Nutshells of Thermal Analysis

Heat it up!
Burn it!
## Thermal Analysis (TA)

<table>
<thead>
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<th>Abbreviations</th>
<th>Full Names</th>
<th>Measure</th>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
<td>Heat difference</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
<td>Mechanical Stiffness and Damping</td>
</tr>
<tr>
<td>TMA</td>
<td>Thermomechanical Analysis</td>
<td>Dimension</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
<td>Mass</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
<td>Temperature Difference</td>
</tr>
<tr>
<td>DIL</td>
<td>Dilatometry</td>
<td>Volume</td>
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<td>DEA</td>
<td>Dielectric Thermal Analysis</td>
<td>Dielectric Permittivity and Loss Factor</td>
</tr>
<tr>
<td>EGA</td>
<td>Evolved Gas Analysis</td>
<td>Gaseous Decomposition Products</td>
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<tr>
<td>TOA</td>
<td>Thermo-Optical Analysis</td>
<td>Optical Properties</td>
</tr>
<tr>
<td>Many more….</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Thermogravimetric Analysis (TG, TGA)

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 …

<table>
<thead>
<tr>
<th>Type</th>
<th>Process</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical changes</td>
<td>Gas adsorption</td>
<td>Gain</td>
</tr>
<tr>
<td></td>
<td>Gas desorption</td>
<td>Loss</td>
</tr>
<tr>
<td></td>
<td>Phase transition - Vaporization</td>
<td>Loss</td>
</tr>
<tr>
<td></td>
<td>Phase transition - Sublimation</td>
<td>Loss</td>
</tr>
<tr>
<td>Chemical changes</td>
<td>Decomposition</td>
<td>Loss (when losing gases)</td>
</tr>
<tr>
<td></td>
<td>Breakdown reaction</td>
<td>Loss (when losing gases)</td>
</tr>
<tr>
<td></td>
<td>Gas reaction</td>
<td>Gain or Loss</td>
</tr>
<tr>
<td></td>
<td>Chemisorption</td>
<td>Gain</td>
</tr>
</tbody>
</table>
Thermogravimetric Analysis (TG, TGA)

Temperature vs Time Programs

Constant heating

Gradually isothermal

Isothermal

Heating/cooling rate: 1 – 50 °C / min (typically 5 – 10 °C / min)

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

Atmosphere: In air or inert gas (He, Ar, N₂) or slow oxidation atm (1-5 % O₂ in He, N₂)

Run: at least three times
Thermogravimetric Analysis (TG, TGA)

Balance types:
- Horizontal – sample pan and reference pan
- Vertical – sample pan
  (usually no reference pan
  - cannot perform DTA, DSC)
TGA of CaC$_2$O$_4$•H$_2$O
Thermogravimetric Analysis (TG, TGA)

TGA of CaC$_2$O$_4$•H$_2$O

TG curve

DTG curve
Thermogravimetric Analysis (TG, TGA)

**Temperature and Mass Definitions**

- Onset temperature ($T_{\text{onset}}$)
  - Temperature of the process - temperature of the maximum mass loss rate ($T_0$)
- Residual Mass ($M_{\text{res}}$)
Thermogravimetric Analysis (TG, TGA)

TGA of CaC$_2$O$_4$•H$_2$O

In air (or inert gas)

Inert gas

CaC$_2$O$_4$•H$_2$O
(FW:146.111, 100%)

- 12.33% (-H$_2$O)

CaC$_2$O$_4$
(FW:128.096, 87.67%)

- 19.17% (-CO)

CaCO$_3$
(FW:100.086, 68.50%)

CaO
(FW:56.077, 68.50%)

- 30.12% (-CO$_2$)
Common gaseous molecules originating from inorganic compounds decomposing before melting point

\[ \text{H}_2\text{O, CO, CO}_2, \text{SO}_x, \text{NO}_x, \text{Cl}_2, \text{F}_2, \text{CH}_3\text{OH}, \text{other solvents} \]
Thermogravimetric Analysis (TG, TGA)

Software: NETZSCH Proteus® (Marsh procedure)
Quantification of portlandite (Ca(OH)$_2$) content in cement

~430°C: Ca(OH)$_2$ -> CaO + H$_2$O↑
Thermogravimetric Analysis (TG, TGA)

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

\[ \text{~430}^\circ\text{C: Ca(OH)}_2 \rightarrow \text{CaO + H}_2\text{O}\uparrow \]

Mass Loss (Marsh):
Onset: \(431.7\ ^\circ\text{C}\)
Inflection: \(440.4\ ^\circ\text{C}\)
Mass Change: \(-0.258\ \text{mg}\)
Thermogravimetric Analysis (TG, TGA)

Software: NETZSCH Proteus® (Marsh procedure)
Quantification of portlandite (Ca(OH)$_2$) content in cement

~430°C: Ca(OH)$_2$ -> CaO + H$_2$O↑
Thermogravimetric Analysis (TG, TGA)

Factors affecting TG curve

<table>
<thead>
<tr>
<th>Instrumental</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate</td>
<td>Mass</td>
</tr>
<tr>
<td>Furnace atmosphere and flow-rate</td>
<td>Particle size <em>(Make fine powders)</em></td>
</tr>
<tr>
<td>Geometry of pan and furnace</td>
<td>Sample history/pre-treatment</td>
</tr>
<tr>
<td>Material of pan</td>
<td>Packing <em>(Make compact solids)</em></td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td></td>
<td>Heat of reaction</td>
</tr>
<tr>
<td></td>
<td>Sample purity</td>
</tr>
</tbody>
</table>

**TG of CaC$_2$O$_4$•H$_2$O**

- In air
- In N$_2$
Thermogravimetric Analysis (TG, TGA)

Backward TG curve (when combustion occurs)
Thermogravimetric Analysis (TG, TGA)

(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)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Noise / Erratic records</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical buoyancy</td>
<td>Static</td>
</tr>
<tr>
<td>Effect temp. on balance</td>
<td>Vibration</td>
</tr>
<tr>
<td>Convection and/or turbulence</td>
<td>Pressure pulses in lab.</td>
</tr>
<tr>
<td>Viscous drag on suspension</td>
<td>Uneven gas flow</td>
</tr>
</tbody>
</table>

Errors
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 Al₂O₃) as a function of time or temperature.**

<table>
<thead>
<tr>
<th>Type</th>
<th>Process</th>
<th>Heat process</th>
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<tr>
<td>Physical changes</td>
<td>Adsorption</td>
<td>Exothermic</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>Change in crystal structure</td>
<td>Endo- or Exothermic</td>
</tr>
<tr>
<td></td>
<td>Crystallization</td>
<td>Exothermic</td>
</tr>
<tr>
<td></td>
<td>Melting, Vaporization, Sublimation</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Chemical changes</td>
<td>Oxidation</td>
<td>Exothermic</td>
</tr>
<tr>
<td></td>
<td>Reduction</td>
<td>Endothermic</td>
</tr>
<tr>
<td></td>
<td>Breakdown reaction</td>
<td>Endo- or Exothermic</td>
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<tr>
<td></td>
<td>Chemisorption</td>
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</tr>
<tr>
<td></td>
<td>Solid state reaction</td>
<td>Endo- or Exothermic</td>
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Differential Thermal Analysis (DTA)

**Principle**

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

DTA curve – endothermic process
Differential Thermal Analysis (DTA)

* Peak temperature is affected by heating rate & sample mass, but not by $\Delta H$ and $T_{onset}$

Measuring

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

*Depending on instruments

exothermic

endothermic
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.**

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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.)

\[ \Delta H = \int_{t_1}^{t_2} (\text{Heat Flow} - C_p \cdot \beta) \, dt \]
Differential Scanning Calorimetry (DSC)

*Directions of endo- and exo- depends on instruments

*Offset
*Heat flow
*Temperature
*EN
*EX
Differential Scanning Calorimetry (DSC)

*Directions of endo- and exo- depends on instruments
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).
TGA - DTA

Reading Data

![Graph showing TGA and DTA data with temperature change and weight percentage over temperature range. Peaks indicate Crystallization and Dehydroxylation.]
SUMOF-2
Crystal: $C_{24}H_{12.25}O_{14}Zn_{4.125} \Rightarrow [Zn_4O(BDC)_3](Zn(OH)_2)_{0.125}O_{w0.75}$
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: $C_{75}H_{50}NO_{31.7}Zn_8 \Rightarrow [Zn_4O(NDC)_3]_2(DMF)(H_2O)_3.5O_{w1.2}$
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: $C_{33}H_{24}NO_{15}Zn_4 \Rightarrow [Zn_4O(BDC)_2(BPDC)](H_2O)(DMF)(OH)$
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
SUMOF-2 (MOF-5)
Crystal: $\text{C}_{24}\text{H}_{12.25}\text{O}_{14}\text{Zn}_{4.125} \rightarrow [\text{Zn}_4\text{O(BDC)}_3](\text{Zn(OH)})_2\text{O}_{0.125}\text{O}_{0.75}$
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: $\text{C}_{75}\text{H}_{50}\text{NO}_{31.7}\text{Zn}_8 \rightarrow [\text{Zn}_4\text{O(NDC)}_3]_2(\text{DMF})(\text{H}_2\text{O})_3\text{O}_{1.2}$
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: $\text{C}_{33}\text{H}_{24}\text{NO}_{15}\text{Zn}_4 \rightarrow [\text{Zn}_4\text{O(BDC)}_2(\text{BPDC})](\text{H}_2\text{O})(\text{DMF})(\text{OH})$
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
SUMOF-2 (MOF-5)
Crystal: $\text{C}_{24}\text{H}_{12.25}\text{O}_{14}\text{Zn}_{4.125}$ $\rightarrow$ $[\text{Zn}_4\text{O(BDC)}_3](\text{Zn(OH)}_2)_{0.125}\text{O}_{w0.75}$
FW: 794.33
Wt% (calc. C 36.29, H 1.55, N 0) (exp. C 36.61, H 1.742, N 0.034) activated

$[\text{Zn}_4\text{O(BDC)}_3](\text{ZnO})_{0.125}$
$\text{C}_{24}\text{H}_{12}\text{O}_{13.125}\text{Zn}_{4.125}$
FW: 780.08
Wt% (calc. C 36.95, H 1.55, N 0) (exp. C 36.61, H 1.742, N 0.034) activated

$\text{(ZnO)}_{4.125}$
FW: 335.73
335.73/780.08 = 0.430
31.8/74.2 = 0.429
SUMOF-3 (IRMOF-8)
Crystal: C_{75}H_{50}NO_{31.7}Zn_{8} => [Zn_{4}O(NDC)_{3}]_{2}(DMF)(H_{2}O)_{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_{4}O(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
SUMOF-4
Crystal: $C_{33}H_{24}NO_{15}Zn_4 \Rightarrow [Zn_4O(BDC)_2(BPDC)](H_2O)(DMF)(OH)$
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
$325.56/864.02 = 0.377$
$26.4/68.2 = 0.387$