

Thermogravimetric Analysis – TGA

Technique, Instrument, Applications



TGA Method

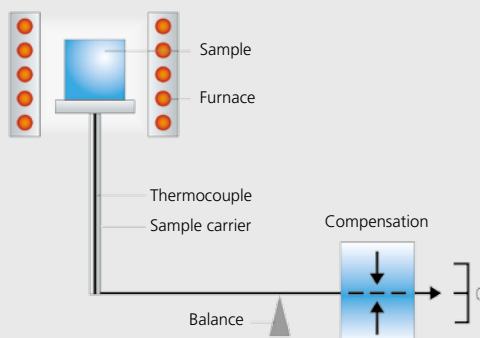
Thermogravimetry (TG) or Thermogravimetric Analysis (TGA) is a well proven Thermal Analysis method. TGA is used in the research & development of various substances and engineering materials – solid or liquid – in order to obtain knowledge about their thermal stability and composition.

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 thermo-gravimetry for polymers (ISO 11358) or other specific applications, such as compositional

analysis for rubber (ASTM D6370) and evaporation loss of lubricating oils (ASTM D6375).

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.



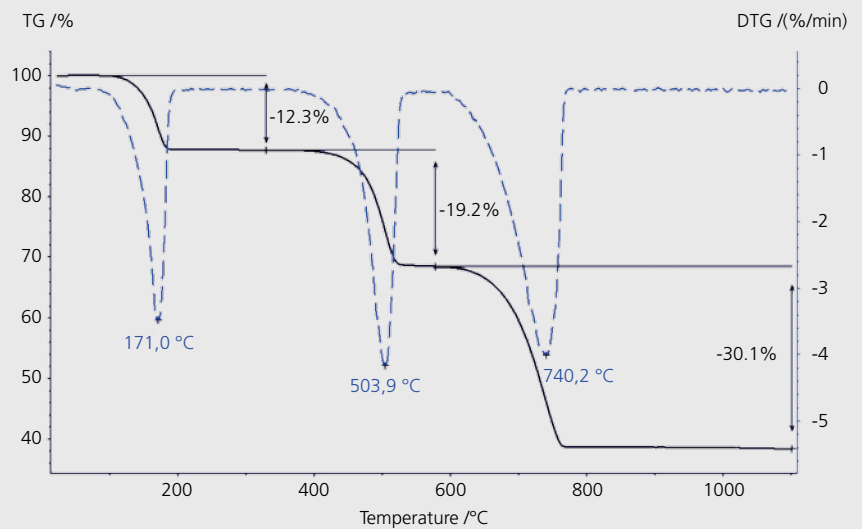
Measuring Principle

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 TGA plot shows the decomposition of calcium oxalate monohydrate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, in air at a heating rate of 10 K/min. The decomposition occurs in three mass-loss steps (black curve) with the release of water (12.3%), carbon monoxide (19.2%) and carbon dioxide (30.1%).

The corresponding 1st derivative of the TGA curve (dotted line, DTGA) provides the decomposition rate and is helpful for evaluating the mass-loss steps accurately.



TGA and DTGA curves for the decomposition of calcium oxalate monohydrate



TG 209 **F1** Libra® with automatic sample changer (ASC)

At a Glance

- Precise ultra-microbalance
- Vacuum-tight design
- Vertical, top-loading design
- Corrosion-resistant ceramic furnace
- Automatic sample changer (ASC) for up to 64 samples
- Integrated gas supply unit with three mass flow controllers
- *BeFlat*®: Automatic baseline correction
- *c-DTA*®: Caloric effects made visible
- Coupling to evolved gas analysis

TG 209 **F1** *Libra*[®] – Trendsetting Technology



Safe and Easy Handling

One advantage of the 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 Temperature and Fast Heating Rates in a Ceramic Furnace

The maximum temperature of the corrosion-resistant micro-furnace 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-furnace with fast cooling and therefore allows for high sample throughput.

Thermostatic Control – Optimum Stability

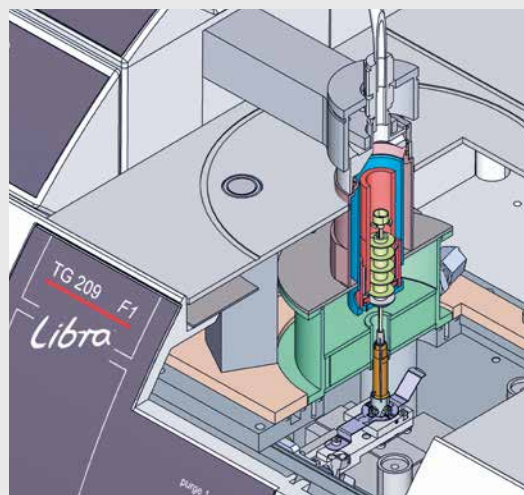
The precise ultra-microbalance under thermostatic control provides high resolution of 0.1 µg in the large mass measurement range of 2000 mg. Samples with a large mass change can be continuously analyzed at a high precision level without switching measurement ranges.

c-DTA[®] for Additional Information on Caloric Effects

The sample carrier type P (Platinel[®]) provides the highest sensitivity for the c-DTA[®] signal, which serves for recording endothermic and exothermic effects via calculated DTA in a manner similar to DSC (Differential Scanning Calorimetry). Temperature calibration can be carried out by means of the melting point determination – easily and without any modification of the hardware (see page 11).

Defined Gas Conditions for Reproducible Measurements

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 gas supply unit with mass flow controllers (MFCs) accommodates up to two purge gases and one protective gas. The MFCs can be controlled, recorded and evaluated via the software. Automatic gas switching allows for the implementation of identical measurement conditions, thus improving the reproducibility of the measurement.



Scheme of the TG 209 **F1** Libra®

AutoVac 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. Better separation from the decomposition of the polymer component can be achieved: the volatiles evolve at lower temperatures whereas the decomposition temperature of the polymer remains nearly at the same temperature.

Technical Key Data

Temperature range	(10°C) 20°C to 1100°C
Heating and cooling rates	0.001 K/min to 200 K/min
Cooling time (1100°C to 100°C)	~ 12 min in nitrogen atmosphere ~ 4.7 min in helium atmosphere
Temperature precision	±0.2K
Measuring range	2000 mg
Weight loss/gain (max.)	2000 mg (minus weight of crucible)
Resolution	0.1 µg
Atmospheres	inert, oxidizing, static, dynamic
Vacuum-tight design	<10 ⁻² mbar
Integrated gas supply unit	3 mass flow controllers
Sample carrier	Various types, easy exchangeable
<i>BeFlat</i> ®	Automatic baseline correction
<i>c-DTA</i> ®	Endo- and exothermal effects and temperature calibration
<i>AutoVac</i>	Automatic evacuation and refilling (option)
<i>Super-Res</i> ®	Rate-controlled mass change (option)
Automatic sample changer (ASC)	64 positions, piercing device, different crucibles (option)
Couplings for gas analysis	FT-IR, integrated FT-IR (<i>Perseus</i> TG), MS, GC-MS (options)

TG 209 **F1** *Libra*[®] – Automatic Sample Changer and Accessories

Automatic Sample Changer – High Efficiency and Flexibility

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.

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.

Piercing Device – Sensitive Samples Kept Safe

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



TG 209 **F1** *Libra*[®] with ASC

Crucible Types for Various Applications¹

Application	Material	Diameter/Height	Volume
Standard TGA tests ²	Al ₂ O ₃	6.8 mm/4 mm	85 µl
Standard TGA tests ² , high sample input	Al ₂ O ₃	8.0 mm/8 mm	300 µl
Standard TGA tests ² , higher sample input	Al ₂ O ₃	9.0 mm/7 mm	350 µl
Especially for c-DTA ^{®3}	Pt/Rh (80/20)	6.8 mm/2.7 mm	85 µl
Especially for c-DTA ^{®3} , high volume	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

² Standard Al₂O₃ crucibles may not be used for all salts and glasses; reactions may occur prior to or during melting.

³ Pt/Rh crucibles may not be used for metals; reactions may occur prior or during melting



Wide range of crucibles

Exchangeable Sample Carrier Types⁴

Application	Material of the Sample Support	Sensor Type	For Crucible Types
Standard TGA	Al ₂ O ₃	Type P	6.7 mm to 9 mm Ø, 85 µl to 350 µl
Ideal for c-DTA [®]	PdPt/Au/AuPd (Platinel [®])	Type P (disk)	6.7 mm to 9 mm Ø, 85 µl to 350 µl
For corrosive media	Al ₂ O ₃	Type P, protected	6.7 mm to 9 mm Ø, 85 µl to 350 µl

⁴ For ASC: max. diameter of the crucible is 8 mm



Radiation shield of the TGA sample carriers

Sample carrier type P for c-DTA[®]

Al₂O₃ sample carrier for corrosive gases

Proteus[®] Software – Flexible, Intelligent, Complete

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 work station or laboratory computers, e.g., for evaluations.

General Software Features

- For Windows[®] XP and Windows[®] 7 operation systems
- 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 (option)

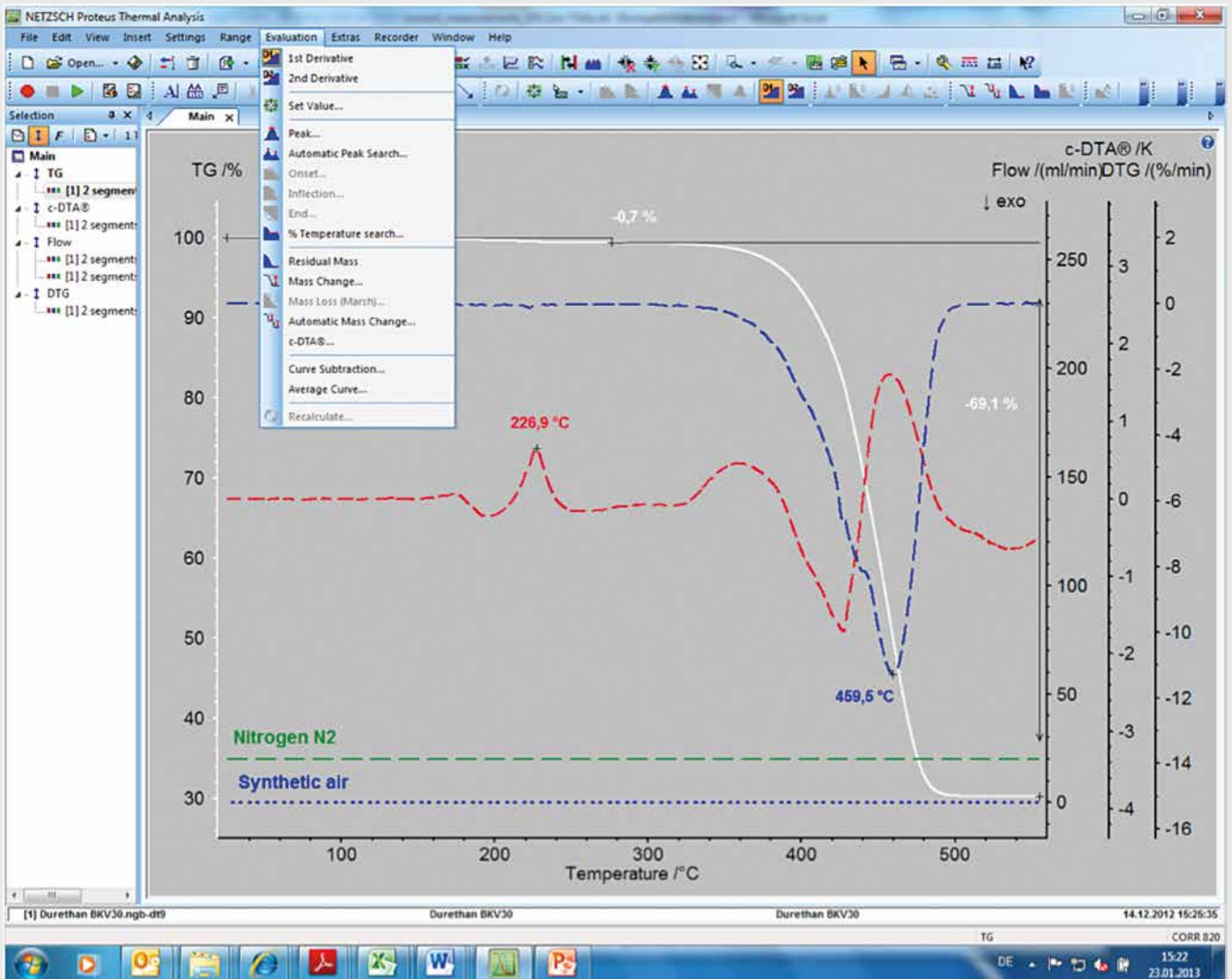
Main TGA Features

- Mass change in % or mg
- Automatic evaluation of mass change steps and characteristic temperatures
- Extrapolated onset and endset
- Peak temperatures and values of the 1st and 2nd derivatives
- *c-DTA*[®] for multi-point temperature calibration and evaluation of endo- and exothermal effects (calculated DTA signal)
- *BeFlat*[®]: Automatic correction of buoyancy and drift for rapid TGA results
- Multi-curve analysis of simultaneous evaluation of several TGA and DTGA curves
- *Super-Res*[®] (Rate-controlled mass change) for improved resolution and separation of superimposed mass-change steps

Advanced Software¹

- *Peak Separation* for separation of DTGA peaks which are in close proximity. Improved quantitative determination of super imposed mass-change steps
- *Thermokinetics* for accurate process prediction and optimization such as lifetime and composition behavior via multivariate nonlinear regression. Process optimization through freely selectable time/temperature programs for time and cost reduction.

¹ The Advanced software is an option and also available after delivery.



User interface of the *Proteus*® software during evaluation: presentation of the TGA curve (white) together with the DTGA curve (blue, dashed line), the c-DTA® curve (red) and two gas flow curves (blue, dotted line and green, dashed line) in the main frame.

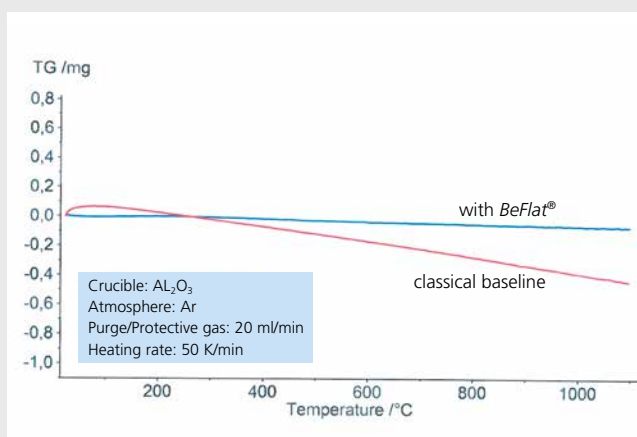
TG 209 **F1** *Libra*[®] – Smart Tools Integrated

BeFlat[®] – Measurement Results Quickly Obtained

No More Baseline Run – Faster to Your Results

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.

In contrast, the TG 209 **F1** *Libra*[®] generally no longer requires a separate baseline run. This greatly simplifies routine test work, especially for quality control in industry.

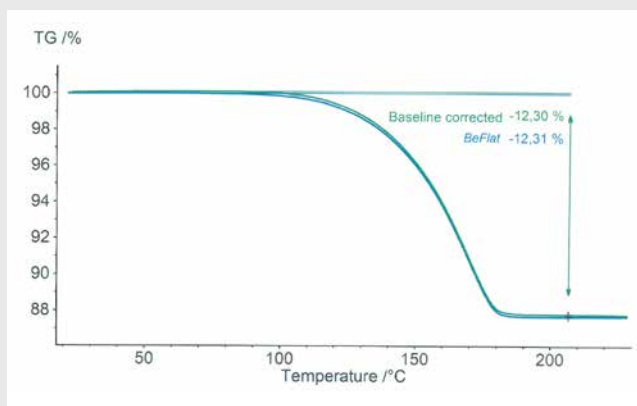


Stable baseline (blue) due to automatic correction of external influences

Intelligent TGA – Automatic Correction for External Influences

The *Libra*[®] takes the physics behind the external influences into consideration and corrects these effects automatically (depicted in the graphic above). The software stores the *BeFlat*[®] data as well as the raw data (upper plot).

The plot below depicts the water loss in a sample from 50°C to 250°C. The green curve represents data with a conventional correction by a separate baseline run; the blue curve represents the automatic *BeFlat*[®] corrected data and the results show a very good congruence.

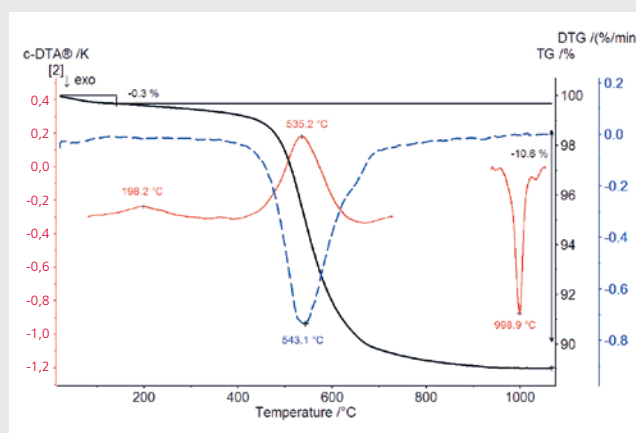


Water loss in a sample

c-DTA® – Calculated DTA for Endothermic and Exothermic Effects

More Information through Caloric Effects

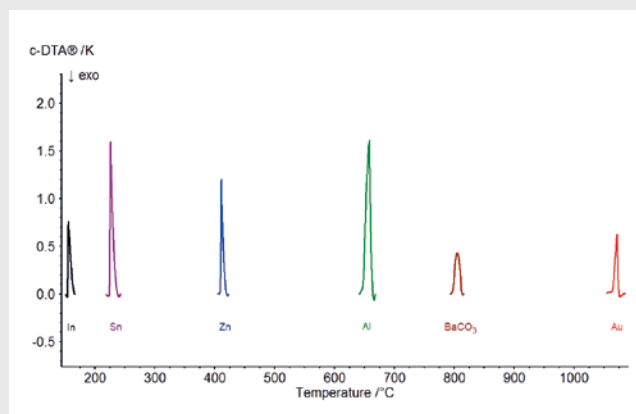
In addition to the TGA and DTGA curves, this plot depicts endothermic and exothermic effects determined by means of the calculated DTA signal, c-DTA®. Kaolinite was heated to 1100°C in a nitrogen atmosphere at 10 K/min. The two endothermic c-DTA® peaks (198°C and 535°C) are directly related to the occurring mass-loss steps and are caused by dehydration and dehydroxylation: loss of adsorbed water from the surface (0.3%) and loss of water from inter layers (10.6%). The exothermic c-DTA® peak at 999°C represents the formation of mullite.



TGA measurement on a kaolinite sample (37.17 mg); common presentation of the TGA curve (black), the DTGA curve (blue, dashed line) and the c-DTA® curves (red)

Easy and Reliable Temperature Calibration

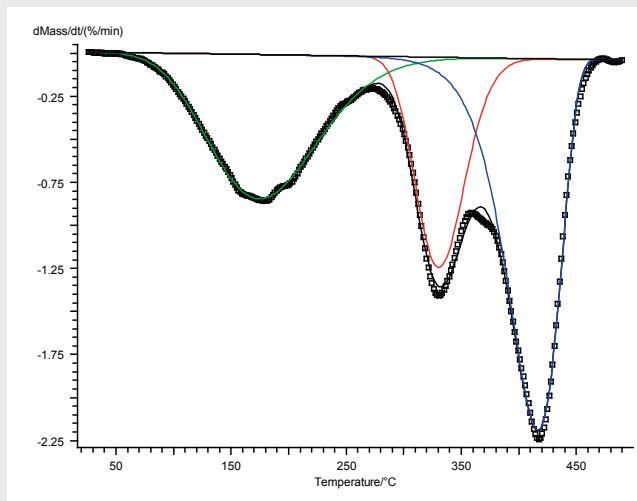
The multiple-point temperature calibration carried out by means of c-DTA® is in accordance with standardized methods and can therefore be easily used for validation purposes. To carry it out, the onset temperatures of the melting peaks of high-purity reference materials are determined across the entire temperature range for the TG 209 **F1 Libra**®. This plot shows the melting peaks of In, Sn, Zn, Al, BaCO₃ and Au at a heating rate of 10 K/min. Temperature calibration by means of c-DTA® is simple and does not require any modifications to the thermobalance.



c-DTA® effects of several materials suitable for temperature calibration

Peak Separation – Improved Separation of Overlapping Mass-Change Steps

By applying *Peak Separation* to DTGA peaks, the quantitative mass-loss steps during material decomposition can be separated much more clearly. This 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 three separated mass-loss steps were determined to 34.1%, 22.3% and 43.6%.



Good agreement between the experimental data (symbols) and the cumulative curve (black) of the calculated peaks (colored lines) as a result of applying *Peak Separation*

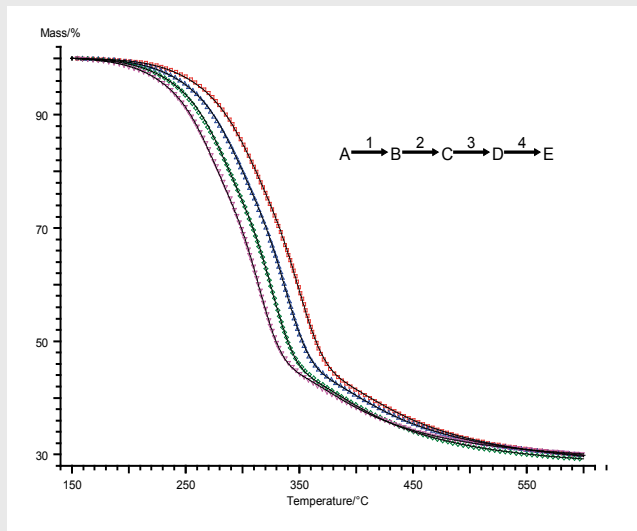
Super-Res[®] for Event-Based TGA

Normally, a defined constant heating rate is applied to the sample in order to study its decomposition behavior.

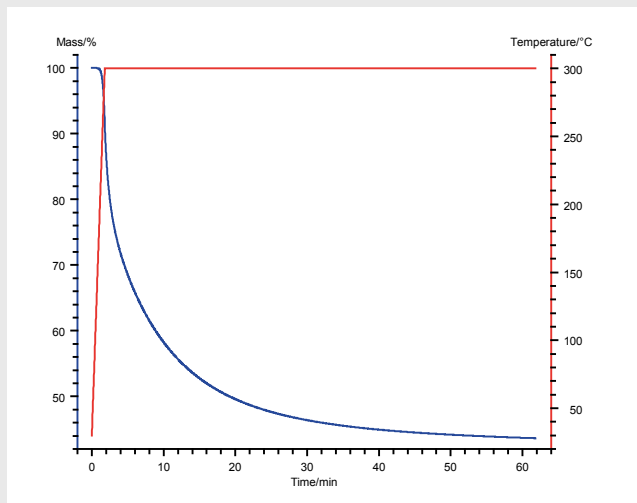
Super-Res[®] provides a rate-controlled heating rate according to defined thresholds with respect to the mass-loss

rate (DTGA curve) set by the operator. This often results in much better separation of overlapping mass-loss steps.

Thermokinetics for the Optimization of any Process



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



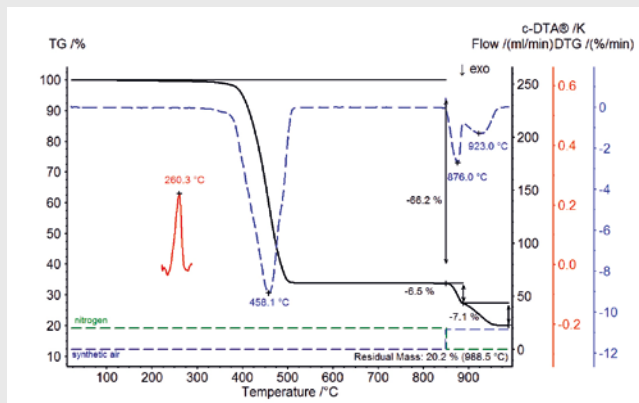
Prediction of the mass change for a defined temperature/time program

With the unique NETZSCH *Thermokinetics* software, any process can be modeled. The kinetic parameters such as activation energy, pre-exponential factor and order of reaction can be determined.

The TGA plot (upper illustration) presents 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.

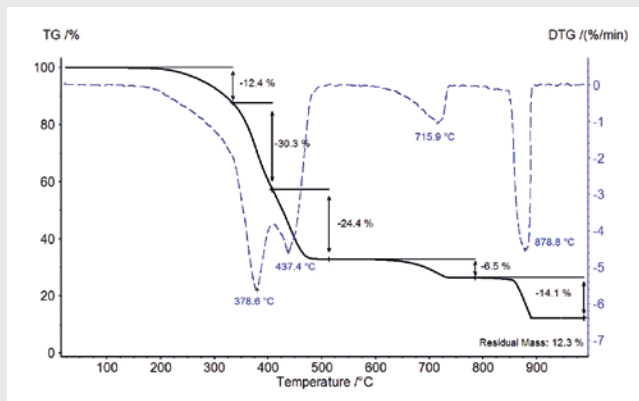
Based on this model, a prediction was computed: Starting at 30°C, heating to 300°C at a heating rate of 150 K/min, and then holding the temperature constant at 300°C for 1 hour yields the blue mass-change curve shown here (lower illustration). The calculation forecasts a residual mass of about 45% after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

TG 209 **F1** *Libra*[®] for a Wide Variety of Applications



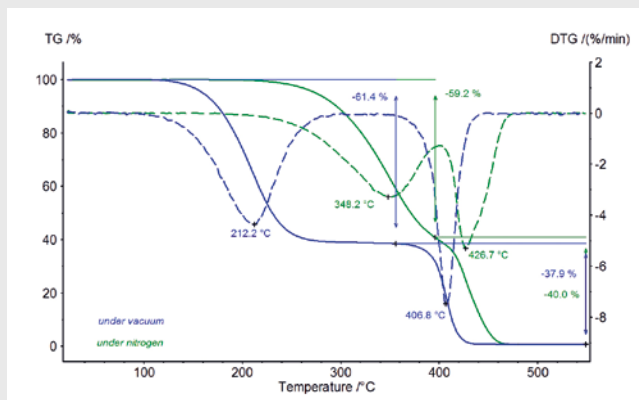
Polyamide

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 with Inorganic Filler

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. The DTGA peak at 716°C and the corresponding mass-loss step of 6.5% can be attributed to the release of CO₂ resulting from the decomposition of chalk. By switching to an oxidizing atmosphere at 850°C, the burning of the carbon black could be observed.

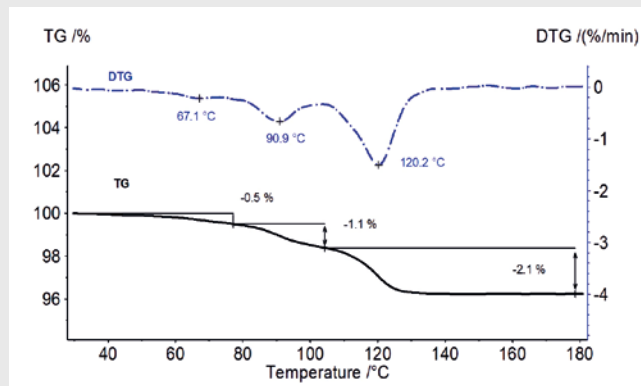


SEBS+PP

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.

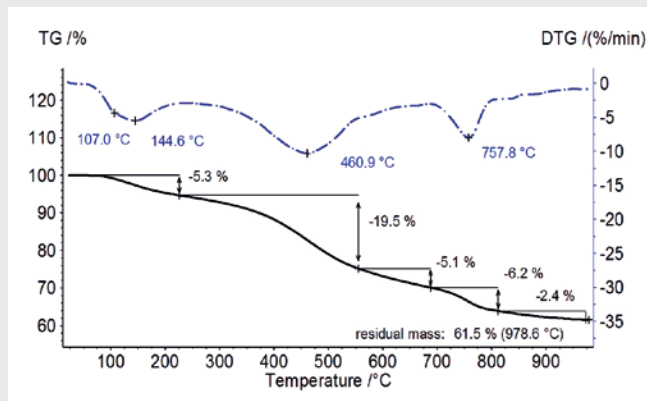
Magnesium Stearate

Commercially available magnesium stearate, a widely used excipient for pharmaceutical formulations, is a mix of several fatty acid salts. 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 180°C. In the corresponding TGA-FT-IR experiment (not shown here), it was possible to identify all volatile components as water.



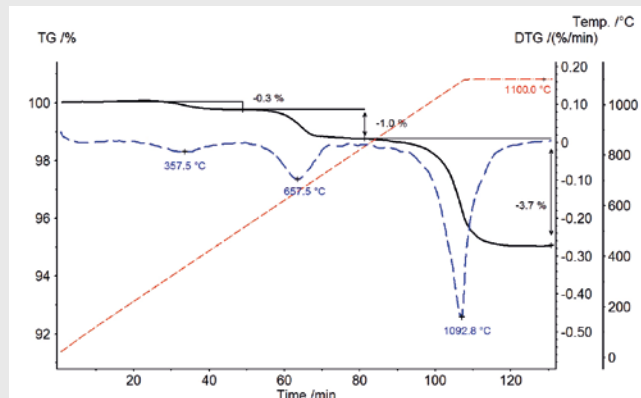
Coal

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 first mass loss (below 210°C) can be most probably related to the release of moisture; while the other steps are mainly related to organic volatiles.



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 ceramic furnace of the TG 209 **F1 Libra**[®], which permits measurements up to 1100°C, that makes this mass-loss step experimentally accessible.



TG 209 **F1** *Libra*[®] with Evolved Gas Analysis (EGA)

Different Methods

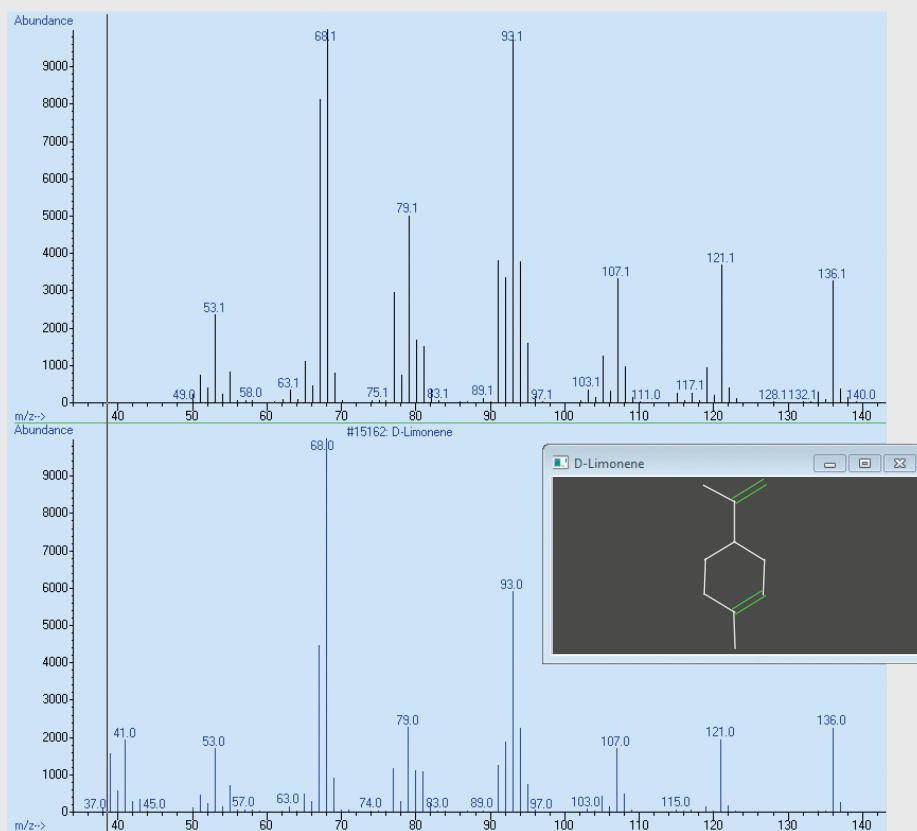
By coupling TG 209 **F1** *Libra*[®] to a gas analysis technique such as an FT-IR (Fourier Transform Infrared) spectrometer, MS (Mass Spectrometer), or GC-MS (Gas Chromatograph - Mass Spectrometer), information regarding the type of evolved gases as a function of time or temperature can be obtained, 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.

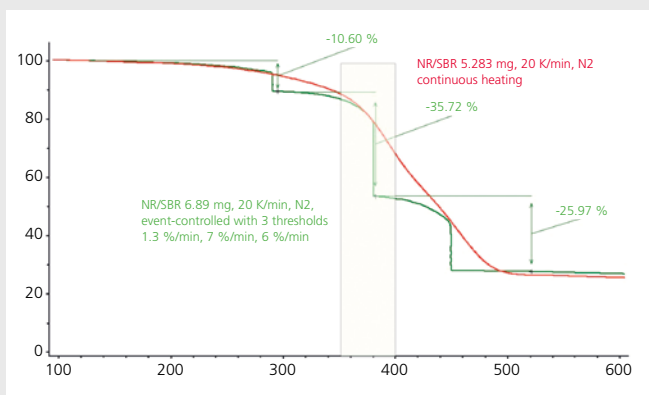
GC-MS provides detailed structural information on most compounds for an accurate identification of the gas components.



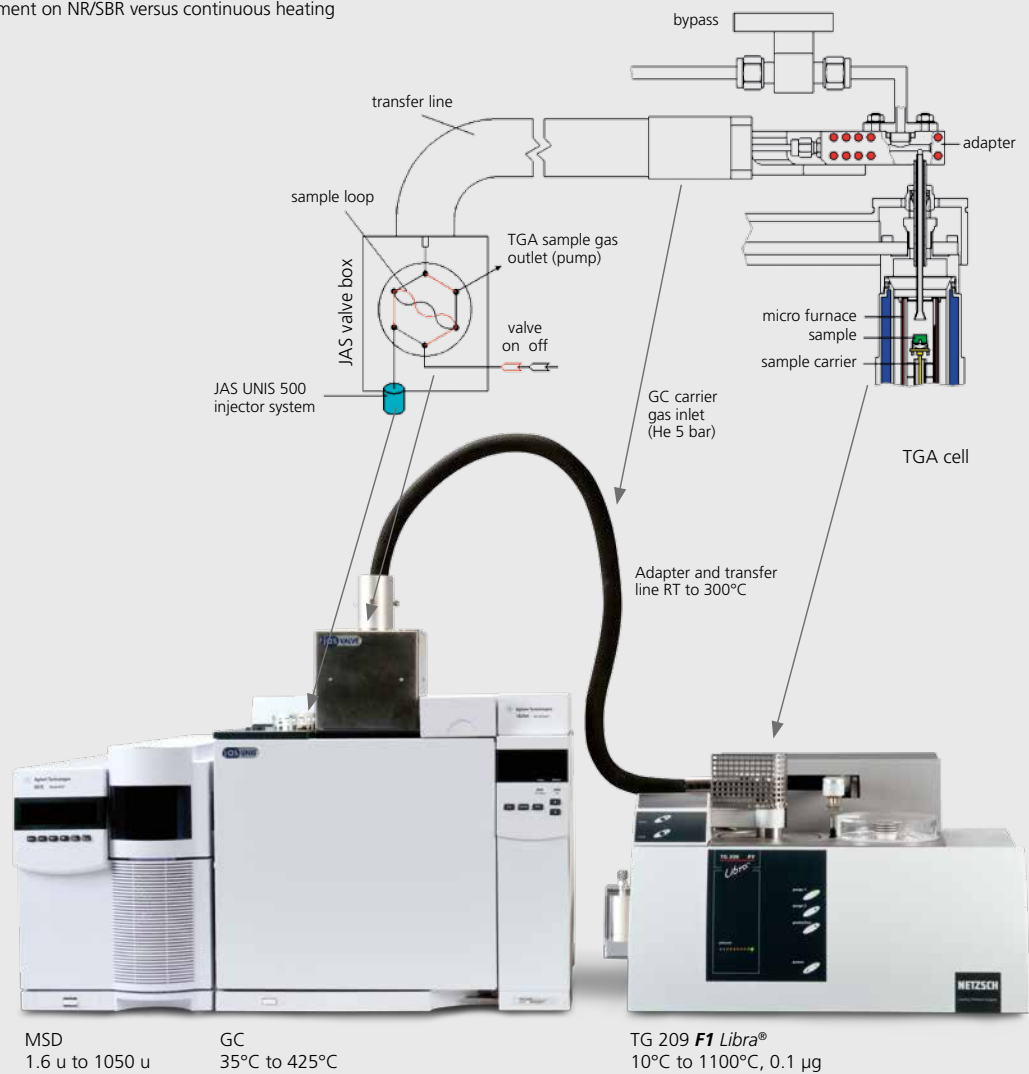
Additional Information

www.netzsch.com/gcms

Evaluation of GC-MS-TIC chromatograms



Event-controlled TGA-GC-MS measurement on NR/SBR versus continuous heating



Detailed diagram of the functional elements of the TGA-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. By

means of the *Perseus* TG 209 **F1** *Libra*[®], a TG-FT-IR system was created that is an excellent alliance with a compact Bruker Optics FT-IR spectrometer. The integrated design for both systems sets new standards for state-of-the-art coupling techniques. The built-in heatable gas cell is directly connected with the gas outlet of the TGA furnace. The small volume of the short transfer path guarantees fast transport and is advantageous for condensable gases.



Perseus TG 209 **F1**

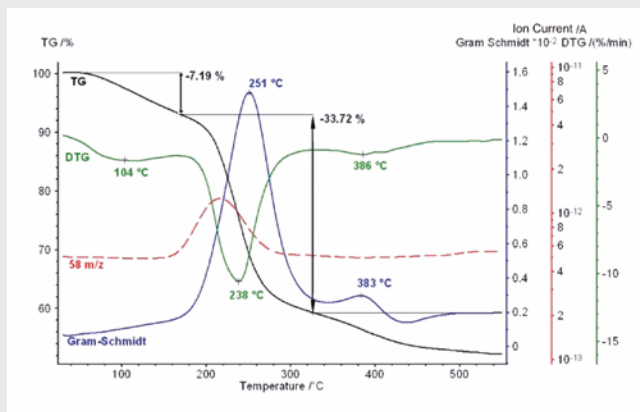
Additional Information

www.netzsch.com/ftir

Simultaneous TGA-MS-FT-IR Coupling and *PulseTA*[®]

The unique heated coupling adapter allows simultaneous TGA-MS-FT-IR measurements, even when the automatic sample changer (ASC) is running. Only one operational software package on a single PC is needed for TGA-MS-FT-IR. Comprehensive evaluations can be displayed in one plot. Calibration and quantification of the evolved gas components can be achieved by the *PulseTA*[®] technique.

Take advantage of nearly 40 years of coupling experience and ask for our special coupling brochures.



Comprehensive evaluation of TGA, DTGA, FT-IR (Gram-Schmidt), and QMS (m/z) versus temperature



Coupling of TENSOR 27, external gas cell, TG 209 *F1 Libra*[®] with ASC and QMS 403 D *Aëolos*[®]

The NETZSCH Group is a mid-sized, family-owned German company engaging in the manufacture of machinery and instrumentation with worldwide production, sales, and service branches.

The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 3,000 employees at 163 sales and production centers in 28 countries across the globe guarantee that expert service is never far from our customers.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction) 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