Thermal Analysis

TGA with Evolved Gas Analysis

Thermogravimetric Analysis (TGA) provides quantitative information on the change in mass of a sample as a function of time as it is heated, cooled or held at constant temperature. The combination of TGA with a mass spectrometer (MS) or a Fourier transform infrared spectrometer (FTIR) allows the nature of the gaseous reaction products formed in the TGA to be investigated online. When several compounds are evolved, the MS or FTIR can track their evolution profiles. Mass spectra and infrared spectra are substance-specific. The spectra can be used to characterize the substance or substance class through spectral interpretation and comparison with database reference spectra. Decomposition pathways can thereby be elucidated.

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Theory

**Mass spectrometry** characterizes substances by identifying and measuring the intensity of molecular fragment ions of different mass-to-charge ratio (m/z).

The incoming gas molecules are first ionized in the ion source. The positive molecular ion and fragment ions formed are then separated according to their m/z value by a combination of magnetic and electrostatic fields. A mass spectrum is recorded by scanning the field strength so that ions of increasing m/z ratio arrive at the detector.

In **TGA-MS**, the mass spectrometer is usually set to monitor m/z values characteristic for specific structural features.

**Infrared spectroscopy** measures the light absorbed by different types of vibrations in molecules.

Infrared radiation from the light source is divided into two beams by the beam splitter. One beam is reflected onto a moving mirror and the other onto a stationary mirror. Both beams are then recombined and pass through the sample to the detector. Fourier transformation of the resulting interferogram yields an mid-infrared transmission spectrum.

In **TGA-FTIR**, the absorption bands of each spectrum are usually simultaneously integrated over the entire spectral range or over characteristic spectral regions. The intensity is presented as a function of time as so-called Gram-Schmidt curves or chemigrams.

Coupling the TGA to a gas analyzer

The TGA/SDTA851® is coupled to the MS via a fused silica capillary tube heated at 200 °C to prevent condensation. Part of the gases evolved from the sample in the TGA is sucked into the MS. The sensitivity is so great that only about 1% of the effluent gas is required. The purge gas is argon or nitrogen.

In contrast, the TGA-FTIR combination uses the total volume of purge gas and gaseous decomposition products from the TGA. The gases are transferred through a heated glass-coated steel transfer capillary line into a heated gas cell in the FTIR spectrometer. Nitrogen, which does not exhibit IR-absorption, is used as purge gas.
TGA-MS and TGA-FTIR are used in research and development, in quality control and to investigate material failure. Typical applications are:

- Thermal degradation processes (oxidation, pyrolysis)
- Vaporization and sublimation
- Detection of additives in a matrix
- Characterization of starting materials and end products
- Investigation of chemical reactions (catalysis, syntheses, polymerization)
- Outgassing and adsorption/desorption behavior

### Tutorial examples

**Decomposition of calcium oxalate monohydrate (TGA-MS)**

The diagram shows that calcium oxalate monohydrate decomposes in 3 distinct steps. The MS fragment ion curves for water (m/z 18), CO (m/z 28) and CO$_2$ (m/z 44) display peaks that correspond closely to the individual TGA steps. The first weight loss step relates to the elimination and vaporization of water of crystallization (1); the second step to the decomposition of anhydrous calcium oxalate with formation of CO (2); and the third step to the decomposition of calcium carbonate to calcium oxide and CO$_2$ (3). The m/z 44 ion curve shows that CO$_2$ is also formed in the second step at 550 °C (besides CO). This is a result of the disproportionation reaction of CO to CO$_2$ and carbon (2CO $\rightarrow$ CO$_2$ + C).

\[
\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O} \quad (1) \\
\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO} \quad (2) \\
\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2 \quad (3)
\]

**Pyrolysis of PVC (TGA-FTIR)**

This example describes the thermal degradation of PVC. The TGA weight loss curve exhibits two clear steps. The IR spectrum (above left) measured at the maximum of the peak at 310 °C corresponds to HCl formed through the reaction \((\text{CH}_2\text{-CHCl})_n \rightarrow (\text{CH}==\text{CH})_n + n\cdot\text{HCl}\). The spectrum measured at the maximum of the second peak at 465 °C (above right) is due to benzene formed through the cyclization of \((\text{CH}==\text{CH})_n\). The curve in the lower part of the diagram shows a chemigram in the wavenumber range 3090 to 3075 cm$^{-1}$. Absorption bands in this region are characteristic for molecules with aromatic rings (C-H stretching vibrations).
**Application examples**

**Detection of solvents in pharmaceutical substances (TGA-MS)**

Different solvents are normally used in the synthesis of a pharmaceutical substance and afterward for purification/recrystallization. The presence of residual amounts of solvents can influence the properties of the substance and must therefore be kept as low as possible.

The TGA curve exhibits several weight loss steps. In the final step above 250 °C, the substance begins to decompose. The two steps in the range 70—240 °C indicate the loss of moisture or solvents through heating. The simultaneously recorded MS ion curves confirm that the weight loss steps correspond to methanol (m/z 31) and acetone (m/z 43, the main fragment ion of acetone).

The methanol is released over a wide temperature range. In comparison, the acetone is eliminated in a much narrower temperature range. This indicates that the acetone is more firmly bound, possibly as a solvate.

**Decomposition of BHET**

BHET (bis-hydroxyethyl terephthalate) is an intermediate used in the production of PET. It is produced by the esterification of terephthalic acid with ethylene glycol.

Two weight loss steps were observed on heating BHET in the TGA. A direct comparison of the IR spectrum measured at 300 °C with database spectra showed that the first step is due to the elimination of excess ethylene glycol.

The second step was investigated by recording several different chemigrams. The results show that BHET decomposes in this temperature range with the formation of various esters, alcohols and compounds containing carboxylic acid groups.

The side chains of the aromatic ring of BHET are cleaved at temperatures above 400 °C with the formation of hydroxy formic acid ester (H-CO-O-(CH₂)₂-OH). The combination of IR spectra and chemigrams allows both simple and complex mixtures of substances to be characterized.
Curing and decomposition of a melamine-formaldehyde resin

The monomers used for preparing amino resins (aminoplasts) are urea (for UF resins) or melamine (for MF resins) together with formaldehyde. The latter reacts with amino groups with the formation of methylol groups. In the curing reaction, the amino resin undergoes cross-linking as a result of condensation reactions. The methylol groups react with amino or other methylol groups and form either methylene bridges, or ether bridges. Correspondingly, the cross-linking reaction results in the elimination not only of water but also methanol. The conversion of ether bridges to methylene bridges with the elimination of formaldehyde does not occur until higher temperatures. The aim of the TGA-MS study was to gain an insight into the reactions taking place by analyzing the volatile substances evolved.

The TGA curve shows that the sample undergoes a significant weight loss between room temperature and 220 °C. Above this temperature, the weight loss increases markedly as shown by the change of slope in the DTG curve. From these results one can assume that residual curing is completed by 220 °C and that afterward degradation begins. In the condensation reaction only water is eliminated (m/z 17, 18). Methanol (m/z 31) and formaldehyde (m/z 30) are not detected until temperatures above 220 °C. The rapid increase of m/z 17 compared with m/z 18 from about 220 °C onward is due to the elimination of ammonia (m/z 17). This proves that the dominant reaction is that between methylol groups and amino groups. (For further details, see UserCom 14, page 9)

Quality control of ETFE

ETFE, a copolymer of ethylene and tetrafluoroethylene, is used as insulation for cables. These types of materials are analyzed to determine the nature of gaseous products formed on thermal degradation. This information is needed to optimize the corrosion protection of metallic contacts used in the cable. In any thermal treatment of the final product, the emission of corrosive gases should be minimized. This problem can be easily tackled by TGA-EGA. The diagram shows the TGA curves of the raw material (pellet) and the processed material (insulation). Both samples lose volatile additives from about 200 °C onward.

The actual decomposition begins at about 440 °C. The IR spectra of the insulation material proved that HF was formed at temperatures above 450 °C. The results showed that the product is therefore unsuitable for its intended use.

For more information on evolved gas analysis see the Collected Applications booklet Evolved Gas Analysis available from METTLER TOLEDO (ME-51726056).