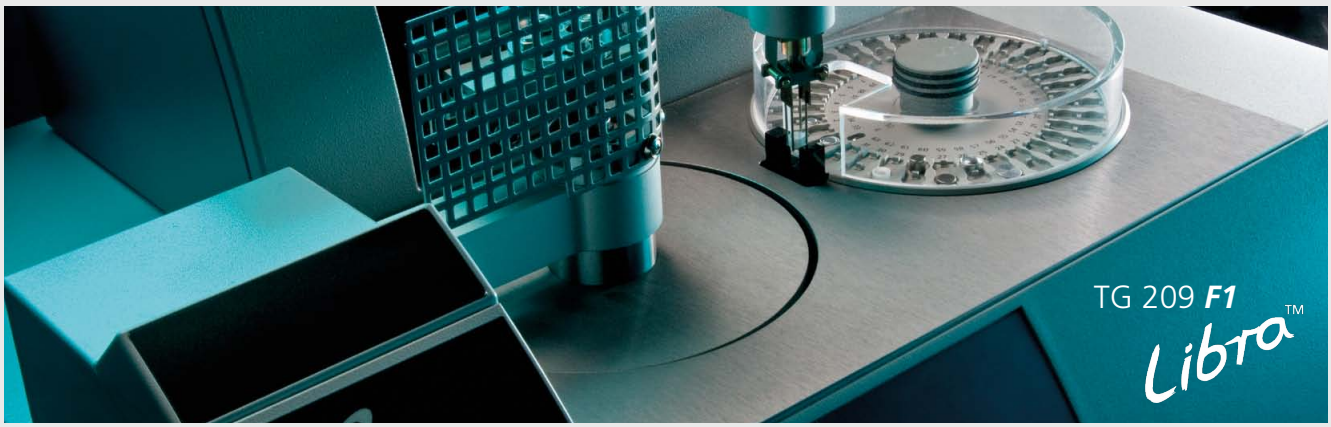
NETZSCH

Analyzing & Testing

Thermogravimetric Analysis – TGA

Method, Technique, Applications



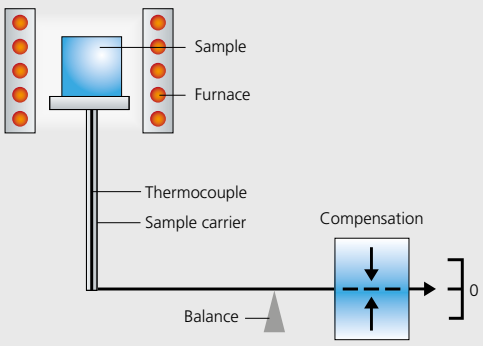
Leading Thermal Analysis

TGA – Method

Thermogravimetry (TG) or Thermogravimetric Analysis (TGA) is a well proven Thermal Analysis method. TGA is used in the research & development of various substances and engineering materials – solid or liquid – in order to obtain knowledge about their thermal stability and composition.

In recent decades, TGA has been used increasingly for the quality control and assurance of raw materials and incoming goods as well as for failure analysis of finished parts, especially in the polymer processing industry. Various international standards describe the general principles of thermogravimetry for polymers (ISO 11358) or other specific applications, such as compositional analysis for rubber (ASTM D 6370) and evaporation loss of lubricating oils (ASTM D 6375).

NETZSCH Analyzing & Testing has been manufacturing thermo-microbalances for many years. Our vertical, top-loading design not only provides for easy operation and sample loading, but also allows gases to flow naturally in an upward direction. Evolved gas analyzers such as mass spectrometers, FT-IR spectrometers and/or GC-MS (gas chromatograph-mass spectrometers) can then be coupled directly at the top of the unit. The Automatic Sample Changer (ASC) can also be used to conduct routine measurements around the clock.

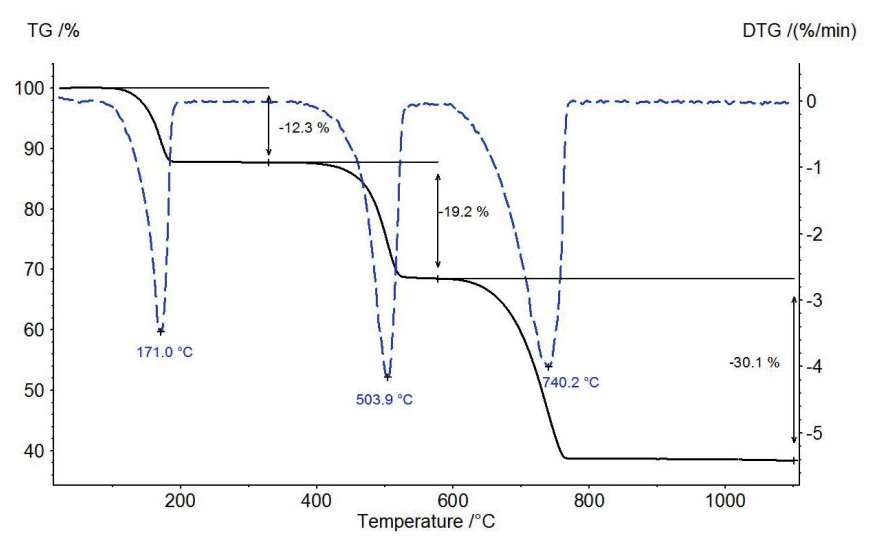


Measuring Principle

A thermobalance is used to measure the mass change of a sample as a function of temperature or time, under a defined and controlled environment with respect to heating rate, gas atmosphere, flow rate, crucible type, etc.

Measurement Result

This TG plot shows the decomposition of calcium oxalate monohydrate, $CaC_2O_4 * H_2O$, in air at a heating rate of 10 K/min. The decomposition occurs in three mass loss steps with the release of water (12.3%), carbon monoxide (19.2%) and carbon dioxide (30.1%). The corresponding 1st derivative of the TG curve, DTG, provides the decomposition rate and is helpful for evaluating the mass loss steps accurately.



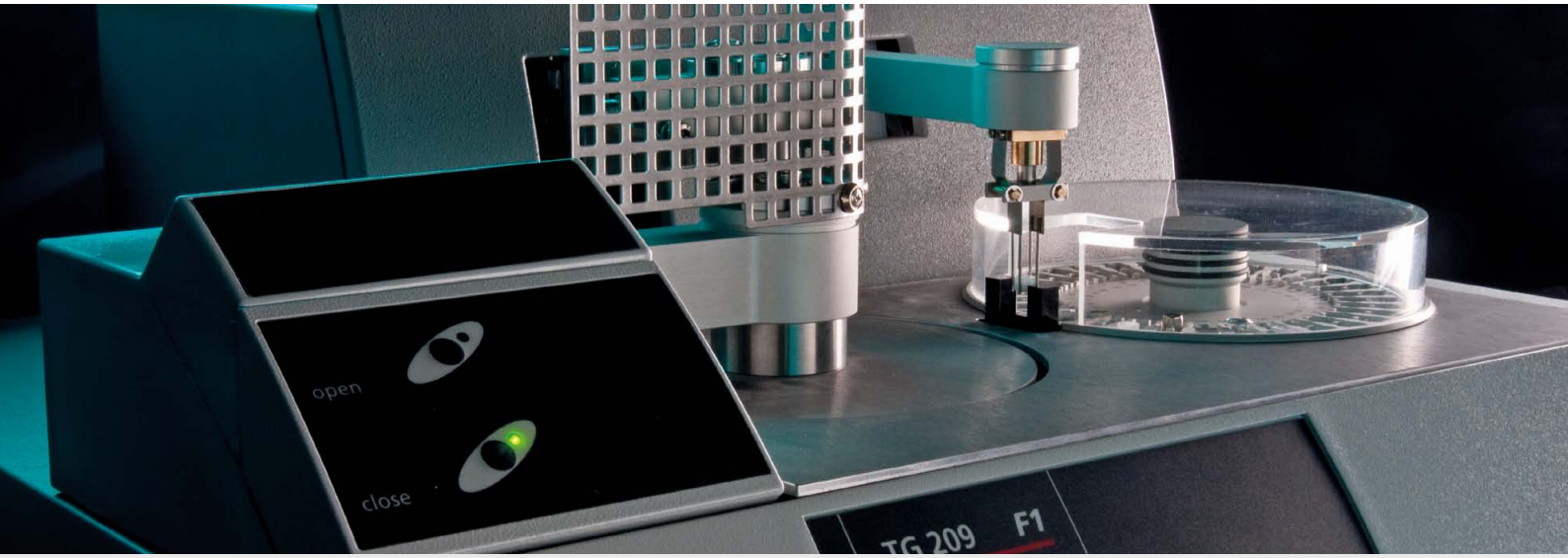
TG and DTG curves for the decomposition of calcium oxalate

TG 209 ***F1*** *Libra*™ with Automatic Sample Changer (ASC)

At a Glance

- Intelligent TGA
- Vertical, top-loading design
- Precise ultra-microbalance
- Vacuum-tight design
- Integrated mass flow controllers
- Exchangeable sample carrier types
- Coupling to evolved gas analysis
- Automatic Sample Changer (ASC) for up to 64 samples

TG 209 ***F1*** *Libra*™ – Trendsetting Technology Safe



Safe and Easy Handling

One advantage of the new TG 209 ***F1*** *Libra*™ is its vertical, top-loading design which guarantees free and safe access to the crucible – there is no hang-down wire with any danger of bending, and no horizontal beam where crashing can occur. When placing the crucible on the sample carrier, there is no effect to the microbalance since the sample carrier is detached by an automatic lifting device. Sample placement is therefore always trouble-free.

High Resolution under Thermostatic Control

The precise ultra-microbalance under thermostatic control provides high resolution of 0.1 µg in the large mass measurement range of 2000 mg. Samples with a large mass change can be continuously analyzed at a high precision level without switching measurement ranges.

High Temperature at Fast Heating Rates in a New Ceramic Furnace

The maximum temperature of the corrosion-resistant microfurnace amounts to 1100°C (sample temperature). Its high heating rates of up to 200 K/min are suited for identifying the material by a fast QC check. A water-cooled jacket provides the micro-furnance with fast cooling and therefore allows for high sample throughput.

Defined Gas Conditions via Three MFCs

The vacuum-tight design allows a pure and defined inert gas atmosphere to be established for the pyrolysis of the sample. No superimposed oxidation by residual air can occur. The integrated mass flow controllers (MFCs) for two purge gases and one protective gas can be controlled, recorded and evaluated via the software. Of course, gas switching can be implemented automatically under reproducible conditions.

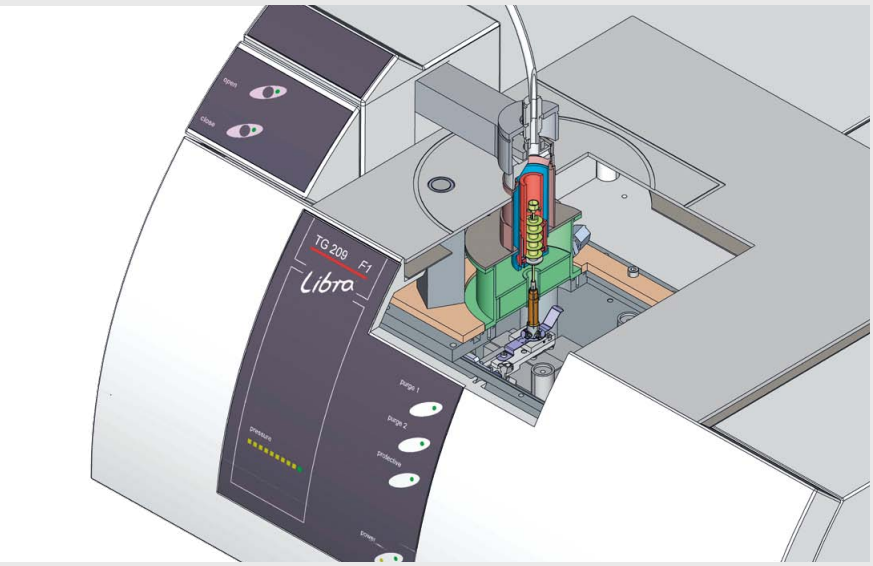
NETZSCH

AutoVac™ and Vacuum Technique for More Accurate and Reproducible Results

The optional *AutoVac*™ feature for programmable automatic evacuation and gas filling provides uniform measurement conditions and therefore ensures reproducible TGA results. When polymer mixtures or blends are measured in a vacuum, the boiling point depression of low volatiles (e.g., solvents or plasticizers) can be realized. A better separation from the decomposition of the polymer component can be achieved.

Exchangeable Sample Carriers and Various Crucible Types

Depending on the mass, volume, shape and reactivity of the sample, crucibles of various materials are available with volumes of up to 350 µl, as well as corrosion-resistant sample carrier types in different geometries. The sample carrier type P (Platinel®) provides the highest sensitivity for the c-*DTA*® signal, which serves for recording endothermal and exothermal effects via calculated DTA in a manner similar to DSC (Differential Scanning Calorimetry).



Design of the TG 209 ***F1*** *Libra*™

Technical Specifications	
Temperature range	(10°C) 20°C to 1100°C
Heating and cooling rates	0.001 K/min to 200 K/min
Cooling time (1000°C to 100°C)	12 min
Measuring range	2000 mg
Resolution	0.1 µg
Atmospheres	inert, oxidizing, static, dynamic
Vacuum-tight design	$<10^{-2}$ mbar
Integrated Mass Flow Controllers (MFCs) for 2 purge gases and protective gas	
Exchangeable sample carrier types	
c-*DTA*® for calculated DTA signal	
AutoVac™ for automatic evacuation and refilling (optional)	
Super-Res® for rate-controlled mass change (optional)	
Automatic Sample Changer (ASC) for 64 different crucibles (optional)	
Coupling to MS, GC-MS, FTIR for Evolved Gas Analysis (optional)	

TG 209 ***F1*** *Libra*™ – Automatic Sample Changer and Accessories

The Automatic Sample Changer (ASC) is designed for routine quality control and assurance measurements. The single carousel accommodates up to 64 samples, even if these are in different crucible types with different geometries. Crucibles can be changed safely and reliably around the clock – even over the weekend. This provides higher efficiency at lower costs.

Of course, each sample can be assigned a different measurement and evaluation program. The macro recorder features easy-to-understand input fields. Unplanned analyses can also be inserted into a pre-programmed series of tests already in progress.

For unstable substances or samples with volatile or oxygen-sensitive components, an automatic piercing device is available which perforates the sealed aluminum crucible just prior to the start of the measurement.

Additional Information

visit www.netzsch.com/tg209f1

TG 209 ***F1*** *Libra*™ with ASC

Crucible Types for Various Applications[1]

Application	Material	Diameter/Height	Volume
Standard TGA tests, not for salts and glass	Al_2O_3	6.8 mm/4 mm	85 µl
Standard TGA tests, not for salts and glass, high sample input	Al_2O_3	8.0 mm/8 mm	300 µl
Standard TGA tests, not for salts and glass, higher sample input	Al_2O_3	9.0 mm/7 mm	350 µl
Especially for c-*DTA*®, not for metals	Pt/Rh (80/20)	6.8 mm/2.7 mm	85 µl
Especially for c-*DTA*®, high volume, not for metals	Pt/Rh (80/20)	6.8 mm/6 mm	190 µl
Especially for c-*DTA*®, up to max. 600°C	Al (99.5%)	6.7 mm/2.7 mm	85 µl

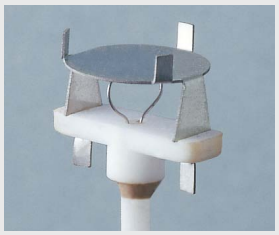
[1] For special applications, there are also crucibles available in other materials

Exchangeable Sample Carrier Types[2]

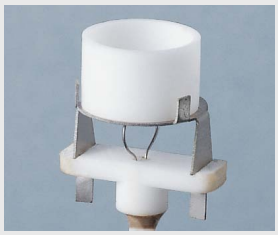
Application	Material of the sample support	Sensor type	For crucible types
Standard TGA	Al_2O_3	Type P	7 mm to 9 mm diameter, 85 µl to 350 µl
Ideal for c-*DTA*®	PdPt/Au/AuPd (Platinel®)	Type P (disk)	7 mm to 9 mm diameter, 85 µl to 350 µl
For corrosive media	Al_2O_3	Type P, protected	7 mm to 9 mm diameter, 85 µl to 350 µl

[2] For ASC: max. diameter of the crucible is 8 mm

Standard Al_2O_3 sample carrier for corrosive gases



Sample carrier with Platinel® thermocouple



Sample carrier with Al_2O_3 sample crucible

Proteus® Software for TG 209 ***F1*** *Libra*™ – User-Friendly and Versatile

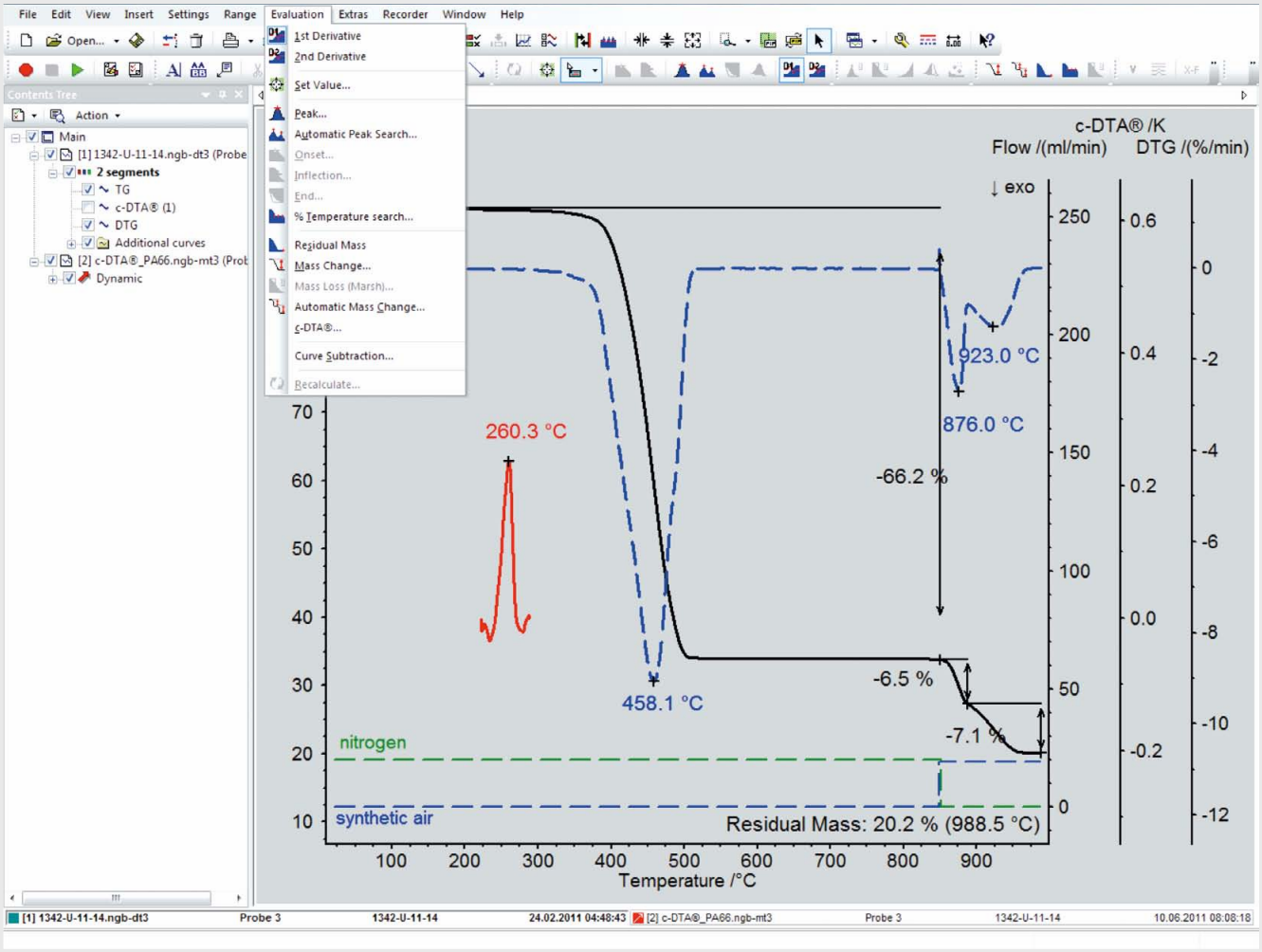
The TG 209 ***F1*** *Libra*™ runs under the versatile *Proteus*® software on a Windows® operating system. The *Proteus*® software includes everything you need to carry out a reliable measurement and evaluate the resulting data – or even carry out complicated analyses. The *Proteus*® software is licensed with the instrument and can also be installed on other computer systems. The data security and absolute quality that it provides are prerequisites for usage conforming to GLP, GMP and 21 CFR, part 11.

General Software Features

- Multi-tasking for simultaneous measurement and evaluation
- Multi-moduling for up to 4 different instruments
- Multi-method analysis for curve comparison and evaluation of various methods
- Snapshot for on-line evaluation of the running measurement
- Picture-in-picture presentation (PIP and FLIP)
- Graphic and data export
- Storage and restoration of analyses
- Context-sensitive help system
- Macro recorder (optional)

Main TGA Features

- Mass change in % or mg
- Automatic evaluation of mass change steps and characteristic temperatures
- Extrapolated onset and end-point
- Peak temperatures and values of the 1st and 2nd derivatives
- Multi-point temperature calibration via c-*DTA*®; calculated DTA
- c-*DTA*® for evaluation of endothermal and exothermal effects
- Automatic correction of buoyancy and drift for rapid TGA results



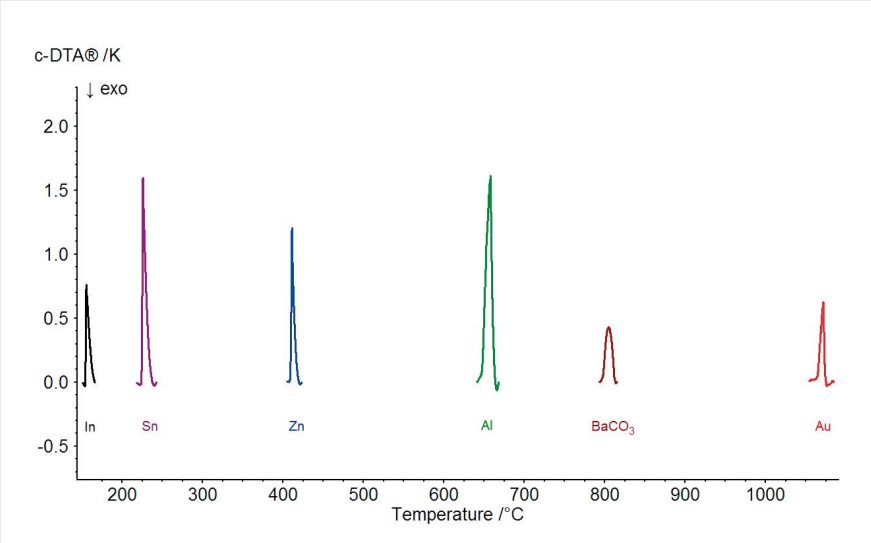
Key Advanced Software Features

Feature	Advantage	Benefit
c-DTA®	Calculated DTA for endothermal and exothermal effects	Better curve interpretation through a DSC-like signal
Super-Res®	Rate-controlled mass change	Better resolution and better separation of superimposed mass change steps
Peak Separation	Separation of DTG peaks which are in close proximity	Better quantitative determination of superimposed mass change steps
Thermokinetics	Accurate process prediction such as lifetime and decomposition behavior via multivariate non-linear regression	Process optimization through freely selectable time/temperature programs saves time and money

Calculated DTA – c-*DTA*®

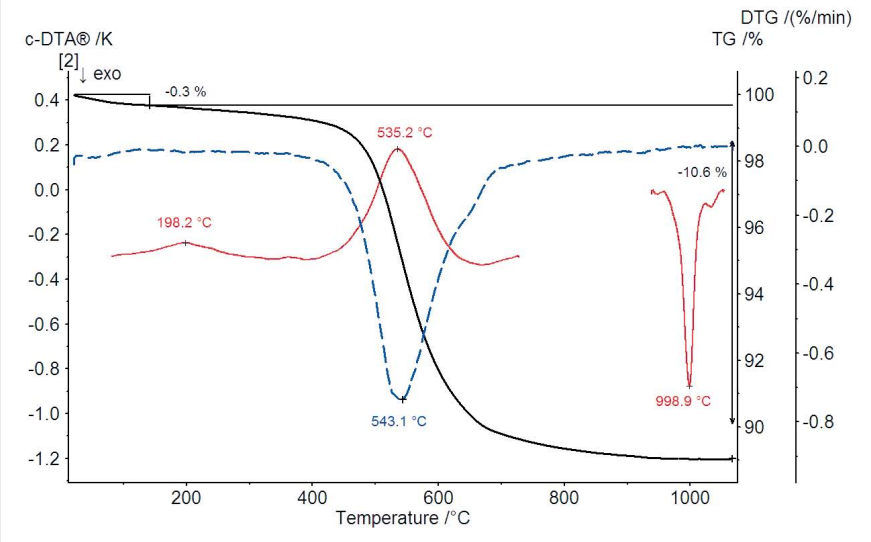
Easy and Reliable Temperature Calibration

The multi-point temperature calibration executed by means of c-*DTA*® conforms to standardized methods, and can therefore be easily validated. The onset temperatures of the melting of highly pure reference metals are taken over a broad temperature range. This plot shows the melting of In, Sn, Zn, Al and Au at a heating rate of 10 K/min.



More Information through Caloric Effects

In addition to the TGA and DTG curves, this plot depicts endothermal and exothermal effects determined by means of the calculated DTA signal.

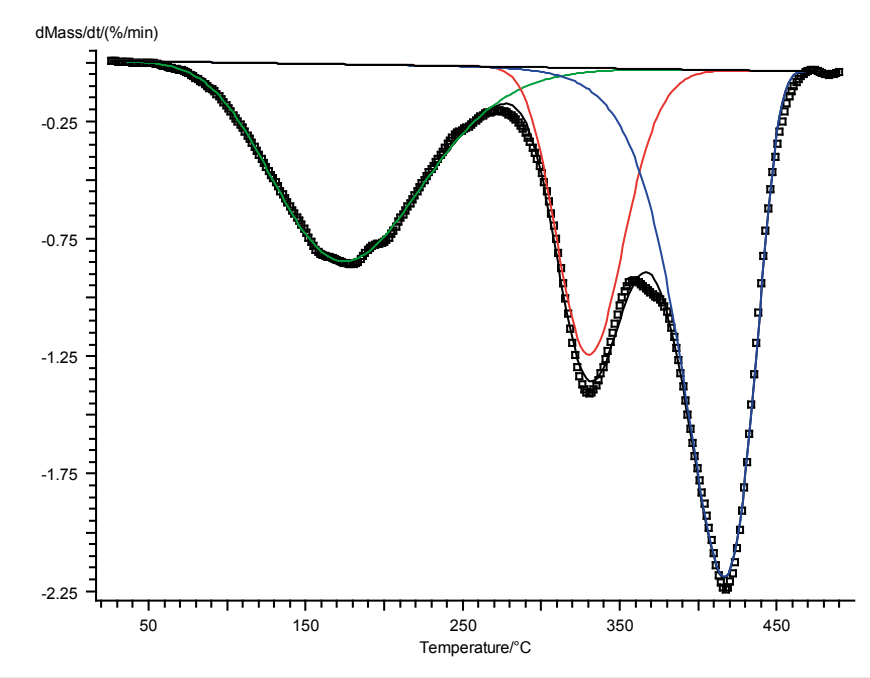


Super-Res® for Event-Based TGA

Normally, a defined constant heating rate is applied to the sample in order to study its decomposition behavior. If two mass-loss steps are superimposed, a lower heating rate (longer time) provides better separation of the individual peaks and therefore allows for more accurate mass loss steps. *Super-Res*® provides a rate-controlled mass loss step according to defined thresholds with respect to the mass loss rate (DTG curve) set by the operator. This results in much better separation of the individual mass loss steps.

Peak Separation for Better Accuracy of Mass Change Steps

Peak Separation software is increasingly used for superimposed, asymmetric DSC peaks according to the Frazer-Suzuki algorithm in order to achieve better separation of the individual phases. By applying *Peak Separation* to DTG peaks, the quantitative mass loss steps during material decomposition can be separated much more clearly. This provides higher accuracy with regard to the individual mass loss steps. The following plot shows the TGA result on a rubber mixture (NR/SBR) for tires, measured under vacuum (approx. 10^{-2} mbar). The symbols depict the measured raw data, the colored lines represent the separated peaks and the solid black line is the cumulative curve of the colored ones. The experimental and the calculated data match very well, resulting in three separate mass loss steps of 34.1%, 22.3% and 43.6%.



Thermokinetics for the Optimization of any Process

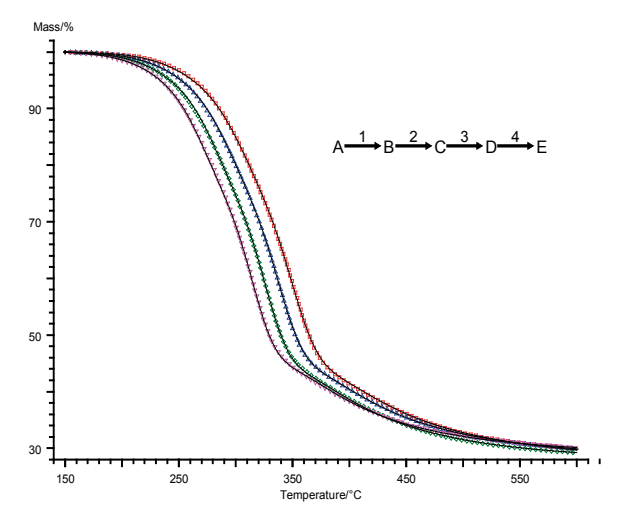


Fig. 1: Comparison of the TGA raw data (symbols) and the curves (solid lines) calculated on the basis of a 4-step reaction model

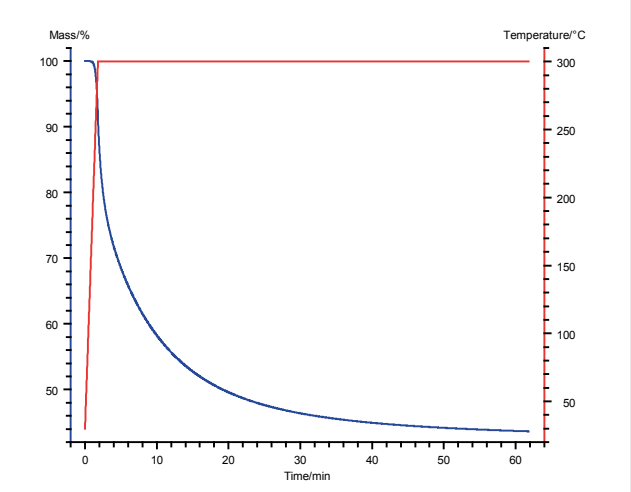


Fig. 2: Prediction of the mass change for a temperature program including heating at 150 K/min to 300°C, followed by an isothermal step (60 minutes)

With the unique NETZSCH *Thermokinetics* software, any process can be modeled via multivariate non-linear regression. The kinetic parameters such as activation energy, pre-exponential factor and order of reaction can be determined. From this modeling result, various predictions of the process can be established for any temperature/time program.

Thermogravimetry is ideal for determining the decomposition behavior of a substance. The lifetime of the material can thus be predicted as a function of time and/or temperature.

Fig. 1 shows the TGA plot of a biomass sample measured at 4 different heating rates – from 5 K/min to 40 K/min – in an inert gas atmosphere. The higher the heating rate, the more the curves are shifted to higher temperature values. This is typical behavior for effects caused by kinetic processes. There is an excellent congruence between the TGA raw data (symbols) and the calculated curves (solid lines). The formal model used consists of four consecutive reactions. For the first one, a 3-dimensional diffusion type was selected; the other three are n-th order reactions.

Based on this model, a prediction was computed: Starting at 30°C, heating to 300°C at a heating rate of 150 K/min, and then holding the temperature constant at 300°C for 1 hour yields the blue mass change curve shown in fig. 2. The calculation forecasts a residual mass of about 45% after 62 minutes.

TG 209 ***F1*** *Libra*™ – The Clever Solution

Tedious Baseline Run Eliminated

In order to ensure correct mass change values, a baseline run is usually carried out under identical test conditions such as heating rate, gas type, gas flow rate, crucible type and geometry, etc., and subtracted from the sample measurement. The baseline takes instrument and buoyancy influences into consideration.

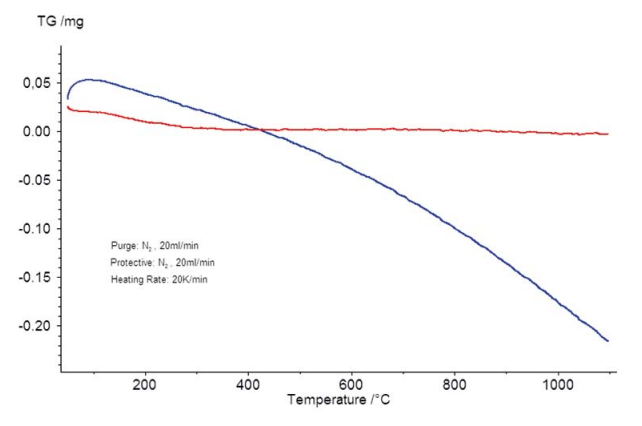


Fig. 1: Stable baseline (red) due to automatic correction of external influences

The Intelligent TGA – Automatic Correction of External Influences

Contrary to conventional models, the TG 209 ***F1*** *Libra*™ no longer requires a separate baseline run. This greatly simplifies routine test work, especially for quality control in industry.
The *Libra*™ takes the physics behind the external influences into consideration and corrects these effects automatically (depicted in fig. 1). The software stores the corrected data as well as the raw data.

Fig. 2 depicts the water loss in a sample from 50°C to 300°C. The blue line represents data without correction of the external influences; the red line represents corrected data.

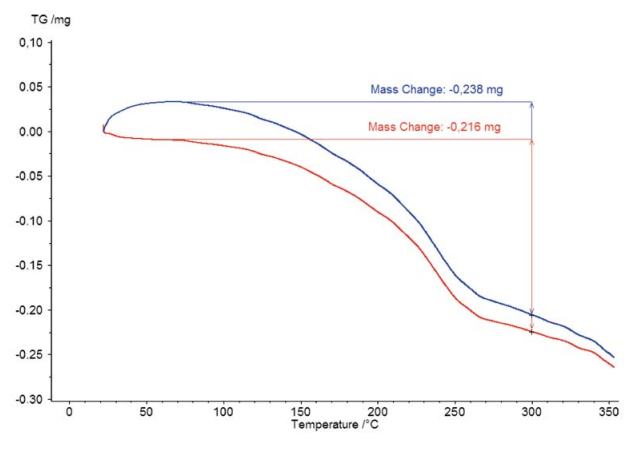
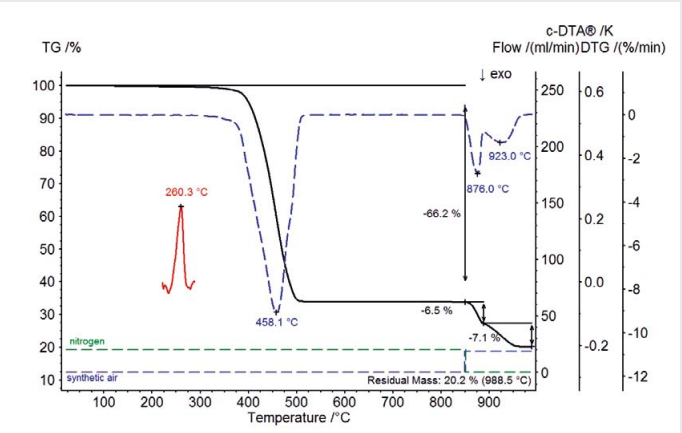


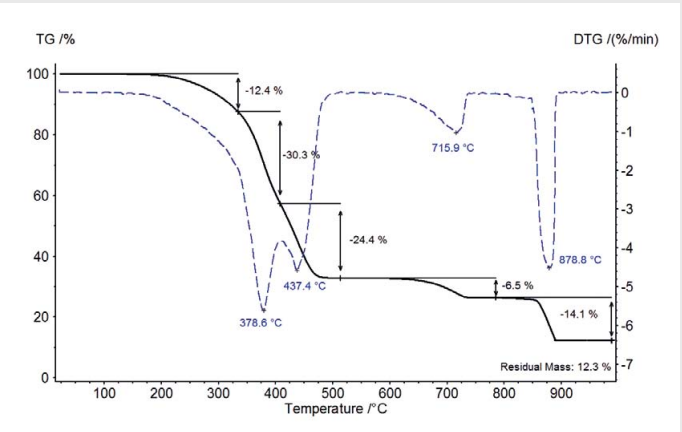
Fig. 2: Water loss in a sample

TG 209 ***F1*** *Libra*™ for a Wide Variety of Applications



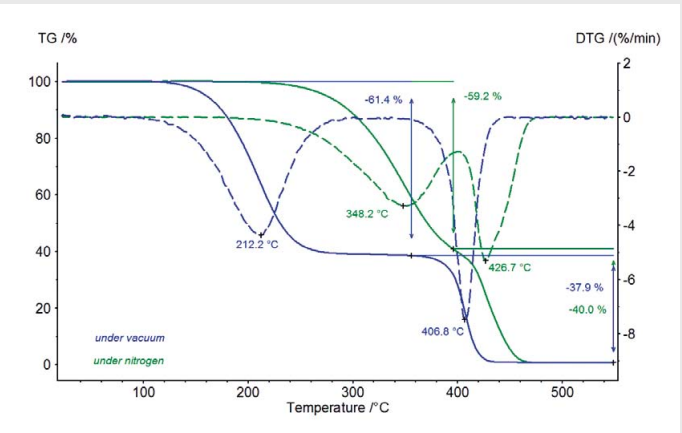
Polyamide

Polyamide 66 is a thermoplastic polymer which is used for a wide variety of technical parts. The stiffness of the PA66 can be increased by suitable fillers such as glass fibers. By means of TGA, not only can the decomposition of the polymer be determined, but the precise glass fiber content as well. The TGA curve also shows the content of pyrolytic soot and added carbon black.



NR/SBR Rubber

The TGA analysis on rubber is a standard analytical method for the determination of plasticizer content and rubber components. The example shows an NR/SBR rubber mixture which exhibits a plasticizer content of 12.4%. The two-step decomposition of the rubber (NR and SBR) can be separated precisely. This compound also has a chalk content as inorganic filler. By switching to an oxidizing atmosphere at 85°C, the burning of the carbon black could be observed.

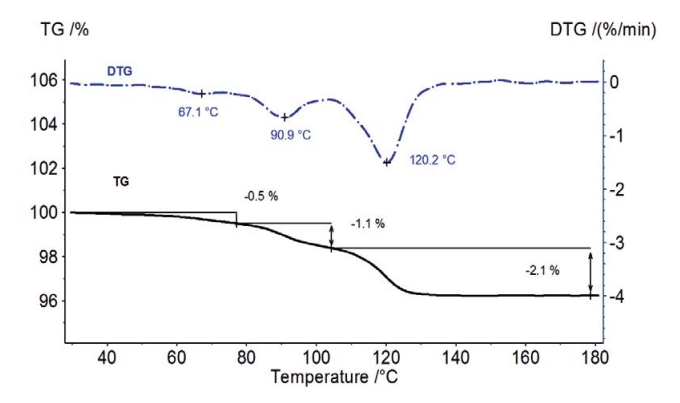


SEBS+PP

Thermoplastic elastomers are a class of copolymers or polymer mixtures with both thermoplastic and elastomeric properties. They can be used very easily in the manufacturing process, e.g., by injection molding. For investigating the plasticizer content, the advantage of conducting the TGA analysis under vacuum conditions is evident (blue curves). By reducing the vapor pressure of the plasticizer, two mass loss steps were clearly separated.

Magnesium Stearate

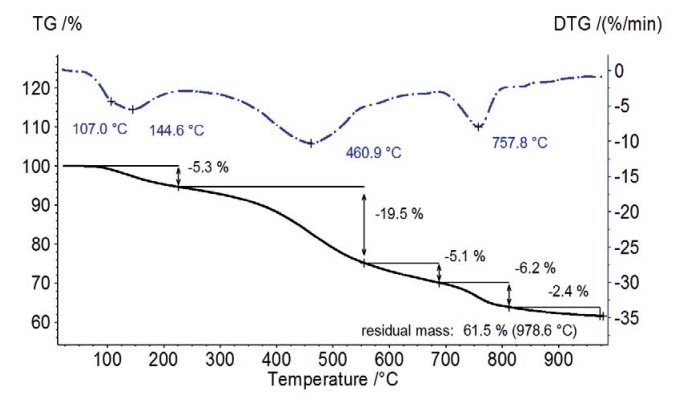
Commercially available magnesium stearate, a widely used excipient for pharmaceutical formulations, is a mix of several fatty acid salts that may vary in proportion. The magnesium stearate used in the present study shows three mass-loss steps of 0.5%, 1.1% and 2.1% in the temperature range up to 200°C. In the corresponding TG/FTIR experiment (not shown here), it was possible to identify all volatile components as water.



TGA measurement of magnesium stearate, sample mass. 5.8 mg, heating rate: 10 K/min, N_2 atmosphere

Coal

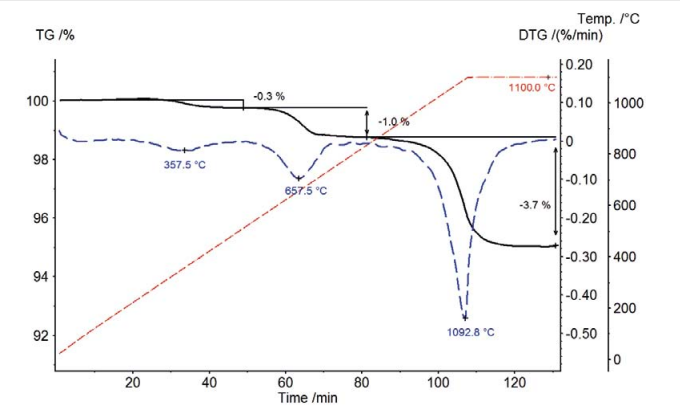
Coal pyrolysis is a complex process involving a large number of chemical reactions. During heating, mainly volatiles (gases and tars) and solid carbon (coke) are produced. 10 mg of coal was measured in a nitrogen atmosphere at a heating rate of 100 K/min. The corresponding TGA curve reveals several steps. The first mass loss (below 210°C) can be most probably related to the release of moisture; the calculated residual mass is 61.5%.



TGA measurement of finely ground coal

Mica

The TGA analysis on mica shows mass loss steps at lower temperatures for the dehydration and the dehydroxylation of the material. In addition, a characteristic mass loss step can be observed at 1093°C. It is the new ceramic furnace of the TG 209 ***F1*** *Libra*™, which permits measurements up to 1100°C, that makes this mass loss step experimentally accessible.



TGA measurement of mica

TG 209 ***F1*** *Libra*™ with Evolved Gas Analysis (EGA)

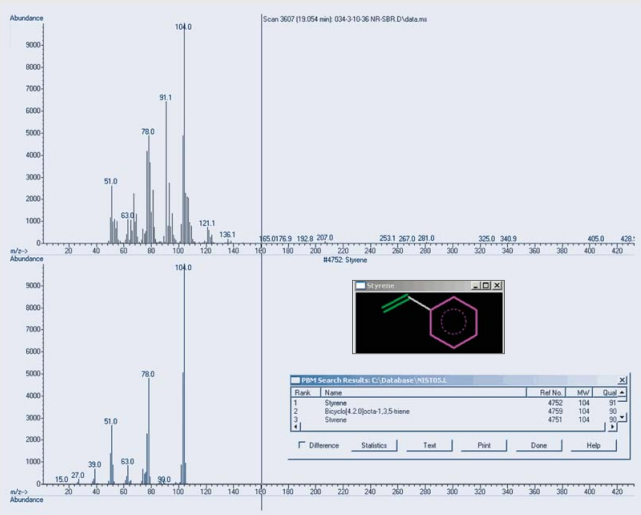
Different Methods

By coupling TG 209 ***F1*** *Libra*™ to a gas analysis technique such as an FTIR (Fourier Transform Infrared) spectrometer, MS (Mass Spectrometer), or GC-MS (Gas Chromatograph – Mass Spectrometer), information regarding the type of evolved gases as a function of time or temperature can be obtained, which yields a fingerprint of the analyzed material.

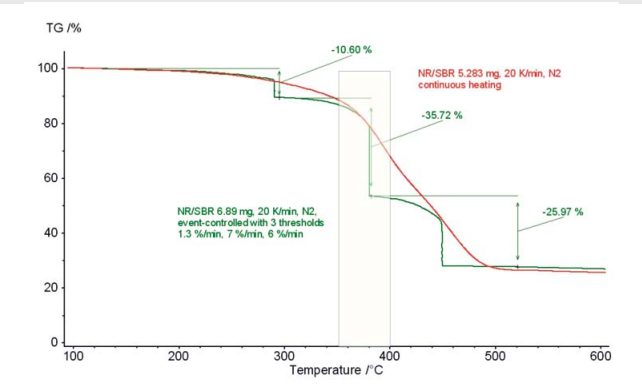
Coupling to GC-MS

GC (Gas Chromatography) is a high-resolution method for separating volatile and semi-volatile compounds. The gas mixtures are separated based on the differences in component distribution between a stationary phase (e.g., inner coating of a capillary) and a mobile phase (purge gas). This leads to different time delays or retention times of the gas components.

MS (Mass Spectrometry) is applied as a highly sensitive detection system at the outlet of the GC separation column and will register the time distribution of the separated gas components in the purge gas flow.
GC-MS provides detailed structural information on most compounds for an accurate identification of the gas components.



Evaluation of GC-MS-TIC chromatograms

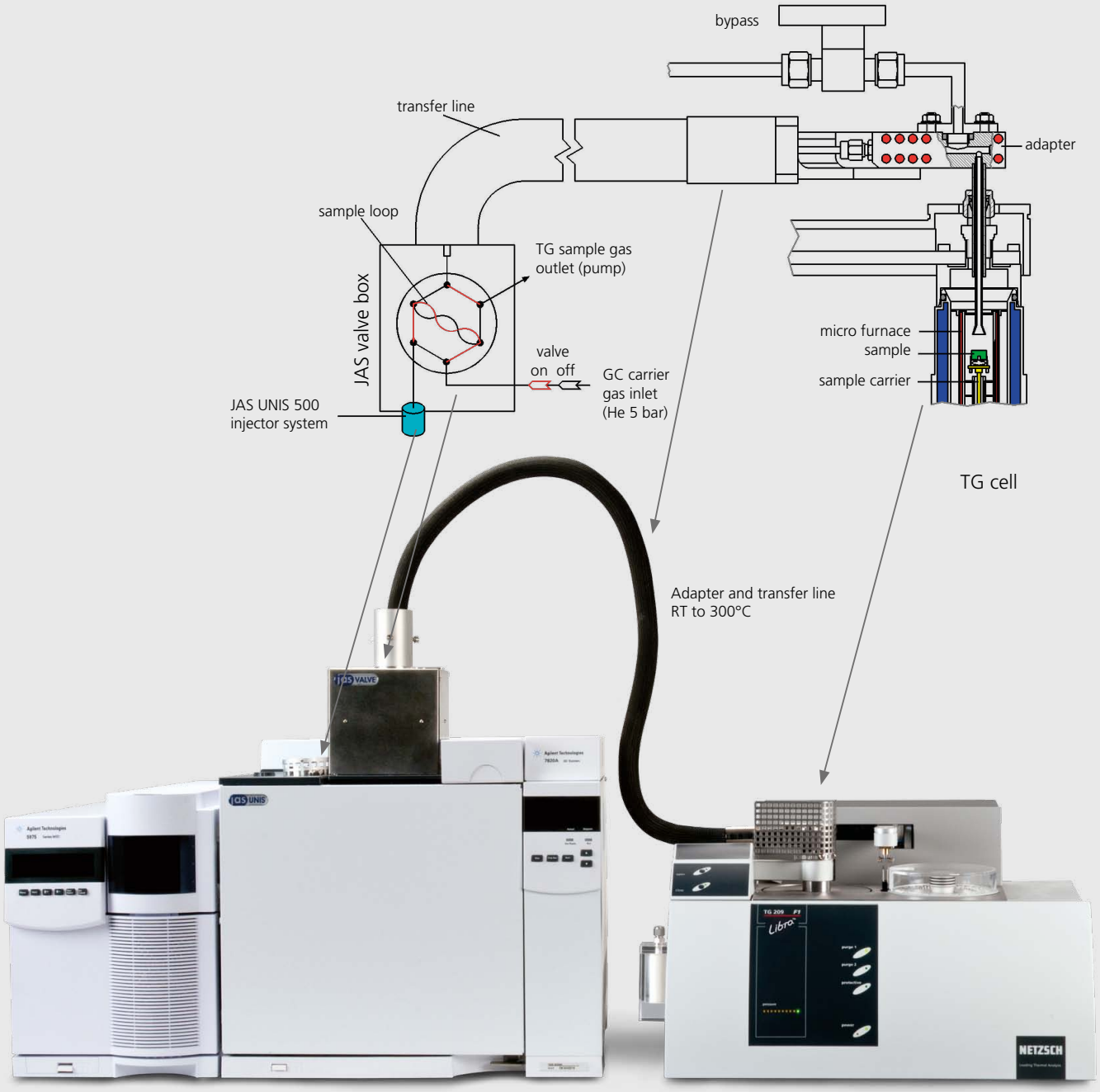


Event-controlled TG-GC-MS measurement on NR/SBR

- Nearly complete identification of the evolved gases with exact temperature correlation to TG and DTG curves
- Integration of the chromatogram
- Library search report for quantification of each gas component

Additional Information

visit www.netzsch.com/gcms



Detailed diagram of the functional elements of the TG-GC-MS coupling

TG 209 ***F1*** *Libra*™ with Evolved Gas Analysis (EGA)

Coupling to MS

High-level material research and characterization can be achieved by coupling the TG 209 ***F1*** *Libra*™ to our QMS 403 *Aëolos*® Quadrupole Mass Spectrometer. Any gases evolved are introduced directly into the electron impact ion source of the MS through a quartz glass capillary heated to 300°C.

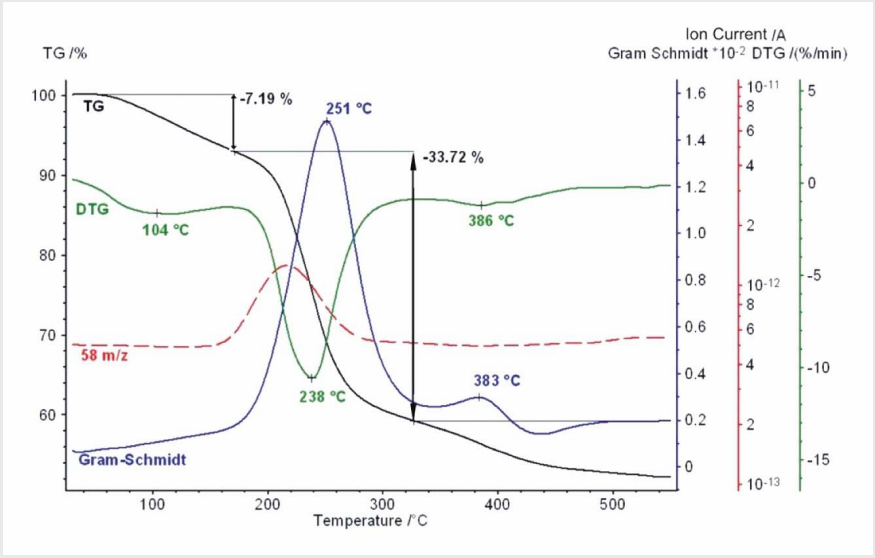
Coupling to FT-IR

"More than just the sum of its parts" is the motto for our comprehensive coupling system incorporating an FT-IR (Fourier Transform Infrared) Spectrometer manufactured by our cooperation partner, Bruker Optics. The purge gas flow from the TGA carries the volatiles through a short heated transfer line to the vacuum-tight gas cell of the FT-IR. All evolved gases with a changing dipole moment are identified by their typical absorption spectrum, and complex gas mixtures can be spectroscopically separated.

Simultaneous TG-MS-FTIR Coupling and *PulseTA*®

The unique heated coupling adapter allows simultaneous TG-MS-FTIR measurements, even when the Automatic Sample Changer (ASC) is running. Only one operational software package on a single PC is needed for TG-MS-FTIR. Comprehensive evaluations can be displayed in one plot.

Calibration and quantification of the evolved gas components can be achieved by the sophisticated *PulseTA*® technique. Take advantage of nearly 40 years of coupling experience and ask for our special coupling brochures.



Comprehensive evaluation of TGA, DTG, FTIR (Gram-Schmidt), and QMS (u) versus temperature

Coupling of Tensor 27, external gas cell, TG 209 ***F1*** *Libra*™ and QMS 403 C *Aëolos*®

Additional Information

visit www.netzsch.com/ftir

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When it comes to Thermal Analysis, Adiabatic Reaction Calorimetry and the determination of Thermophysical Properties, NETZSCH has it covered. Our 50 years of applications experience, broad state-of-the-art product line and comprehensive service offerings ensure that our solutions will not only meet your every requirement but also exceed your every expectation.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42
95100 Selb
Germany
Tel.: +49 9287 881-0
Fax: +49 9287 881 505
at@netzsch.com

www.netzsch.com

NGB · TG 209 **F1** *Libra*™ · EN · 2000 · 06/11 · MD · Technical specifications are subject to change.