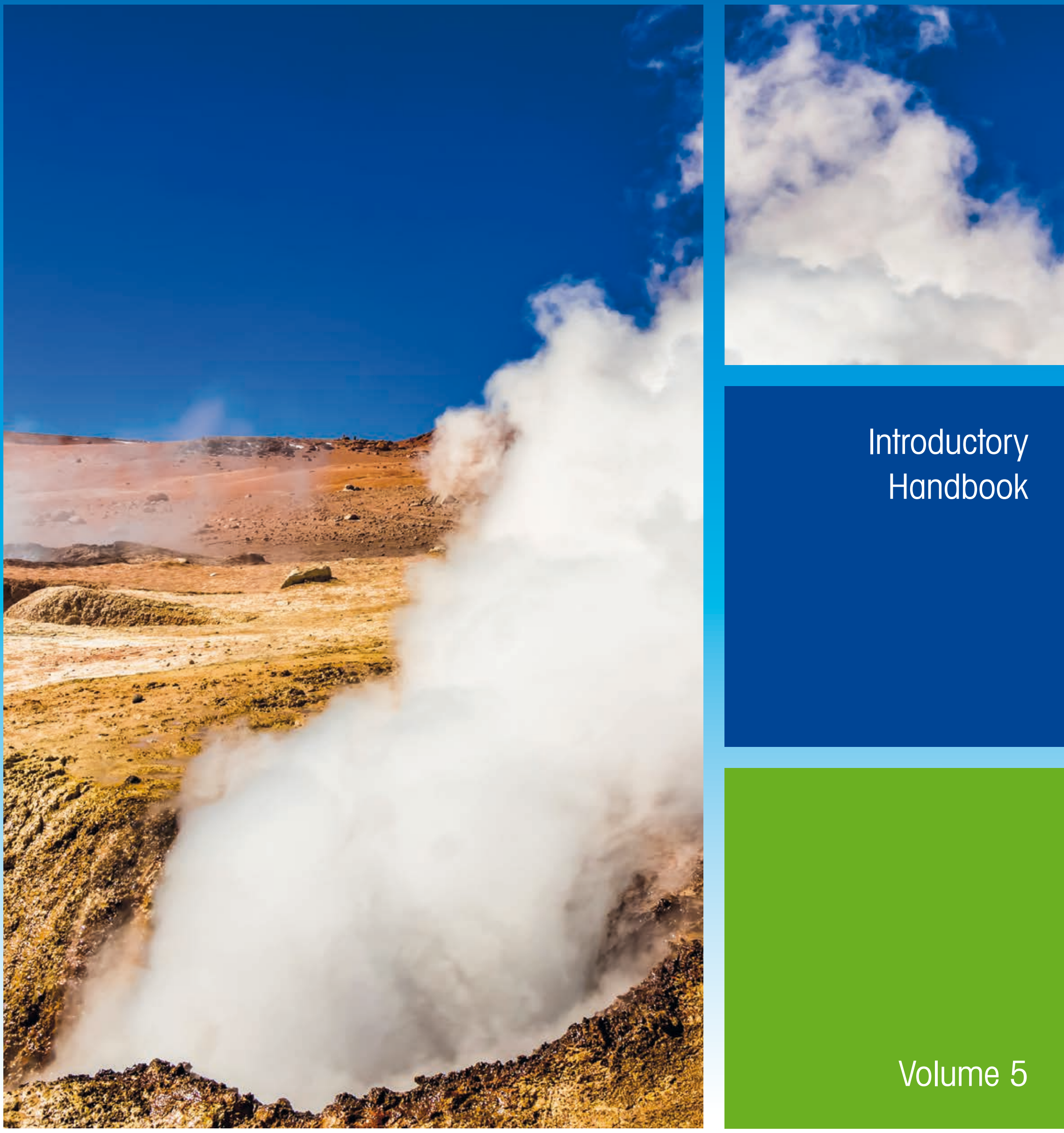
Thermal Analysis



Introductory
Handbook

Volume 5

Thermal Analysis in Practice

Evolved Gas Analysis

METTLER TOLEDO

Selected Applications
Thermal Analysis

Evolved Gas Analysis

Preface

A thermogravimetric analyzer (TGA) coupled on-line to an evolved gas analysis (EGA) system provides quantitative (mass loss) and qualitative (identification) information about gaseous reaction or decomposition products produced by a material during a TGA measurement.

The thermogravimetric analyzer records the mass loss of a sample while the sample is exposed to a temperature program (dynamically) or to a specific temperature as a function of time (isothermally) in a controlled atmosphere. METTLER TOLEDO also supplies TGA/DSC instruments which simultaneously record the heat flow to and from a sample.

Evolved gas analysis includes several techniques that allow gaseous products evolved during the mass change to be detected and identified. METTLER TOLEDO offers four different EGA techniques, namely Fourier transform infrared spectroscopy (FTIR), mass spectrometry (MS), gas chromatography-mass spectrometry (GC/MS), and micro gas chromatography-mass spectrometry (Micro GC(/MS)). The techniques can be coupled to a TGA and produce a large amount of complementary information. The data obtained can be directly correlated with the measured mass losses.

The chapters covering TGA-MS, TGA-FTIR, TGA-GC/MS and TGA-Micro GC(/MS) were previously published in different issues of UserCom, our biannual technical customer magazine (www.mt.com/ta-usercoms).

This booklet provides an overview of TGA coupled to EGA techniques and demonstrates how powerful that combination can be for material characterization.

Dr. Teresa Dennenwaldt and the editorial team of the METTLER TOLEDO materials characterization group:

Dr. Andreas Bach
Nicolas Fedelich
Dr. Angela Hammer
Dr. Elke Hempel
Ni Jing
Dr. Melanie Nijman
Dr. Domenico Regonini
Dr. Jürgen Schawe
Dr. Markus Schubnell

Contents

1. Thermogravimetry and Gas Analysis, Part 1: Basic Principles and Overview

Dr. Markus Schubnell

A thermobalance coupled to a suitable Evolved Gas Analysis (EGA) system allows qualitative information to be obtained about the gaseous reaction or decomposition products formed in a TGA experiment in addition to purely quantitative information about mass changes. The five chapters of this handbook discuss the various measurement techniques that METTLER TOLEDO offers for such analyses.

1.1. Introduction

In thermogravimetric analysis, the mass of a sample is continuously measured as a function of temperature. Changes in mass of just a few micrograms can be detected with high accuracy. Modern thermobalances such as the METTLER TOLEDO TGA/DSC can also simultaneously measure the heat flow to and from the sample. This provides information about thermal changes that occur during the mass change and also about effects that are not associated with a change in mass such as melting, crystallization, or solid-solid transitions.

Questions regarding the identity of the gaseous products evolved during the mass change however remain unanswered. This information can be obtained by coupling the TGA to a suitable system for gas analysis. In these five chapters of this handbook, we will discuss the various techniques that METTLER TOLEDO offers for such analyses. The first chapter presents an overview of the different techniques and discusses their application possibilities.

In the four chapters that follow, we show how TGA-MS (thermogravimetric analysis coupled with mass spectrometry), TGA-FTIR (thermogravimetric analysis coupled with Fourier transform infrared spectroscopy), TGA-GC/MS (thermogravimetric analysis coupled with gas chromatography and mass spectrometry), and TGA-Micro GC(/MS) (thermogravimetric analysis coupled with micro gas chromatography and (optionally) mass spectrometry can be applied in practice.

1.2. The various techniques

The gas analysis techniques discussed here all have something in common, namely that 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.

In TGA-GC/MS, the decomposition gases are however normally not measured online, in contrast to TGA-MS, TGA-FTIR and TGA-Micro GC(/MS). Instead, gas samples are taken at particular furnace temperatures during the TGA measurement and stored in a special interface. The gas samples are analyzed afterward by GC/MS after the TGA measurement has finished.

1.3. TGA-MS

The operating principle of a mass spectrometer is shown schematically in Figure 1. Gas molecules entering the ionization chamber from the TGA are bombarded with electrons. The molecules are ionized and form both

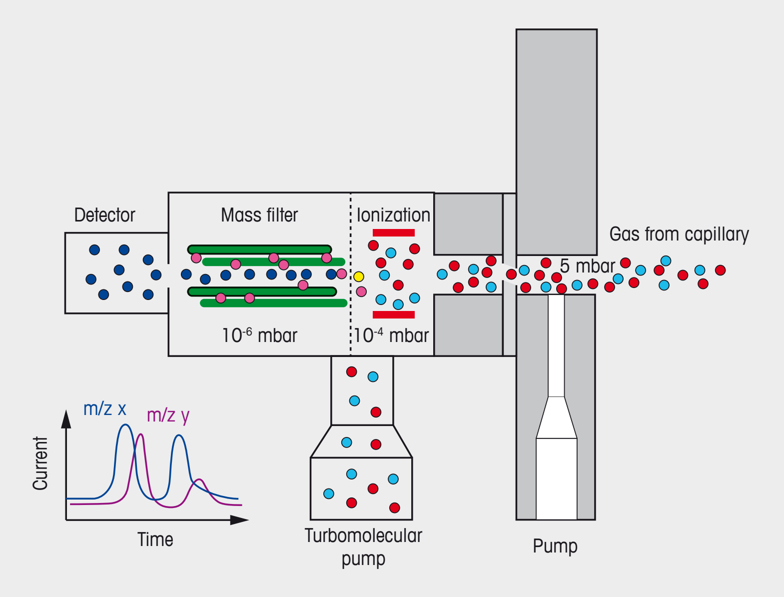


Figure 1. Schematic diagram showing the operating principle of a mass spectrometer.

positively charged molecular ions and numerous fragment ions. The ions produced and their relative intensities depend on the energy of the electrons used for ionization. This can be set on the mass spectrometer and is typically 70 eV. This voltage produces mainly singly charged ions.

The ions then enter an alternating electromagnetic field, a so-called mass filter, that separates the ions so that at any one instant only ions of a particular mass-to-charge ratio, (m/z) reach the detector.

In mass spectrometry, the ions are characterized by the ratio of their mass, m, and their electrical charge, z. After passage through the filter, ions of a particular m/z ratio arrive at the detector where their intensity is measured.

The mass spectrometer can be operated in several different ways. A so-called mass spectrum can be obtained by scanning the whole or part of the mass range, for example from m/z 18 to m/z 80. This is done by periodically varying the alternating electromagnetic field. The intensities of the different ions are presented as a function of m/z. The mass spectrum provides information about the nature and structure of the molecule being measured.

In combination with TGA, the user often sets the MS to detect and monitor the intensity of one or more individual masses (e.g. m/z 18, m/z 28, and m/z 44). This mode is extremely sensitive and is known as selected ion monitoring (SIM) or multiple ion detection (MID). The resulting m/z curve shows the intensity of the selected ion as a function of time. Peaks in the ion current signal for a particular m/z mean that molecules are present in the gas flow that after ionization fragment to ions of this mass-to-charge ratio.

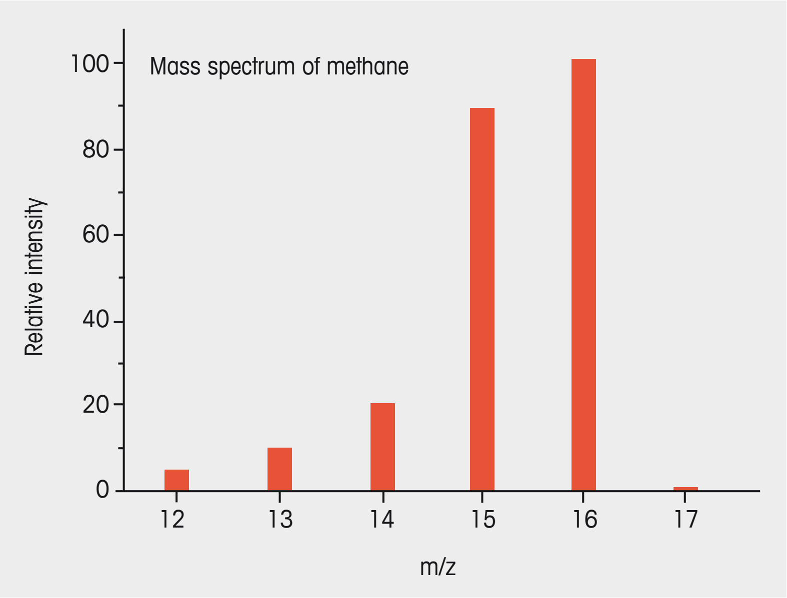


Figure 2.
Mass spectrum of methane (CH_4). The m/z 17 ion corresponds to the singly charged CH_4 molecule containing a ^{13}C atom. On the Earth, the two stable carbon isotopes ^{12}C and ^{13}C are present in a ratio of about 99 to 1.

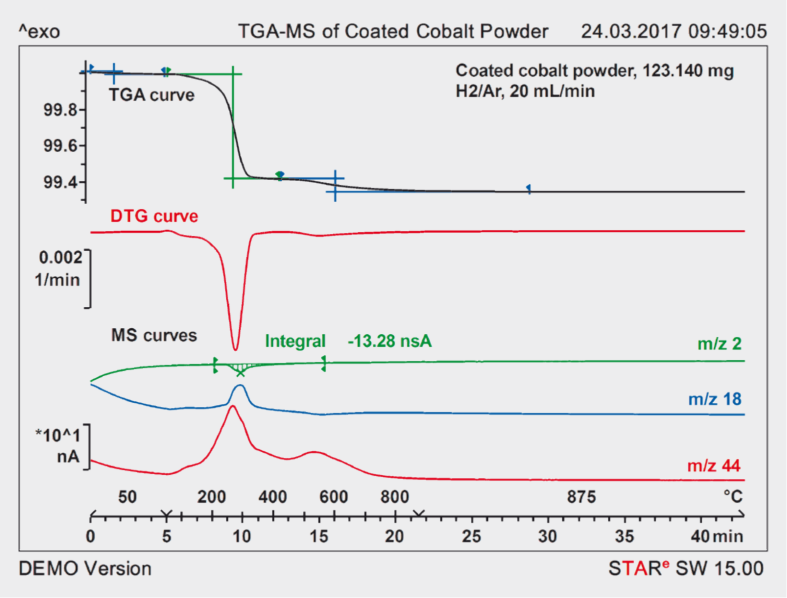


Figure 3.
TGA-MS curves of coated cobalt powder measured in inert hydrogen.

As an example, Figure 2 displays the mass spectrum of methane (CH_4). The singly charged CH_4 molecule is detected by the m/z 16 and m/z 17 ions (the molecular peaks correspond to $^{12}CH_4^+$ and $^{13}CH_4^+$). Besides this, electron bombardment produces numerous fragment ions that are formed by the removal of different numbers of hydrogen atoms from the methane molecule (e.g. m/z 12, 13, 14, and 15 fragment peaks, corresponding to C^+, CH^+, CH_2^+, CH_3^+).

In certain cases, doubly charged ions can also be formed through the removal of two electrons from the molecule. For example, the mass spectrum of argon consists mainly of singly charged $^{40}Ar^+$ (m/z 40) and doubly charged $^{40}Ar^{++}$ (m/z 20).

The mass spectrum of a substance allows a substance to be unambiguously identified and can be recorded in a few seconds. This means that TGA and MS measurements are effectively performed simultaneously. In TGA experiments, a number of different compounds are often evolved at the same time. In such cases, the identification of the substances is not always easy because different compounds often exhibit fragment ions with the same mass-to-charge ratio in their mass spectra (for example, ammonia yields the fragment ions m/z 14 (N^+), m/z 15 (NH^+), m/z 16 (NH_2^+) and m/z 17 (NH_3^+) just like for methane. Information about the interpretation of mass spectra will be given in Chapter 2.

In summary, the interpretation of the mass spectra of gas mixtures containing many "large" molecules (for example a mixture of long chain organic molecules) is difficult because of their fragmentation. On the other hand, TGA-MS is extremely useful for the detection of small molecules (for example water, CO_2, HCl, SO_x, NO_x, NH_x, etc.). For further details, see the METTLER TOLEDO Evolved Gas Analysis Handbook [1].

1.3.1. TGA-MS: Example

Cobalt powder is used in the manufacture of pigments in the glass, enamel and ceramic industries. Cobalt oxidizes very rapidly to cobalt oxide (Co_3O_4) in air. To prevent oxidation, finely powdered cobalt is coated with a very thin protective film of paraffin, polyethylene glycol or polyethylene.

Despite the protective coating, cobalt oxide is still formed. The content can be determined by performing TGA-MS measurements. The cobalt powder is heated in an inert hydrogen atmosphere (4% H_2, 96% Ar) in a TGA coupled to a mass spectrometer.

Figure 3 displays some typical measurement curves. The figure shows the TGA and DTG (first derivative) curves together with the MS curves for hydrogen (m/z 2), water (m/z 18) and CO_2 (m/z 44). Three mass loss steps can be seen. The first step corresponds to the loss of moisture. The second step is mainly due to the reduction of the cobalt oxide in the sample.

This process consumes hydrogen and produces water as a reaction product ("negative" peak with a decrease in the m/z 2 signal, and a "positive" peak with an increase of the m/z 18 signal). At the same time, part of the coating degrades (signal on the m/z 44 curve). The rest of the coating decomposes from about 400 °C onward, mainly with the production of CO_2. However, the content of cobalt oxide in the sample cannot be reliably determined from the TGA measurement because the decomposition of the coating and the reduction of the cobalt oxide overlap.

The content could however be determined if we knew how much hydrogen is needed to reduce a known amount of cobalt oxide. This information was obtained from a TGA-MS measurement of cobalt oxide performed in a similar way as before in inert hydrogen (see Figure 4). In this experiment, the cobalt oxide is reduced to metallic cobalt by the hydrogen with the release of water. This can be seen from the opposing MS curves of m/z 2 and m/z 18.

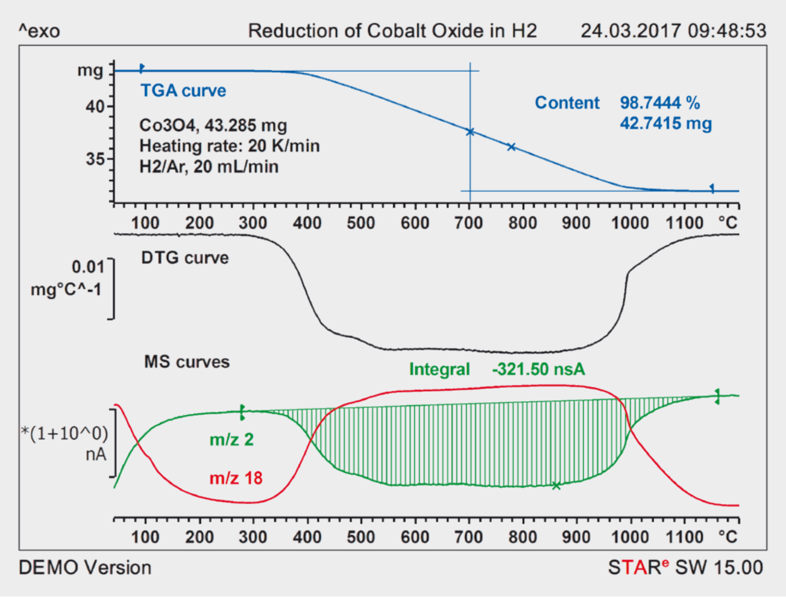


Figure 4.
TGA-MS curves of cobalt oxide (Co_3O_4) measured in inert hydrogen.

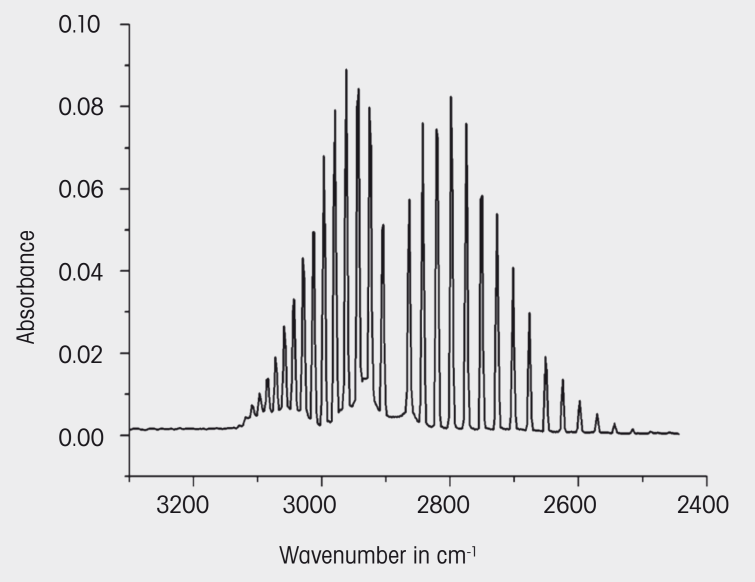


Figure 5.
FTIR spectrum showing the rotational-vibrational fine structure of hydrogen chloride at room temperature.

Figure 4 shows that a hydrogen equivalent of 321.5 nCb is needed (integration of the broad peak in the m/z 2 curve) for the reduction of 42.75 mg Co_3O_4. The MS curve in Figure 3 showed that a hydrogen equivalent of 13.28 nCb was needed to reduce the Co_3O_4 present in the coated cobalt powder. This evaluation gives a mass of 1.77 mg Co_3O_4 in the coated cobalt powder sample and corresponds to a Co_3O_4 content of 1.44%.

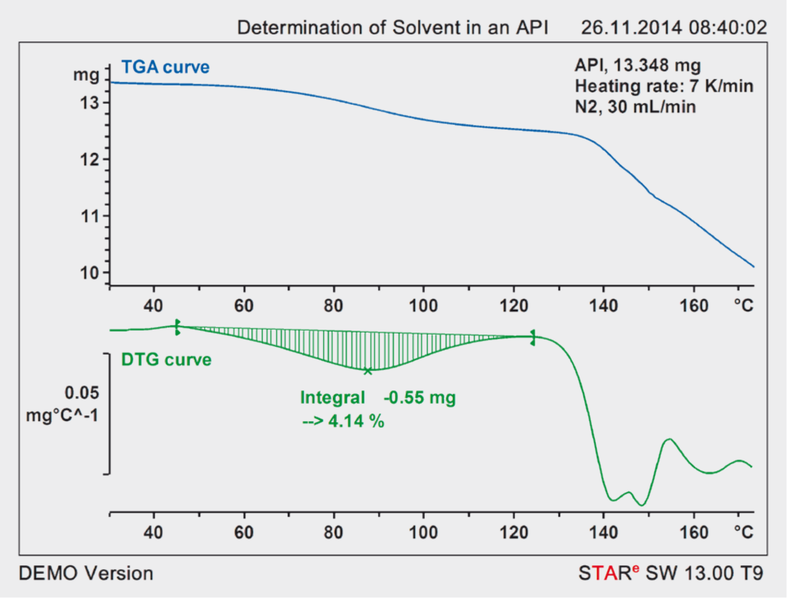


Figure 6.
TGA-FTIR measurement of an active pharmaceutical ingredient (API) that had been recrystallized in an unknown solvent.

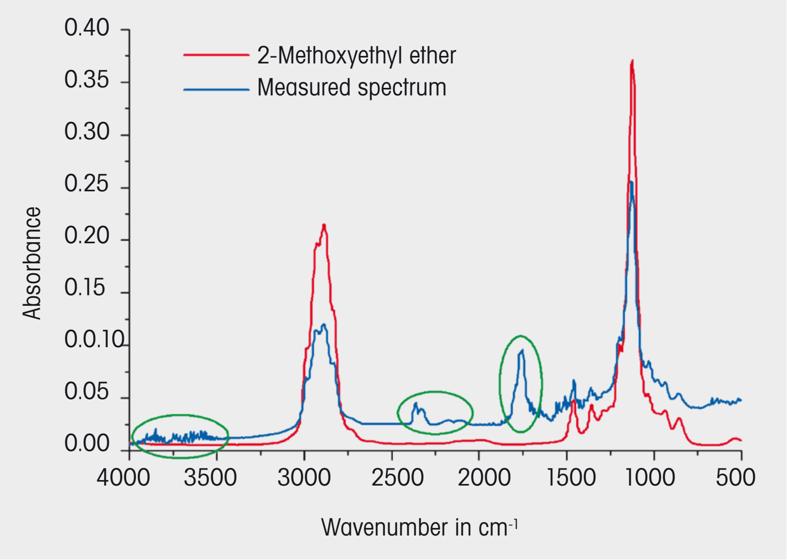


Figure 7.
Measured IR spectrum (blue curve) at a TGA temperature of 88 °C and the database IR spectrum of 2-methoxyethyl ether (best fit, red curve).

1.4. TGA-FTIR

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

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

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 5 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. The transmittance (T) is the ratio of the light intensity transmitted by the sample (I) to that incident on it (I_0), that is I/I_0 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 = –log T. Compared with transmittance, the absorbance has the advantage that it is a linear function of concentration.

The wavenumber is expressed in cm^{-1}. It is the reciprocal of the wavelength (λ) of the absorbed light and is calculated by dividing 10,000 by the wavelength (λ) in microns. The unit is a linear function of energy.

Fourier transform infrared spectroscopy (FTIR) is nowadays the usual method for recording infrared spectra. In contrast to the previously used dispersive IR spectrometers, an 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.

In TGA experiments, several gaseous substances are often evolved at the same time. Each of these compounds exhibits a characteristic IR spectrum. The measured IR spectrum is therefore usually the sum of numerous individual spectra. Even with the aid of reference spectra, the complete interpretation of the measured spectra is a difficult task.

Quite often, however, the identification of specific functional groups (e.g. of alcohols or of aromatic compounds, etc.) in the reaction products is also important. For further details, see the METTLER TOLEDO Evolved Gas Analysis Handbook [1].

1.4.1. TGA-FTIR: Example

Figures 6 and 7 show a typical application example of TGA-FTIR. The sample analyzed was an active pharmaceutical ingredient (API) that had been recrystallized in a solvent. The purpose of the TGA-FTIR analysis was to identify the solvent that had been used and to determine how much of it was still present in the product.

Figure 6 shows the TGA of the API and the calculated DTG curve. The TGA and DTG curves show three main processes: The small mass loss from room temperature up to about 50 °C is presumably due to the loss of moisture. We interpret the first clear mass loss step between 50 and about 125 °C as being due to the loss of the residual solvent. The substance finally decomposes from about 125 °C onward.

To identify the solvent, the IR spectrum of the gases evolved at a TGA temperature of 88 °C was examined more closely. Comparison of the spectrum with database spectra gave good agreement with 2-methoxyethyl ether, MEE, (Figure 7). This was therefore the solvent used to recrystallize the API.

Close comparison of the spectrum measured at 88 °C with the reference spectrum of MEE (Figure 7) shows that weak absorption bands occur in the measured spectrum that are not present in the reference spectrum von MEE. For example, there are indications for the presence of water (bands around 3700 cm^{-1}), CO_2 (bands around 2300 cm^{-1}), and carbonyl compounds (bands around 1750 cm^{-1}).

Altogether, this indicates that several other minor processes occur during the mass loss step between 50 and 125 °C besides the release of MEE, which is clearly the main process.

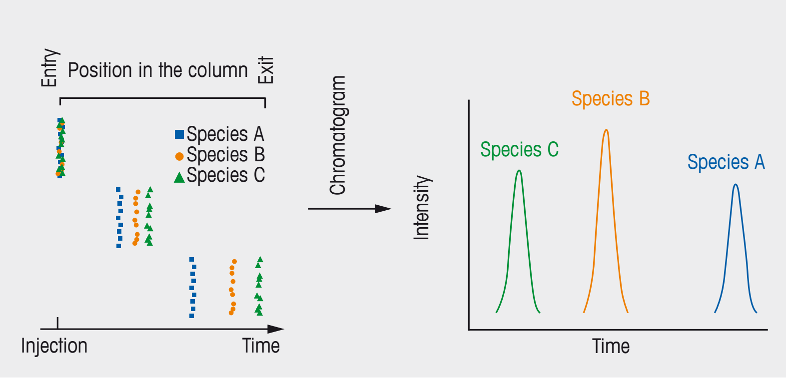


Figure 8. Separation of gases by gas chromatography: Different species of molecules take different times to pass through the column. The graph showing the intensity of the species arriving at the end of the column as a function of time is the gas chromatogram.

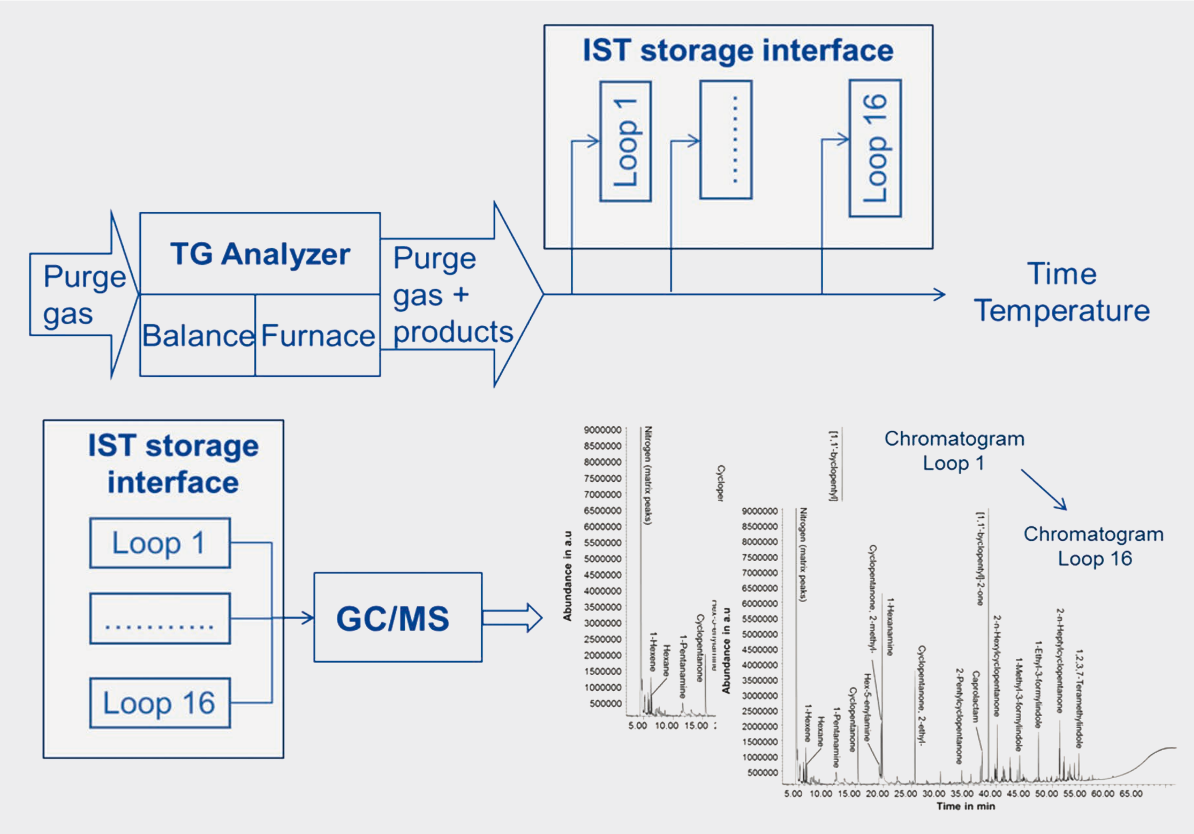


Figure 9. Setup of a TGA-GC/MS system. The decomposition gases taken from the TGA at different furnace temperatures are stored in storage loops.

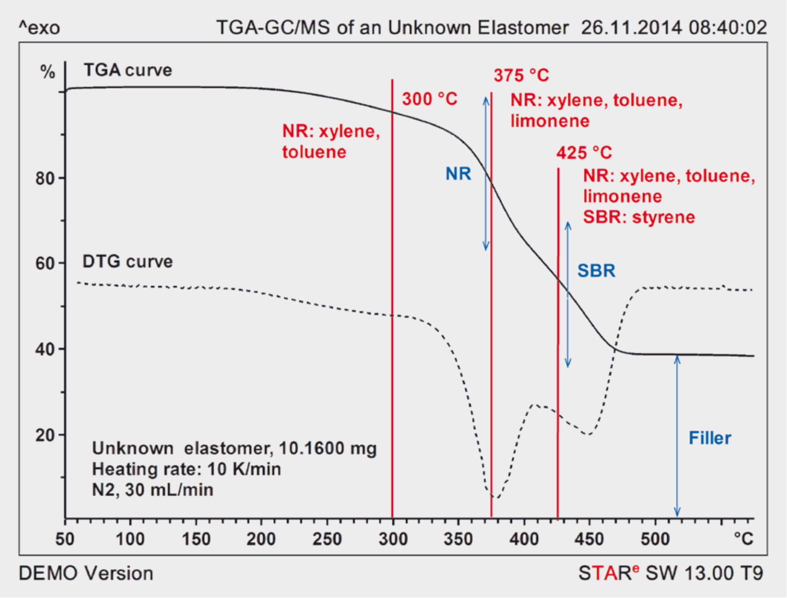


Figure 10.
The TGA and DTG curves and results of gas analysis using GC/MS of an unknown elastomer. The measurement was performed at a heating rate of 10 K/min and a flow rate of 30 mL/min nitrogen.

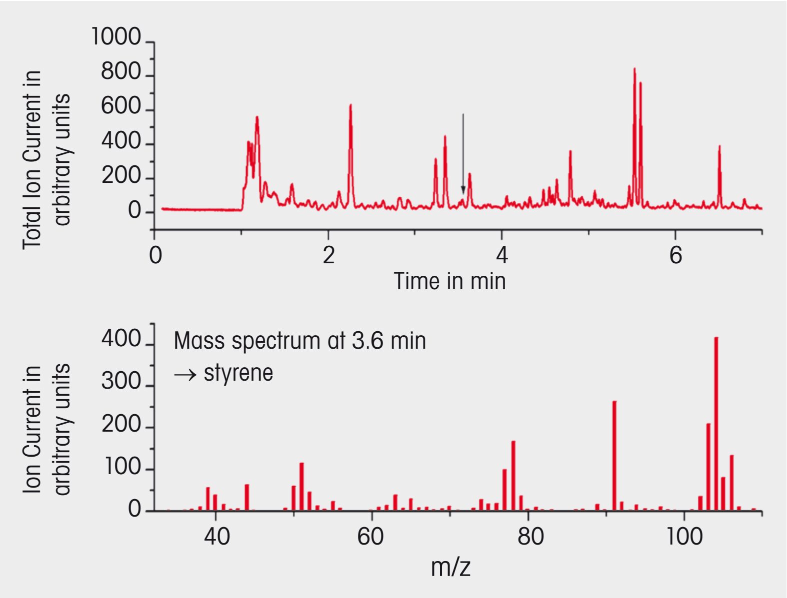


Figure 11.
Above: Chromatogram of the decomposition products of an unknown elastomer collected at a TGA furnace temperature of 425 °C. Below: The mass spectrum of the substance (styrene) corresponding to the peak marked by the black arrow in the chromatogram.

In this particular case, it is best to determine the mass loss and hence the residual content of MEE in the product from the DTG curve as indicated in Figure 6. This yields an MEE content of about 4.1%.

1.5. TGA-GC/MS

As previously mentioned, the interpretation of mass spectra or infrared spectra is more difficult when several unknown gaseous products are simultaneously released. In such cases, we recommend the combination of a separation technique and an identification technique to unequivocally identify the different compounds. The separation technique most often used for gas mixtures is gas chromatography (GC).

The principle of gas chromatographic separation is shown schematically in Figure 8. The gas mixture containing different types of molecules is injected onto the GC column. The different molecular species are transported through the column by a carrier gas and interact with the material used to fill or coat the column (the stationary phase). Depending on their relative affinity for the stationary phase, the individual molecules take different times to reach the end of the column. This so-called retention time is different for each type of molecule and can be used for identification purposes. The retention time however depends on several different parameters such as the column used, the carrier gas flow rate, and the temperature program used for heating the column.

For this reason, a GC is often coupled to a mass spectrometer (MS). This enables the different molecules to be unequivocally identified, independently of the above-mentioned GC operating parameters. METTLER TOLEDO offers two different GC systems: One is a GC-MS combination and the other a so-called Micro GC, which if needed can also be coupled to an MS. These two systems will be discussed in more detail in the following sections.

1.5.1. TGA-GC/MS

A TGA-GC/MS system uses a classical GC in which the column is heated using a suitable temperature program. The analysis of a gas mixture typically takes about 50 minutes.

During the TGA experiment, gas samples are taken at different furnace temperatures in order to obtain information about the composition of the decomposition gases evolved at those particular temperatures of interest. The METTLER TOLEDO GC/MS system is therefore additionally equipped with a storage interface system that can store up to 16 gas samples in separate 250-µL storage loops. Each of these samples represents the composition of the decomposition gases at the temperatures chosen by the user.

The samples are then analyzed offline by the GC/MS after completion of the TGA measurement (for further details see Chapter 4, Thermogravimetry and Gas Analysis, Part IV: TGA and GC/MS).

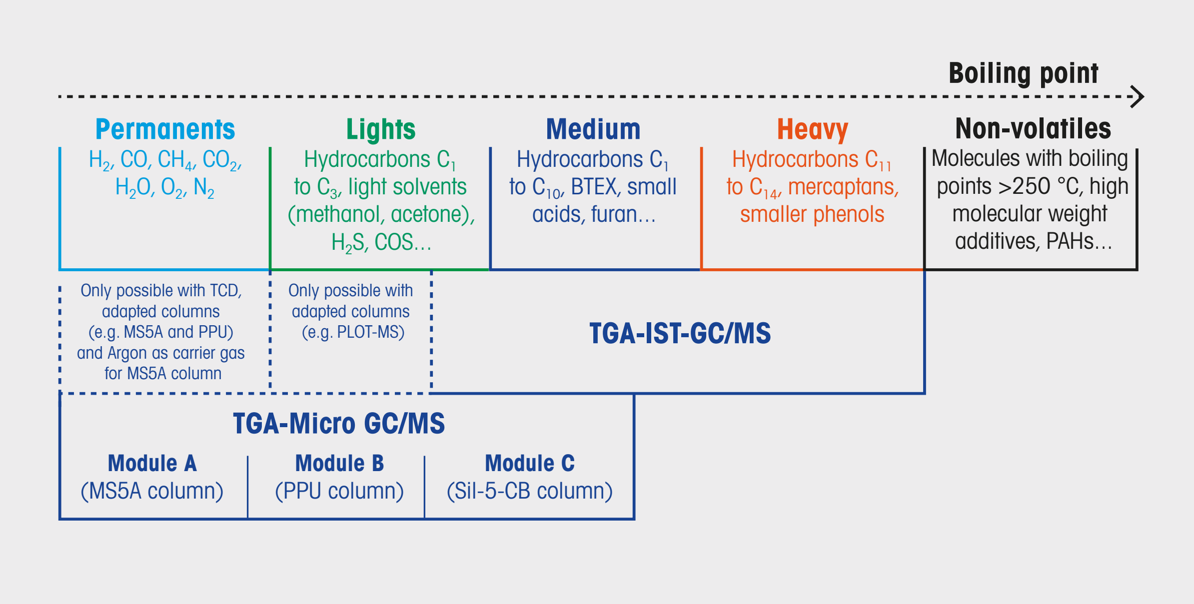


Figure 12.
Application range of TGA-Micro GC(/MS) and TGA-IST-GC/MS.

The basic setup of a TGA-GC/MS system is shown schematically in Figure 9. The IST storage interface can store up to 16 gas samples. The gas samples are analyzed one after the other in the GC/MS after the TGA experiment. Each peak in the chromatogram corresponds to a substance that can be identified by the MS.

1.5.2. Example

As an example, Figures 10 and 11 show the results of a TGA-GC/MS measurement of an unknown elastomer in nitrogen. The purpose of the measurement was to identify the elastomer. Figure 10 shows the resulting TGA and DTG curves.

The curves indicate two pyrolysis steps. This suggests that the elastomer sample consists of two different elastomers. The DTG curve was used to select the temperatures at which the gas samples were taken in a second experiment. Three such temperatures are marked in the figure by vertical red lines. The gas samples were analyzed by GC/MS after the TGA experiment. An example of such an analysis is shown in Figure 11. The upper diagram shows the chromatogram of the gas sample at a TGA temperature of 425 °C. Mass spectra were recorded for every peak in the chromatogram. The mass spectrum corresponding to the peak marked by the black arrow in the chromatogram is displayed in the lower part of Figure 11. Comparison of this spectrum with reference spectra in a database indicated that the measured MS spectrum was that of styrene. This allows us to conclude that SBR is also present in the unknown elastomer. In a similar way, decomposition products were detected that are typical for natural rubber, NR, (limonene, toluene, xylene, see Figure 10). The unknown elastomer therefore appears to be a mixture of NR and SBR.

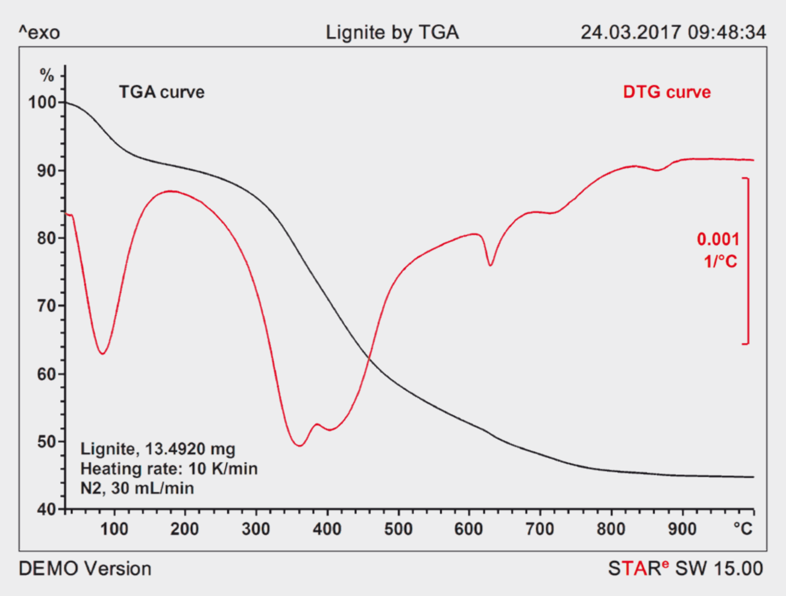


Figure 13.
TGA curve and its first derivative (DTG curve) of lignite (brown coal).
The measurement was performed at 10 K/min in nitrogen.

The composition of elastomers can be estimated from the TGA curve, namely about 30% NR, 30% SBR and 40% carbon black (filler). It would not have been possible to identify the two elastomer components by MS alone, and only with considerable difficulty by FTIR.

1.6. TGA-Micro GC/MS

In contrast to conventional GC, a gas sample can be analyzed in a Micro GC

Table 1. Comparison of MS, FTIR, GC/MS and Micro GC(/MS).

Technique	**Advantages**	**Limitations**	**Typical applications**
MS Pfeiffer Vacuum Thermostar GSD 320 T	- Online technique, typical resolution[1] 2 °C - High dynamic sensitivity (>5 decades) - Quantitative evaluation is possible	- Maximum mass 300 amu - Interpretation of the data requires previous information about the sample - Gas inlet can become blocked by large molecules (condensation) - Data format is not compatible with other data bases	- Detection of small molecules (CO_x, NO_x, SO_x, H_2O, HCl, etc.) - Residual solvents in active pharmaceutical ingredients
FTIR Thermo Scientific Thermo Nicolet iS10/50	- Online Technique, typical temperature resolution[2] 2 °C - Can also be used for the analysis of solids but needs an ATR accessory, (only iS50) - It also provides information about the structure of the detected gases	- Dynamic sensitivity is about 3 decades (DTGS detector) - Quantitative evaluation is difficult - Interpretation of the IR data requires experience and previous information about the sample - Less sensitive than MS and GC/MS	- Detection of simple and complex compounds - Residual solvents in active pharmaceutical ingredients
GC/MS SRA IST16 Agilent 7590 GC Agilent 5975 MS	- Gas mixtures can be easily analyzed (separation by GC, identification by MS) - Quantitative evaluations are possible (chromatogram) - GC/MS can also be used as a "stand alone" system for the analysis of liquids	- Storage mode: up to a maximum of 16 gas samples can be stored during a TGA experiment; GC/MS measurements need much time - Online operation: poor separation power of the GC column - Maximum mass 1050 amu	- Volatile molecules up to about 250 amu
GC and Micro GC/MS	- Quasi online-technique, typical temperature resolution 30 °C[3]; - Up to 2 different columns can be used simultaneously for different groups of gases - Quantitative analyses are possible (concentrations) - Can be used in combination with MS	- Columns are only sensitive for a limited number of gases - Acidic gases cannot be detected (e.g. HCl, SO_x, HF).	- Detection of small molecules ("permanents") possible without MS - Detection of light and medium weight compounds by Micro GC/MS

[1] Single ion (MID) scan with 20 masses, integration time 0.5 s, heating rate 10 K/min
[2] Resolution 4 cm^{-1}, averaging over 8 spectra, heating rate 10 K/min
[3] Heating rate 10 K/min, analysis time of Micro GC 3 min

within a few minutes. Micro GC is therefore an online method, like MS or FTIR, except that the temperature resolution is not so good as with MS and FTIR: an analysis time of 3 minutes and a heating rate of 10 K/min results in a temperature resolution of 30 K.

The METTLER TOLEDO Micro GC is modular and can be equipped with up to 4 modules. Each of these modules is a Micro GC that has its own column. This enables different "groups" of gases be identified depending on the number of columns used.

A Micro GC is of course ideal for the detection of small molecules (e.g. CO, CO_2, H_2O, NOx, hydrocarbons up to C_{10}) which cannot be detected or only detected with difficulty using a conventional GC (e.g. H_2O, H_2).

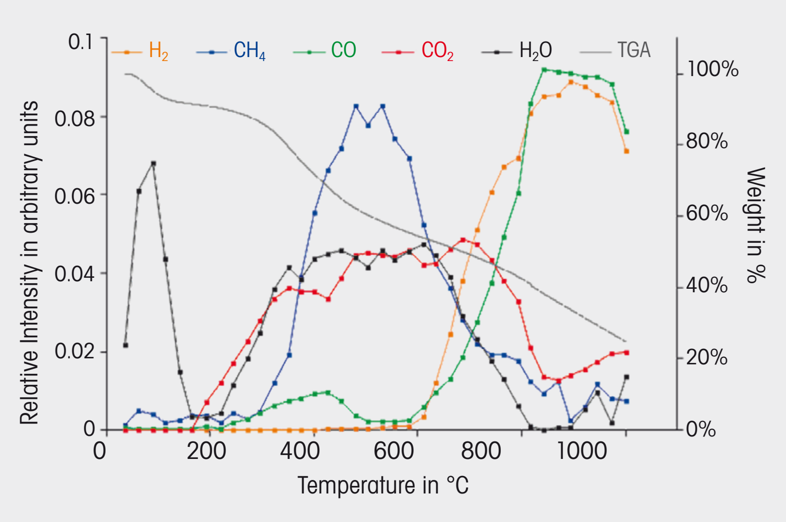


Figure 14. TGA curve and temperature profiles of different decomposition gases measured using a Micro GC equipped with a TCD detector. The profiles are normalized and do not represent the actual composition of the pyrolysis gases.

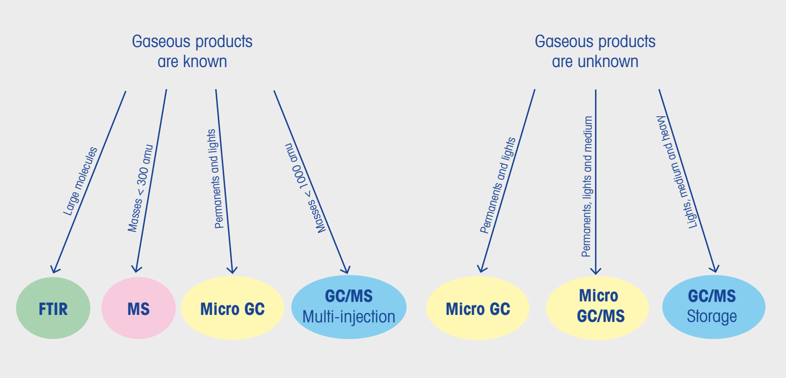


Figure 15. Recommendations for choosing an EGA technique.

Figure 12 illustrates the application range of TGA-Micro GC/MS and TGA-GC/MS. If a column for C_4 to C_{10} hydrocarbons is used in the Micro GC, the identification of the particular compound based on its retention time is difficult. MS detection is recommended for such columns instead of the TCD (thermal conductivity detector) normally used in the Micro GC. For further details on Micro GC see Chapter 5, Thermogravimetry and Gas analysis, Part V: TGA and Micro GC/MS.

1.6.1. Example

As an example, Figure 13 shows the TGA and DTG curves of a sample of brown coal (lignite). The measurement was performed at a heating rate of 10 K/min in nitrogen. Mainly CO_2, H_2O, H_2, CH_4 and CO are expected as pyrolysis gases. The Micro GC is ideal for the detection of these gases.

Figure 14 shows the emission profiles of the main decomposition gases expected as a function of temperature. For better visualization, the profiles were normalized to their total intensity (area under the emission profile). This representation does not therefore indicate the actual concentrations of the different decomposition gases.

Up until about 180 °C, mainly moisture is evolved. Between 200 °C and 600 °C, methane and CO are also released besides water and CO_2. From about 600 °C onward, the actual gasification of carbon occurs whereby mainly CO and hydrogen (synthesis gas) are produced.

1.7. Conclusions and recommendations

TGA-MS, TGA-FTIR, TGA-GC/MS and TGA-Micro GC(/MS) are powerful techniques that yield both quantitative (mass loss) and qualitative (identification) information about the gaseous products released during a TGA measurement. Table 1 presents a comparison of the four methods.

Not all techniques are equally suitable for dealing with specific questions. The overview in Figure 15 shows which technique is best for solving a particular application problem.

The GC/MS multi-injection mode is a special operating mode of the GC in which the separation power of the GC is greatly reduced. The advantage of this operating mode is that GC/MS can be performed online like MS or FTIR.

References

[1] N. Fedelich, METTLER TOLEDO Collected Applications Handbook: Evolved Gas Analysis, Second Edition.

2. Thermogravimetry and Gas Analysis, Part 2: TGA-MS

Dr. A. Hammer

TGA experiments in combination with a suitable EGA technique not only provide quantitative information about the change in mass of a sample but also qualitative information about the gaseous reaction or decomposition products that are evolved. In the previous chapter, we presented an overview of the advantages of coupling a thermobalance to a gas analyzer for the qualitative analysis of the reaction or decomposition products [1]. In this chapter, we show in more detail how TGA-MS experiments are performed and evaluated.

2.1. Introduction

TGA-MS is used as an analysis method to detect small gaseous molecules such as H_2O, HCl or CO_2 evolved from samples that are not too complex. A typical example is the detection of residual solvents in pharmaceutical products. In this analysis method, the evolved gases from the TGA experiment are transferred online through a capillary tube into the MS. The temperature at which substances are evolved can therefore be determined exactly.

Normally, short lengths of heated capillary tubing (about 0.5 to 1 m long) are used to transfer the gases from the TGA into the MS. The capillaries are solely for gas transfer and have no separation function. This is different to GC/MS where suitable GC capillary columns are used to separate the evolved substances. For TGA-MS experiments, METTLER TOLEDO recommends coupling the TGA to a Pfeiffer Vacuum ThermoStar Analysis system [2].

2.2. TGA-MS setup

The schematic diagram in Figure 1 shows the setup of a TGA-MS instrument combination. The MS capillary embedded in a heated transfer line (normally at 200 °C) is inserted into the TGA furnace by means of a special TGA-MS interface. The interface consists of a glass body, a support for the capillary, and a second gas outlet through which the excess gas emitted from the TGA can be vented to the surroundings. The position of MS capillary in the TGA furnace is very important.

2.3. Influence of the position of the capillary in the TGA-furnace on the MS signal

The tip of the MS capillary in the TGA furnace should be positioned as close as possible to the sample holder and hence the sample and the gases that are evolved. The length of the capillary varies depending on the TGA and the sensor. The position of the end of the capillary in the furnace influences the amplitude of the MS signal.

This is illustrated in Figure 2. It shows the CO_2 peak area obtained from four $CaCO_3$ samples of equal mass that were heated at 10 K/min from 550 to 750 °C in argon at 20 mL/min. The peak area decreases by about 6% per cm displacement from the optimum position of the tip of the capillary. In addition, the peak maximum is somewhat delayed. At a flow rate of 20 mL/min, the delay in the large TGA furnace is about 9 s per cm displacement [3].

2.4. Gases

Argon is most frequently used as a purge gas for TGA-MS experiments. Besides argon, nitrogen and helium are also used. Air or oxygen is less recommended because oxygen reduces the lifetime of the filament in the mass spectrometer. When nitrogen is used, samples which evolve CO cannot be investigated because CO has the same molecular mass as nitrogen (28) – the CO cannot then be identified.

Helium is expensive and requires the use of a flow rate meter specially adjusted for this gas. Since the thermal

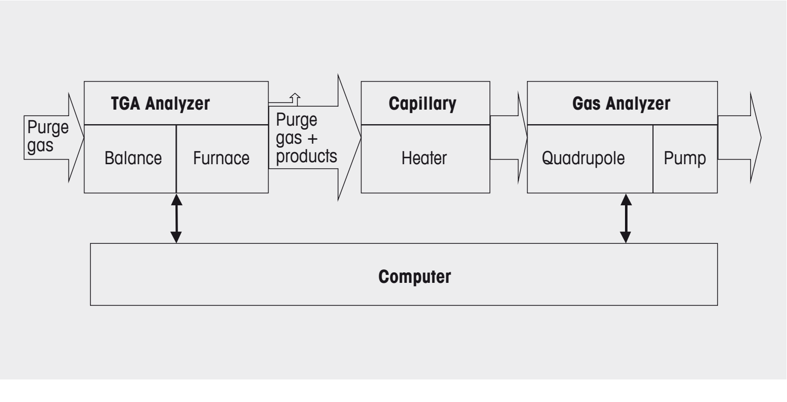


Figure 1. Schematic diagram of the TGA-MS setup.

conductivity of helium is higher than that of argon or nitrogen, special attention must be paid to the adjustment of the heat flow with TGA/DSC instruments. Furthermore, with helium, the TGA furnace chamber must be adequately purged. It is therefore advisable to purge the TGA overnight with helium before performing the first measurement.

The gas flow rate (sum of protective gas, purge gas and reactive gas) through the furnace is very important. With decreasing flow rate, the gases produced are less diluted and the MS signal is larger.

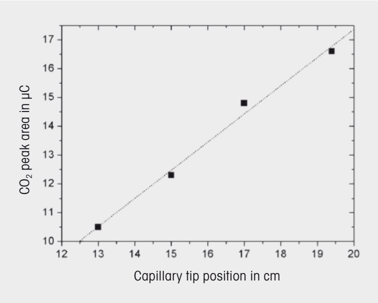


Figure 2.
Influence of the position of the capillary tip in the furnace on the sensitivity [3].

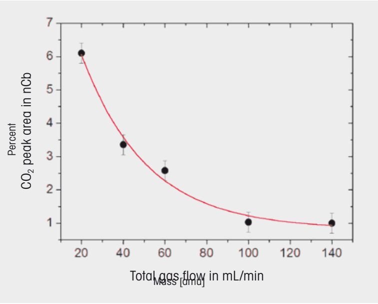


Figure 3.
Influence of the gas flow rate on the peak area of CO_2 (m/z 44). The peak area was normalized to 1 at a flow rate of 140 mL/min. The peak areas were corrected for different sample masses [3].

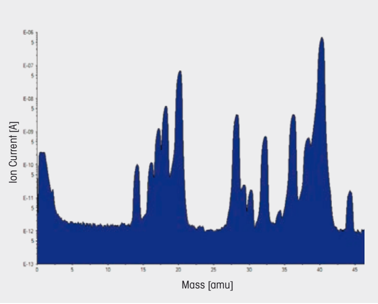


Figure 4.
MS spectrum in the analog mode of a mixture of alkanes from the decomposition of PE or PP.

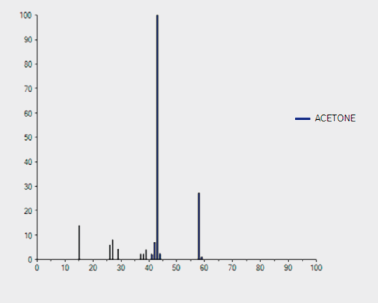


Figure 5.
MS spectrum of acetone in the bar graph presentation mode.

This is illustrated in Figure 3 which shows the influence of gas flow rate on the peak area of the CO_2 peak using the decomposition of calcium carbonate as an example. The samples were heated at 15 K/min. This diagram shows that the sensitivity of the MS at low gas flow rates depends strongly on the flow rate. This means that a very stable gas supply is needed for the reliable measurement of MS signals particularly at low flow rates [3].

2.5. Measurement modes

Three main operating modes are used to record MS spectra:

- scan analog
- scan bar graph
- MID scan

In the so-called scan analog mode shown in Figure 4, the fragment ions and molecular ions are measured continuously between two different masses, for example between m/z 5 and 150. The same is true for the scan bar graph mode shown in Figure 5 except that the presentation of the measurement results is different.

Measurements can also be made in the MID mode (multiple ion detection), also referred to as the SIM mode (selected ion monitoring). This measurement mode is very sensitive because only a few specific masses are detected.

If nothing is really known about the decomposition products expected from a particular sample, a measurement is first performed in the scan analog or scan bar graph mode over a wide mass range to identify the main fragment ion peaks.

This is followed by a second experiment in which only the masses of these particular fragment ions are measured in the MID mode. This results in better time resolution and greatly improved sensitivity compared with the initial survey analyses. Furthermore, there is the possibility of quantifying the masses found.

The following steps illustrate the procedure for unknown and known samples:

Procedure for the TGA-MS analysis of an unknown sample:

- Perform the TGA measurement and evaluate the results.
- Perform the TGA-MS analysis with the MS in the scan analog or scan bar graph mode.
- Evaluate the MS data and identify the masses of interest.
- Perform the TGA-MS analysis with the MS in the MID mode for the detection of specific masses.

Procedure for the TGA-MS analysis of a known sample:

- Perform the TGA-MS analysis with the MS in the MID mode to detect specific masses.

2.6. Detecting low concentrations

If you want to identify low concentrations in samples, it is best to perform a blank curve subtraction. This is done by carrying out an identical TGA-MS experiment with empty crucibles and subtracting the MS curves from the MS curves obtained from the sample measurement. Small peaks can then be more easily identified.

2.7. Overlap of fragments of the same mass

It is possible that different products form fragment ions that have the same mass. For example, ionization of a water molecule produces ions with masses m/z 17 and 18. Likewise, when ammonia (NH_3) is evolved in a TGA measurement, an ion of mass m/z 17 is obtained. Whether masses 17 and

18 originate from the same source or not can be investigated by observing the ratio of the curves of m/z 17 to 18. If the ratio is constant, both masses probably originate from the same source. If the ratio is not constant, it is most likely that both water and NH_3 are present as fragment ions.

Figure 6 shows an experiment involving the curing of an amino resin as an example. Curing involves a polycondensation reaction in which water is eliminated. From about 50 to 160 °C, the ratio of the MS curves for masses m/z 17 and 18 is constant, which indicates the release of water.

From about 220 °C onward, the curves of masses m/z 17, 30 and 31 then exhibit a marked increase. This is accompanied by a decrease in the DTG curve, which indicates that decomposition of the sample has begun. At the same time, the m/z 18 curve shows a noticeable decrease. Since water is characterized by masses m/z 17 and 18, we expect the ratio to remain constant as long as water is released. From 220 °C onward, the ratio changes thereby indicating a fragment other than water is detected. Since the sample is an amino resin, we conclude that NH_3 is produced as a decomposition product above 220 °C. This was confirmed by analyzing the sample with another technique (TGA-FTIR).

2.8. Quantitation

Normally, TGA-MS is used to perform qualitative measurements. The aim of a TGA-MS measurement is to identify decomposition products by identifying molecular ions or their fragment ions and so elucidate the composition of the sample. In quantitative measurements, the measurement conditions should be kept constant. The example shown in Figure 7 illustrates how methyl salicylate can be determined in a sample of butadiene rubber (BR). This was done by measuring the original BR sample without methyl salicylate and samples of BR to which 0.5, 1 and 5 µL of methyl salicylate had been added. The main fragment ion of methyl salicylate has a mass of 92. The m/z 92 ion was recorded for each sample and the results evaluated. The detection limit in this case was about 1 µL. In addition, a calibration curve was constructed which enabled unknown amounts of methyl salicylate in BR above the detection limit to be determined.

The upper diagrams in Figure 7 show the TGA weight loss curve of BR without the methyl salicylate additive and the curves of BR samples containing different amounts of the substance.

The lower diagram shows the MS curves of the 92 m/z fragment ion. Since the concentrations were very low, the m/z 92 curves of the samples containing the additive were corrected by subtracting the m/z 92 curve of the sample without the additive.

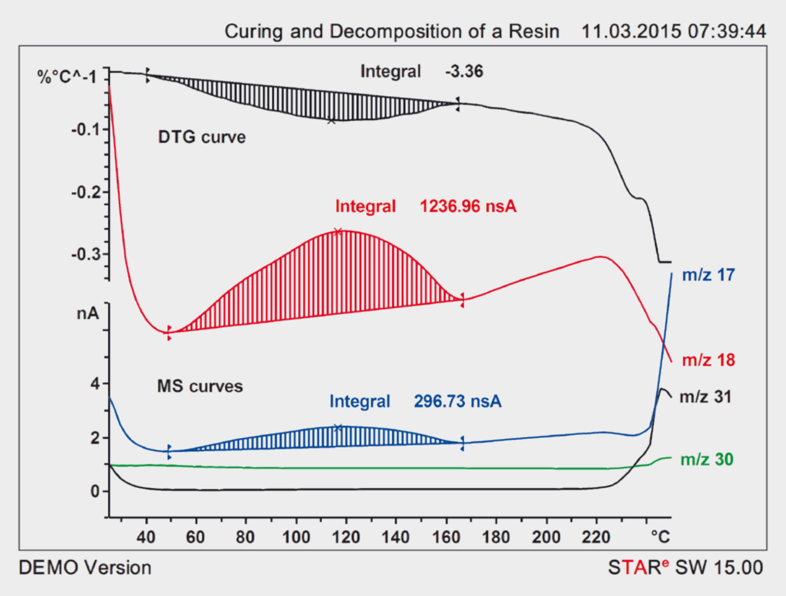


Figure 6. Decomposition of an amino resin: DTG curve and MS curves of masses m/z 17, 18, 31 (methanol) and 30 (formaldehyde).

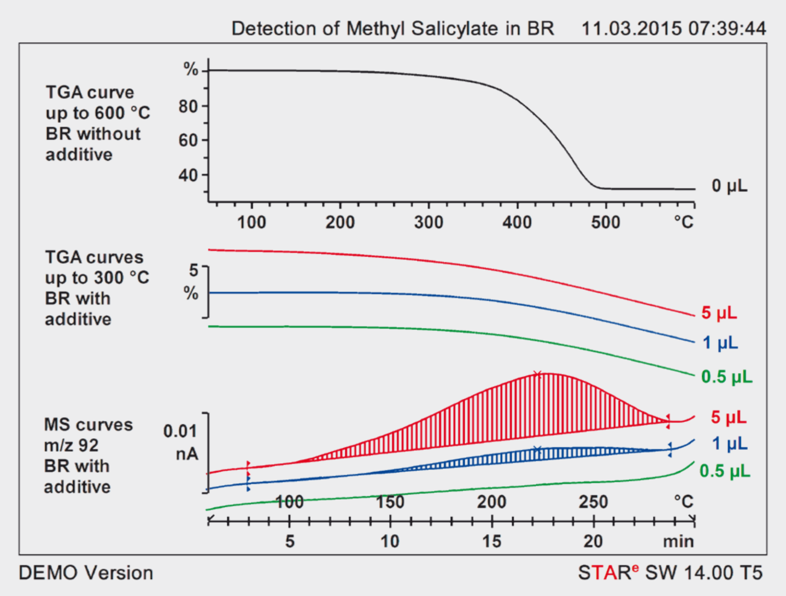


Figure 7. Quantification of methyl salicylate in a butadiene rubber sample.

2.9. Examples

The first example describes how the decomposition of ammonium perchlorate (NH_4ClO_4) in an argon atmosphere was investigated. The resulting TGA, DTG, and MID curves are displayed in the diagram in Figure 8.

About 7 mg of sample was weighed into an aluminum oxide crucible. The sample was first held isothermally at 35 °C for 20 minutes and then heated to 500 °C at a heating rate of 10 K/min. The isothermal step is recommended for samples that are thermally stable at this temperature. It ensures that there is sufficient time for the purge gas (e.g. argon) to remove any oxygen and water present after inserting the sample into the TGA furnace.

The measurements were performed in the MID mode. The ammonium perchlorate is expected to decompose to the following main products: N_2, O_2, H_2O and Cl_2. All four gases were detected. Table 1 presents an overview of the masses detected and the possible molecules. It is worth noting that the sample decomposes in three steps and that decomposition products are evolved in all three steps.

Table 1.
Masses of ions formed in the decomposition of ammonium perchlorate and the possible molecules.

Masses detected, m/z	Possible molecules
14, 28	N_2
16, 32	O_2
17, 18	H_2O
35, 70, 72	Cl_2

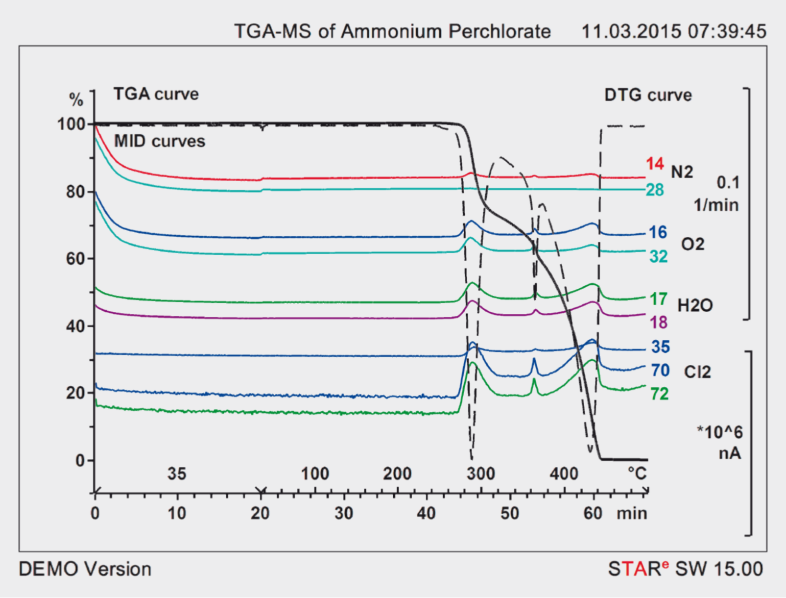


Figure 8.
Above: TGA and DTG curves. Below: MID curves resulting from the decomposition of ammonium perchlorate.

The second example describes the decomposition of a sample of limestone in argon. The results are summarized in Figure 9. The sample first loses about 0.1% moisture. This is followed by a large weight loss step of 43.2% due to the decomposition reaction in which mainly CO_2 (m/z 44) and CO (m/z 28) were detected. The weight loss corresponds to a content of 98.2% $CaCO_3$ indicating that the sample also contained small amounts of inorganic impurities.

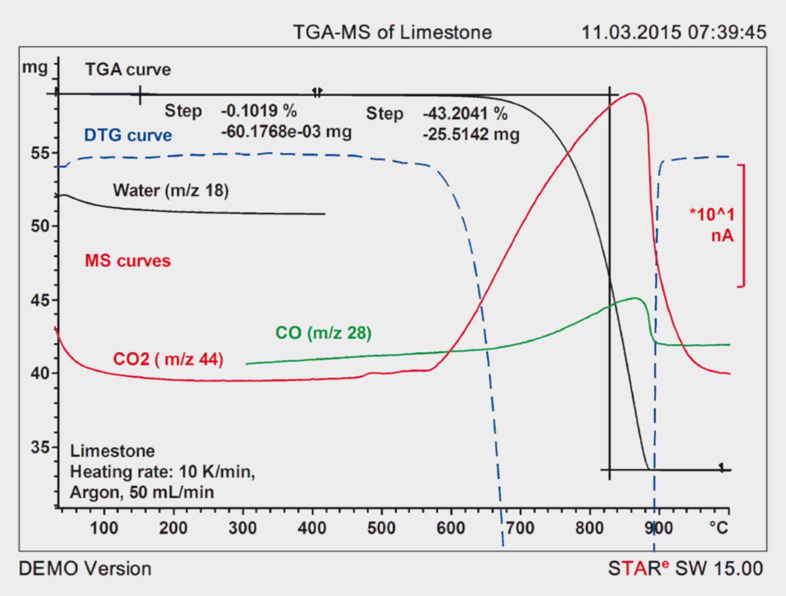


Figure 9.
TGA, DTG and MS curves obtained from the decomposition of a sample of limestone.

Both examples show how TGA-MS can be used to reliably detect decomposition products evolved from less complex samples.

In the third example, a complex rubber compound was measured at a heating rate von 10 K/min up to 550 °C in a nitrogen atmosphere. The TGA and MID curves are displayed in Figure 10.

The results show that about fifty different decomposition products were detected. Identification of the individual substances is difficult because the molecules are simultaneously detected in the mass spectrometer and are not separated. Furthermore, when polymeric materials such as elastomers and thermoplastics are measured, only small amounts of samples should be used. Otherwise, there is always the possibility that the capillary line or the baffle in the MS becomes blocked. In this example, we used a sample of about 5 mg.

For this type of sample, we recommend TGA-GC/MS as the best method. Chapter 4 will cover different aspects of TGA-GC/MS in detail.

2.10. When to use TGA-MS

The online combination of a TGA with an MS is recommended when we expect small molecules as reaction or decomposition products and when we are dealing with starting materials that do not simultaneously evolve a large number of substances. Gases such as CO_2, CO, O_2, N_2, H_2O, NH_3, NO_2 or solvents such as acetone or ethanol can be easily identified. If many unknown substances are simultaneously evolved, for example in the decomposition of an elastomer, we recommend TGA-GC/MS because in this technique the components are first separated by GC and then identified by MS using suitable databases.

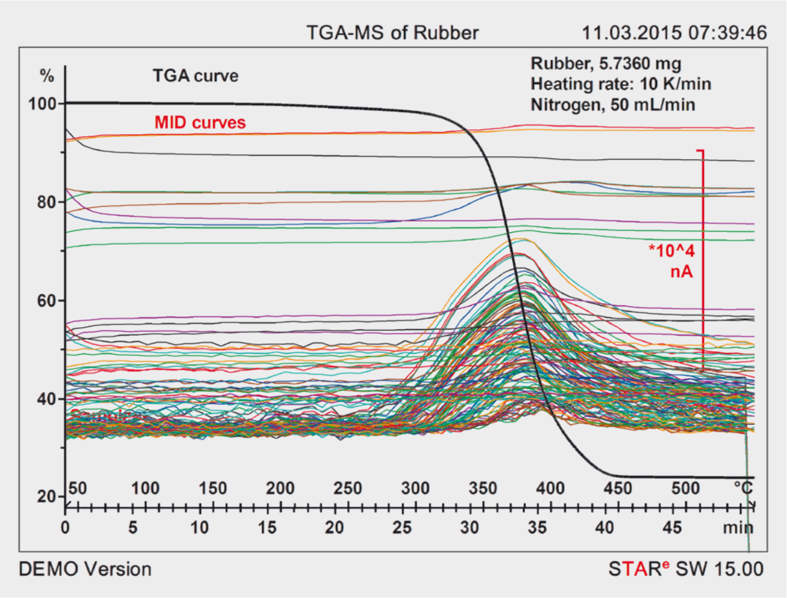


Figure 10.
TGA and MID curves resulting from the decomposition of a rubber sample in nitrogen.

2.11. Conclusions

TGA-MS is an excellent technique. It enables you to identify gases evolved in a TGA analysis even at very low concentrations (ppm level). This is particularly the case when we are dealing with small molecules and mixtures that are not too complex.

References

[1] M. Schubnell, Thermogravimetry and gas analysis, Part 1: Basic principles and overview, UserCom 45, 1–9.
[2] Vacuum Technology Know How, Pfeiffer Vacuum.
[3] M. Schubnell, The TGA-MS combination, UserCom 27, 15–17.

3. Thermogravimetry and Gas Analysis, Part 3: TGA/DSC-FTIR

Dr. Melanie Nijman

TGA experiments combined with EGA not only provide quantitative information about the change in mass of a sample but also supply qualitative information about the gaseous reaction or decomposition products that are evolved. In this chapter, we will show how TGA-FTIR experiments are performed and evaluated.

3.1. Introduction

Chapter 1 presented different techniques for the analysis of gaseous decomposition or reaction products evolved in a TGA experiment.

This chapter describes the use of a TGA coupled to a Fourier transform infrared spectrometer (FTIR). What parameters are vital for the successful operation of the TGA and the FTIR, what is important regarding the sample, and how do we evaluate the vast amount of data that is collected? These and other topics are discussed in the following sections.

3.2. TGA-FTIR setup

TGA-FTIR measurements are performed using a normal TGA/DSC or TGA instrument. METTLER TOLEDO offers an optimized TGA furnace interface for connecting the TGA to the FTIR spectrometer and recommends the Thermo Scientific™ TM iS™50 or iS™10 FTIR spectrometer equipped with a gas cell as spectrometer. In principle, any FTIR spectrometer equipped with a suitable gas cell can be used.[1]

The TGA is connected to the gas cell in the FTIR by means of a heated transfer line. Both the gas cell and the transfer line are maintained at 200 °C to prevent condensation. The decomposition products produced in the TGA are transferred by the purge or reactive gas together with the balance protection gas through the transfer line into the gas cell.

In TGA-FTIR measurements the balance protection gas is usually nitrogen at a flow rate of about 20 mL/min. The purge or reactive gases are typically nitrogen, air or oxygen at a flow rate of 50 mL/min). Figure 1 shows a schematic diagram of a TGA/DSC-FTIR setup.

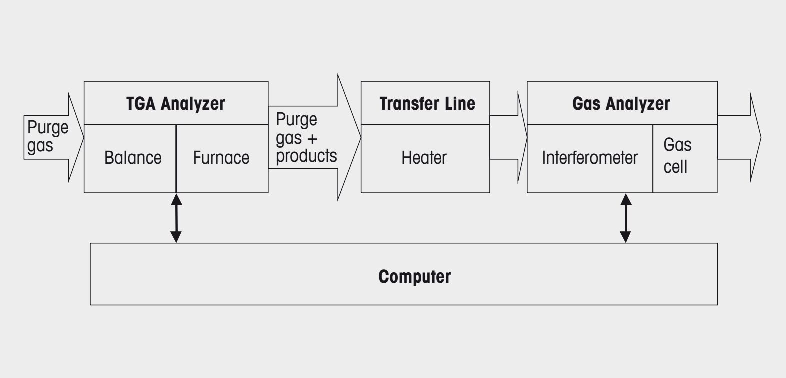


Figure 1.
Schematic diagram of a TGA coupled to an FTIR spectrometer.

Table 1.
Overview of FTIR measurement parameters.

Parameter	Measurement time	Effect	Typical value
Mirror speed ↑	↓	Poorer noise suppression	0.4747 cm/s
Number of scans ↑	↑	Better noise suppression	8
Resolution ↑	↑	Better resolution	$4\ \text{cm}^{-1}$

3.3. Sample mass and sample preparation

The sample mass should be chosen so that each of the compounds we want to detect makes up about 100 µg. For most purposes, a sample mass of about 10 mg is sufficient. For smaller concentrations, the sample mass must be increased in proportion or a more sensitive type of gas analyzer system (GC/MS or just MS) must be used.

3.4. Measurement parameters and data generation

3.4.1. TGA

In general, TGA-FTIR measurements are performed using the usual TGA

---

[1] The automatic synchronization of the TGA with the spectrometer cannot be guaranteed with other spectrometers.

methods, for example a heating rate of 10 or 20 K/min. The entire TGA temperature range from 22 to 1600 °C can be used.

3.4.2. FTIR

Default parameters are given by the manufacturer for the most important settings of the FTIR spectrometer (e.g. amplification, Fourier transformation, filter, etc.). These guarantee optimum infrared measurement conditions (e.g. for noise).

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 (this is shown in the OMNIC™ software of the iS™50 or iS™10) multiplied by the heating rate yields the temperature resolution with which information about the composition of the evolved gases is recorded.

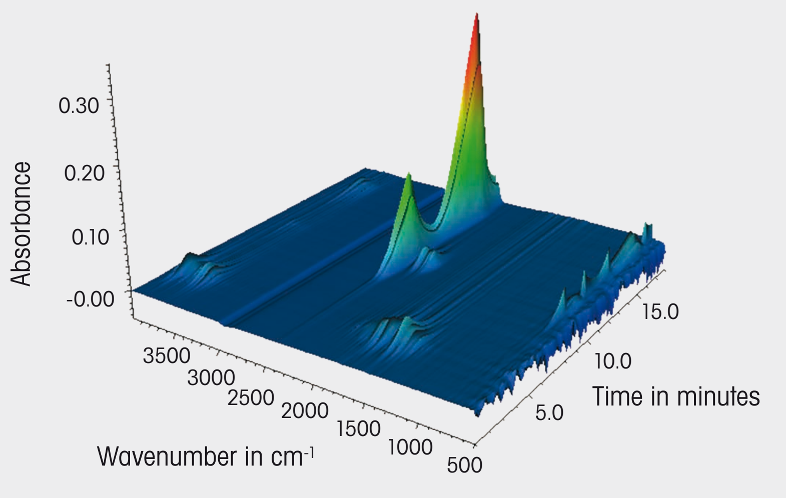


Figure 2.
FTIR spectra recorded during a TGA measurement. The x-axis shows the wavenumbers of the individual spectra, the y-axis the time at which the particular spectrum was recorded, and the z-axis the absorbance.

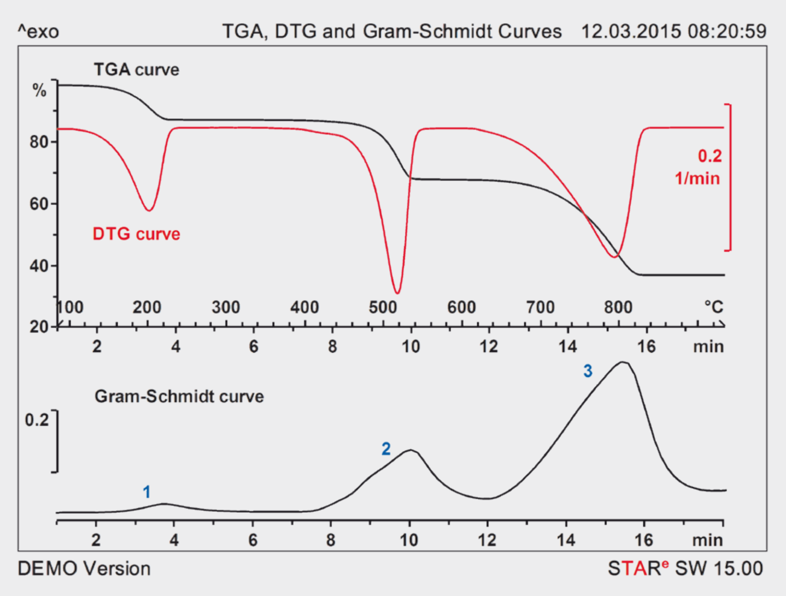


Figure 3.
TGA, DTG (above) and Gram–Schmidt (below) curves of calcium oxalate monohydrate.

An example using the parameters is shown in Table 1: At a resolution of 4 cm^{-1}, a scan takes about 1 second. A spectrum based on eight scans therefore takes about 10 seconds. At a TGA heating rate of 10 K/min, this means that a spectrum is recorded every 1.67 °C. This results in 360 spectra for a temperature range of 150 to 750 °C.

Figure 2 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-axis. The y-axis is the time axis and the z-axis shows the absorbance.

A section at right angles to the time axis yields a spectrum, and a section at right angles to the wavenumber axis the absorbance of the sample for this wavenumber as a function of time.

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 measurement, the blank correction eliminates the unwanted absorption signals from these two gases.

The blank spectrum is measured immediately before the start of the TGA-FTIR experiment and subtracted from every spectrum recorded during the TGA measurement. The blank spectrum must be measured using the same parameters as were used to record the spectra.

3.4.3. Evaluation of a TGA-FTIR measurement

As has already been explained, a TGA-FTIR experiment produces a large number of FTIR spectra besides the TGA/DSC measurement curves. The assignment of a particular spectrum to a particular temperature is done via the point in time when the FTIR spectrum was recorded.

The evaluation of the TGA-FTIR measurement takes place in two steps. First, the TGA/DSC data is evaluated, for example step valuation with the aid of the first derivative of the TGA curve (the DTG curve).

After this the FTIR spectra are evaluated. This is usually done in three steps:

1. Generation of a Gram–Schmidt curve
2. Interpretation of spectra at selected temperatures
3. Construction of chemigrams

The following example illustrates the procedure and evaluation of results obtained from a TGA-FTIR analysis of calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$. The measurement was performed using a TGA/DSC and an iS™50 FTIR spectrometer. The TGA heating rate was 10 K/min. The measurement was performed in nitrogen at 50 mL/min. The FTIR measurement parameters used were the standard values given in Table 1.

3.4.4. TGA, DTG, and Gram–Schmidt curves

The upper diagram in Figure 3 displays the TGA curve (black) and its first derivative (red). The curves show that the calcium oxalate monohydrate loses mass in three steps. During the mass loss steps, spectra are recorded with the FTIR which are characteristic for the decomposition products.

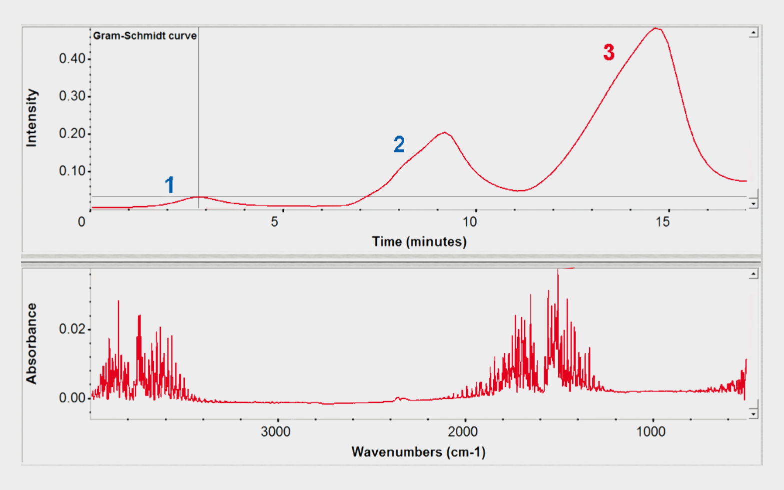


Figure 4.
Gram–Schmidt curve with FTIR spectrum at the first mass loss.

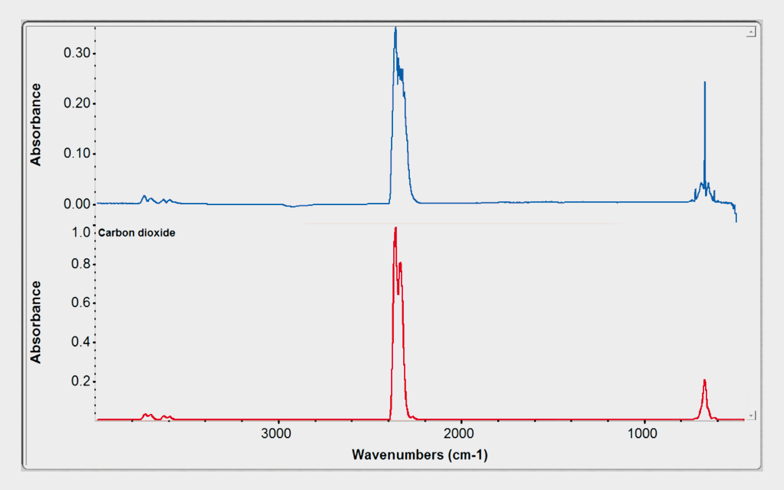


Figure 5.
FTIR spectrum measured during the third weight loss step together with the best fit from the database.

The area under a spectrum corresponds to the total infrared intensity. If the total IR intensity for each spectrum is calculated and plotted as a function of time or temperature, a so-called Gram–Schmidt curve is obtained.

The Gram–Schmidt curve for the TGA-FTIR experiment on calcium oxalate monohydrate is displayed in the lower diagram in Figure 3.

The DTG curve is generally a mirror image of the Gram–Schmidt curves. The intensity of the individual peaks in the DTG and Gram–Schmidt curve are however different because the infrared absorption is not the same for all decomposition products. This can be seen in Figure 3.

3.5. Identification of substances or their functional groups from individual FTIR spectra

In order to identify the decomposition products, the individual spectra must be more closely examined. Normally, this involves looking at spectra recorded at specific temperatures. These temperatures are usually chosen based on features in the Gram–Schmidt curve: spectra are analyzed where shoulders or peaks occur (shoulders indicate overlapping decomposition processes, peaks the maximum concentration of the decomposition products in the gas flow). In the example, these are the spectra measured at 200, 520 and 790 °C.

Figure 4 shows the analysis procedure using the Thermo Scientific™ OMNIC™ software. The upper diagram displays the Gram–Schmidt curve.

The cursor in the Gram–Schmidt curve determines which spectrum is shown in the lower part of the evaluation window in the OMNIC™ software. The cursor can be moved using the cursor keys or the mouse.

The spectrum at the first mass loss shows very many absorption bands in the range 4000 to 3500 cm^{-1} and from 2000 to 1200 cm^{-1}. These bands are typical for water. The first mass loss is due to the loss of the water of crystallization from $CaC_2O_4{\cdot}H_2O$ and occurs at about 200 °C.

Frequently, several different substances are evolved during a mass loss step. Their IR spectra overlap, making the interpretation of a measured spectrum much more difficult. In this case, a database containing the spectra of hundreds of different gaseous compounds can be very helpful.

The measured spectrum (or part of it) is compared with the reference spectra in the database. The software presents a list of compounds that could produce the measured spectrum.

The upper spectrum (blue) in Figure 5 is the spectrum measured at 790 °C. The lower spectrum (red) is the spectrum from the database that agrees best with the measured spectrum. In this case, it is carbon dioxide.

For a successful database search, it is important that the database used contains spectra of gaseous substances and that the resolution of the spectra in the database is about the same at that used to record the measured spectra.

In Figure 5, the resolution of the measured spectrum is clearly better than that of the spectrum stored in the database.

The second mass loss step is due to the formation of carbon monoxide.

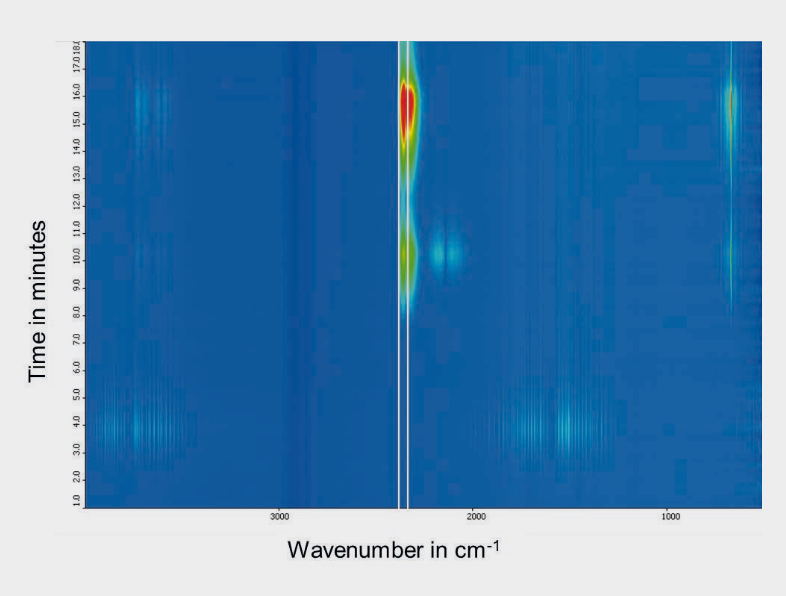


Figure 6.
2D contour plot of spectra obtained from the analysis of calcium oxalate monohydrate. The white lines define the region used to monitor CO_2 as a function of time and temperature.

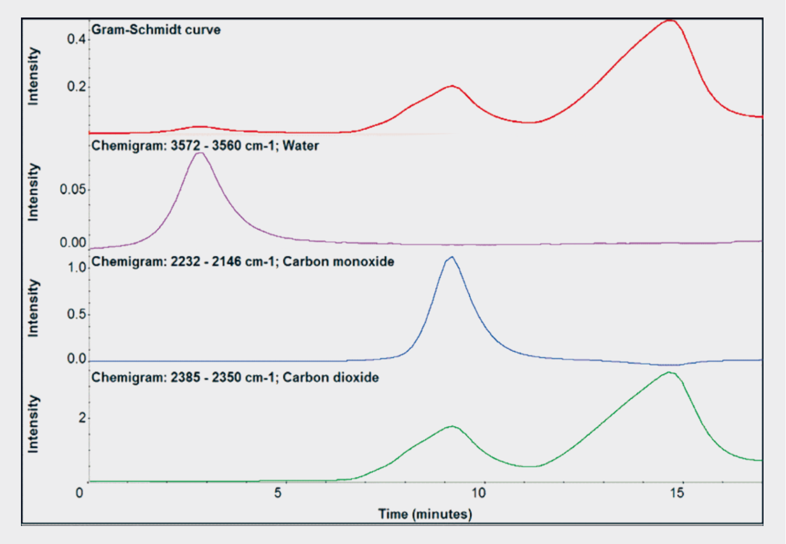


Figure 7.
Chemigrams for water (violet), carbon monoxide (blue) and carbon dioxide (green). The Gram–Schmidt diagram is shown above for reference (red).

3.6. Chemigrams of the evolved substances

Once the evolved substances have been identified, a profile that describes the release of the substance in question as a function of time is often useful.

This can be obtained by defining a wavenumber range that is characteristic for the spectrum of the substance in question. The area under this part of the spectrum is integrated as a function of time or temperature for all the measured spectra. The resulting curve is known as a chemigram.

Figure 6 shows the spectra recorded during the TGA analysis of calcium oxalate monohydrate displayed in a 2D plot.

The colors characterize the intensity of the infrared absorption. The individual spectra correspond to horizontal lines. The wavenumber region (2385 to 2350 cm^{-1}) defined by the two vertical white lines corresponds to a wavenumber region characteristic for carbon dioxide. The chemigram for this wavenumber range is displayed in Figure 7 together with the chemigrams for water (3572 to 3560 cm^{-1}) and carbon

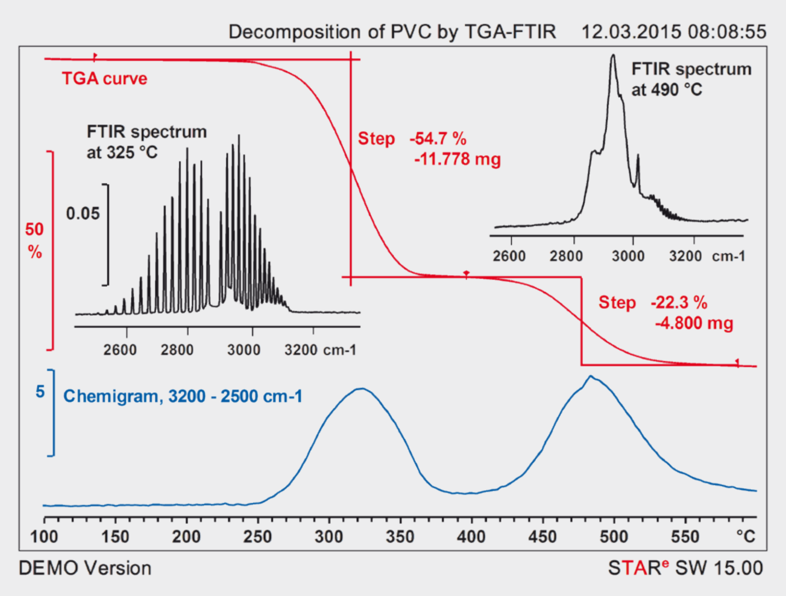


Figure 8.
TGA curve, chemigram and spectra resulting from the TGA-FTIR analysis of PVC. Two different decomposition products are identified. Their infrared absorption bands occur in the wavenumber range used for the chemigram.

monoxide (2232 to 2146 cm^{-1}) and the Gram–Schmidt curve.

The chemigrams show that water is released at the first mass loss (violet curve), carbon monoxide (blue curve) at the second mass loss, and carbon dioxide (green curve) and at the third.

This result does not agree with that expected from the equations written to describe the decomposition of calcium oxalate monohydrate namely step 1: water; step 2: carbon monoxide; and step 3: carbon dioxide.

Based on this, the release of carbon monoxide is only expected in the second mass loss step.

The mass loss steps measured by the TGA agree well with the mass changes expected from the stoichiometry of the decomposition reactions [1, 2].

The question however is, why does the FTIR chemigram for carbon dioxide indicate the presence of this substance besides carbon monoxide in the second mass loss step? In fact, this is a result of the disproportionation reaction of CO to CO_2 and C known as the Boudouard reaction [3].

The interpretation of the chemigrams discussed here assumes that the spectra in the particular wavenumber region used are always due to the same chemical compound. This is also the case for calcium oxalate monohydrate. However, it is also possible that other compounds also absorb infrared light in the same wavenumber range.

An example of this is shown in Figure 8 which summarizes the decomposition of polyvinylchloride (PVC). The TGA curve shows that PVC decomposes in two steps.

The blue curve in the lower part of the diagram is the chemigram for the wavenumber range 3200 to 2500 cm^{-1}. The two maxima in the chemigram correspond to the two mass loss steps. The black curves are the infrared spectra that were measured at 325 °C and 490 °C (maxima of the chemigrams). The two spectra show large differences. Using the database, the spectrum at 325 °C was assigned to hydrogen chloride (HCl), and the second spectrum to benzene. This yields information on the decomposition process of PVC. In the first step, dehydrochlorination of the polymer chain takes place while in the second step chain rearrangements occur with the release of benzene.

The two different processes can only be identified when the spectra obtained from the TGA-FTIR analysis are more closely examined at different temperatures.

3.7. Conclusions

TGA-FTIR is a powerful technique that can be used to quantify the mass losses of a sample and at the same time identify the gaseous substances evolved.

When several complex substances are simultaneously released, interpretation and identification of the measured spectra requires experience or the use of a suitable database. Chemigrams can be used to follow the release of particular substances such as carbon dioxide or water as a function of temperature.

This chapter gives a step-by-step overview of the procedure for data analysis and shows that a few simple measurements can provide a lot of relevant information.

References

[1] Atlas of Thermoanalytical Curves, G. Liptay (Ed.), Akadémiai Kiadó, Budapest 1973.
[2] J. Paulik and F. Paulik, Comprehensive Analytical Chemistry, Vol. 12, Part A Elsevier, Amsterdam 1981, p. 83.
[3] E. Charsley et al., American Laboratory, January, 1990

4. Thermogravimetry and Gas Analysis, Part 4: TGA-GC/MS

Nicolas Fedelich

A thermogravimetric analyzer coupled to a suitable EGA system allows qualitative information to be obtained about the gaseous reaction or decomposition products formed in a TGA experiment in addition to purely quantitative information about mass changes. In Chapter 4 of this series, we discuss the combination of a TGA with a GC/MS system.

Figure 1.
Right: the TGA-GC/MS system.
Middle: the storage interface (IST16 or IST1).
Left: the GC/MS.

4.1. Introduction

In thermogravimetric analysis, the mass of a sample is measured as a function of temperature. Changes in mass of just a few micrograms can be detected with high accuracy but no information is obtained about the identity of the gaseous products evolved during the mass change.

The information can however be obtained by coupling the TGA to a suitable system for gas analysis. The combination of a TGA with an infrared spectrometer or a mass spectrometer has been discussed in the previous chapters [1, 2].

The disadvantage of these two techniques is that gaseous compounds simultaneously evolved are measured as mixtures of gases at the same time. This makes the interpretation of the measured spectra more difficult. In fact, FTIR and MS are mainly used when the composition of the decomposition gases is dominated by just a few gases and the other decomposition gases only occur at low concentrations. If the composition of the decomposition gases consists of a large number of different gases, then the combination of a TGA with a GC/MS or a Micro GC(/MS) is recommended. In this chapter, we discuss the setup of a TGA-GC/MS system and show how TGA-GC/MS analyses are performed using polyamide 66 (PA 66) as an example. The coupling of a TGA to a Micro GC(/MS) will be described in Chapter 5.

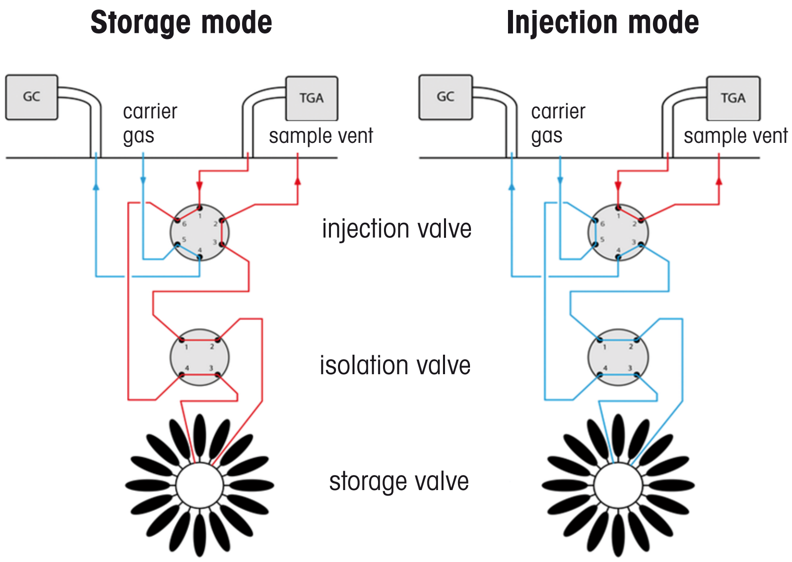


Figure 2.
Schematic diagram of the storage mode (left) and the injection mode (right) of the IST16 storage interface.

4.2. Setup of a TGA-GC/MS system

A TGA-GC/MS system consists of several different components as shown in Figure 1. In the TGA (on the right of the picture), the sample is heated and decomposition gases are evolved. The gases are transferred to the IST16 storage interface (in the middle of Figure 1) which can store up to 16 gas samples at temperatures predefined by the user.

When the TGA measurement is completed, the individual gas samples are injected one after the other into the GC/MS. The different compounds in a gas sample exit the GC column at different times and are identified at the outlet by the MS. This allows gaseous decomposition products to be unequivocally detected even at very low concentrations. In the following sections, we will discuss the different components that make up a TGA-GC/MS system.

4.3. The storage interface

The IST16 storage interface consists of a series of valves and 16 steel loops each with a volume of 250 µL. In the "storage mode", the gas flow from the TGA passes through the next loop to be filled to the outlet of the storage interface. When the desired TGA program temperature reaches the temperature chosen for filling the loop, the inlet and outlet sides of the loop are closed and the gas flow from the TGA is switched to the next loop.

This allows gas samples to be collected at up to a maximum of 16 different TGA temperatures. The samples correspond to the composition of the decomposition gases at each particular temperature. The first storage loop is usually filled with the protective and method gas used in the TGA before the actual TGA-GC/MS measurement. This gas sample is later used to clean and the column and transfer line from the IST16 to the GC/MS.

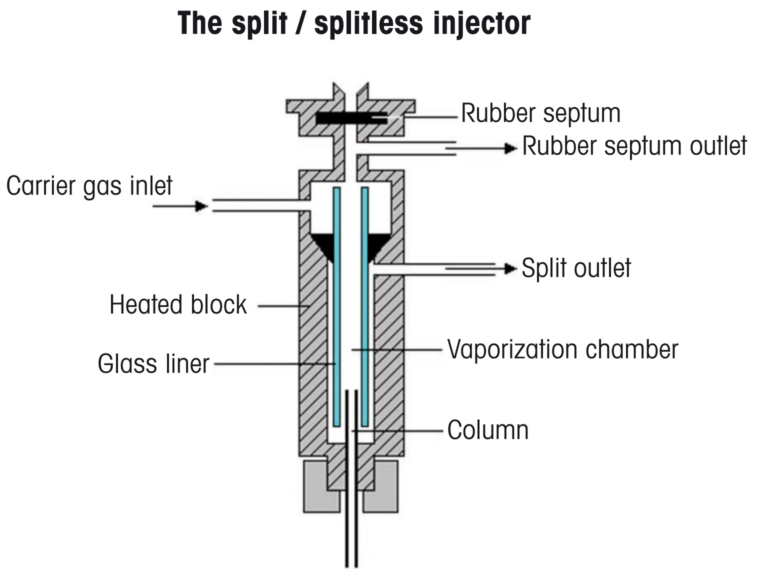


Figure 3. Schematic diagram of a split/splitless injector. Source: http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm

Tip

For the analysis of materials expected to produce decomposition gases with an m/z greater than 250, we recommend installing a 10-cm long tube (for example made of PTFE or PEEK) between the TGA furnace outlet and the heated transfer line. The tube acts as a cold trap to condense less volatile decomposition products. This protects the TGA to IST16 transfer line, the storage interface and the GC/MS against excessive contamination. The condensation products in the tube can also be analyzed by GC/MS. This is done by first dissolving the condensation products in a suitable solvent (e.g. isopropanol). The solution is then injected into the GC using a syringe (typical volume 5 µL). Vaporization of the dissolved substances and the solvent takes place in the so-called liner which is part of the injector and can be heated to 400 °C. In this case, a much larger split ratio is used (typically greater than 20).

With unknown samples, a trial TGA experiment is first performed in order to choose the temperatures at which gas samples are to be taken. The temperatures are determined from the first derivative of the TGA curve. Gas samples are then stored at these temperatures in the storage interface during the TGA-GC/MS experiment.

Both the storage interface (storage loops and valves) as well as the two transfer lines (from the TGA to the IST16, and from the IST16 to the GC/MS) are heated (typically at 250 to 300 °C) in order to prevent condensation of gases. As soon as the storage loops are filled with gas samples, the storage interface switches automatically from the storage to the injection mode.

In this mode, the gas samples are transferred by a carrier gas (usually helium) one by one through the second transfer line into the GC/MS and analyzed with respect to their composition. A schematic diagram of the storage and injection operating modes is shown in Figure 2.

The storage interface can also be operated in the ”multi-injection mode” and in a "fast GC mode" in addition to the storage and injection modes. In both of these operating modes, only one storage loop is required.[2)] In the multi-injection mode, the GC column is held at a constant temperature (e.g. 250 °C). In this case, practically no chromatographic separation of the decomposition gases occurs, so that the multi-injection mode is comparable to direct coupling of the MS to the TGA.

In the fast GC mode, typical heating rates of 80 K/min (GC) and 2 K/min (TGA) are used. This reduces the GC analysis time considerably (but also lowers the GC separating power). The fast GC mode allows about five to ten GC/MS analyses to be performed during a TGA measurement depending on the temperature range. The multi-injection and fast GC modes do not take full advantage of the possibilities offered by the TGA-GC/MS coupling and will therefore not be further discussed in this chapter.

4.4. The GC/MS

Gas chromatography is an analytical technique that is used to separate gases from one another in a gas mixture. The main components of a GC are the injector, the column (or the stationary phase) and the detector. The gas to be analyzed is injected into the injector of the GC, transferred by a carrier gas (the mobile phase, usually helium) onto the column, and detected at the end of the column using a suitable detector.

There are several different types of injector. In a TGA-GC/MS combination, the GC is equipped with a split-splitless injector. A split-splitless injector allows either the total amount of gas (splitless) or just part of the gas (split) to be introduced onto the column. This determines the amount of gas that enters the column and avoids overloading the column.

In TGA-GC/MS, the gas sample is flushed into the GC/MS from the corresponding storage loop using helium. The decomposition gases are therefore diluted by the balance protection gas and (if used) the reactive gas and additionally with helium. In TGA-GC/MS, a relatively low split ratio of typically 5:1 is used.

This means that 5 parts or 83.3% of the gas flow arriving at the injector is passed directly to the outlet of the GC, and 16.7% of the gas stored in a loop passes through the column. Figure 3 shows a schematic diagram of a split-splitless injector. From the injector, the gas sample and carrier gas pass onto the column. Capillary columns are nowadays mostly used. They are made from quartz capillary tubing coated on the outside with a thin layer of polymer. The internal diameter of such a capillary column is 0.05 to 0.5 mm and its length varies from 10 to 60 m.

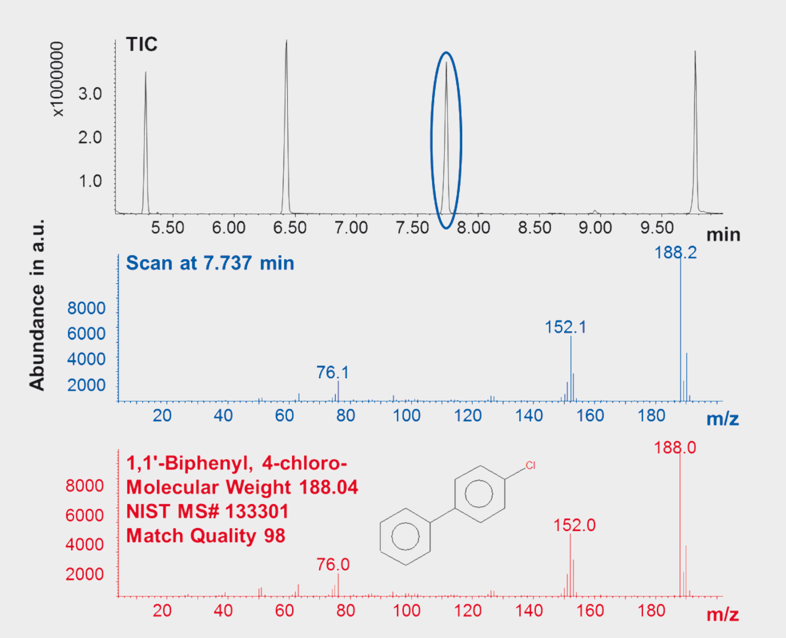


Figure 4.
GC/MS analysis of a gas sample. Mass spectra are continuously measured at the outlet of the GC.

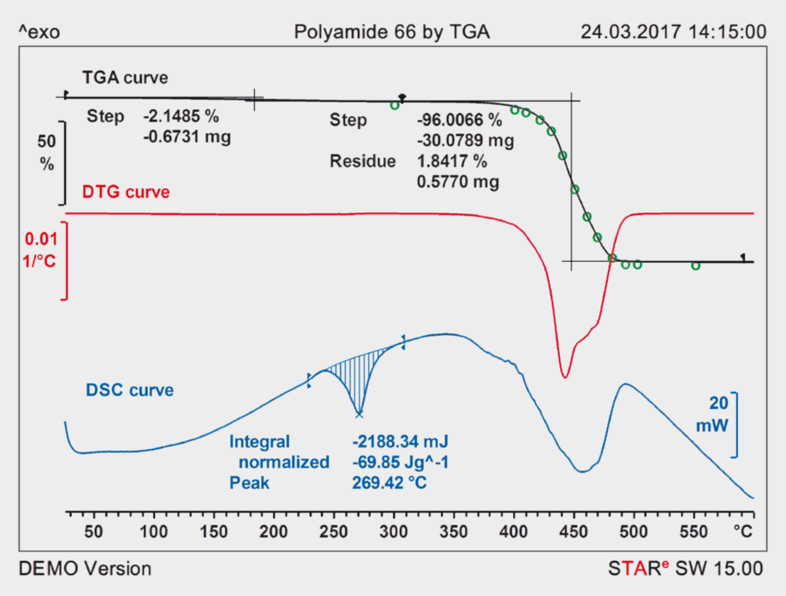


Figure 5.
TGA, DTG and TGA/DSC curves of polyamide 66. The small green circles on the TGA curve mark the temperatures at which gas samples were stored in the IST16 storage interface.

[2)] If someone only wants to work in these modes, the IST1 storage interface is available. It has just one storage loop.

The inside wall is coated with the stationary phase, usually a silicone-based polymer (poly-siloxane thickness 0.1 to 10 µm). Information about which column to use for a particular application is given in reference [3]. The column is mounted in an oven which is heated during a GC/MS analysis using a temperature program specific for the column.

The time needed by gas molecules to pass through the column is different for each gas. This so-called retention time can therefore in principle be used as an identification criterion for a particular gas.

At the outlet of the column, the amount of substance leaving the column is measured by a detector as a function of time. This results in a so-called chromatogram. This consists of a series of peaks, each of which corresponds to a particular gas. The most frequently used detectors are thermal conductivity detectors (TCD) and flame ionization detectors (FID). With detectors like this, identification of the measured gases is based solely on the retention time. The retention time of a gas depends however on a number of instrumental parameters such as the column (geometry, stationary phase), the mobile phase, the gas flow, column pressure, temperature program of the column, etc.

For GC columns, the retention times of many substances are available in tables for particular GC measurement parameters. This however limits the detectable substances to those listed in the tables. Apart from this, the measurement parameters cannot be freely chosen. These disadvantages can be overcome by using a mass spectrometer which allows the gases leaving the column outlet to be identified independently of the measurement conditions. Furthermore, there are no limitations regarding the substances that can be detected.

In a mass spectrometer, the molecules that enter are first ionized. This produces electrically charged fragment ions that are characterized by the ratio of their mass to electrical charge (m/z). The distribution of the fragments as a function of m/z (i.e. the so-called mass spectrum) is characteristic for the original molecule.

The distribution is determined using an analyzer (usually an electrical quadrupole) and a detector (often an SEM, secondary electron multiplier).

The measurement quantity is the ion current that the fragment ions produce at the detector of the MS. The sum of the ion currents of all the fragments of a type of molecule is called the total ion current or TIC. The TIC is thus proportional to the concentration of the corresponding gas in the gas mixture. If the TIC is recorded as a function of the GC analysis time, a curve with numerous peaks is obtained.

The TIC curve is therefore a chromatogram in which each peak corresponds to a particular substance. The retention times for each peak can be determined from the TIC curve. The mass spectrum associated with each peak unequivocally characterizes the substance in question. Identification is achieved using databases. We use the NIST/Wiley library, which contains more than 950,000 spectra [4]. Figure 4 shows an example of the evaluation of a GC-MS measurement.

The ion currents for the measured masses, m/z, are summed together for each spectrum. This produces a curve as a function of time for the total ion current (top diagram: TIC, total ion current).

Peaks on this curve indicate that at the corresponding time a particular type of molecule arrives at the outlet of the GC. The MS supplies the mass spectrum (middle diagram: mass spectrum for the TIC peak circled blue in the top diagram). Molecules are identified by comparing the measured mass spectrum with reference spectra of a library spectrum (bottom diagram). The quality of agreement is characterized by the so-called Match Quality. An ideal match is 100.

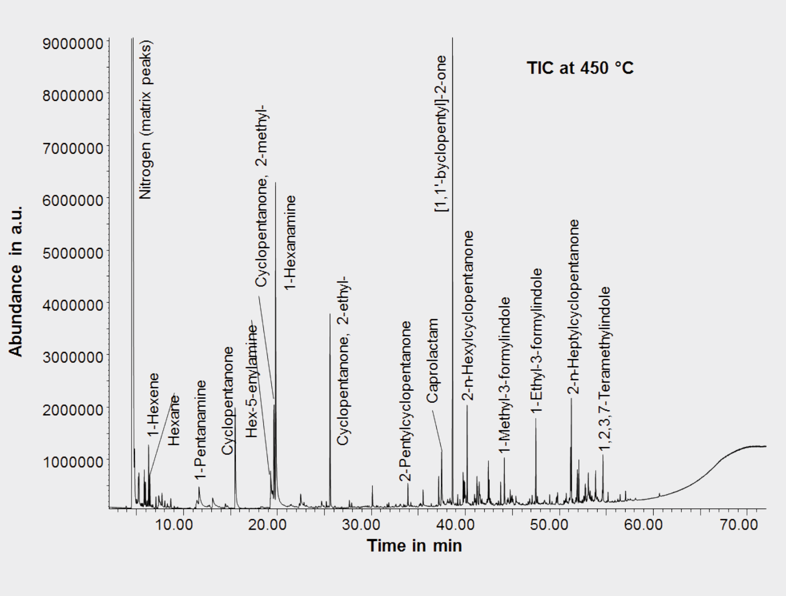


Figure 6.
TIC of loop 8 corresponding to a TGA temperature of 450 °C.

4.5. Example: Analysis of polyamide 66 by TGA-GC/MS

4.5.1. Experimental details

The sample used was a polyamide 66 from the ResinKit™ of The Plastics Group of America.[3] The measurements were carried out using a TGA/DSC coupled to an Agilent 7890 GC gas chromatograph equipped with an Agilent 5975C MSD mass spectrometer detector via an SRA Instruments IST16 storage interface.

The TGA measurements were performed in nitrogen (20 mL/min balance gas, 30 mL/min method gas) between room temperature and 600 °C; the heating rate was 10 K/min. The storage interface and the transfer lines were held at 250 °C.

The GC injector temperature was 280 °C. The temperature program for the GC column consisted of an isothermal segment at 40 °C (15 minutes), a temperature ramp of 5 K/min from 40 to 300 °C, and a further isothermal segment at 300 °C (5 minutes). The column was an HP-5ms and the carrier gas helium.

The gas flow through the column was kept constant at 0.8 mL/min. The split was 5:1. The mass range from m/z 10 to m/z 300 was analyzed with the mass spectrometer. The previously mentioned NIST library was used to interpret the spectra.

4.6. Results

First of all, about 30 mg PA 66 was measured using the TGA. The results are displayed in Figure 5. It shows the TGA curve, the DTG curve, and the simultaneously measured DSC curve. Two mass loss steps can be seen: a first step (step height 2.1%) begins practically at room temperature and ends at about 300 °C. This is due to the release of moisture, an effect that often occurs with PA 66. The second step corresponds to the pyrolysis of the polymer, which is completed by about 500 °C. A residue of about 2% of the original mass is left. The DSC curve shows the melting of PA 66 at about 270 °C [8]. The broad endothermic peak correlates with the mass loss and also characterizes the pyrolysis.

This first measurement allowed the temperatures to be set at which to analyze the decomposition gases in a TGA-GC/MS experiment. These are marked on the TGA curve in Figure 5 as green circles. The first storage loop was filled at the beginning of the TGA-GC/MS measurement with the protection and method gas used in the TGA. The storage loops were filled one after the other as the TGA measurement progressed. After the last storage loop had been filled, the gas samples were analyzed individually using the GC/MS.

As an example, Figure 6 shows the TIC of the gas sample taken at 450 °C. Each peak in the TIC corresponds to a different decomposition product. The particular decomposition product was identified based on the measured mass spectrum and comparison with the reference spectrum stored in the NIST library. Some of the substances assigned to different peaks are also shown in Figure 6.

Altogether over 60 different decomposition products were identified. Table 1

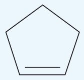
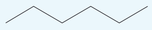
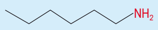
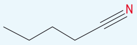
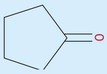
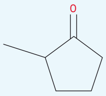
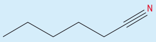
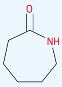
Substance name	RT in min	Targetion	Formula	Structure
Cyclopentene	6.43	67	C_5H_8	
1-Hexene	7.05	41	C_6H_{12}	
Hexane	7.25	57	C_6H_{14}	
1-Hexanamine	8.95	41	$C_6H_{15}N$	
Pentanitrile	18.61	43	C_8H_{18}	
Cyclopentanone	19.94	55	C_5H_8O	
Cyclopentanone, 2-methyl-	24.29	42	$C_6H_{10}O$	
Hexanenitrile	26.40	54	$C_6H_{11}N$	
Caprolactam	35.18	55	$C_6H_{11}NO$	

Table 1.
Some of the decomposition gases identified during the pyrolysis; RT is the retention time.

---

[3] www.plasticsgroup.com/resinkit.php

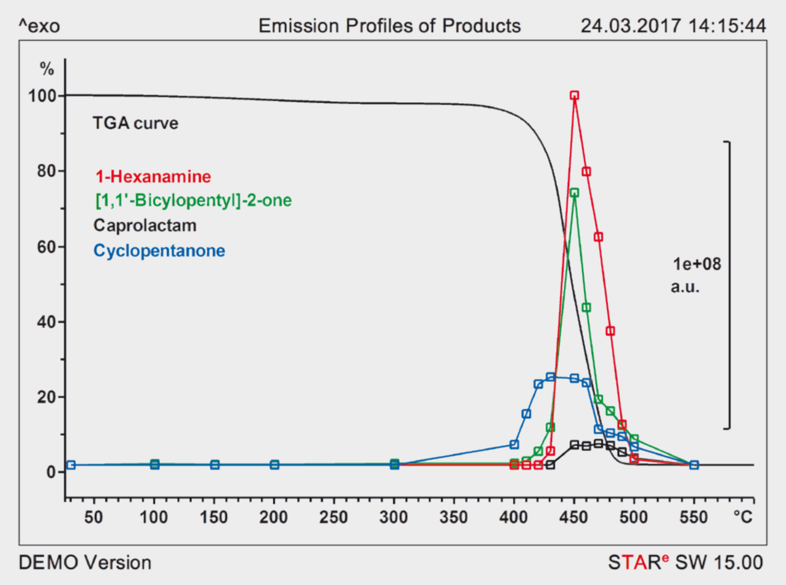


Figure 7.
Emission profiles for selected decomposition products of PA 66. Concentrations cannot be readily determined from the ratio of the peaks.

lists the most important decomposition products that were formed during the pyrolysis together with their retention times (RT) and chemical formula and structures. Also listed is the ion which is measured with the greatest abundance in the MS (main fragment, target ion).

Numerous decomposition products were found that are characteristic for polyamides and in particular for PA 66: cyclopentanone [5, 6], nitriles, e-caprolactam, hexane-1 amine, and alkenes/alkanes such as cyclopentene/cyclopentane [7–9].

Small molecules (e.g. H_2O, CO_x, CH_4) all have practically the same retention time in the column we used and therefore cannot be chromatographically separated.

There are however two ways to obtain information about these gases:

1. Perform a second TGA-GC/MS measurement using an empty sample crucible and then subtract the TIC curves of the two measurements at each temperature. The intensities of the characteristic m/z values of the small molecules (e.g. 18 for water, 44 for CO_2, etc.) are then determined from the mass spectra that occur in the first peak in the TIC (this peak is produced by all the small molecules).
2. Use the TIC curve of the gas sample in the first storage loop (it does not contain any decomposition gases) as a blank curve for the TIC curves of the storage loops with the decomposition gases. The intensities for the typical m/z values for the small molecules (e.g. 18 for water, 44 for CO_2, etc.) in the first peak of the corrected TIC curves are then evaluated.

So-called emission profiles of a substance can be created from the mass spectrum of a particular TIC peak by plotting the intensity of the main fragment ion of the substance as a function of temperature. Alternatively, the surface areas of the TIC peaks at the same retention time can be used to create emission profiles. Suitably normalized, the concentration of individual gases can also be estimated. Figure 7 shows such emission profiles (not normalized).

4.7. Conclusions

A TGA coupled to a GC/MS via a storage interface allows the composition of the decomposition gases of a sample at up to 16 freely selectable temperatures to be determined. The gas samples stored are individually analyzed by GC/MS following completion of the TGA measurement.

The GC separates the different gases contained in a gas mixture from one another. These are then identified by the MS. This allows emission profiles for individual decomposition products to be created. After suitable calibration, the composition of the decomposition gases can also be quantitatively determined.

The procedure for performing a TGA-GC/MS measurement was illustrated using PA 66 as an example. More than 60 different decomposition products were identified. The main decomposition products were cyclopentanone with numerous derivatives and amines. Furthermore, different nitriles, e-caprolactam and alkenes/alkanes were also identified.

References

[1] A. Hammer, Thermogravimetry and gas analysis, Part 2: TGA-MS, UserCom 46, 1–5.
[2] M. Nijman, Thermogravimetry and gas analysis, Part 3: TGA/DSC-FTIR, UserCom 47, 1–6.
[3] http://www.chem.agilent.com/cag/cabu/PropPhase1.htm
[4] Wiley 10th/NIST 14 Combined Library 978-1-119-00414-1.
[5] P. Gijsman, R. Steenbakkers, C. Furst, J. Kersjes, Differences in the flame retardant mechanism of melamine cyanurate in polyamide 6 and polyamide 66. Polymer Degradation and Stability, 2002; 78:219 24.
[6] S. V. Levchik, E.D. Weil, M. Lewin, Thermal decomposition of aliphatic nylons, Polymer International. 1999; 48:532–57.
[7] D. M. MacKerron and R. P. Gordon, Polym. Degrad. Stab., 12: 277 (1985).
[8] S. Tsuge, H. Ohtani, H. Matsubara, and M. Ohsawa, J. Anal. Appl. Pyrol., 17: 181 (1987).
[9] E. Braun, B. C. Levin, Nylons - a Review of the Literature on Products of Combustion and Toxicity. Fire and Materials. 1987; 11:71–88.

5. Thermogravimetry and Gas Analysis, Part 5: TGA-Micro GC/MS

Nicolas Fedelich

In the previous chapters, we described the online combination of TGA with FTIR, MS and GC/MS. In this final chapter, we will discuss the combination of TGA with a Micro GC optionally equipped with a mass spectrometer.

5.1. Introduction

5.1.1. Operation and setup of a Micro GC

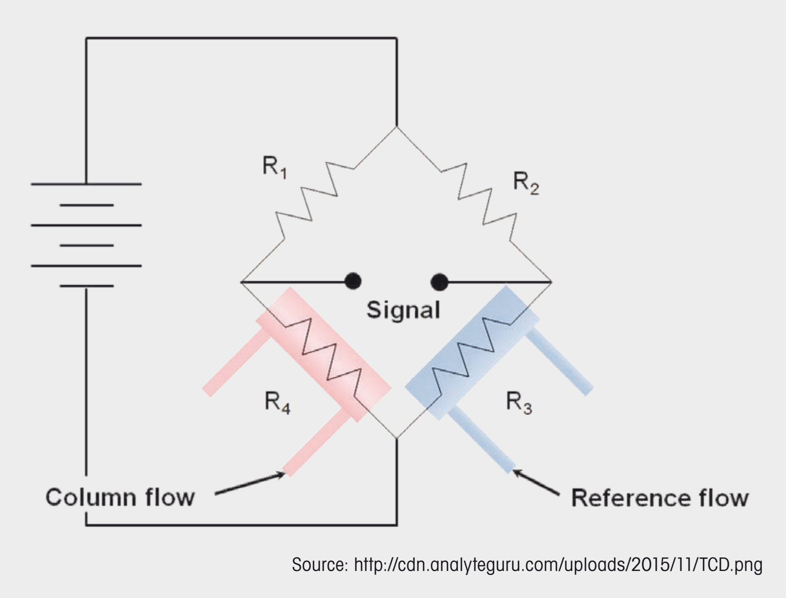
The mode of operation and the basic setup of a Micro GC are in principle the same as for a classical GC [1].

However, the most important components of a Micro GC (injector, separating column, detector) are distinctly smaller than in a classical GC. As in GC, different separating columns are available for the Micro GC depending on the compounds that have to be detected.

However, the number of compounds that can be separated with a particular column is more limited in comparison to GC columns. A Micro GC therefore usually consists of several modules with different columns through which the gases being analyzed flow in parallel.

The time needed to record a chromatogram is much shorter (typically 3 minutes) due to the comparatively short columns used. Table 1 summarizes the most important differences between a Micro GC and a GC/MS with storage interface (IST).

Each Micro GC module is equipped with a thermal conductivity detector (TCD).



Source: http://cdn.analyteguru.com/uploads/2015/11/TCD.png

Figure 1. Functional principle of a TCD detector (for details, see text).

Table 1. Gas analysis by GC and Micro GC: the most important differences.

	GC/MS	Micro GC(/MS)
Typical length of separating column	20–60 m; usually one column	4–20 m; usually several columns
Typical temperature program of separating column	Isothermal: 50 °C, 10–20 min. Dynamic: 50–300 °C at 5–20 K/min.	Isothermal: 60–160 °C (depends on the column).
Typical analysis time for a chromatogram	Isothermal: 15–30 min. Dynamic: 20–75 min.	2–3 min.
Typical analysis mode coupled with TGA	Analysis of the decomposition gases stored during the TGA measurement takes place after the TGA measurement (offline method)	Analysis of the decomposition gases takes place simultaneously with the TGA measurement (online method)

As shown in the schematic diagram in Figure 1, a TCD consists of a thermostated metal block containing two identical measuring cells. The measurement gas being analyzed flows through one of these cells from the separating column; the carrier gas (as reference gas) flows through the other cell.

Each cell contains a filament which is

---

[4] Argon is normally used as carrier gas if hydrogen or helium is to be detected in the Micro GC. A suitable column is also required.

heated to a temperature higher than that of the detector block. As a consequence, heat flows from the filament to the detector block. This lowers the temperature of the filament. The measurement gas and the carrier gas have different thermal conductivities, depending on the composition of the measurement gas.

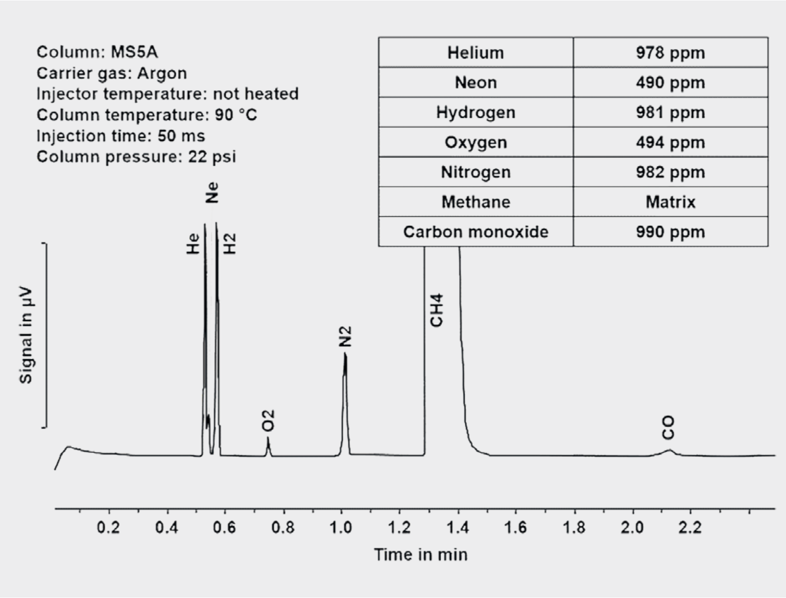
For this reason, the temperatures and hence the electrical resistance of the two filaments differ. The measurement and reference cells are connected to two additional resistances to make up a Wheatstone bridge circuit. This allows a temperature difference between the two filaments to be measured as a voltage.

The thermal conductivity of helium is much higher than all other gases except hydrogen. Helium is therefore usually employed as the carrier gas.[4] Furthermore, the thermal conductivities of substances which are gaseous at room temperature differ only insignificantly from each other. This means that a TCD shows practically the same sensitivity toward most gases.

This makes the usual time-consuming calibration measurements for quantitative determinations unnecessary. To a good approximation, the concentration of a particular gas corresponds the ratio of the peak height (or peak area) of the gas in a chromatogram to the sum of the peak heights (or peak areas) of all the peaks present in the chromatogram. TCDs also exhibit by linear behavior over a wide concentration range (a few ppm to 100%).

The separating column is a key component that determines which of the simultaneously injected gases can be separated from one another. Several separating columns and therefore several Micro GC modules are required to separate as many gases as possible.

Table 2 lists the currently most frequently used Micro GC columns and their applications. The columns marked yellow are used most often. They allow about 95% of the gases currently detectable with Micro GC columns to be separated. Figure 2 shows a chromatogram from



Helium	978 ppm
Neon	490 ppm
Hydrogen	981 ppm
Oxygen	494 ppm
Nitrogen	982 ppm
Methane	Matrix
Carbon monoxide	990 ppm

Figure 2.
Example of a TCD chromatogram.

Table 2.
Overview of the most frequently used Micro GC separating columns and the most important gases that can be detected with the various columns.

Compounds / Columns	Helium	Hydrogen	Neon	Argon	Oxygen	Nitrogen	Methane	Carbon monoxide	Carbon dioxide	Chlorofluorocarbons	Nitrous oxide	Ethylene	Ethane	Acetylene	Propane	Propylene	Propyne	Hydrogen sulfide	carbonyl sulfide	Sulfur dioxide	Amines	Alkenes	Polar solvents	Apolar solvents	Hydrocarbons C1-C3	Hydrocarbons C1-C4	BTEX	Alcohols	Water
Molsieve 5	√	√	√	√	√	√	√	√																					
CP-PoraPLOT U									√	√		√	√	√	√			√	√	√				√					√
CP-Sil 5 CB										√											√		√	√		√	√	√	
CP-PoraPLOT Q									√	√	√			√	√	√									√				√
CP-Sil 52 CB																					√		√				√	√	√
PLOT Al_2O_3																√	√	√				√							
CP-COx		√			√	√	√	√	√																				
Si-PLOT										√								√	√	√									

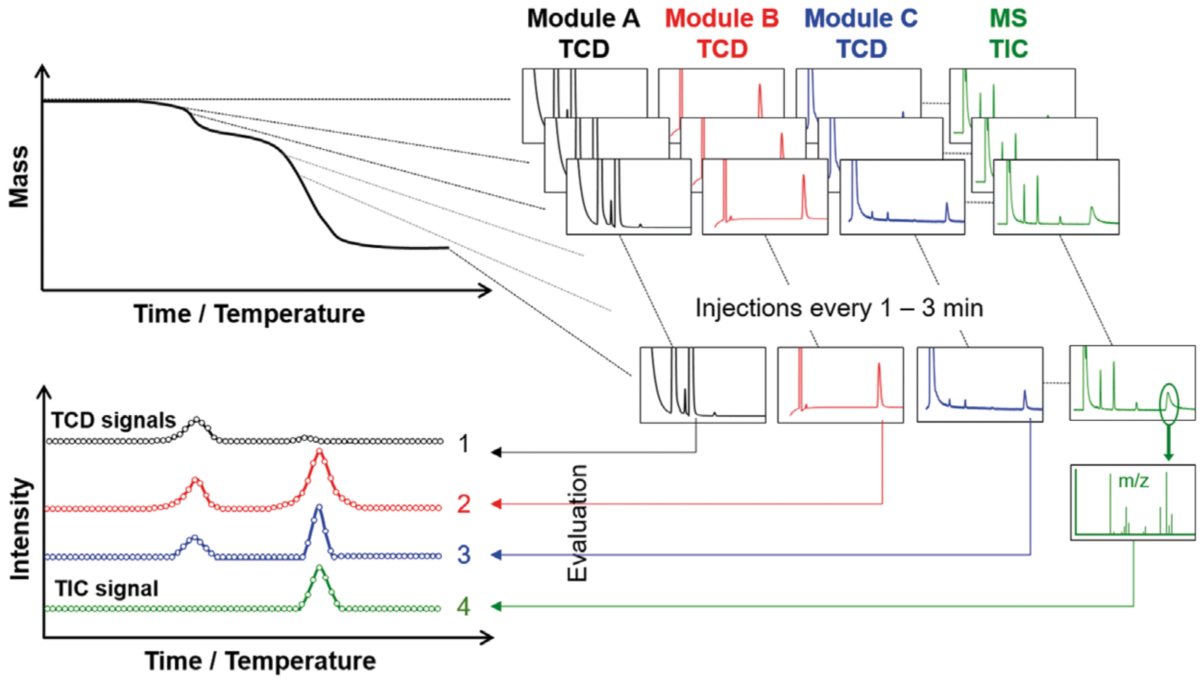


Figure 3.
Setup of a TGA-Micro GC(/MS) system.

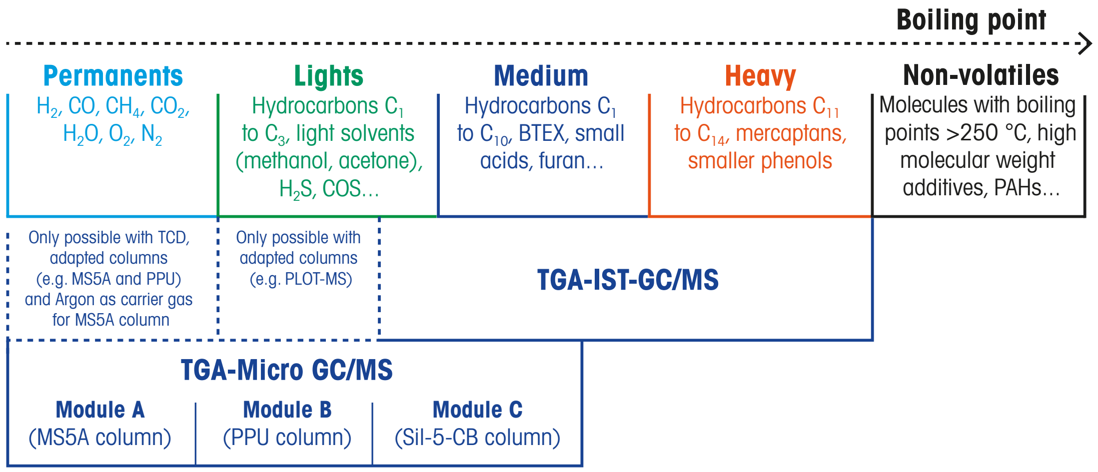


Figure 4.
Application range of TGA-Micro GC(/MS) and TGA-IST-GC/MS.

a Molsieve 5 separating column. This column is used when so-called permanent gases (permanents: H_2, CO, CH_4, CO_2, H_2O, N_2, O_2) are to be detected. The identification of the gases is based on the retention time (the time a gas takes to pass through the separating column), which is different for every gas.

With separating columns that allow larger molecules to be detected (e.g. the CP-Sil 5 CB column), the identification of gases based on retention time is difficult because of the large number of separable gases. An MS detector (which is much more sensitive) 5) is therefore recommended for such columns besides the TCD detector.

5.2. TGA-Micro GC and TGA-Micro GC/MS

A TGA is coupled to a Micro GC or a Micro GC/MS via a transfer line which is typically heated to about 80 °C 6) as shown schematically in Figure 3. The gas flow from the TGA is distributed equally between the modules installed in the Micro GC. A Micro GC-MS interface is required if an MS detector is used in addition to the TCD detector.

The analysis of a gas sample (in the Micro GC, typical volume about 10 µL) takes about 2 to 3 minutes. The results from a TGA-Micro GC(/MS) experiment can afterward be used to create so-called emission profiles. An emission profile reflects the concentration of a volatile compound in the decomposition gas as a function of temperature or time. Together with the TGA curve and its first derivative, it allows a better understanding of the processes that occur during the mass changes. Figure 4 summarizes the application possibilities of TGA-Micro GC(/MS) and TGA-IST-GC/MS.

---

5) The TCD detector can detect concentrations down to about 1 to 10 ppm. The detection limit of the MS detector is an order of magnitude better.

6) This temperature is low compared with the temperature of the transfer line in a TGA-GC/MS system (typically 250 °C). This is because the Micro GC only detects volatile compounds.

5.3. TGA-Micro GC/MS: Example

Figure 5 shows the TGA and DTG curves of a phenol-formaldehyde resin. The measurement was performed from 100 to 1000 °C at 5 K/min in nitrogen (protective gas 20 mL/min, reactive gas 50 mL/min). The initial sample mass was about 30 mg.

A 150-µL aluminum oxide crucible was used. The curves show that the mass loss of about 65% occurred in several steps. To determine the products released in the different decomposition steps, we first performed a TGA-IST-GC/MS measurement. Eight volatile decomposition products were identified (benzene, toluene, m- and p-xylene, phenol, 2-methylphenol, 4-methylphenol, 2,5-dimethylphenol and 2,6-dimethylphenol). Figure 6 summarizes the results obtained from 16 gas samples that were analyzed at different temperatures by GC/MS. The curves show the emission profiles for phenols (red curve) and BTX compounds (benzene, toluene, xylene; blue curve) together with the TGA curve (black).

Figure 5.
TGA and first derivative (DTG) curves of a phenol-formaldehyde resin.

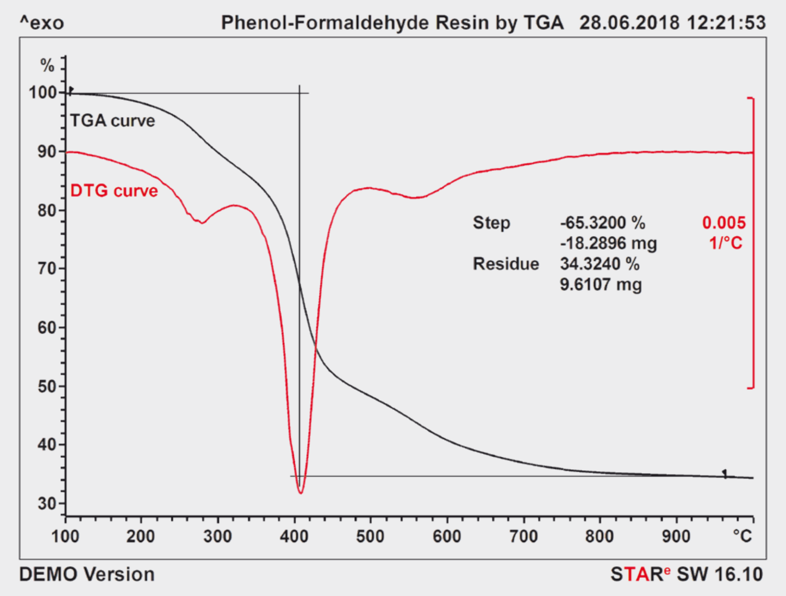
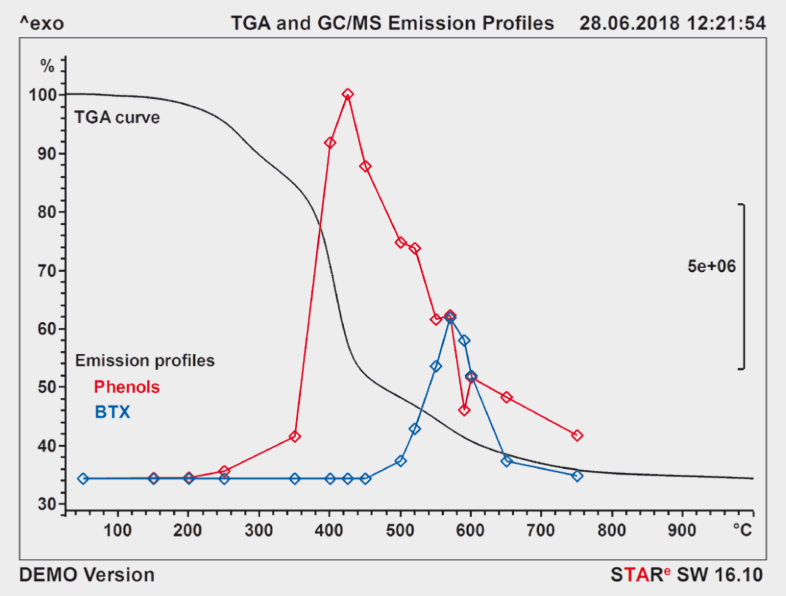


Figure 6.
TGA curve and emission profiles calculated from GC/MS measurements for phenols and BTX compounds (benzene, toluene and xylene).



Phenols are released from about 300 °C onward and compounds of the BTX group between 500 and 650 °C. Small molecules (for example CO_2 or H_2O) that were also expected as decomposition products based on the chemical composition of the sample could not be detected. The reason for this is that these small molecules were not separated from one another with the column used; they arrived at the column exit at the same time as the carrier gas (in this experiment N_2).

The same material was then investigated by TGA-Micro GC/MS. The TGA measurement parameters were identical to those used for the TGA-GC/MS measurement. The sample weight was also the same (about 30 mg). The Micro GC was equipped with three modules using the following separating columns: Molsieve 5 (argon as carrier gas, to detect any hydrogen), CP-PoraPLOT U, and CP-Sil 5 CB (helium as carrier gas). An MS detector was used in addition to the TCD detector with the CP-Sil 5 CB column.

Figures 7a to 7c show the TCD chromatograms obtained with the three columns mentioned above and Figure 7d the TIC chromatogram (total ion current) recorded with the MS detector and the CP-Sil 5 CB column, in all cases measured at a TGA furnace temperature of 620 °C.

Hydrogen, oxygen, and methane were identified in the chromatogram obtained using the Molsieve 5 column (Figure 7a). The chromatogram from the CP-PoraPLOT U column identified water and CO_2 (Figure 7b). Larger molecules (phenol, benzene, toluene) were detected using the CP-Sil 5 CB column (Figure 7c).

Comparison of the TCD chromatogram with the TIC chromatogram in Figure 7d shows that the MS detector also detects xylene and tetrahydrofuran. This demonstrates that the MS detector is clearly superior to the TCD detector with regard to sensitivity and detection limit.

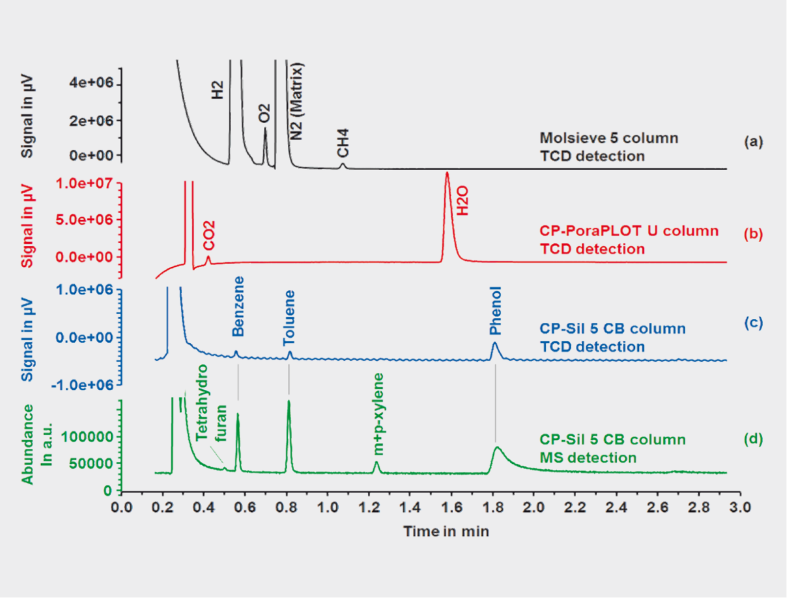


Figure 7.
TCD and TIC chromatograms of gases measured at a TGA furnace temperature of 620 °C:
(a) Molsieve 5 column;
(b) CP-PoraPLOT U column;
(c) CP-Sil 5 CB column;
(d) TIC chromatogram from the MS detector using the CP-Sil 5 CB column.

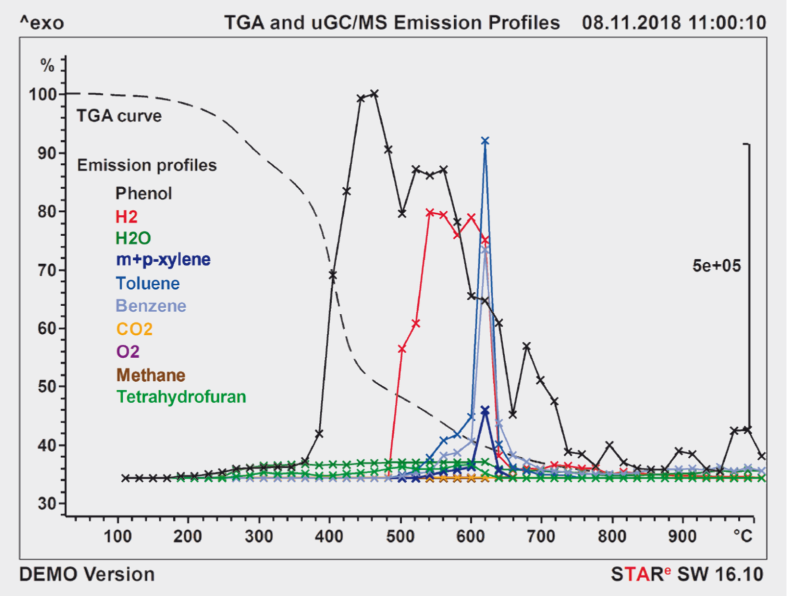


Figure 8.
TGA curve and emission profiles of all the evolved compounds.

Table 3 summarizes the compounds identified using the Micro GC together with details of the columns used, the retention time and the detector. As shown in Figure 8, the data obtained from the various chromatograms allows emission profiles to be created for all the different decomposition products. The figure shows quite clearly that besides hydrogen mainly phenols and BTX compounds are released. The temperature dependence of the phenol and BTX emissions agrees well qualitatively with the profiles obtained from the GC/MS measurements (see Figure 6). The other compounds (water, CO_2, tetrahydrofuran, oxygen and methane only occur in low concentrations.

5.4. Summary and conclusions

TGA measurements provide information on the thermal decomposition of materials under particular atmospheric conditions. The decomposition products that occur can be identified using different techniques [1–7]. In this chapter, we have presented the combination of a TGA coupled to a Micro GC which was additionally equipped an MS detector. The Micro GC(/MS) can detect permanent gases (permanents, e.g. H_2, CO, CH_4, CO_2, H_2O, O_2), as well as low molecular weight compounds (lights; e.g. hydrocarbons C_1 to C_3, solvents such as methanol or acetone, H_2S, COS) and low to medium molecular weight compounds (medium, e.g. hydrocarbons C_4 to C_6, BTX).

In comparison, TGA-IST-GC/MS can be used to detect medium to higher molecular weight compounds (medium/heavy, e.g. hydrocarbons C_6 to C_{14}). The two techniques complement one another and can be coupled to a TGA.

The short analysis time (2 to 3 minutes) needed to measure a chromatogram with a Micro GC allows simultaneous TGA-Micro GC(/MS) measurements to be performed.

The measurement time for a TGA-Micro GC(/MS) measurement is much shorter compared with a TGA-IST-GC/MS measurement. At the same time, TGA-Micro GC(/MS) measurements provide emission profiles with a better temperature resolution than TGA-IST-GC/MS measurements.

In this chapter, we investigated the decomposition of a phenol-formaldehyde resin as an example. Using TGA-IST-GC/MS, eight volatile decomposition products (benzene, toluene, m and p xylene, phenol, 2-methylphenol, 4-methylphenol, 2,5-dimethylphenol and 2,6-dimethylphenol) were identified.The emission profiles show that the phenols occur from about 320 °C onward, and compounds belonging to the BTX group from about 500 °C. Using TGA-Micro GC/MS, water, CO_2, tetrahydrofuran,

Name	Chemical formula	Column	Retention time (s)	Detector	Signal used for profile
Hydrogen	H_2	Molsieve 5	34.7	TCD	TCD
Oxygen	O_2	Molsieve 5	41.8	TCD	TCD
Methane	CH_4	Molsieve 5	66.3	TCD	TCD
Carbon dioxide	CO_2	CP-PoraPLOT U	24.8	TCD	TCD
Water	H_2O	CP-PoraPLOT U	94.1	TCD	TCD
Tetrahydrofuran	C_4H_8O	CP-Sil 5 CB	31.7	MS	MS (m/z 42)
Benzene	C_6H_6	CP-Sil 5 CB	32.7	TCD and MS	MS (m/z 78)
Toluene	C_7H_8	CP-Sil 5 CB	47.9	TCD and MS	MS (m/z 92)
m-xylene	C_8H_{10}	CP-Sil 5 CB	76.3	MS	MS (m/z 91)
p-xylene	C_8H_{10}	CP-Sil 5 CB	76.3	MS	MS (m/z 91)
Phenol	C_6H_6O	CP-Sil 5 CB	105.4	TCD and MS	MS (m/z 94)

Table 3. Decomposition products from a phenol-formaldehyde resin sample identified by Micro GC/MS.

oxygen as well as traces of methane and hydrogen were detected in addition to BTX and phenol.

A combination of TGA with a Micro GC(/MS) is recommended for samples that are expected to produce mainly low molecular weight decomposition products (permanents, e.g. H_2O, CO_2, CO, CH_4, etc.). If higher molecular weight decomposition products are of interest, the coupling of a TGA with an IST-GC/MS is the better solution.

References

[1] M. Schubnell, Thermogravimetry and gas analysis, Part 1: Basic principles and overview, UserCom 45, 1–9.

[2] A. Hammer, Thermogravimetry and gas analysis, Part 2: TGA-MS, UserCom 46, 1–5.

[3] N. Fedelich, Investigation and identification of constituents of a rubber compound, UserCom 42, 21–25.

[4] A. Hammer, Identification of an unknown polymer sample using TGA-GC/MS, UserCom 43, 15–18.

[5] N. Fedelich, METTLER TOLEDO Collected Applications Handbook: Evolved Gas Analysis, Second Edition.

[6] M. Nijman, Thermogravimetry and gas analysis, Part 3: TGA/DSC-FTIR, UserCom 47, 1–6.

[7] M. Schubnell, Thermogravimetry and gas analysis, Part 4: TGA-GC/MS, UserCom 48, 1–7.

More detailed information on these topics can be found at:
▶ www.mt.com/ta-ega

6. For More Information

Outstanding Services

METTLER TOLEDO offers you valuable support and services to keep you informed about new developments and help you expand your knowledge and expertise, including:

News on Thermal Analysis

Informs you about new products, applications and events.

- **www.mt.com/ta-news**
- **www.mt.com/ta-app**
- **www.mt.com/ta-knowledge**

Handbooks

Written for thermal analysis users with background information, theory and practice, useful tables of material properties and many interesting applications.

- **www.mt.com/ta-handbooks**

Tutorial

The Tutorial Kit handbook with twenty-two well-chosen application examples and the corresponding test substances provides an excellent introduction to thermal analysis techniques and is ideal for self-study.

Title	Order number
Tutorial Kit (handbook only)	30281946
Tutorial Kit (handbook and samples)	30249170

- **www.mt.com/ta-handbooks**

Videos

Our technical videos explain complex issues concerning thermal analysis instrumentation and the STAR^e software – whether it's sample preparation, installation, creating experiments or evaluating measurement results.

- **www.mt.com/ta-videos**

UserCom

Our popular, biannual technical customer magazine, where users and specialists publish applications from different fields.

- **www.mt.com/ta-usercoms**

Applications

If you have a specific application question, you may find the answer in the application database.

- **www.mt.com/ta-applications**

Webinars

We offer web-based seminars (webinars) on different topics. After the presentation, you will have the opportunity to discuss any points of interest with specialists or with other participants.

- **www.mt.com/ta-webinars** (Live Webinars)
- **www.mt.com/ta-ondemand** (On Demand Webinars)

Training

Classroom training is still one of the most effective ways to learn. Our User Training Courses will help you get the most out of your equipment. We offer a variety of one-day theory and hands-on courses aimed at familiarizing you with our thermal analysis systems and their applications.

- **www.mt.com/ta-training** (Classroom)
- **www.mt.com/ta-etraining** (Web-based)

Overview of METTLER TOLEDO
Thermal Analysis Application Handbooks

The following application handbooks are available and can be purchased:
www.mt.com/ta-handbooks

Introductory Handbooks	Language	Order number	Details
Thermal Analysis in Practice Volume 1 Fundamental Aspects (350 pages)	English	51725244	
Thermal Analysis in Practice Volume 2 Tips and Hints (48 pages)	English	30306885	
Thermal Analysis in Practice Volume 3 Tutorial Examples (92 pages)	English	30281946	Handbook and Tutorial samples 30249170
Thermal Analysis in Practice Volume 4 Validation (280 pages)	English	51725141	
Thermal Analysis in Practice Volume 5 Evolved Gas Analysis (40 pages)	English	30748024	

Applications Handbooks	Language	Order number	Details
Thermal Analysis of Elastomers Volumes 1 and 2 Collected Applications (290 pages)	English	51725061 51725057 51725058	Volumes 1 and 2 Volume 1 Volume 2
Thermal Analysis of Thermoplastics Collected Applications (154 pages)	English	51725002	
Thermal Analysis of Thermosets Volumes 1 and 2 Collected Applications (320 pages)	English	51725069 51725067 51725068	Volumes 1 and 2 Volume 1 Volume 2
Thermal Analysis of Pharmaceuticals Collected Applications (104 pages)	English	51725006	
Thermal Analysis of Food Collected Applications (68 pages)	English	51725004	
Evolved Gas Analysis Collected Applications (216 pages)	English	51725056	
Thermal Analysis of Polymers Selected Applications (40 pages)	English	30076210	

www.mt.com/ta-news
For more information

METTLER TOLEDO Group
Analytical Instruments
Local contact: www.mt.com/contacts

Marketing MatChar / MarCom Analytical