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THERMAL AND EVOLVED GAS ANALYSIS -TGA-DTA-DSC AND FTIR SPECTROSCOPY-

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- INTRODUCTION
- THERMOGRAVIMETRIC ANALYSIS - TGA
- DIFFERENTIAL THERMAL ANALYSES - DTA
- DIFFERENTIAL SCANNING CALORIMETRY - DSC
- THERMOGRAVIMETRIC ANALYSIS (TGA) - FOURIE TRANSFORM INFRARED SPECTROSCOPY-FTIR
- FOURIE TRANSFORM INFRARED SPECTROSCOPY-FTIR

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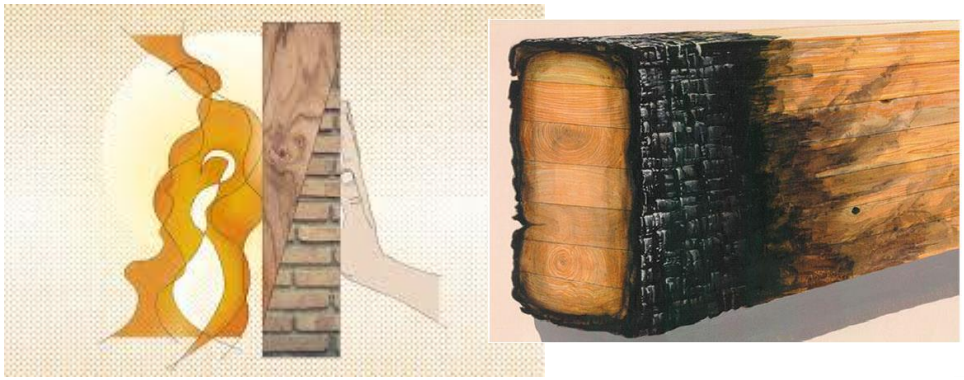
INTRODUCTION

Fire resistance is the property of materials or their assemblies that prevents or retards the passage of excessive heat, hot gasses or flames under conditions of use (NYCBC 2008).

Fire resistance rating is typically determined by measuring the ability of a passive fire protection material or assembly to withstand a fire resistance test. *This is quantified either as a measure of period of time for which a material or assembly withstands by specific fire resistance test or by evaluating through quantifiable criteria set by a specific fire resistance test, the ability of a material or assembly to perform a specific structural functionality.*



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INTRODUCTION

The fire resistance is necessary but not sufficient condition for obtaining the protection of construction against fires that presents a complex system containing the following measures:

- **Active fire protection** methods–include measures at the moment of fire and it necessitates to be switched on in the event of fire. It contains *fire suppression systems (fire extinguishers and water sprinklers), fire detection systems and hypoxic air as well as ventilation systems.* These actions may be manually operated, like a fire extinguisher or automatic, like a sprinkler [1,2,3]

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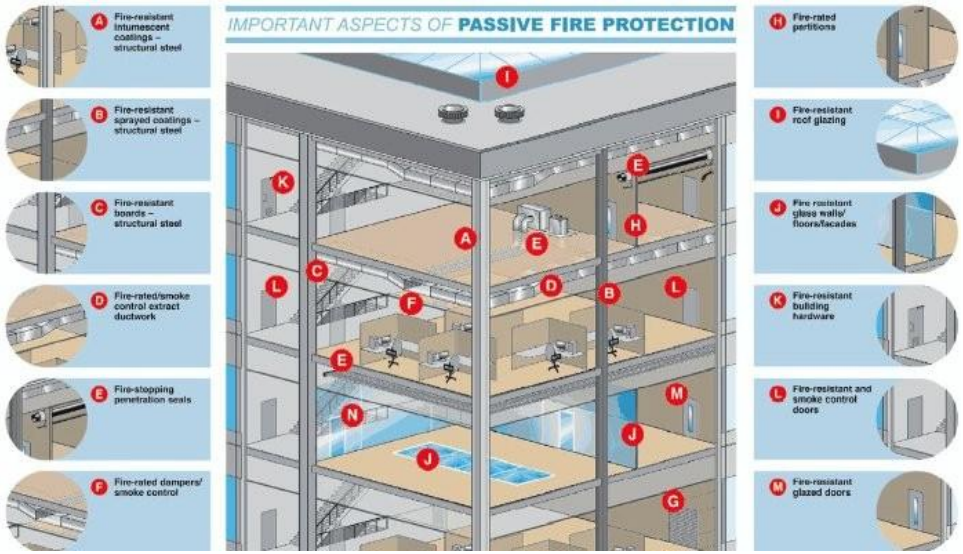
- **Passive fire protection** methods containing measures **aiming to** keep the fire from spreading quickly and providing time to escape for people in the building. It is built into the structure to provide stability and into walls and floors to separate the **building** into areas of manageable risk. These areas are designed to restrict the growth and spread of fire allowing occupants to escape and offering **protection** for firefighters. On the other hand, passive fire protection measures are those related to the features of the construction itself. *They are an integral part of the construction, present throughout its lifetime and serving as a fire spreading barrier as well as a thermal energy barrier preventing the failure of construction elements [4].*



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INTRODUCTION

- **Passive fire protection -** *For instance, application of special mortars and boards as well as radiation shielding could be used for passive fire protection [5*]. The cementitious mortars, sprayed on the construction element surface could prevent the mechanical deterioration of concrete structures exposed to fires above 300°C and diminish explosive spalling of concrete. *The boards* used for the passive fire protection are incombustible, made of endothermic materials such as gypsum or calcium silicate reinforced by inert fibers to avoid their disintegration. They are not effective for high temperature and long-duration fires. The materials used for passive fire protection are tested through standard tests, but some basic information regarding structural integrity, endothermic /exothermic effects as well as release of volatile gases could be obtained by thermal analysis like hyphenated TGA/DSC-FTIR analysis in order to determine material/product fire resistance performance [1,6,7,8].

- **Management systems** (such as evacuation procedures, communication procedures, compartmentalization, smoke extraction, etc.) [9].

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INTRODUCTION

From the above-mentioned measures it is evident that materials properties are most important for passive fire protection.

Drysdale [10] reported that basic function of a fire resistant material is to set a barrier that prevents or retards the transfer of excessive heat and spreading of hot gasses and flames.

The spreading of heat is coupled to the thermal conductivity and endothermicity of materials (endothermal effects could be determined by DSC analysis). The spreading of fire, release of gasses is related to the incombustibility and structural integrity of materials. The loss of structural integrity permit the materials or their assembly to prevent of acting as an effective barrier (this could also be determined by TGA/DSC coupled with FTIR thermal analysis) [11].

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THERMAL ANALYSIS

Thermal analysis (TA) is a group of techniques that study the properties of materials as they change with temperatures. It can provide information on the mechanism and the kinetics of thermal decomposition which may provide insight as to how material might react to a fire.

The studies about thermal degradation of solid material, are necessary for construction fire safety to understand the compartments of those materials in case of fire.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) coupled with Fourier transformation infrared spectroscopy (FTIR) are traditional methods for investigations of thermal degradation and release of volatile gasses.

They provide information of the type of phase change by determining the characteristics of weight loss in different heating rates and atmosphere conditions [11]. Beside the above-mentioned technique also is present differential thermal analysis (DTA).

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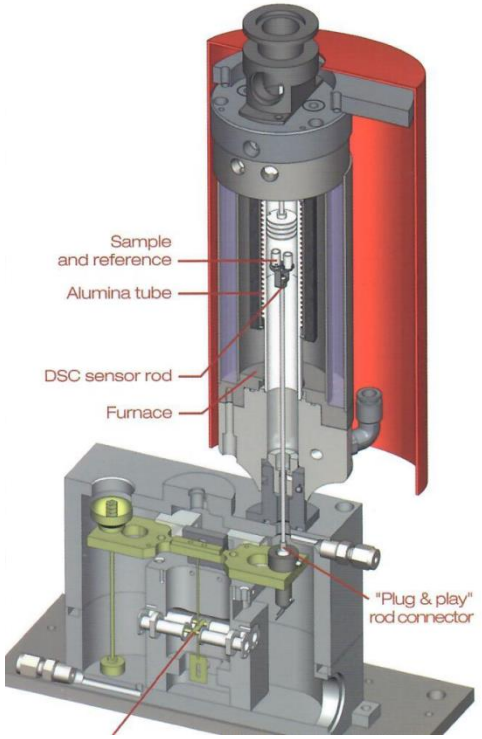
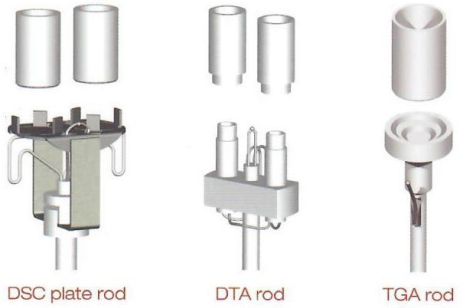
THERMAL ANALYSIS

TGA/DSC device-outside



TGA/DSC device-inside



Crucible and plate rod for TGA, DTA and DSC

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THERMOGRAVIMETRIC ANALYSIS **TGA**

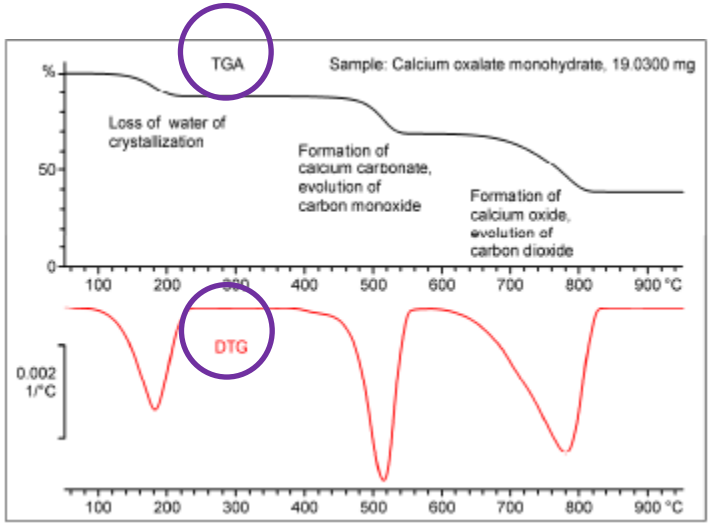
TGA measures the weight and hence mass of a sample as a function of temperature.

The acronym TG was previously used. Nowadays TGA is preferred in order to avoid confusion with Tg- the glass transition temperature.

TGA allows to

- detect changes in sample mass (gain or loss),
- determine stepwise changes in mass, usually as a percentage of the initial sample mass, and
- determine temperatures that characterize a step in the mass loss or mass gain curve.

DTG, Differential Thermogravimetry corresponds to the 1st derivative of the TGA curve.



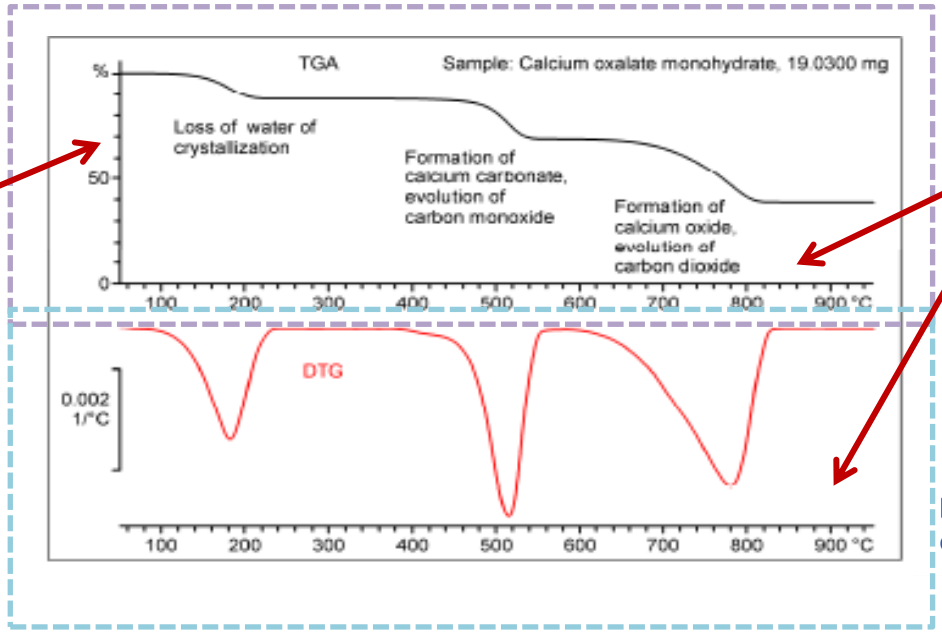
THERMOGRAVIMETRIC ANALYSIS **TGA**

TGA is an experimental technique in which the weight or strictly speaking the mass of a sample is measured as a function of sample temperature or as a function of the time in isothermal experiments.

The results of a TGA measurement are usually displayed as a TGA curve in which mass change is plotted against temperature or time. This shows the rate at which the mass changes and is known as the differential thermogravimetric or DTG curve. TGA measures the mass loss when it is heated, cooled or held isothermally in a defined atmosphere.

TGA

Mass change



Temperature change

DTG

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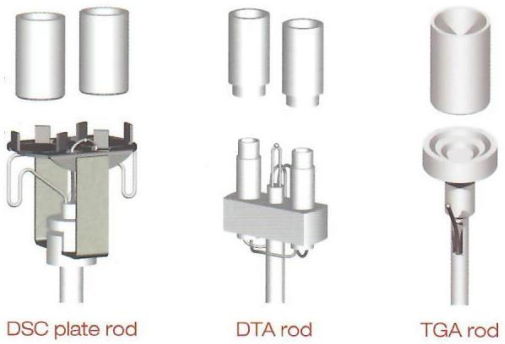
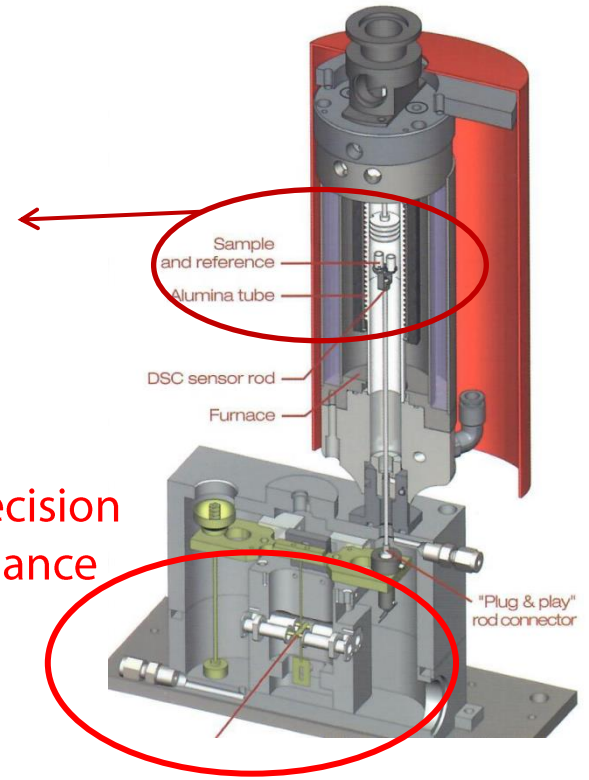
THERMOGRAVIMETRIC ANALYSIS **TGA**

A TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment.





A sample purge gas controls the sample environment. This gas may be inert (argon in our experiment) or a reactive gas (synthetic air) that flows over the sample and exits through an exhaust.

TGA can be tested with milligram-sized samples (in our experiments 30 mg)

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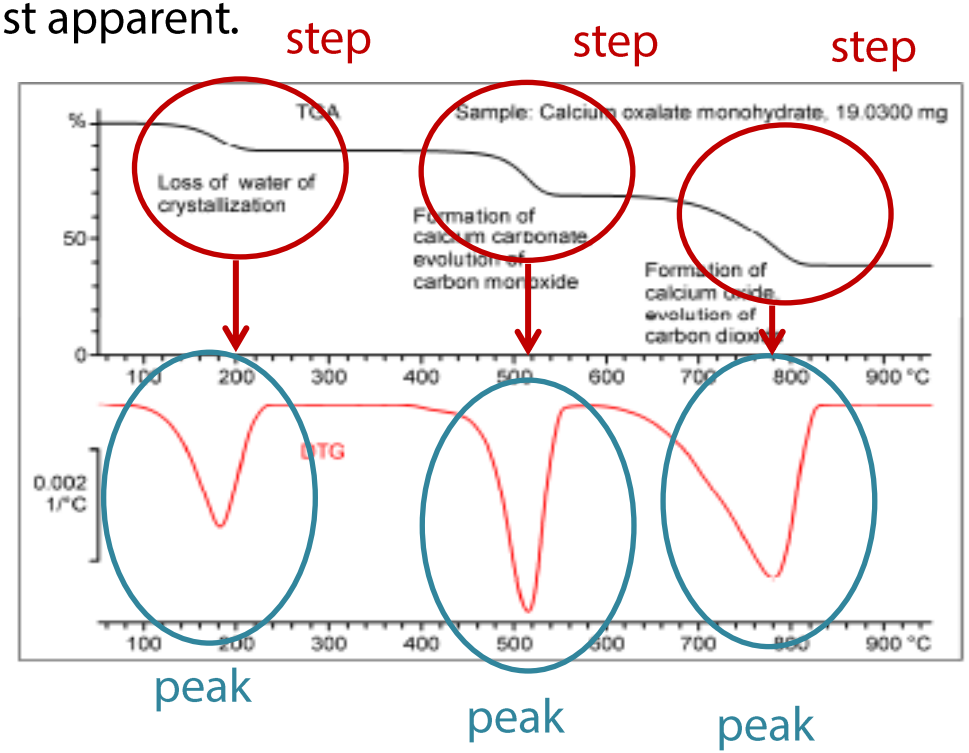
THERMOGRAVIMETRIC ANALYSIS **TGA**

Mass changes occur when the sample loses material or reacts with the surrounding atmosphere.

A number of different effects can cause a sample to lose, or even gain, mass and so produce steps in the TGA curve. This produces ***steps in the TGA curve*** or ***peaks in the DTG curve***. Derivative weight loss (DTG) curve can be used to tell the point at which weight loss is most apparent.



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THERMOGRAVIMETRIC ANALYSIS **TGA**

Application of thermogravimetry is **limited to events with detectable mass changes** Otherwise, other techniques, such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC), must be used.

The main thermal events recorded by TG are summarized in Table:

Physical phenomena	
Sublimation	A (solid) → A (gas)
Vaporization	A (liquid) → A (gas)
Adsorption	A (solid) + B (gas) → A (solid) (Bgas-ads)
Absorption	A (solid) + B (gas) → A (solid) (Bgas-abs)
Desorption	A (solid) (Bgas-ads) → A (solid) + B (gas) A (solid) (Bgas-abs) → A (solid) + B (gas)
Chemical phenomena	
Oxidation	A (solid) + B (gas) → C (solid)
Pyrolisis	A (solid) → B (solid) + Gases
Volatilization	A (solid) + B (gas) → Gases

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THERMOGRAVIMETRIC ANALYSIS **TGA**

Performing of measurements

The results of TGA measurements are influenced by various **factors** such as [13]:

- *Method parameters: heating rate, atmosphere (air, nitrogen, argon; pressure).*
- *Sample preparation: sample size, homogeneity and morphology of the sample: coarse crystals, fine powder.*
- *Choice of crucible .*
- *Instrumental influences such as buoyancy and gas flow effects. These can be reduced or eliminated by performing blank curve subtraction.*
- *Changes in the physical properties of the sample during the measurement. For example, a change in emissivity (which affects the heat transfer within the sample and from the furnace to the sample), or the volume (which leads to a change in buoyancy).*
- *The sample may spit or move and artifacts caused by such events can be minimized by grinding the sample or covering with a platinum mesh.*

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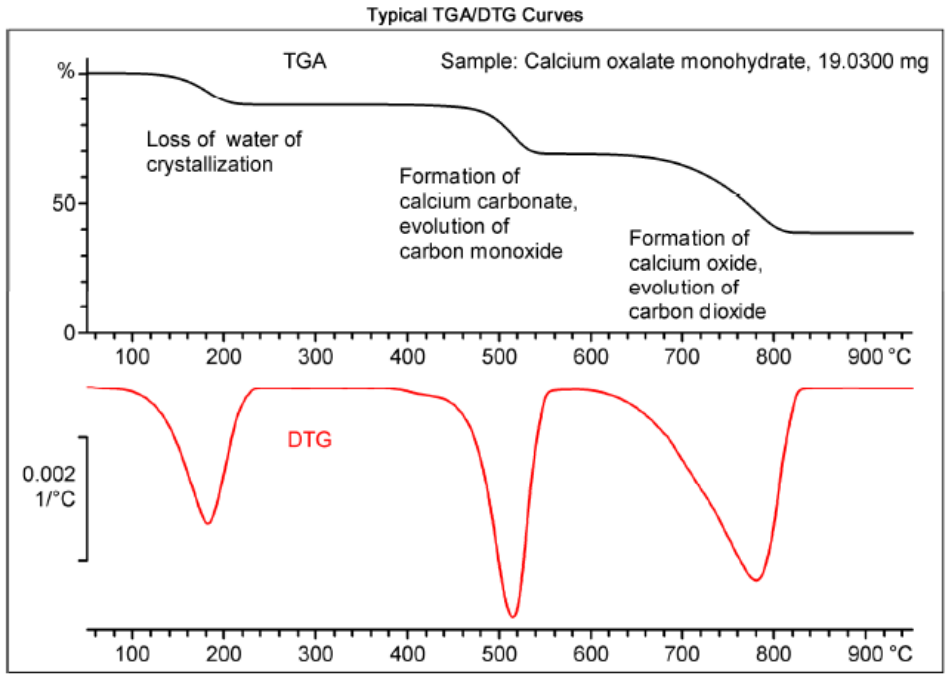
THERMOGRAVIMETRIC ANALYSIS **TGA**

Example

A TGA thermal curve is displayed from left to right. The descending TGA thermal curve indicates a weight loss occurred.

A 19.03 mg sample of calcium oxalate monoxydrate was analyzed (Figure).

Temperature Program: Heat from 40 °C to 900 °C heating rate 30 °C/minute in nitrogen atmosphere with a purge rate of 20 mL/minute.



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THERMOGRAVIMETRIC ANALYSIS **TGA**

Decomposition of Calcium monooxalate can be expressed according the following reactions:

- Loss of water of crystallization:

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O\uparrow$$

- Decomposition of calcium oxalates and formation of calcium carbonate and carbon monoxide:

$$CaC_2O_4 \rightarrow CaCO_3 + CO\uparrow$$

- Calcium carbonate decomposition and formation of calcium oxide and evolution of carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

The TGA curve has been normalized (divided by the sample mass) and therefore begins at 100%. The temperature range of the three mass loss steps is particularly clear in the first derivative or DTG curve.

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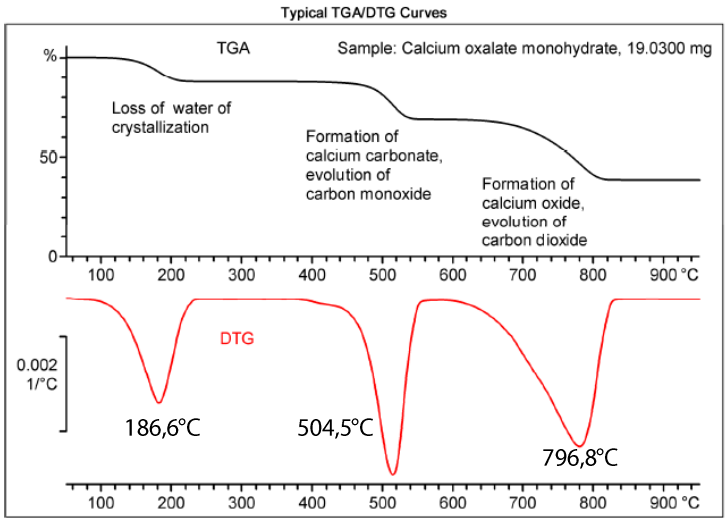
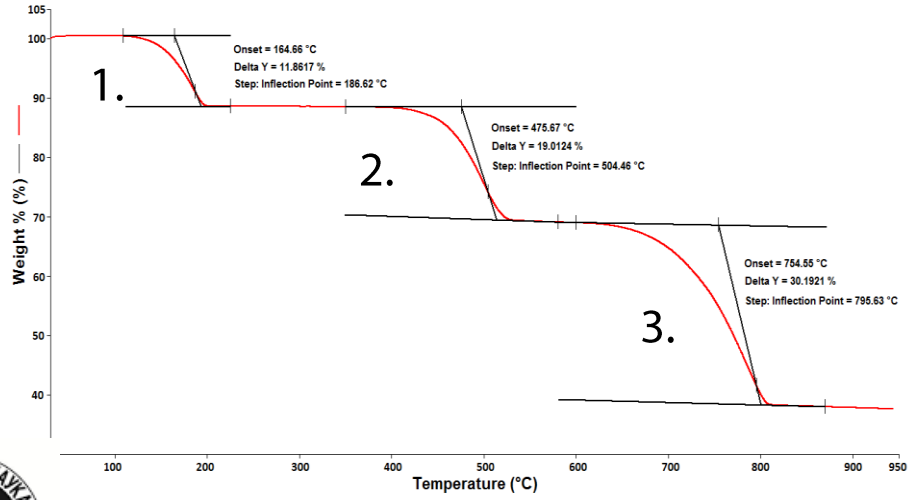
THERMOGRAVIMETRIC ANALYSIS **TGA**



In Figure are presented TGA and DTG curves for phase changes during heating of calcium monooxalate. TGA curve shows three steps followed by mass changes.



In all three cases mass changes were caused by the release of the following gasses:

1. H_2O (11.86%),
2. CO (19%), and
3. CO_2 (30.2%)

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THERMOGRAVIMETRIC ANALYSIS **TGA**

Unfortunately, the temperature of above-mentioned reactions could not be precisely determined from the TGA curve. The position of DTG peaks determined the temperature with highest mass changes: water loss temperature (186.6°C), decomposition of calcium oxalate (504,5°C) and decomposition of calcium carbonate (796,8°C).

DTG curve presents the rate of mass change. For the evaluation of the properties of materials during exposure to fire, very informative could be peaks intensities of DTG peaks.

Namely, they indicates, that at temperatures denoted by peak position, the rate of releasing of volatile gasses. If the rate is higher the release of gasses is more intensive which would provoke higher pressure inside material. For instance, in Figure is showed that temperature 504,5°C is the one with highest rate of gas release.

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Differential Thermal Analyses **DTA**

In **DTA** the temperature difference between the sample and an inert reference substance is measured as a function of temperature. The DTA signal is °C or K. Previously, only the thermocouple voltage in mV or µV was displayed.

The measurement signal represents the temperature difference between the sample and a previously measured and stored blank sample.

DTA allows:
- to detect endothermic and exothermic effects, and
- to determine temperatures that characterize thermal effects.

In DTA, temperature differences ΔT relative to a thermally inert material are measured during heating or cooling of a sample. The DTA curve records these differences during reactions in the sample, showing thermal effects as deviations from the zero line.

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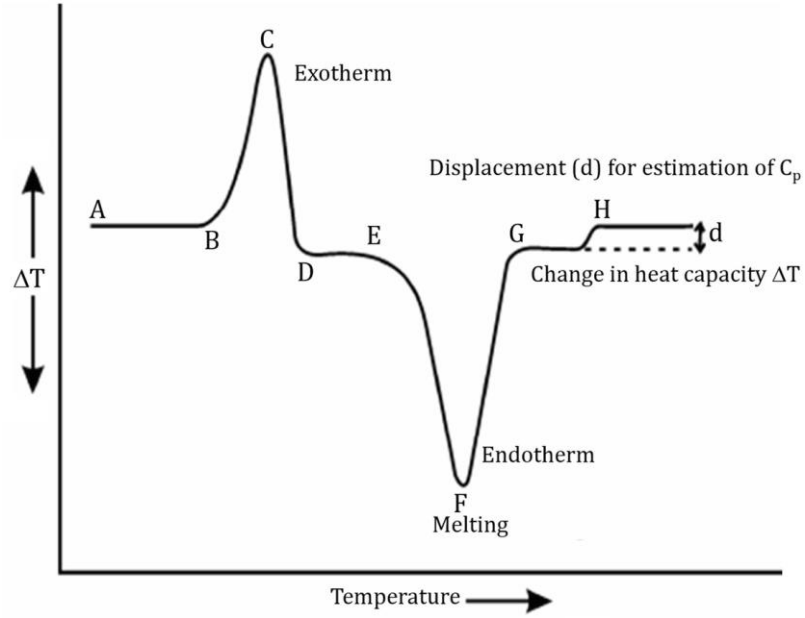
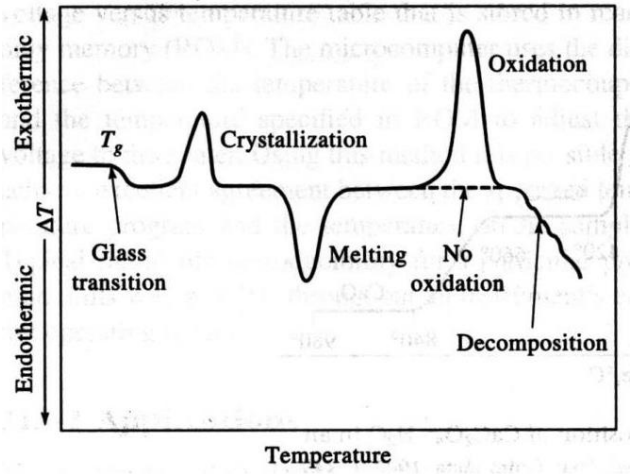
Differential Thermal Analyses **DTA**

Coordinates of the resulting DTA diagrams are ΔT(ordinate) and sample temperature (abscissa), both given in ^{0}C. Accordingly, whether a reaction requires heat (endothermic reaction) or releases heat (exothermic reaction), the curve slopes toward one side or the other of the zero line. Conventionally, an endothermic reaction is graphed sloping down (see figure).





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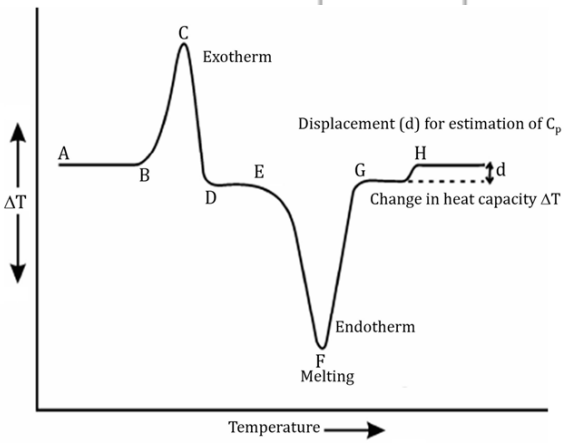
Differential Thermal Analyses **DTA**

When the differences in heat capacity and heat conduction between a sample and a simultaneously heated inert substance are ignored, the sample and inert substance should be at the same temperature during heating as long as there is no reaction in the sample. Such is the case with a small sample and an inert reference material that does not differ greatly from the sample chemically.

At the free ends of two thermocouples, the welded ends of which are imbedded in the sample and the inert substance, respectively (see Figure), there is initially no potential. The graph of the difference in voltage as a function of time and/or temperature is parallel to the axis. As soon as an endothermic or exothermic reaction begins, the heating of the sample (and the sample holder block) either remains below or rises beyond the furnace temperature. The sample remains colder (through the use of the supplied heat as reaction heat) or becomes warmer (through heat released by an exothermic reaction) than the inert reference material. The potential is measured at the free ends of the thermocouples' differential connections, and the deviation from the zero line on the DT A curve is thus obtained.



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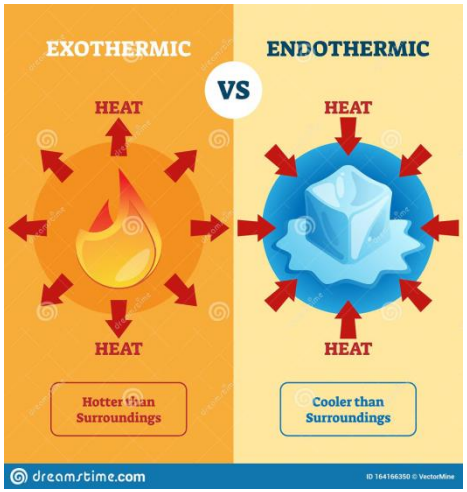
Differential Thermal Analyses **DTA**

Endothermic, heat consuming reactions include:

- dehydration (releasing adsorbed water and water bound in the structure as H20 or OH),
- structural decomposition,
- melting, evaporation and sublimation reactions,
- structural transformations (heating),
- magnetic transformations (demagnetizing of a ferromagnetic substance).
- reduction.

Exothermic, heat releasing reactions include:

- oxidation, including combustion,
- processes of freezing,
- reconstruction of a crystal structure,
- structural transformations (cooling).



For the materials that are used for passive fire protection is preferential to have endothermic effects, as these effects heat is consumed on these effect instead on increase of material surface temperature

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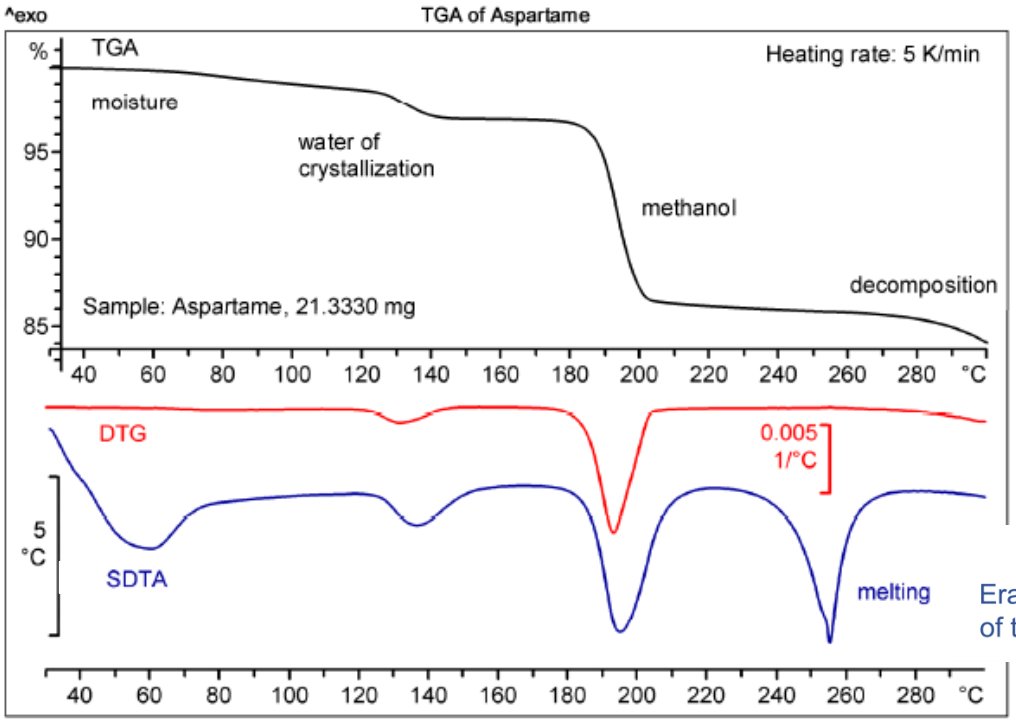
Differential Thermal Analyses **DTA**

EXAMPLE

In the Figure is presented the changes during thermal treatment of artificial sweetener aspartame. It is interesting to point out the differences in information obtained by DTG and DTA curves. Peaks of DTG curves give information related to temperatures of phase transformations followed by mass changes. DTA peaks provide information about phase transformation which are followed by mass change and without mass change (like melting, solidification, etc). Futhermore, DTA effects presented in Figure are endothermic.



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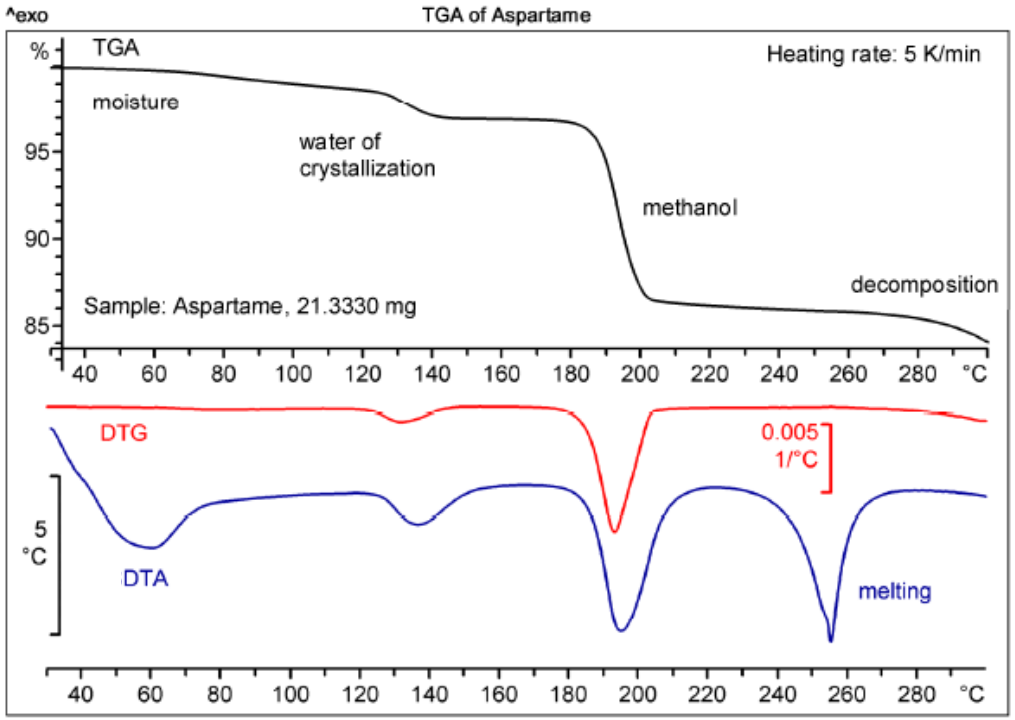
Differential Thermal Analyses **DTA**

First, the phase transformation at 60°C is not followed by mass change, but the water of crystallization lost at 130 °C is followed by mass change. Latter on this is followed by the elimination of methanol at 180 °C and the formation of a piperazine ring. This reaction takes place in an extremely narrow temperature range of just 20 K for 1 to 99% conversion. The DTA curve shows that the piperazine derivative melts at 250 °C.



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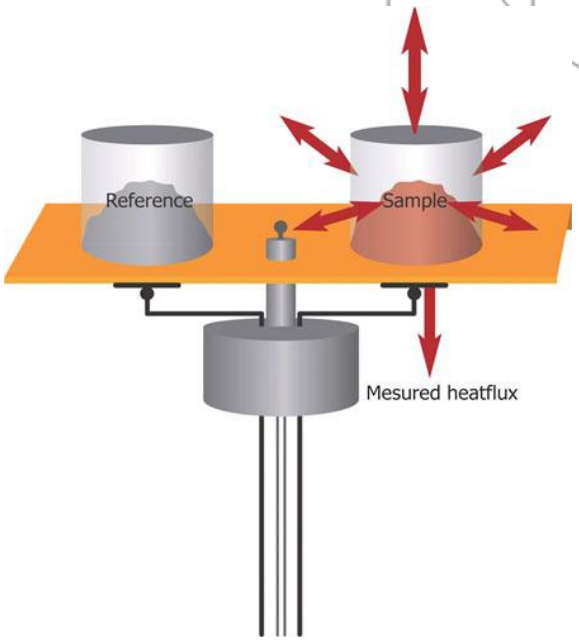
Differential Scanning Calorimetry **DSC**

DSC is defined as followed by ICTAC: "*A technique in which the heat flux (thermal power) to (or from) a sample is measured versus time or temperature while the temperature of the sample is programmed, in a controlled atmosphere. The difference of heat flux between a crucible containing the sample and a reference crucible (empty or not) is measured.*"

In a heat flux DSC, the specimen surroundings (generally the furnace and detector) are at constant temperature (isothermal mode) or at a variable temperature (scanning temperature mode).



A defined exchange of heat takes place between the specimen and its surroundings. The amount of ***heat flux*** (heat flow rate) is determined.

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Differential Scanning Calorimetry **DSC**

True differential scanning calorimetry (DSC) gives a quantitative measure of the electrical energy, for resistance heating, which must be supplied to, or withheld from, the sample in order to maintain a zero-temperature difference between the sample and an inert reference material during heating.

This principle of operation limits the useful range of true DSC to temperatures where conduction, not radiation, is the main heat transfer mechanism, i.e.<1000 K.

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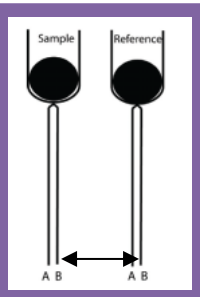
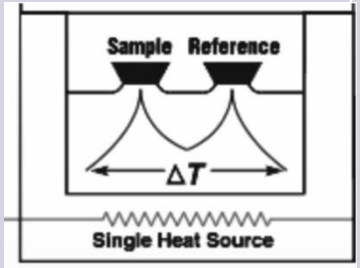
Differences between **DTA** and **DSC**

DTA is registration of temperature differences ΔT relative to a thermally inert material which are measured during heating or cooling of a sample. It is similar to the objective of **DSC**. But, there is also great difference. **DSC** is rather more versatile than **DTA**. **DSC** allows quantitative determination of heat capacity, and also the enthalpy of a phase transformation. The differences between DTA and DSC method could be summarized as:

DTA	 **ΔT between sample and reference**	**Measuring:** **ΔT (temperature difference)** **Characteristics:** **More robust, measurements can be done in wider T range, in more aggressive environment (oxidation atmosphere), possible combination with TGA to measure mass change**	**Application:** **Phase reaction, phase diagram**
DSC	 ΔT between sample and reference	**Measuring:** T and ΔH of transformation, Cp measurements **Characteristics:** DSC is more sensitive than DTA	**Application:** Specific heat, heat of transition

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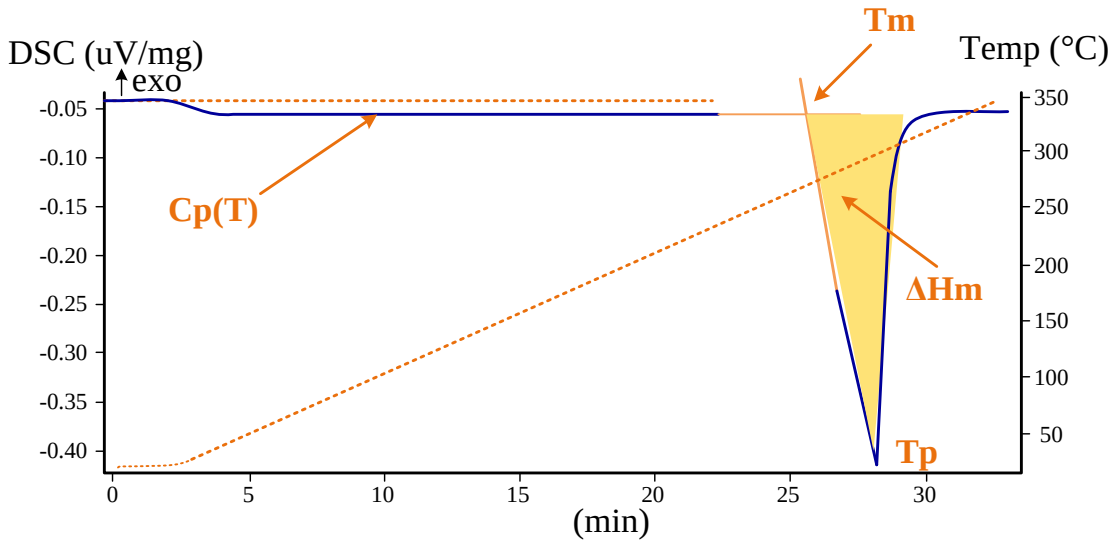
Differential Scanning Calorimetry **DSC**

From the **DSC curve** different important information are obtained (Figure):

- the temperature of the transformation (generally measured at the top of the peak), **Tp**
- the heat related to the transformation (area under peak), **ΔHm**
- the rate of the transformation,
- specific heat capacity, c_p



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Differential Scanning Calorimetry **DSC**

In order to get accurate measurements of temperature of transition, the DSC has to be **calibrated** using reference materials. The experimental procedures for such a correction are described in different standards, especially ISO standard.

As the DSC signal is equivalent to a thermal power (expressed in mW), the integration of the DSC peak between the time related to start of the peak and time corresponding to the end of the peak, will generate its value.

In this manner it is possible to evaluate material properties such as:

- *glass transition temperature,*
- *melting,*
- *crystallization,*
- *specific heat capacity,*
- *cure process,*
- *purity,*
- *oxidation behavior, and*
- *thermal stability.*

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Differential Scanning Calorimetry **DSC**

Sample preparation

DSC samples are analyzed in small vessels known as crucible or pans, designed for optimal thermal conductivity and minimum reaction with the samples.

Crucibles

Crucibles

The choice of the crucible is a very important step. It is needed that there is no interaction between the crucible and the sample during the test. In the same time it is needed that the crucible is a good heat conductor in order to ensure a good heat transfer between the sample and the thermocouple. Different materials are used to produce adequate crucibles:

- **Aluminium** (up to 500 ◦C), (organic products, polymer materials, studying the dehydration of mineral substances (plaster, gypsum, etc.).
- **Alumina** (especially required for metallic samples),
- **Platinum** (especially required for inorganic samples),
- **Graphite and tungsten** (for temperature above 1750 ◦C).

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Differential Scanning Calorimetry **DSC**

Atmosphere

As the crucible is open, the control of the gas above the sample is a very important parameter. Different types of gas atmosphere are available according to the experiment to be run:

- **Inert atmosphere** (nitrogen, argon, helium) to protect the sample from any oxidation.
- **Oxidative atmosphere** (air, oxygen) to be used for oxidation and combustion investigations.
- **Reactive gas** (hydrogen, carbon monoxide, ammonia, . . .) for adsorption and absorption reactions.
- **Water vapour** for hydration reactions.

In our experiment could be used argon and synthetic air.

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Differential Scanning Calorimetry **DSC**

Definition of experimental conditions are required for DSC analysis.

At first is necessary to define the temperature range than the heating rate. Definition of these parameters for the measurement are based on someone knowledge of the physical and chemical properties of the sample.

In our experiment (Setaram, Labsys Evo):

- *Temperature range:* maximum temperature 1150°C
- *Heating rate*: in the range from 5 up to 100 K/min

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Differential Scanning Calorimetry **DSC**

Interpretation of DSC diagrams

Thermal effects are distinct deviations from the more or less straight line DSC curve. *They are caused by the sample undergoing physical transitions or chemical reactions.*

The interpretation of DSC curves requires considerable experience in thermal analysis as well as knowledge of the possible reactions that sample could undergo.

- Interpretation is often facilitated by measuring a cooling curve directly afterward.
- It is a good idea to heat the sample a second time. Differences between the first and the second heating curves can be very informative.

If two effects overlap, than it is necessary to separate them by using faster or slower heating rates, and smaller sample weights. Here, one should take into account that faster heating rates cause a marked shift in the peak maxima of chemical reactions to higher temperatures.

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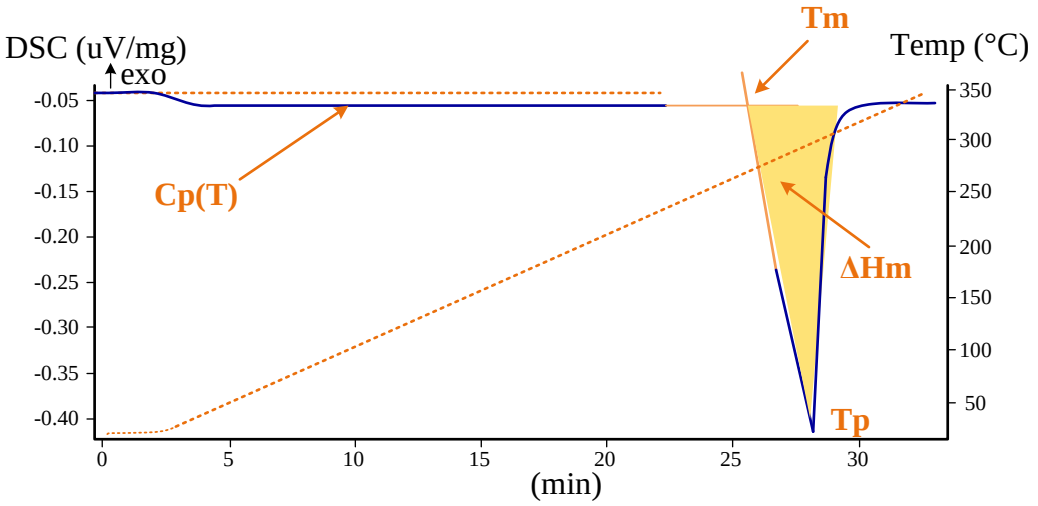
Differential Scanning Calorimetry **DSC**

During interpretation of the curve it is necessary to determine (Figure):

- The onset temperature, T_m
- The temperature of the reaction-peak temperature, T_p
- The enthalpy of the reaction, ΔH_m, peak area determined by integration.



If someone is interested in determination of c_p value than certain blank curve should be determined.

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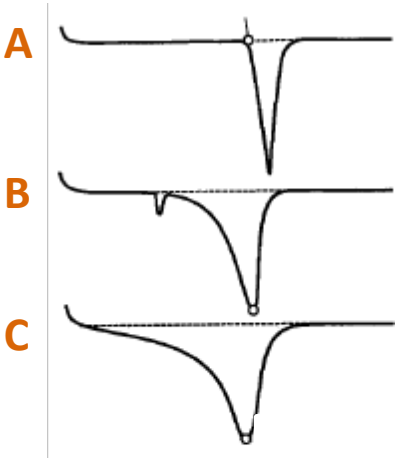
Differential Scanning Calorimetry **DSC**

The shape of the DSC curve is usually very characteristic and helps to identify the nature of the effect. The shape depends on whether the transformation is physical or chemical.



A-When the substance is pure, the low temperature side of the melting peak is almost a straight line, while the melting point (melting temperature) corresponds to the onset.

B,C-Impure and polymeric samples, whose melting curves are concave in shape, are characterized by the temperatures of their peak maxima.
Substances with eutectic impurities exhibit two peaks (B): first the eutectic peak, whose size is proportional to the amount of impurity, and then the main melting peak. Sometimes the eutectic is amorphous so the first peak is missing.

C-Partially crystalline polymers give rise to very broad melting peaks because of the size distribution of the crystallites.
The structure of some type of polymers cannot be completely, but partly crystalline.

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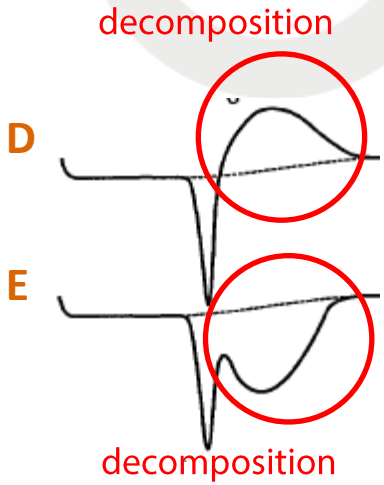
Differential Scanning Calorimetry **DSC**



D,E-Many organic compounds melt with decomposition (exothermic or endothermic). An endothermic peak in a DSC heating curve is a melting peak if the sample weight does not decrease significantly over the course of the peak. A number of substances exhibit a marked degree of sublimation around the melting temperature. If hermetically sealed pans are used, the DSC curve is not affected by sublimation and evaporation. The sample appears to have visibly melted after the measurement. Powdery organic substances, in particular, form a melt that on cooling either solidifies to a glass (with no exothermic crystallization peak) or crystallizes with an exothermic peak.

Comment: Many metals have a high melting point oxide layer on their surface. After melting, the oxide layer remains behind as a rigid envelope. This impure samples and mixtures often show several peaks.

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Differential Scanning Calorimetry **DSC**

The other important information associated with the DSC peak is related to the kinetics of the transformation- ***dh/dt*** denotes the rate of transformation.

As fire resistance depends on kinetics as well as on the fact whether the material has endothermic or exothermic peaks, the DSC signal corresponds to a heat flow rate, while the shape of the peak directly informs on the kinetics of transformation.

It is of really great importance for the evolution of fire resistance. For example, a sharp peak indicates a high rate of reaction. At the top of the peak, dh/dt_{max} , the rate of the reaction reaches the maximum value.

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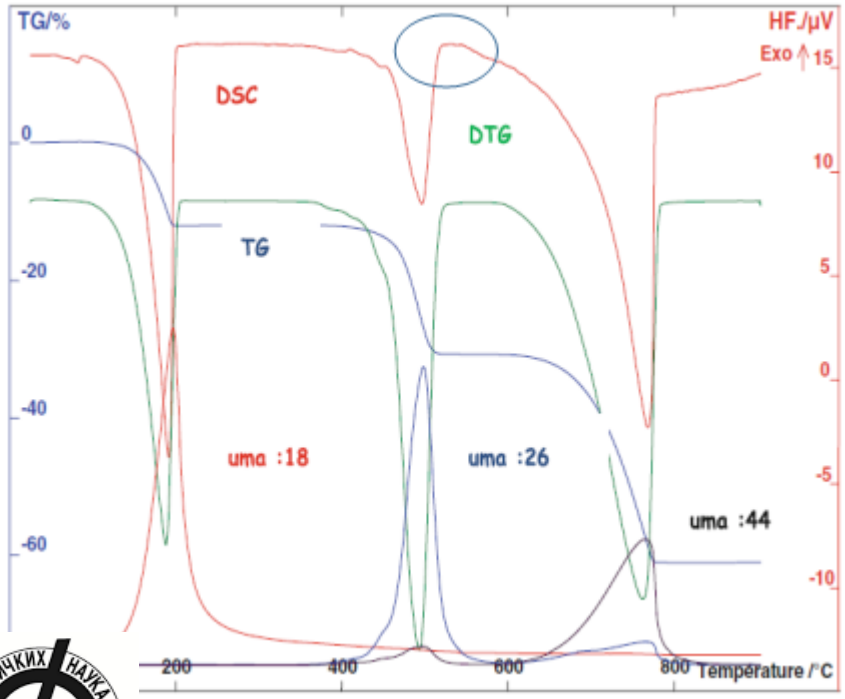
Differential Scanning Calorimetry **DSC**

EXAMPLE

An example of the significance of DSC curve shape could be seen in the following example. In the Figure is presented decomposition of calcium oxalate CaC_2O_4,H_2O. The analysis was performed by TG, DSC analysis coupled with MS (mass spectroscopy).

H_2O | $CaCO_3;CO$ | $CO_2;CO$



The decomposition of this compound is given through three stages:

- the decomposition of the hydrate (H_2O);
- the decomposition of calcium oxalate in calcium carbonate and carbon monoxide (CO); and
- the decomposition of the calcium carbonate in calcium oxide and calcium dioxide (CO_2).

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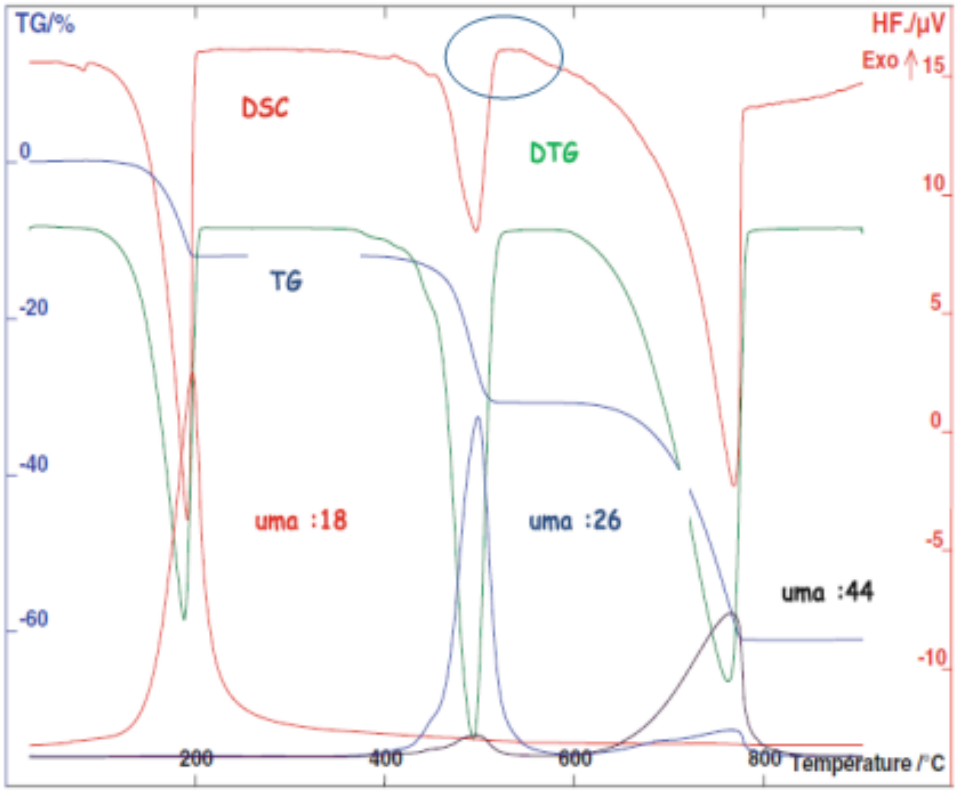
Differential Scanning Calorimetry **DSC**

Small exothermic deviation at the end of the second endothermic peak, but it is not detectable on the TGA curve (denoted as circle in Figure), indicates the presence of some traces of air in the furnace that reacts with CO. Concerning the fire resistance, the presence of endothermic peaks indicate that calcium oxalate **will not contribute to fire spreading.**



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Coupled Fourier transform infrared spectrometer **FTIR** and **TGA**

TGA-FTIR analyses is a system that allows qualitative information related to determination the gaseous reaction or decomposition products formed in experiment while quantitative information are about mass changes (TGA).

One type of reaction is decomposition. In a decomposition process, chemical bonds break and complex compounds or polymers decompose to form gaseous products such as water, carbon dioxide or hydrocarbons. Volatile decomposition products can be identified by connecting the TGA to a Fourier transform infrared spectrometer (FTIR).

Questions regarding the identity of the gaseous products evolved during the mass change however will remain unanswered without the device for evolved gas analysis, i.e. if TGA is not coupled to a suitable system for gas analysis.

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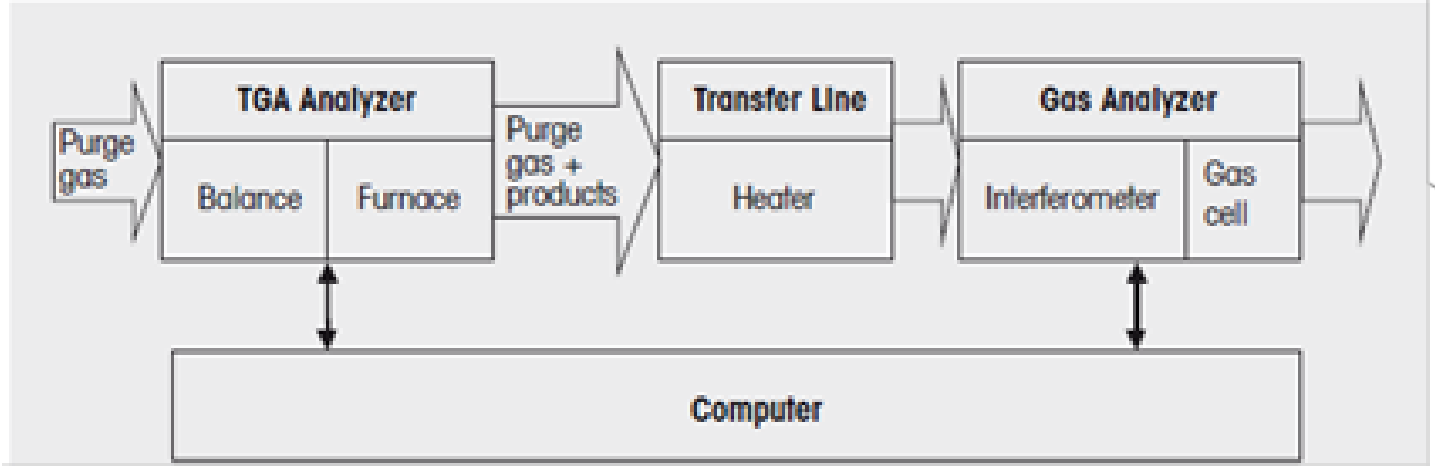
Fourier transform infrared spectrometer **FTIR**

The gases and volatile products evolved during the heating process in the TGA have to be transferred to the gas analysis system. This is accomplished using a transfer line, This is typically maintained at a temperature of 200°C to prevent gaseous products from condensing. The schema for TGA-FTIR measurements is presented in the Figure:



The gas analysis technique, presented in Figure, shows that the gases and volatile products evolved during the heating process in the TGA have to be transferred to the gas analysis system.

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Fourier transform infrared spectrometer **FTIR**

FTIR spectroscopy is based on the interaction of molecules with electromagnetic radiation in the mid-infrared spectral region 4000 to 400 cm^{-1}. The energy used for analysis is so low that ionization, fragmentation or dissociation cannot occur.

If a molecule is irradiated with broad-band infrared light, it absorbs energy at certain frequencies corresponding to the vibration or rotations it excites in that molecule. The infrared spectrometer measures the transmittance of the incident radiation as a function of wavelength.

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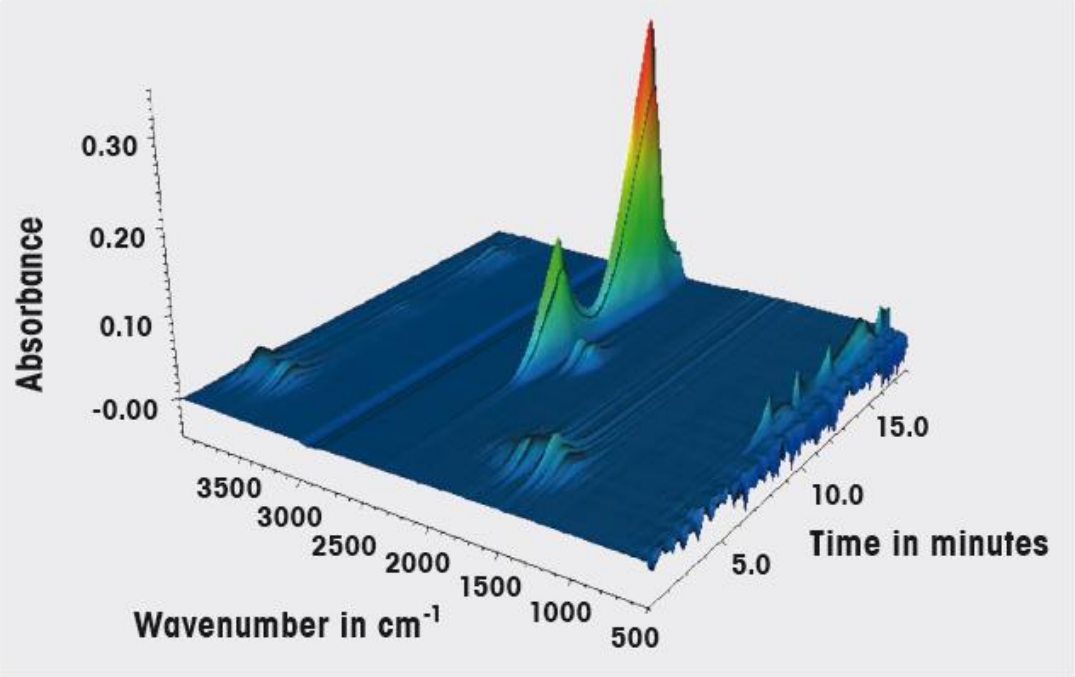
Fourier transform infrared spectrometer **FTIR**

The resulting infrared spectrum is characteristic for the particular molecule and allows the functional groups of a molecule to be identified. The technique is therefore ideal for the identification of small molecules produced during TGA analysis.

This is illustrated in Figure which displays the infrared spectrum of gaseous HCl. In this example, the absorbance (ordinate) is plotted as a function of the wavenumber (abscissa). This is the usual presentation for FTIR spectra.



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Fourier transform infrared spectrometer **FTIR**

The transmittance (T) is the ratio of the light intensity transmitted by the sample (I) to the incident on it (I_o) that is I/I_o at a particular wavelength and is usually expressed as a percentage value. The absorbance (A) is the negative logarithm of the transmittance and is given by A=-logT. Compared with transmittance, the absorbance has the advantage that it is a linear function of concentration.

FTIR spectrometer can record a spectrum in just a few seconds or even less. This means that TGA and FTIR measurements are effectively performed simultaneously.

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Fourier transform infrared spectrometer **FTIR**

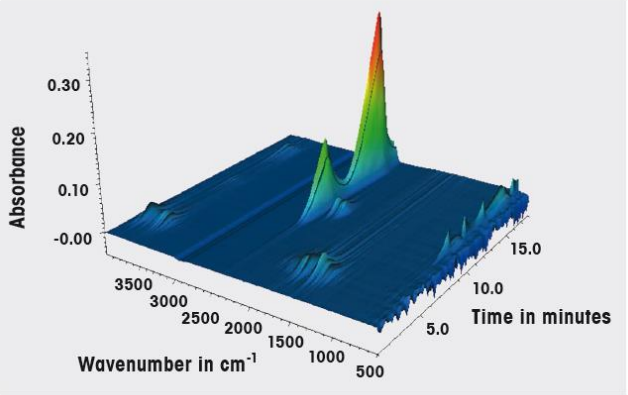
MEASURMENTS

For combined TGA-FTIR measurements, the user must set the following parameters:

- the speed at which the mirror in the interferometer moves;
- the number of scans to be accumulated for a spectrum; and
- the resolution in wavenumbers for recording the spectrum.

These three parameters determine how long the spectrometer takes to measure a spectrum. The time multiplied by the heating rate yields the temperature resolution with which information about the composition of the evolved gases is recorded.

Figure shows an example of how a series of FTIR spectra from a measurement can be displayed. In this diagram, the x-axis is the wavenumber axis, that is, the individual spectra are plotted parallel to the x-xis. The y-axis is he time axis and the z-axis shows the absorbance.



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Fourier transform infrared spectrometer **FTIR**

Water and carbon dioxide absorb infrared light very strongly so that even the smallest amounts are visible in FTIR spectra. It is therefore usual to correct measurement spectra by subtracting a so-called blank spectrum because low concentrations of water and carbon dioxide are always present in the spectrometer.

Since the atmosphere in the laboratory remains more or less constant within the time frame of the TGA-FTIR measurements, the blank correction eliminates the unwanted absorption signals from these two gases.

The same investigation of calcium oxalate, described previously with the coupling, is used to see the difference between the two coupling techniques → Figure.

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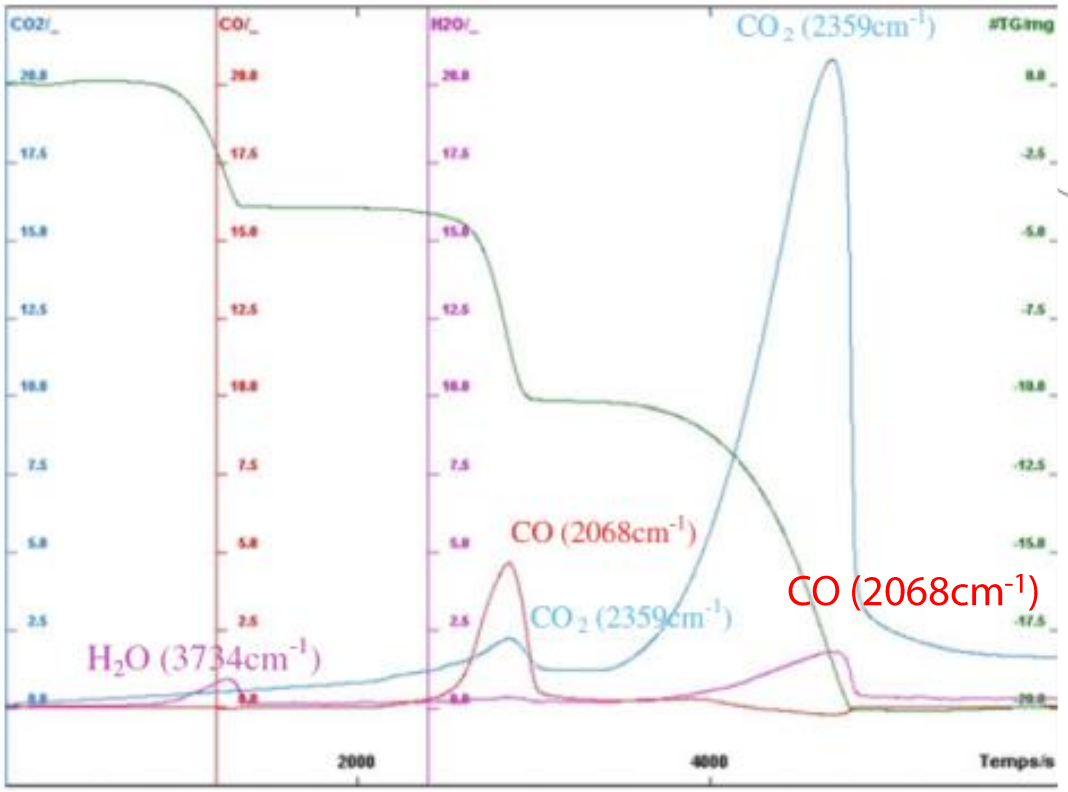
Fourier transform infrared spectrometer **FTIR**

The characteristic wavelengths of the expected emitted gas are recorded together with the three mass losses corresponding to the different steps of decomposition of the calcium oxalate:

FTIR spectra

- H_2O (3734 cm^{-1}) for the decomposition of the hydrate.
- CO(2068 cm^{-1}) for the decomposition of the calcium oxalate in calcium carbonate.
- CO_2 (2359 cm^{-1}) for the decomposition of the calcium carbonate in calcium oxide.



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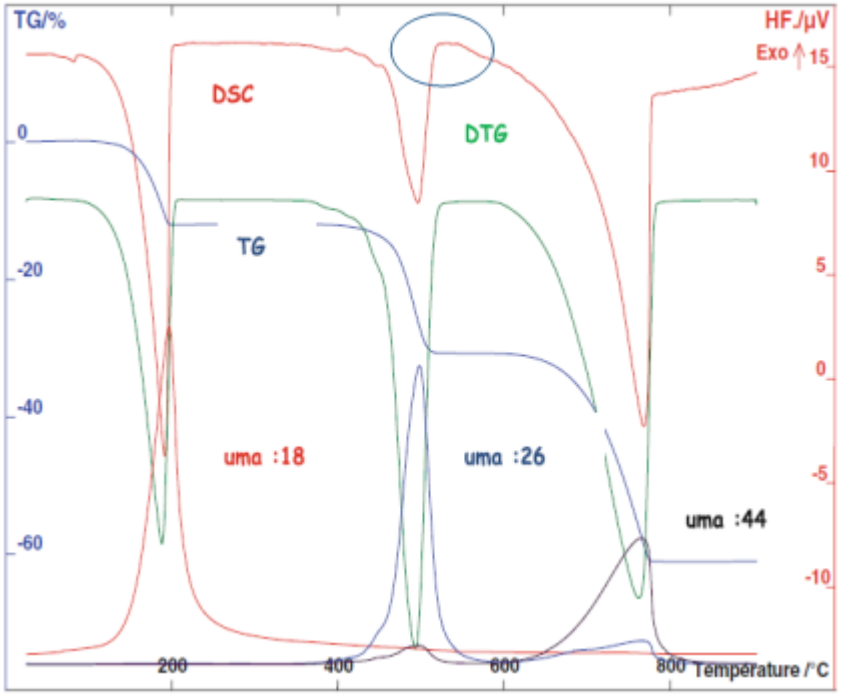
Fourier transform infrared spectrometer **FTIR**

As mentioned above related to DSC measurements, the TG-FTIR coupling also shows that during the second step, when CO is formed, traces of a fraction of CO_2 were detected during the second loss, and a fraction of CO during the third mass loss, indicating the presence of some trace of air in the furnace during the experiment. That was indicated also in Figure with DSC, in the second stage.



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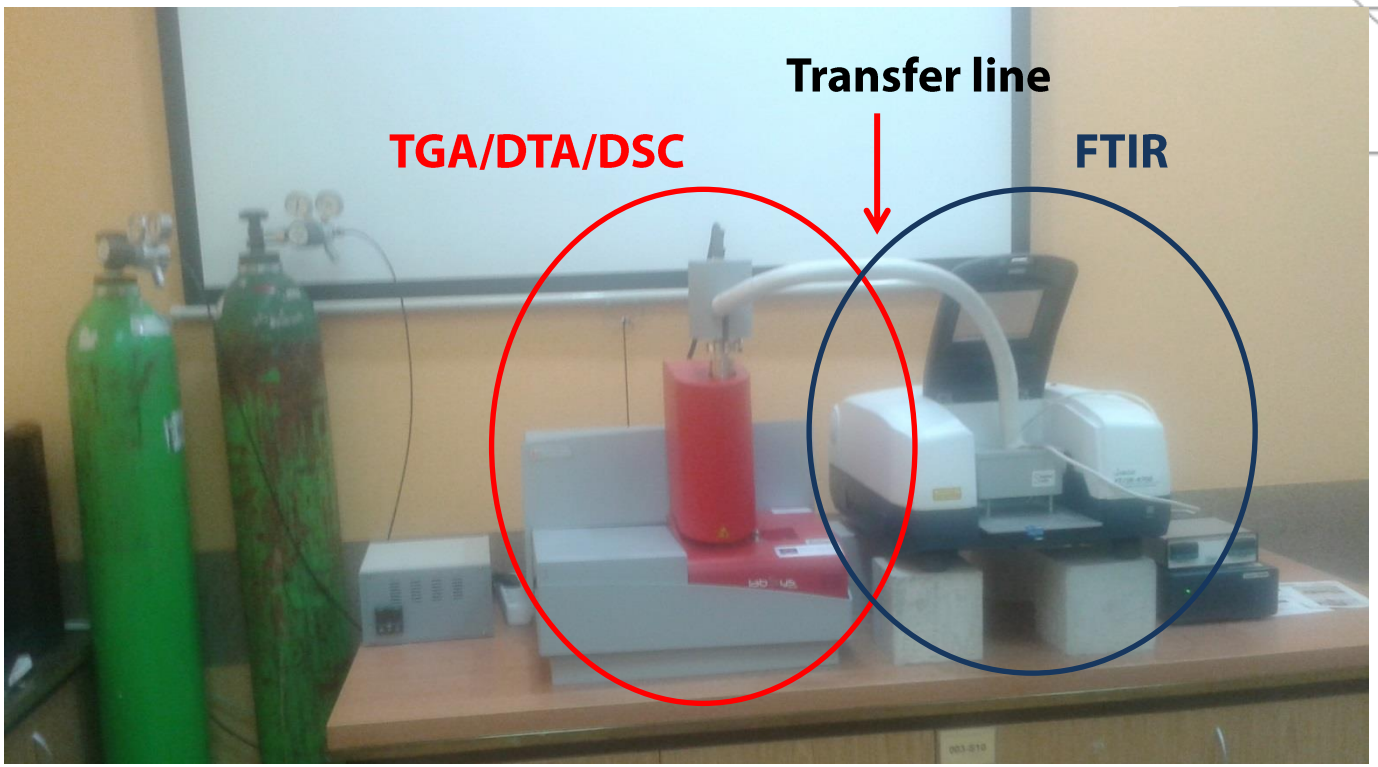
TGA coupled with FTIR



Devices on Department for civil engineering and geodesy at Faculty of Technical Sciences

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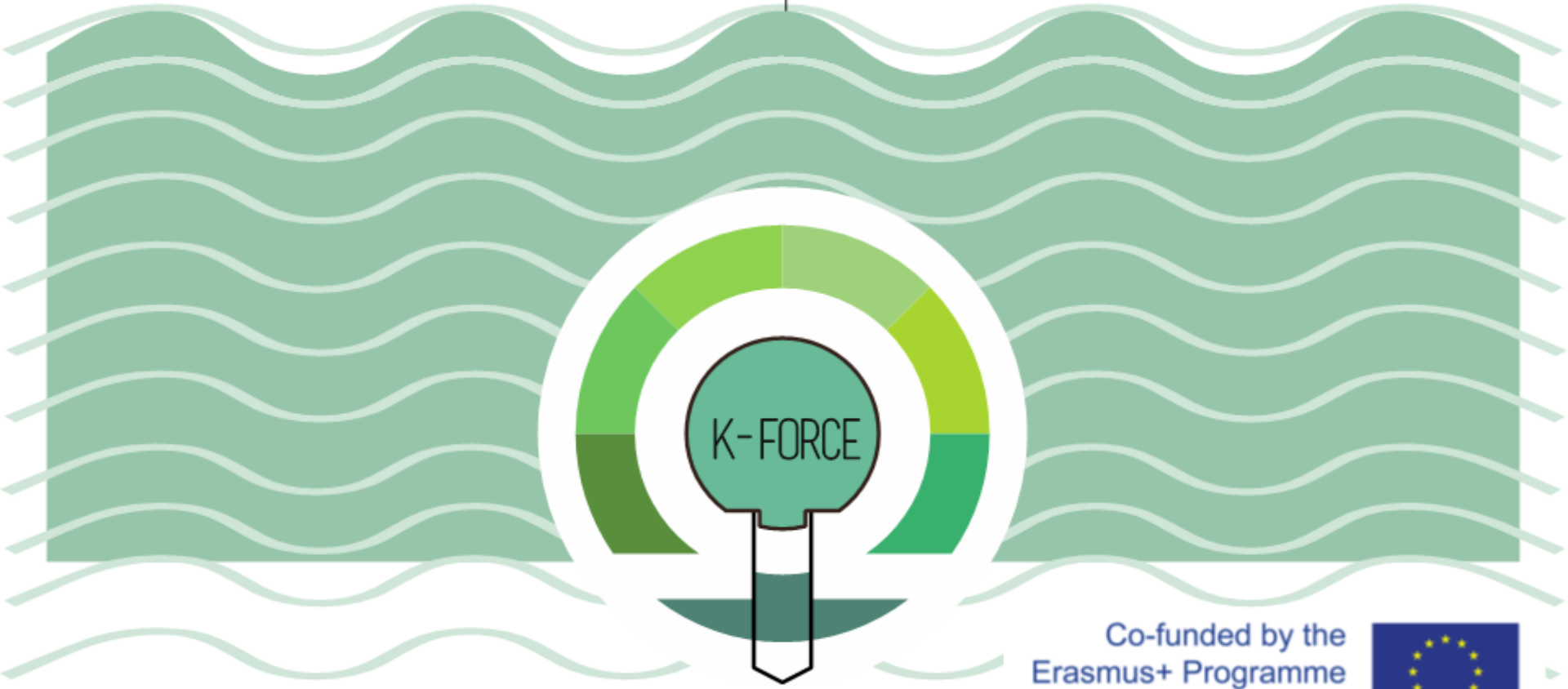

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Thank you
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