NETZSCH

Analyzing & Testing

TA-QMS Coupling

Evolved Gas Analysis

Leading Thermal Analysis

Thermogravimetry and Evolved Gas Analysis

Thermoanalytical techniques are universal tools for characterizing solids and liquids with respect to their thermal behavior. Especially Thermogravimetry finds its broad application for testing the weight changes of the sample during a programmed heat treatment. A multitude of information on material properties, composition and stability is provided. However, the chemical and analytical information about the products causing the weight changes of the sample is often lacking. EGA can supply this additional information.

Decomposition
- Dehydration
- Stability
- Residual Solvent
- Pyrolysis

Solid-Gas Reactions
- Combustion
- Oxidation
- Corrosion
- Adsorption
- Desorption
- Catalysis

Compositional analysis
- Polymer content
- Proximate analysis
- Binder burn-out
- Dewaxing
- Ash content

Evaporation
- Vapor pressure
- Sublimation

Complementary Information

Physical changes detected by thermal analysis are explained by the gas analysis in the mass spectrometer forming a workstation for analytical chemistry. Evolved species are detected down to the ppm level, which exceeds the standard sensitivity of thermal analysis methods. High-class material research and characterization is the result of coupled thermal analysis and mass spectrometry.

Quadrupole Mass Spectrometry (QMS)

The sensitive, selective, fast and continuous function of a quadrupole mass spectrometer makes this system ideally suited for evolved gas analysis in combination with Thermogravimetry. Further key features which help provide an optimal coupling with thermal analyzers include the small dimensions of the quadrupole mass filter, the efficient and reproducible ionization of gases in the electron impact ion source, and the resolution in the detection of molecules, atoms and fragments.

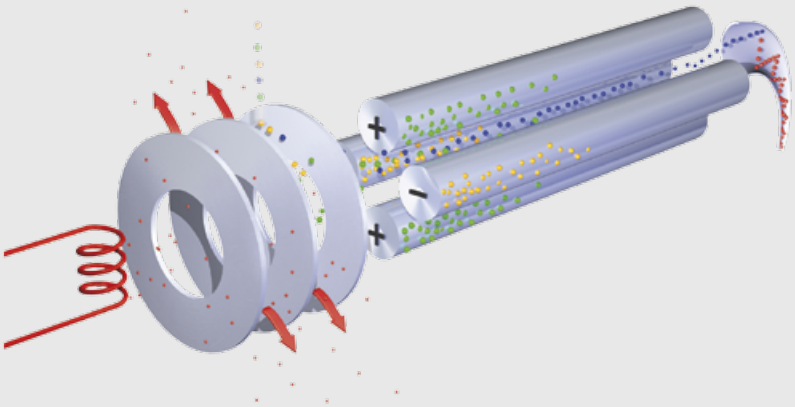
Identification

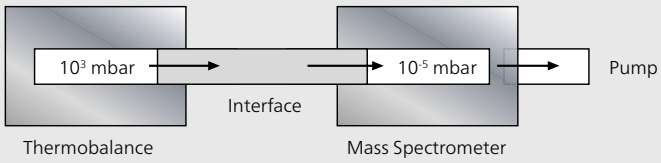
- Gas composition
- Fingerprint
- Partial pressure
- Fragmentation
- Solid-gas interactions

TA-QMS Coupling

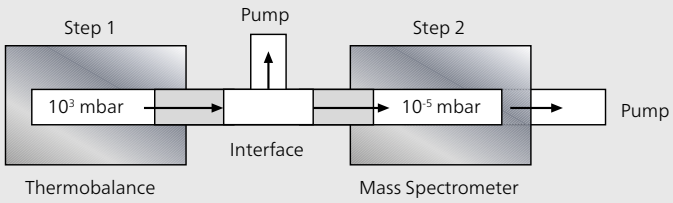
Interface for Pressure Adjustment

Mass spectrometers, composed of a mass filter, an electron impact ion source and ion detector, work only in high vacuum. Therefore an interface is required for the coupling of a thermobalance, which works with a purge gas flow at atmospheric pressure, to the mass spectrometer. Different versions of pressure reduction interfaces are realized, depending on instrumentation and applications.





Capillary Coupling



Orifice Coupling *SKIMMER*® Coupling

Single-Step Pressure Reduction

A capillary of small internal diameter connects the gas outlet at the furnace of the thermobalance with the gas inlet at the mass spectrometer. The pressure continuously drops from atmospheric pressure down to high vacuum in one step.

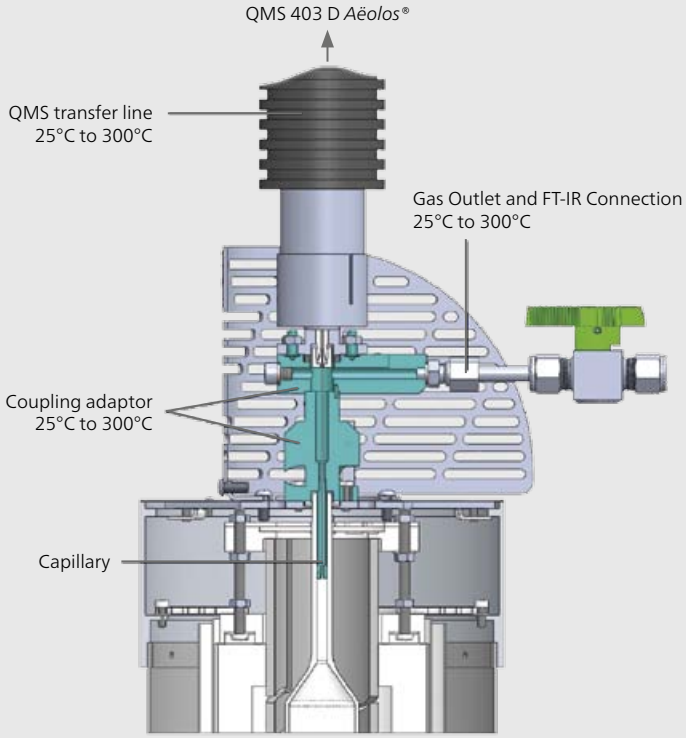
Double-Step Pressure Reduction

Different systems, such as laminar flow capillary, nozzle, and orifice, are used to reduce the pressure in the first step down to the range from 10^{-1} mbar to 10 mbar. A membrane pump, rotary pump or drag stage of the turbo molecular pump is applied to achieve this pressure reduction.

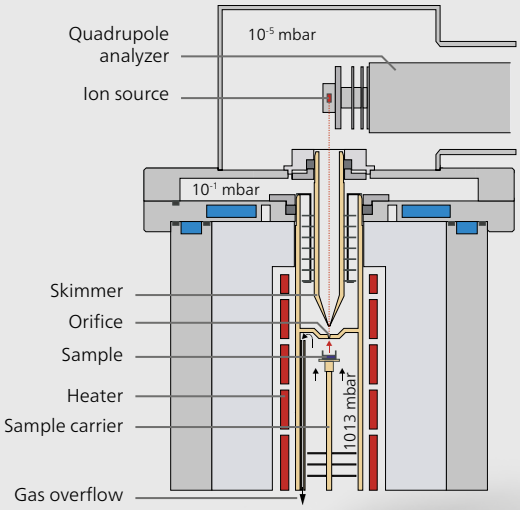
The second step is either an orifice or a skimmer as a molecular leak for the gas inlet into the high vacuum recipient of the mass spectrometer.

Perfect Gas Flow Conditions

The aim of coupling is to have all relevant gases and vapors transported from the sample area into the ion source of the mass spectrometer for precise qualitative and quantitative analysis. This is only achieved through perfect gas flow conditions in the thermal analyzer, the coupling interface and the gas inlet of the mass spectrometer. As only a small quantity of gas is required for the analysis, a bypass is used at the gas outlet of the thermobalance for the excess purge gas flow not going through the coupling interface.



Capillary Coupling



SKIMMER® Coupling

SKIMMER K

Coupling TA-QMS 403 D *Aëolos*®

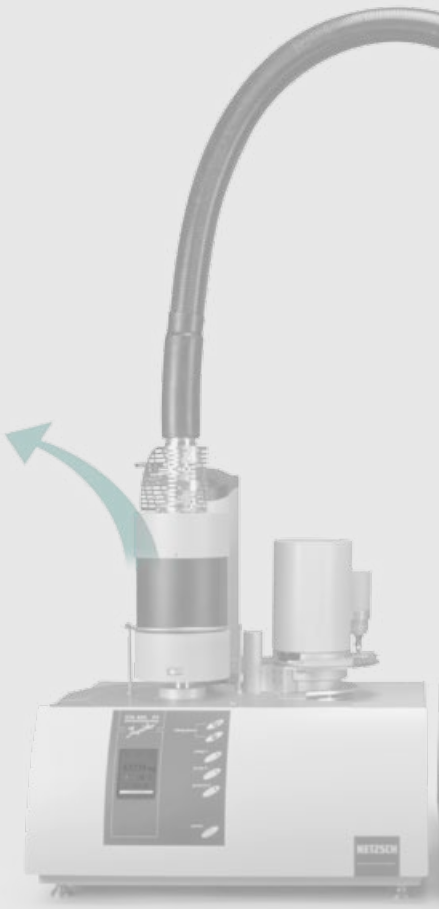
Top Line Capillary Coupling

An elaborated concept for capillary coupling to NETZSCH thermobalances (TGA) and STA instruments (simultaneous TGA-DSC) has been realized with the introduction of the QMS 403 D *Aëolos*® Quadrupole Mass Spectrometer. Volatile sample materials in a controlled temperature treatment are directly transferred into the electron impact ion source of the MS via a fused silica capillary which can be heated up to 300°C.

The Coupling System is Improved for

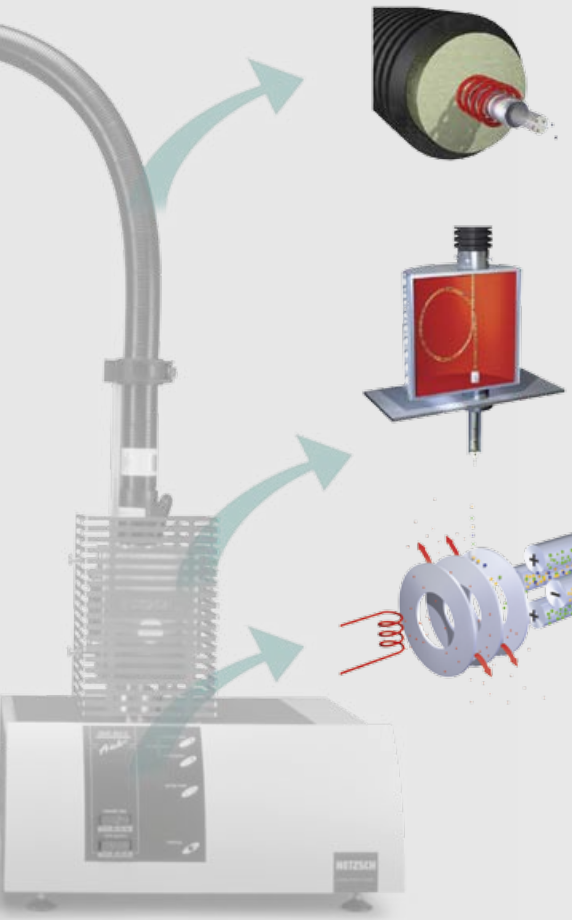
- Minimized condensation losses through the increased overall temperature of 300°C at the whole gas transfer system from the furnace exit over the capillary to the MS gas inlet
- Single step pressure reduction to eliminate clogging of orifices.
- Flexibility of the coupling to allow as well standard TGA measurements and also simultaneous TGA, MS, (GC-MS), and FT-IR measurements

The QMS 403 D *Aëolos*® can also be independently employed for the analysis of other gas sources.



Natural vertical gas flow through the STA furnace to the heated adaptor with capillary inlet and bypass

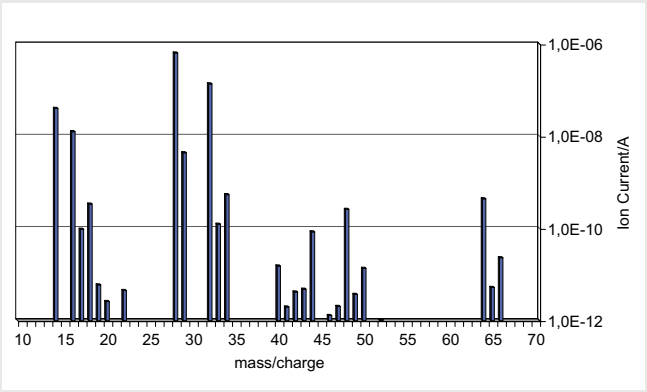
TA specifications			
STA 449 ***F1*** *Jupiter*®	-150°C to 2400°C	max. 5 g, resolution TG 0.025 µg	DSC < 0.1 µW
STA 449 ***F3*** *Jupiter*®	-150°C to 2400°C	max. 35 g, resolution TG 1 µg	DSC < 0.1 µW
DSC 404 ***F1/F3*** *Pegasus*®	-150°C to 2000°C	resolution	DSC < 0.1 µW
DSC 204 ***F1*** *Phoenix*®	-180°C to 700°C	resolution	DSC < 0.1 µW
TG 209 ***F1*** *Libra*®	RT to 1100°C	max. 2 g, resolution TG 0.1 µg	
TMA 402 ***F1/F3*** *Hyperion*®	-150°C to 1550°C	max. 5000 µm, resolution up to 0.125 nm, sample dimension up to 30 mm	
DIL 402 C	-180°C to 2000°C	max. 5000 µm, resolution min. 0.125 nm, sample dimension up to 50 mm	



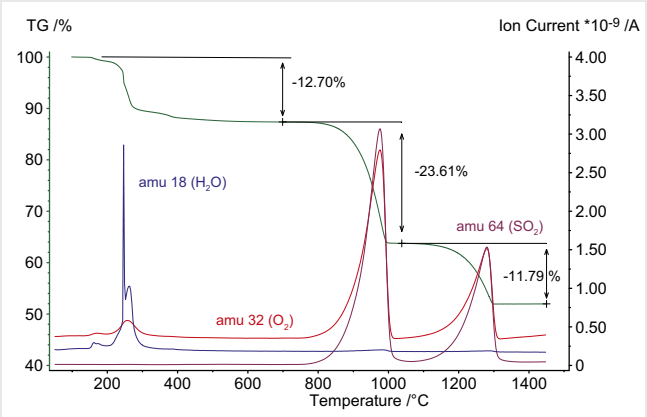
The inert quartz-glass capillary with controlled heating to 300°C for loss-free gas transfer to the QMS

Heated chamber for easy handling and precise adjustment of the capillary inlet to the QMS

Quadrupole MS with cathode, electron and ion lenses, mass filter and channeltron detector



A Scan-Bargraph is often the basis for complete information on all evolved species and allows selection of all or individual interesting mass numbers for import into the *Proteus*® software as continuous MID curves. Here, one scan out of the repeated scans is shown for $Nd_2(SO_4)_3$*5 H_20 measured in air at 950°C.



$Nd_2(SO_4)_3$*4.7 H_20 (29.53 mg) was heated at a rate of 10 K/min up to 1400°C in a nitrogen flow. The MID curves, directly imported from the coupled *Aëolos*®, show the well separated gas evolution for water, oxygen and sulfur dioxide in perfect correlation with the TGA steps.

QMS 403 D *Aëolos*® specifications		
QMS mass range 300 u*	resolution > 0.5 u*	Scan, Scan-Bargraph, MID
Electron impact ionization	ionization energy: 25 eV to 100 eV	iridium cathodes 2 Y_2O_3 coated
Channeltron SEM	detection limit > $2 \cdot 10^{-14}$ mbar partial pressure	> 1 ppm

* unified atomic mass unit

STA 409 CD with QMS 403/5 *SKIMMER*® Coupling

Unique Supersonic jet Gas Transfer

The *SKIMMER*® coupling is the shortest possible solution for the gas transfer from the sample to the QMS. The aerodynamic beam *SKIMMER*® collimates the molecules from the barrel-shaped jet expansion behind the divergent nozzle towards the QMS ion source. The pressure reduction of the purge gas flow at atmospheric pressure down to the high vacuum behind the *SKIMMER*® orifice is achieved in two steps along a distance of less than 20 mm. All components are heated to at least the sample temperature and therefore no chance for any condensation exists. Even metal vapors are detected by this unrivaled coupling system.

The nozzle and *SKIMMER*® are precisely machined from either alumina or amorphous carbon (glassy carbon), allowing application temperatures of 1450°C or 2000°C in the corresponding furnaces. The molecular beams are analyzed by a quadrupole mass spectrometer up to high mass numbers of 512 u or optionally 1024 u.

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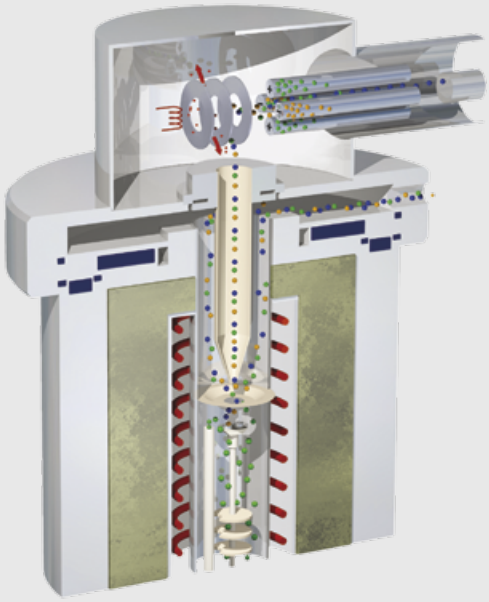
Technical Key Data STA – QMS *SKIMMER*® Coupling

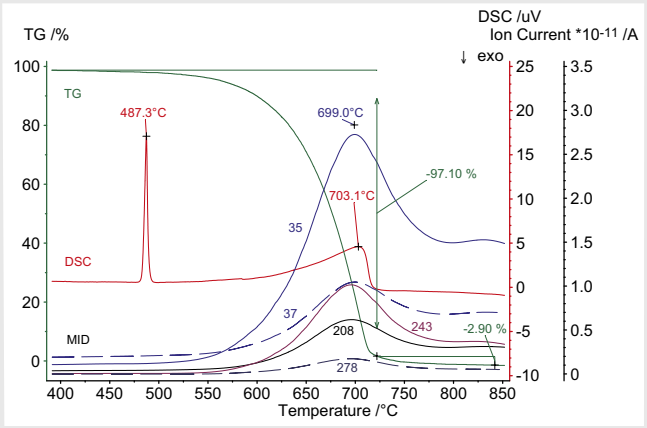
STA 409 CD		QMS	
Temperature range	■ RT to 1450°C with SiC furnace ■ RT to 2000°C with graphite furnace	QMS system options	■ 1 to 512 u ■ 1 to 1024 u
Balance weighing range	15 g	Measuring modes	Analog scan, Scan-bargraph, MID
TGA resolution	2 µg	Ion source	Electron impact ionization: Electron impact, Energy* 0…125 eV, in steps of 1 eV adjustable, for "soft" and "hard" ionization
Sensor types	TGA, DTA, DSC	Cathodes	Tungsten
		Detection limit	< $1x10^{-14}$ mbar (SEM) partial pressure

* Note: limits below 40 eV require a reduction of emission and adaption of further ion source voltages in order to avoid superheating of the cathode

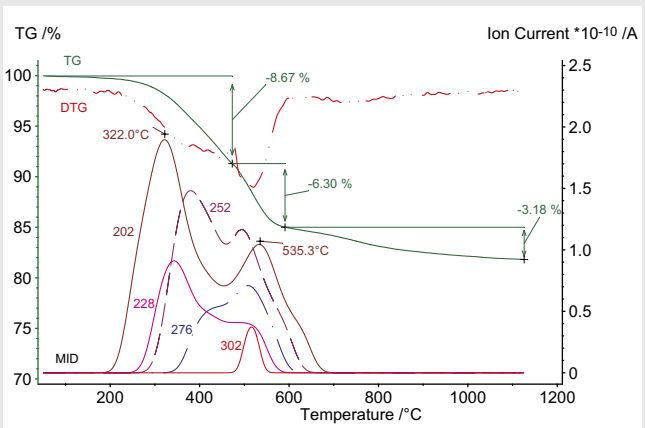


Shortest possible connection between *SKIMMER*® cone and QMS-ion source with perfect gas flow conditions

Gas outlet, nozzle and *SKIMMER*® are heated together with the sample



Lead chloride (7.92 mg) in an argon flow of 150 ml/min shows evaporation starting in the melting range (487°C). The molecule ion (PbCl2 m/z 278) and fragment ions caused by dissociation and ionization (PbCl m/z = 243, Pb m/z = 208, Cl m/z 37, Cl m/z = 35) are clearly detected far below the boiling temperature of the starting material.



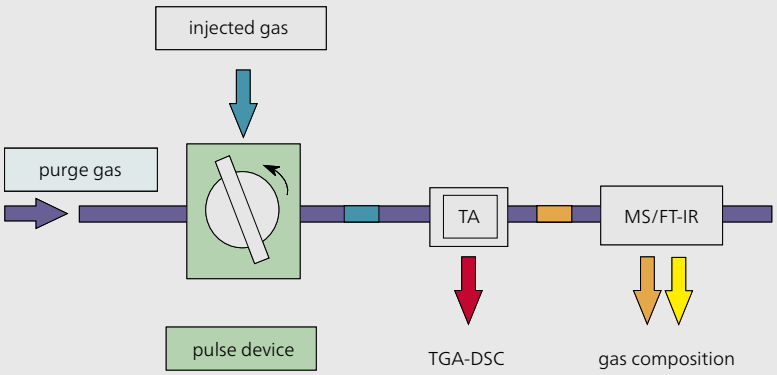
Pitch carbon powder (55.2 mg) decomposes in nitrogen flow (50 ml/min) into aromatic compounds of high molecular weight, mainly up to 600°C. Only selection is shown by MID curves for pyrenes (m/z = 202), Triphenylenes (m/z = 228), Benzo(a)pyrenes (m/z = 252), Benzo(ghi)perylenes (m/z = 276) and Dibenzopyrenes (m/z = 302).

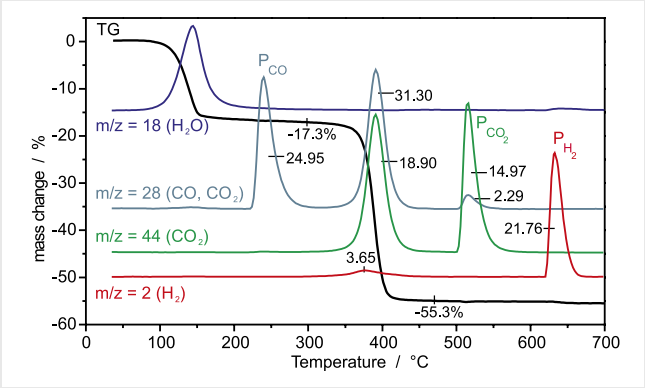
Calibration/Quantification

Quantification of the signals from gas analyzers requires a calibration of the whole coupled system with a known type and amount of gas or solvent to control the temperature dependent flow properties. The unique pulse thermal analysis technique (*Pulse*TA®) is a perfect tool to achieve quantitative gas detection in separate calibration runs or even online during a sample measurement. A known amount of gas is injected into the sample gas stream and the registered signal of the resulting pulse is integrated.

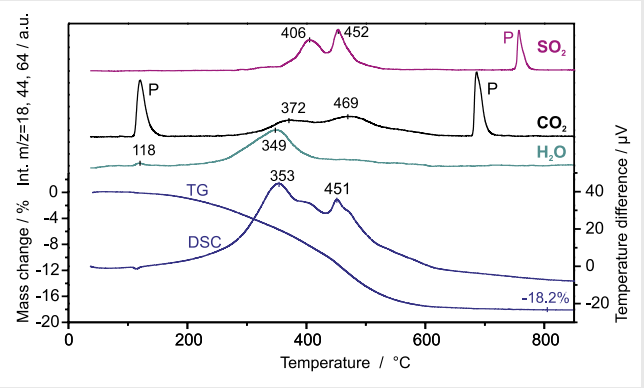
The application of *Pulse*TA® also increases the sensitivity of thermoanalytical measurements, allows studying gas solid reactions with stepwise control of the process by the pulsed supply of the reactive gas, and simplifies adsorption/desorption experiments.

PULSETA®





This plot shows the thermal decomposition STA of $ZnC_2O_4*2H_2O$ in a helium gas flow (50 ml/min). With corresponding pulses of CO and CO_2, marked by P, a quantification of the evolved gases in the MS is possible, even with the overlapping contributions to m/z 28 by CO and the fragmentation of CO_2. The reaction between CO and traces of water is shown by the H_2 signal and quantified by the H_2 pulse PH_2 (red).



The determination of carbon and sulfur content in a petrol rock was achieved by STA-MS measurements. During calcination in air, the CO_2 and SO_2 signals can be exactly quantified through corresponding pulses, even with the contribution of water to the detected weight loss.

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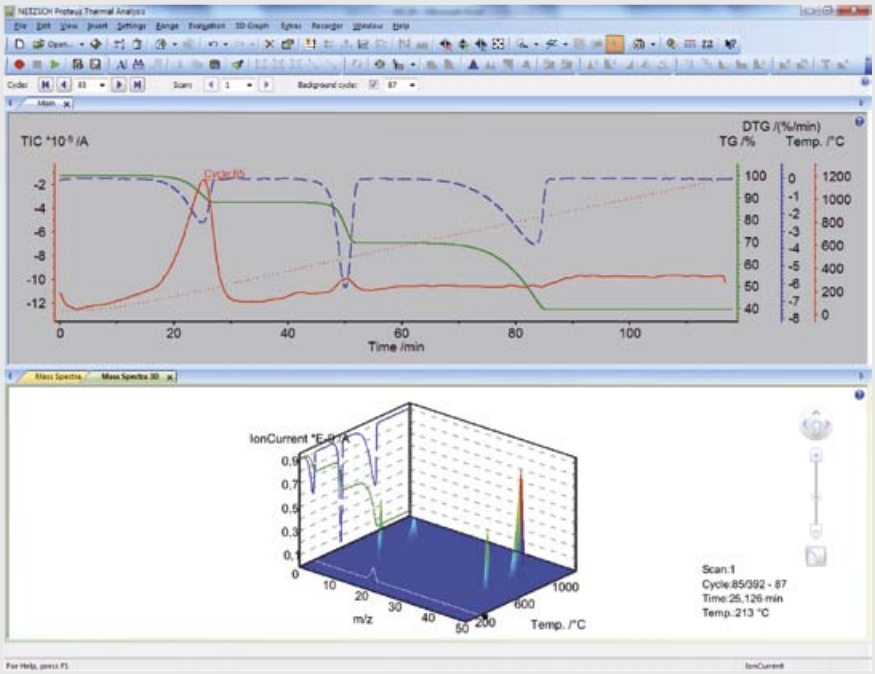
Fully Integrated TA-MS Software

The control of measurements with coupled TGA-QMS instruments is governed by the *Proteus*® software. The user gives the command for data acquisition once both the QMS and the *Proteus*® software are ready with parameter inputs and checking of pressure and ion source conditions. The online data collection is simultaneous and synchronized through triggered start to guarantee a precise time and temperature correlation between all the signals from the two coupled analytical systems during evaluation. The user works with the two software packages on one computer and has all possibilities to evaluate data and display results in the *Proteus*® software according to his preferences. The integration of the TA and QMS software based on effective data exchange from acquisition to evaluation makes the coupled TGA-QMS a real functional unity.



Fast Parameter Input for Routine Experiments

- fast MID input of 8 mass numbers
- fast mass range input for scan-bargraphs

Versatile Programming for Research Work

- selection of up to 64 MID mass numbers
- selection of analogue scans in max. 64 channels
- selection of scan-bargraphs or scan analog graphs with optimized rate and sensitivity in 4 different channels

Common Evaluation in *Proteus*® Software

- TGA-DSC/DTA-MID curves: characteristic temperatures, peak areas
- TGA-DSC/DTA-scan-bargraph envelope curves: characteristic temperatures, peak areas
- TGA-DSC/DTA Total Ion Current
- Evalution of MS spectra
- Export of MS data in NIST-library compatible format
- Three-dimensional presentation of spectra data together with temperature, TGA, DTG and/or DSC curves

NETZSCH

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 2,700 employees at 140 sales and production centers in 27 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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