Evolved Gas Analysis
Collected Applications
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**TGA-MS**

**Measurement principles**

Mass spectrometry is an extremely sensitive method for the detection and identification of traces of gaseous substances. The technique can quantify atoms or molecules and provide chemical and structural information (functional groups and side chains) on the compounds analyzed.

In the mass spectrometers typically used for hyphenated techniques, sample molecules enter the mass spectrometer through an ion source where they are bombarded with a beam of high-energy electrons (usually about 70 eV). This energy is greater than the ionization potentials and bond strengths of organic substances. It is in fact sufficient to remove one (or more) electrons from molecules to form positively charged molecular ions. The excess energy also causes extensive fragmentation of the molecule with the formation of many different positively charged fragment ions according to complex pathways. The fragment ions formed are, however, directly related to the structure of the molecule under investigation, e.g.

\[
\begin{align*}
ABC + e^- & \rightarrow ABC^+ + 2e^- \\
AB^+ + C + 2e^- & \\
BC^+ + A + 2e^- & \\
A^+ + BC + 2e^- & \\
A^+ + B + C + 2e^- & \\
\ldots &
\end{align*}
\]

The mass spectrometer separates the ions according to their mass-to-charge ratio m/z. With hyphenated techniques we are normally only interested in the singly charged molecule and fragment ions. For a number of reasons, quadrupole mass spectrometers have been widely used over the past twenty-five years in preference to conventional magnetic field sector analyzers in instrument combinations. A quadrupole mass analyzer consists of two pairs of parallel rod electrodes located between an ion source and a detector. The four rods are mounted opposite to each another and are connected in pairs (see diagram). Mass separation is achieved by the combination of a continuous electrostatic field and a high-frequency alternating field. The ions transmitted through the system are recorded at the SEM detector. Steadily increasing (scanning) the field strength causes ions of increasing m/z value to arrive at the detector and thereby produce a mass spectrum.

Mass spectrometers operate under high vacuum (typically 10^{-5} mbar). This is necessary to prevent ions colliding with residual gas molecules along their path from the ion source to the detector, which would prevent them from reaching the detector.
Measurement modes

Scan analog: The ion current is continuously measured as a function of the mass-to-charge ratio (i.e. for singly charged ions, the mass). The intensity and mass of the fragment ions provide information on the nature of the material under investigation.

Scan bargraph: Only those masses are displayed whose signal intensity exceeds a particular value (i.e. that are above a certain threshold). The increment in m/z is therefore not continuous. The spectrum can be transformed into time-dependent intensities curves.

MID: Multiple Ion Detection (also known as Selected Ion Monitoring, SIM) enables you to continuously monitor the intensity of ions at defined m/z values, e.g. as shown in the following diagram at m/z 78 and 148.

In this technique the whole mass spectrum is not scanned, only a selected number of ions with particular m/z values are analyzed and the instrument rapidly switches between the selected ions until the measurements are completed. The amount of time (the so-called dwell time) that the analyzer remains at a given m/z value is thereby greatly increased. This in turn increases the fraction of these ions that reach the detector and results in a major improvement in sensitivity. Thus while subnanogram ($10^{-10}$ to $10^{-9}$ g) quantities of compounds can normally be detected using full-scan
# Applications List

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<td></td>
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<td>Polymer</td>
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<td>Expandable material</td>
<td>Polymer</td>
<td>Expansion, decomposition</td>
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</table>
3 Influence of the Heating Rate on MS Response

Purpose
The aim of the experiment was to investigate the influence of different heating rates on the response of the mass spectrometer.

Sample
Malonic acid (COOH-CH2-COOH).

Conditions
Measuring cells: TGA/SDTA coupled to a Balzers Thermostar® mass spectrometer
Pan: Aluminum 40 μl, no lid
Sample preparation: The crystals were ground in a mortar. Sample weights of approx. 10 mg were used.
TGA measurement: Heating from 50 °C to 640 °C at 5, 10, 20, 30, 40 and 50 K/min, blank curve corrected
Atmosphere: Nitrogen, 50 ml/min

Interpretation
Samples of malonic acid were measured with TGA at heating rates between 5 and 50 K/min and the corresponding TGA signals recorded. The thermal decomposition of malonic acid exhibits a single weight loss step that shifts toward higher temperatures with increasing heating rates.

The SDTA curves indicate that the sample begins to melt at approximately 134 °C (onset temperature), and that this is independent of the heating rate. The decomposition process in the liquid phase depends on the heating rate; higher heating rates shift the onset of decomposition and the decomposition range to higher temperatures.
**Interpretation**

The decomposition of malonic acid results in the elimination of acetic acid, which was confirmed by the m/z 60 ion curve (see MS spectrum of acetic acid in Application 1). The m/z 60 ion curve was measured at each different TGA heating rate and the corresponding peak areas calculated. The results are summarized in the above diagram. The TGA curve showed that the weight losses were the same for each sample, i.e. the amount of acetic acid evolved was independent of the heating rate. Constant peaks areas for the m/z 60 curves were therefore also expected. In fact the calculated peak area shows a slight increase at higher heating rates.

**Evaluation**

<table>
<thead>
<tr>
<th>Heating rate, K/min</th>
<th>Onset / peak temperatures SDTA, °C</th>
<th>MS peak area (m/z 60), nsA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Melting</td>
<td>Decomposition</td>
</tr>
<tr>
<td>5</td>
<td>134.2</td>
<td>173.6</td>
</tr>
<tr>
<td>10</td>
<td>134.1</td>
<td>182.9</td>
</tr>
<tr>
<td>20</td>
<td>134.1</td>
<td>188.7</td>
</tr>
<tr>
<td>30</td>
<td>134.0</td>
<td>194.3</td>
</tr>
<tr>
<td>40</td>
<td>134.0</td>
<td>191.5</td>
</tr>
<tr>
<td>50</td>
<td>134.0</td>
<td>203.7</td>
</tr>
</tbody>
</table>
**Conclusion**  The weight loss step due to the decomposition of malonic acid to acetic acid is independent of the heating rate. The m/z 60 peak area depends to a slight extent on the heating rate, although similar quantities of material are transported to the mass spectrometer. This effect might be due to the fact that because the heating rates are different, the concentration of acetic acid in the evolved gases is in each case very different.
8 Decomposition of Copper Sulfate Pentahydrate (Tutorial)

**Purpose**
This reaction is used as tutorial experiment to demonstrate the combination of thermogravimetry with FTIR spectroscopy. Copper sulfate pentahydrate loses its water of crystallization in several steps. The resulting anhydrous copper sulfate decomposes in three further reaction steps as given by the following equations:

\[
\begin{align*}
(1) & \quad 2 \text{CuSO}_4 & \rightarrow & \text{Cu}_2(\text{SO}_4)O + \text{SO}_3 \\
(2) & \quad \text{Cu}_2(\text{SO}_4)O & \rightarrow & 2 \text{CuO} + \text{SO}_3 \\
(3) & \quad 2 \text{CuO} & \rightarrow & \text{Cu}_2O + \frac{1}{2} \text{O}_2
\end{align*}
\]

**Sample**
Copper sulfate pentahydrate (CuSO$_4$.5 H$_2$O).

**Conditions**

<table>
<thead>
<tr>
<th>Measuring cells:</th>
<th>TGA/SDTA851$^\circ$ coupled to a Nicolet Nexus FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan:</td>
<td>Alumina 70 $\mu$l, no lid</td>
</tr>
<tr>
<td>Sample preparation:</td>
<td>As received, no preparation. 33.139 mg</td>
</tr>
<tr>
<td>TGA measurement:</td>
<td>Heating from 25 $^\circ$C to 1000 $^\circ$C at 10 K/min, blank curve corrected</td>
</tr>
<tr>
<td>Atmosphere:</td>
<td>Nitrogen, 50 ml/min</td>
</tr>
</tbody>
</table>

**Interpretation**
The dehydration process takes place in three steps between room temperature and 300 $^\circ$C. Afterward, according to the reaction scheme, SO$_3$ is expected to be formed in the range 600 $^\circ$C to 800 $^\circ$C. Above 800 $^\circ$C oxygen is evolved. The measured weight losses agree well with the stoichiometric values.

In contrast to the DTG curve, which shows a small maximum, the Gram-Schmidt curve does not show any clear change in signal above 800 $^\circ$C. This point will be discussed in the following section.
Interpretation

The initial dehydration of copper sulfate pentahydrate in three steps is confirmed by the IR spectrum of water in each case. The weight loss measured from 600 °C to 800 °C does not correspond directly to the loss of SO₃ as the comparison of the measured spectra with a database spectrum of SO₂ shows. In fact SO₃ is unstable at high temperatures and decomposes to SO₂ and O₂. Unfortunately, symmetrical diatomic molecules such as oxygen are IR inactive and cannot be detected by means of FTIR analysis.

<table>
<thead>
<tr>
<th>Evaluation</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Theoretical step (stoichiometry), %</th>
<th>Measured step, %</th>
<th>Peak temperatures DTG, °C</th>
<th>Possible products</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.1</td>
<td>36.0</td>
<td>97.6</td>
<td>water of crystallization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>124.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>245.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.1</td>
<td>32.3</td>
<td>718.4</td>
<td>SO₂, O₂</td>
</tr>
<tr>
<td></td>
<td>767.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>3.2</td>
<td>908.2</td>
<td>O₂</td>
</tr>
</tbody>
</table>

Conclusion

The initial stepwise loss of water of crystallization was clearly confirmed by the FTIR spectra of water. The loss of SO₃ according to the above reaction scheme appeared to be more complicated since the equilibrium of the reaction SO₃ ↔ SO₂ + ½ O₂ is shifted to the right above about 757 °C. This was confirmed by the spectra of sulfur dioxide that were measured. Oxygen could not be identified by means of FTIR because symmetrical diatomic molecules do not absorb infrared energy.
## 12 Detection of Methyl Salicylate in a Sample of Rubber

### Purpose
The aim of the experiment was to detect very small amounts of methyl salicylate in rubber and establish a detection limit.

### Sample
Butyl rubber (BR; 130 mg) spiked with 0.5, 1, 5 μl methyl salicylate (methyl o-hydroxybenzoate).

### Conditions
- **Measuring cells:** TGA/SDTA coupled to a Balzers Thermostar© mass spectrometer
- **Pan:** Aluminum 40 μl, no lid
- **Sample preparation:** As received, no preparation. Sample weights of about 7 mg were taken from the spiked samples
- **TGA measurement:** Heating from 60 °C to 300 °C at 10 K/min, blank curve corrected
- **Atmosphere:** Nitrogen, 50 ml/min

### Interpretation
A sample of NR that did not contain any methyl salicylate was measured up to 600 °C for reference purposes. The weight loss detected in this case is due solely to the decomposition of the rubber.

The spiked samples of rubber were measured up to 300 °C, by which temperature the methyl salicylate had been completely eliminated. The weight loss curves of the samples containing low amounts (i.e. low concentrations) of methyl salicylate (0.5 μl and 1 μl) were almost identical to that of the reference sample.
The m/z 92 ion curve of methyl salicylate was recorded simultaneously with the TGA curve. The elimination of methyl salicylate is characterized by a deflection of the ion curve from the baseline over a broad temperature range of some 200 K. The peak area is directly proportional to the amount of the organic substance in the rubber. Under the experimental conditions used, the MS detection limit was found to be 0.5 µl because at this level no specific signal could be detected.

**Evaluation**

<table>
<thead>
<tr>
<th>Amount of methyl salicylate in µl in the original sample (ca. 130 mg)</th>
<th>MS peak area (m/z 92), nsA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.67</td>
</tr>
<tr>
<td>5</td>
<td>4.37</td>
</tr>
</tbody>
</table>

**Conclusion**

The high sensitivity of the mass spectrometer enabled the quantification of volatile materials in the microgram range even after the detection limit of the thermobalance had been reached.