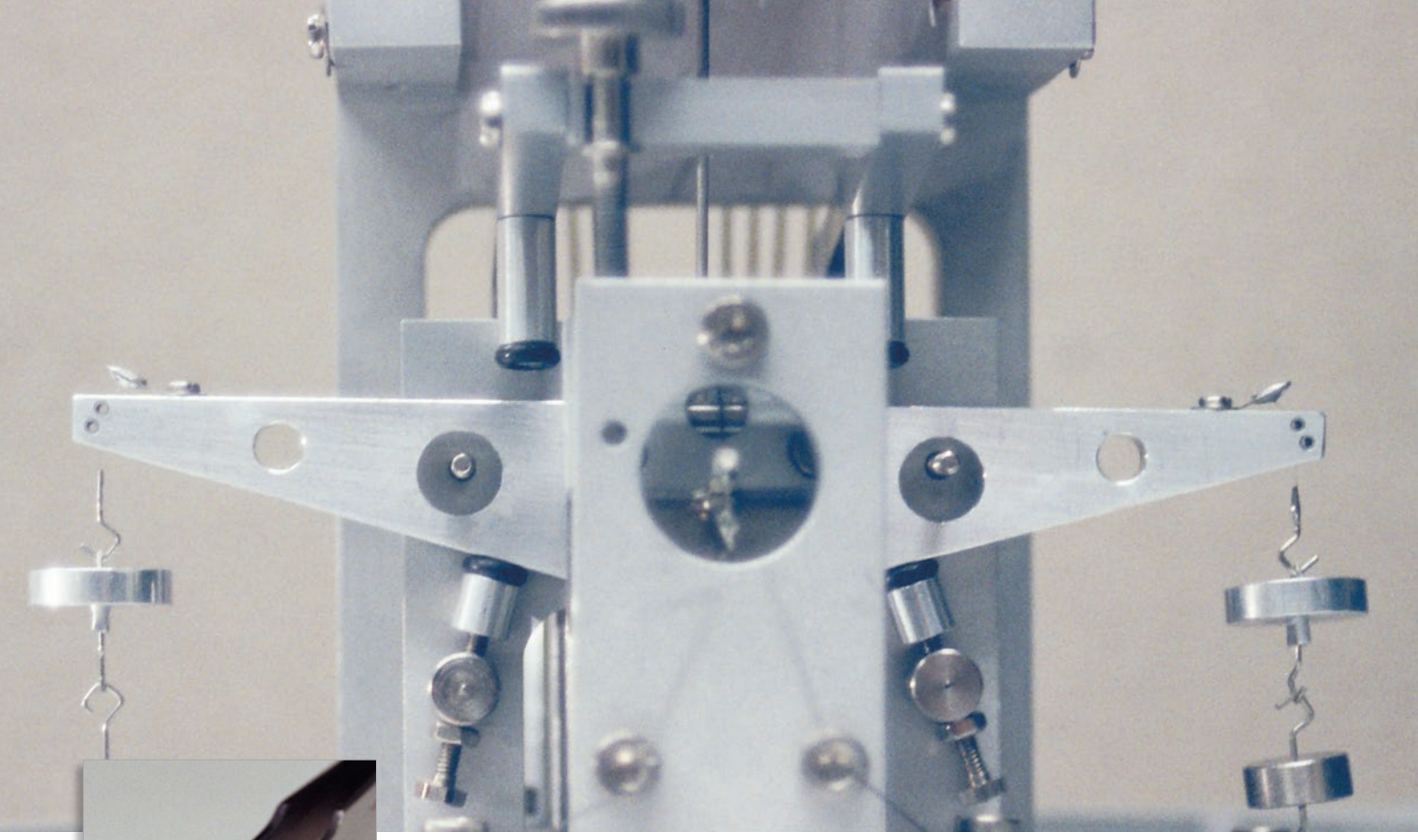

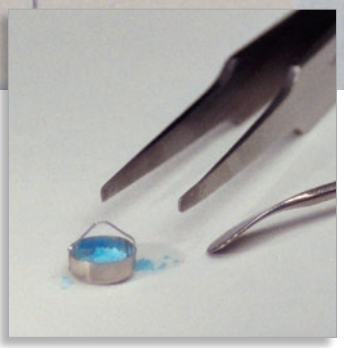

Thermal Analysis

(TA)

- quality control
- purity
- phase changes
- thermal behavior

When a material is heated its structural and chemical composition can undergo changes such as fusion, melting, crystallization, oxidation, decomposition, transition, expansion and sintering. Using Thermal Analysis such changes can be monitored in every atmosphere of interest. The obtained information is very useful in both quality control and problem solving.

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Technique	Abbreviation	Property	Applications
Thermogravimetric Analysis	TGA	Mass difference	Sample purity Decomposition Dehydration Oxidation
Differential Thermal Analysis	DTA	Temperature difference	Phase changes Dehydration Decomposition Reactions
Differential Scanning Calorimetry	DSC	Energy difference	Heat capacity Phase changes Reactions Calorimetry

Table 1: Different TA techniques and their applications.

Instrumentation

A thermal analysis system contains a graphite resistor furnace that can heat a sample from room temperature to 1750°C. The atmosphere in the system can be either inert (vacuum, nitrogen, helium, argon) to protect the sample from oxidation or active (air, oxygen, hydrogen) to react with the sample. To determine small weight changes of the sample during heating a microbalance is used (frontpage) that has a resolution of 0.03 µg.

Options

Thermal analysis is a general name for a group of analytical techniques used to monitor the behavior of a material as a function of temperature (or time at a specific temperature). Table 1 shows an overview of the different techniques that will be discussed in this note.
To characterize a variety of samples, different sample holders are available (fig. 1). Homemade sample holders are also available that allow the detailed characterization of thin layers.

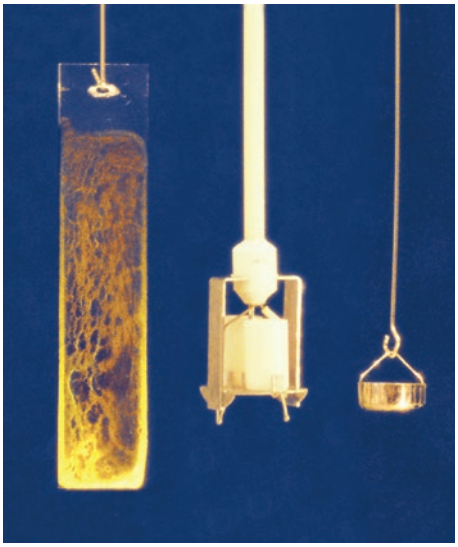
Thermogravimetric Analysis (TGA)

In TGA the exact mass of a sample is determined while it undergoes a temperature treatment. It is possible to keep the sample at a constant temperature or a linear temperature gradient can be applied.
Alternatively, the sample can be heated until a constant mass is obtained.

Differential Thermal Analysis (DTA)

Differential Thermal Analysis is an analytical method in which the sample and an inert reference material are heated concurrently, each having its own temperature sensing and recording apparatus. The temperature changes that occur in the course of heating are plotted. This thermogram provides data on the chemical and physical transformations that have occurred, such as melting, sublimation, glass transitions, crystal transitions, and crystallization.

Fig. 1: Sample holders as used in TGA (right) DSC (middle) and for thin films (left).



Example 1: Dehydration and decomposition of calcium oxalate

Starting materials in production can contain impurities like an unknown quantity of water. This water can reduce reactivity or add unwanted weight to the material – both of which can cause production problems. To prevent this from happening a TGA analysis can help to identify the state of the material.
In this example calcium oxalate is analyzed using TGA (fig. 2). The first loss of sample weight is due to the dehydration of water (12 %). The loss of sample weight is equal to the quantity of one mole of crystal water.
The second loss of sample weight is due to loss of CO (19 %) and the third step to loss of CO_2 (30 %). When the sample would have been contaminated with e.g. barium or strontium oxalate more peaks would be visible. Absence of these peaks indicates that the material is a monohydrate and no other major contamination is present in this material.

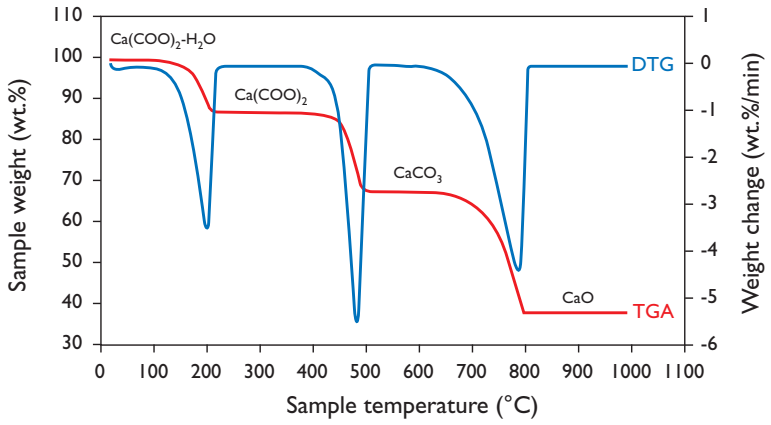


Fig. 2: Thermogravimetric analysis of calcium oxalate, the first derivative signal (DTG) shows how fast the weight change occurs.

Example III: Dehydration of copper sulphate pentahydrate

Figure 4 shows the results of a TGA-DSC measurement of copper sulphate pentahydrate. The different dehydration steps that occur during heating of the material are difficult to distinguish in the TGA-signal, but are clearly visible in the DSC-result. The majority of the water is lost below 150°C, but the monohydrate is stable until 244°C. The loss of water from the monohydrate corresponds to a weight loss of 7.0%.

Example II: The combustion rate of carbon

In production processes, gas purity can be critical. When carbon parts are heated to high temperatures, the presence of oxygen can decrease lifetime. With TGA it is possible to determine what oxygen concentration can be tolerated without degrading the carbon parts. To do so, a carbon sample is heated to 1100°C in a few minutes using a nitrogen atmosphere with different oxygen concentrations (<2, 200, 500 vol.ppm). The weight loss is monitored during 2 hours at 1100°C. The combustion rate is calculated by measuring the loss of weight during a specified time. The results of the TGA measurements are shown in figure 3, where the sample mass is plotted as function of time. The combustion rate is determined from the slope of the curves. By plotting the combustion rate of carbon at 1100°C against the oxygen concentration, a linear relation is observed in this concentration range. The maximum oxygen concentration in nitrogen that can be tolerated in a process can be determined on the basis of this information.

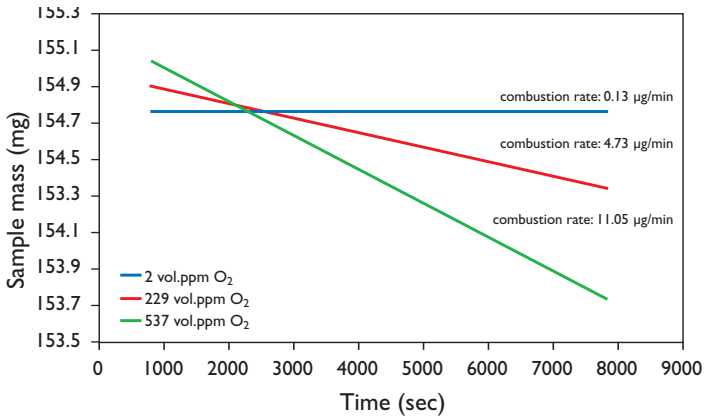
Differential Scanning Calorimetry (DSC)

DSC is used to determine the temperature and enthalpy of a phase transformation. This type of information is very useful for quality control as phase transformations are very sensitive for purity, thermal stability and compositions of mixtures. DSC uses additional metal calibration standards which make it possible to calculate the energy emitted or absorbed by a sample (enthalpy).

Hyphenated techniques

The above described thermal analysis techniques can be performed stand-alone or combined. The most common hyphenated techniques are TGA-DSC and TGA-DTA. It is also possible to couple a gas analyzer to the thermal analysis system to identify the emitted vapors, for example to unravel mechanisms of transformations. Typical analyzers are a mass-spectrometer (MS) or a fourier-transform infrared instrument (FT-IR). Emitted vapors can also be absorbed in gas-trapping bottles or organic sampling tubes. In this way analyses can be performed off-line.

Fig. 3: Carbon oxidation as studied at different oxygen concentrations.



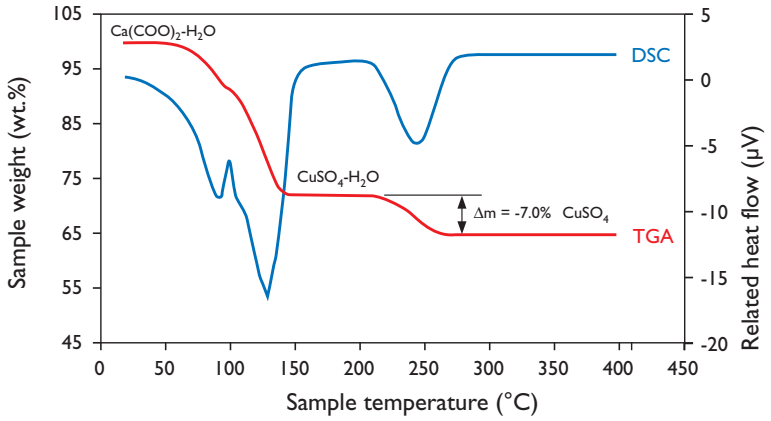


Fig. 4: The analysis of copper sulphate pentahydrate with TGA-DSC.

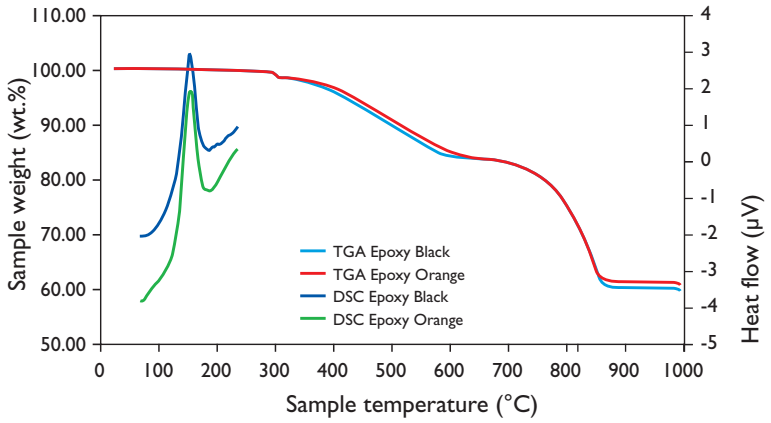


Fig. 5: Epoxy resin analysis with TGA-DSC.

Example IV: Characterization of epoxy resins with TGA-DSC

TGA-DSC can also be used to investigate the thermal and chemical properties of a material. In this example a customer wanted to replace a standard epoxy resin with a new epoxy resin. The most obvious difference between the old and new epoxy resin is the color, due to the addition of another pigment. It is important to know the thermal and chemical differences between both epoxy resins before this change is made in the factory. By using the coupled TGA-DSC the thermal effect of the hardening reaction was determined using DSC and the ash residue was measured simultaneously by TGA.

The samples are first put in a nitrogen atmosphere at 30°C. Then, the temperature is increased to 300°C and held there for 15 minutes. During this period the atmosphere is changed from nitrogen to air, which allows combustion of the sample. Subsequently, the temperature is increased to 1000°C. The TGA and DSC signals are monitored during the whole procedure. The results of the TGA and DSC measurements are shown in figure 5. The DSC result of the black epoxy is comparable with that of the orange epoxy resin. An exothermic reaction is observed at 155°C. The enthalpy is 17 J/g for both materials. The TGA results are comparable too. For both epoxy resins an ash residue of 59 wt.% is found. The TGA-DSC results show that relevant properties of the epoxy resins are the same and that the process parameters do not have to be changed.

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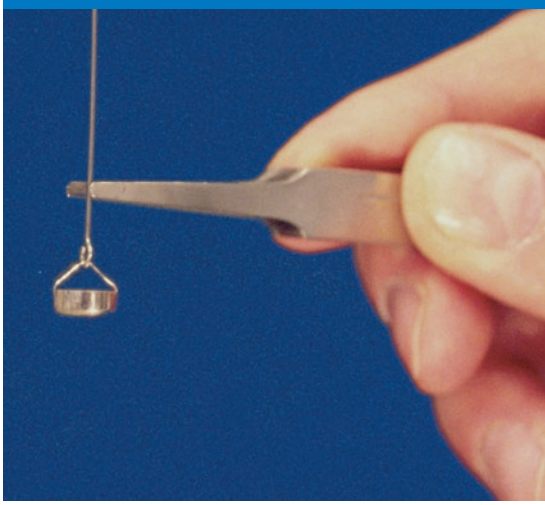

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