TGA with Evolved Gas Analysis

Introduction

In thermogravimetric analysis (TGA) the weight of a sample is recorded as a function of temperature or time under defined atmospheric conditions. Quantitative compositional analysis can be performed and the reaction kinetics investigated. Qualitative information on the gaseous products evolved is obtained by coupling the thermobalance online with a mass spectrometer (MS) or a Fourier transform infrared spectrometer (FTIR).

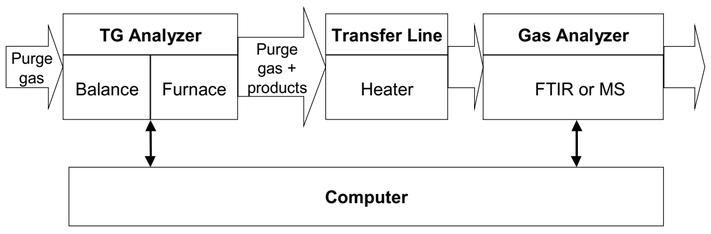

Fig. 1. The coupling of TGA and gas analysis

The data from the gas analyzer is then compared with the TGA weight loss curve. The DTG (derivative weight loss) and SDTA (single DTA) curves are also often displayed to aid interpretation. SDTA monitors temperature differences due to enthalpy changes.

The combination of a thermobalance with a mass spectrometer, TGA-MS

The TGA/SDTA851e is coupled to the MS via a heated quartz glass capillary tube. One end of the glass capillary is positioned close to the sample in the thermobalance. Part of the evolved gases is sucked into the capillary by the vacuum in the MS. The MS repeatedly measures either the entire mass spectrum or, as shown in Figure 2, monitors the intensity of characteristic fragment ions (m/z, the mass to charge ratio). The decomposition of calcium oxalate monohydrate is shown as an example.

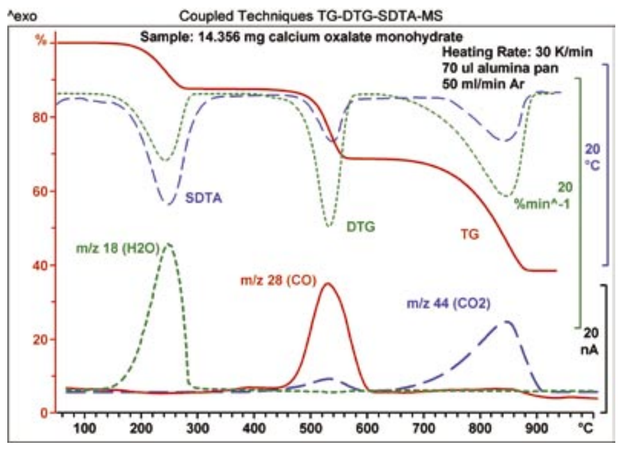

Fig. 2. The decomposition of $CaC_2O_4 \cdot H_2O$ was investigated by monitoring the m/z values 18, 28 and 44. The first step in the TGA curve corresponds to the elimination of water of crystallization, the second step to the release of carbon monoxide from the anhydrous calcium oxalate, and the third step to the liberation of CO_2 from the calcium carbonate formed in the second reaction step. The m/z 44 curve also shows that a small amount of CO_2 is formed in the second step. This effect is due to the disproportionation reaction of CO to CO_2 and carbon.

The combination of the thermobalance with an FTIR spectrometer, TGA-FTIR

The TGA is coupled to the FTIR spectrometer via a glass-coated transfer line. This transports the volatile products evolved during the decomposition of the sample to a gas cell installed in the FTIR spectrometer. Both the transfer line and the gas cell are heated to prevent condensation of the decomposition products.

The FTIR spectrometer measures the spectra of the gases in the gas cell rapidly at frequent intervals. Afterward, a spectral range characteristic for a particular functional group can be selected and the infrared absorption bands in this range integrated and displayed as a function of time.

The resulting curve, known as a chemigram, is a very useful way to compare the results of the spectroscopic analysis with the TGA weight loss curve. This is illustrated in Figure 3.

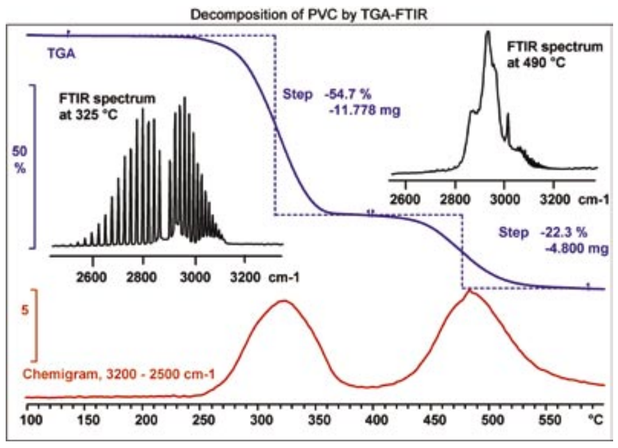

Fig. 3. Thermal degradation of PVC measured by TGA-FTIR. The TGA curve and the chemigram show two clearly defined steps. A FTIR spectrum measured at the first maximum corresponds to HCl. The spectrum measured at the second maximum is, however, very different and is identified as benzene formed through the cyclization of $(-CH=CH-)_n$.

Applications

Hyphenated TGA-MS or TGA-FTIR analysis is an invaluable aid in research and development, and is also a very useful tool for quality control and the investigation of material failure or damage. Typical applications are:

- detection and identification of compounds (Fig. 4)
- characterization of raw materials and final products (Fig. 5 and 6)
- chemical reactions (catalysis, synthesis, polymerization)
- thermal degradation processes (oxidation, pyrolysis) (Fig. 7)
- degassing and adsorption behavior

Conclusions

Combining a thermobalance with a mass spectrometer or an FTIR spectrometer opens up many important new application possibilities for thermogravimetric analysis. Qualitative information on the substances evolved can be obtained in addition to the quantitative results from the weight loss steps. The online combination of thermogravimetric and spectrometric measurements provides comprehensive details on the processes that occur.

	Features	Benefits
TGA-MS	• High sensitivity	• Extremely low concentrations of evolved gases can still be identified (e.g. impurities in pharmaceutical substances
	• High resolution (timescale)	• Overlapping weight losses can be qualitatively interpreted
TGA-FTIR	• High chemical specificity	• Direct identification of compounds and functional groups
	• High resolution (timescale)	• Overlapping weight losses can be qualitatively interpreted

Table 1. Features and benefits of TGA-MS and TGA-FTIR

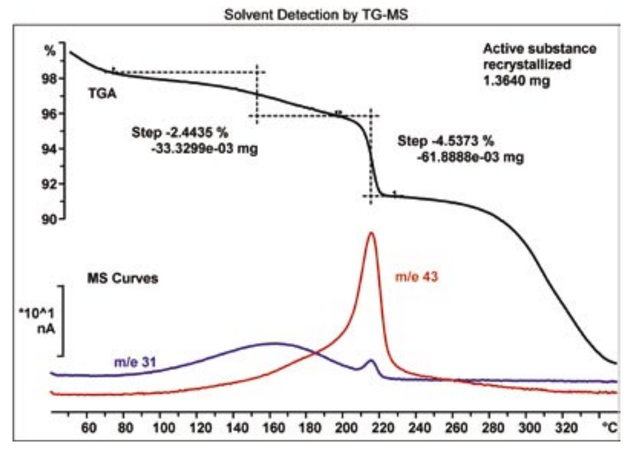

Fig. 4. Methanol and acetone were used to recrystallize a pharmaceutical substance. Residues of both solvents can be clearly detected by TGA-MS. The high temperature observed for the elimination of the relatively large amount of acetone indicates that acetone is more firmly bound in the substance, possibly as a solvate.

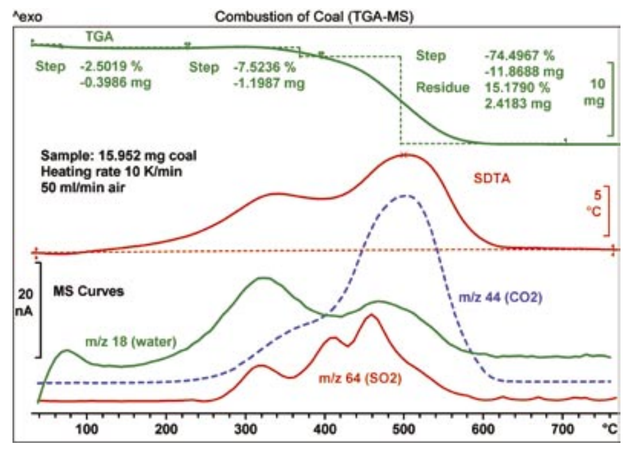

Fig. 5. The TGA curve shows three weight loss steps. The first is due to the evaporation of moisture. The combustion of the coal takes place in the two steps that follow. The MS data shows that appreciably more water is evolved in the first of these two steps. Besides carbon, a greater proportion of hydrogen and hydrogen-containing compounds (e.g. CH_4) is burned. In addition, the formation of SO_2 (m/z 64) proves that sulfur-containing substances are present in the coal.

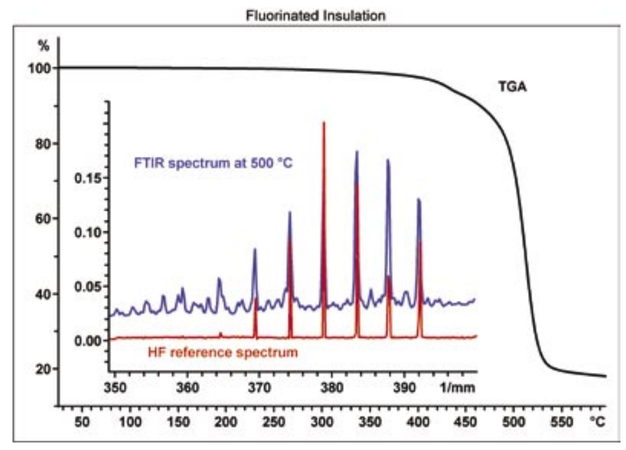

Fig. 6. ETFE is used as cable insulation material. An important point is whether hydrogen fluoride is formed when the material undergoes thermal degradation. The TGA-FTIR data of a sample of ETFE shows that volatile additives are evolved from about 200 °C onward. Degradation begins at about 440 °C. The FTIR spectra prove that hydrogen fluoride is formed above about 450 °C.

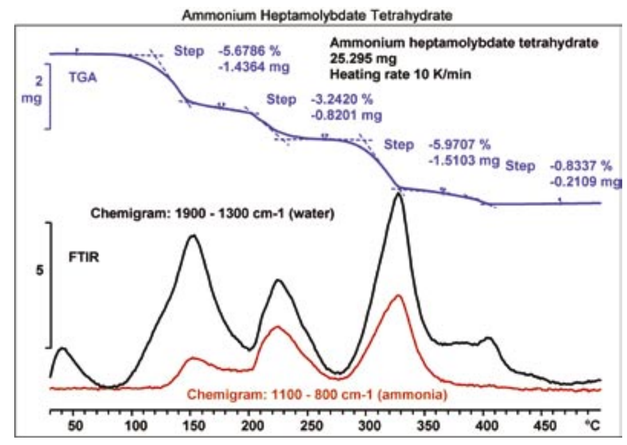

Fig. 7. $(NH_4)_6Mo_7\ O_{24} \cdot 4H_2O$ decomposes in three steps with the elimination of 6 molecules of NH_3 and 7 molecules of H_2O. Except in the last weight loss step, it can be seen that water and ammonia are formed simultaneously but not in a fixed ratio to each other. This indicates that the decomposition is non-stoichiometric.

Literature

A more detailed description of the use of evolved gas analysis is given in the **Collected Applications** booklet **Evolved Gas Analysis** available from METTLER TOLEDO (ME 51 725 056).

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