CHEM*3440

Chemical Instrumentation

Topic 14

Thermal Analysis

Thermal Methods

We will examine three thermal analytical techniques:

- Thermogravimetric Analysis (TGA)
- Differential Thermal Analysis (DTA)
- Differential Scanning Calorimetry (DSC)

TGA and DTA have found important roles to play in industrial chemistry, particularly with the analysis and development of polymers.

DSC is an important research tool, providing access to accurate thermodynamics data as well as information regarding reactivity and phase transformations.

Thermogravimetry

Analysis of mass changes in a sample as a function of temperature.

Usually observes mass loss:

- decomposition
- sublimation
- reactivity and desorption of products

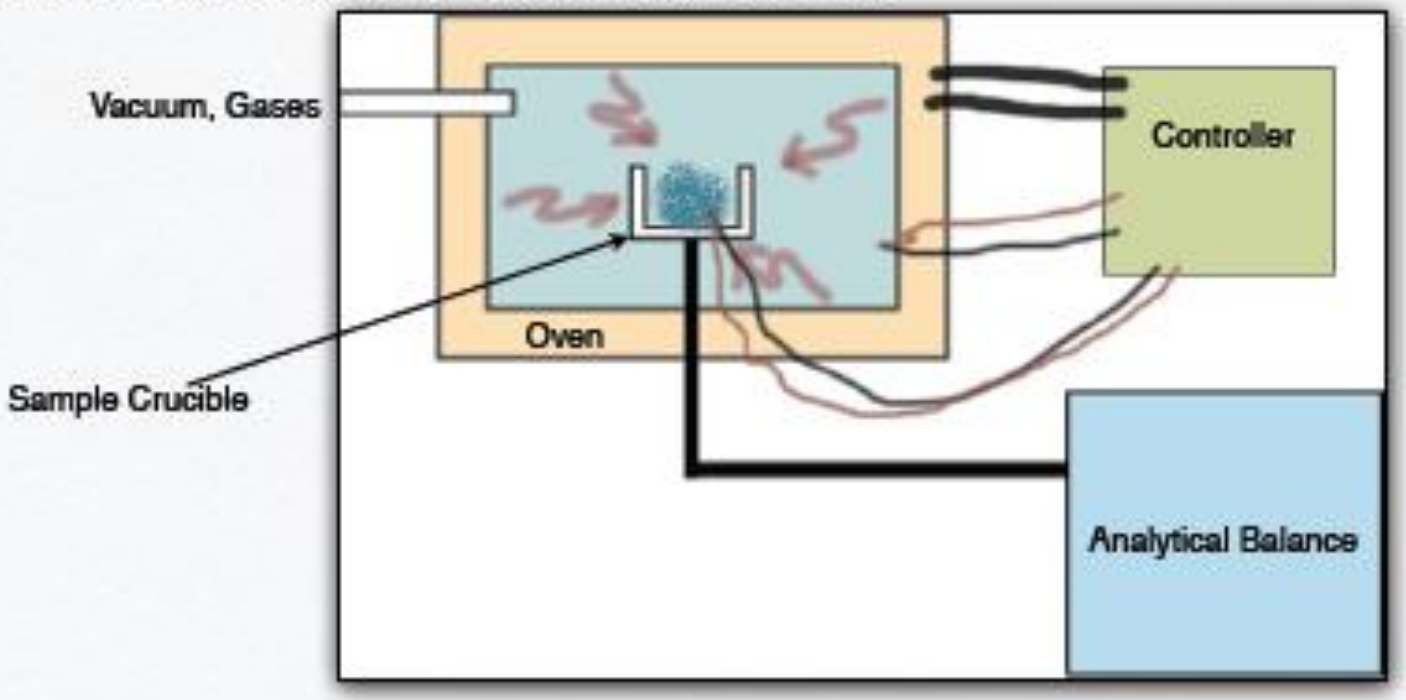
Can observe mass gain:

- oxidation, forming non-volatile oxides

Instrumental Components

There are three principal components in a TGA:

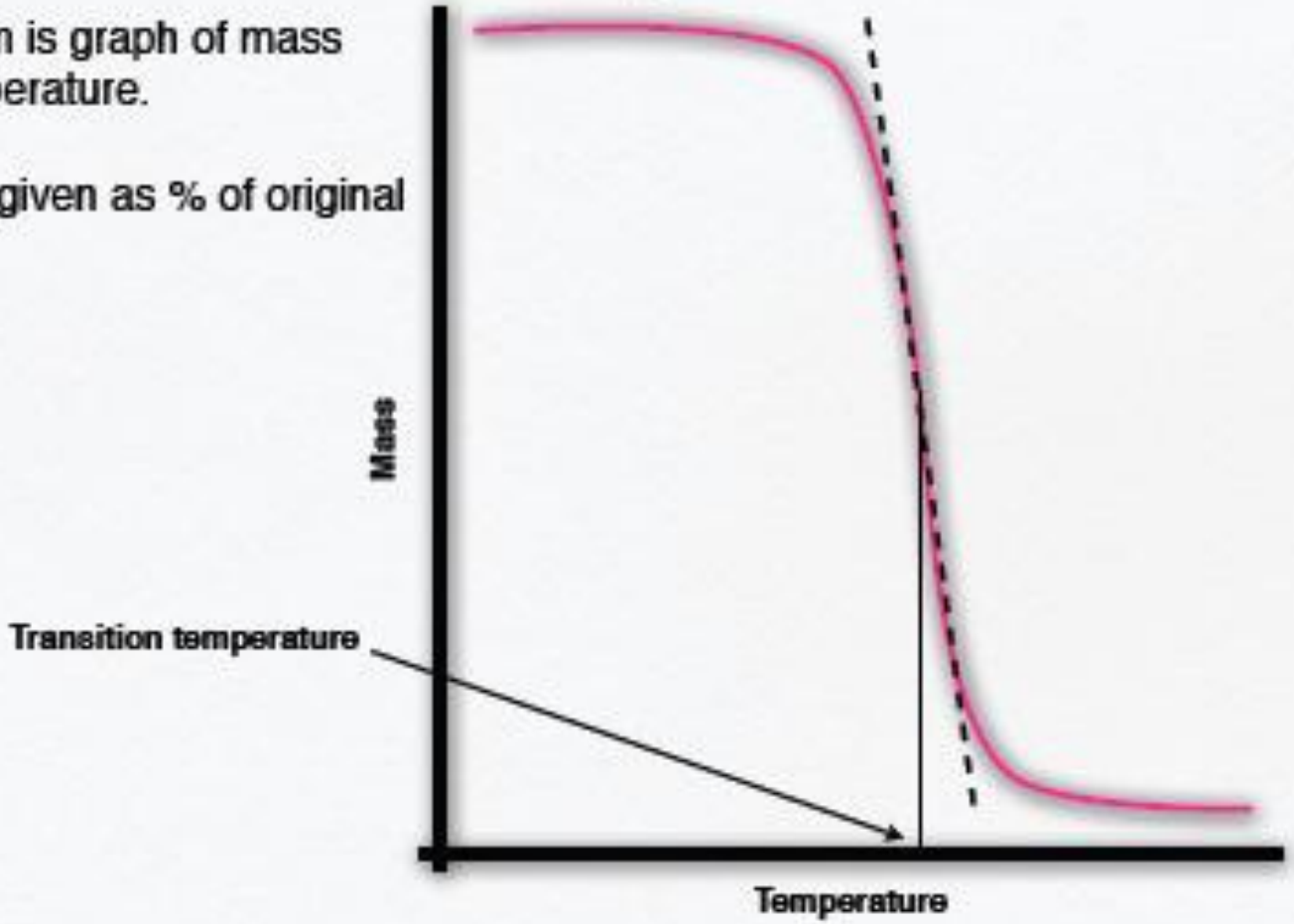
- analytical balance
- furnace and temperature control system
- control of atmospheric gases exposed to sample



TGA Data Analysis

Thermogram is graph of mass *versus* temperature.

Sometimes given as % of original mass.



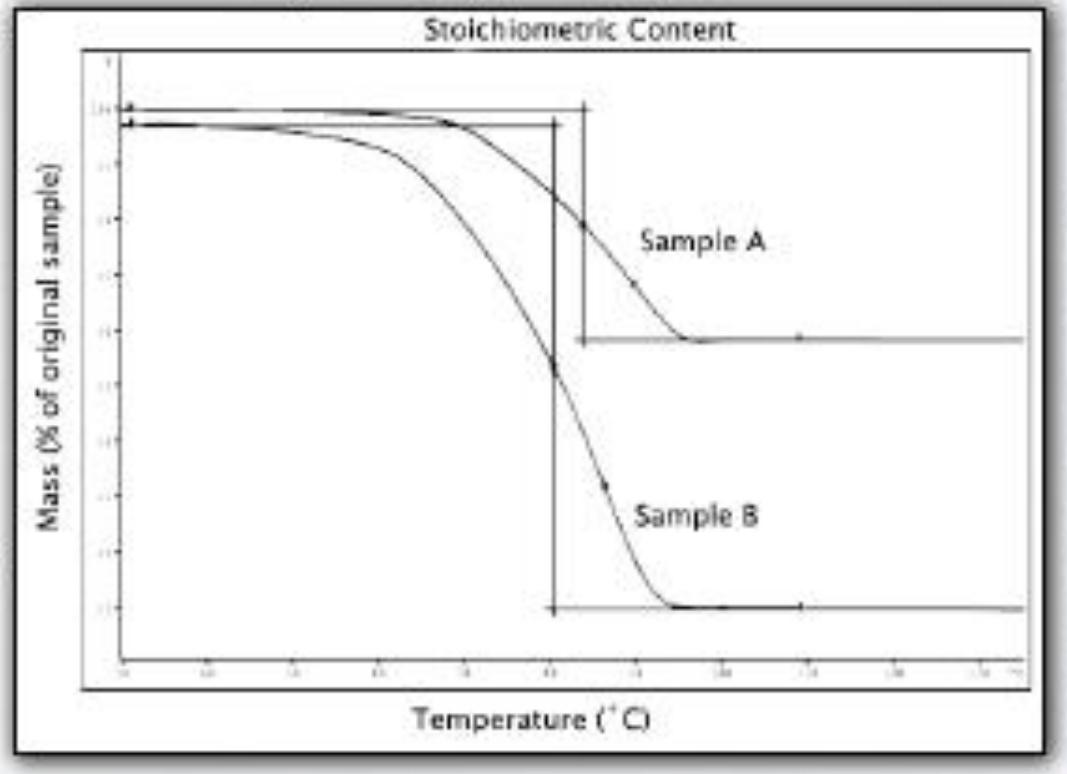
TGA Example1

Theophylline (180.17 g/mol) is a pharmaceutical used for chronic asthma treatment. Its stable form is that of the monohydrate (198.18 g/mol). The amount of water in an actual sample is important to measure in order to ensure accurate dosage. Dehydration is complete at 110 °C.

Complete hydrate should lose 9.1% of mass, based on stoichiometry.

Sample A loses only 4.13%. Hence, it is only 45.54% pure hydrate.

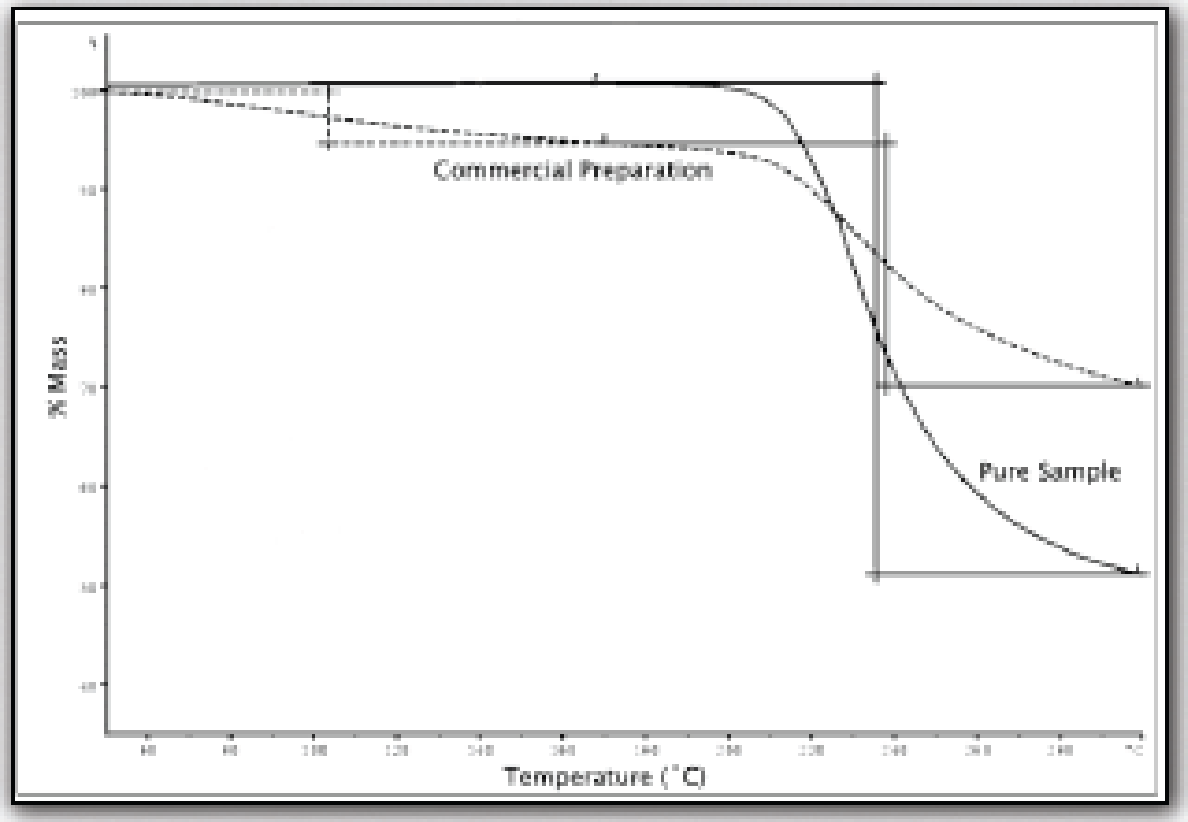
Sample B loses 8.69% and is therefore 95.79% pure. Note that it loses a small amount of adsorbed moisture before scan even started.



TGA Example2

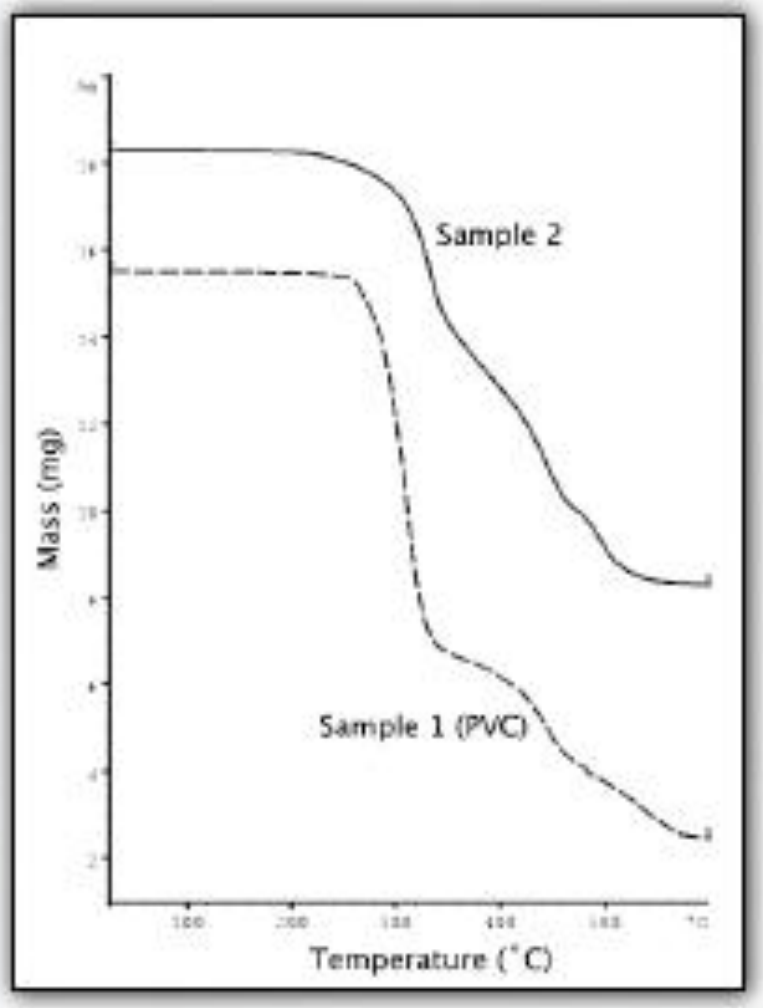
Calcium carbasalate is a salicylate like aspirin with its analgesic effects but seems to do less damage to the stomach lining. The pure, active compound shows a 49.46% weight loss starting at 210 ˚C due to decomposition.

A particular preparation of it (called Alcacyl), shows a 5% weight loss, due to moisture and followed by a 24.45% weight loss at the decomposition temperature. This indicates that the original sample was 49.43% carbasalate.



TGA Example3

The thermal stability of polymeric insulation layers used in coating electrical wires is investigated for quality assurance. Shown here are two different polymers. Note that they both decompose in several steps; the thermogram can be used as a fingerprint for identification and confirmation.



Differential Thermal Analysis

An analysis sample is heated in a linear temperature ramp.
Its temperature is compared to that of a similarly heated inert reference sample.
Any physical or chemical process that occurs in the analysis sample will be accompanied by an additional enthalpic change.

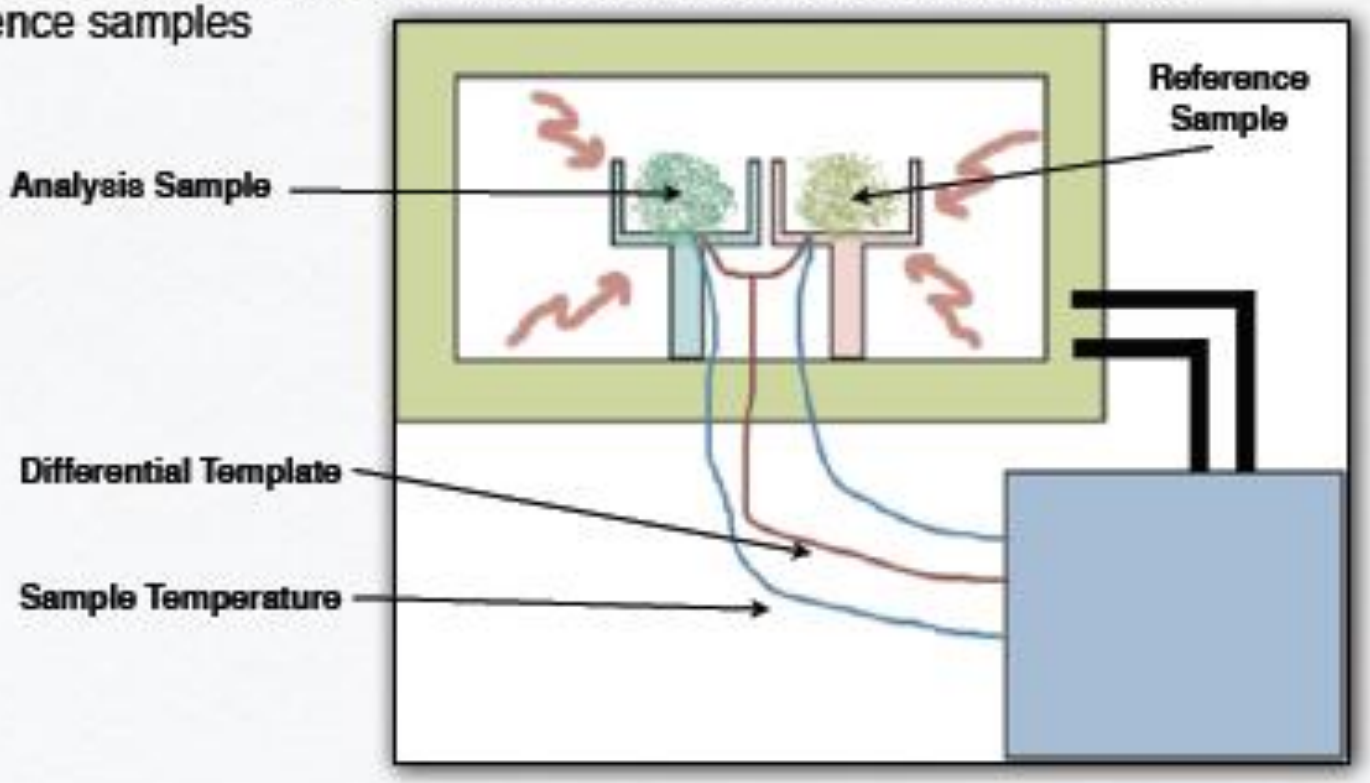
The enthalpic change can be either endothermic or exothermic.

The temperature of the analysis sample will respectively be less than or greater than expected, thereby identifying the physical process.

Instrumental Components

Principal components of the experiment include:

- an oven for the controlled heating of the samples
- separate temperature sensing transducers for both the analysis and reference samples

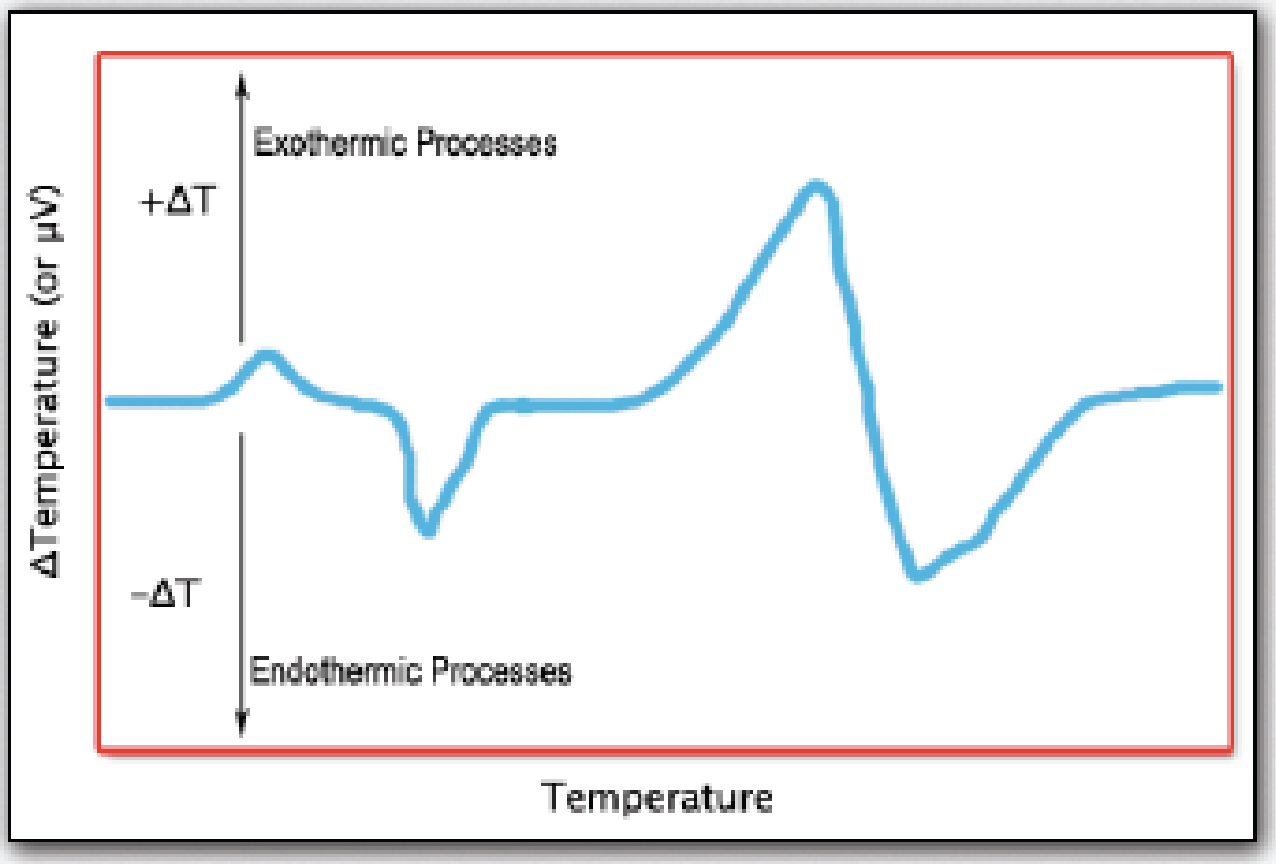


DTA Data Analysis 1

Thermogram is graph of the temperature difference between the analysis and reference samples as a function of the oven temperature.

Sometimes, the temperature difference is plotted directly as the thermocouple potential difference (usually in μV).

Exothermic processes will make the analysis sample hotter than the reference, and *vice versa*.

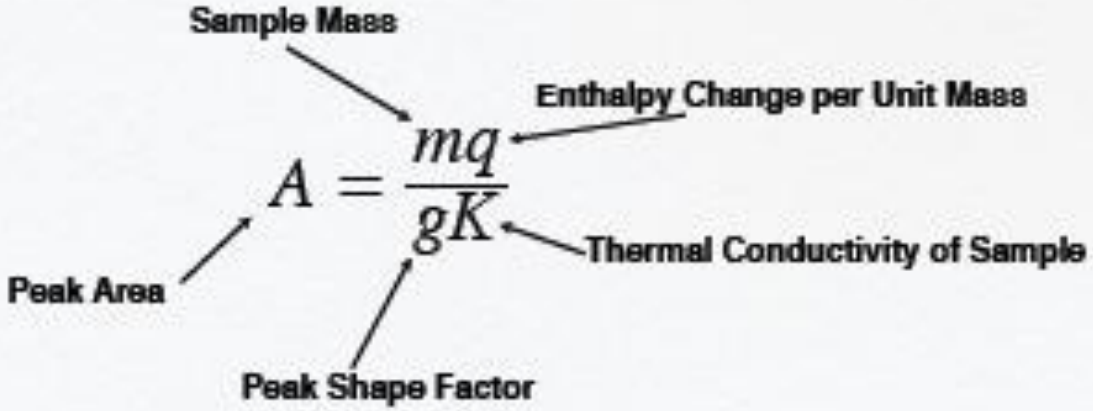


DTA Data Analysis 2

Data can be acquired while either heating or cooling the system. Often both are preferred. Be aware of irreversible processes.

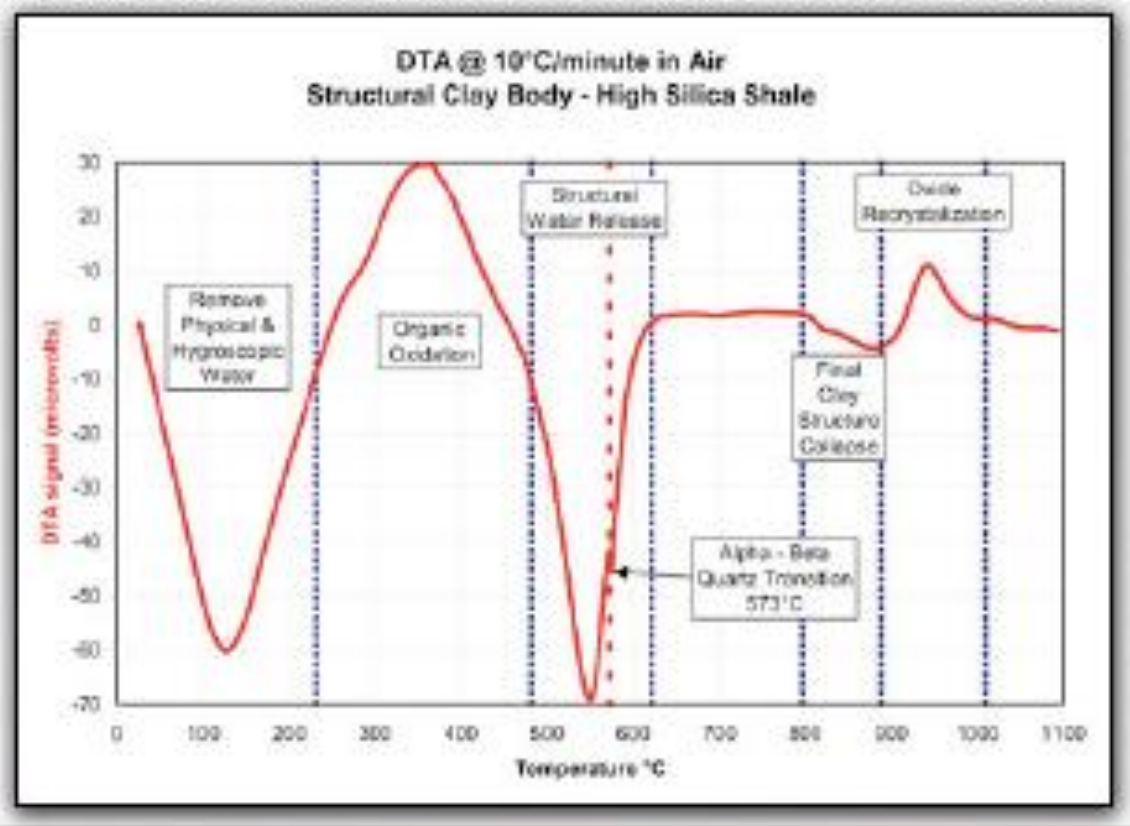
Baseline changes can arise due to differences or changes in heat capacity, even if no enthalpic changes occur - often associated with structural phase transitions.

Area under a DTA peak is proportional to enthalpy change and is independent of heat capacity.



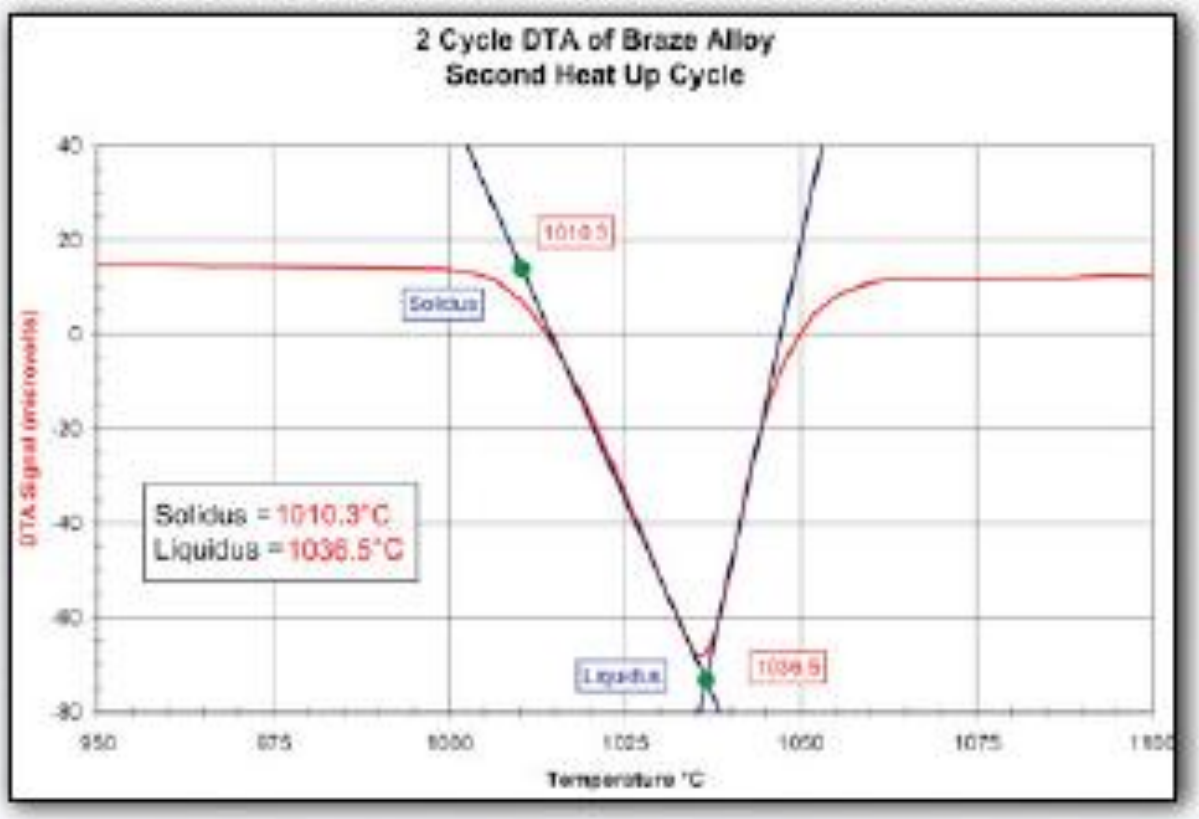
DTA Example1

Here we have a sample of clay. We observe, dehydration, oxidation, phase transitions, and recrystallization process. The enthalpy changes associated with each can be determined by finding the area under the curve for each process.



DTA Example2

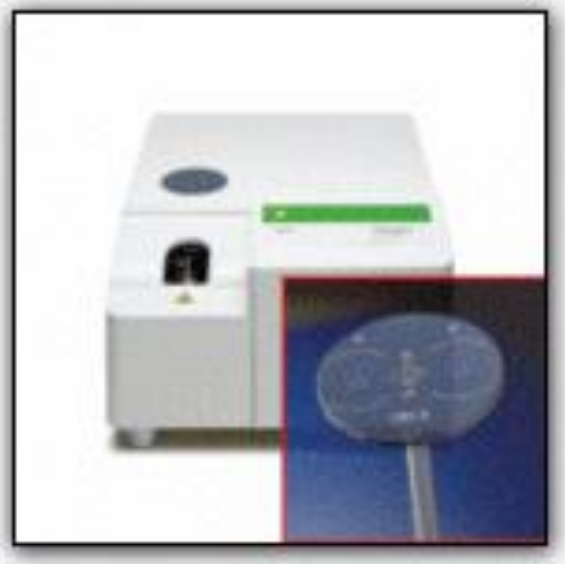
This is a metal alloy used for brazing (high temperature soldering). When automating the joining process, knowledge of the temperature when it becomes a liquid (liquidus) and when it returns to its solid form (solidus) are critical.

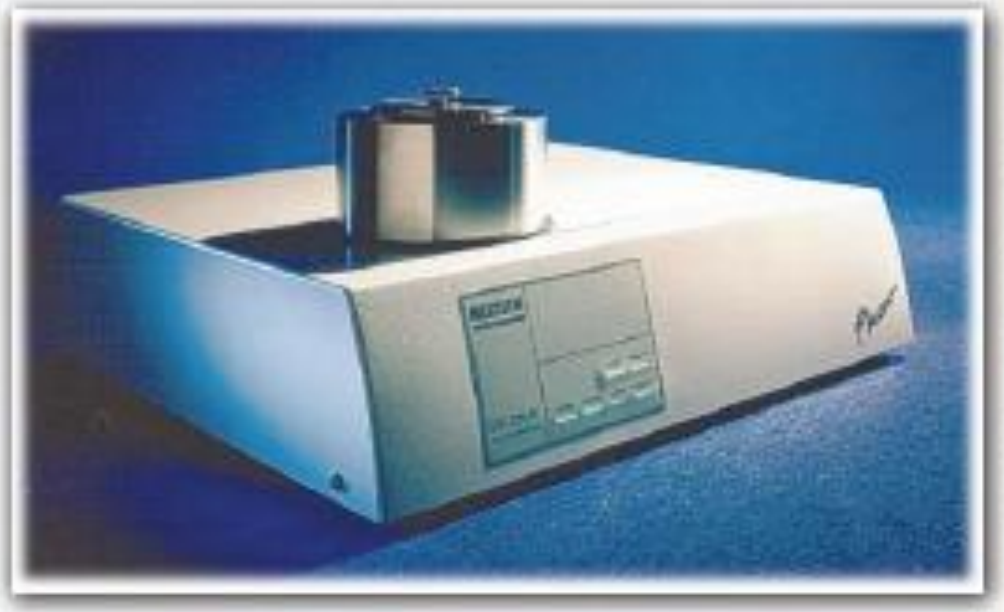


Differential Scanning Calorimetry

DSC is the most sophisticated and advanced of the thermal methods. There are two principal variants:

- heat-flow DSC
- power compensated DSC

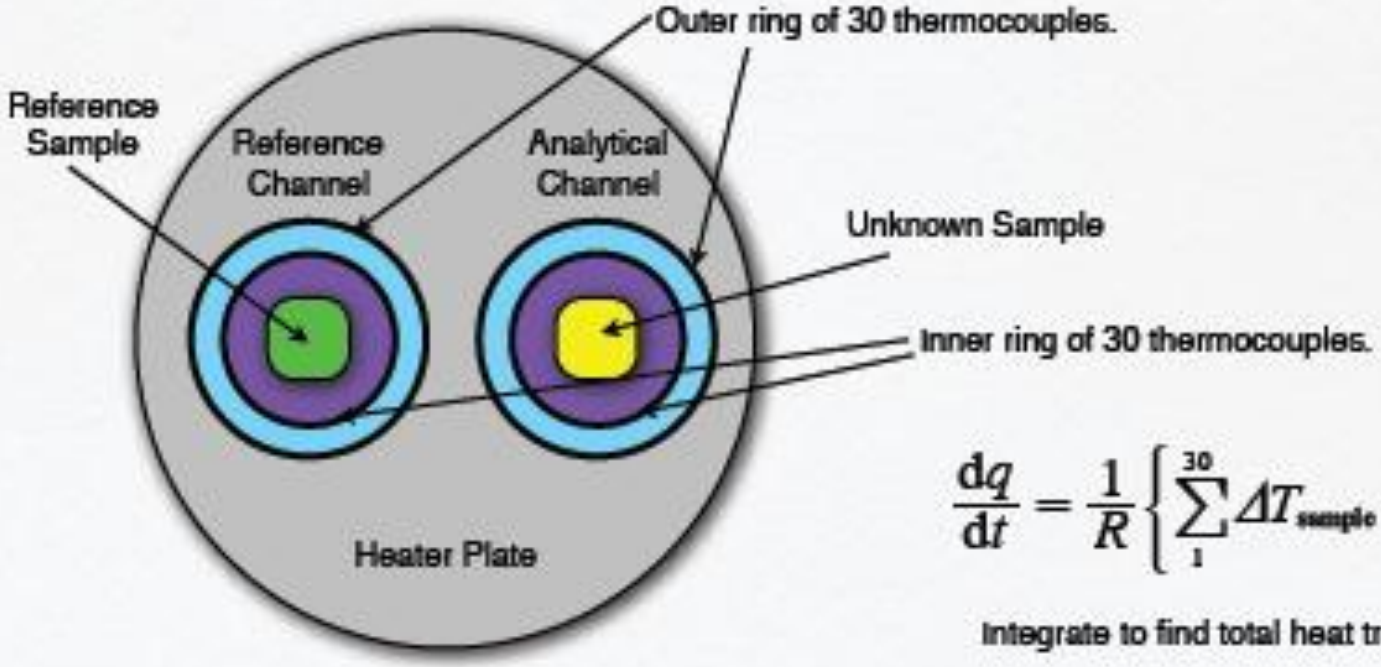




Instrumental Components 1

Set-up is similar to DTA: analysis sample and reference sample.

Heat-Flow DSC: each sample is surrounded by an inner ring and an outer ring of thermocouples. The average temperature difference between the two measures the heat flow into or out of the sample.



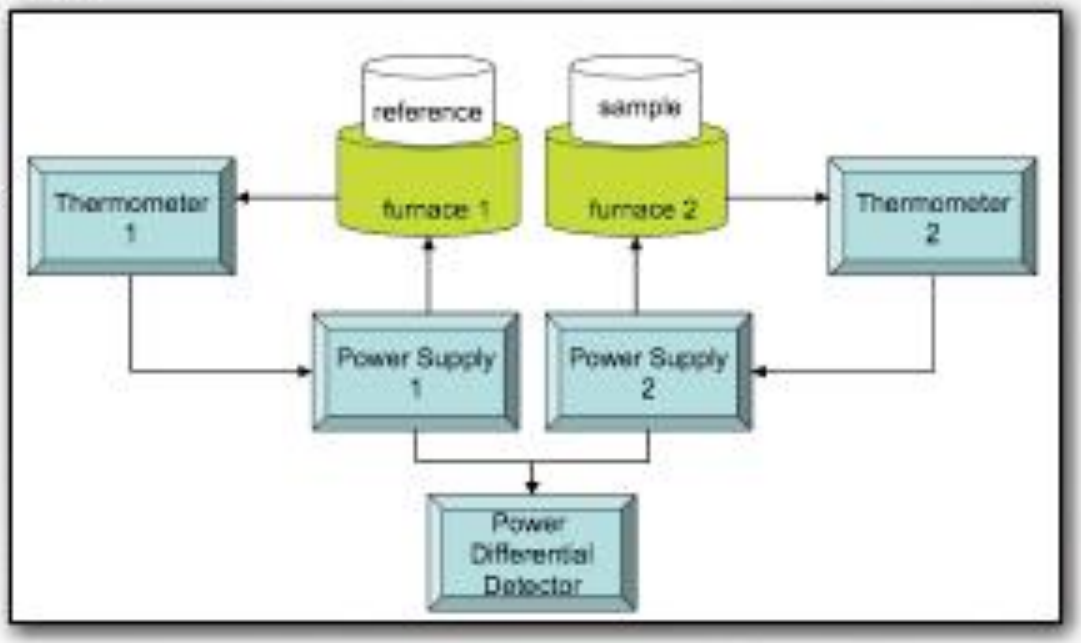
$$\frac{dq}{dt} = \frac{1}{R}\left\{\sum_{1}^{30}\Delta T_{sample} - \sum_{1}^{30}\Delta T_{reference}\right\}$$

Integrate to find total heat transfered.

Instrumental Components 2

Power Compensated DSC: Two samples, each heated independently. Temperature difference is monitored. Control heat flow into analysis sample (adjusting heater power) to keep the temperature difference $\Delta T = 0$. This is a null experiment with feedback.

The power supplies attempt to heat the two samples at an identical rate. When an exothermic process begins to occur in the analysis sample, the power decreases, in order to keep the temperature correlated with the reference. Similarly with an endothermic process. This is the signal.

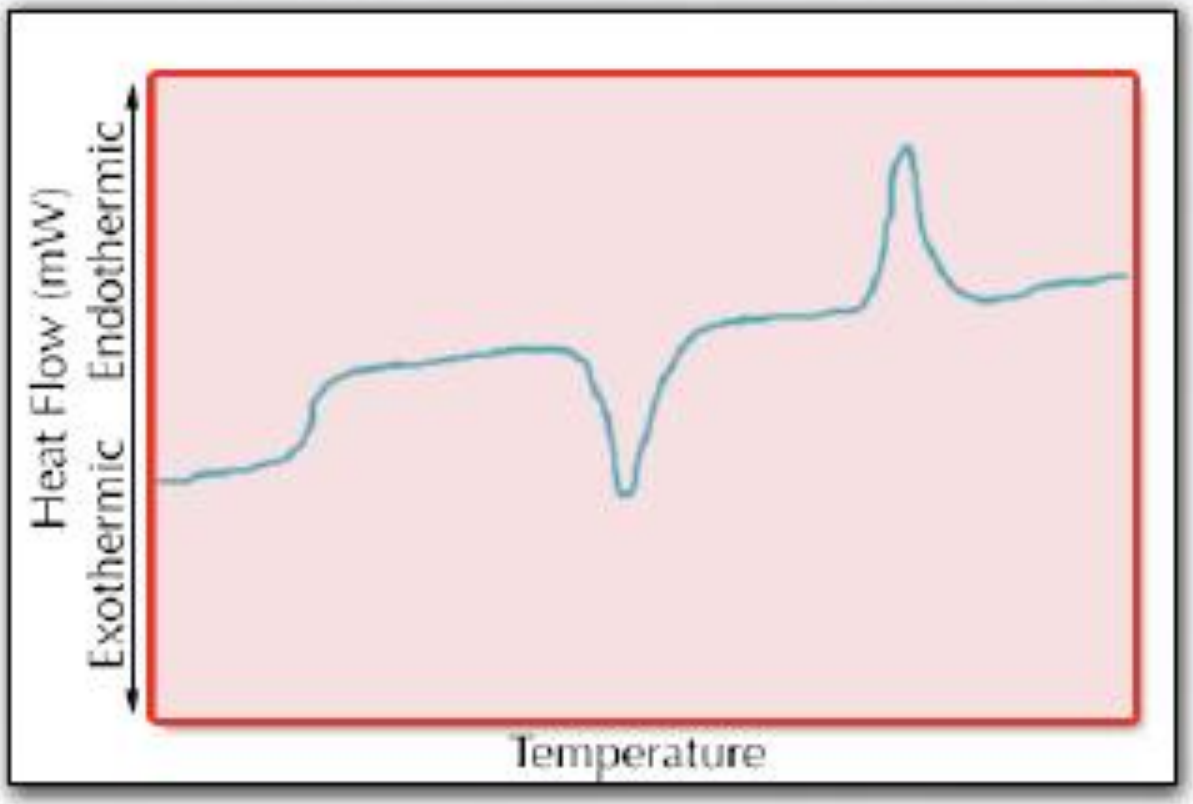


This uses much smaller sample sizes than with heat flow DSC.

DSC Data Analysis 1

The power differences are plotted as a function of the sample temperature. The unit is usually differences in power, given in mW.

Here is the DSC curve for a polymeric material such as high density polyethylene (HDPE). We see three phase transitions temperatures identified: the glass transition temperature, the crystallization temperature, and the melting temperature.



DSC Data Analysis 2

Integrate area under a peak as a function of time: signal is power (W = J/s). Integral gives total energy associated with the process: ΔH.

Can determine average heat capacity and entropy of process.

$$\Delta H = \int_{T_1}^{T_2} C_p \, dT = C_p (T_2 - T_1)$$

$$C_p = \frac{\Delta H}{(T_2 - T_1)}$$

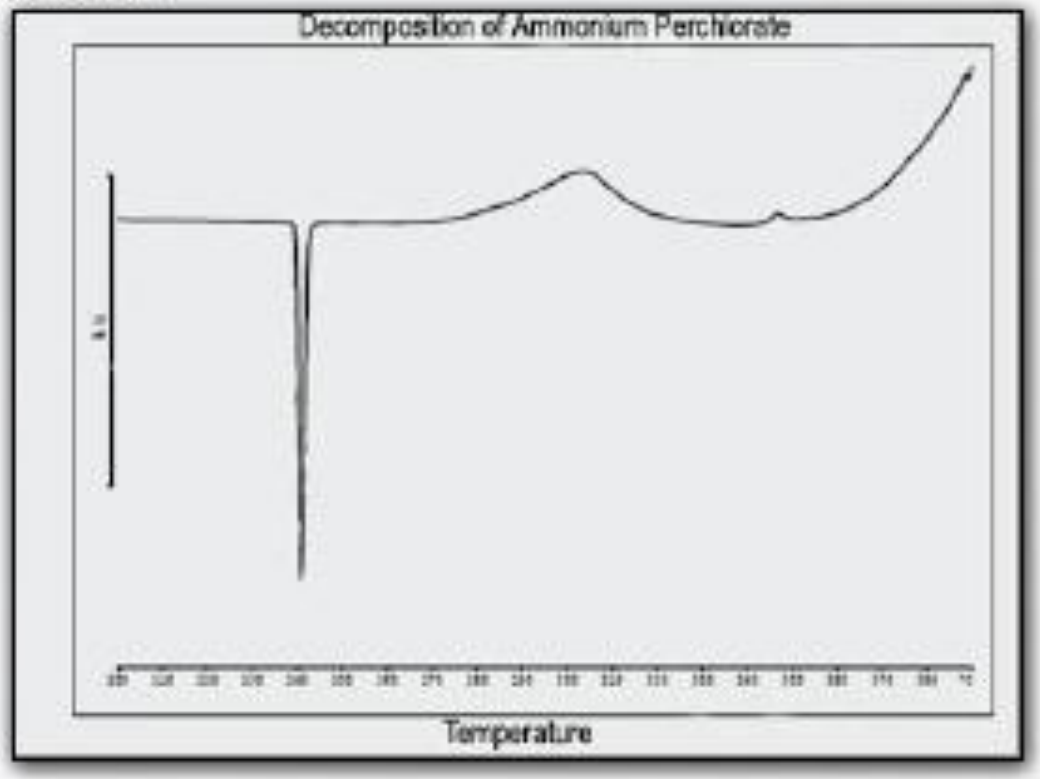
$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT = C_p \ln (T_2 - T_1)$$

When C_p is constant, the enthalpy increases linearly in time. The DSC curve is a straight line with slope C_p.

DSC Example 1

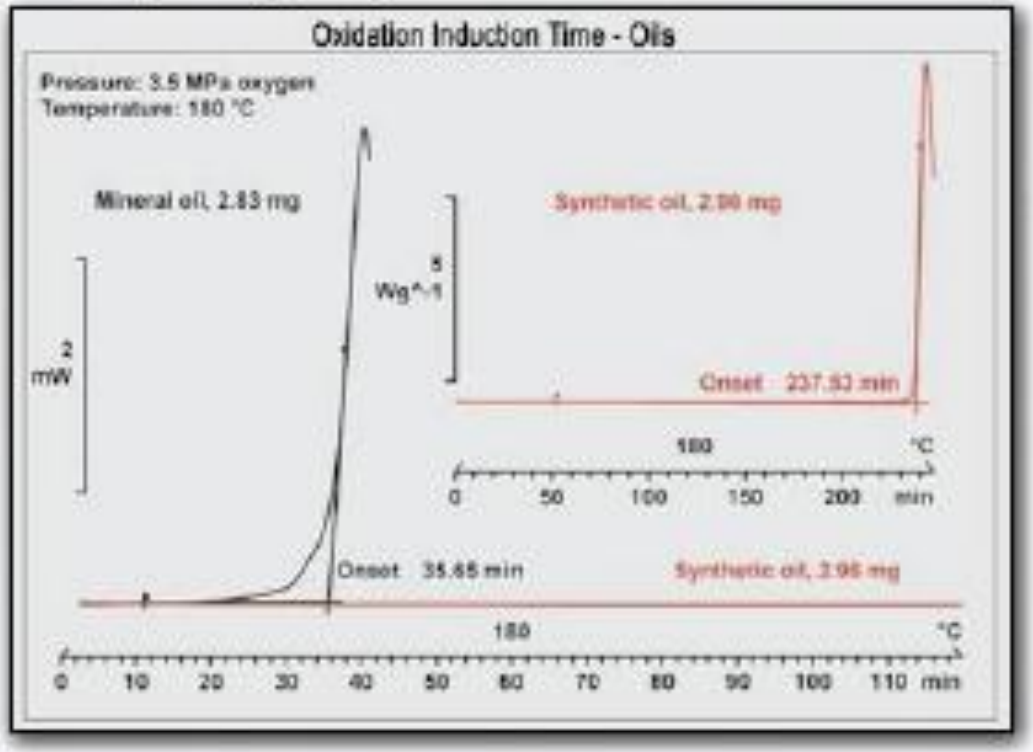
Ammonium perchlorate is an important component of high explosives. The stability of this material is critical to their safe handling. We see at 242 °C, the solid-solid phase transition to the cubic phase. At higher temperatures, one observes decomposition reactions.

This work was part of a study to investigate the mechanism of decomposition. Literature values for the activation energy ranged from 37 to 260 kJ/mol with different mechanisms proposed. This work clarified the mechanism and identified the activation energy as 115 kJ/mol.



DSC Example 2

An important test in the automotive industry is to determine the stability of lubricating oils at elevated temperatures and pressures. This will impact its utility as a lubricant in motors. In these case, the oil is brought to a high operating temperature and held there under an oxygen atmosphere. At some point, the oil begins to oxidize and then quickly decomposes exothermically. Note how the synthetic oil has a much longer Oxidation Induction Time than does the mineral oil.

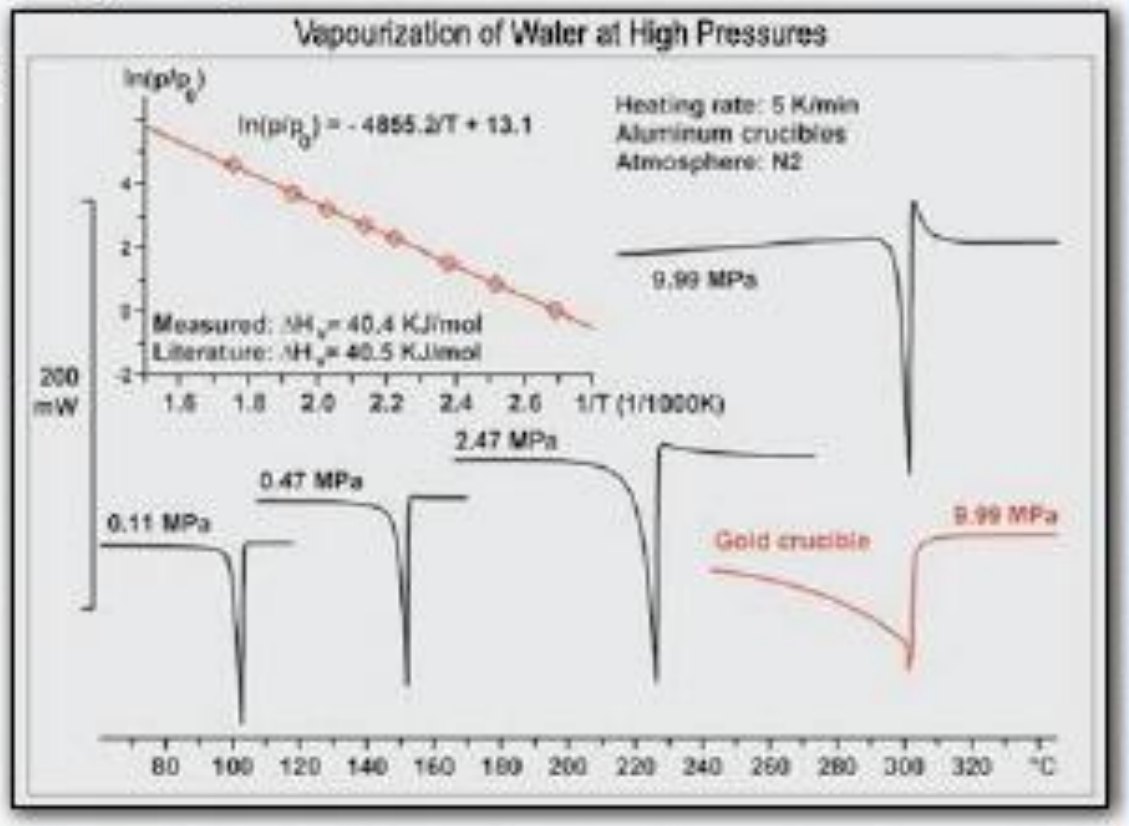


DSC Example 3

40 μL of H_2O is placed in an Al crucible at various elevated pressures. The boiling point is observed as a sharp, endothermic event. With the Clausius-Clapeyron equation, the enthalpy of vapourization can be measured.

$$\ln\left(\frac{P}{P_0}\right) = -\frac{\Delta H_{vap}}{R} \cdot \frac{1}{T} + C$$

Note how there is a small exothermic event that follows the vapourization. It is attributed to a reaction between the water and the aluminum, which is confirmed by carrying out the reaction in a gold crucible.



Crucibles

Choice of crucible is critical.

- Thermal properties of crucible.
- Reactive properties with samples.
- Catalytic behaviour with samples.

Aluminum: inexpensive, low temp

Copper: used as catalyst (testing polymers)

Gold: higher temp, expensive

Platinum: still higher temp, expensive.

Alumina (Al_2O_3): very high temp

Sapphire: crystalline alumina, more chemically resistant than amorphous Al_2O_3.

Combined Techniques

One can improve the utility of these techniques by combining them with other analytical procedures. Two successful instruments are obtained by combining as follows:

- TGA + Mass Spectrometry: TGA-MS
- TGA + Infrared Spectroscopy: TGA-FTIR

A TGA-MS instrument.

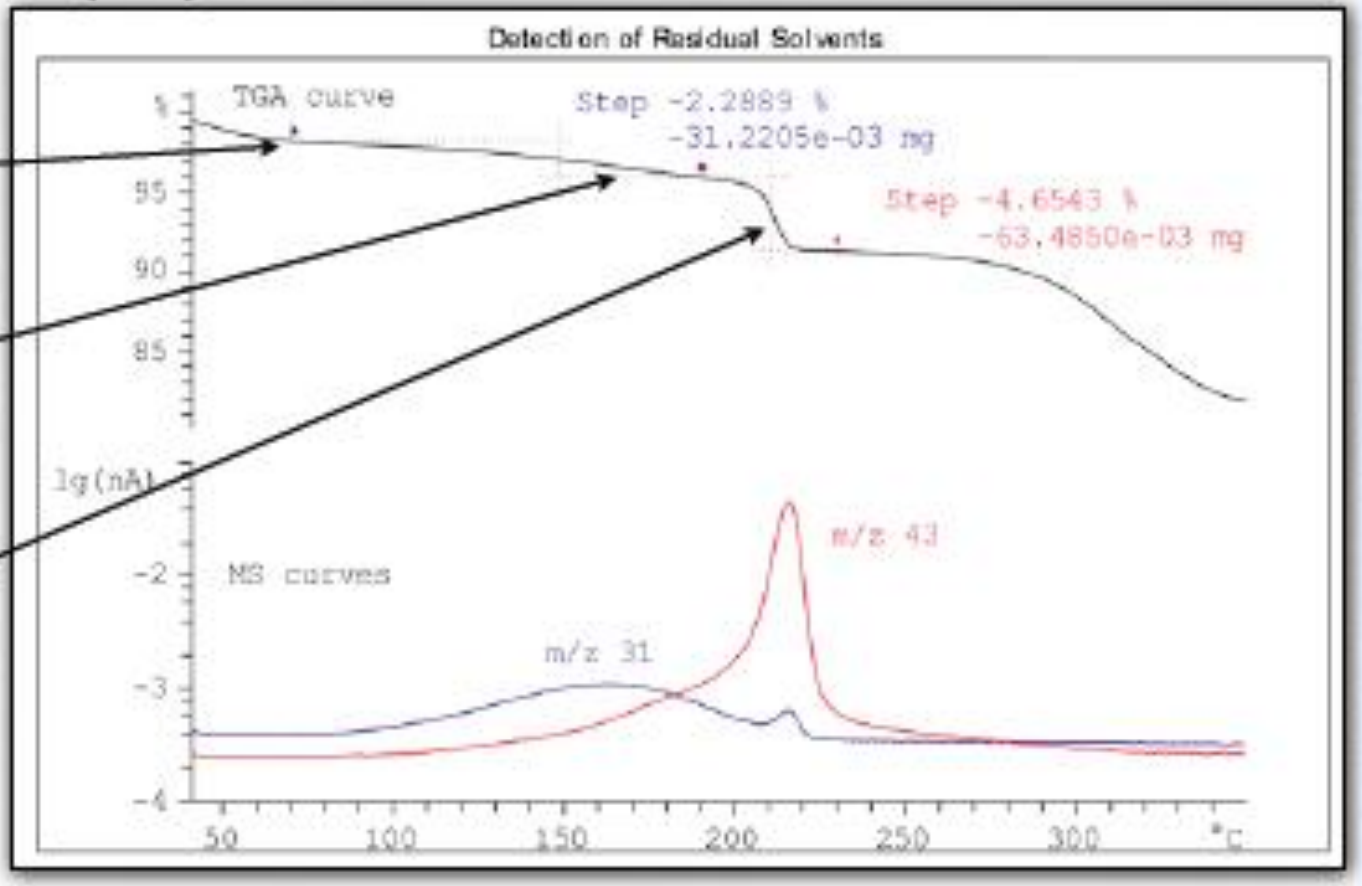
TGA-MS Application

A pharmaceutical compound is studied to determine the presence of solvents used in its precipitation. Both methanol and acetone are found.

Loss of adsorbed moisture

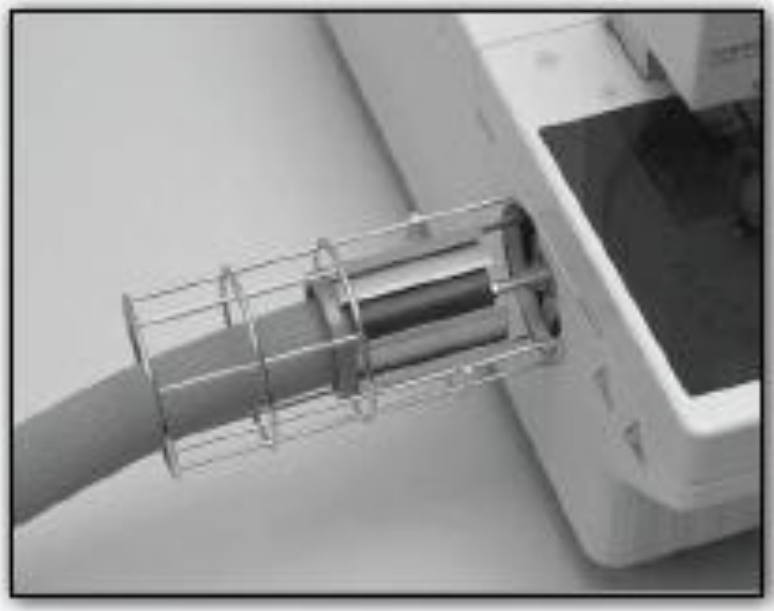
Loss of residual methanol

Loss of strongly bound acetone; must form integral part of precipitate.



TGA-FTIR

Here one couples the desorbing gases into the light path of an FTIR instrument. This helps to identify the molecular nature of the evolving gases associated with the weight loss event.



Such an instrument is coupled here to a Mettler-Toledo TGA.