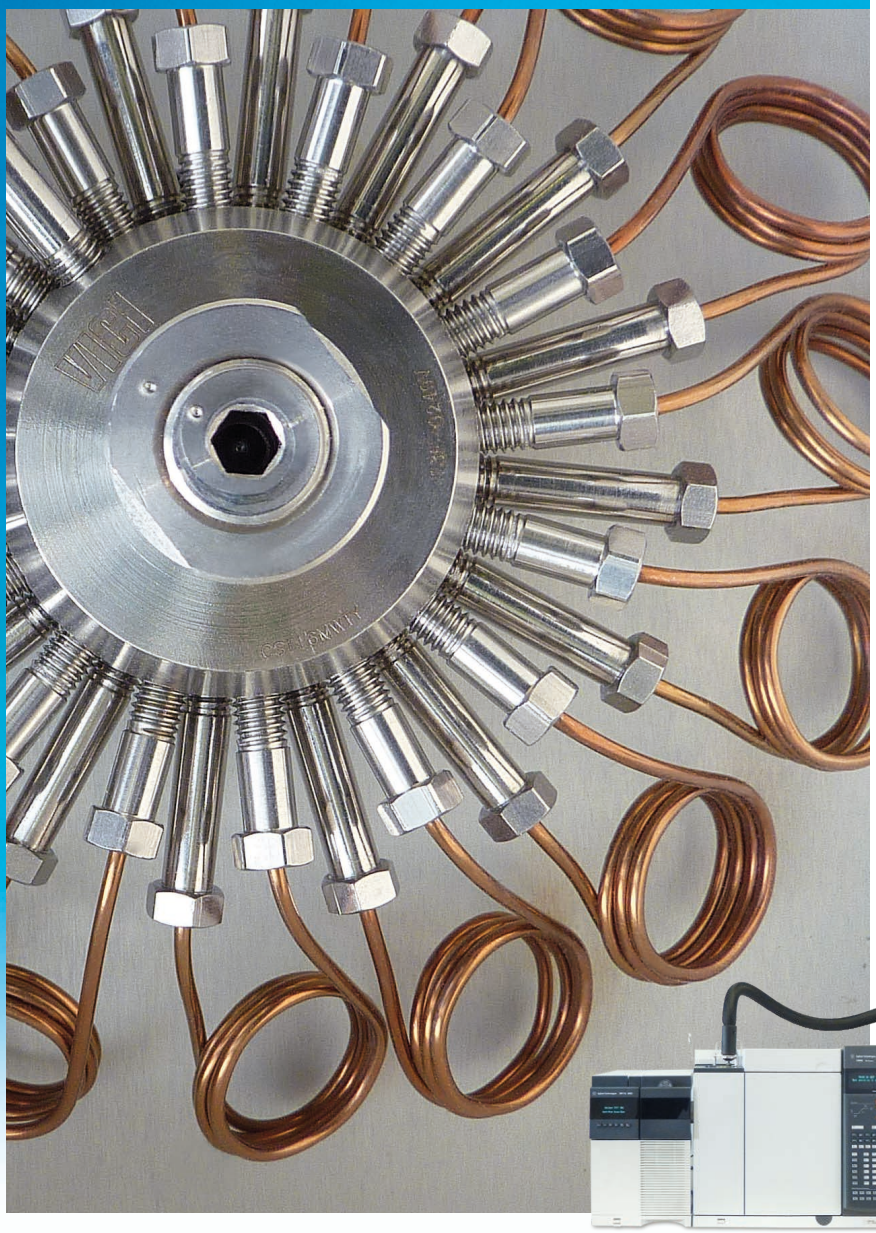
Thermal Analysis Excellence



TGA-MS
TGA-FTIR
TGA-GC/MS
TGA-Micro GC/MS

STAR^{e} System

Innovative Technology

Versatile Modularity

Swiss Quality

Hyphenated Techniques

Enable Compositional Analysis and Identification

METTLER TOLEDO

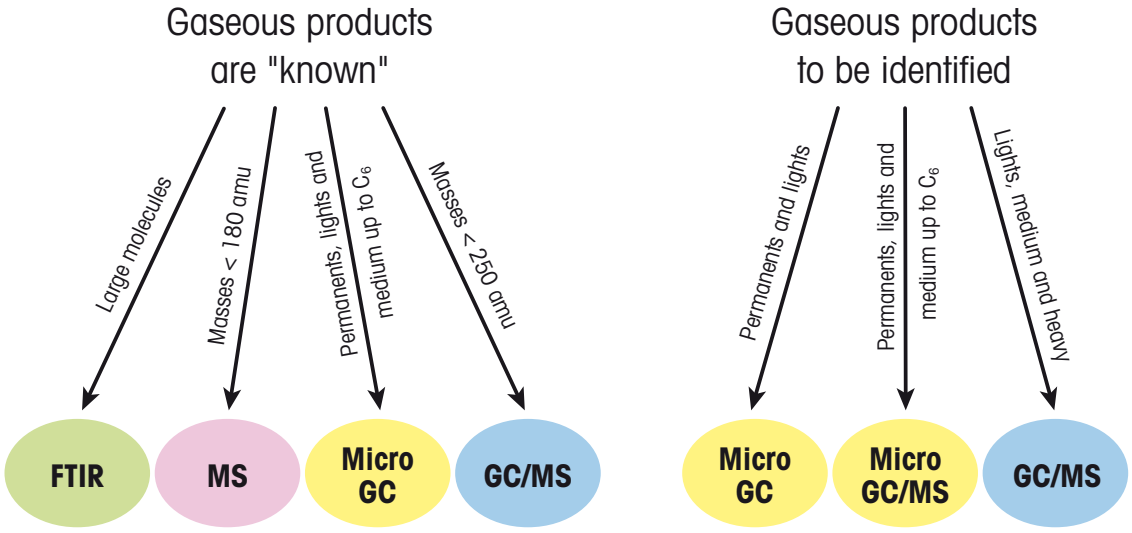
Four TGA-EGA Techniques
More Information From a Single Experiment

Thermogravimetric analysis (TGA) is a quantitative technique used to measure the change in mass of a sample as a function of temperature or time. TGA alone, however, is not an identification technique. It cannot identify or characterize the nature of the gaseous products evolved during a thermogravimetric measurement. The combination of TGA with a gas analyzer makes this possible. The techniques (MS, FTIR, GC/MS and Micro GC/MS) discussed in this brochure provide the complimentary information. The data obtained can be correlated directly with the measured mass losses.

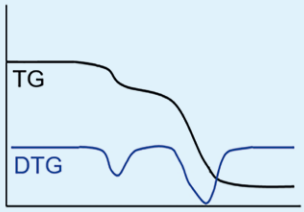
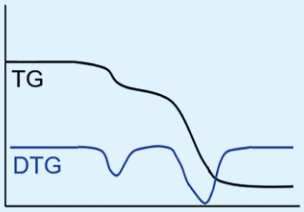
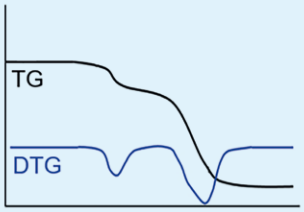
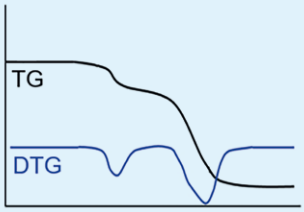
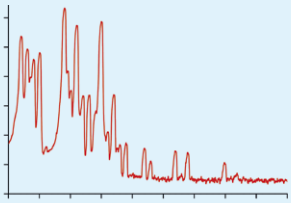
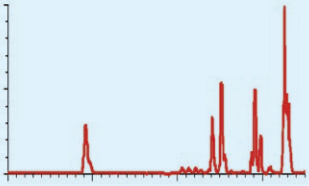
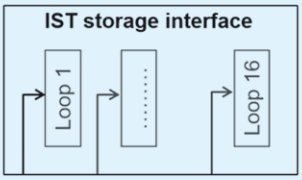
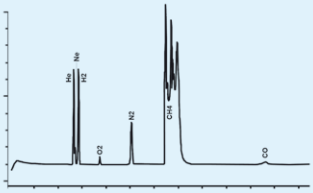
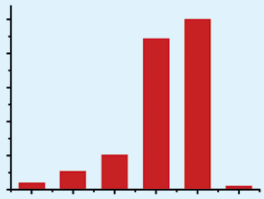
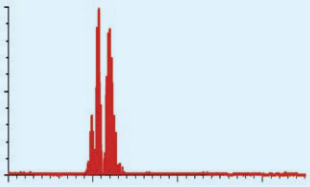
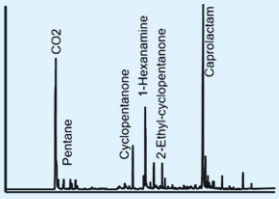
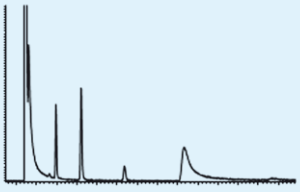
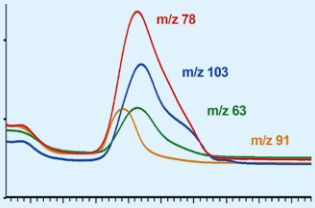
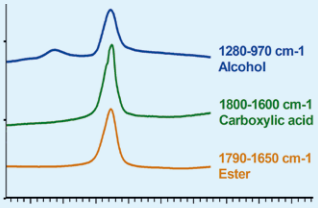
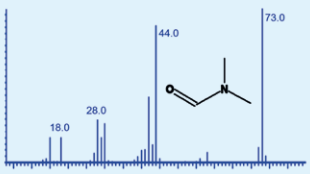
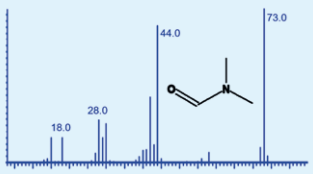
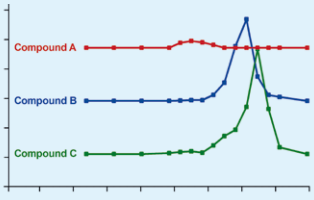
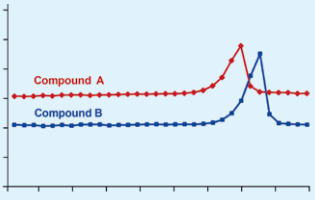
Features and benefits of the TGA evolved gas analysis (TGA-EGA) systems:

- **Automated TGA-EGA systems** – save time by acquiring more information from a single run
- **Simultaneous TGA-EGA** – enables quantitative compositional analysis and material identification
- **Reference databases** – help to identify gaseous decomposition products

The overview below shows which technique is best for solving a particular application problem.



Evolved gas analysis – Applied Techniques

TGA-MS	TGA-FTIR	TGA-GC/MS	TGA-Micro GC/MS
TGA results: 	TGA results: 	TGA results: 	TGA results: 
Mass scan over a range of masses: 	Gram-Schmidt – total absorbance spectrum: 	Up to 16 stored samples: 	TCD chromatogram (with gas detection): 
Analysis of selected ions: 	Functional groups profile (chemigrams): 	Up to 16 total ion chromatograms: 	Total ion chromatogram: 
MS: 	FTIR: 	Identification of evolved compounds: 	Identification of evolved compounds: 
		Gas profiling over the entire range of TGA experiment: 	Gas profiling over the entire range of TGA experiment: 

TGA-MS, TGA-FTIR, TGA-GC/MS and TGA-Micro GC/MS are powerful techniques that yield both quantitative (mass analysis, absorbance) and qualitative (identification, gas profiles) information.

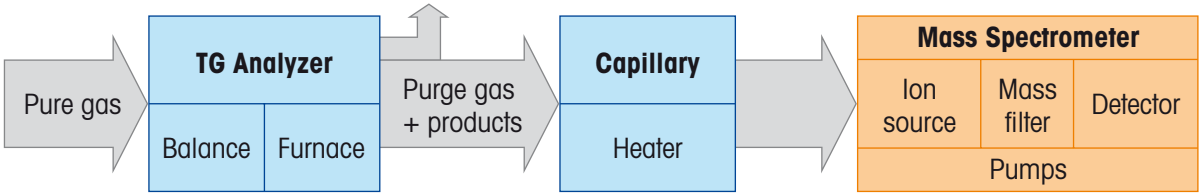
TGA-Mass Spectrometry (MS)
Fast and Highly Sensitive

Mass spectrometry (MS) is an extremely sensitive analytical technique that is used to detect and identify trace amounts of gaseous substances. In a mass spectrometer, the molecules of a substance are first ionized. The molecular and fragment ions produced are then separated according to their mass-to-charge ratios (m/z). The technique can quantify atoms or molecules and provides chemical and structural information (functional groups and side chains) on the compounds analyzed.

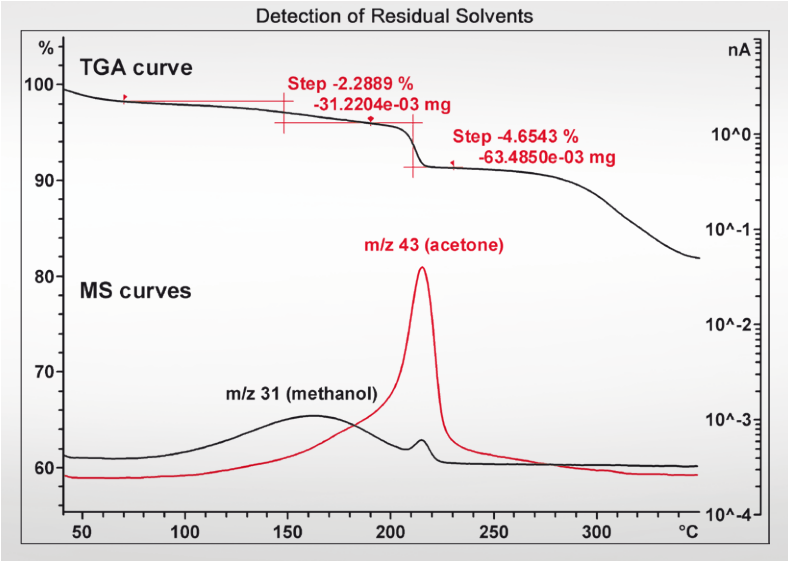
Features and benefits of a TGA-MS system:

- **Gas analysis by MS** – detects small molecular species of known analytes
- **Direct import of MS data into STAR^e software** – comparison of curves from TGA and MS permit better interpretation
- **Different measurement modes** – select the best mode according to your needs and application

The TGA is coupled to the MS via a fused silica capillary tube enclosed in a heated transfer line. Since the MS operates at high vacuum, only about 1% of the effluent gas from the TGA is allowed to pass to the mass spectrometer (otherwise the vacuum would collapse). This small amount is however perfectly adequate because the sensitivity of the MS is extremely high.

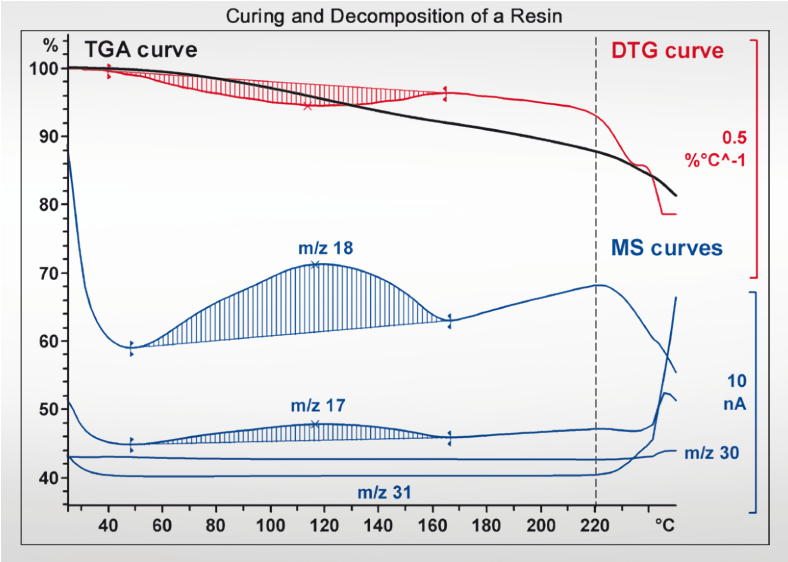


Detection of residual solvents in an active pharmaceutical ingredient (API)



In the production of APIs, traces of solvents often remain in the product. Combined techniques such as TGA-MS are ideal for detecting and identifying such undesired residues. In this example, methanol and acetone were used to recrystallize the active substance. The peaks on the MS curves corresponding to m/z 31 and m/z 43 confirm the presence of these two substances. The results indicate that the weight loss step at 200 °C is almost entirely due to the elimination of acetone. Definite analytical information like this can only be obtained using a mass spectrometer coupled to a TGA instrument.

Curing and decomposition of an amino resin by TGA-MS



In this example, a curing reaction of an amino resin is presented and the main decomposition products are analyzed so as to indicate whether or not the reaction was proceeding favorably. The TGA curve shows a gradual loss of mass in the range of 40 to 220 °C due to the polycondensation reaction of the amino resin. The marked change in the TGA and DTG curves above 220 °C indicates the start of decomposition. The evaporation of water with ion masses of 17 and 18 formed during the polycondensation reaction can be detected from about 50 °C onward. Since it was unclear whether these two signals only come from water, additional measurements with FTIR (not shown here) were performed and confirmed the presence of ammonia, which has a mass-to-charge ratio of 17.

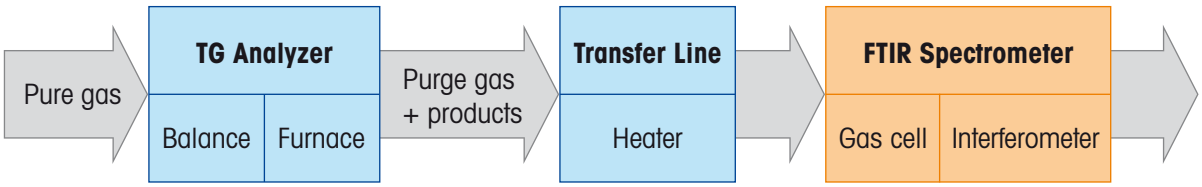
TGA-FT-Infrared Spectroscopy (FTIR)
Identification of Functional Groups

Infrared spectroscopy is based on the interaction of the molecules of a chemical substance with infrared light. The molecules absorb infrared energy at frequencies that depend on the structure of the molecule. The absorption of energy causes the molecule or certain parts of the molecule (the so-called functional groups) to vibrate at the same frequencies at which they absorb the energy. The absorption frequencies are unique for a particular molecule and can therefore be used to characterize or identify a substance or the class of substance through interpretation or the use of spectral libraries.

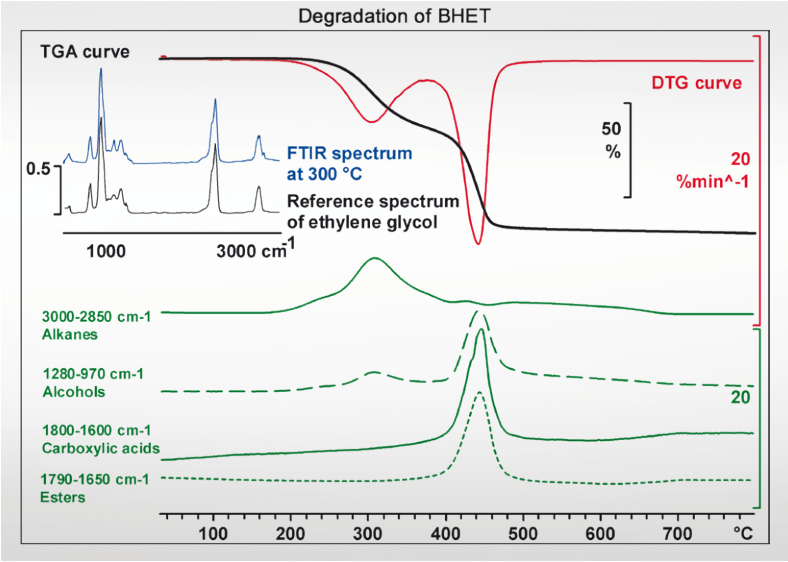
Features and benefits of a TGA-FTIR system:

- **Gas analysis by FTIR** – enables simple and complex compounds to be identified
- **Simple data import** – Gram-Schmidt and chemigram curves can be displayed in S**TA**R^{e} with the TGA curve for better interpretation

A typical TGA-FTIR system is shown below. The FTIR uses the total volume of gas flowing from the TGA. The purge gas and the evolved gases from the sample are transferred from the TGA furnace outlet through a heated transfer line into a heated gas-cell installed in the FTIR. The transfer line and gas cell are kept at about 200 °C in order to prevent condensation of the evolved gases.

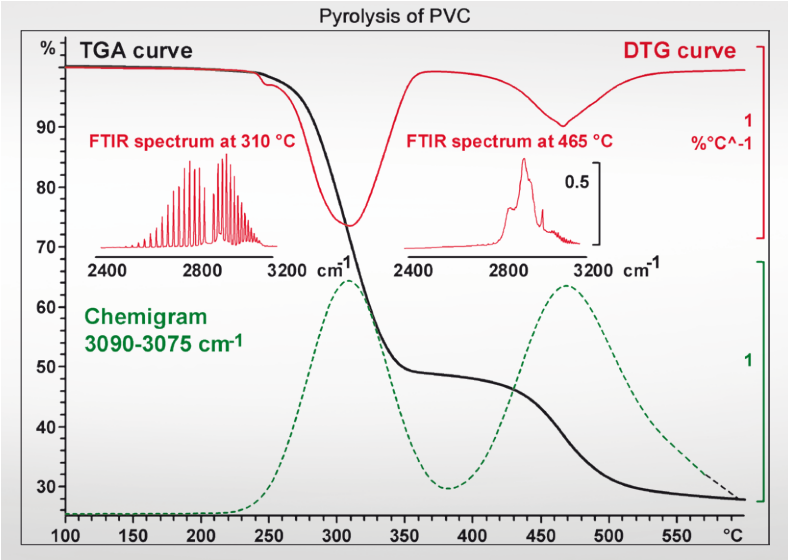


Thermal degradation of bis-hydroxyl-butyl-terephthalate (BHET) by TGA-FTIR



In this example, TGA-FTIR was used to investigate the degradation of BHET, an intermediate product in the synthesis of PET. BHET is normally synthesized from terephalic acid and ethylene glycol. The TGA and DTG curves display a two-step degradation with maxima at about 300 and 440 °C. The evolved gas profile at 300 °C (see upper left inset) showed an excellent match with a reference library spectrum of ethylene glycol. The functional group profiles of the main peak at 440 °C indicated the presence of alcohol, carboxylic acid and ester and led to the assumption that the side chains of BHET are cleaved at temperatures above 400 °C with the formation of hydroxyl formic acid ester.

Pyrolysis of polyvinyl chloride (PVC) by TGA-FTIR



PVC is used in numerous construction materials such as pipes, films and insulation materials and produces harmful chlorine derivatives when exposed to high temperatures. The aim here was to identify the decomposition products. The TGA, DTG and infrared chemigram curves show that the decomposition of PVC occurs in two steps, at about 310 and 465 °C. The FTIR spectrum at 310 °C corresponds to the spectrum of HCl gas, the spectrum at 465 °C is typical in this wavenumber range for benzene. It is well-known that benzene is formed through cyclization of the alkene chains (C = C double bonds form during the cleavage of the HCl group).

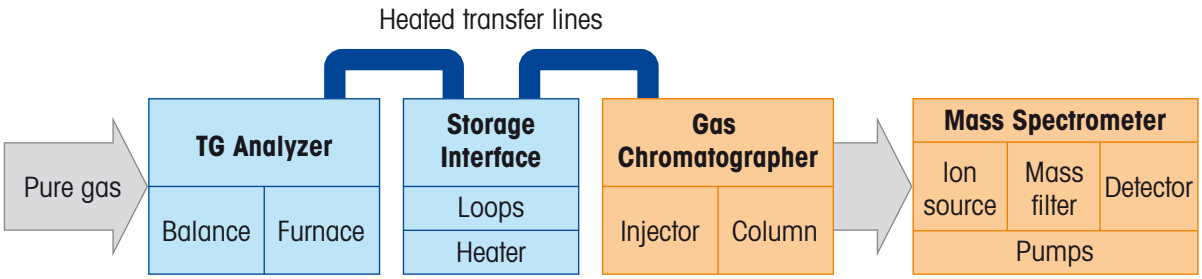
TGA-GC/MS
A Powerful Identification Technique

In TGA-GC/MS, the decomposition products from the TGA are transferred to a storage interface with 16 storage loops (IST16) for subsequent analysis by gas chromatography and mass spectrometry (GC/MS). GC/MS is one of the most sensitive and commonly used techniques due to its ability to separate out components from complex materials.

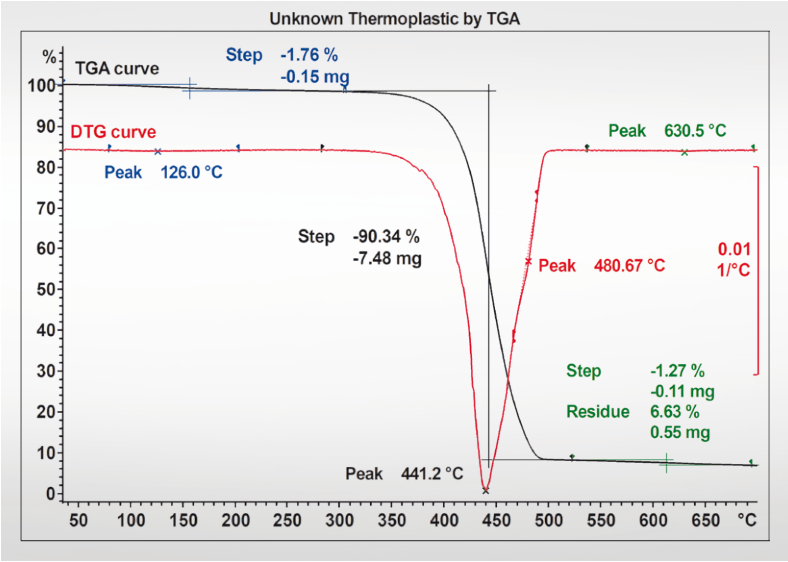
Features and benefits of a TGA-GC/MS system:

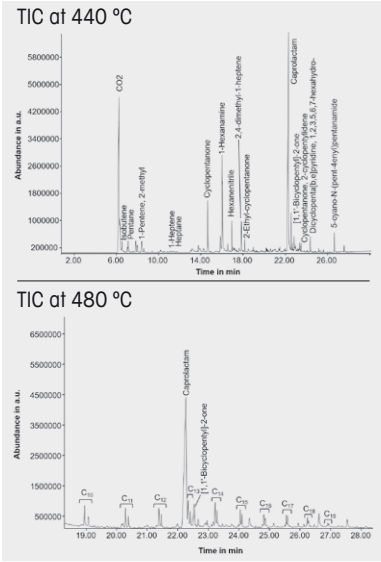
- **Gas analysis by GC/MS** – gas chromatographic separation followed by MS enables accurate identification of unknown samples
- **IST16 interface with 16 storage loops** – improves the resolution of several decomposition steps occurring in one single measurement
- **Different measurement modes** – select the best mode according to your needs and application

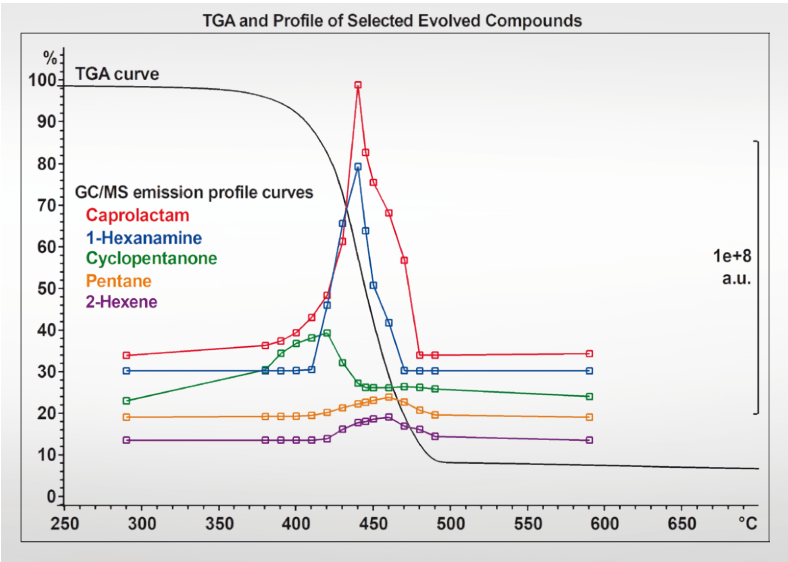
A typical TGA-GC/MS system with the IST16 storage interface is shown below. The gases from the TGA are transferred via a heated transfer line to the IST16 storage interface. From each storage loop, the gases are further transferred to the gas chromatograph column where the various molecular species of the gas mixture are separated from one another. Each species is then transferred to the MS where the mass spectra are continuously measured.



Identification of multi-component thermoplastics by TGA-GC/MS







The identification of unknown materials is an important field in many R&D and QC areas. The following example illustrates how TGA-GC/MS can be applied for such a task. The TGA and DTG curves show that the sample starts to decompose at 300 °C with a 90% mass loss step (DTG peak maximum at about 440 °C and a shoulder peak at 480 °C).

16 samples were taken between 290 and 590 °C. The total ion chromatograms (TIC) are shown for the gas samples withdrawn at 440 and 480 °C, respectively. Over 130 substances could be identified; for the most prominent ones, after integration of the individual peaks, emission profile curves were created. The main decomposition products detected were: cyclopentanone and amine compounds (typical for PA 6.6), caprolactam and nitrile compounds (typical for PA 6) and alkanes/alkenes – characteristic for polyethylene (PE) and polypropylene (PP). So it was concluded that the unknown polymer is a blend of PA 6.6 / PA 6, containing lower amounts of PE and PP.

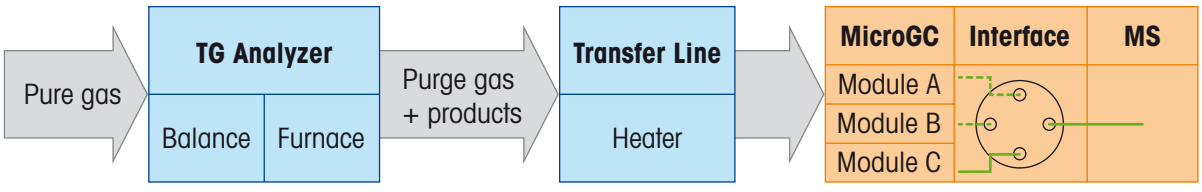
TGA-Micro GC/MS
Real-Time Gas Identification/Quantification

The mode of operation and the basic setup of a Micro GC and a classical GC are in principle the same. Even so, the components of a Micro GC (injector, separating column, detector) are distinctly smaller than in a classical GC. A Micro GC usually consists of several modules with different columns through which the gases being analyzed are injected in parallel. The time needed to record a chromatogram is significantly shorter (typically 2 to 3 minutes) due to the comparatively short columns used.

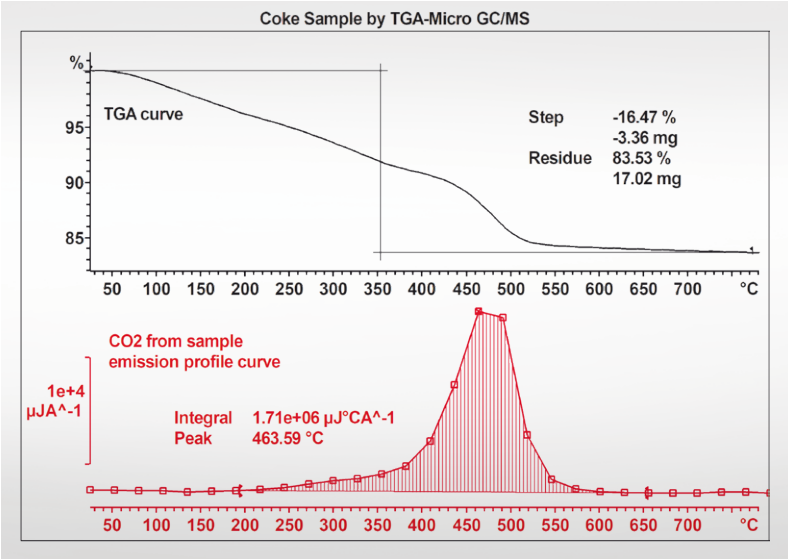
Features and benefits of a TGA-Micro GC/MS system:

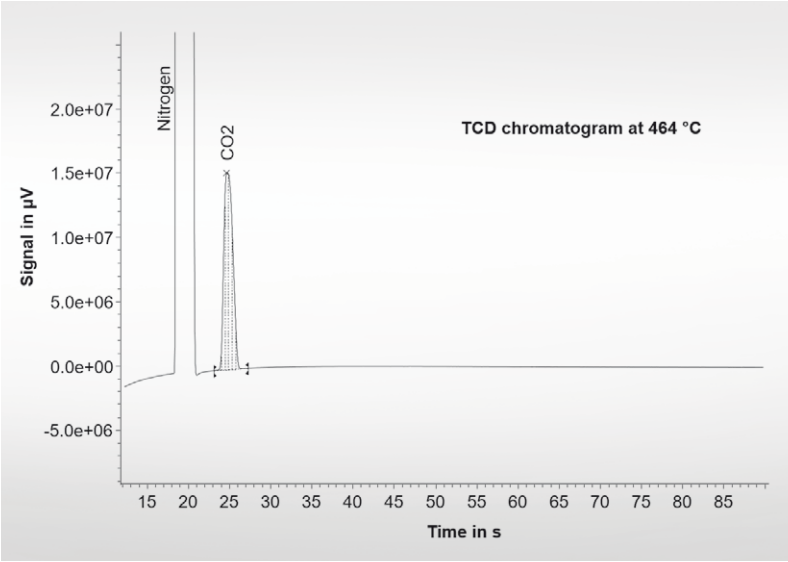
- **Gas analysis by Micro GC/MS** – enables real-time identification and quantification of small unknown molecules
- **Simultaneous TGA-Micro GC/MS** – fast results without prior evaluation
- **Modular concept** – users may add up to three Micro GC modules as needed with optional MS-coupling

A TGA is coupled to a Micro GC without MS or to a Micro GC/MS via a transfer line which is typically heated to about 80 °C as shown schematically below. Each Micro GC contains a GC column with a TCD (thermoconductivity detector); the analysis in the Micro GC typically takes about 2 min per injection. The MS detector is optional and connected via an interface to any module (module C in the schematic below).



Quantification of CO_2 in a coke sample by TGA-Micro GC





Coke is the residue formed after heating bituminous coal to high temperatures in the absence of air, and is typically used in the iron production process. Coke which is one almost pure form of carbon, evolves almost pure CO_2 on burning. The quality of the coke can be determined by the amount of released CO_2.

A coke sample was analyzed by TGA-Micro GC (PoraPLOT U column). The TGA curve showed that about 16.5% of the coke sample decomposed under the experimental conditions. All CO_2 peaks obtained in the TCD chromatograms were integrated to result in the emission profile of evolved CO_2 (red curve). One of these TCD chromatograms with the CO_2 peak is displayed above.

From an analoguous analysis with $CaCO_3$ for which the precise CO_2 content in the decomposition is known, a proportionality factor of the peak areas was determined. This factor enabled the determination of the CO_2 content and resulted in an amount of 2.68 mg CO_2, instead of 3.36 mg as indicated by the TGA experiment. Obviously, about 0.7 mg of the total 3.36 mg came from a gas other than CO_2.

Offering for evolved gas analysis

TGA-MS	
ThermoStar, single quadrupole, 1 – 200 amu	100 - 230 V, for 1 - 200 amu
ThermoStar, single quadrupole, 1 – 300 amu	100 - 230 V, for 1 - 300 amu

TGA-FTIR	
No article offered	Instruments that can be connected (supplied with interface): Nicolet iS10; Nicolet iS50; Nicolet iS5

TGA-IST-GC/MS	
SRA IST1 Coupling Interface / 230 V	Coupling interface IST1 including METTLER TOLEDO TGA installation kit
SRA IST1 Coupling Interface / 115 V	
SRA IST16 Storage Interface / 230 V	Storage interface IST16 including METTLER TOLEDO TGA installation kit
SRA IST16 Storage Interface / 115 V	
Agilent GC/MS, Diffusion Pump	Agilent gas chromatograph combined with single quadrupole MS; DP = diffusion pump, TP = turbo pump
Agilent GC/MS, Turbo Pump	
GC/MS Package with IST1 and GC/MS 230 V	Fixed GC/MS package with IST1, interface kit and NIST library included
GC/MS Package with IST1 and GC/MS 115 V	
GC/MS Package with IST16 and GC/MS 230 V	Fixed GC/MS package with IST16, interface kit and NIST library included
GC/MS Package with IST16 and GC/MS 115 V	
Upgrade Kit (from IST1 to IST16)	The IST1 can be upgraded to IST16

TGA-Micro GC/MS	
Chassis Micro GC SOLIA 1 Module 230 V	SOLIA base instrument prepared for one gas separation module
Chassis Micro GC SOLIA 1 Module 115 V	
Chassis Micro GC SOLIA 2 Modules 230 V	SOLIA base instrument prepared for two gas separation modules
Chassis Micro GC SOLIA 2 Modules 115 V	
Chassis Micro GC SOLIA 3 Modules 230 V	SOLIA base instrument prepared for three gas separation modules
Chassis Micro GC SOLIA 3 Modules 115 V	
Gas Module Molsieve (MS5A)	Most relevant gases: He, H_2, Ar, O_2, N_2, CH_4, CO
Gas Module PoraPLOT U (PPU)	CO_2, H_2O, Cl/F carbons, ethane, ethane, propane
Gas Module PoraPLOT Q (PPQ)	CO_2, H_2O, NO_x, Cl/F carbons, propane, propylene; acetylene
Gas Module Al_2O_3/KCl	Propylene, propyne, hydrogen sulfide
Gas Module Sil5 CB	Alcohols, Cl/F carbons; C_1 to C_3 hydro carbons
Gas Module 52CB	Aromatic hydro carbons (BTEX); amines; polar solvents
Gas Module Si-PLOT	Cl/F carbons; sulfur dioxide, carbonyl sulfide; hydrogen sulfide
Interface for SOLIA / Agilent single quadrupole MS, DP, 230 V	Interface between SRA SOLIA and Agilent single quadrupole MSD, DP = diffusion pump
Interface for SOLIA / Agilent single quadrupole MS, DP, 115 V	
Interface for SOLIA / Agilent single quadrupole MS, TP, 230 V	Interface between SRA SOLIA and Agilent single quadrupole MSD, TP = turbo pump
Interface for SOLIA / Agilent single quadrupole MS, TP, 115 V	

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