

## TGA-GC-MS Coupling

Evolved Gas Analysis with Chromatographic Pre-Separation



# Thermogravimetry and Evolved Gas Analysis

## Thermogravimetry (TGA) and Simultaneous Thermal Analysis (STA)

Thermogravimetry (TGA) and Simultaneous Thermal Analysis (STA), which is primarily simultaneous TGA-DSC (Differential Scanning Calorimetry), are widely applied analytical methods for the research and quality control of all kinds of inorganic and organic materials and products. Often, it is not sufficient to determine only the mass and enthalpy changes resulting from a thermal treatment; additional information may be required about the volatile products evolved during chemical reactions, thermally induced transitions, evaporation, and decomposition in order to gain deeper insight into the nature, structure and composition of the materials.

NETZSCH thermobalances and STA systems are arranged vertically with the sample above the balance, allowing the gases to flow in the natural upward direction. This design is ideal for coupling gas analysis equipment to the top of the furnace.

Mass spectrometry (MS) is the most comprehensive method for gas analysis, providing sensitivity down to the ppb/ppm level, high resolution at the atomic level, and also high speed of detection. Although the direct coupling of quadrupole mass spectrometers (QMS) – e.g., *Aëolos*<sup>®</sup> or SKIMMER to a TG or STA – is a well proven method, it has limitations in determining the individual components of gas mixtures which often hinder clear identification and interpretation. This is where gas chromatography comes into play.

### TG information

- Dehydration
- Desolvation
- Binder burn-out
- Decomposition
- Pyrolysis
- Combustion
- Oxidation
- Corrosion
- Evaporation
- Compositional analysis
- Ash content



## Gas Chromatography (GC) – Mass Spectrometry (MS)

GC 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; e.g., helium, nitrogen, argon, hydrogen).

Gas components with low affinity for the stationary phase but higher affinity for the mobile phase will be rapidly carried away by the purge gas, whereas gases with a high affinity for

the stationary phase will follow with a relatively significant time delay ("retention time").

MS is applied as a 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. Because of this pre-separation of the gases by the GC, and the sensitivity and resolution of the MS, detailed structural information is provided, allowing most compounds to be exactly identified.

### Mobile Phase

The mobile phase in GC is a gas, therefore all analytes must be evaporated and introduced into the column in gaseous form.

### Stationary Phase

In current technology, the stationary phase in the GC is usually a polymeric coating inside a long and narrow fused silica capillary.

### MS information

- Gas detection
- Gas identification
- Solid-gas reaction
- Decomposition products
- Pyrolysis gases
- Combustion products
- Flue gas identification

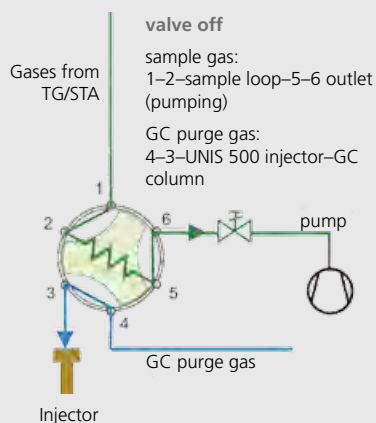


Coupling  
MS-GC-STA 449 **F1** Jupiter®

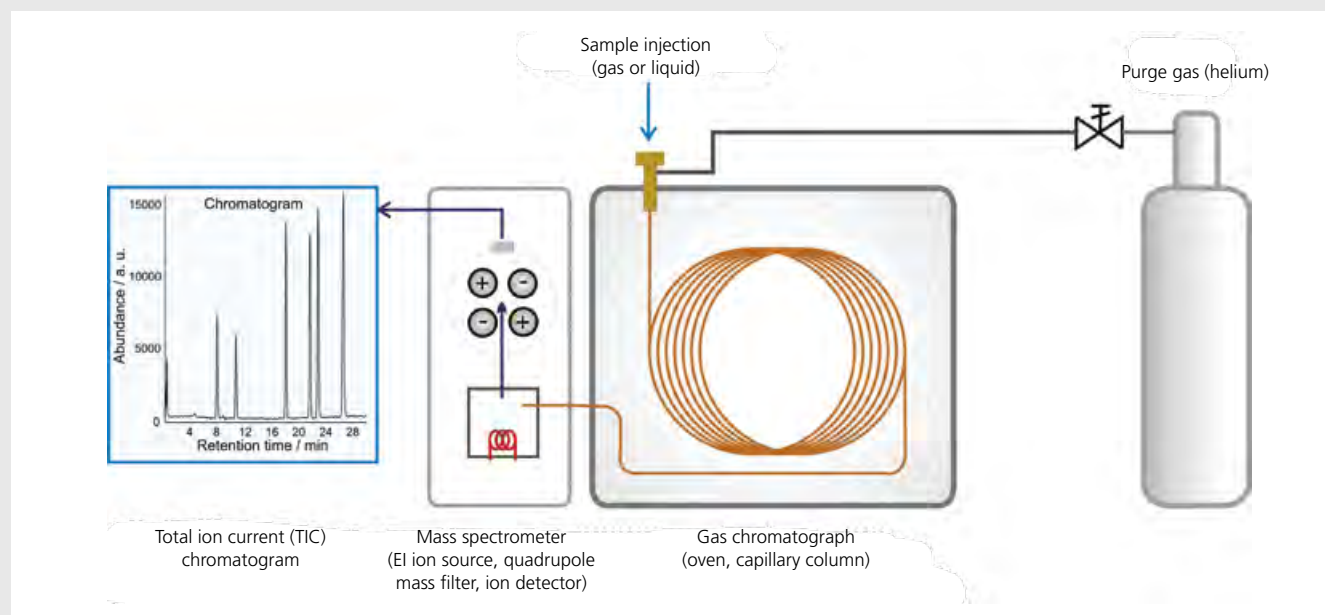
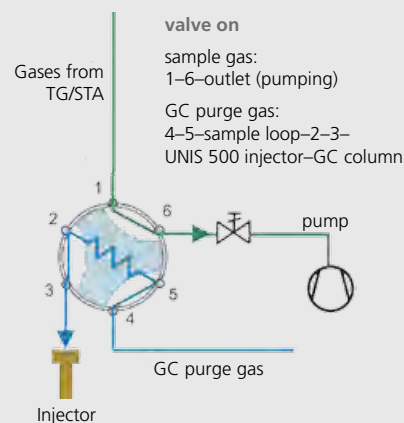
# TGA/STA-GC-MS Coupling

Since the gas separation in the GC column takes a certain amount of time – the duration of which depends upon sample characteristics, column flow rate, column length, and stationary and mobile phase – it is not possible to couple directly into the GC with a continuous online sample gas flow. Our solution, therefore, was to develop a direct coupling in a quasi continuous mode by using heated automatic valves, which allow for software-controlled gas sampling (flow-through sampling loop) and gas injection even at short intervals.

## Gas sampling



## Gas injection



The injected gas mixture of the sampling loop (or parts of it in the split mode) passes the separation column of the GC at the set flow condition (e.g., constant flow of the purge gas 1.5 to 2 ml/min) and arrives, after a final pressure reduction step, as a molecular beam at the ion source of the quadrupole mass spectrometer. The separation column is

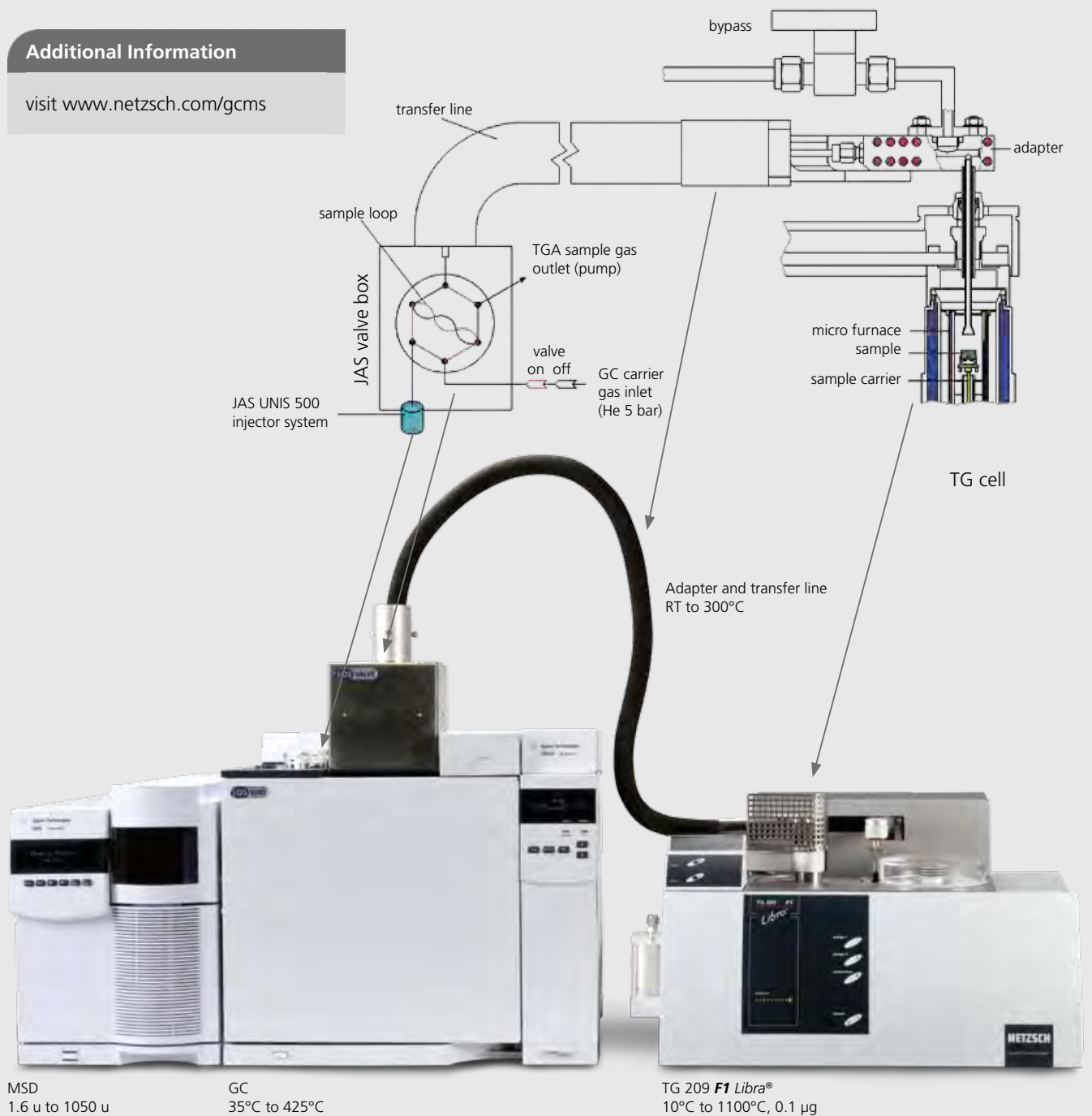
either held at constant high temperature (for the continuous injection mode), or temperature-programmed from a low start temperature to subsequent high temperature (for the event-controlled mode). The mass spectrometer detects all volatile products as a function of time. The curve of the total ion current (TIC) over time (retention time) is called

a chromatogram. Peaks appear in the chromatogram resulting from the sample gas interaction in the stationary and mobile phases, and from the boiling temperature of the individual components. These retention peaks are analyzed by the MS software to determine the contributing substances.

## Detailed Diagram of the Functional Elements of the TGA-GC-MS Coupling

### Additional Information

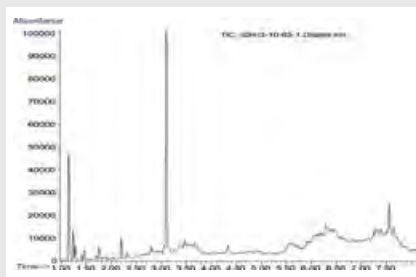
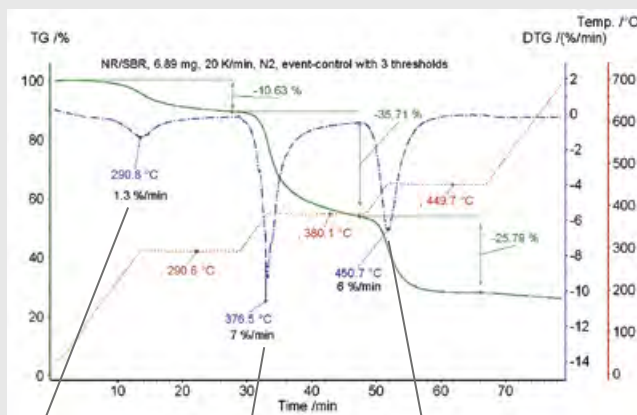
visit [www.netzsch.com/gcms](http://www.netzsch.com/gcms)



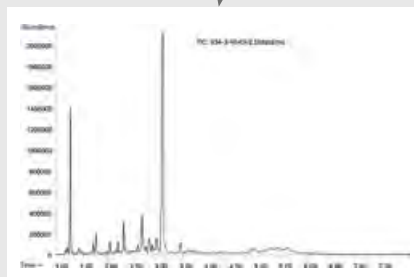
# Event-Controlled Mode, Continuous Mode

## Event-Controlled Mode

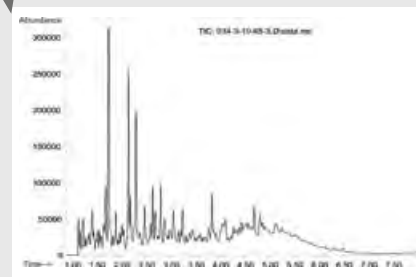
The event-controlled mode uses the automatic detection of mass changes (DTG thresholds) as the trigger for starting the GC-MS. This is called the "reaction-rate-dependent trigger" and operates via the automatic run of the "sequence" function in the ChemStation software. Overlapping reactions can be resolved and the corresponding GC furnace program allows for a nearly complete separation of the evolved gases. Individual thresholds can be selected in every segment of the temperature program.



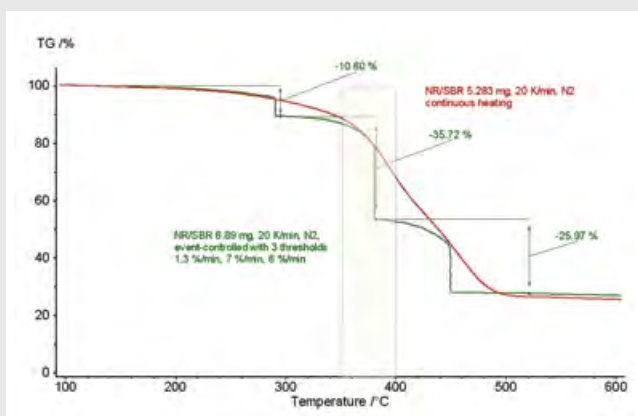
Automatic detection of the TGA step for additives with high volatility: identification of vulcanization agents, plasticizers, or oils in the rubber sample.



First step of rubber decomposition with main fragment isoprene



Second step of rubber decomposition with styrene



### Event-Controlled Run

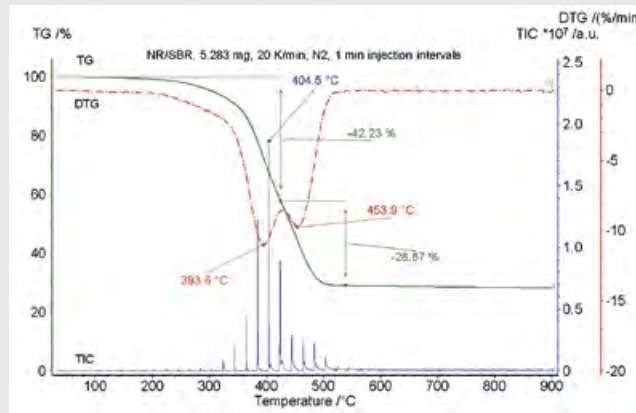
- Nearly complete identification of evolved gases with exact temperature correlation to TGA and DTG
- Integration of chromatogram
- Library search report → quantification



## Continuous Mode

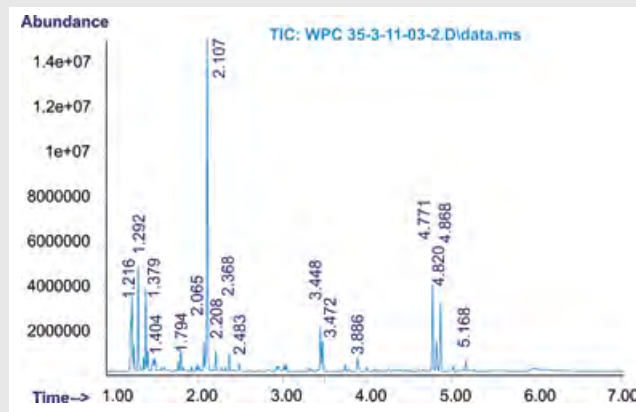
The TG and GC-MS are started simultaneously. Then, when running in continuous mode, the GC-MS operates with a fixed column temperature (e.g. 250°C) and short injection intervals. The evolved gases are identified in good temperature and time correlation with the TGA and DTG results. The total ion chromatogram can be displayed, evaluated, stored and exported together with the thermal analysis curves. A trigger for the start of the GC-MS run can also be programmed in any temperature segment.

- Identification of ions/molecules
- Extraction of ions (shows temperature-time profile, SIM mode)
- Verification of temperature-time correlation with TGA-DTG curves
- Fast and easy method for routine control of gas composition and comparison of samples



## Single Run (or Stand-Alone GC-MS Run)

- Triggered or manual start of GC program
- Complete identification of evolved gases
- Integration of chromatogram
- Library search report → quantification (see table, extract)



peak	RT/min	Area/%	Sample	Hit quality
1	1.216	10.14	Propene	91
2	1.292	9.40	Pentane	91
3	1.379	6.06	1-Pentene, 2-methyl-	94
4	1.404	1.18	2-Pentene, 4-methyl-	91
5	1.794	1.82	Heptane, 4-methyl-	94
6	2.065	2.38	2-Hexene, 4,4,5-trimethyl-	78
7	2.107	32.19	1-Heptene, 2,4-dimethyl-	95

# Software: Easy Handling, Reliable Data Evaluations

## Programming of Measurements

The start of the combined TGA-GC-MS experiment is programmed in the *Proteus*® software together with the usual inputs for the thermal analysis measurement parameters.

The screenshot shows the 'Measurement Definition' dialog box with the following settings:

- Navigation: Fast definition (red), Setup (green), Header (green), Temperature Program (green), Last Items (red).
- Measurement type:  Correction,  Sample,  Correction + sample,  Sample + correction.
- Identity: event-control
- Sample name: WPC
- Sample mass: 8.030 mg
- Crucible mass: 0 mg
- MFC gases table:

Device	Value
Purge 1 MFC	OXYGEN
Purge 2 MFC	HELIUM
Protective MFC	HELIUM
- Laboratory: TG-GC-MS
- Project: Test
- Operator: Kai
- Date: 27.04.2011 10:32:34
- Material: composite
- Temperature calibration:  will be used (selected),  will not be used. Select... button.
- Path: C:\NETZSCH\Proteus\cal5\TG 209 F1\TG 209 F1-20 K\_min.ngb-1
- Bemerk: Helium 30:40 Al2O3 crucible with lid, adaptor 300°C + transfer line heating 280°C
- Footer: Enter the name of laboratory

## Selection of the Trigger Mode

- Trigger (for continuous mode)
- Reaction-rate-dependent trigger (for event-controlled mode), with delay time for the duration of the experiment

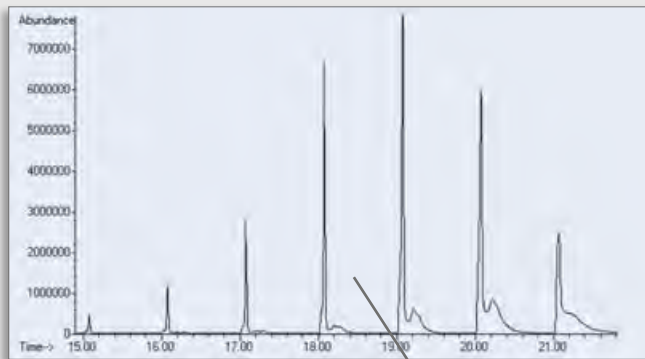
The screenshot shows the 'GC-MS device settings' dialog box with the following settings:

- Mode:  Trigger,  Reaction rate dependent trigger
- Delay: 15 <1...60> min
- Derivative value presentation:  in percent,  absolute
- Parameters of TG signal derivative:

Signal Range /mg	Derivative Range /mg/min	Filter Factor
2000	500	75
	50	150
	5	400
		1000
- Buttons: OK, Cancel, Help

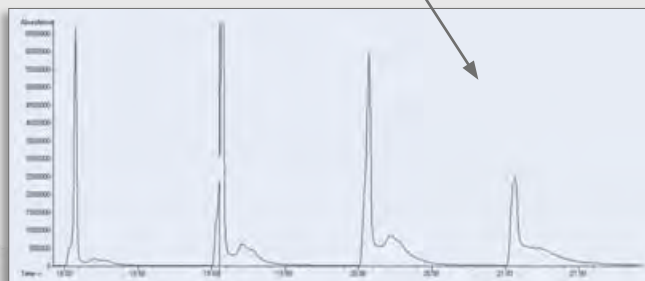


## Evaluation of the GC-MS-TIC Chromatograms

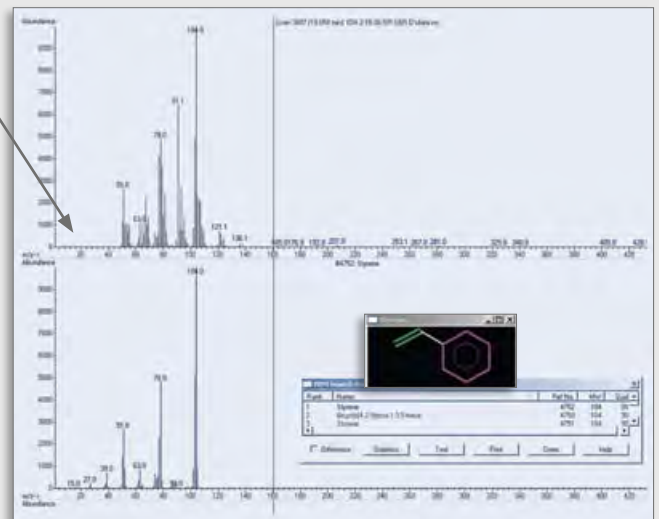
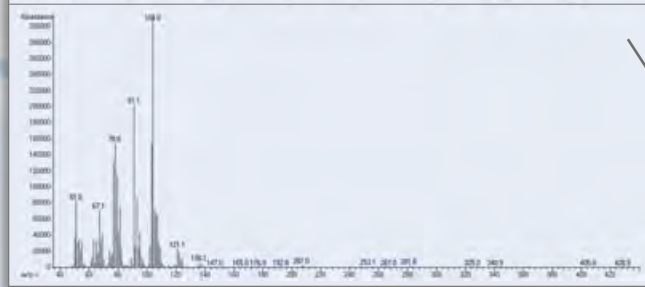


This example shows NR/SBR rubber measured in the continuous mode with 1-min injection intervals and 250°C column temperature.

The MS spectra below every retention peak can be viewed by double-clicking (example spectrum at 19.054 min, 403.5°C).

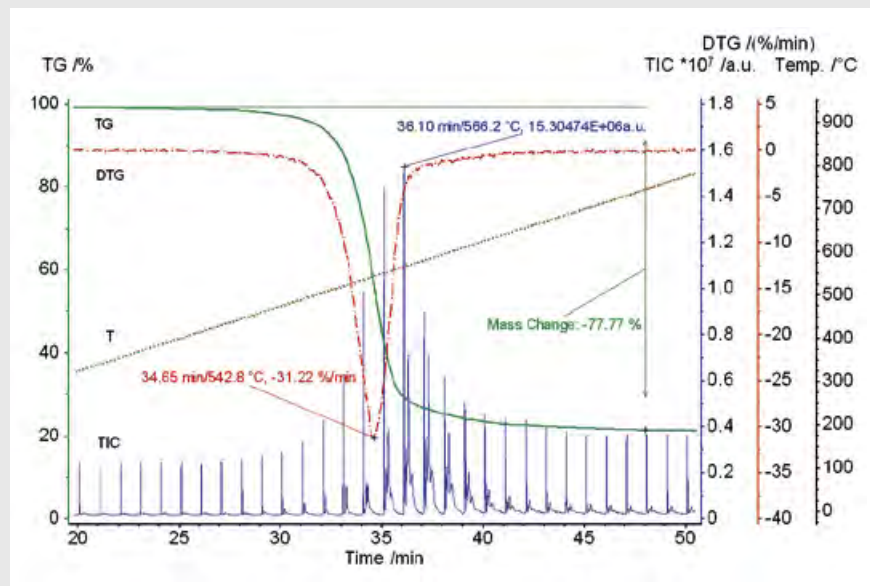


The next double-click displays the hit list of the integrated MS library search program, including the identity, molar mass, structure, and stored spectrum of the chemical compound found. Here, styrene is identified at 19.054 min (403.5°C) with the high hit quality of 91%.



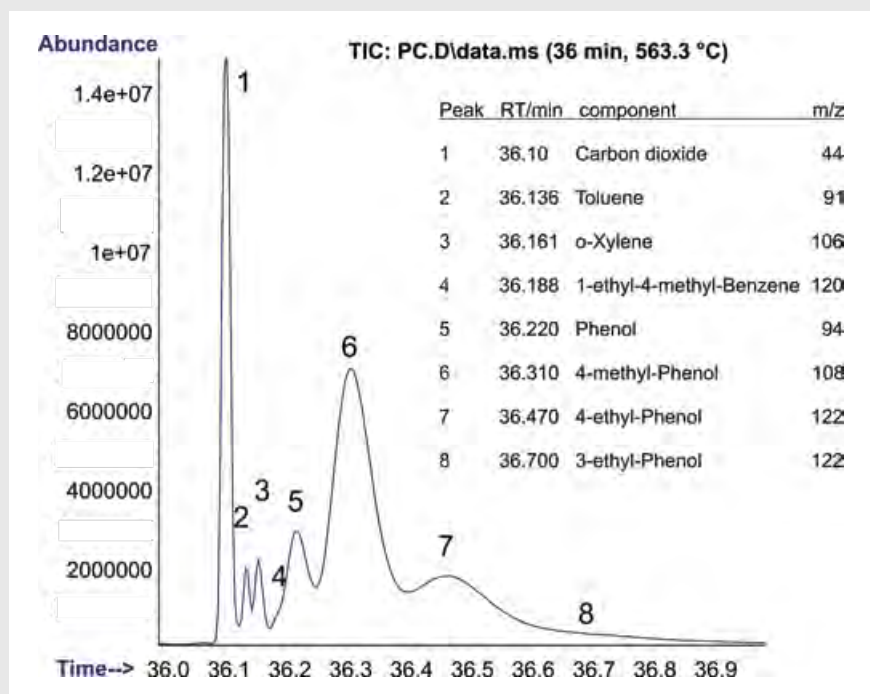
# Unlimited Applications

## Pyrolysis of Polymers



### Polycarbonate (PC)

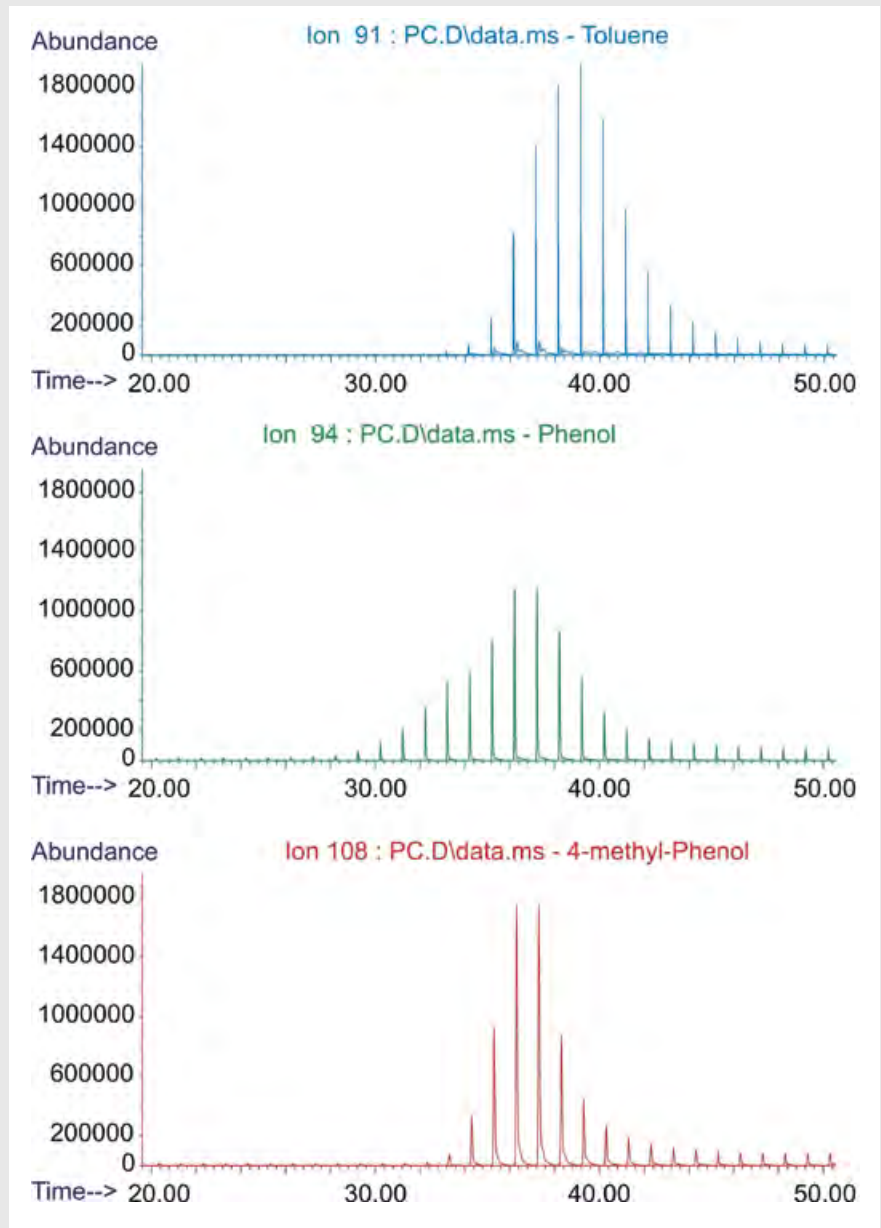
The pyrolysis of 12.42 mg of PC (Lexan 144R) in helium leads to one-step decomposition with the DTG peak at 543°C. The TIC chromatogram of 1-min injection intervals at a column temperature of 250°C (split 10:1) indicates different stages in gas evolution, with the highest intensity at 566°C.



The analysis of the underlying MS spectra of the TIC, beginning at 36 min, leads to the identification of 8 main components with the NIST library search.

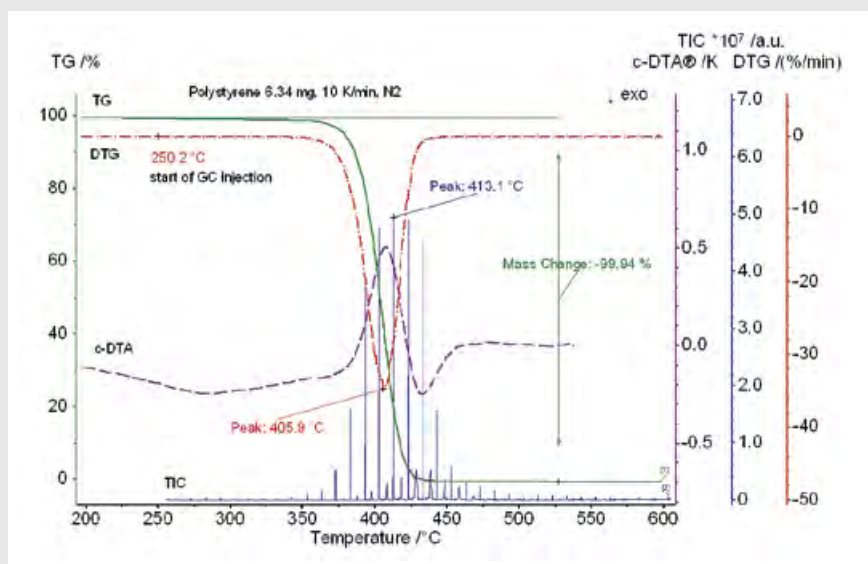


Extracting individual molecule-ions from the total ion chromatogram allows for the monitoring of the temperature and time dependence of gas evolution of individual ions (SIM mode). Clearly visible is the later evolution of toluene compared with phenol and 4-methyl-phenol.



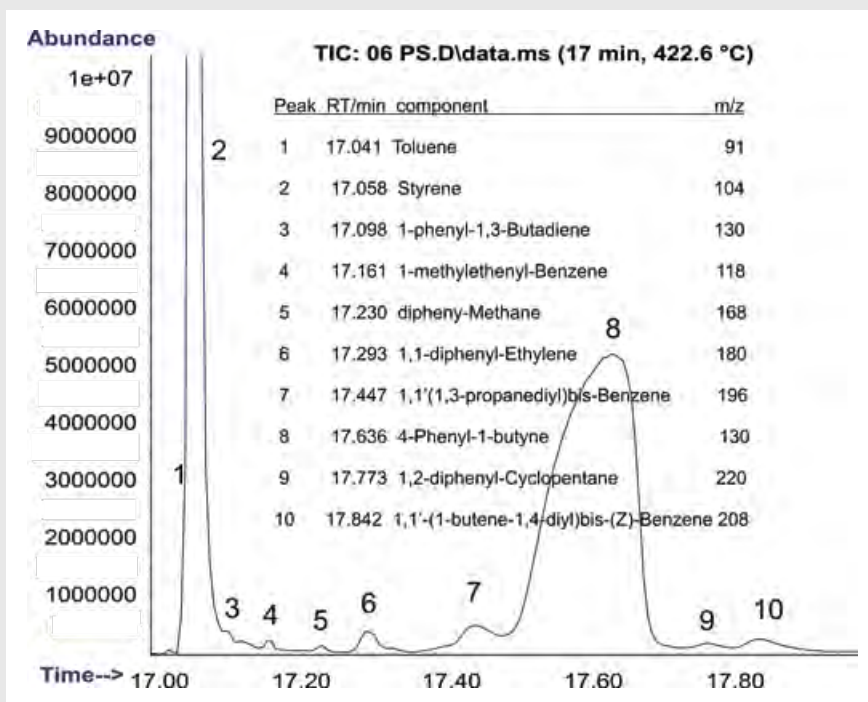
# Unlimited Applications

## Pyrolysis of Polymers



### Polystyrene (PS)

The NIST SRM 705a decomposes in a nitrogen flow in one step at 406°C (DTG peak) and the TIC chromatogram (maximum 413°C) indicates at least two ranges of gas evolution.



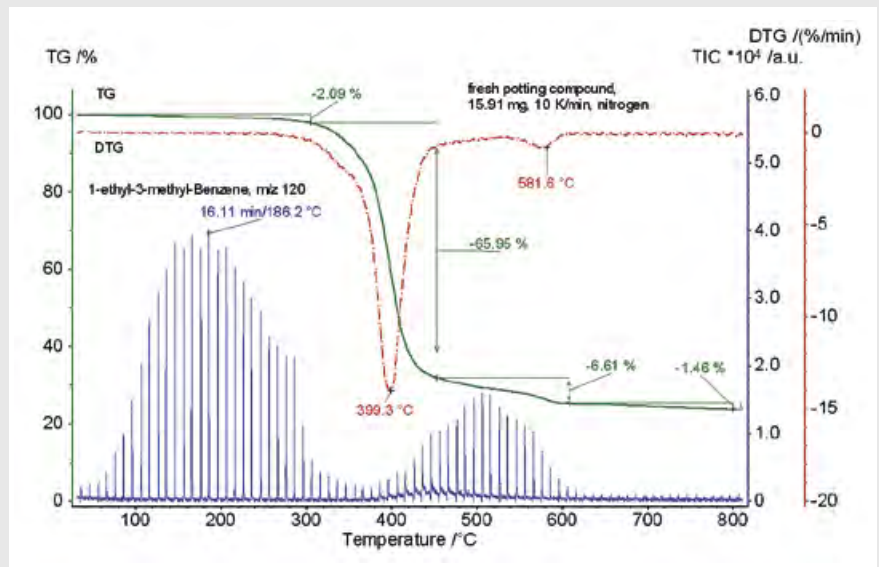
The evaluation of the chromatogram at 17 min (423°C) reveals styrene (m/z 104) as the dominant product (of the whole decomposition), and the styrene dimer (m/z 208) as a component of the second decomposition stage.



## Evaporation of Solvents

### Potting Compound

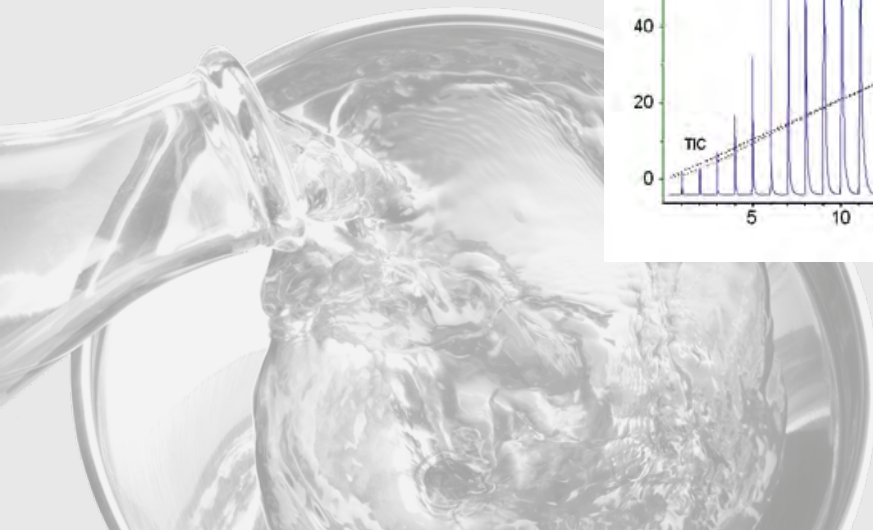
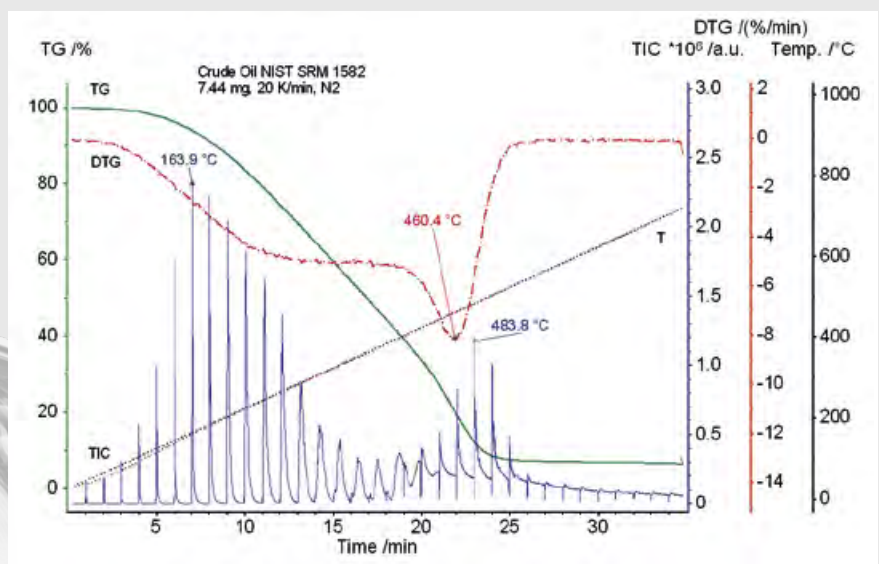
This potting compound for the encapsulation of electronic components, declared to be solvent free, evolves a benzene compound right from the start of the experiment. The selected ion  $m/z$  120 for 1-ethyl-3-methyl-benzene shows the maximum intensity at 186°C, in a range where the TGA curve displays no significant mass loss. The gases evolved during the decomposition of the potting compound were not part of our focus for this plot.



## Fuels

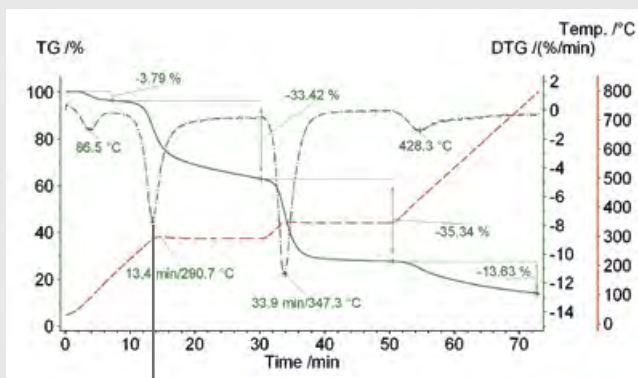
### Crude Oil Pyrolysis

The continuous heating shows the ranges of distillation (characterized by a nearly constant mass loss rate of 5%/min up to 400°C) and pyrolysis of the hydrocarbons (up to 550°C).



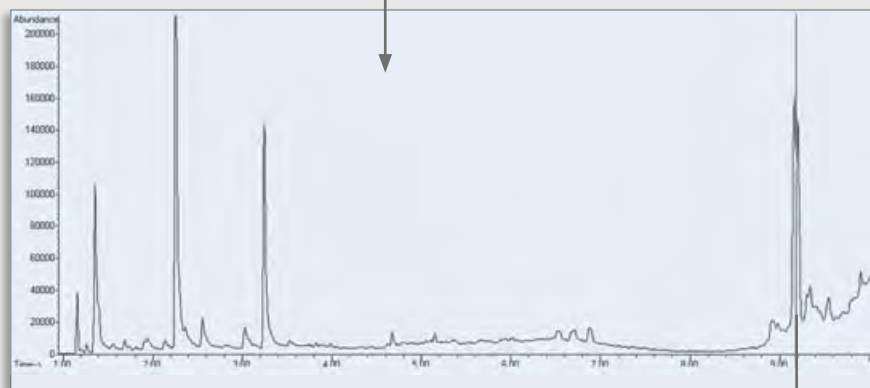
# Unlimited Applications

## Biomass



## Oak Wood Pyrolysis

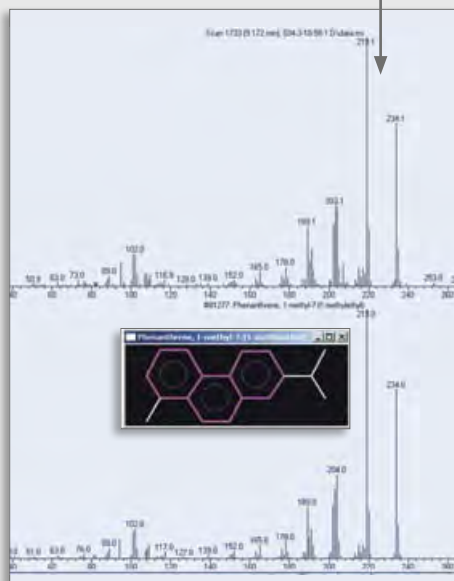
4.370 mg of ground oak wood (*quercus robur*) was pyrolyzed in nitrogen in the event-controlled mode. The DTG threshold of 8%/min resulted in two TGA steps with isotherms at 291°C and 347°C. The gases automatically injected at the GC at these temperatures were separated with the GC furnace program: 60°C for 0.5 min, heating to 310°C at 25 K/min.



The TIC chromatograms for the two events (pyrolysis steps) with peaks in the full range of retention times between 1 min and 10 min are easily evaluated by the library search report. Based on the selected integration parameters, the report shows the major peaks with retention time, percentage of peak area, best hit for the identified molecule, and hit quality (not shown in table).

Any individual peak analysis can be carried out manually by a few mouse clicks, e.g., identifying substituted phenanthrene at 9.209 min retention time in the chromatogram for the gas evolved at 291°C (see bottom figure).

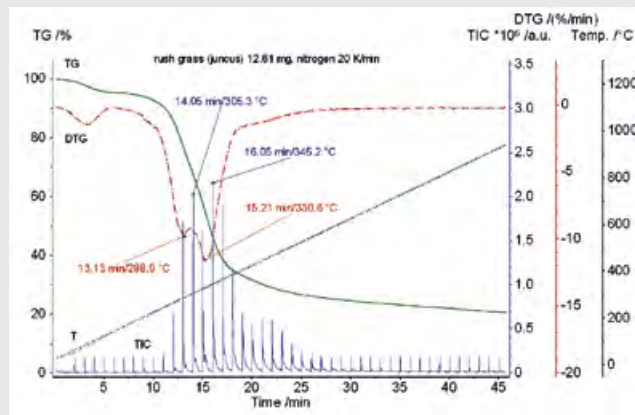
RT	Area%	best hit (NIST/Wiley)
1.157	2.27	6H,8H-Benzopyrano[3,4-b]benzopyran
1.356	8.96	Acetic acid
1.398	2.24	1-Penten-3-ol
2.253	26.67	Furfural
2.551	1.65	Thiazole
3.018	1.96	1-methyl-1-silacyclohexane
3.243	14.86	3-Methyl Hydantoin
6.881	1.70	Benzenamine, N-methyl-N-phenyl-
9.156	16.97	2-Isopropyl-10-methylphenanthrene
9.209	9.01	Phenanthrene, 1-methyl-7-(1-methylethyl)-
9.298	1.42	Benzene, 1-methyl-4-[(4-propylphenyl)ethynyl]-





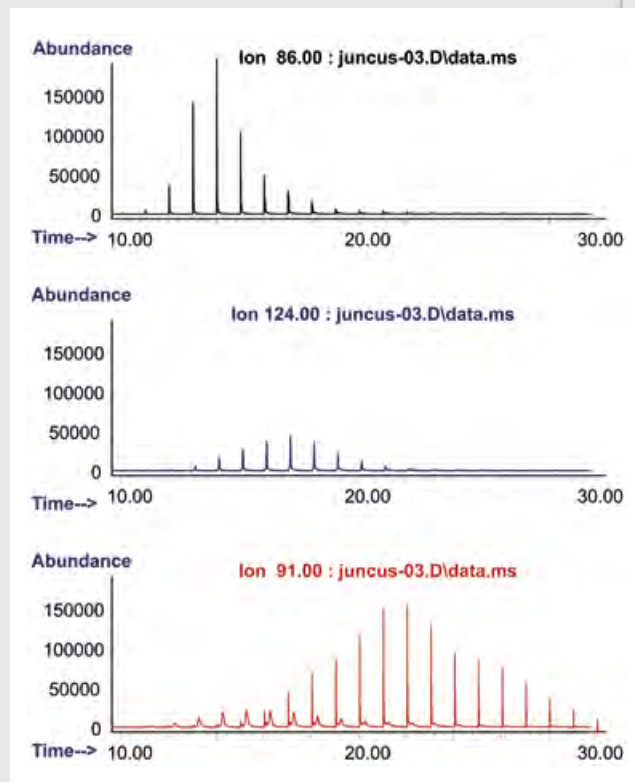
## Rush Grass (*Juncus*) Pyrolysis

After drying (4.6% mass loss), the rush grass decomposes in a nitrogen atmosphere in several steps which are not well separated. The gases evolved represent the cellulose and lignin content of the sample.



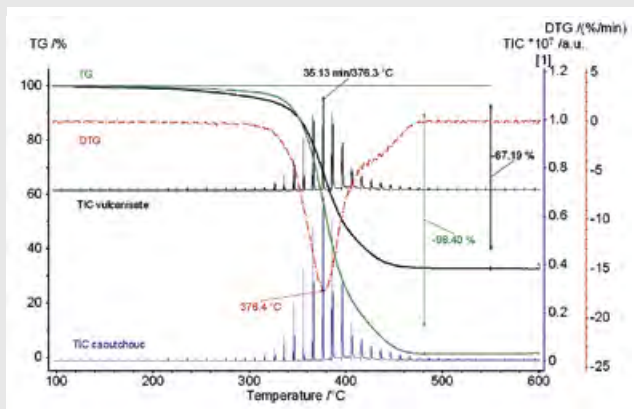
The selected fragment ions (figure right) show significant differences in their temperature distributions (the displayed time range of 10 min to 30 min corresponds to the temperature range 226°C to 626°C):

- m/z 86 for digitoxose (from cellulose)
- m/z 124 for guaiacol (from lignin)
- m/z 91 for toluene (from lignin)



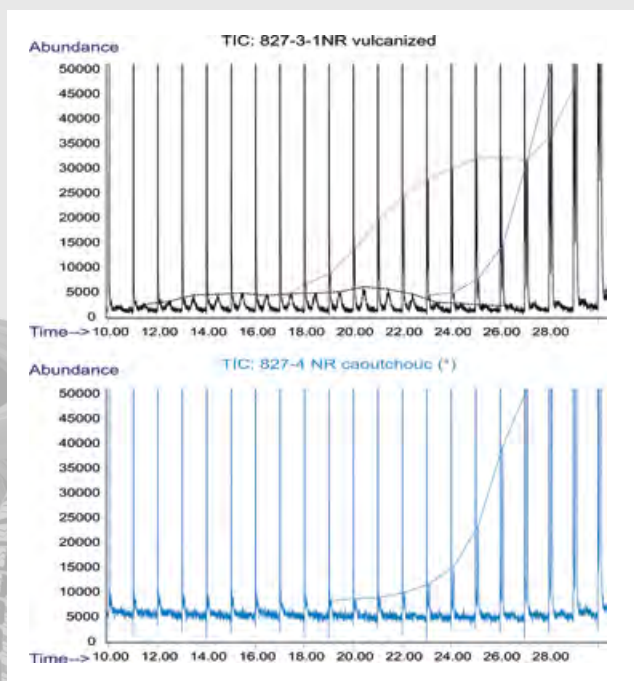
# Unlimited Applications

## Rubber Pyrolysis



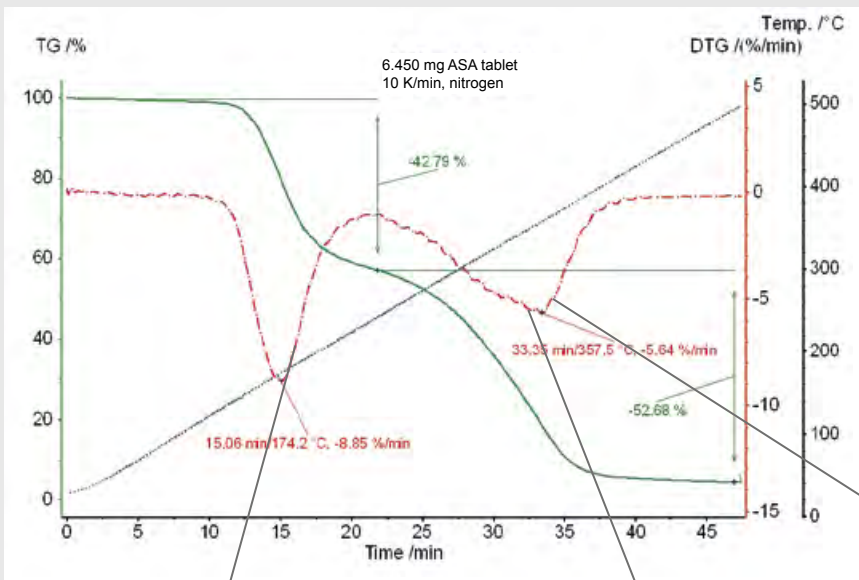
### Differentiation of NR and Vulcanized NR

The difference between the pure NR (natural rubber) caoutchouc and the vulcanized NR is shown by the TIC chromatograms, mainly in the range from 132°C to 294°C (27 min), where TG indicates 0.3%/min difference in the mass loss rate.



Only the vulcanized NR shows the additive benzothiazole (12 - 24 min) and xylene (start at 17 min, 193°C). Significantly, the decomposition of the isoprene (representative for NR) starts in both sample tests at 23 min (254°C).

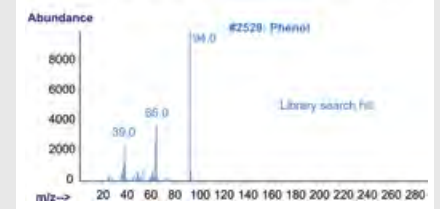
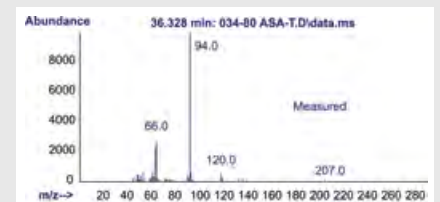
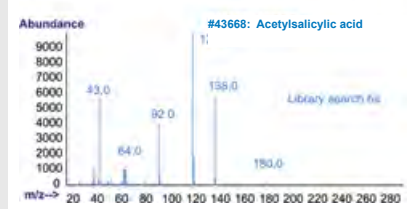
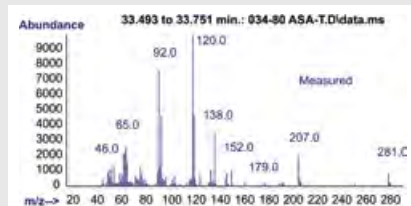
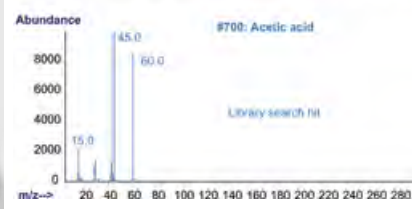
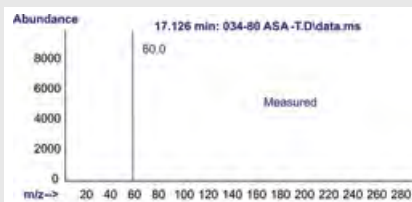
## Pharmaceuticals



### Acetylsalicylic Acid (Trade Name: e.g. Aspirin®)

The evaporation and decomposition of the powdered acetylsalicylic acid tablet sample in nitrogen yields the main products acetic acid (1<sup>st</sup> TG step) and acetylsalicylic acid and phenol (2<sup>nd</sup> TG step).

The GC-MS coupling to the sensitive TG is also an ideal instrument combination for the analysis of residual solvents and impurities in pharmaceutical drugs and excipients.



## Expertise in Service



### Our Expertise – Service

All over the world, the name NETZSCH stands for comprehensive support and expert, reliable service, before and after sale. Our qualified personnel from the technical service and application departments are always available for consultation.

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- Calibration service
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- Moving/exchange service
- Technical information service
- Spare parts assistance



## Our Expertise – Applications Laboratories

The NETZSCH Thermal Analysis Applications Laboratories are a proficient partner for nearly any thermal analysis issue. Our involvement in your projects begins with proper sample preparation and continues through meticulous examination and interpretation of the measurement results. Our diverse methods and over 30 different state-of-the-art measuring stations will provide ready-made solutions for all your thermal needs.

Within the realm of thermal analysis and the measurement of thermophysical properties, we offer you a comprehensive line of the most diverse analysis techniques for materials characterization (solids, powders and liquids).

Measurements can be carried out on samples of the most varied of geometries and configurations. You will receive high-precision measurement results and valuable interpretations from us in the shortest possible time. This will enable you to precisely characterize new materials and components before actual deployment, minimize risks of failure, and gain decisive advantages over your competitors.

For production problems, we can work with you to analyze concerns and develop solutions. The minimal investment in our testing and services will reward you with reduced down time and reject rates, helping you optimize your processes across the board.



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The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 2,500 employees at 130 sales and production centers in 23 countries across the globe guarantee that expert service is never far from our customers.

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.

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