Nutshells of Thermal Analysis

Heat it up !

Burn it !

Thermal Analaysis (TA)

Techniques

Abbreviations	Full Names	Measure
DSC	Differential Scanning Calorimetry	Heat difference
DMA	Dynamic Mechanical Analysis	Mechanical Stiffness and Damping
TMA	Thermomechanical Analysis	Dimension
TGA	Thermogravimetric Analysis	Mass
DTA	Differential Thermal Analysis	Temperature Difference
DIL	Dilatometry	Volume
DEA	Dielectric Thermal Analysis	Dielectric Permittivity and Loss Factor
EGA	Evolved Gas Analysis	Gaseous Decomposition Products
TOA	Thermo-Optical Analysis	Optical Properties
Many more….		

Thermogravimetric Analysis (TG, TGA)

Principle

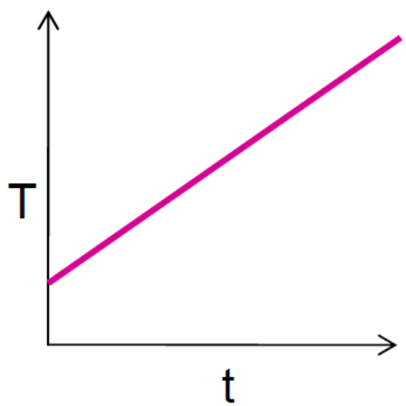
An analytical technique used to determine a material's thermal stability and its fraction of volatile components by **measuring the change of a sample mass as a function of temperature or/and time**.

Mass changes of solid samples occurs when …

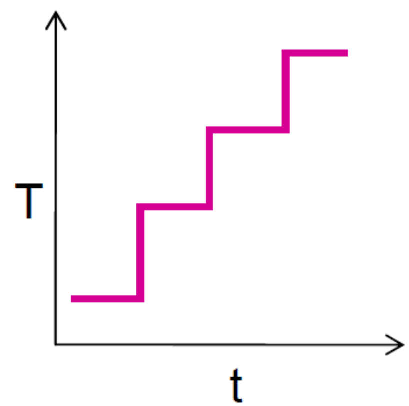
Type	Process	Mass
Physical changes	Gas adsorption	Gain
	Gas desorption	Loss
	Phase transition - Vaporization	Loss
	Phase transition - Sublimation	Loss
Chemical changes	Decomposition	Loss (when losing gases)
	Breakdown reaction	Loss (when losing gases)
	Gas reaction	Gain or Loss
	Chemisorption	Gain

Thermogravimetric Analysis (TG, TGA)

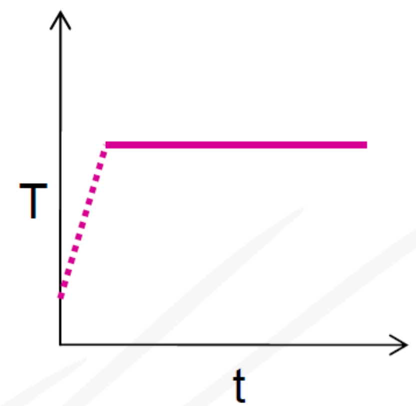
Temperature *vs* Time Programs



Constant heating



Gradually isothermal



Isothermal

Heating/cooling rate : 1 – 50 ^{o}C / min (typically 5 – 10 ^{o}C / min)

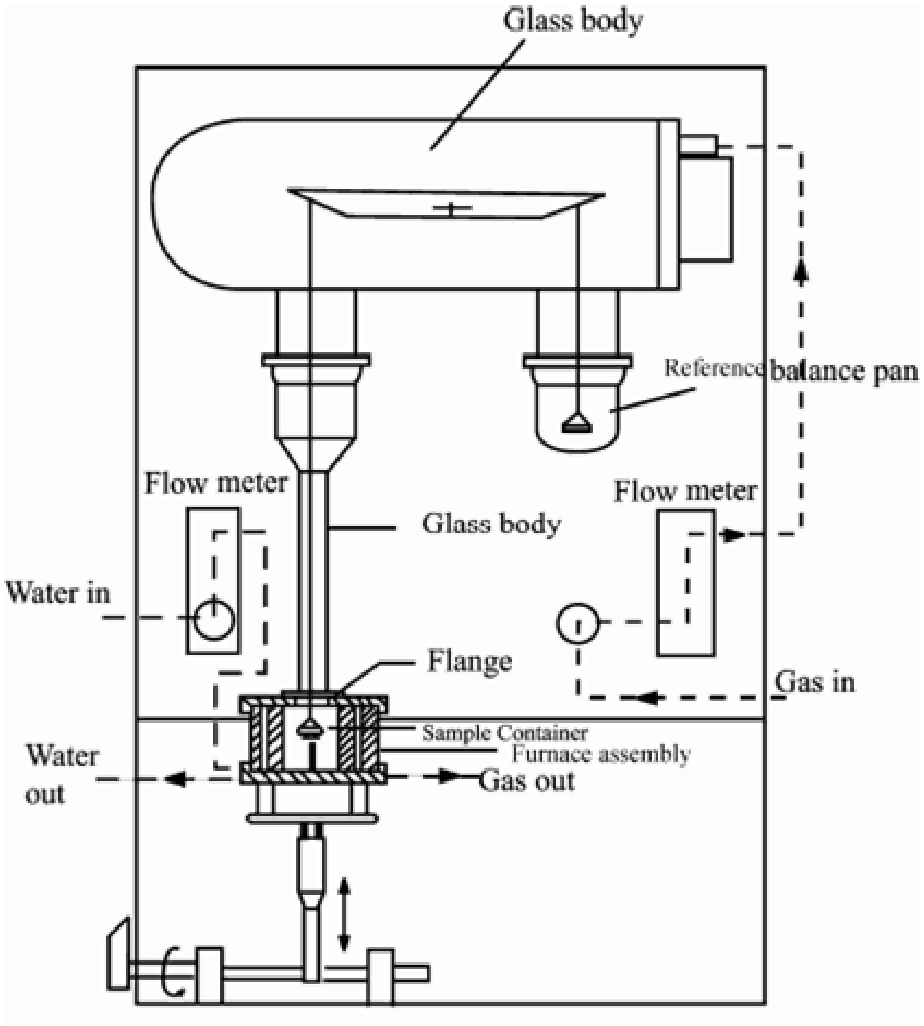
Sample size : 1- 100 mg (typically 5 -20 mg)

Atmosphere: In air or inert gas (He, Ar, N_2) or slow oxidation atm (1-5 % O_2 in He, N_2)

Run: at least three times

Thermogravimetric Analysis (TG, TGA)

Instrument



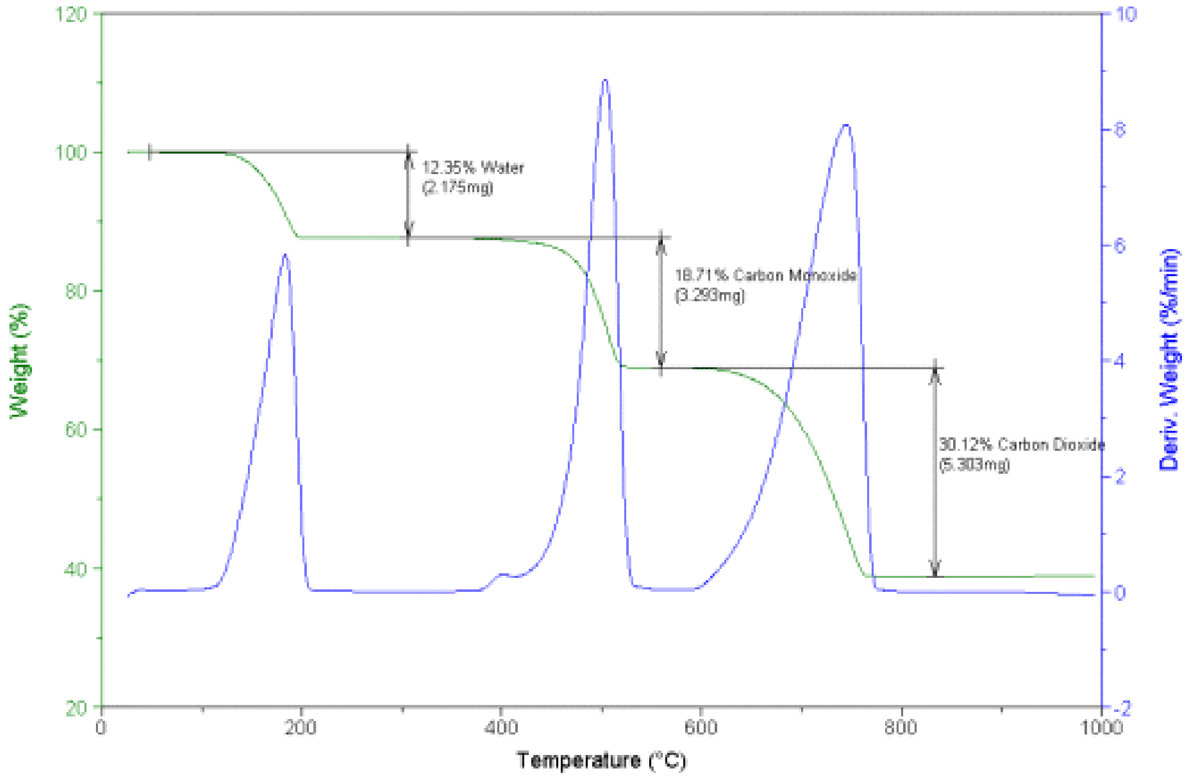
Balance types :

Horizontal – sample pan and reference pan
Vertical – sample pan
(usually no reference pan
- cannot perform DTA, DSC)

Thermogravimetric Analysis (TG, TGA)

Reading Data

TGA of $CaC_2O_4 \cdot H_2O$



Thermogravimetric Analysis (TG, TGA)

Reading Data

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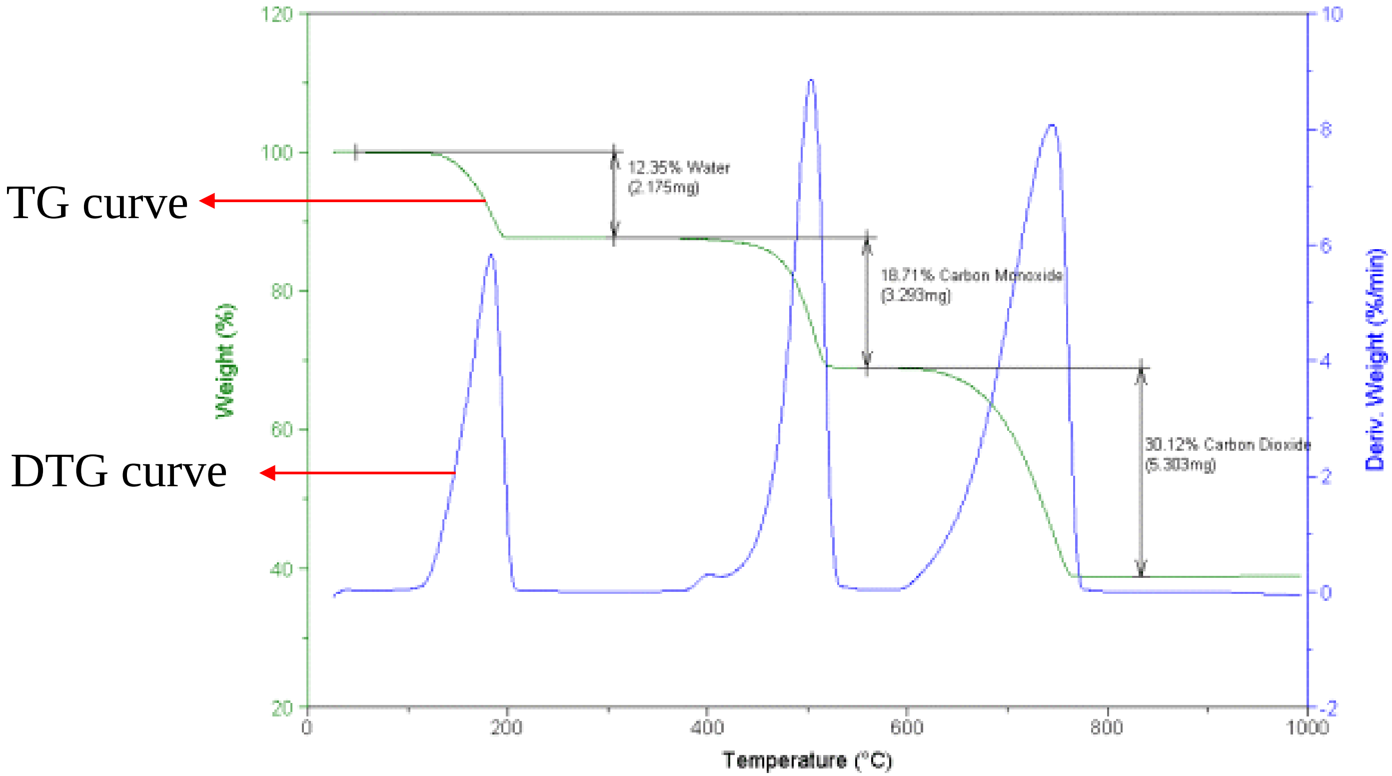
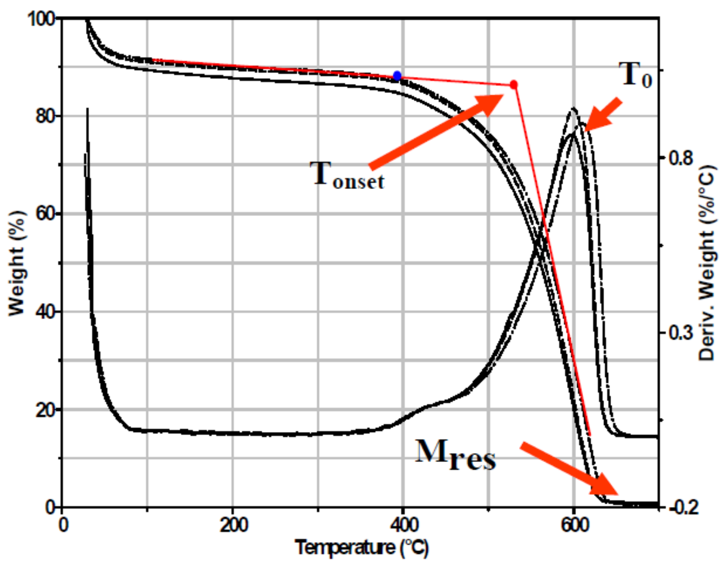


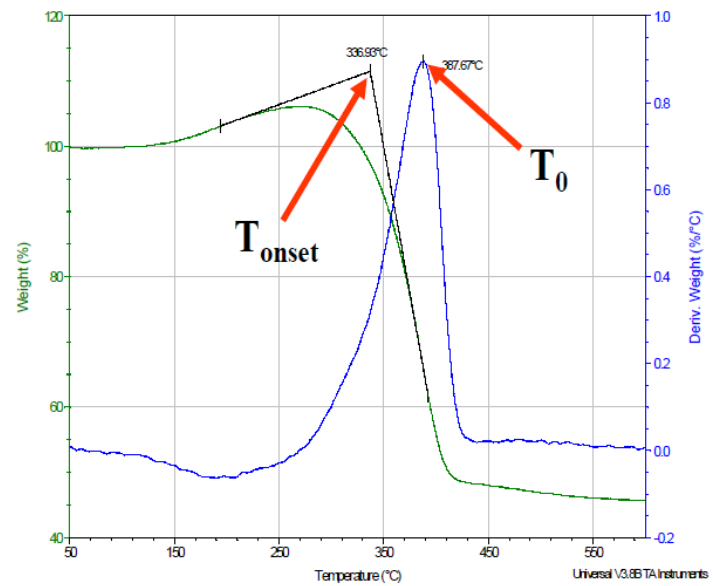
Thermogravimetric Analysis (TG, TGA)

Temperature and Mass Definitions

Onset temperature (T_{onset})
Temperature of the process - temperature of the maximum mass loss rate (T_0)
Residual Mass (M_{res})



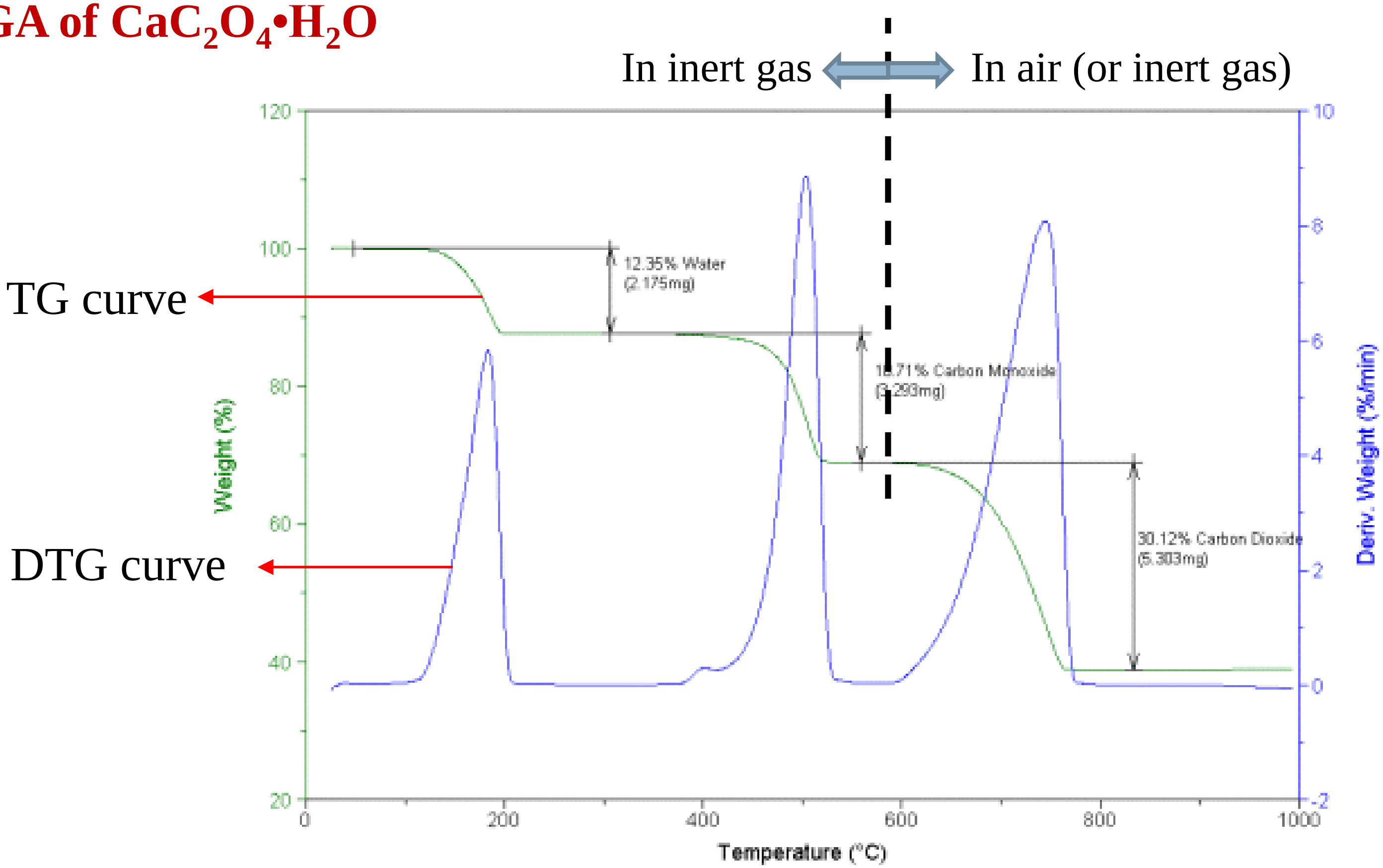
(b)



Thermogravimetric Analysis (TG, TGA)

Reading Data

TGA of $CaC_2O_4 \bullet H_2O$



$CaC_2O_4 \bullet H_2O$	CaC_2O_4	$CaCO_3$	CaO
(FW:146.111, 100%)	(FW:128.096, 87.67%)	(FW:100.086, 68.50%)	(FW:56.077, 68.50%)

- 12.33 % (-H_2O) **- 19.17 % (-CO)** **- 30.12 % (-CO_2)**

Thermogravimetric Analysis (TG, TGA)

Common gaseous molecules originating from inorganic compounds decomposing before melting point

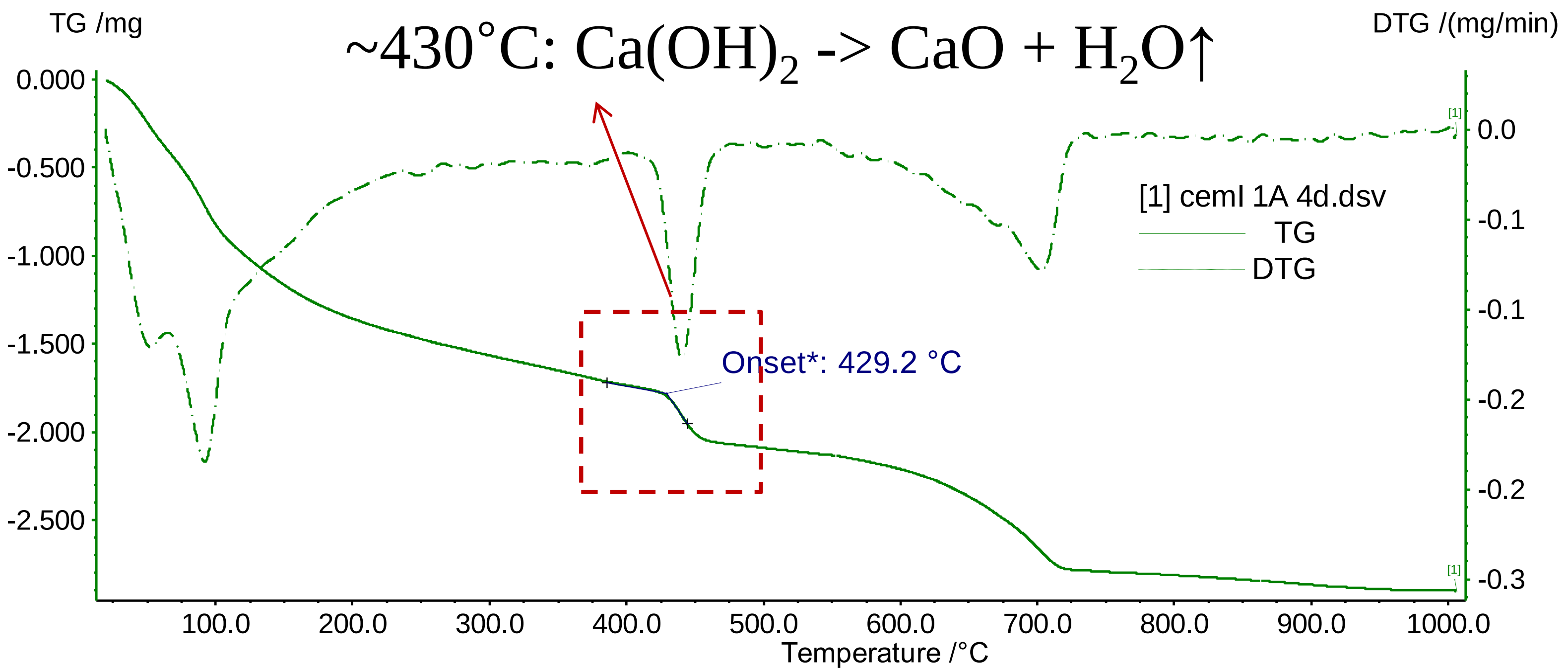
H_2O, CO, CO_2, SO_x, NO_x, Cl_2, F_2, CH_3OH, other solvents

Thermogravimetric Analysis (TG, TGA)

Reading Data

Software: NETZSCH Proteus® (Marsh procedure)

Quantification of portlandite ($Ca(OH)_2$) content in cement



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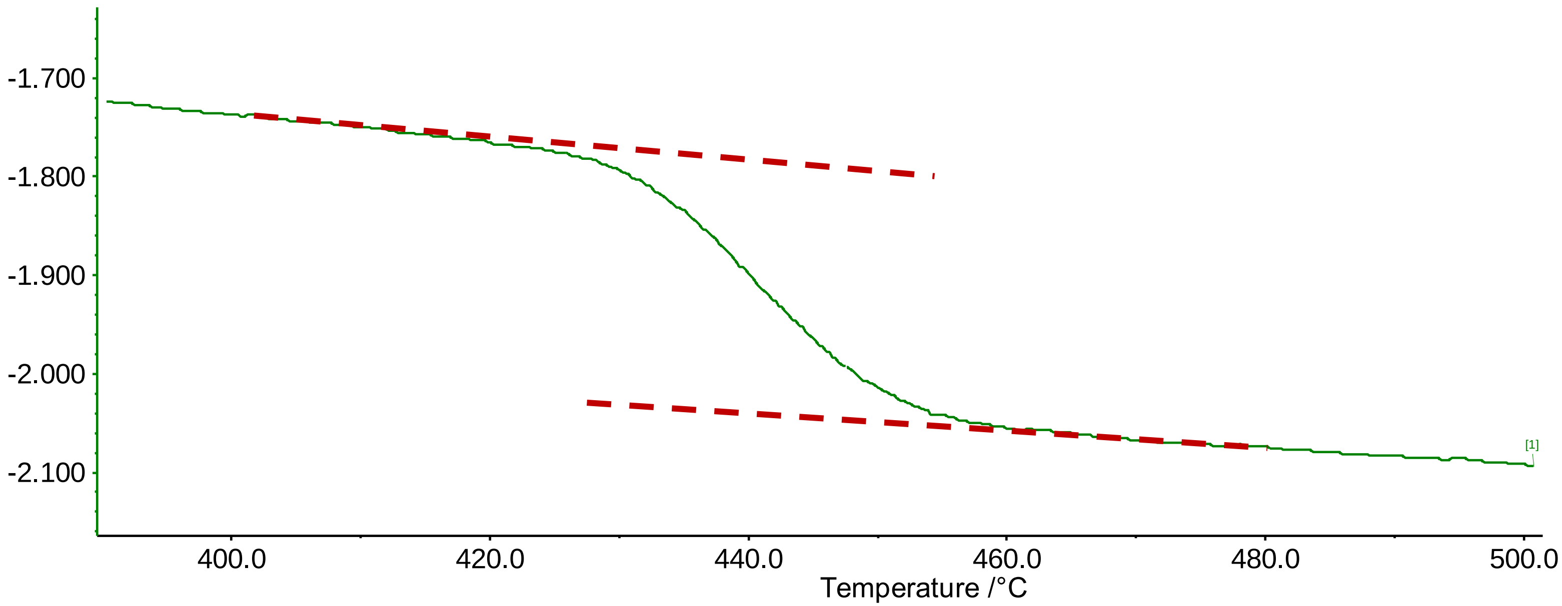
Thermogravimetric Analysis (TG, TGA)

Reading Data

Software: NETZSCH Proteus® (Marsh procedure)

Quantification of portlandite ($Ca(OH)_2$) content in cement

$$\sim 430^{\circ}C: Ca(OH)_2 \rightarrow CaO + H_2O\uparrow$$



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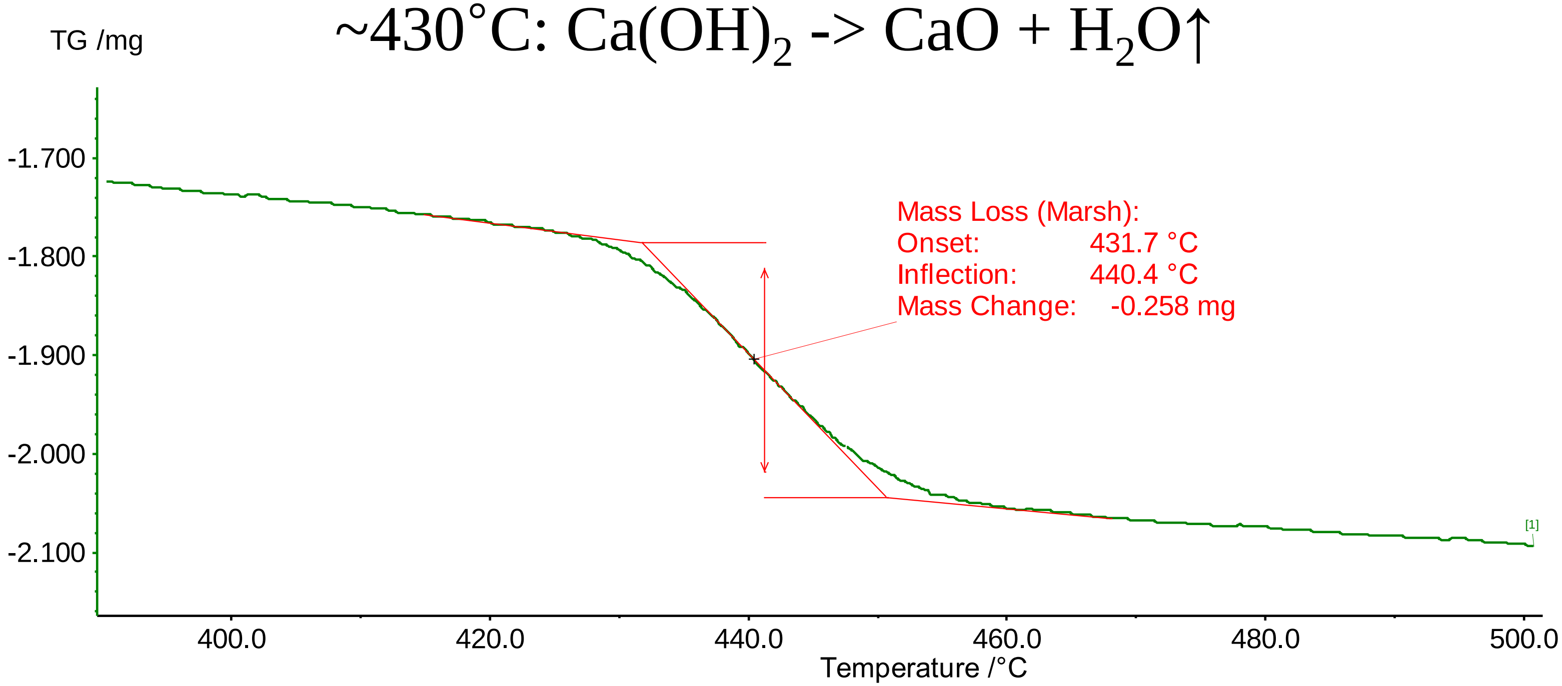

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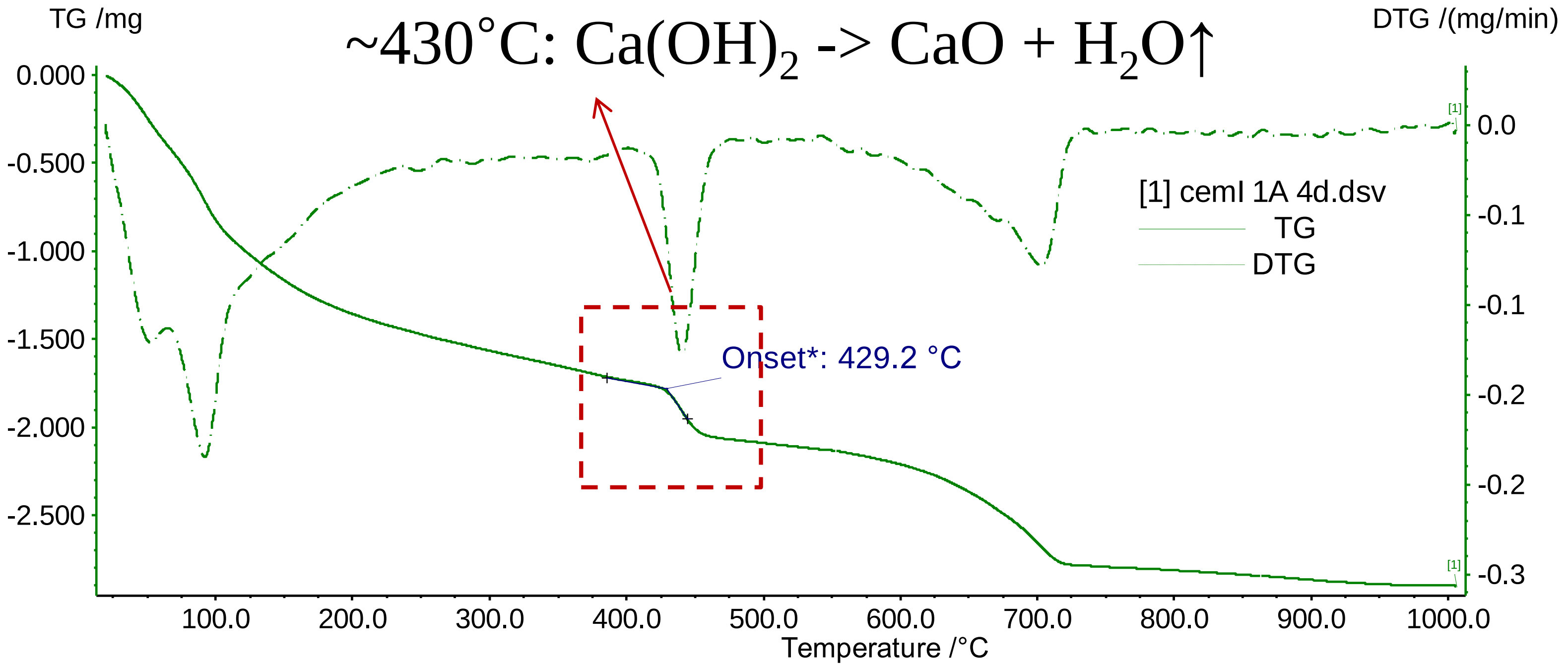
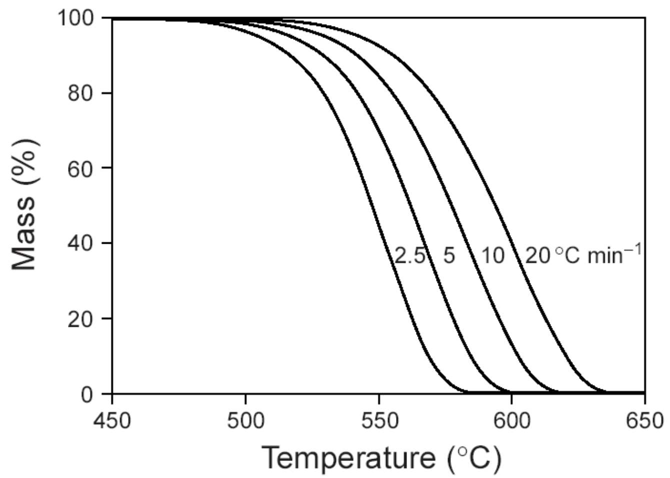


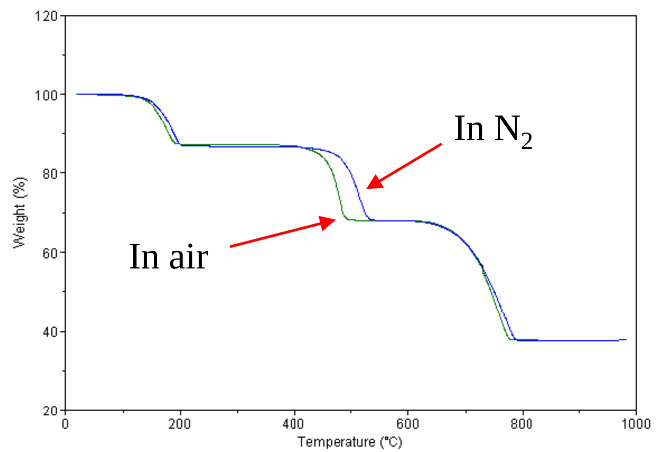
Thermogravimetric Analysis (TG, TGA)

Reading Data

Factors affecting TG curve

Instrumental	Sample
Heating rate Furnace atmosphere and flow-rate Geometry of pan and furnace Material of pan	Mass Particle size **(Make fine powders)** Sample history/pre-treatment Packing **(Make compact solids)** Thermal conductivity Heat of reaction Sample purity



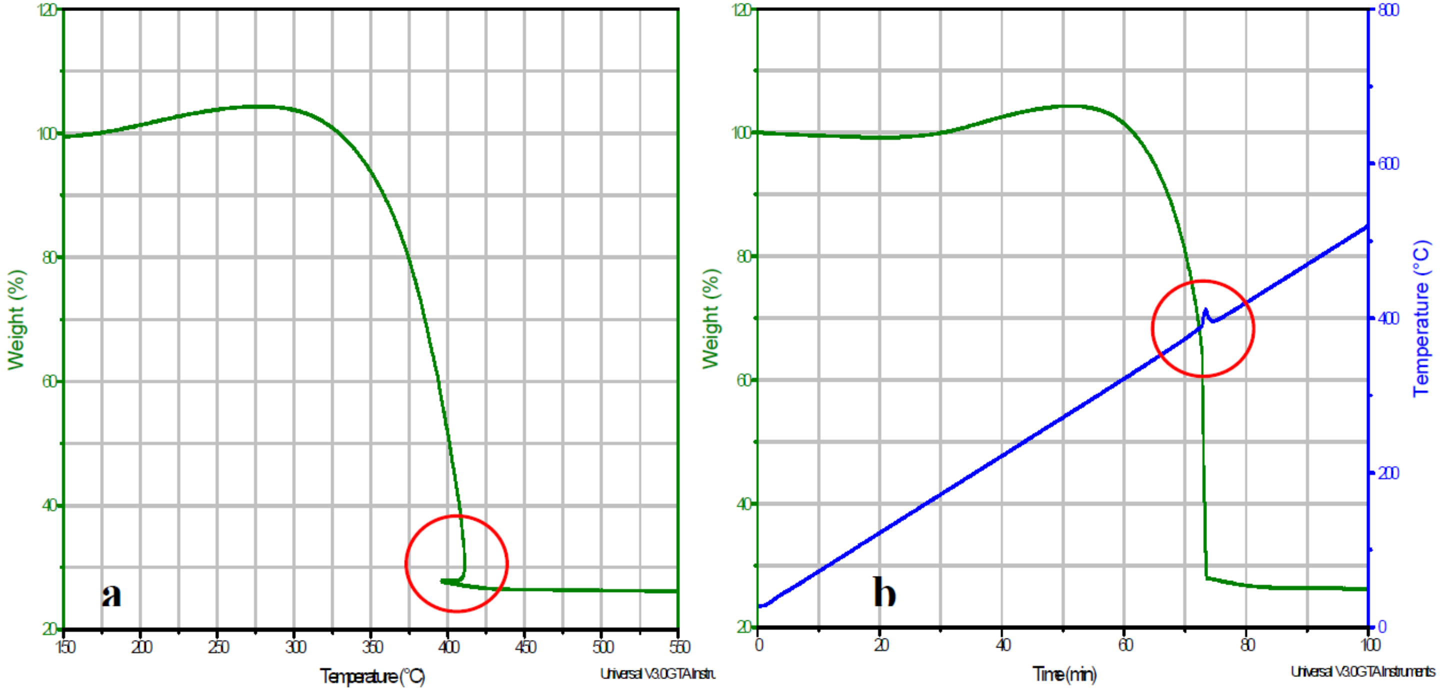


TG of $CaC_2O_4{\bullet}H_2O$

Thermogravimetric Analysis (TG, TGA)

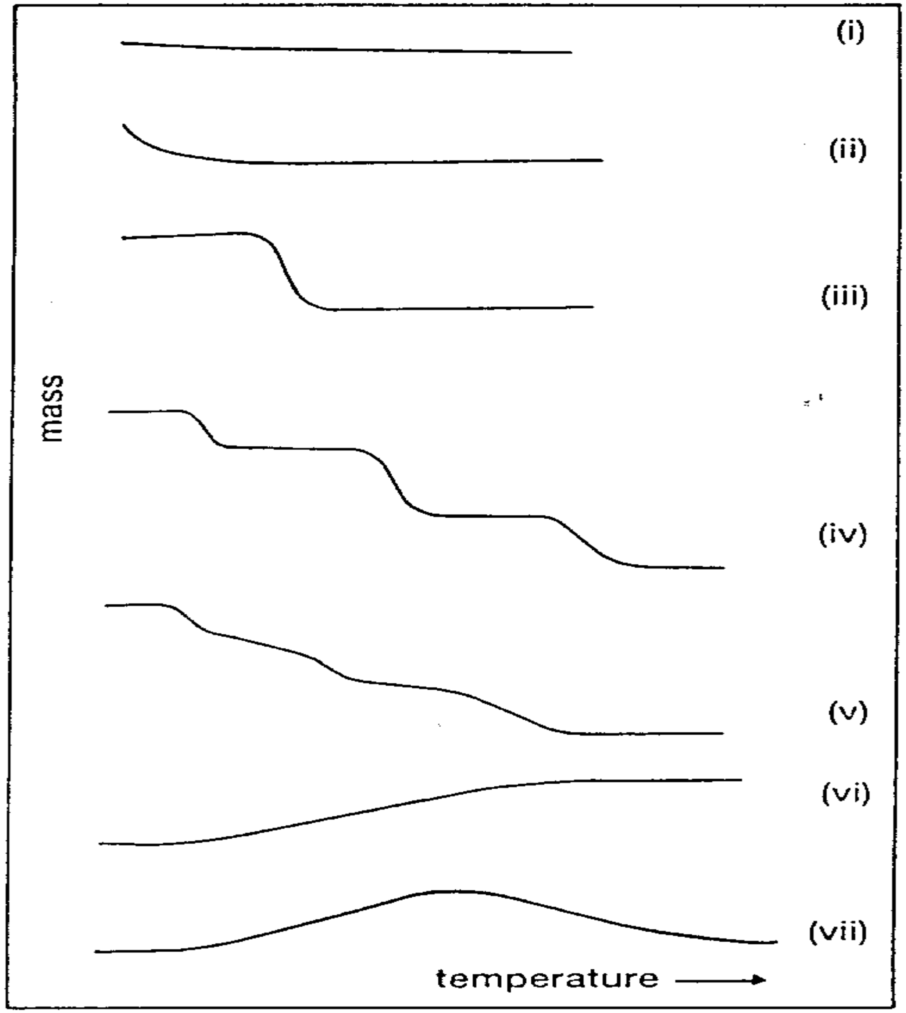
Reading Data

Backward TG curve (when combustion occurs)



Thermogravimetric Analysis (TG, TGA)

Reading Data



(i) no decomposition with loss of volatile products

(ii) The rapid initial mass loss is characteristic of desorption or drying **(dry the sample, redo the experiment)**

(iii) Single stage decomposition,

(iv) Multi-stage decomposition with relatively stable intermediates

(v) Multi-stage decomposition with no stable intermediate product. However heating-rate effect must be considered. At low heating rate, type (v) resemble type (iv)

(vi) Gain in mass due to reaction with atmosphere, e.g. oxidation of metals.

(vii) Oxidation product decomposes again at higher temperature; this is not often encountered.

Thermogravimetric Analysis (TG, TGA)

Errors

Mass	Noise / Erratic records
Classical buoyancy Effect temp. on balance Convection and/or turbulence Viscous drag on suspension	Static Vibration Pressure pulses in lab. Uneven gas flow

Differential Thermal Analysis (DTA)

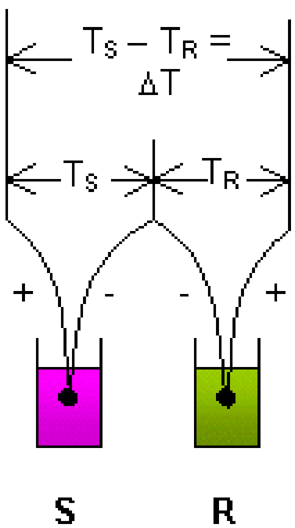
Principle

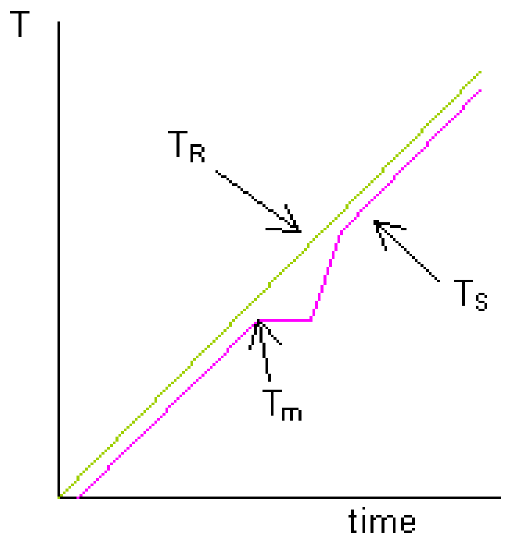
An analytical technique used to determine a material's phase diagram, heat change, and decompositions by **measuring the any temperature difference between sample and reference (usually Al_2O_3) as a function of time or temperature**.

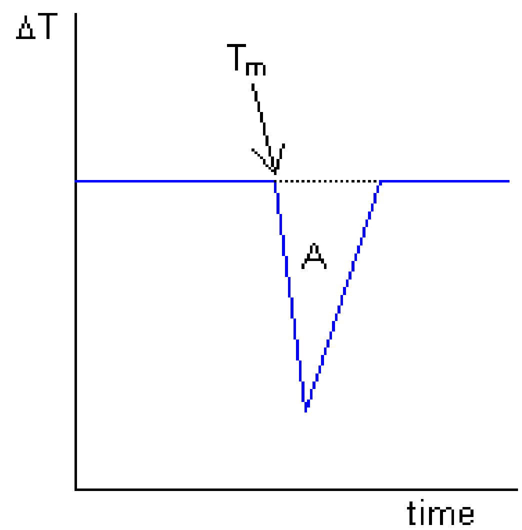
Type	Process	Heat process
Physical changes	Adsorption	Exothermic
	Desorption	Endothermic
	Change in crystal structure	Endo- or Exothermic
	Crystallization	Exothermic
	Melting, Vaporization, Sublimation	Endothermic
Chemical changes	Oxidation	Exothermic
	Reduction	Endothermic
	Breakdown reaction	Endo- or Exothermic
	Chemisorption	Exothermic
	Solid state reaction	Endo- or Exothermic

Differential Thermal Analysis (DTA)

Principle







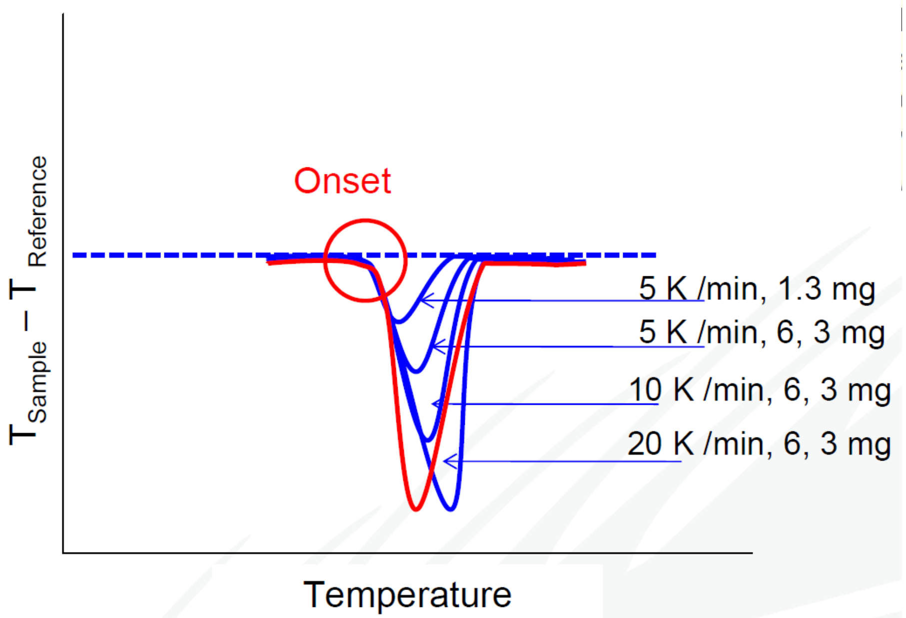
DTA curve – endothermic process

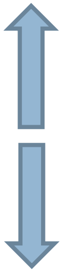
* Constant Heating Rate

* DTA – Temperature of sample minus temperature of reference *vs* Time (Temp.)

Differential Thermal Analysis (DTA)

Reading data





exothermic

endothermic

*Depending on instruments

Measuring
Onset temp Endset temp Integral – enthalpy change Peak temp Peak height Peak width

* Peak temperature is affected by heating rate & sample mass, but not by ΔH and T_{onset}

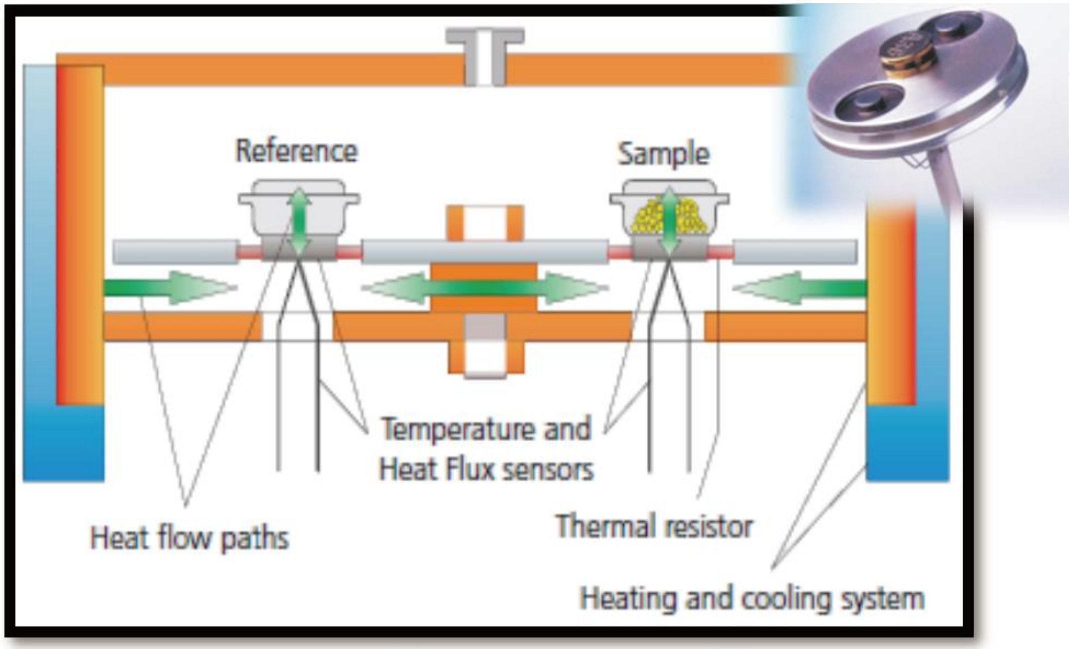
Differential Scanning Calorimetry (DSC)

An analytical technique used to determine a material's phase diagram, heat change, and decompositions by **measuring the difference in the amount of heat required to increase the temperature of a sample and reference.**

Type	Process	Heat process
Physical changes	Adsorption	Exothermic
	Desorption	Endothermic
	Change in crystal structure	Endo- or Exothermic
	Crystallization	Exothermic
	Melting, Vaporization, Sublimation	Endothermic
Chemical changes	Oxidation	Exothermic
	Reduction	Endothermic
	Breakdown reaction	Endo- or Exothermic
	Chemisorption	Exothermic
	Solid state reaction	Endo- or Exothermic

Differential Scanning Calorimetry (DSC)

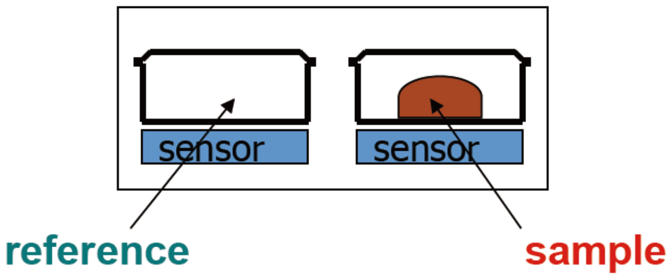
Principle

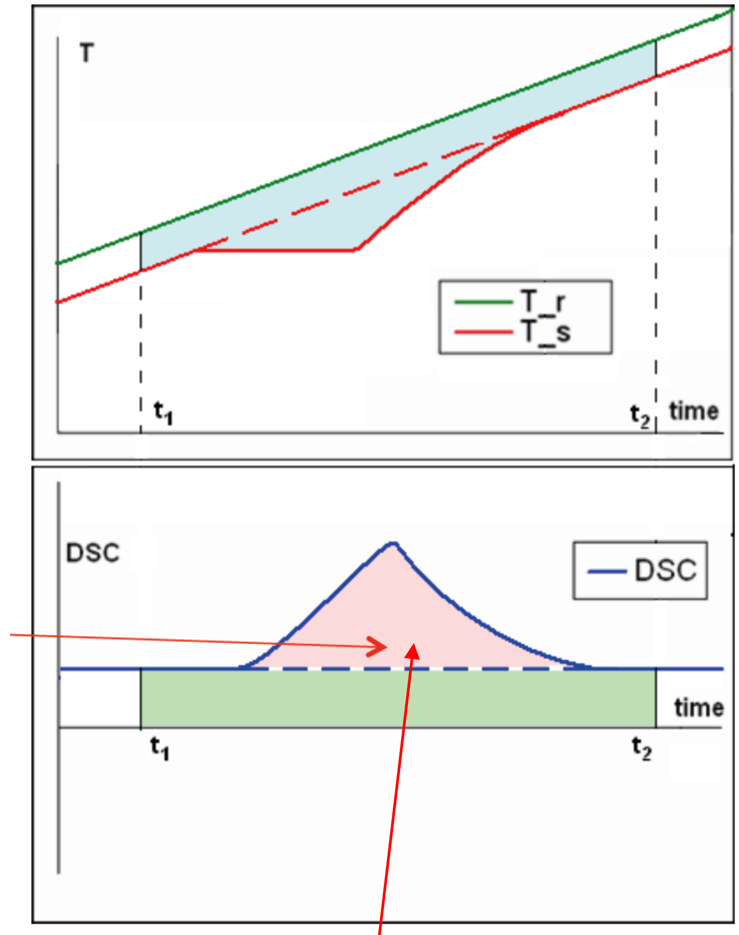


$$\phi \equiv \frac{dQ}{d\tau} = m \cdot C_p \cdot \frac{dT}{d\tau}$$

Differential Scanning Calorimetry (DSC)

Principle





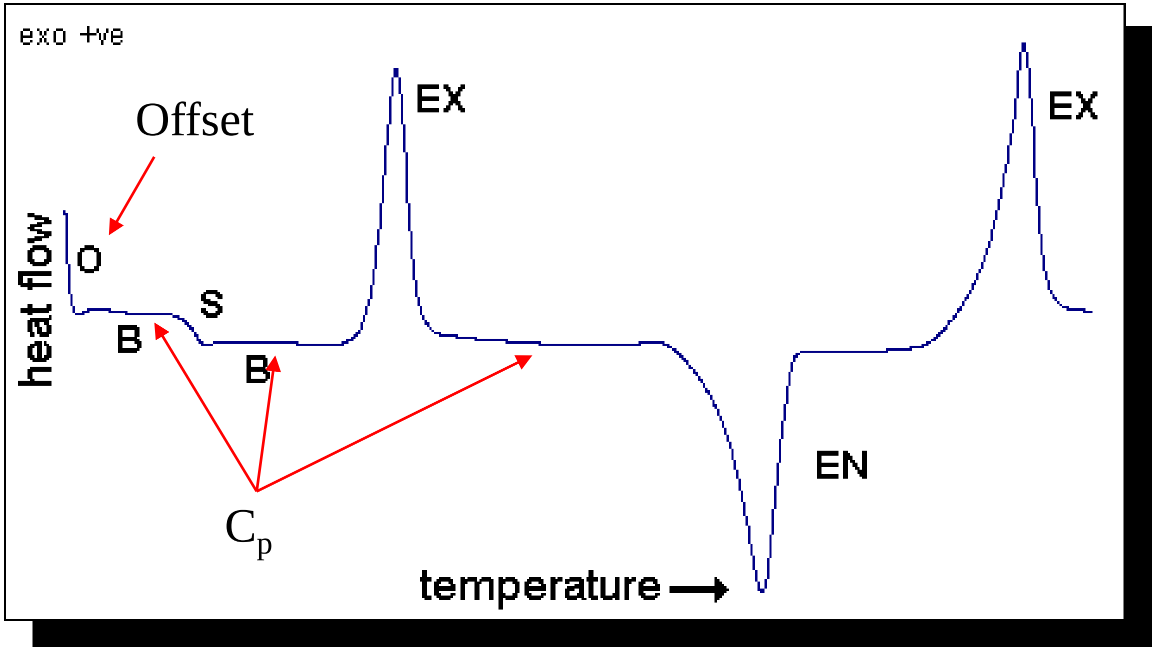
* Constant Heating Rate

* DSC - Heat flow to sample minus Heat flow to reference *vs* Time (Temp.)

$$\Delta H = \int_{t_1}^{t_2} \left(HeatFlow - Cp \cdot \beta \right) dt$$

Differential Scanning Calorimetry (DSC)

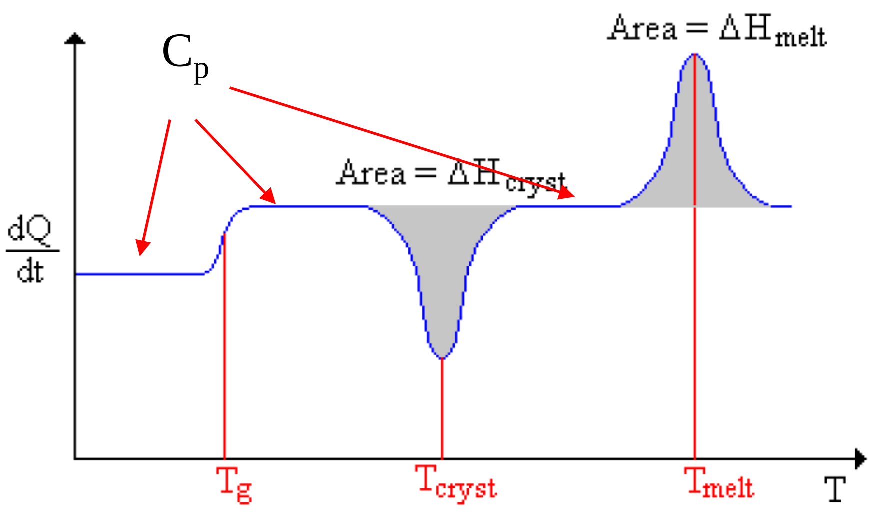
Reading Data

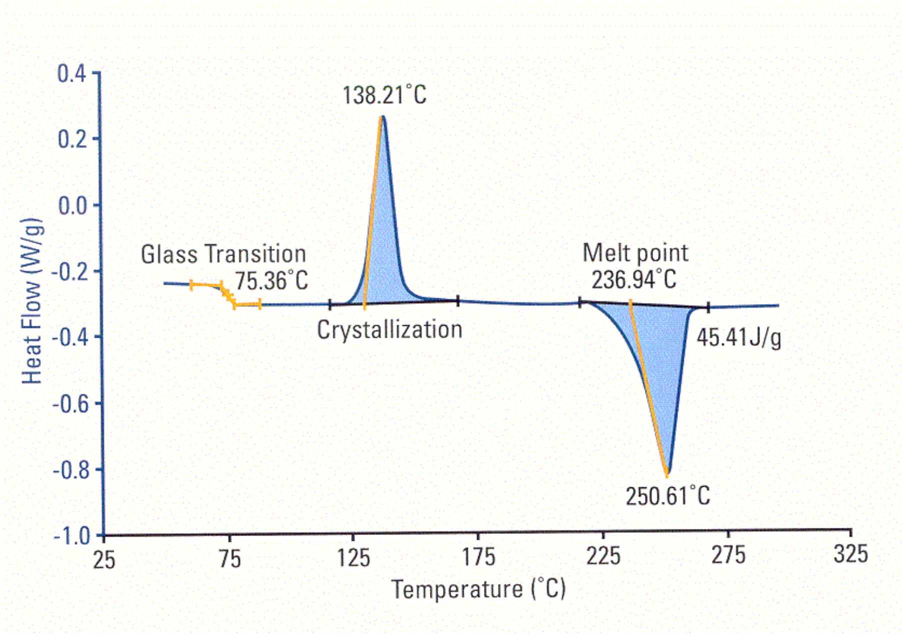


*Directions of endo- and exo- depends on instruments

Differential Scanning Calorimetry (DSC)

Reading Data



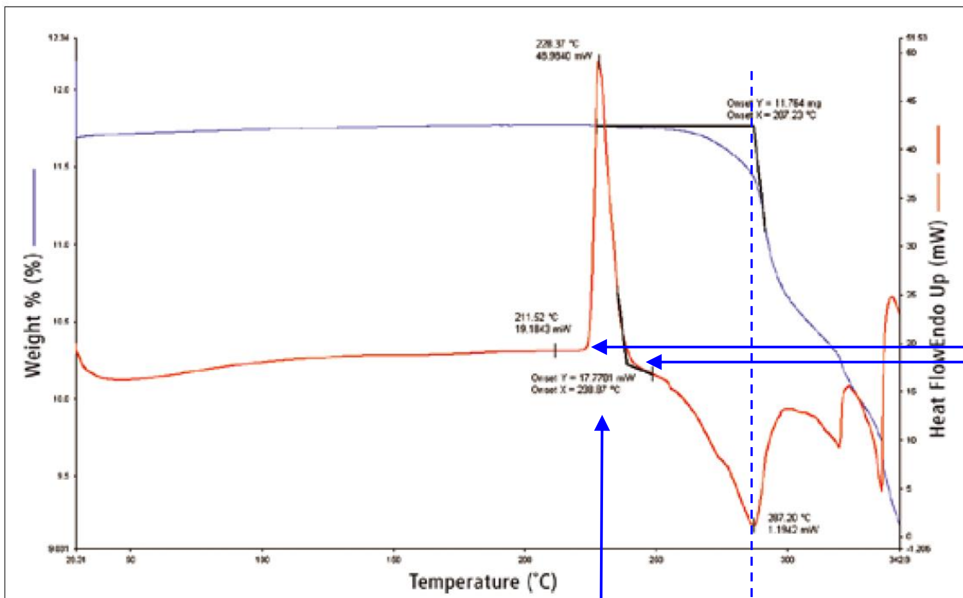


DSC Curve of a Thermoplastic Polymer

*Directions of endo- and exo- depends on instruments

TGA-DSC

TGA reveals changes of a sample due to weight, whereas DTA and DSC reveal changes not related to the weight (mainly due to phase transitions)



A pharmaceutical sample

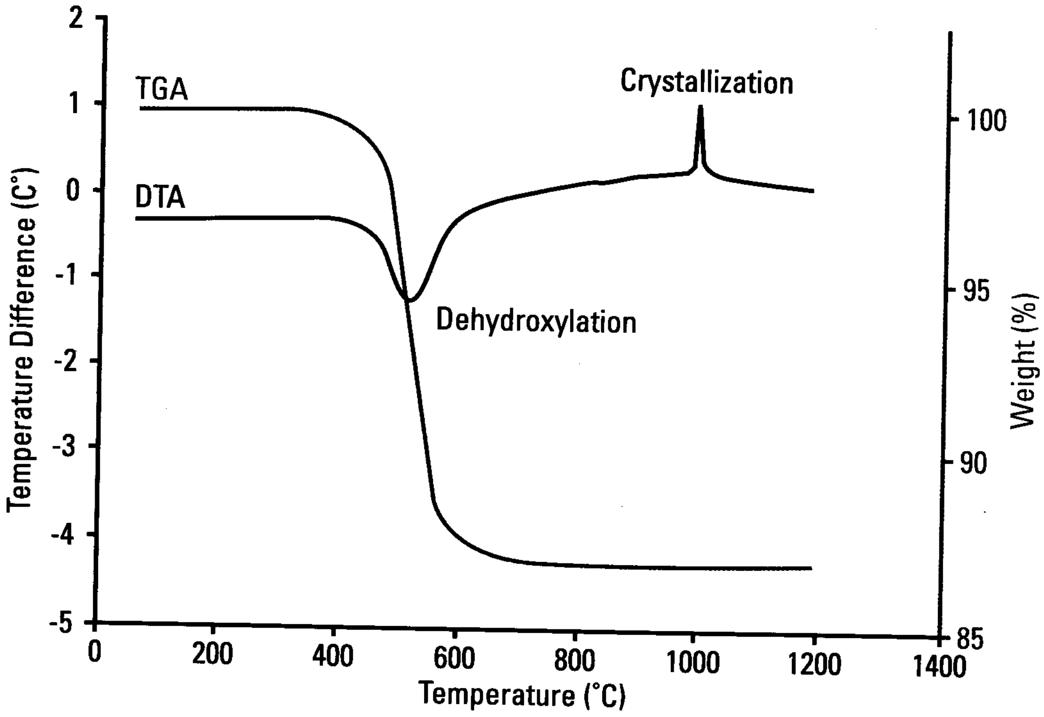
C_p of crystalline > C_p of liquid

Crystalline melt

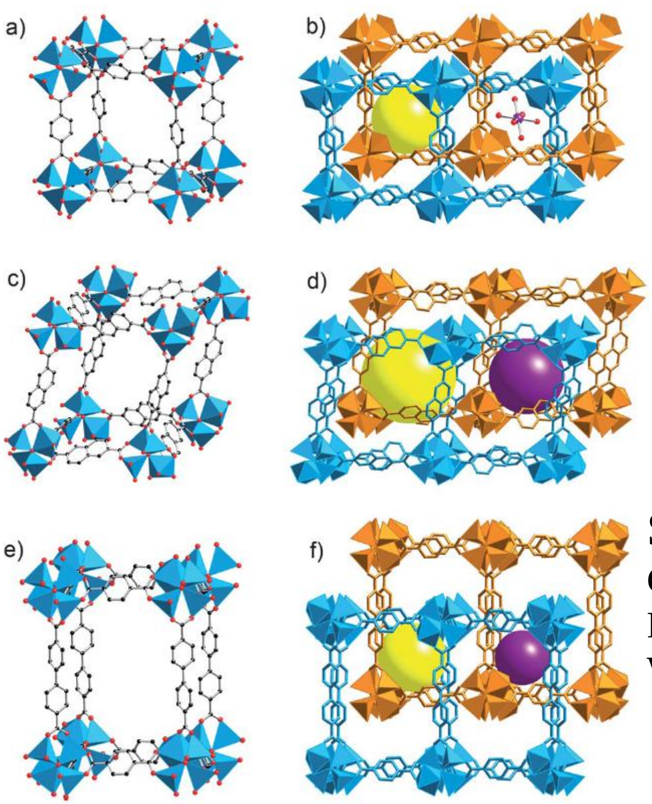
Decomposition temperature

TGA - DTA

Reading Data



Example



SUMOF-2

Crystal: $C_{24}H_{12.25}O_{14}Zn_{4.125}$ => $[Zn_4O(BDC)_3](Zn(OH)_2)_{0.125}O_{w0.75}$

FW: 794.33

Wt% (calc. C 36.29, H 1.55, N 0) (exp. C 36.61, H 1.742, N 0.034) activated

SUMOF-3 Crystal: $C_{75}H_{50}NO_{31.7}Zn_8$ => $[Zn_4O(NDC)_3]_2(DMF)(H_2O)_{3.5}O_{w1.2}$

FW: 1995.52

Wt% (calc. C 45.14, H 2.53, N 0.71) (exp. C 46.36, H 2.24, N 0.051) activated

SUMOF-4

Crystal: $C_{33}H_{24}NO_{15}Zn_4$ => $[Zn_4O(BDC)_2(BPDC)](H_2O)(DMF)(OH)$

FW: 936.10

Wt% (calc. C 42.34, H 2.58, N 1.50) (exp. C 41.24, H 2.205, N 0.029) activated

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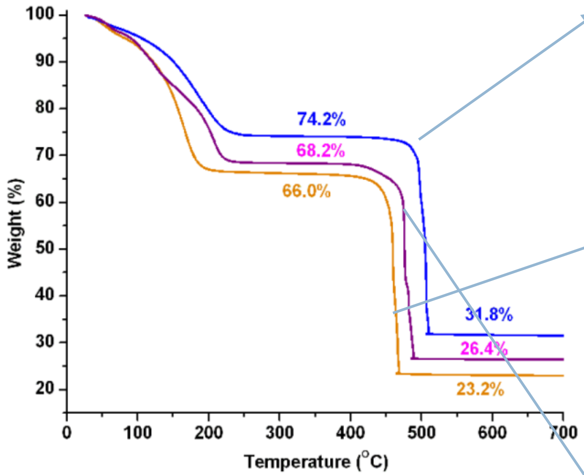
Example



SUMOF-2 (MOF-5)

Crystal: $C_{24}H_{12.25}O_{14}Zn_{4.125}$ => $[Zn_4O(BDC)_3](Zn(OH)_2)_{0.125}O_{w0.75}$

FW: 794.33

Wt% (calc. C 36.29, H 1.55, N 0) (exp. C 36.61, H 1.742, N 0.034) activated

SUMOF-3 (IRMOF-8)

Crystal: $C_{75}H_{50}NO_{31.7}Zn_8$ => $[Zn_4O(NDC)_3]_2(DMF)(H_2O)_{3.5}O_{w1.2}$

FW: 1995.52

Wt% (calc. C 45.14, H 2.53, N 0.71) (exp. C 46.36, H 2.24, N 0.051) activated

SUMOF-4

Crystal: $C_{33}H_{24}NO_{15}Zn_4$ => $[Zn_4O(BDC)_2(BPDC)](H_2O)(DMF)(OH)$

FW: 936.10

Wt% (calc. C 42.34, H 2.58, N 1.50) (exp. C 41.24, H 2.205, N 0.029) activated

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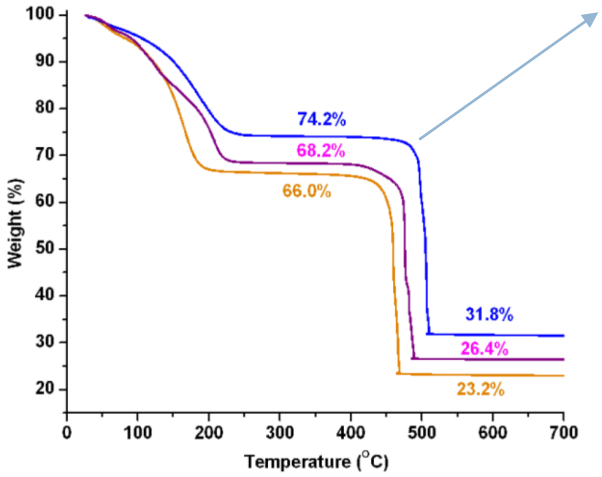

SUMOF-2 (MOF-5)

Crystal: $C_{24}H_{12.25}O_{14}Zn_{4.125}$ => $[Zn_4O(BDC)_3](Zn(OH)_2)_{0.125}O_{w0.75}$

FW: 794.33

Wt% (calc. C 36.29, H 1.55, N 0) (exp. C 36.61, H 1.742, N 0.034) activated

$[Zn_4O(BDC)_3](ZnO)_{0.125}$

$C_{24}H_{12}O_{13.125}Zn_{4.125}$

FW: 780.08

Wt% (calc. C 36.95, H 1.55, N 0) (exp. C 36.61, H 1.742, N 0.034) activated

$(ZnO)_{4.125}$

FW: 335.73

335.73/780.08 = 0.430

31.8/74.2 = 0.429

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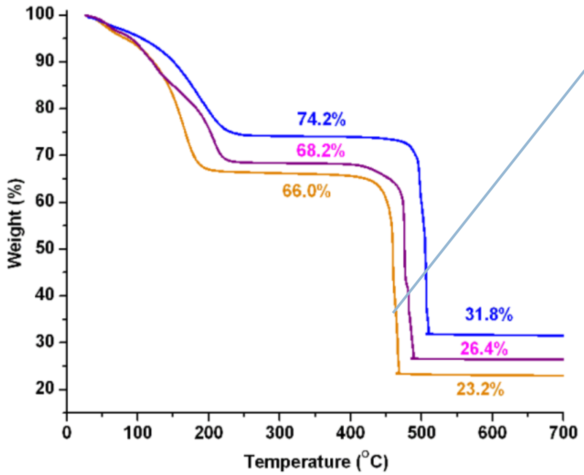
Example



SUMOF-3 (IRMOF-8)

Crystal: $C_{75}H_{50}NO_{31.7}Zn_8$ => $[Zn_4O(NDC)_3]_2(DMF)(H_2O)_{3.5}O_{w1.2}$

FW: 1995.52

Wt% (calc. C 45.14, H 2.53, N 0.71) (exp. C 46.36, H 2.24, N 0.051) activated

$[Zn_4O(NDC)_3]$

$C_{36}H_{18}O_{13}Zn_4$

FW: 920.09

Wt% (calc. C 47.00, H 1.92, N 0) (exp. C 46.36, H 2.24, N 0.051) activated

$(ZnO)_4$

FW: 325.56

325.56/920.09 = 0.354

23.2/66.0 = 0.352

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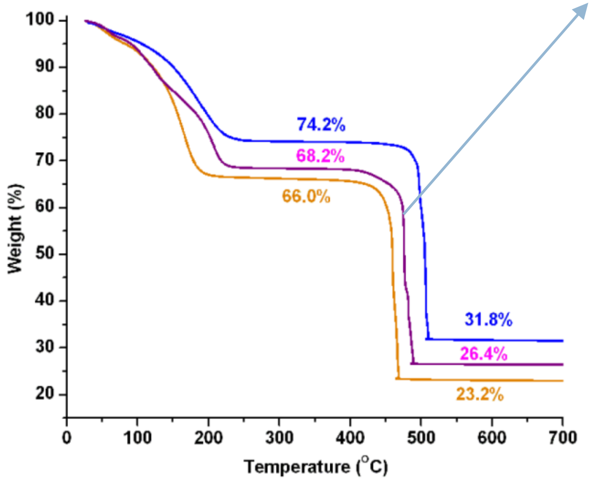
Example



SUMOF-4

Crystal: $C_{33}H_{24}NO_{15}Zn_4$ => $[Zn_4O(BDC)_2(BPDC)](H_2O)(DMF)(OH)$

FW: 936.10

Wt% (calc. C 42.34, H 2.58, N 1.50) (exp. C 41.24, H 2.205, N 0.029) activated

$[Zn_4O(BDC)_2(BPDC)(H_2O)]$

$C_{30}H_{18}O_{14}Zn_4$

FW: 864.02

Wt% (calc. C 41.70, H 2.10, N 0) (exp. C 41.24, H 2.205, N 0.029) activated

$(ZnO)_4$

FW: 325.56

325.56/864.02 = 0.377

26.4/68.2 = 0.387

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