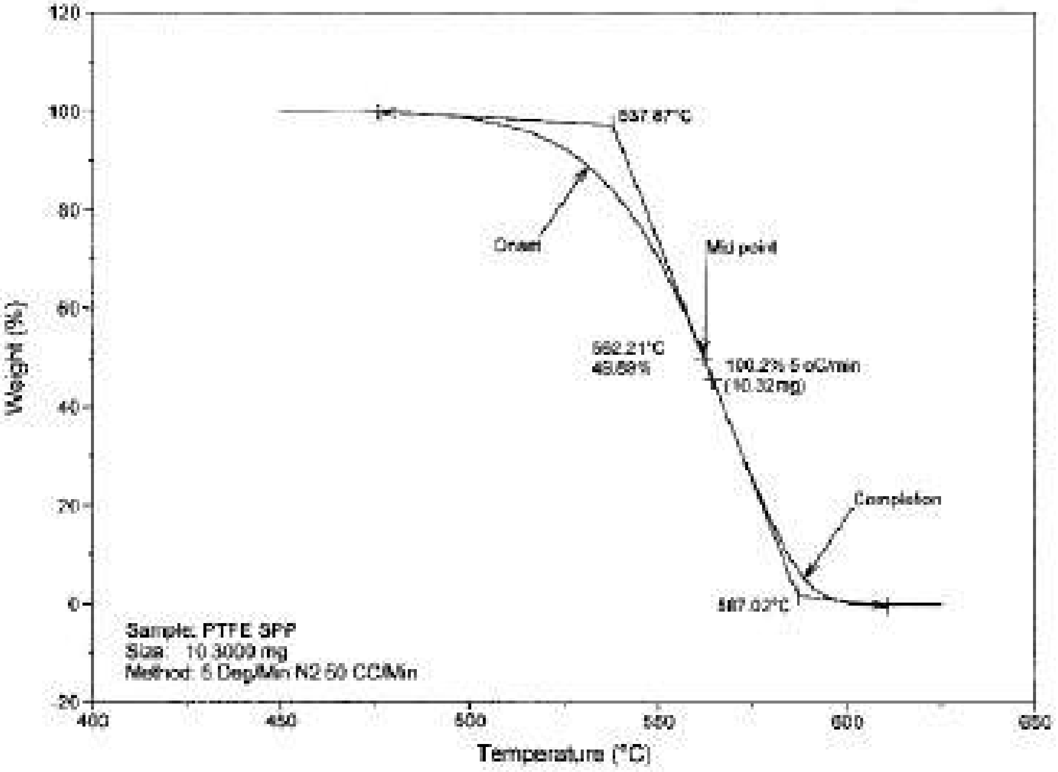
Schematic of general thermal analysis or calorimetry apparatus



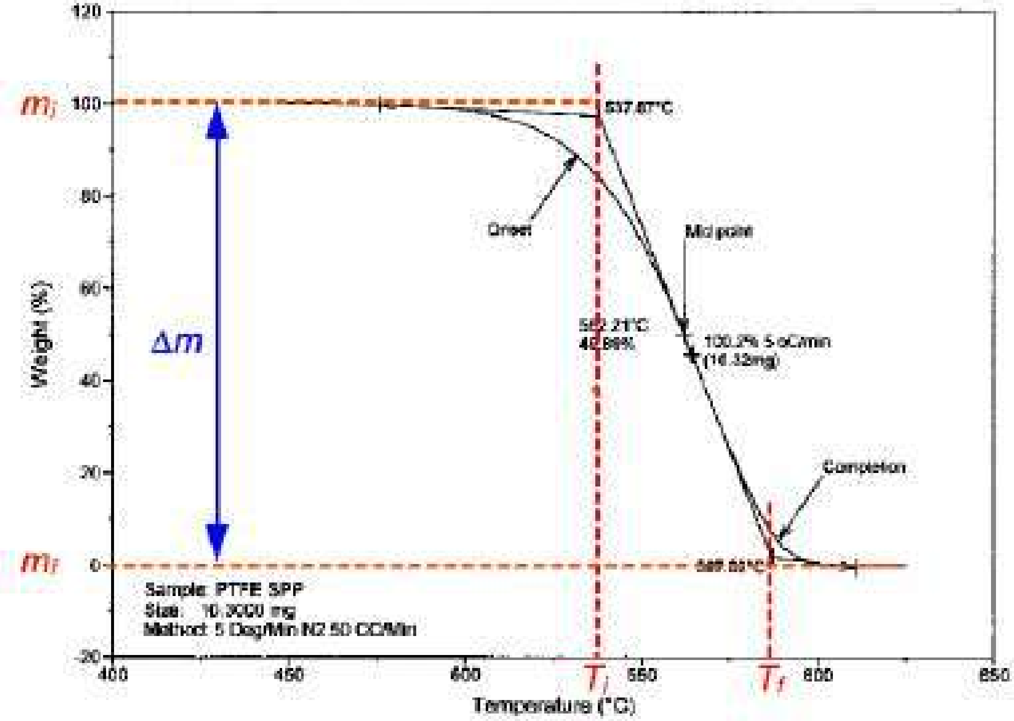
A(Solid) →B(Solid) + C(Gas)

The thermal stability is the ability of the substance to maintain its property as nearly unchanged even on heating.


DERIVATIVE THERMOGRAVIMETRY
1.00
0.00
-1.00
-2.00
-3.00
-4.00
-5.00
-6.00
dm/dt
400.0
450.0
500.0
550.0
600.0
Temperature/°C



Draw tangents of the curve to find the onset and the offset points



m_i, m_f and Δm are fundamental properties of the sample

T_i and T_f depend on operating variables

SOME FACTORS AFFECTING THERMOGRAVIMETRIC CURVES

1. Instrumental (thermobalance) factors

a. Furnace heating rate

b. Recording or chart speed

c. Furnace Atmosphere

d. Geometry of sample holder and furnace

e. Sensitivity of recording mechanism

f. Composition of sample container

SOME FACTORS AFFECTING THERMOGRAVIMETRIC CURVES

2. Sample Characteristics

a. Amount of sample
b. Solubility of evolved gases in sample
c. Particle size
d. Heat of reaction
e. Sample packing
f. Nature of the sample
g. Thermal conductivity

a. Furnace Heating Rate

For initial procedural decomposition temperature, T_i:

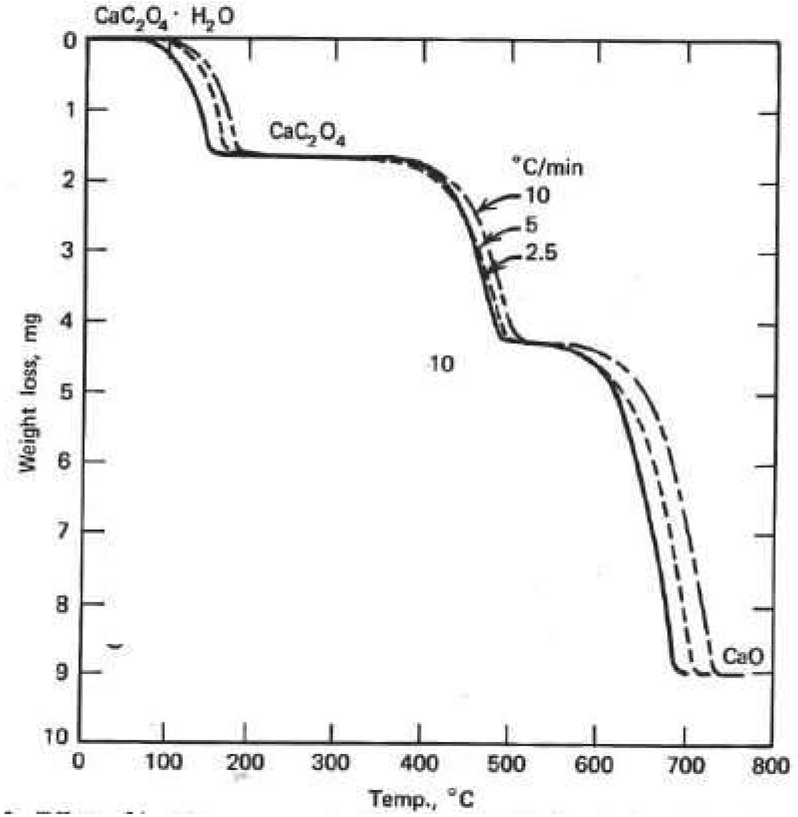
$(T_i)_F > (T_i)_S$

For final procedural temperatures, T_f

$(T_f)_F > (T_f)_S$

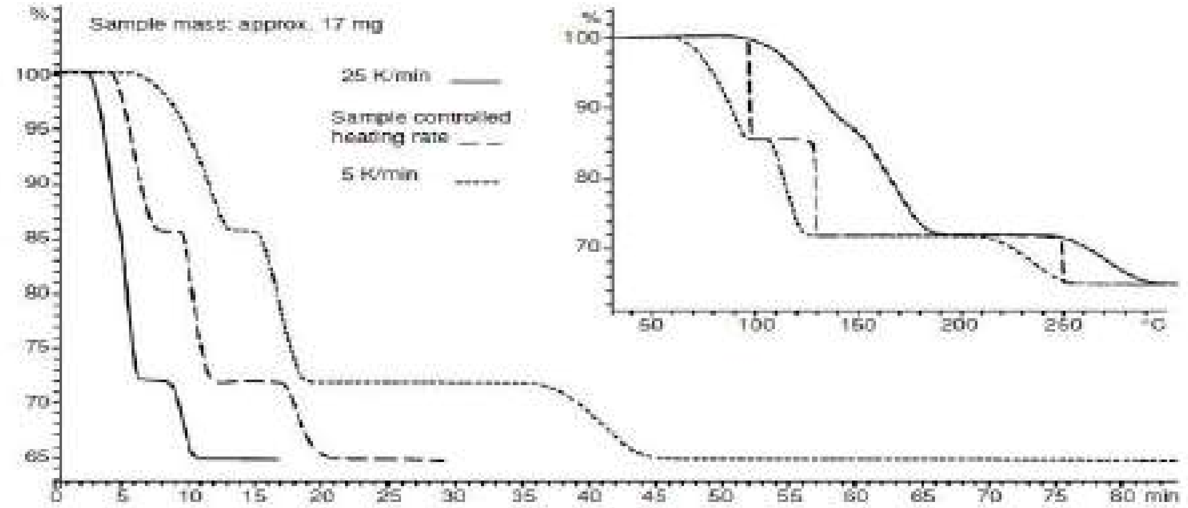
Reaction interval, $T_f - T_i$

$(T_f - T_i)_F > (T_f - T_i)_S$



Slower heating =
better resolution

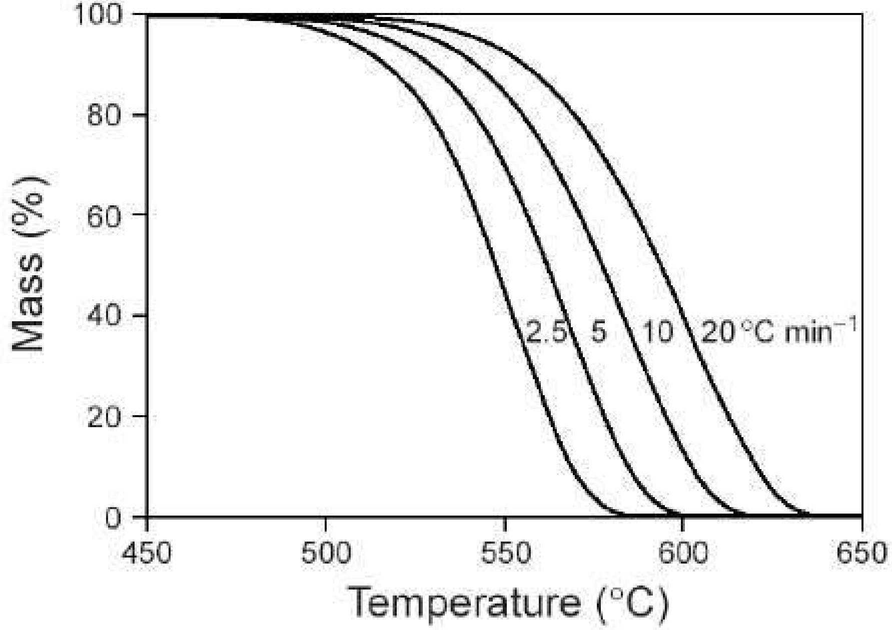
Usually,
Higher heating rate =
shift to higher temperature



Influence of the heating rate on the resolution of partial reactions, in the inserted diagram on the right, the dotted and solid curves of copper sulphate pentahydrate were measured conventionally at 5 and 25 K/min, whereas the dashed curve was recorded using sample controlled heating rate. In this presentation of mass against temperature, the steps in the curve appear to be nearly vertical because, at low heating rates, the reaction takes place almost isothermally. In contrast, in the mass against time presentation (main diagram), the shapes of the three curves at first appear similar. On closer inspection, the better separation obtained using sample controlled heating rates – especially in the first two steps – becomes apparent.

Sample controlled TG: A quite different approach for separating overlapping reactions makes use of rate of change in sample weight to automatically control the heating rate: the faster the change in mass, the slower the heating rate.

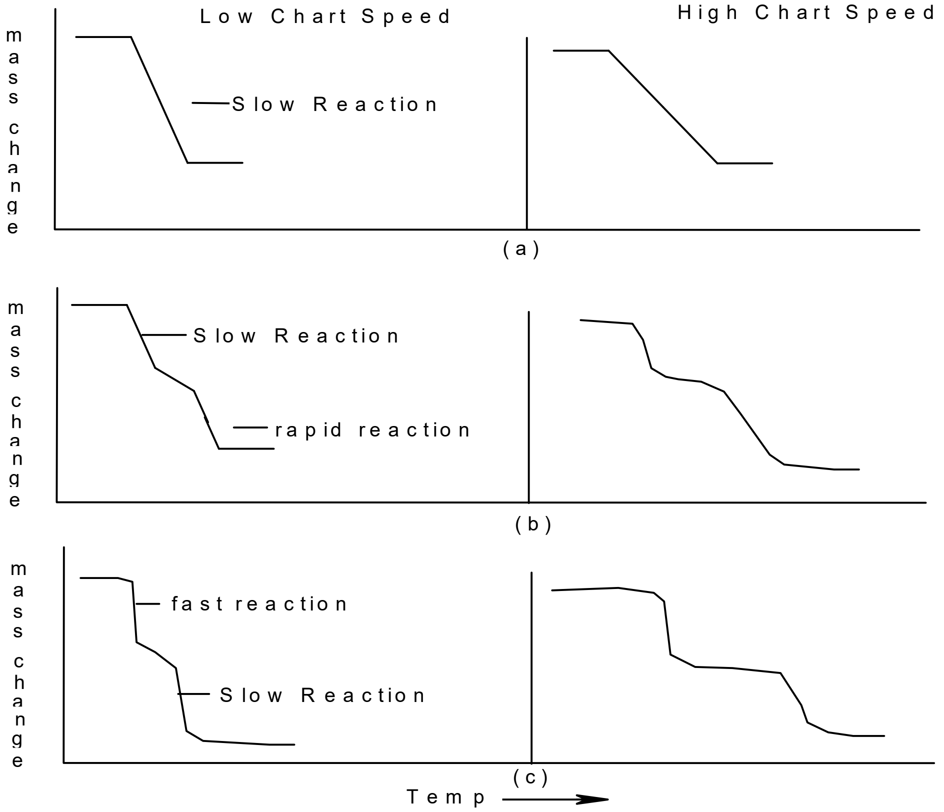
Effect of heating rate



10 mg samples of PTFE, heated at 2.5, 5, 10 and 20 °C/min in nitrogen

b. Recording / Chart Speed

The chart speed of the TG curves for rapid or slow reactions can have pronounced effect on the shape of the curves.



There is definite Flattening of the curve as the chart speed is increased for a slow thermal decomposition reaction.

In case of slow reaction followed by a rapid one, the lower chart speed curve shows less separation of the two steps.

For a fast reaction followed by a slower one, an effect similar to that of curve (b) was observed.

C. Effect of furnace atmosphere :-

The effect of furnace atmosphere depends upon:

i) Type of reaction.
ii) The nature of decomposition products.
iii) The type of atmosphere employed.

Normally function of the atmosphere is to remove the gaseous products evolved during the reaction.

Common atmospheres used are:-

a) Static air i.e. air from the surrounding flows through the furnace.
b) Dynamic air i.e. compressed air from the cylinder flows through the furnace with definite flow rate.
c) Ar-gas / O_2 free N_2-gas is used as inert atmosphere
   Nitrogen or Argon are usually used to purge the furnace and prevent oxidation of the sample.

$$\text{A (solid)} \rightarrow \text{B (solid)} + \text{C (gas)}$$

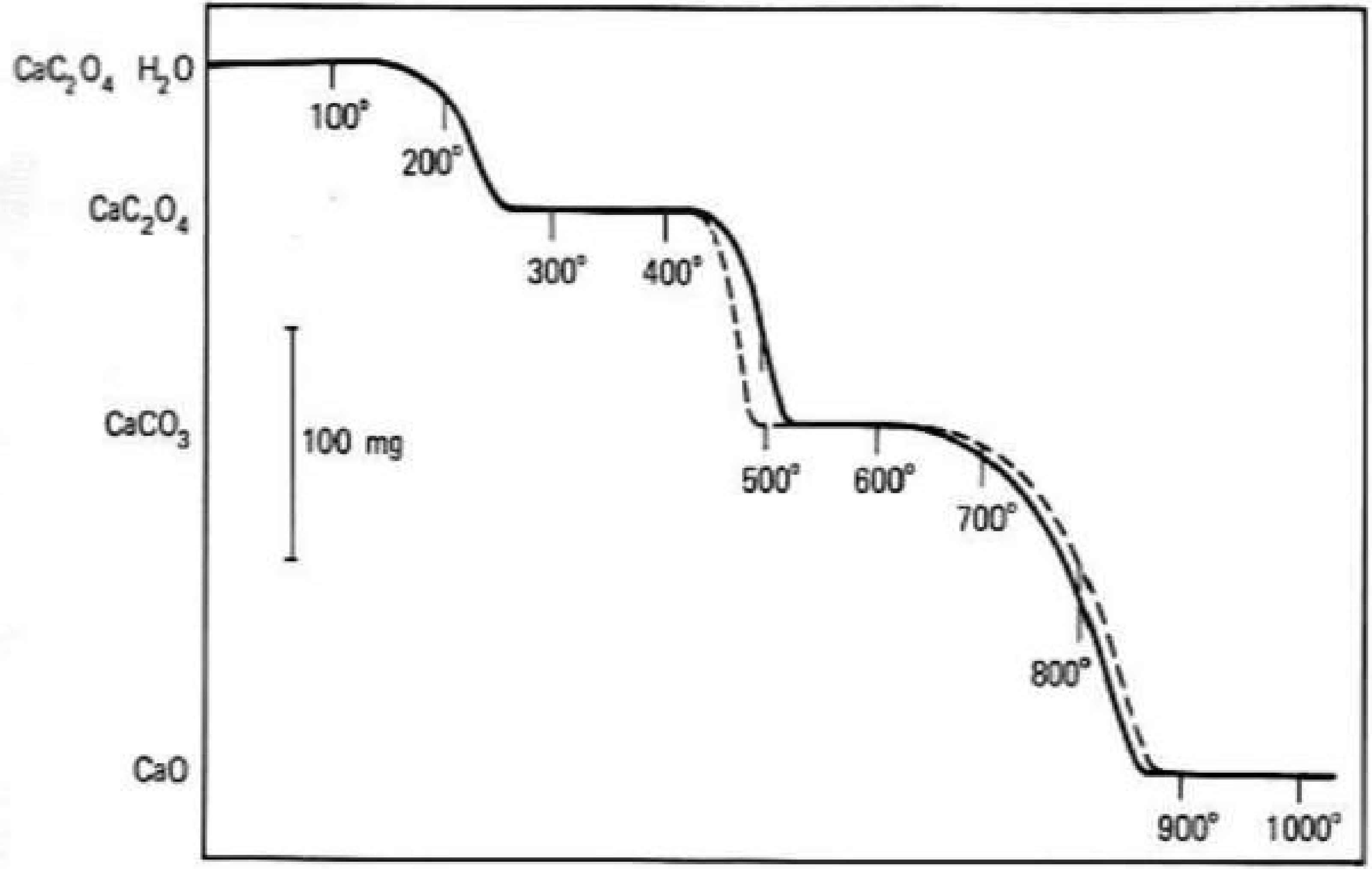
$$\text{A (solid)} \leftrightarrow \text{B (solid)} + \text{C (gas)}$$

$$\text{A (solid)} + \text{B (gas)} \rightarrow \text{C (solid)}$$

$$\text{A (solid)} + \text{B (gas)} \leftrightarrow \text{C (solid)}$$

$$\text{A (solid)} + \text{B (gas)} \rightarrow \text{C (solid)} + \text{D (gas)}$$

$$\text{A (solid)} + \text{B (gas)} \leftrightarrow \text{C (solid)} + \text{D (gas)}$$



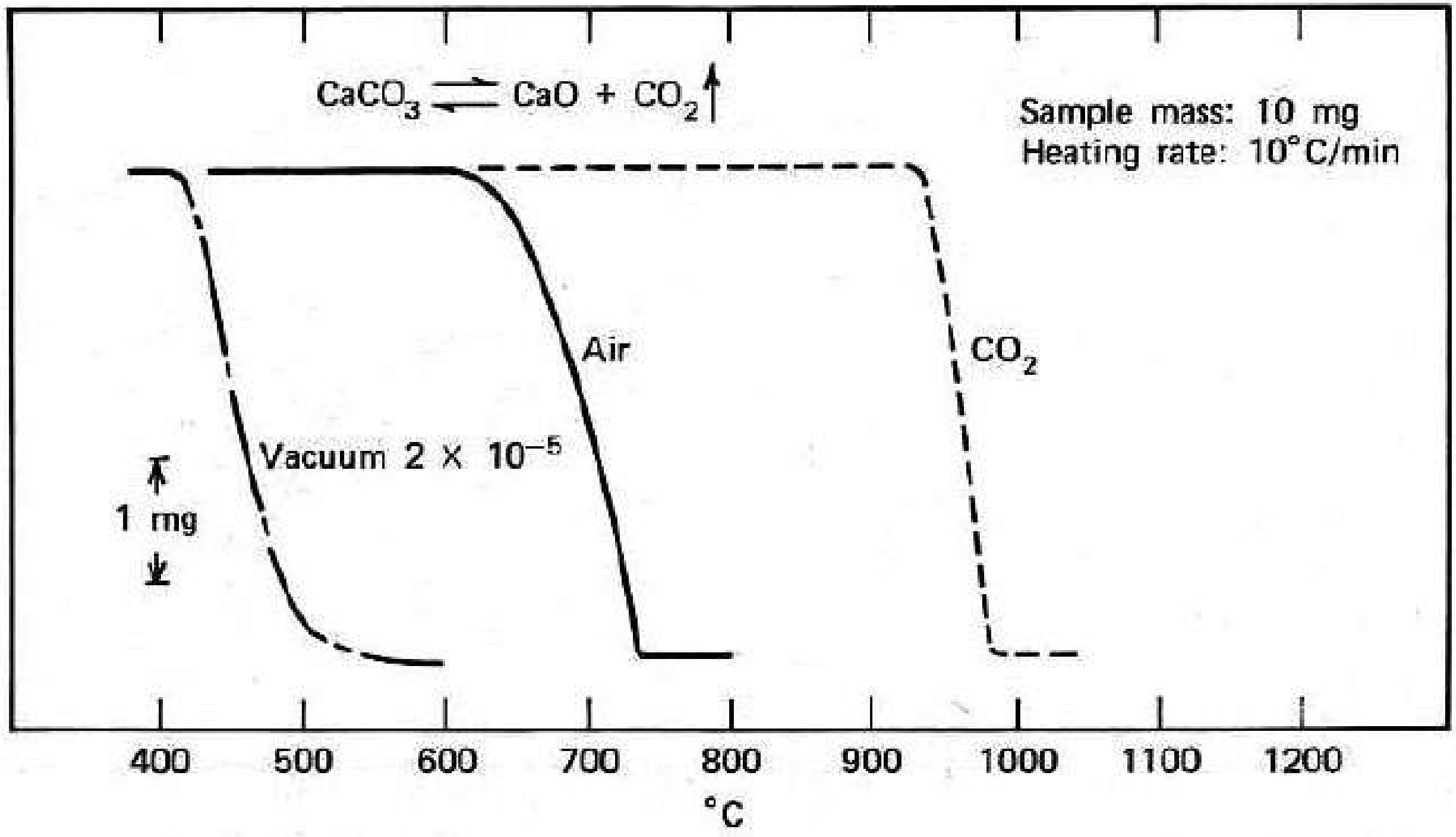
$CaC_2O_4.H_2O\ (s) \rightleftharpoons CaC_2O_4(s) + H_2O\ (g)$

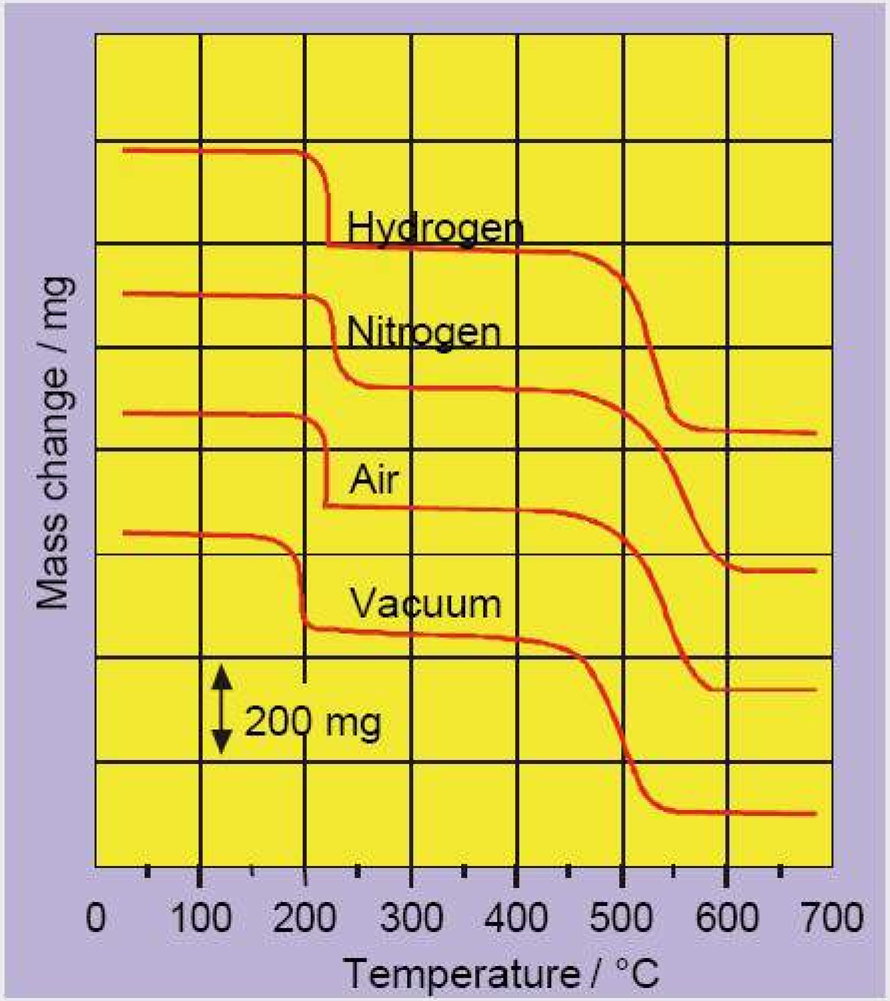
$CaC_2O_4(s) \rightarrow CaCO_3(s) + CO\ (g)$ (in N_2)

$CaC_2O_4(s) + \frac{1}{2}\ O_2(g) \rightarrow CaCO_3(s) + CO_2(g)$ (in O_2)

$CaCO_3(s) \rightleftharpoons CaO + CO_2(g)$

Solid line: N_2 ; dashed line: O_2


$CaCO_3 \rightleftharpoons CaO + CO_2\uparrow$
Sample mass: 10 mg
Heating rate: 10°C/min
Air
CO_2
Vacuum 2×10^{-5}
1 mg
400
500
600
700
800
900
1000
1100
1200
°C



Fast and reversible dehydration in air and hydrogen.

Slower dehydration in nitrogen.

Dehydration and decomposition is slow but occurs at lower temperatures

$MgC_2O_4 \rightarrow MgO + CO + CO_2$

Fast decomposition in hydrogen and air due to following reactions:

in H_2: $CO + CO_2 + 7\ H_2$
$\rightarrow 2\ CH_4 + 3\ H_2O$

in O_2: $CO + CO_2 + 1/2\ \ H_2O$
$\rightarrow 2\ CO_2$

d. Geometry of the Sample Holders :

The geometry of the sample holder can change the shape of TG curve.

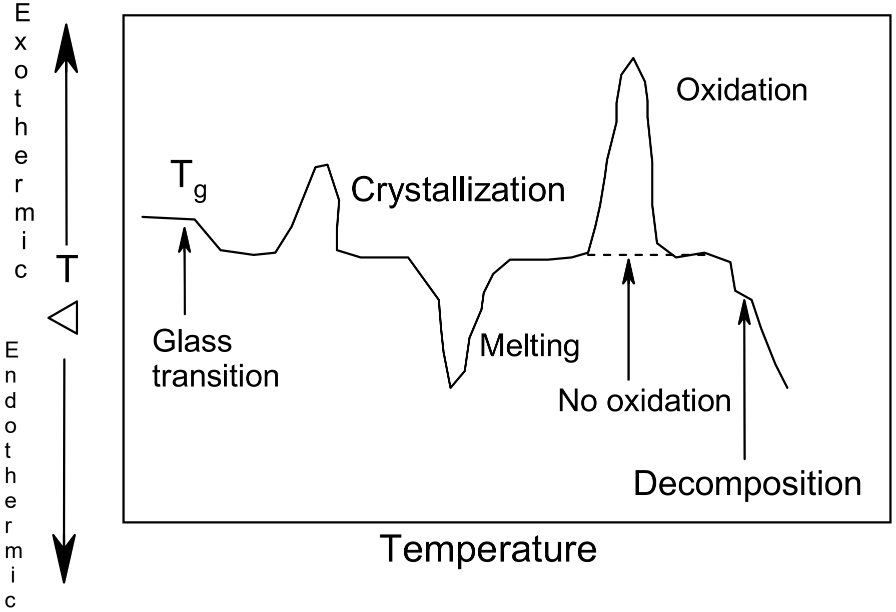
Sample Holders may be range from flat plates to deep crucibles of various capacities.

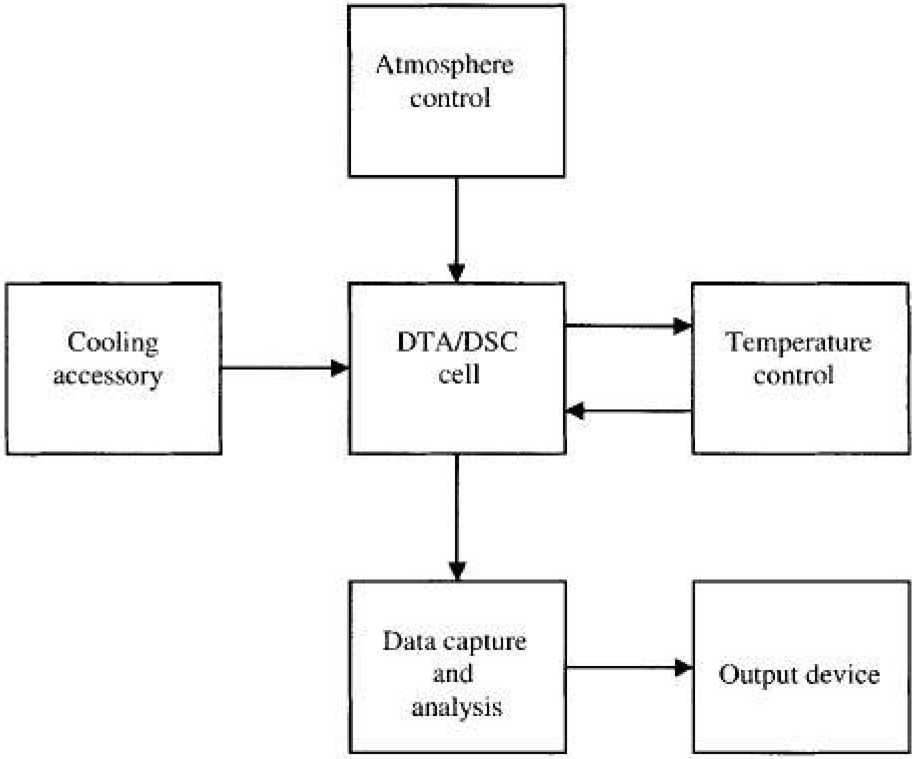
Materials used in their construction may vary from glass, alumina, ceramics, various metals and Metallic alloys.

Generally shallow disc is preferred to cone shape crucible because there is rapid gas exchange between sample and surrounding atmosphere

Differential Thermal Analysis

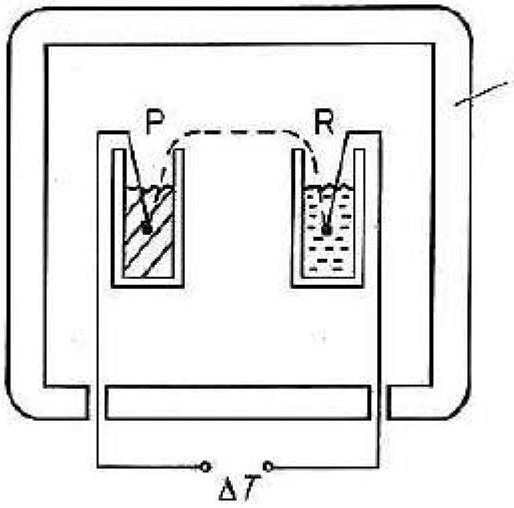
It is the technique in which the difference in temperature between a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program.





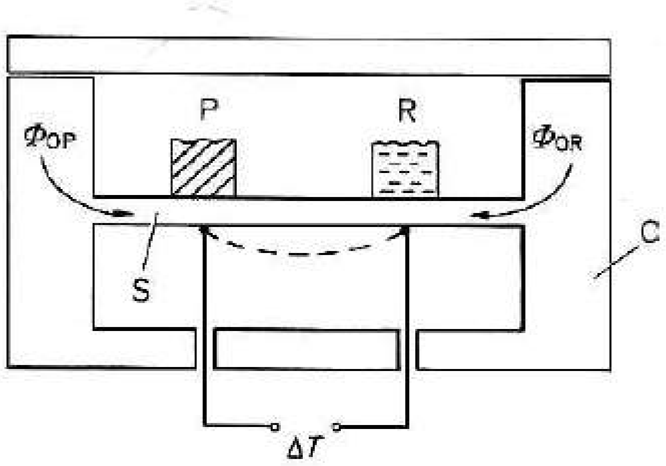
Schematic representation of a DTA or DSC instrument

DTA

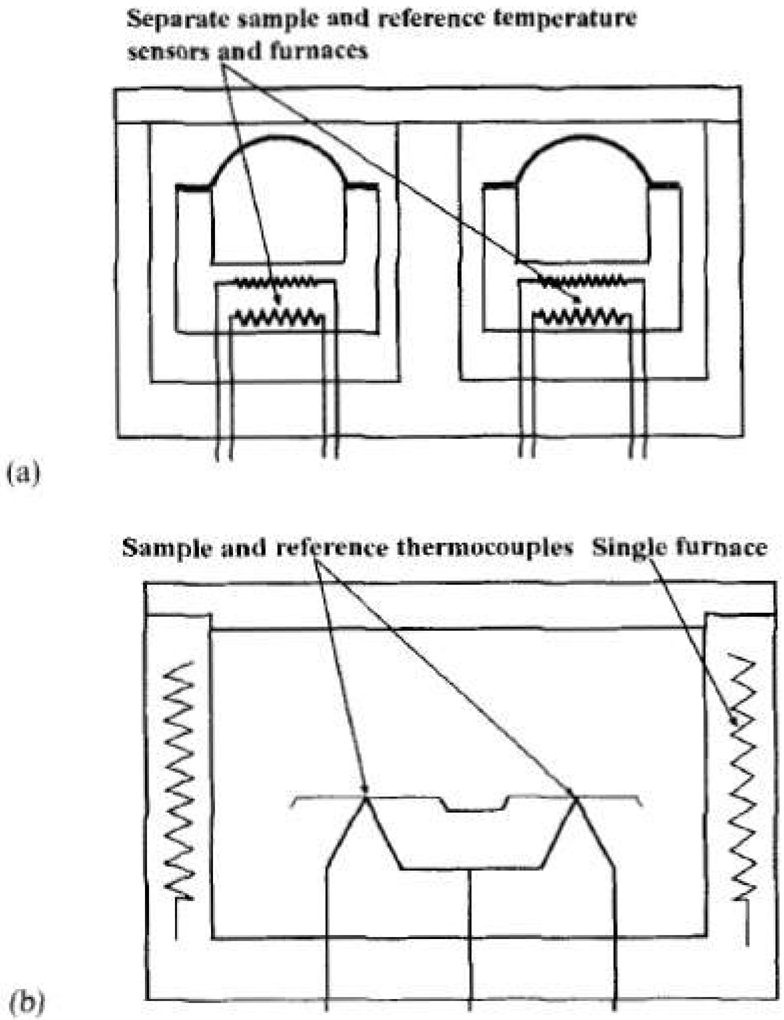


Measure temperature difference between sample and reference while they are being heated.

DSC



Measure difference in heat flow to sample and reference while they are being heated.



(a) *Power-compensation differential scanning calorimeter*. (b) *Heat flux differential scanning calorimeter*

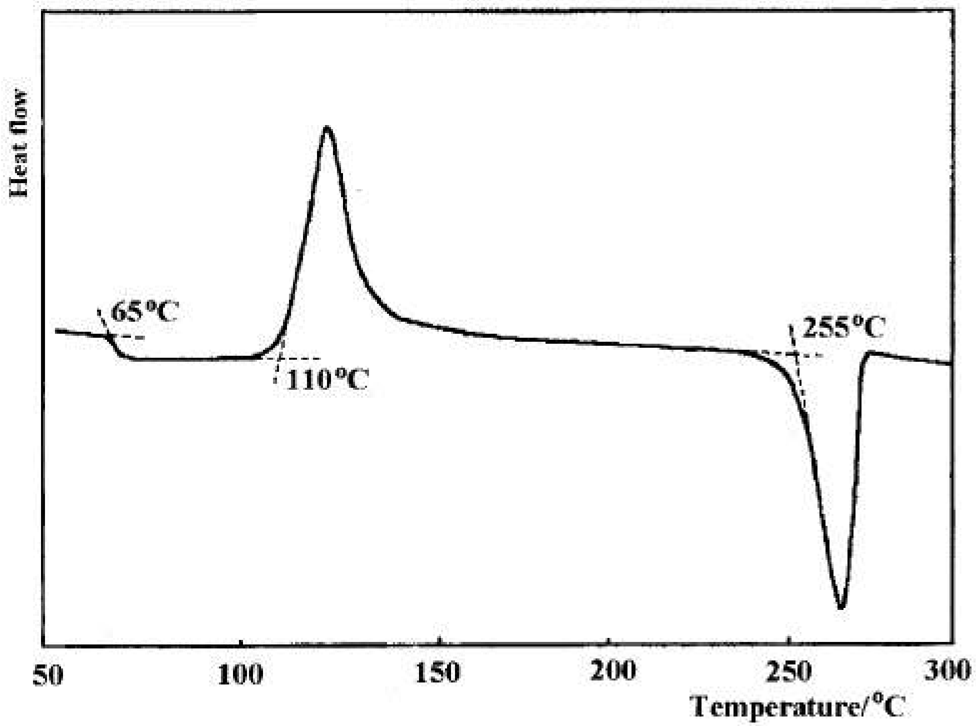
Reference Materials

Reference should have same physical properties as sample

Reference should not have any transformations during heating

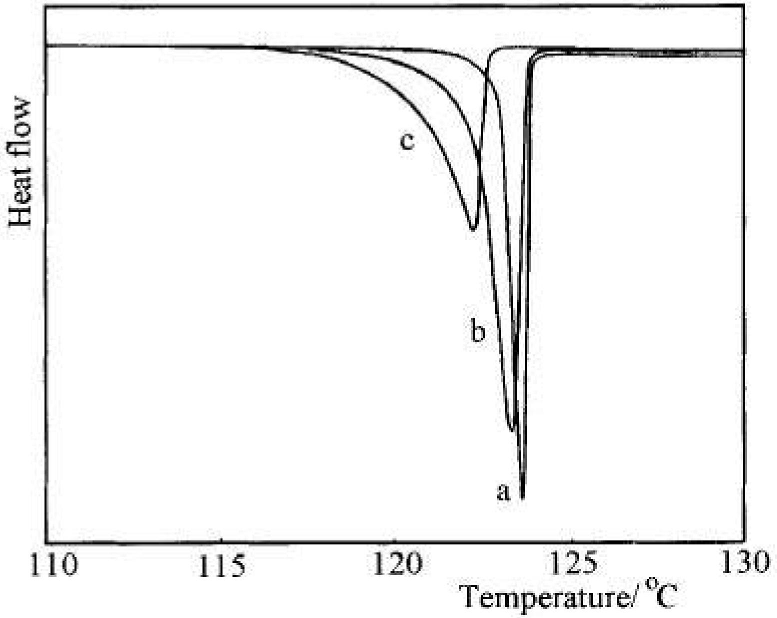
Reference for sample which looses weight?

Commonly used, SiC, Al_2O_3, empty crucible

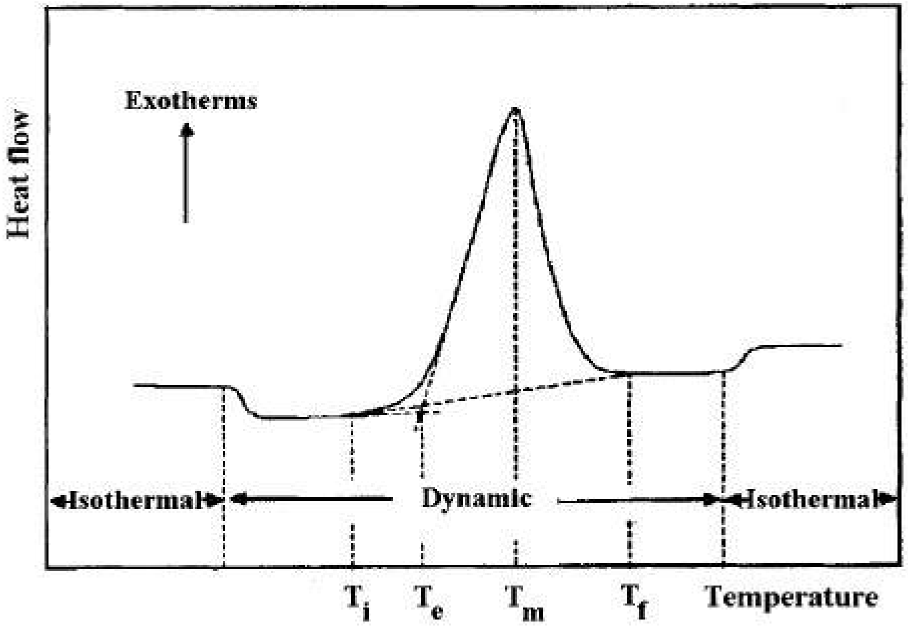


Thermal analysis curve for poly(ethylene terephthalate)

65°C: glass transition temp.; Onset at 110°C: Crystallization: Onset at 255 °C melting

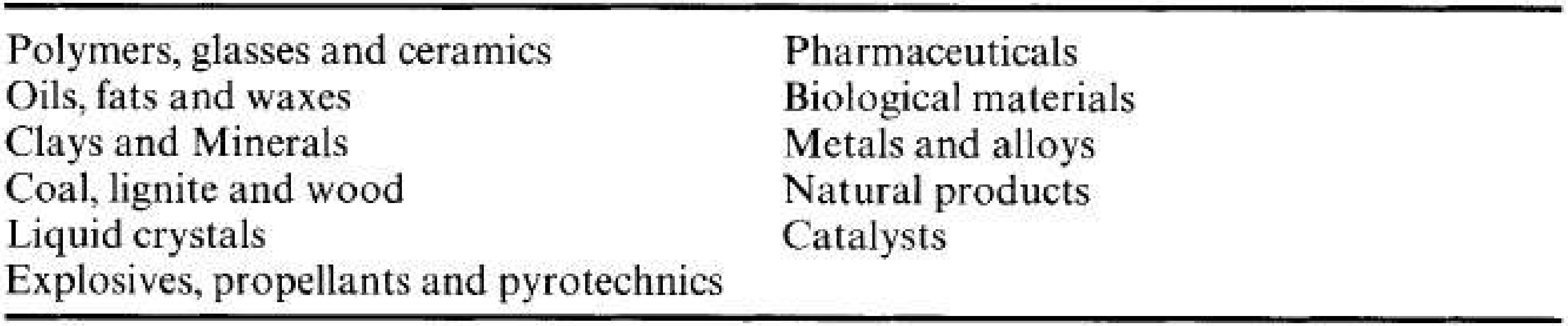


Melting endotherms for benzoic acid: (a) *99.9*, (b) *99 and* (c) *97 mol% purity*

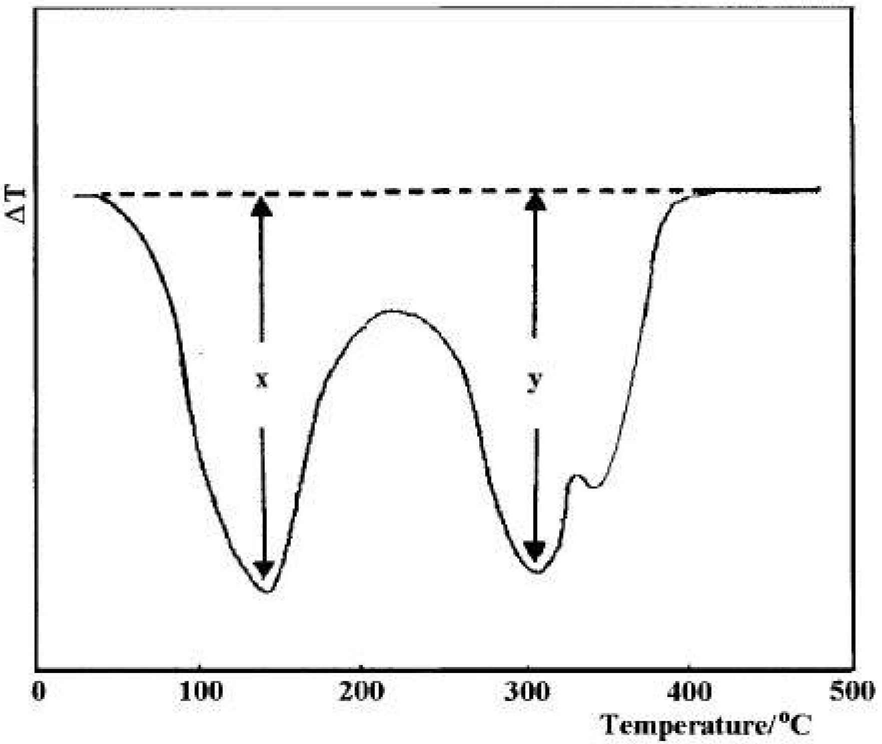


Schematic representation of a thermal analysis curve

Materials studied by DTA/DSC

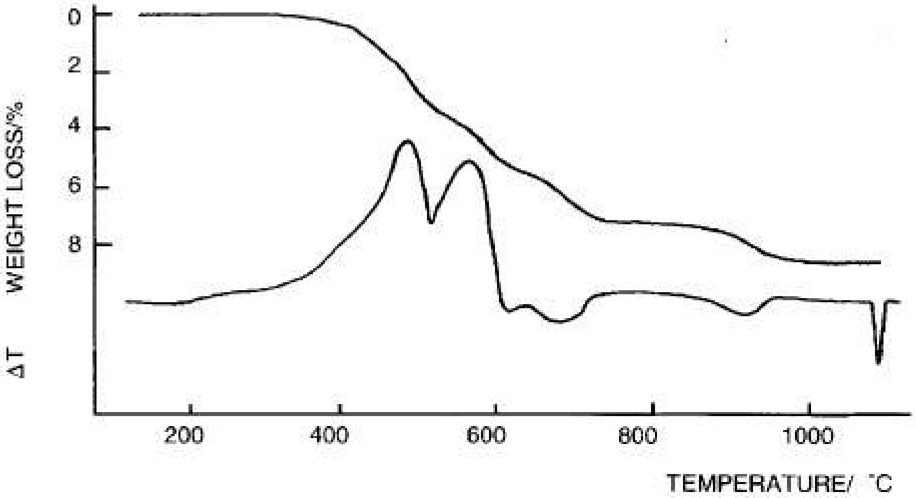


Polymers, glasses and ceramics
Oils, fats and waxes
Clays and Minerals
Coal, lignite and wood
Liquid crystals
Explosives, propellants and pyrotechnics
Pharmaceuticals
Biological materials
Metals and alloys
Natural products
Catalysts

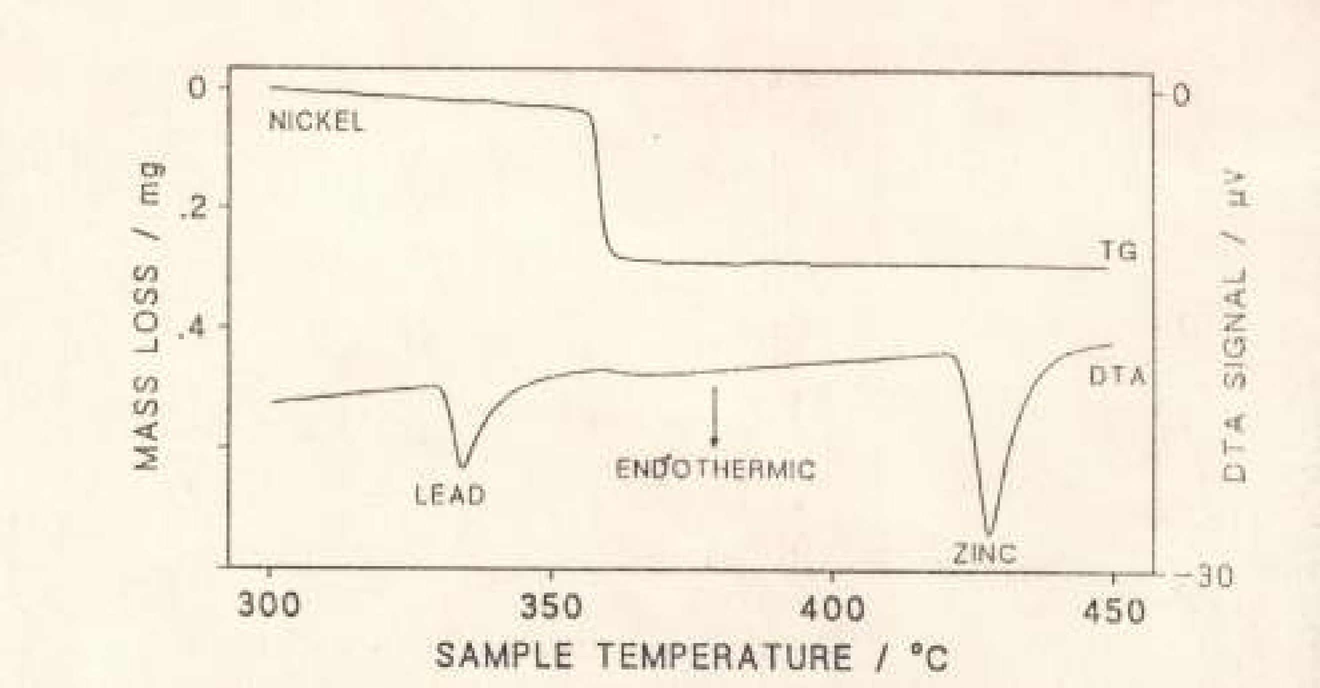


Thermal analysis curve for high alumina cement

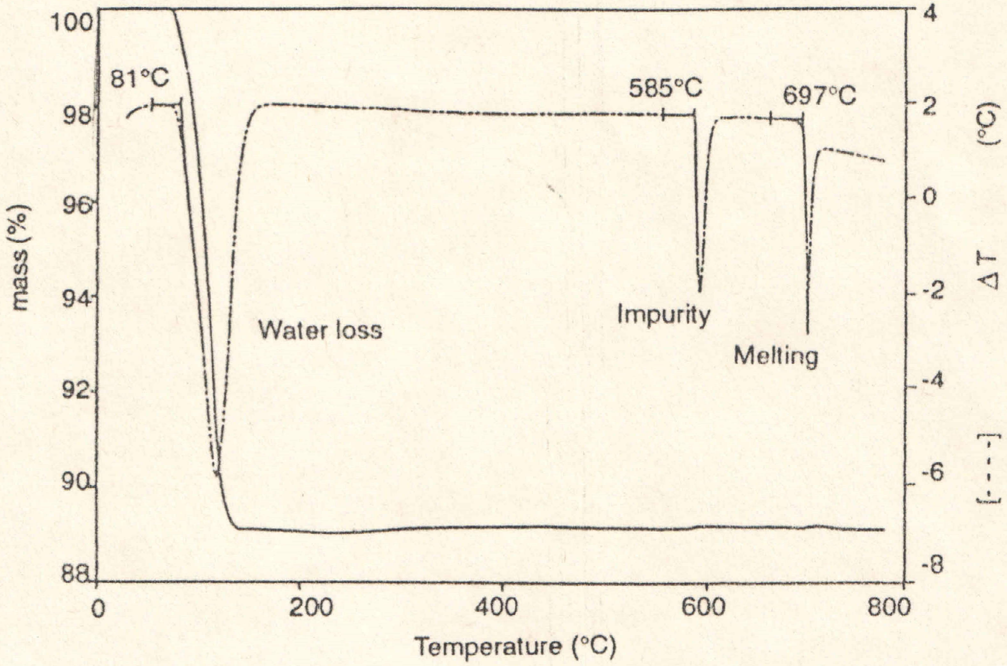
Process	*TG effect*		*DTA/DSC effect*	
	Gain	*Loss*	*Exotherm*	*Endotherm*
Adsorption	✓		✓	
Desorption		✓		✓
Dehydration/desolvation		✓		✓
Sublimation		✓		✓
Vaporisation		✓		✓
Decomposition		✓	✓	✓
Solid–solid transition			✓	✓
Solid–gas reaction	✓	✓	✓	✓
Solid–solid reaction	Maybe	Maybe	✓	✓
Crystallisation			✓	
Melting				✓
Polymerisation		Maybe	✓	
Catalytic reactions	Maybe	Maybe	✓	



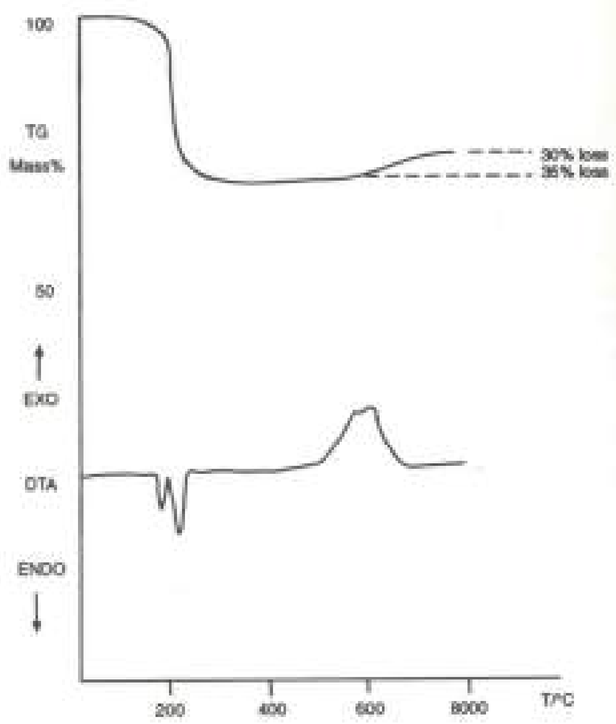
TG and DTA curves for the reduction of a $YBa_2Cu_3O_7$ *superconductor: 50 mg sample, 15°C min*$^{-1}$*, 5%* H_2 *in* N_2



Determination of an accurate value for the Curie point of Nickel using simultaneous TG-DTA in a magnetic field.
327 °C: melting endotherm of lead;
419 °C: melting endotherm of zinc Curie point transition is seen only on the TG.

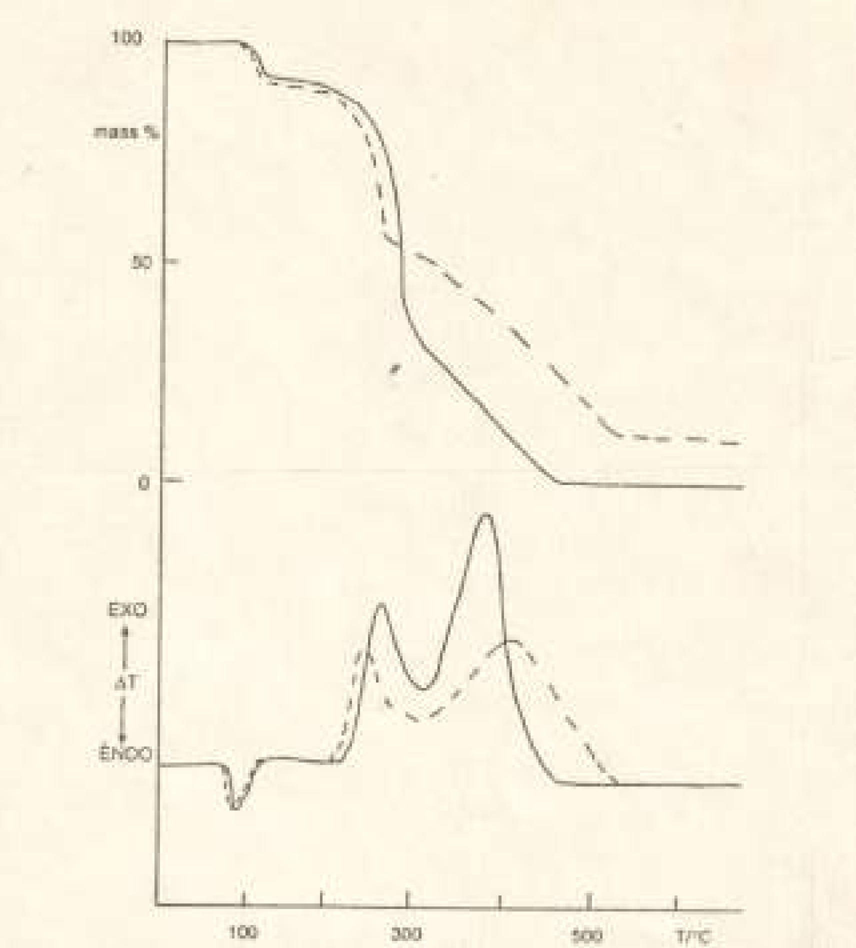


STA of sodium tungstate dihydrate.
Typical conditions: 10 K/min, nitrogen at 100 cm^3/min, 10 mg powdered sample



Thermal analysis curve of tin(II) formate:

(i) A loss of about 35% near 200 °C
(ii) A gain in mass starting near 600 °C

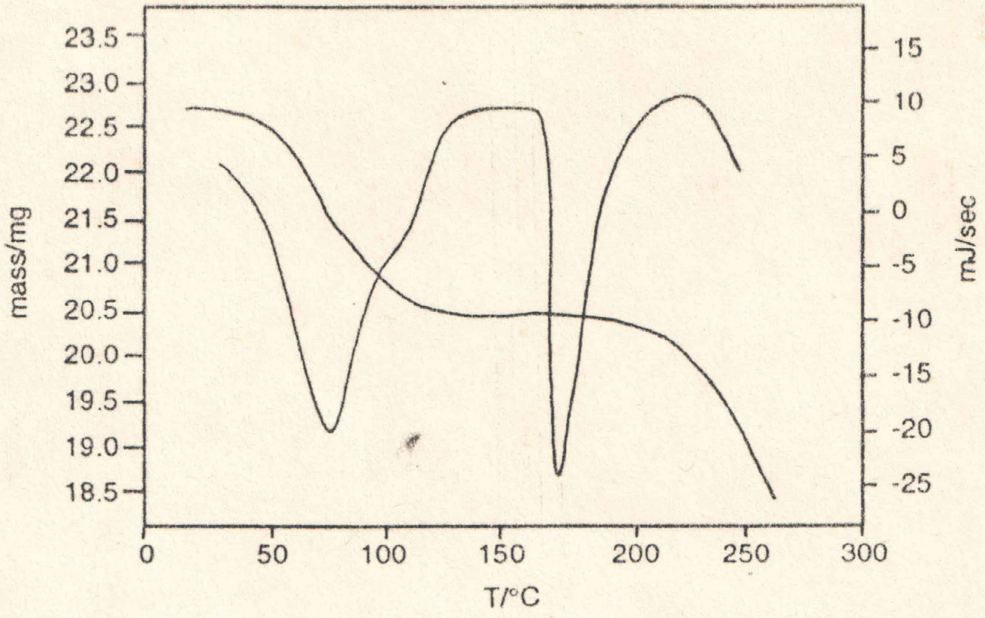


10 K/min, air

STA of wood sample: Stages of combustion of cellulose have been identified
Dehydration and decomposition to laevoglucosan, followed and accompanied by production of flammable volatiles, tars, carbon and gases such as water vapour and oxides of carbon.
Dashed curve: treatment of the materials with fire retardants such as borates, phosphates, or Al salts.

Residue of around 10 % in air comes from mineral additives; In nitrogen due to uncombusted material and fillers such as carbon black

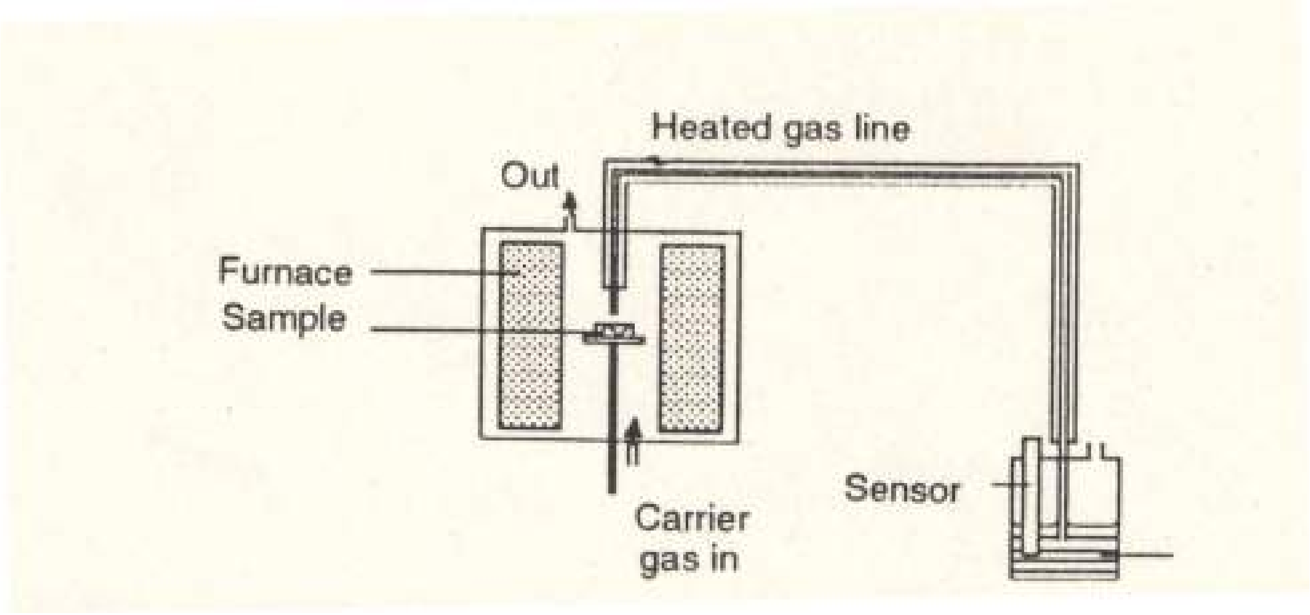
STA of poly(vinyl chloride) sample; 20 mg sample, 5 K/min, Air (full line) or nitrogen (dashed line) at 60 cm^3/ min.
Glass transition at around 80 °C, dehydrochlorination reaction at around 270 °C (weak endotherm).
Loss of volatiles is very exothermic in air but less so in nitrogen
Small peaks due to fillers, fire retardants etc.

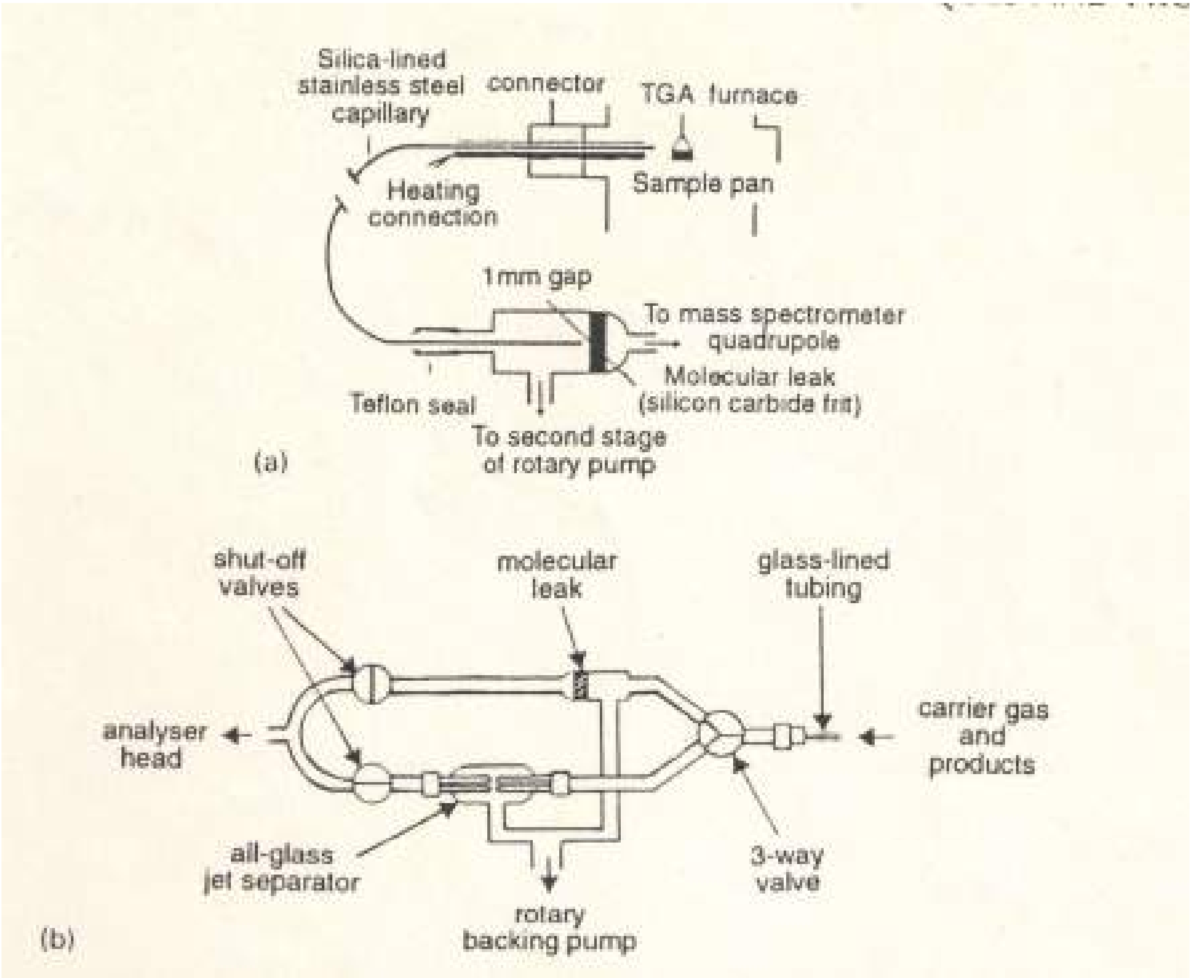


STA of pharmaceutical compound (22.6 mg, 10 K/min, nitrogen at 50 cm^3/min)
Stages: Loss of water from hydrated pharmaceutical, followed by the melting of anhydrous material at about 170 °C without decompostion.

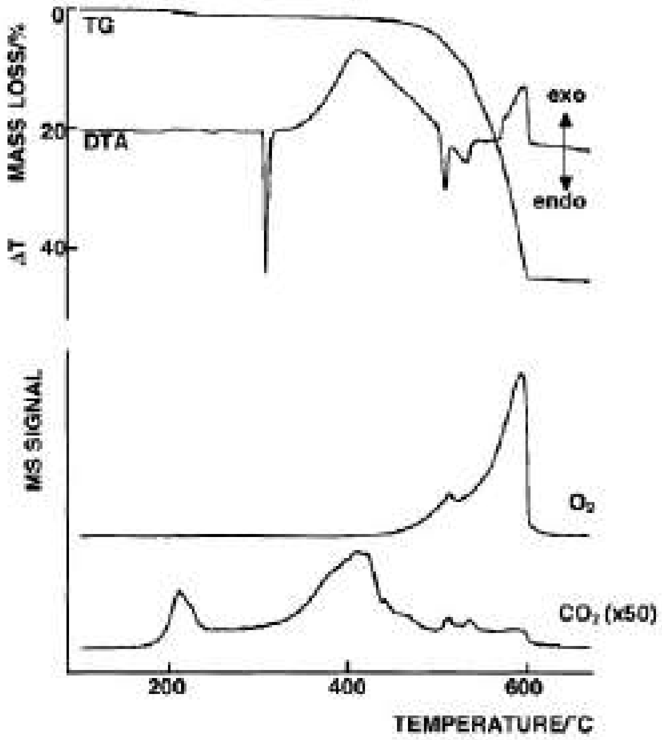
EVOLVED GAS ANALYSIS

1. Physical methods: conductivity, density
2. Chemical methods: reaction, colour indication, electrochemical
3. Spectroscopic methods: mass spectrometry, IR spectroscopy



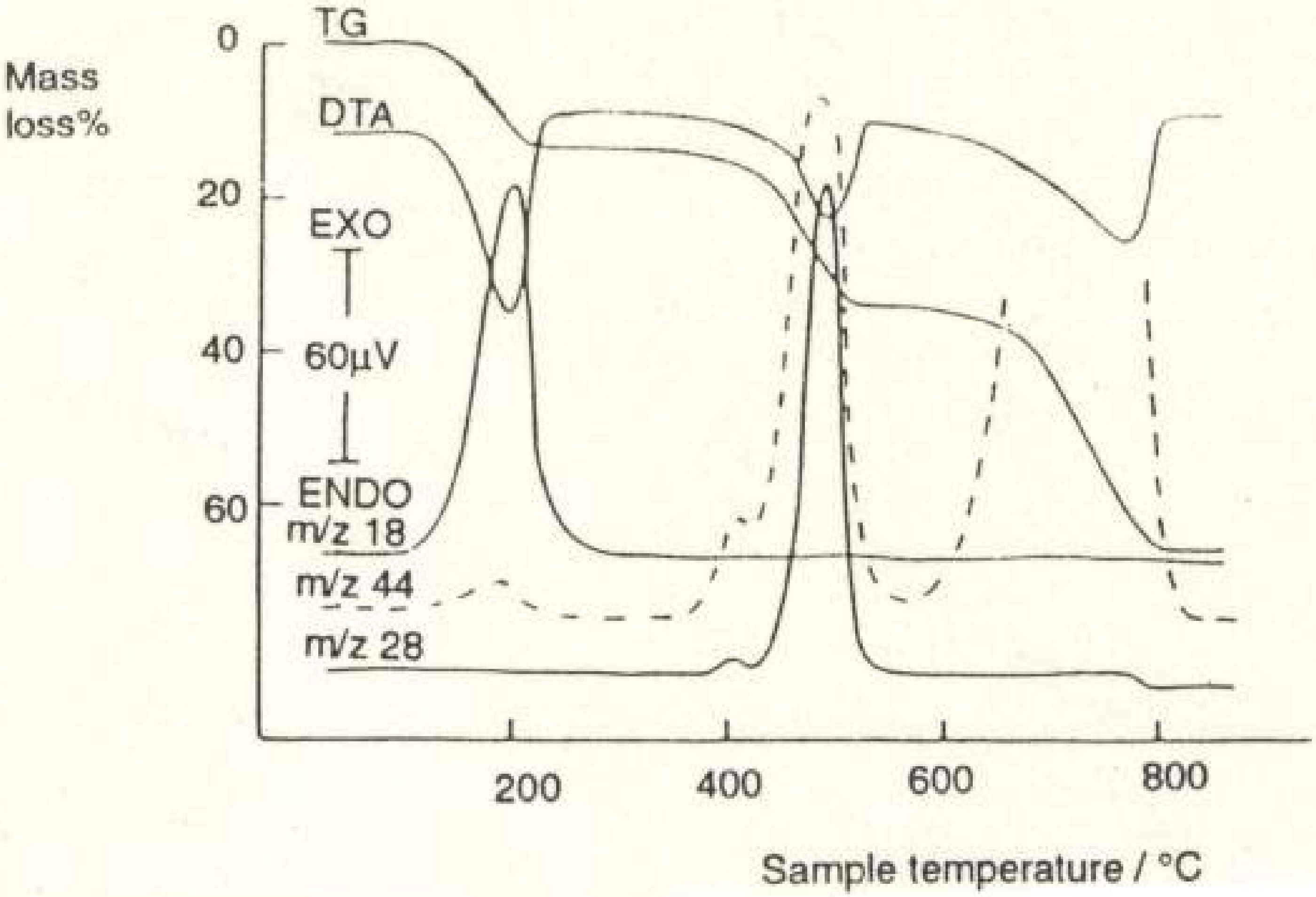


(a) TG-MS system (b) dual inlet system

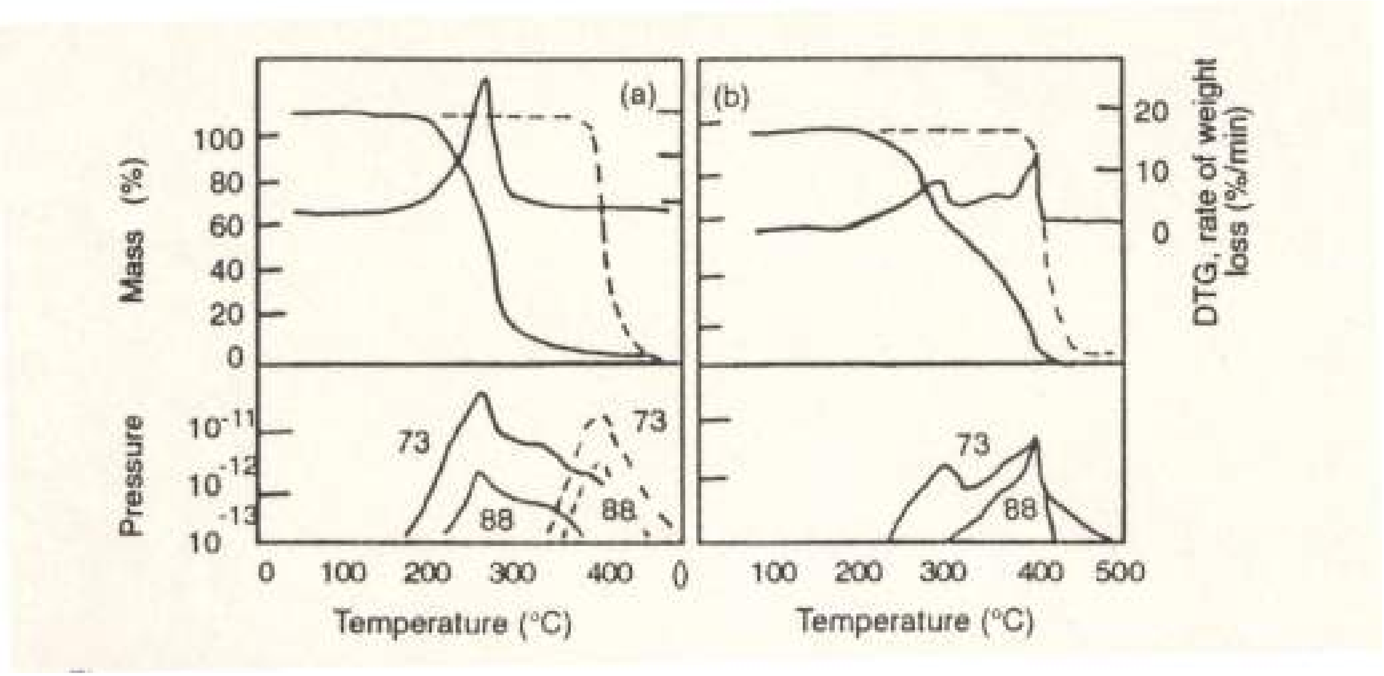


TG, DTA and MS curves for oxygen and carbon dioxide, for a mixture of 10% zirconium, 89% potassium perchlorate and 1% nitrocellulose. 10 mg sample, 10°C min^{-1}, helium

First the nitrocellulose decomposes around 200°C, leaving a carbon rich residue of only *ca.* 10% of the weight of nitrocellulose. Following the sharp orthorhombic–cubic phase transition in potassium perchlorate at 300°C, an exothermic reaction takes place between the zirconium and perchlorate while, at the same time, the carbon residue is oxidised by the perchlorate, as shown by the CO_2 curve. The persistence of CO_2 evolution up to *ca.* 600°C is a real and repeatable phenomenon, and remains unexplained. Oxygen evolution from excess perchlorate starts around 400°C, where it is more sensitively detected by the MS than the TG curve.

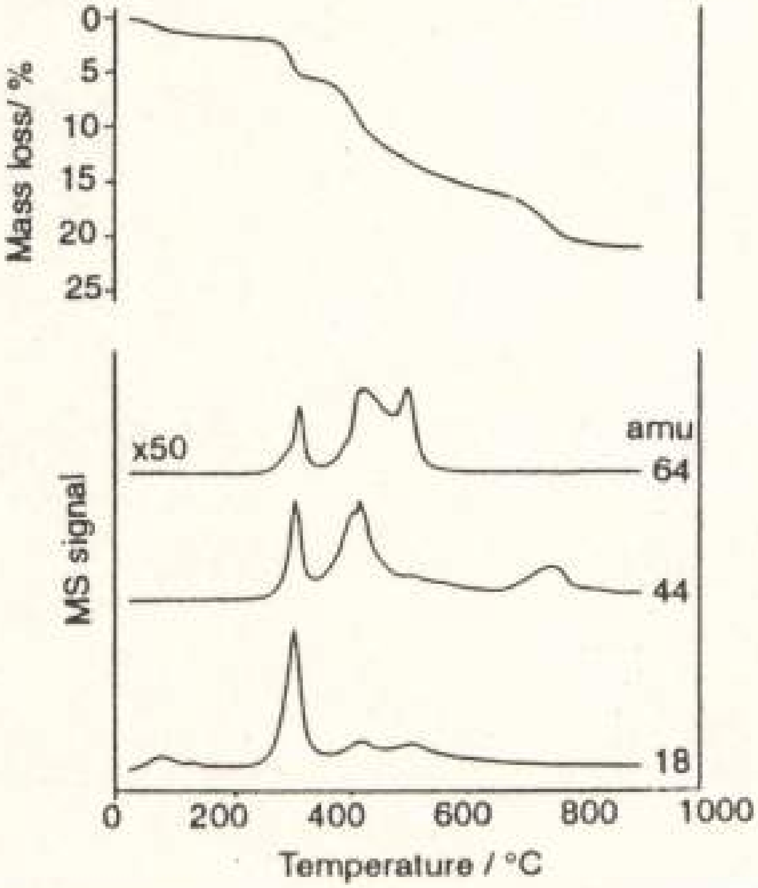


TG-DTA-MS curves for calcium oxalate monohydrate
(15 mg, 15 K/min, argon)

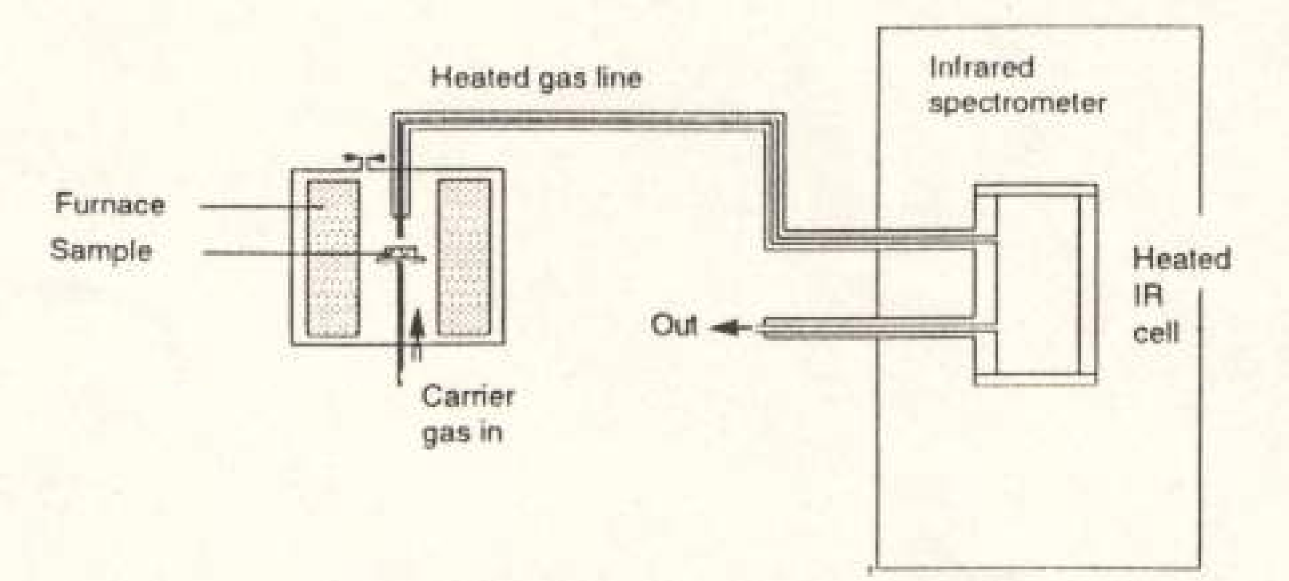


TG-MS curves for poly(ethylene oxide) $M_w = 5 \times 10^6$, from two suppliers (10 K/min, gas flow 100 cm^3/min)
Top curves show the TG under air (full line) or nitrogen (dashed line) and
The lower curves the mass spectral response curves.

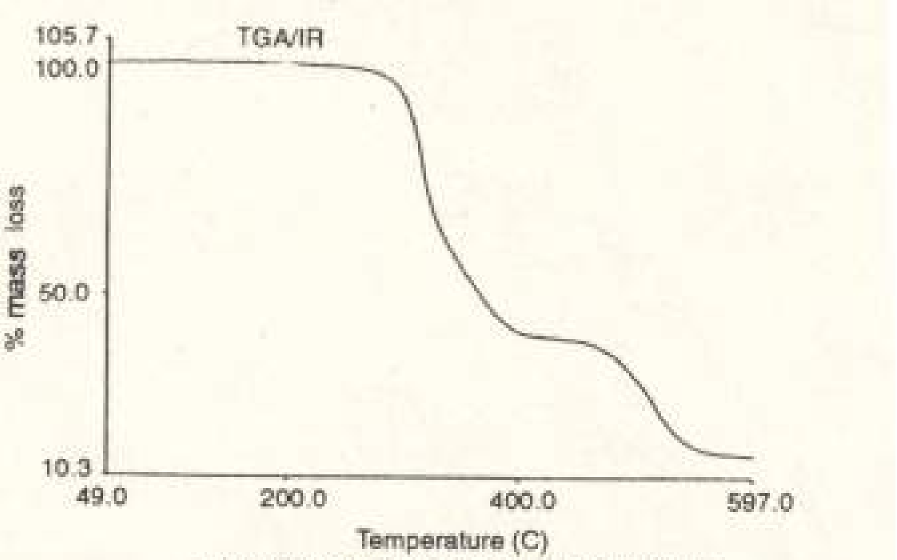
$m/z = 73$ (probably a $C_3H_5O_2$ species) and $m/z = 88$ (*p*-dioxane, $C_4H_8O_2$)



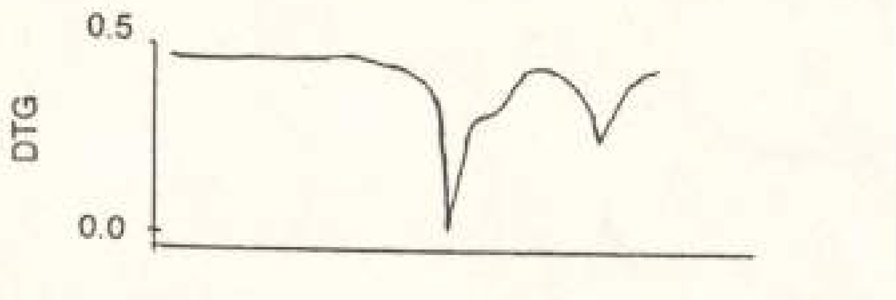
TG-MS curves for an Oxford clay* (40 mg, 20 K/min, air)
∗Used in the manufacture of common bricks
m/*z* = 18 (H_2O); *m*/*z* = 44 (CO_2); *m*/*z* = 64 (SO_2)



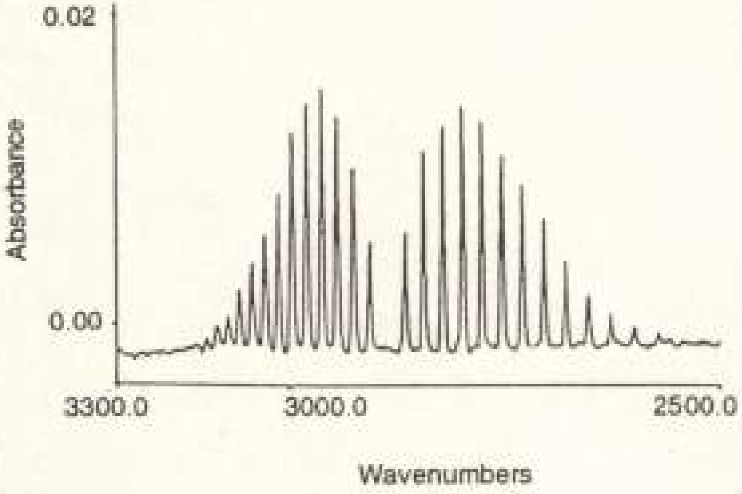
Schematic of a thermal analysis-infrared system



weight loss versus temperature for PVC pipe

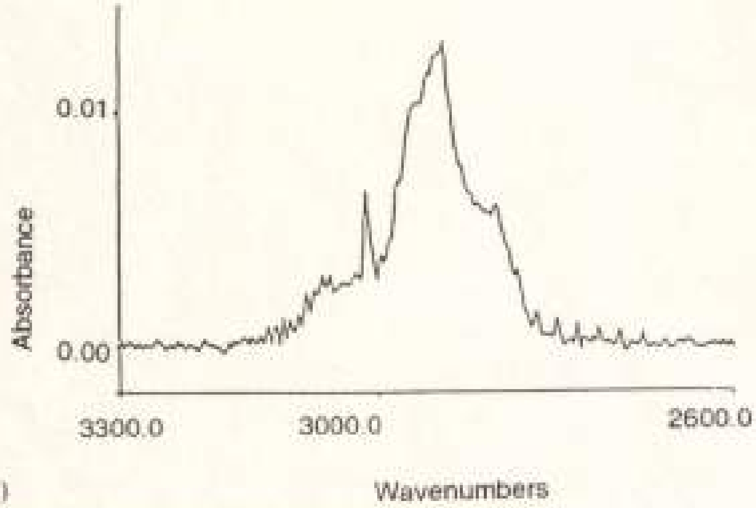


TG and DTG curves for PVC degradation



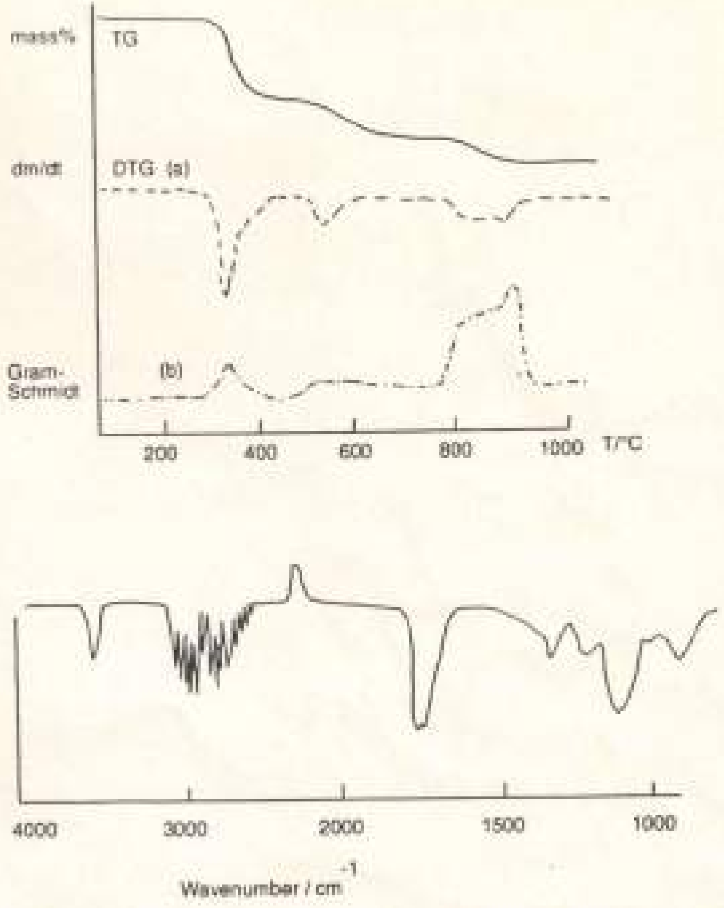
(d)

(d) Spectrum of HCl

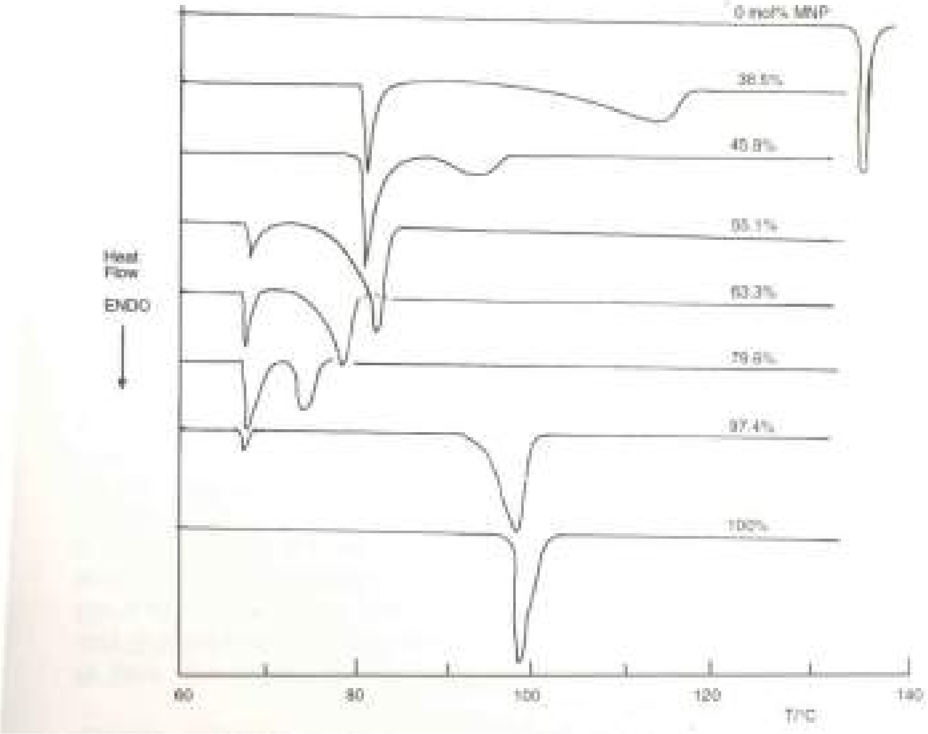


(c)

(e) Hydrocarbon band at 3000 cm^{-1} at 515 °C



TG-FTIR trace for PVC/PVAc copolymer (blend of copolymer of vinyl Chloride and vinyl acetate): shows evolution of HCl, ethanoic acid when Heated in nitrogen and production of CO_2 due to combustion in air at high temperatures



Urea-*m*-nitrophenol system

Tube	U/g	MNP/g	Tube	U/g	MNP/g
1	0.500	0.000	5	0.100	0.400
2	0.194	0.285	6	0.050	0.450
3	0.144	0.282	7	0.003	0.248
4	0.100	0.285	8	0.000	0.500