Thermal analysis

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Thermal analysis
Definitions and uses

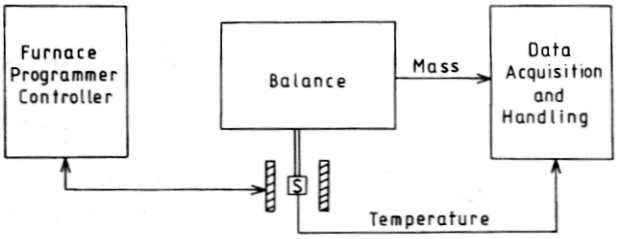
Thermal analysis encompasses a group of techniques in which a property of the sample is monitored against time and temperature, while the temperature of the sample, in a specified atmosphere, is programmed.

- **Thermogravimetry**, TG/TGA/DTG (mass change *vs.* T)
- **Differential thermal analysis** DTA/DSC (heat flux *vs.* T)
- **Evolved gas analysis** (volatiles *vs.* T)
- *etc.*

Basically, methods of thermal analysis allow the study of all chemical processes that are associated with heating/cooling. And there is a lot of these: decomposition, pyrolysis, ignition, phase changes, calorimetry, etc. All this can be studied on a small amount of sample and in a highly automated way.

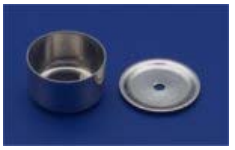
Thermogravimetry (thermogravimetric analysis)
The thermobalance

Thermogravimetry (TG/TGA) is the basic and hence the simplest of all thermoanalytical methods. The instrument is built around a furnace where the sample is mechanically connected to an analytical balance. It records the Δm *vs.* T curve.

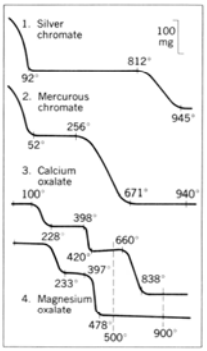


Thermogravimetry
Typical conditions

Maximum temperature: 1100 °C
Sensitivity is on the order of 1 μg
Typical sample load is 10 to 50 mg (up to 1 g is possible)
Crucible material can be aluminum, alumina, Pt, Cu, Au, etc.
Atmosphere is typically vacuum, air, nitrogen, oxygen, or helium



Thermogravimetry
Example TG/TGA curves of precipitates



Curve 1: initial loss of excess wash water of the precipitate, then constant weight up to 812°C when oxygen release starts

$$Ag_2CrO_4 \xrightarrow{812^\circ C} O_2 + Ag + AgCrO_2$$

Curve 2: loss of wash water, then decomposition from 256°C on, then sublimation of Hg_2O

$$Hg_2CrO_4 \xrightarrow{256^\circ C} Hg_2O + CrO_3 \xrightarrow{\text{up to } 671^\circ C} CrO_3$$

Curve 3: Hydrate water release and then decomposition in two steps:

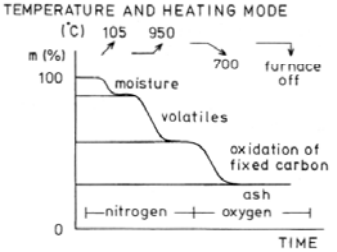
$$Ca(COO)_2 \xrightarrow{398^\circ C} CaCO_3 + CO \xrightarrow{660^\circ C} CaO + CO_2$$

Curve 4: Hydrate water release and then decomposition in one step:

$$Mg(COO)_2 \xrightarrow{397^\circ C} MgO + CO + CO_2$$

Thermogravimetry
Application: analysis of coal for carbon content

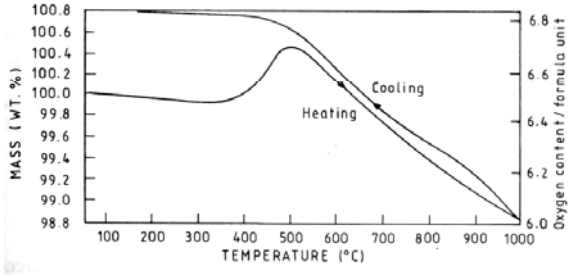
TGA instruments can be also used for routine quantitative analytical work. In this example, a coal sample is first heated in nitrogen gas in order to dry it and to expell any volatiles, and then the atmosphere is switched to oxygen and the carbon content is burnt to CO_2. Weight loss in the last step can be used to calculate the carbon content.



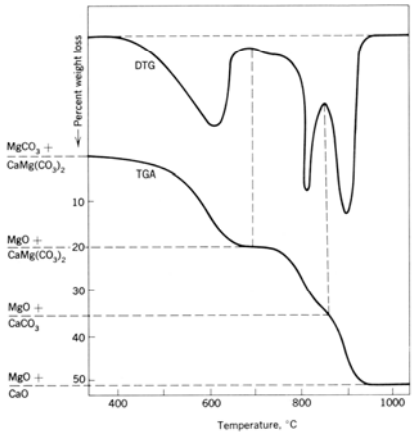
Thermogravimetry

Application: controlled synthesis of superconductors

In this example, the controlled synthesis of $YBa_2Cu_3O_{6.9}$ is performed/monitored by slowly heating and then cooling the superconductor in air. The material looses oxygen upon heating and then takes it up upon cooling. The oxygen content of this type of superconductors largely determines the critical temperature.



Differential thermogravimetry (DTG)

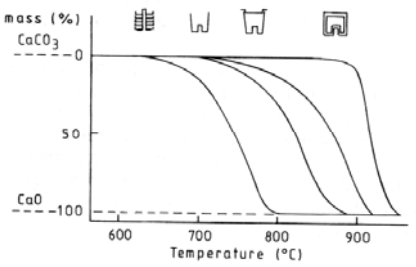


It is very useful to record the first derivative of the TG/TGA curve (DTG) also, because it makes the noticing small features/boulders on the curve much easier (they appear as peaks).

See, for example, the graph on the left that shows the TG/DTG of a mixed carbonate sample. The boulders of the TG curve at around 850°C can hardly be seen, so the corresponding temperatures are difficult to determine. It is much easier done using the DTG curve.

Thermogravimetry
Potential sources of errors

Great care needs to be exercised while loading and operating the instrument if the TG curve is intended to be accurate. Potential sources of error include the effect of heating rate, the geometry of the crucible (see below), gas flow, electrostatic forces, etc.



The geometry of the crucible affects the escape of CO_2 and thus influences characteristic temperature values

Differential thermal analysis (DTA)
Differential scanning calorimetry (DSC)

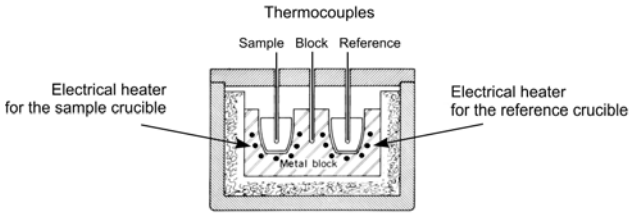
These thermal methods are concerned with ***the measurement of energy changes*** (heat flux) in the sample, usually due to chemical reactions. The most important feature of these methods is that the energy change (endothermic/exothermic) can be read from the DTA/DSC curves by integrating the peak area.

An „inert" reference compound is needed for the measurement (it should not undergo any thermal changes and should not react with the crucible material or the thermocouple). It is typically Al_2O_3 or SiC for inorganics and silicone oil for organics.

Differential thermal analysis (DTA/DSC)

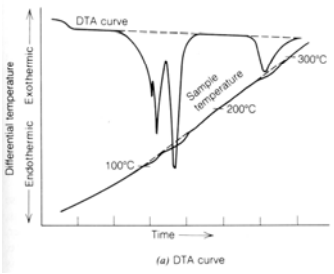
DTA: follows the temperature difference between sample and reference upon heating or cooling. If there is some endothermic chemical reaction then the temperature of the sample will lag behind the temperature of the reference. If the reaction is exothermic, then the situation is the opposite. In the schematic below, the two heaters are driven commonly.

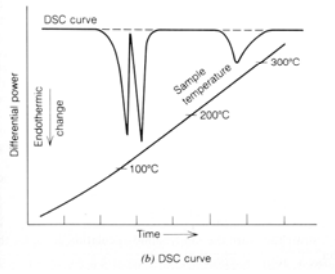
DSC: follows the electrical power (heat) needed to keep the sample and reference at the same temperature. This is the more accurate one. In the schematic below, the heaters are controlled and driven separately.



Differential thermal analysis (DTA/DSC)
Comparison of DTA and DSC

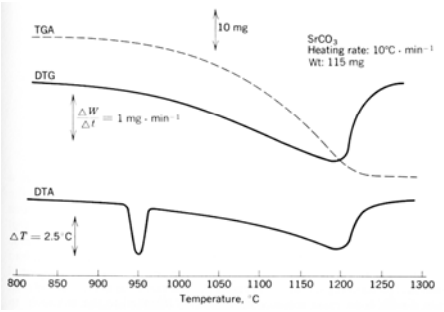
This example DTA/DSC of $CuSO_4 \cdot 5\ H_2O$ shows the superiority of DSC. Peak areas are more accurate and the temperature ramp is less disturbed by thermal events in the sample (e.g. differences in specific heats and thermal conductivities between the sample and reference). In the curves below, the peaks correspond to the loss of two, two and finally one molecule of H_2O.



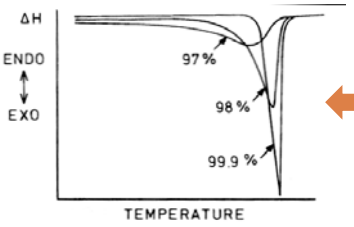


Differential thermal analysis (DTA/DSC)
Applications

An important application of DTA/DSC is the monitoring of ***phase changes or crystalline transitions***. These are not associated by any mass change, so are not reflected in neither TG or DTG curves. This example is for the decomposition of $SrCO_3$ in air, showing the rhombic-hexagonal crystalline transition at 950°C that can only be seen in the DTA curve.

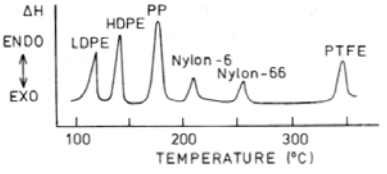


Differential thermal analysis (DTA/DSC)
Applications

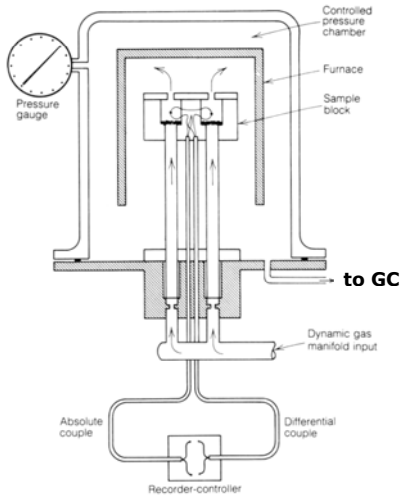


Purity check of a material
(based on the shape and position of the melting curve)

Plastic waste analysis
(fingerprint technique for polimer recognition based on the melting and transition temperatures)



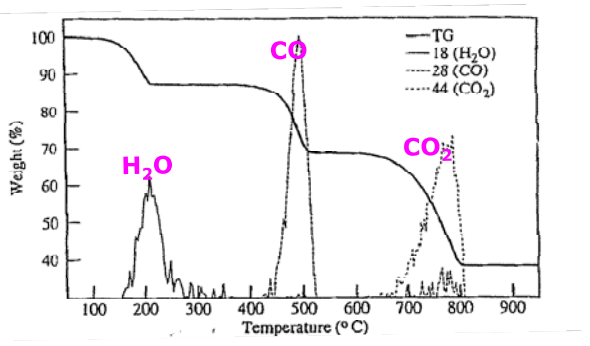
Evolved gas analysis (EGA)
The concept



The concept behind evolved gas analysis is that the study of unknown materials and/or thermal processes is much easier if we also use a detector to selectively identify the released compounds and byproducts (volatiles, combustion products, etc.). This can be done by coupling the gas output of a TG or DTA instrument to a selective detector, such as a spectrometer or a gas chromatograph. This is exemplyfied in the schematic on the left for a DTA-GC combination.

Evolved gas analysis (EGA)
The calcium-oxalate decomposition revisited

The information content of an EGA measurement is illustrated in this example for the decomposition of hydrate water containing Ca-oxalate. The detector was a mass spectrometer in this instance (TG-MS), but could have also been e.g. an FTIR spectrometer (TG-FTIR), or a gas chromatograph (TG-GC).



Thermal analysis

Summary of potential application areas

Illustrative application examples (partially covered):

- determination of drying temperatures for gravimetry
- determination of moisture/hydrate water content
- determination of volatile content
- quantitative analysis of binary samples
  (based on the known stoichiometry of decomposition)
- controlled thermal synthesis of materials
- study of stability of sampes under heating/cooling
- combustion or pyrolysis analysis
- study of gas adsorption/desorption processes
- purity check (melting point determination) of synthetic samples
- identification of compound materials
- calorimetric titration
- quality control of composite man-made materials (fingerprinting)
- *etc.*