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Leading Thermal Analysis

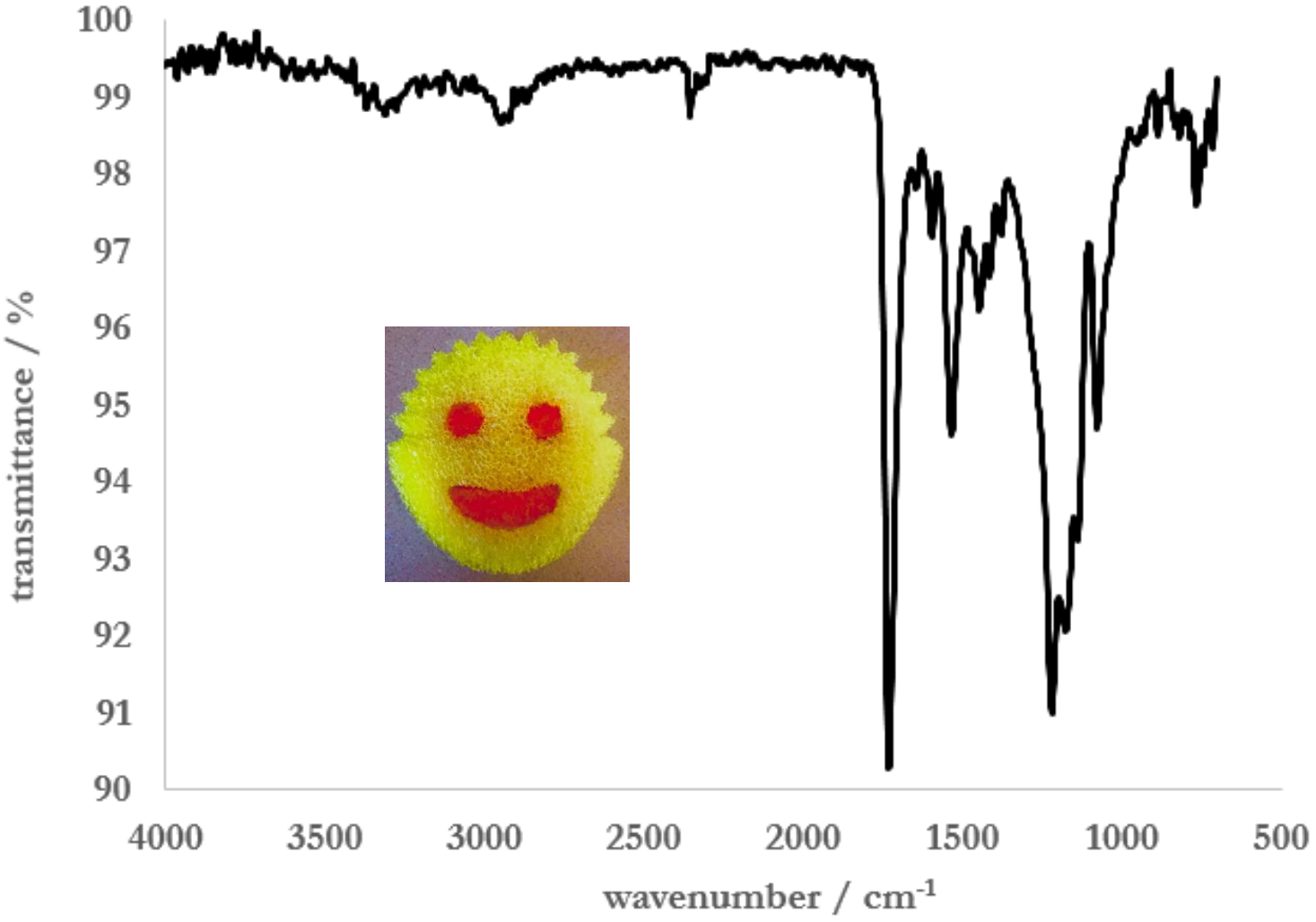
Thermogravimetric Analysis (TGA and STA) with Evolved Gas Coupling Methods

TGA/STA-FTIR-QMS-GCMS

Peter Vichos
NETZSCH Instruments North America, LLC

- Scrub Daddy is a cleaning sponge that can be used wet or dry and change its texture based on the temperature of water used.
- It is firm and rigid in cold water to help remove debris, but also soft, compressible and absorbent in warm water to act as more of a gentle sponge.
- FlexTexture™ is a highly engineered thermoplastic polyurethane foam (polycaprolactone.)
- It changes its structure depending on the temperature to which it is exposed.
- Low melting point of 60°C and a glass transition temperature of −60°C.

Why Evolved Gas Analysis … FTIR Analysis



Main Methods of Thermal Analysis and Evolved Gas Analysis

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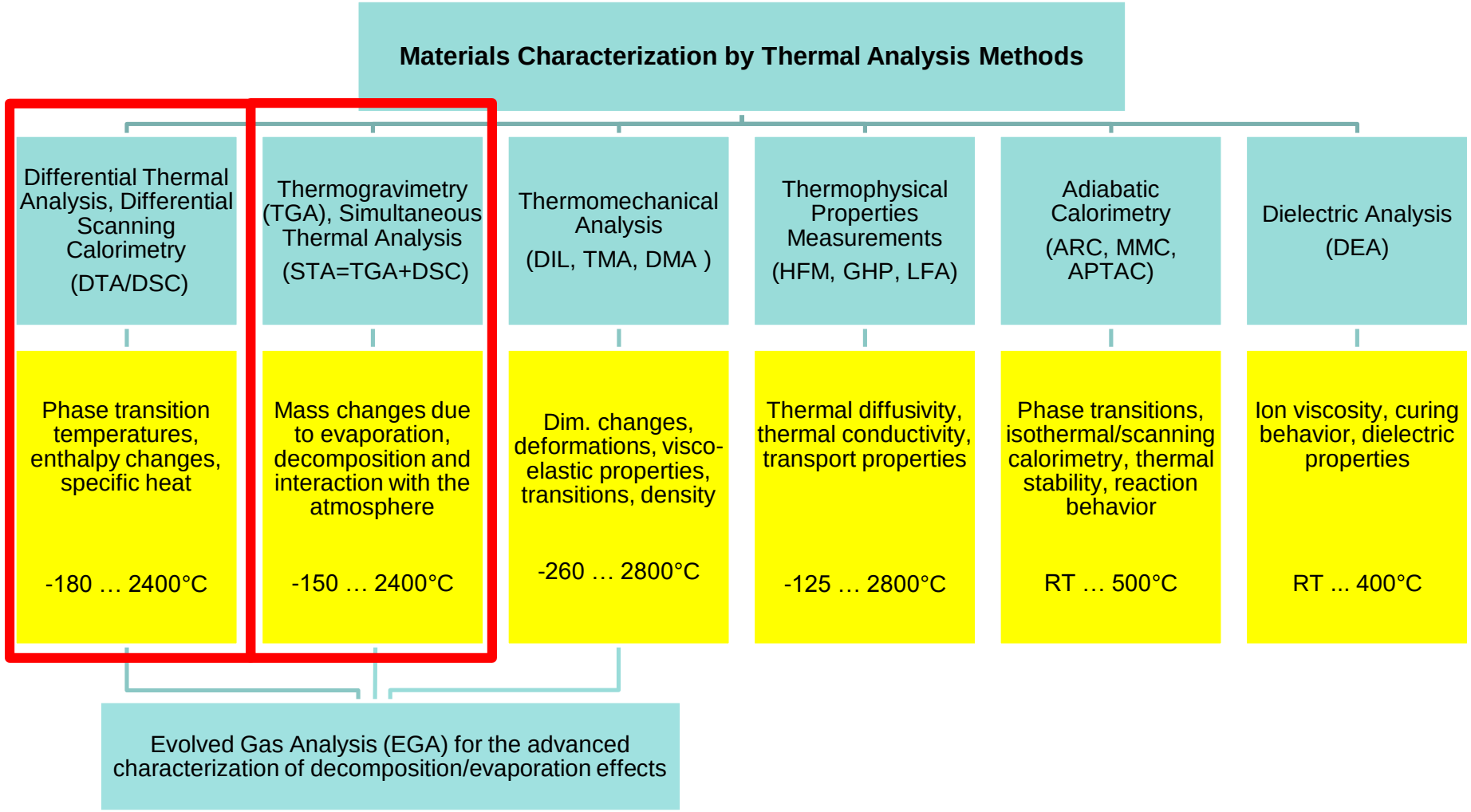

Evolved Gas Analysis (EGA) in Thermal Analysis

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FTIR Coupling:

⇒ Easy interpretation (spectra data bases) of organic vapors without fragmentation. Examples include paints, adhesives, resins, polymer. coatings and drugs.

⇒ Homonuclear diatomic molecules (H_2, N_2, O_2, etc.) cannot be detected

QMS Coupling:

⇒ High sensitivity

⇒ Fast and easy interpretation of atomic/inorganic vapors and standard gases (H_2, H_2O, CO_2, ...)

⇒ Fragmentation, interpretation of organic molecules sometimes difficult

GC-MS Coupling:

⇒ Very high sensitivity

⇒ Separation of the volatiles using the GC column

Principle of Thermogravimetry (TGA)

Respective Standard: ISO 11358, ASTM E1131,…

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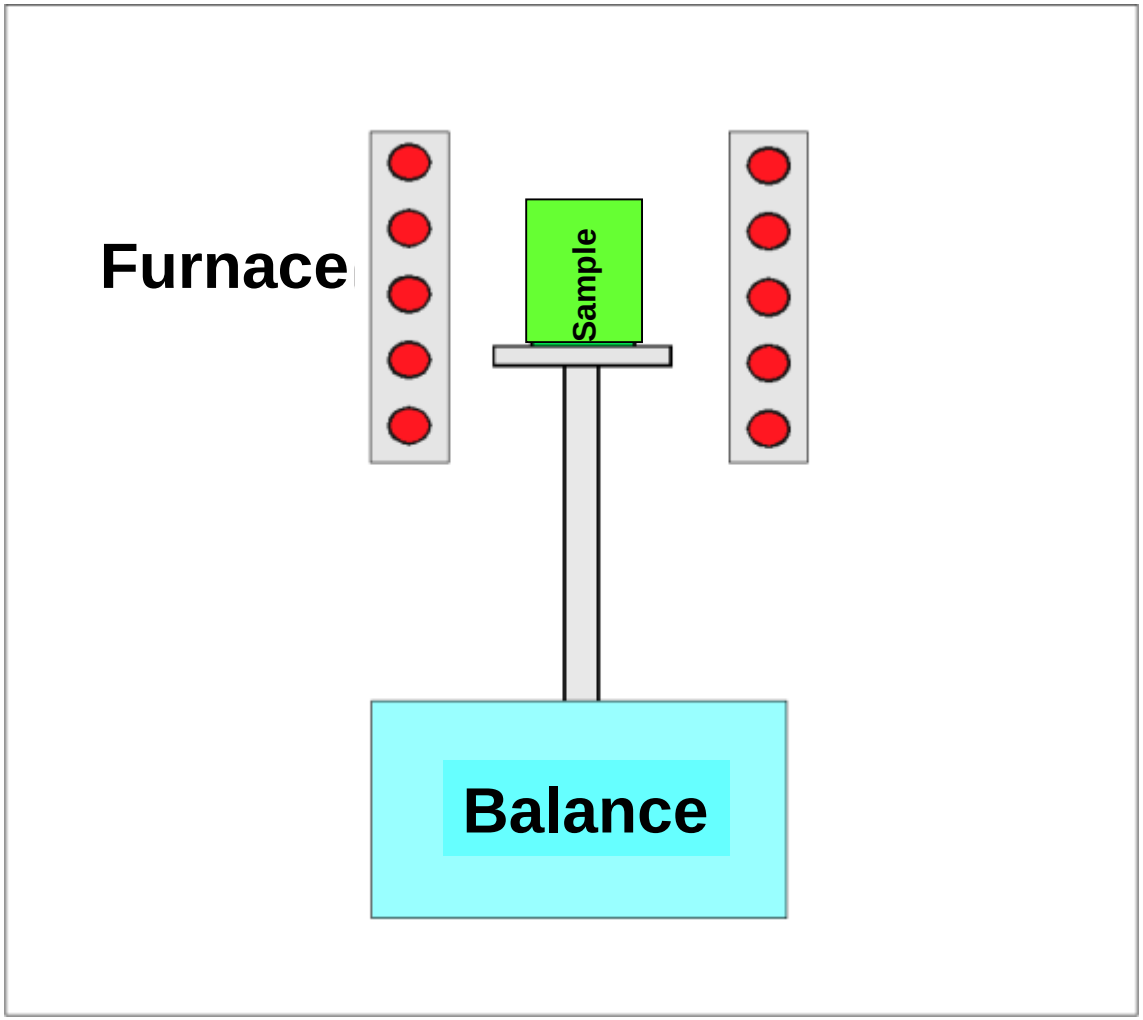


NETZSCH TGA309: Resolution down to 0.01ug, 2gm sample max and 10C to 1100C (optional -150C to 1000C)

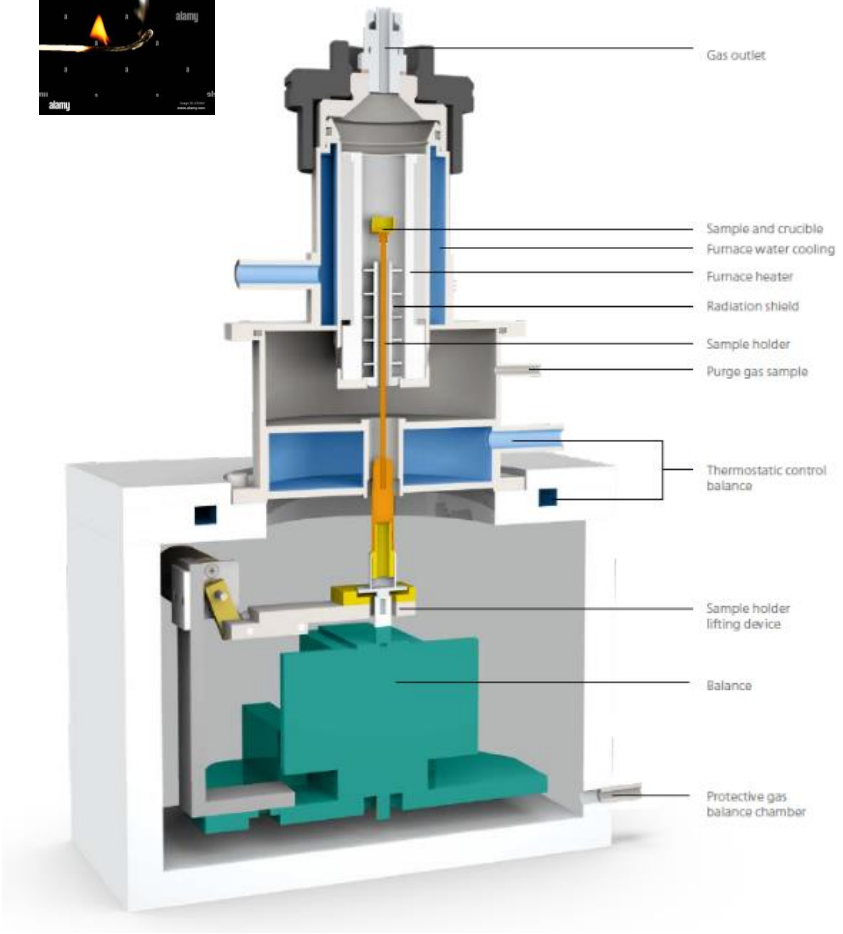
TG 309 Libra Classic

(0.01ug, 0.02ug, 0.05ug)

TG 309 Libra Select/Supreme

Micro-Furnace – A Dynamic System for Efficient Gas Flow

- Low-volume ceramic furnace supports:
  - fast heating rates up to 200 K/min over the entire temperature range.
  - Corrosion resistant furnace
  - fast ballistic cooling by chilling from 1100°C down to room temperature.
  - low purge gas flows ensure less dilution of the evolved gases (to be considered if coupling to evolved gas analysis is planned).
  - short gas path, low volume of the furnace and low dead volume above the sample help prevent condensation of the evolved gases in the furnace
  - vacuum-tightness for reproducible measurement conditions, improved separation of de-composition steps and evolved gas-analysis.



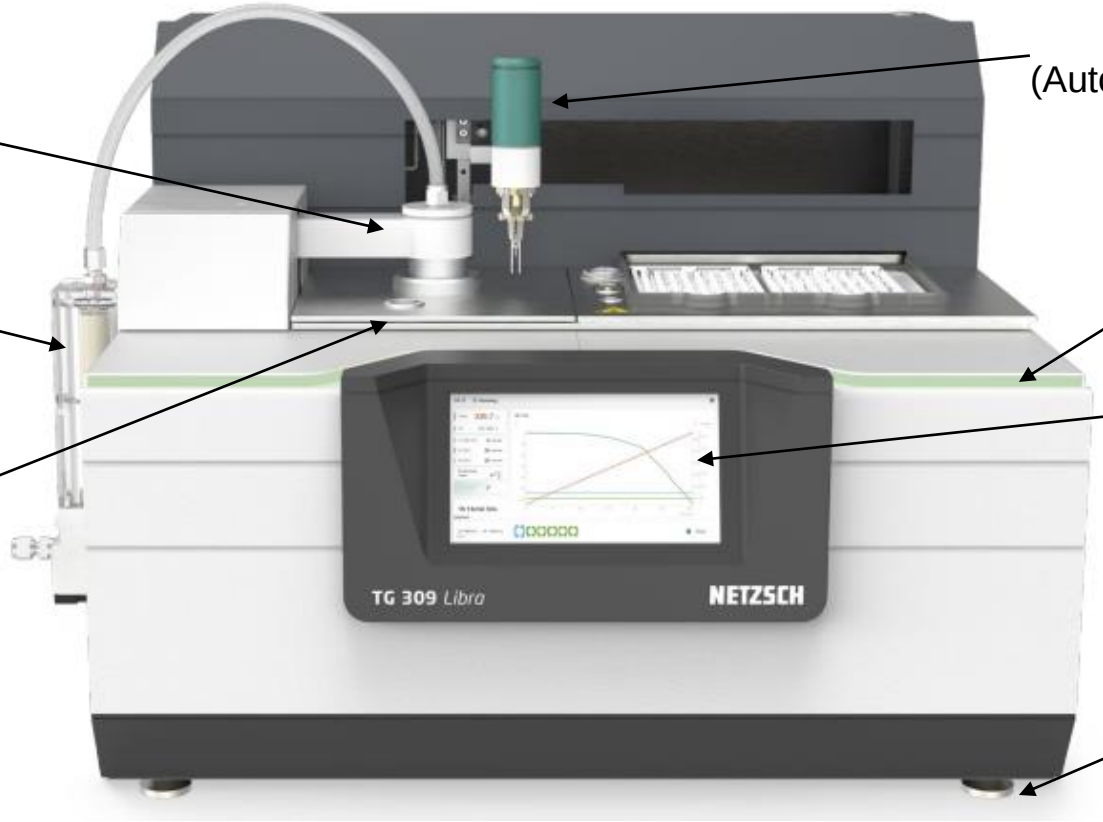
The NETZSCH newly designed TG 309 *Libra*

Furnace cover
with hoisting device

Gas outlet

NETZSCH inside:

- Furnace
- Sensor
- Balance



ASC
(Auto Sampler)

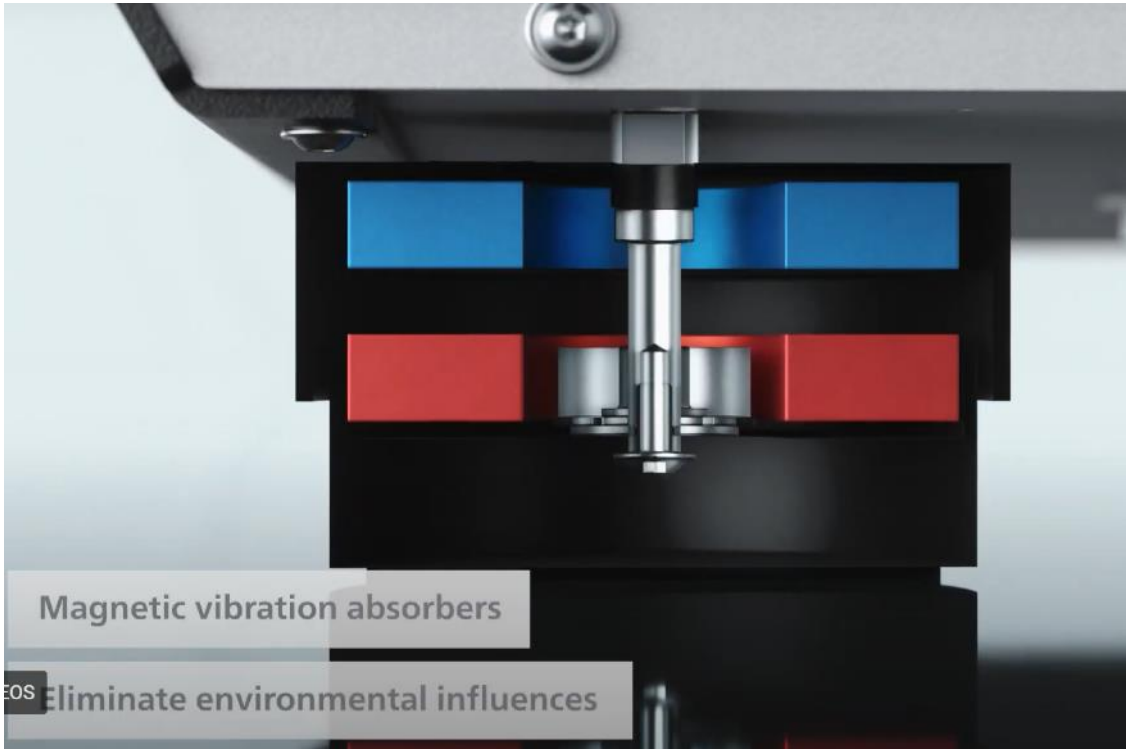
LED status bar

Color touch display

Magnetic shock
absorbers

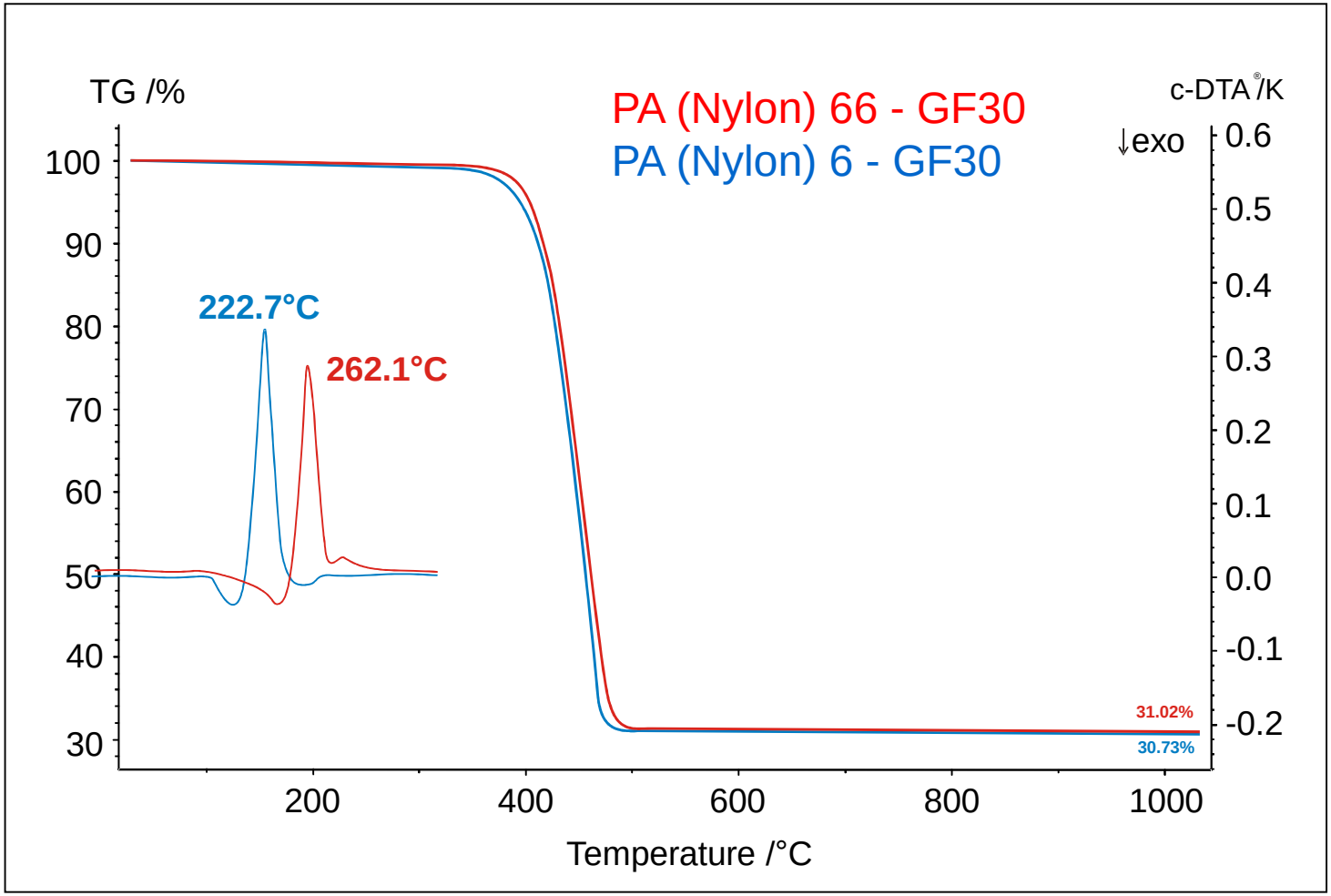
Magnetic Shock Absorber

- The magnetic absorbing feet decouple the TG 309 from undesired vibrations coming from the environment, like steps, door banging or vacuum pumps.
- This results in a stable baseline during the measurement and avoids artefacts in the gravimetric data.
- Thus, heavy stone tables can be eliminated.



Generating Useful Information by Using c-*DTA*®

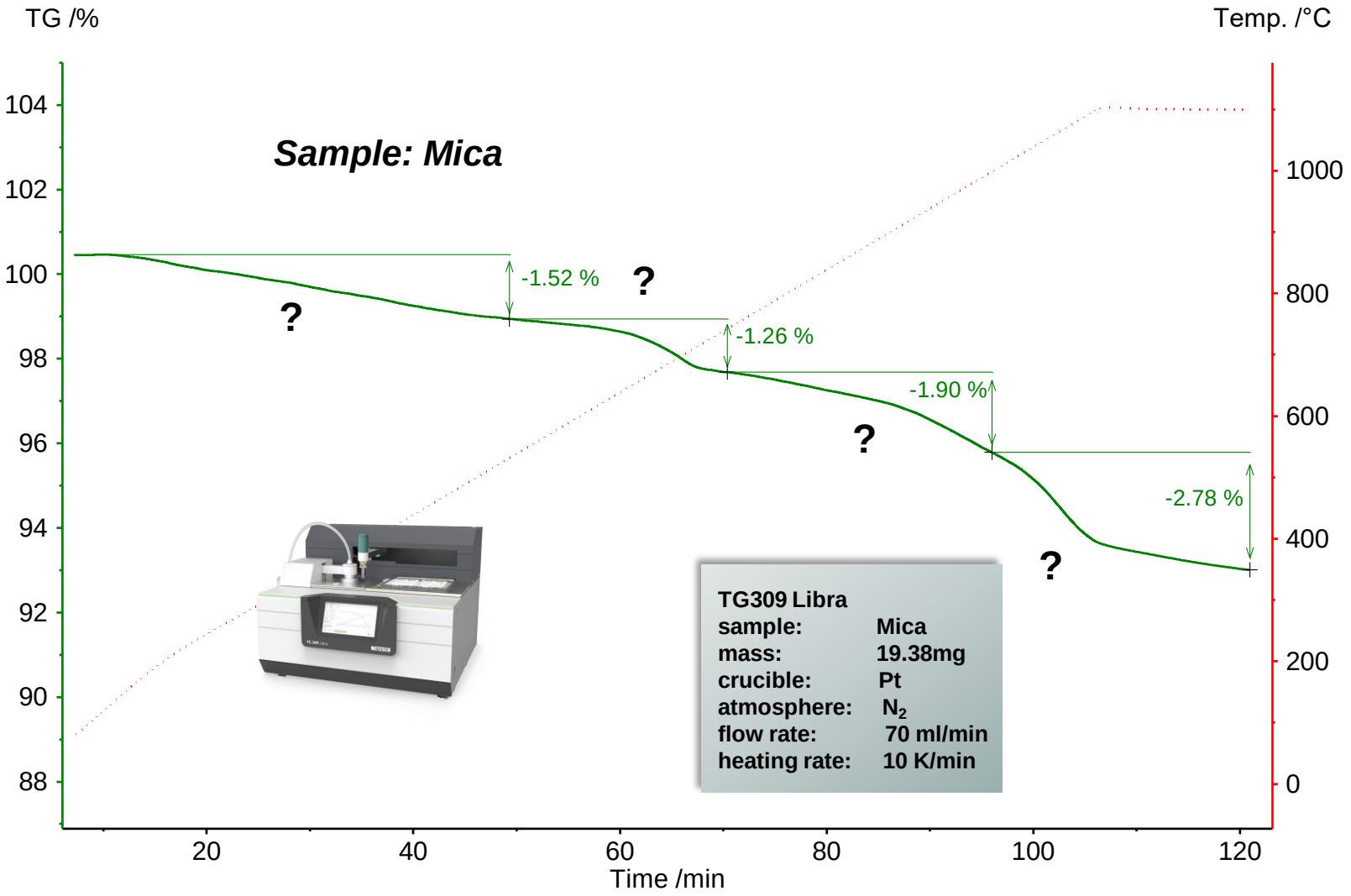
…now we see the difference



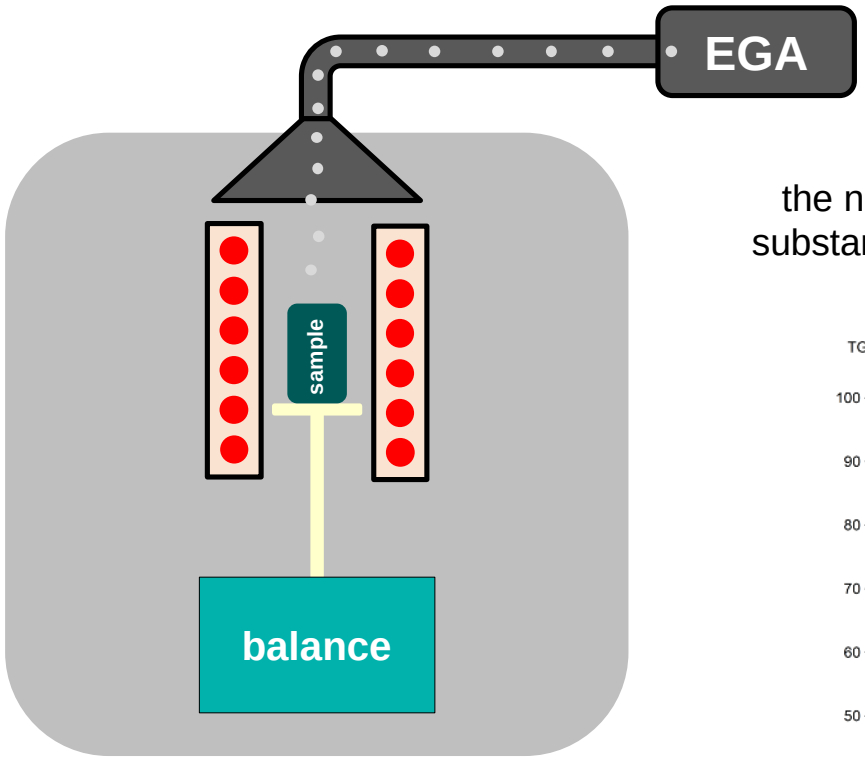
TG 309 *Libra*®, Sample mass: ≈10.6 mg, heating rate: 10 K/min, N_2 atmosphere
(GF30 = glass reinforced fiber of 30%)

Why Coupling with Gas Analysis?

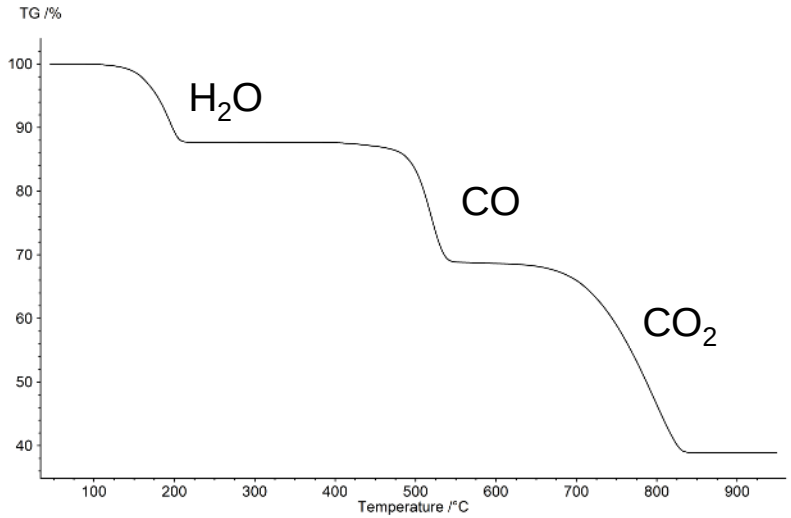
The interpretation of the TGA signal alone is difficult



Evolved Gas Analysis (EGA)



Evolved Gas Analysis (EGA) is a technique in which the nature or amount, or both, of gas or vapor evolved by a substance is measured while the substance is subjected to a controlled-temperature program.



The selection of the best-suited gas analyzer depends on the material

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Analytic Potential

Which kind of material?

Biomass	Organics	Polymers	Building material	Ceramics	Inorganics	Salts	Metals & Alloys

complex matrix — few components

Skimmer — QMS Aëolos — *Skimmer*

FTIR

GCMS

NETZSCH: Several possibilities for Evolved Gas Analysis

FTIR

- *provides good overview about outgassing substance*
- *“The All-Round Solution”*

QMS

- *suitable for all kinds of inorganic and organic gas species*
- *high performance for demanding task like quantification*

GC-MS

- *superior handling of complex outgassing mixtures*
- *Highest sensitivity for demanding task like trace analysis*

What can be analyzed by means of FTIR?

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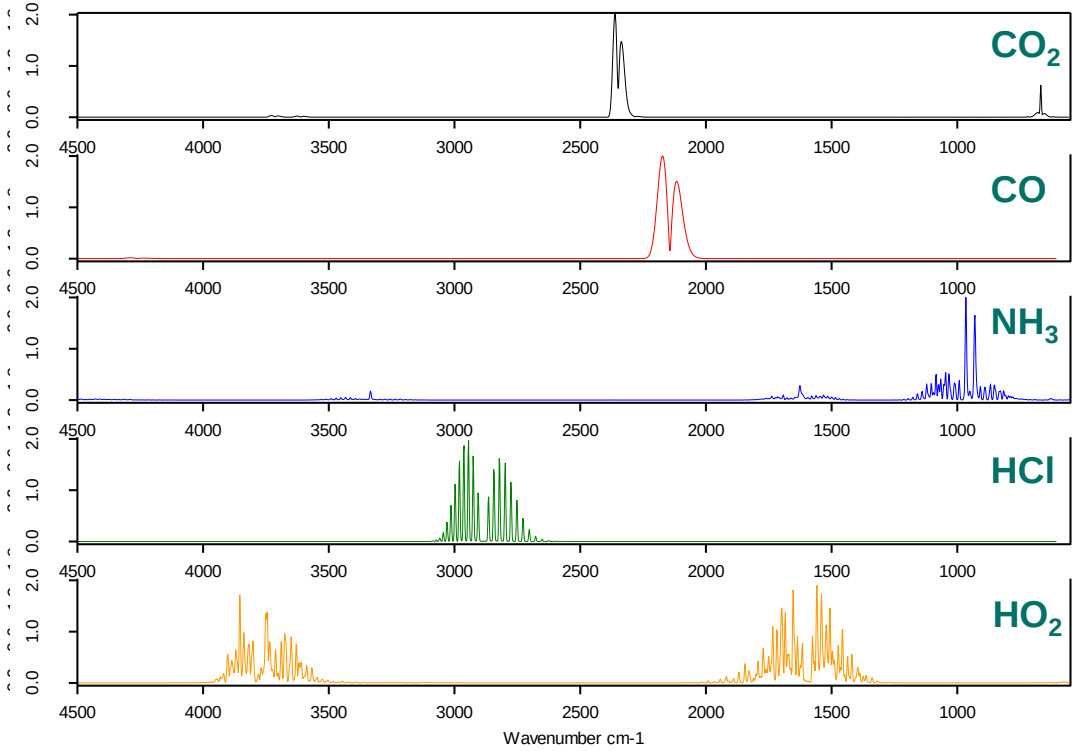
FT-IR coupling



The Coupling Possibilities for TG 309

FT-IR coupling

Key points:

- max. 400 °C Transfer Line Temperature
- max. 370 °C IR Cell Temperature
- Complete Software Integration within Netzsch Proteus for the combined Measurement start
- Automatic data exchange between Netzsch Proteus and Bruker OPUS Software in both directions (e.g., TG, DSC, Temperature, Gram-Schmidt, IR-Traces)
- Two Versions (Capillary & Direct Coupling)

TGA-FTIR Coupling

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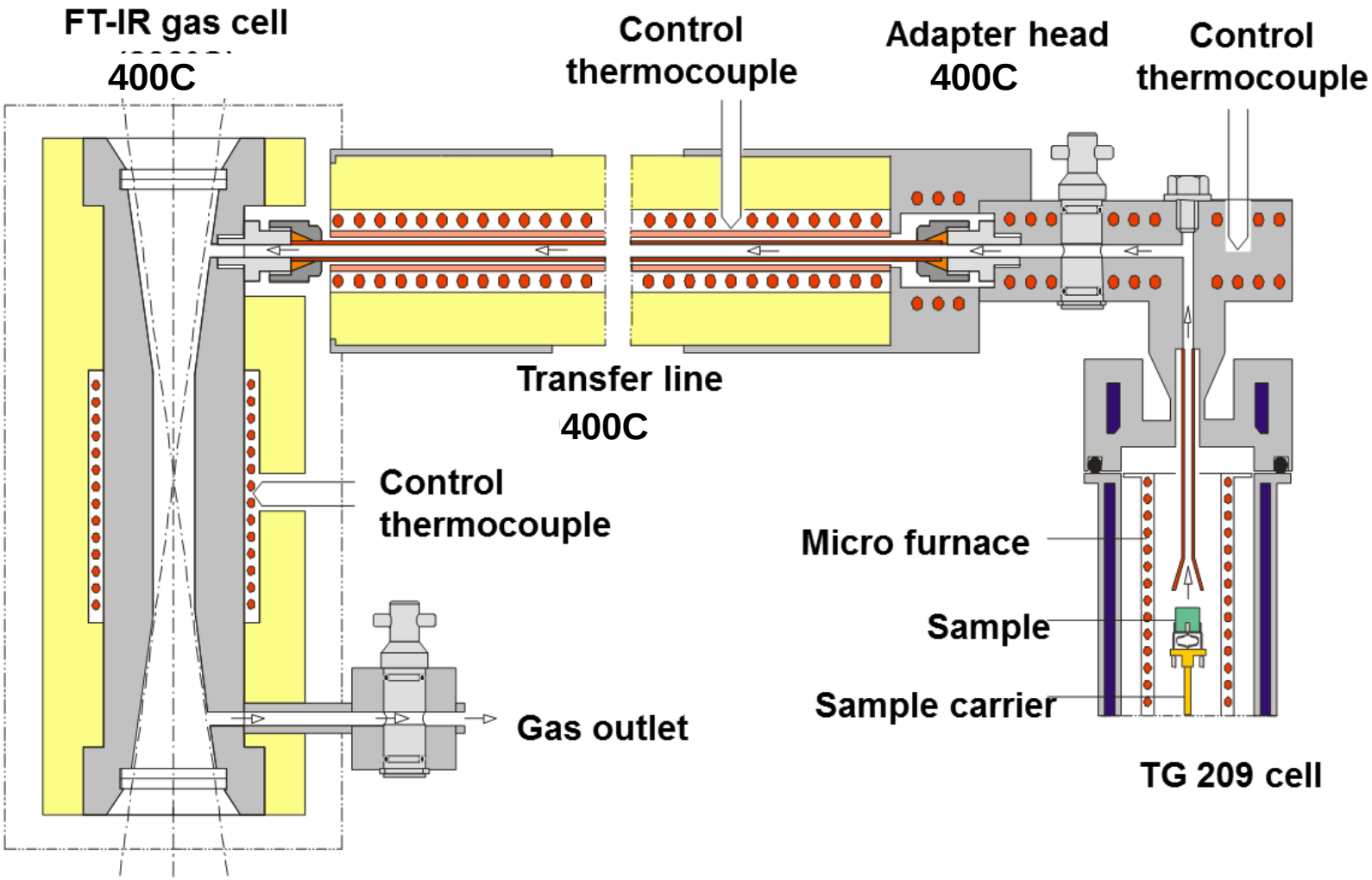

TGA-FTIR (Perseus) with Bruker Alpha II

NETZSCH

- Bruker Alpha II FTIR mounted on TG 309 Libra
- Direct transfer of gases to FTIR gas cell; no transfer line
- FTIR detector does not require LN2 (no detector refill needed; convenient for series of ASC experiments)
- Small size, ideal for glove box; no complicated transfer line connections out of glove box

TGA with FTIR coupling (compact):

Short, heated coupling interface minimizing the risk of condensation

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Perseus FTIR and TGA with Autosampler

Short, heated coupling interface minimizing the risk of condensation

TG 309 *Libra with FTIR*
Soft PVC – Spectrum Extracted

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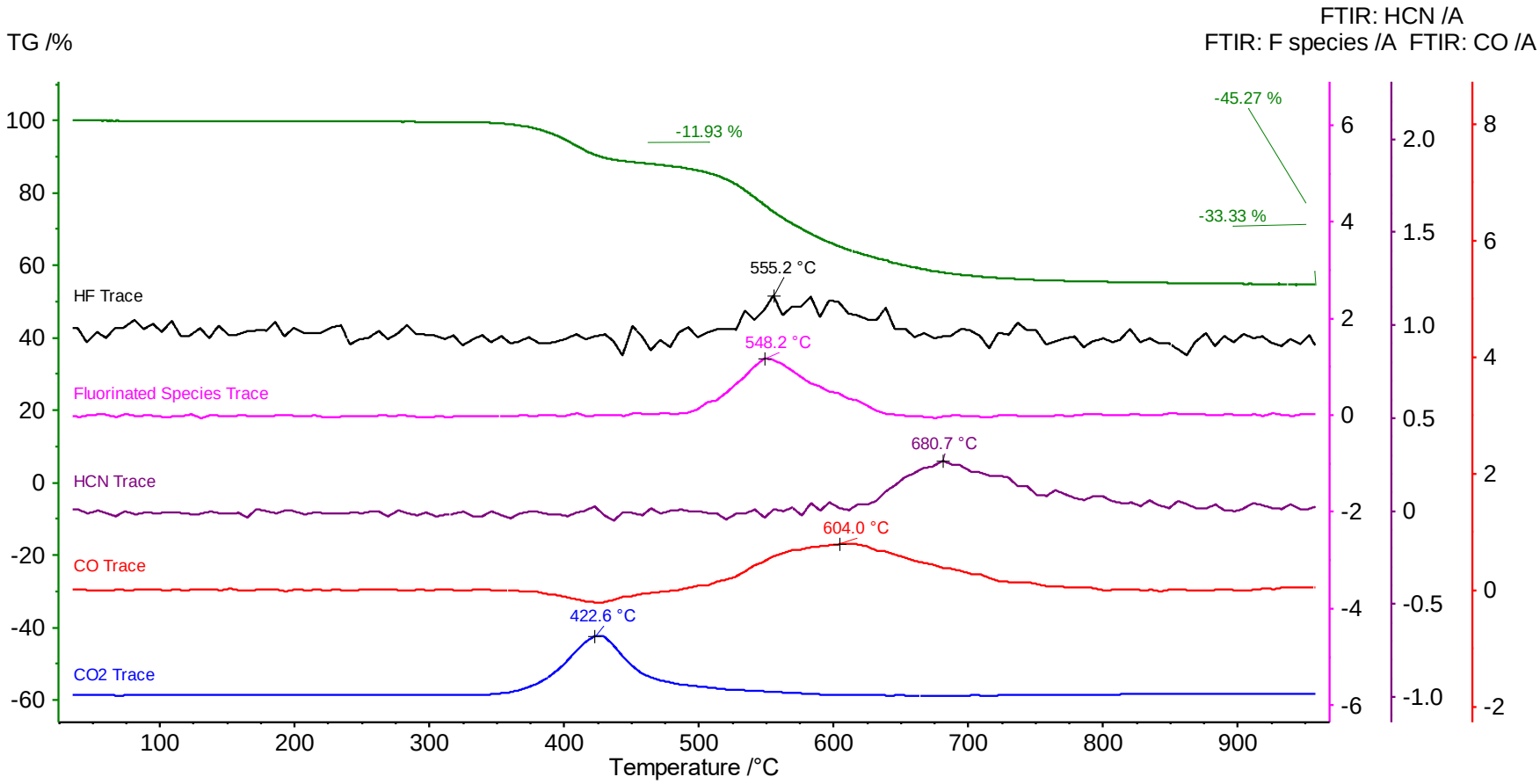
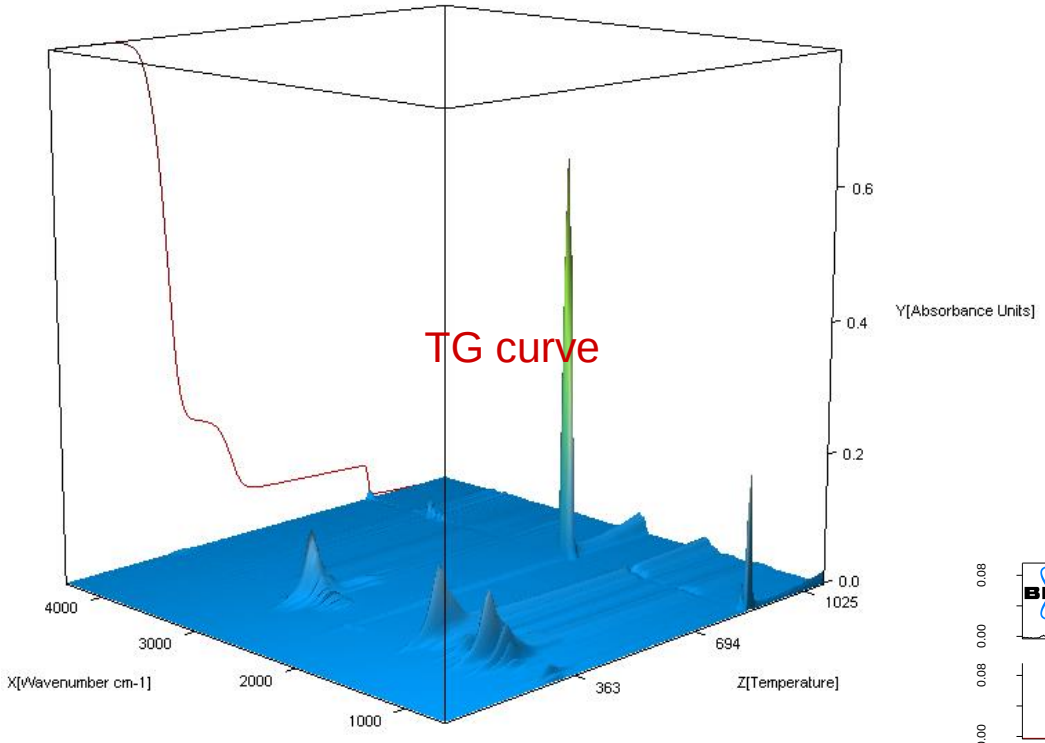
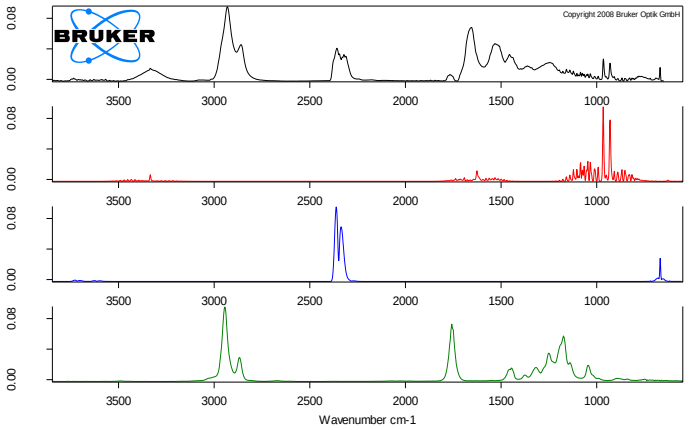


TG 309 Libra with FTIR (Bruker Alpha II)





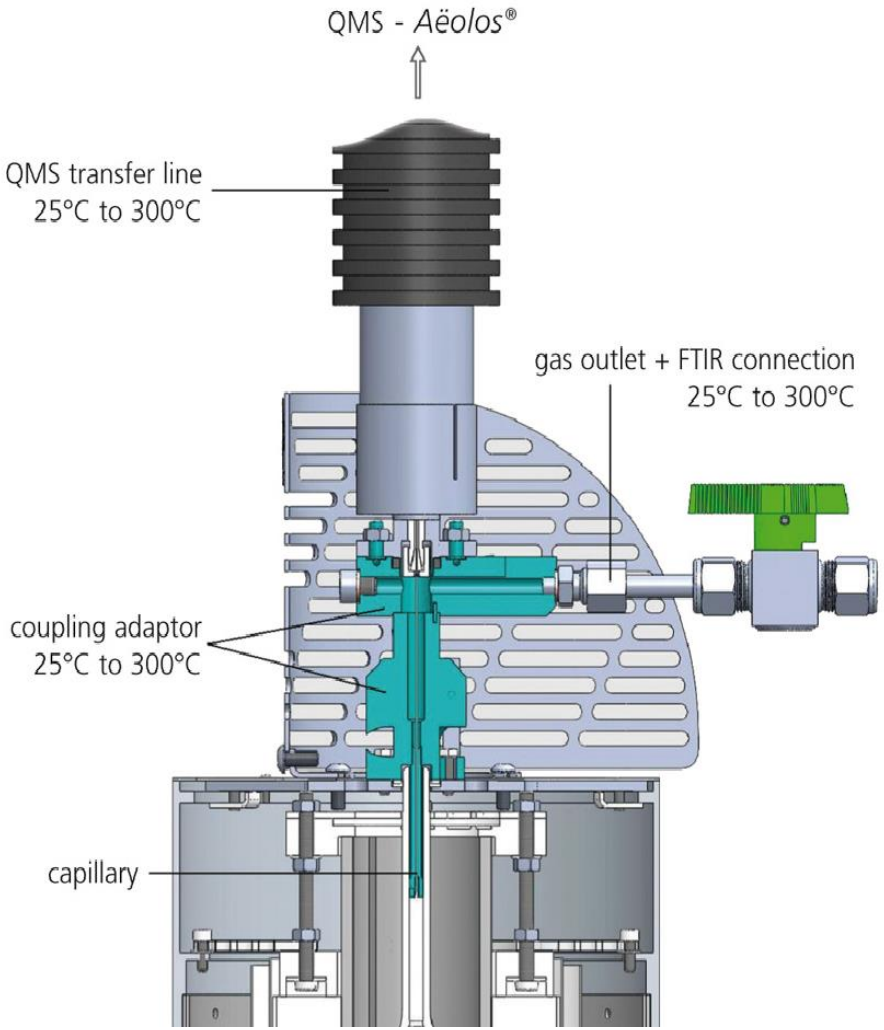
The Coupling Possibilities for TG 309

MS coupling

Key Features

- max. 350°C Transfer Line Temperature
- Complete Software Integration within Proteus for Measurement and Evaluation
- Automatic Tune Options for Mass Scale and Intensity with integrated Calibration Material (PFTBA)
- Two Capillary Versions: Silica Glass & Steel
- Up to 512 amu

The Netzsch Heated Coupling Adaptor to 350C



Gas flow conditions are ideal due to vertical design (remember the match)

Simultaneous measurement of TGA, MS and FTIR possible

Following heating of the entire coupling interface.

→ Prevention of condensation of evolved gases

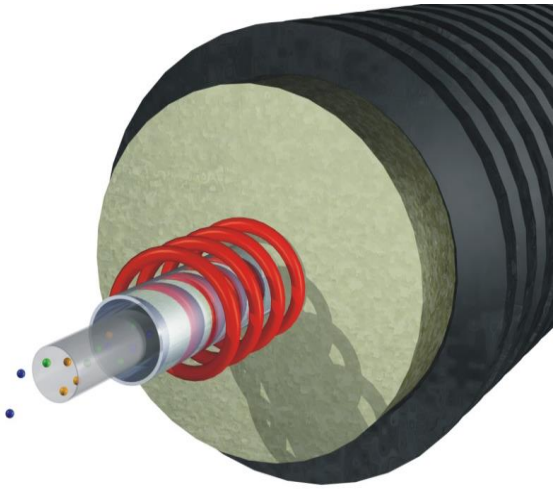
→ Minimized the risk of blocking of the coupling capillary

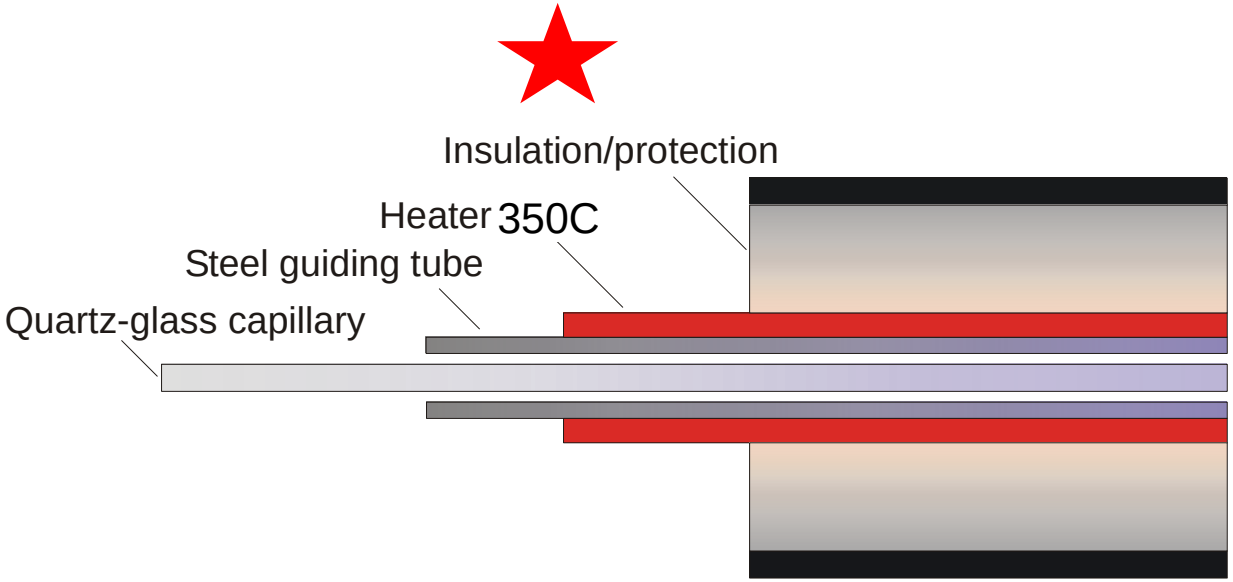
→ Enhanced the traceability of evolved gases

QMS Aëolos®-Transferline: Clever and Robust… Reduce Condensation

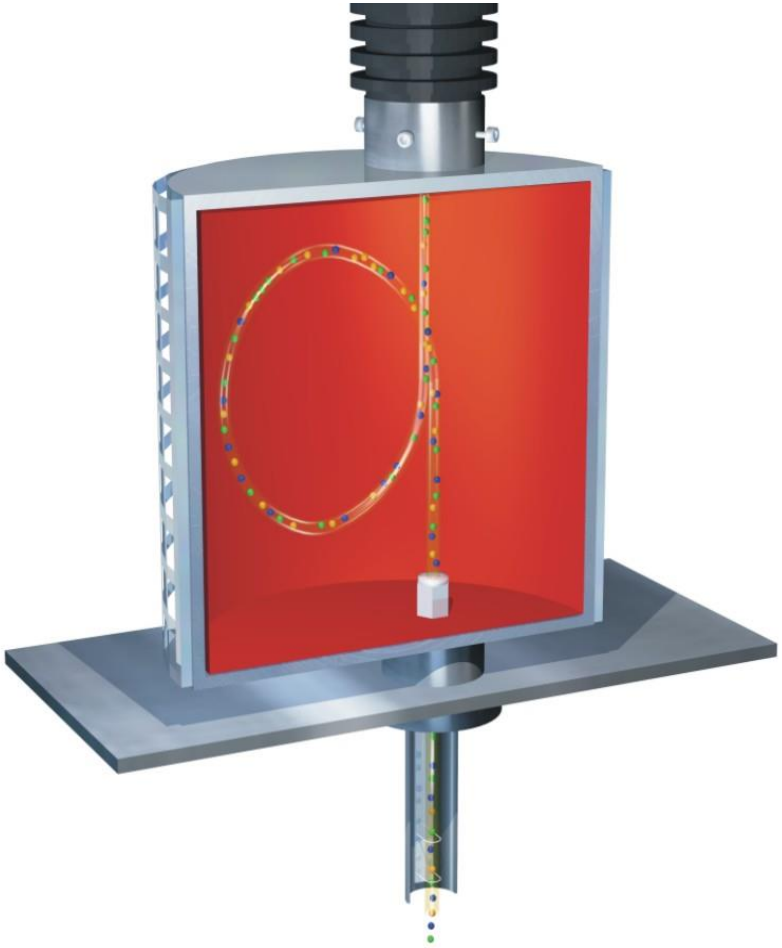
NETZSCH

- Following heating from adaptor to capillary inlet at the MS
- Insulated capillary, flexible and adjustable heating of capillary and QMS inlet system (up to 350°C)
- Easily exchangeable by the operator without opening of the vacuum chamber





Aëolos®-MS inlet: Servicing is easy



- Spare loops of the capillary
- Precise adjustment of the inlet position.
- Easy exchange without opening the vacuum chamber

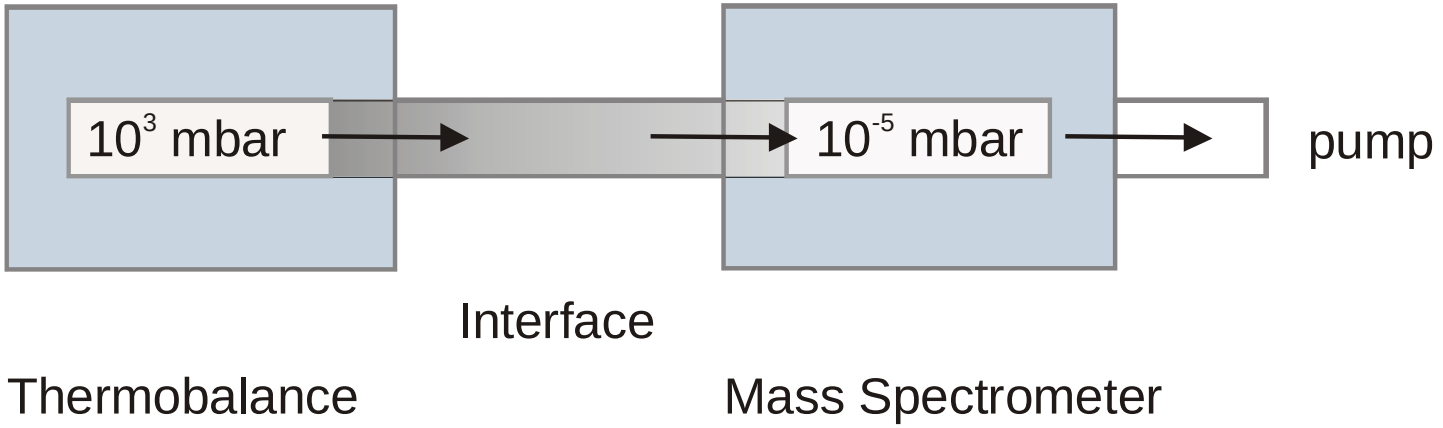
Aëolos® Single-Step-Pressure Reduction: Clever and robust

Single-Step Pressure Reduction

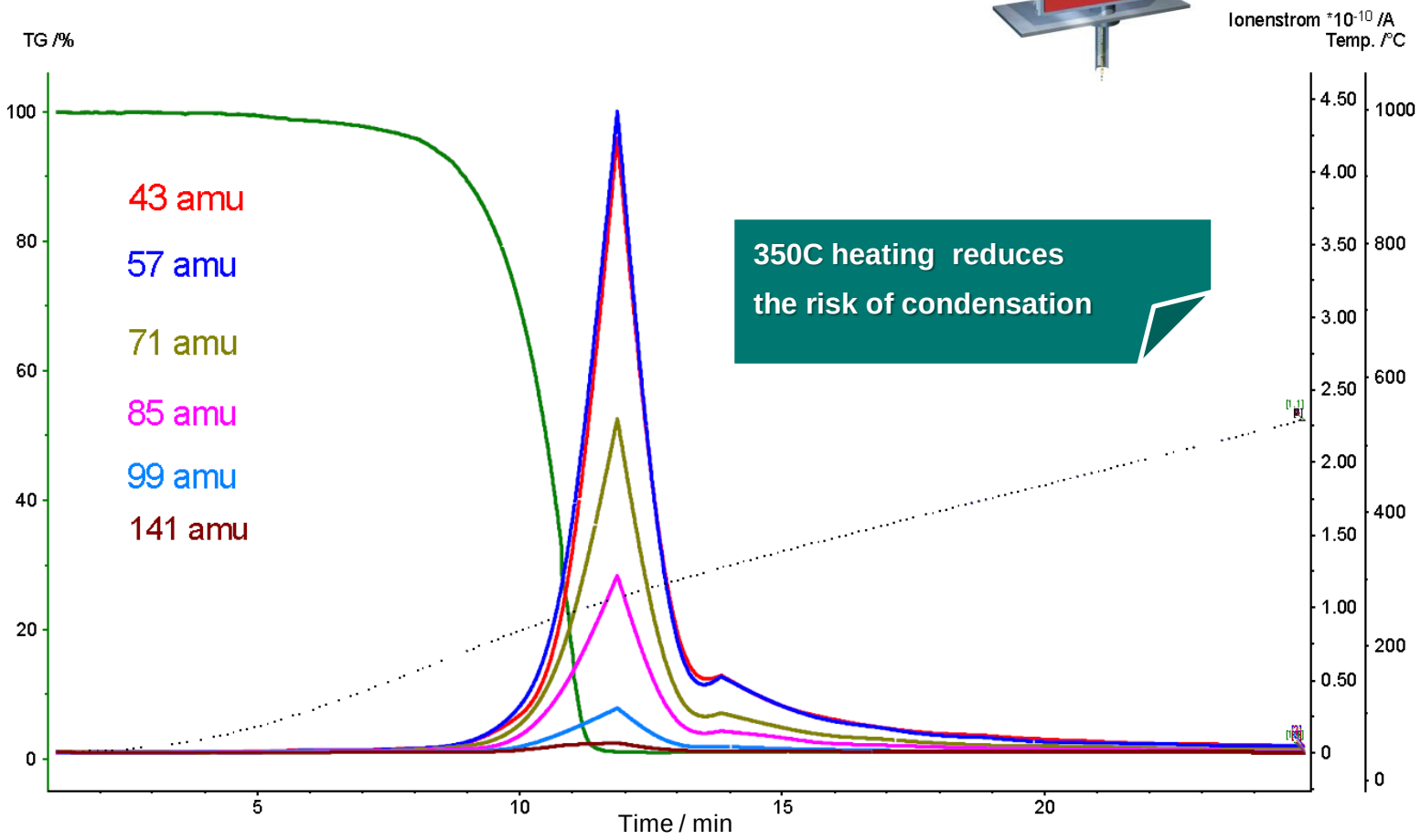
A capillary of small internal diameter (∅ 75 µm) connects the gas outlet at the furnace of the thermobalance with the gas inlet at the mass spectrometer.

The pressure continuously drops from atmospheric pressure down to high vacuum in one step.

Forepump has a high throughput which ensures a faster boot of the system.



QMS Inlet – The effect of 350C Heating



Heptadecane, $C_{17}H_{36}$; b.p.: 301.9°C (Wikipedia)

→ strong MS signal with a good correlation to TGA curve

QMS 403 D *Aëolos*® - Software Analysis

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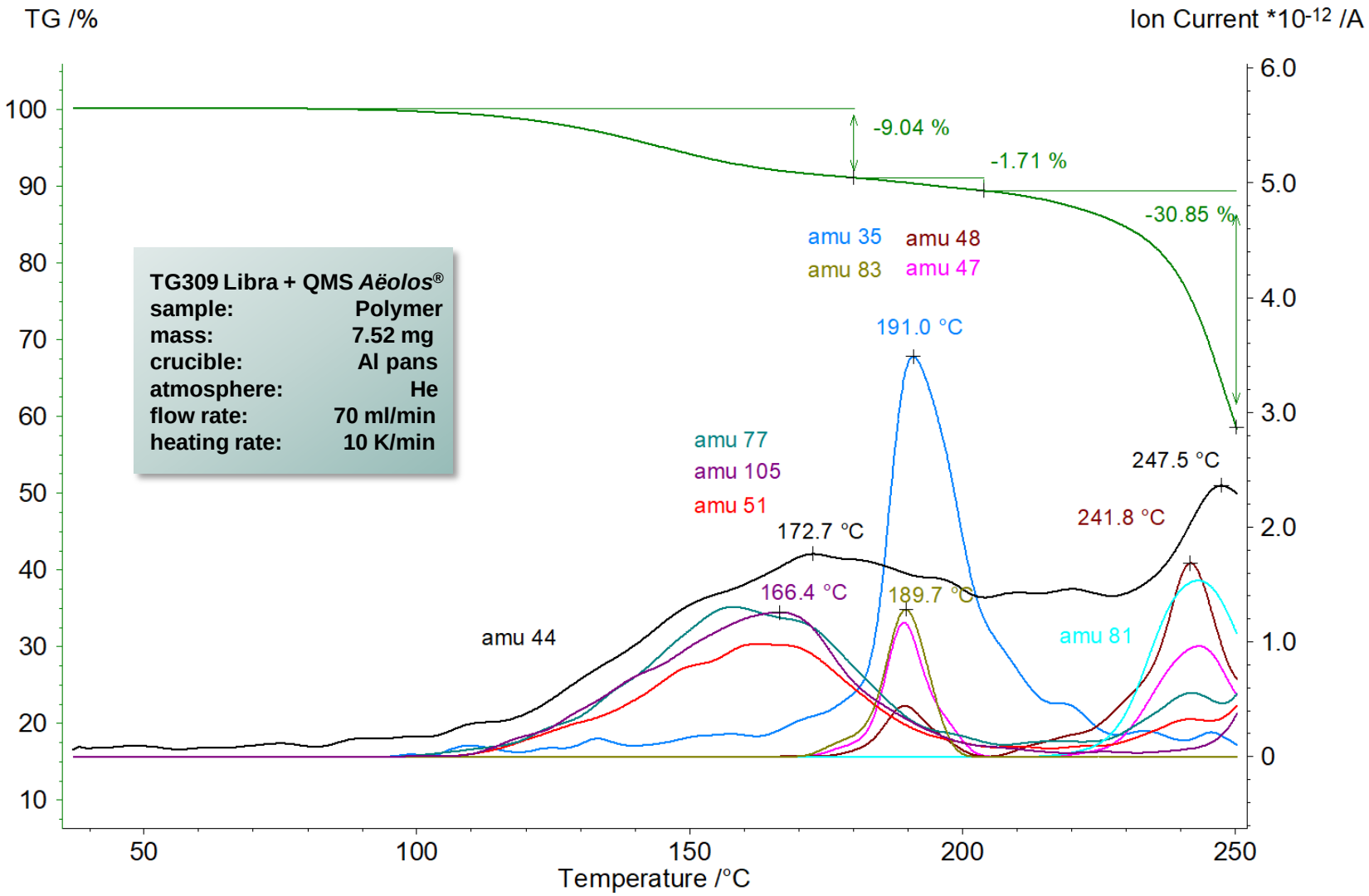


Evaluation of the precisely time and temperature correlated results

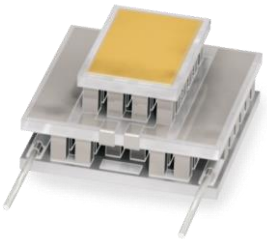
STA 449 *F3 Jupiter*® – Skimmer Coupling up to 1400C

Applications: 1400C transferline

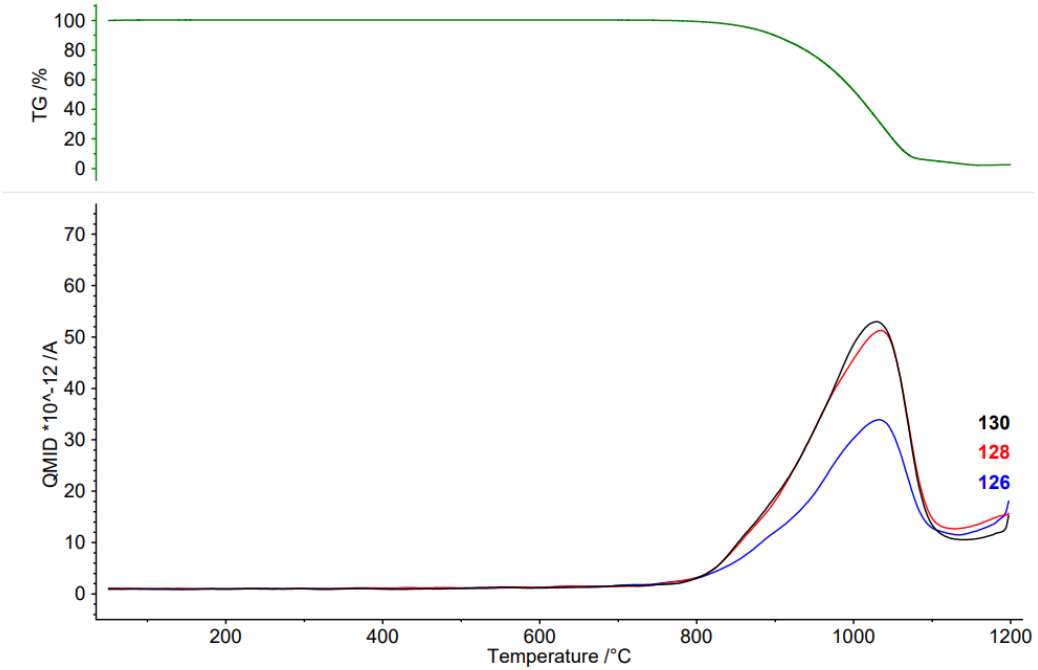
QMS Skimmer is useful if the evolved gases coming from the sample of high boiling point materials such as metal vapors, high boiling point organics and oils.

Lead Tellurie (PbTe)

melting point: 924 °C



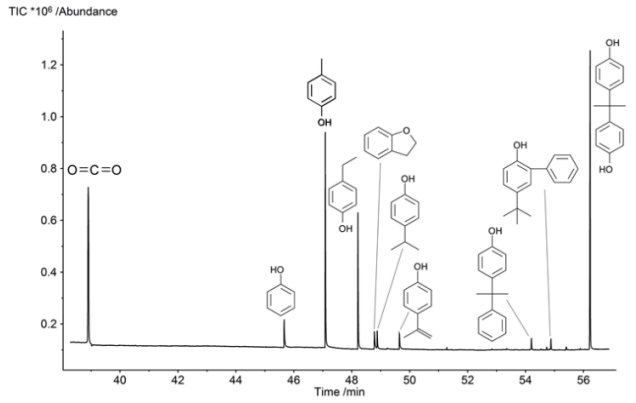
thermoelectric module



(main) isotopes of lead and tellurium: ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{126}Te, ^{128}Te, ^{130}Te

The Coupling Possibilities for TG 309

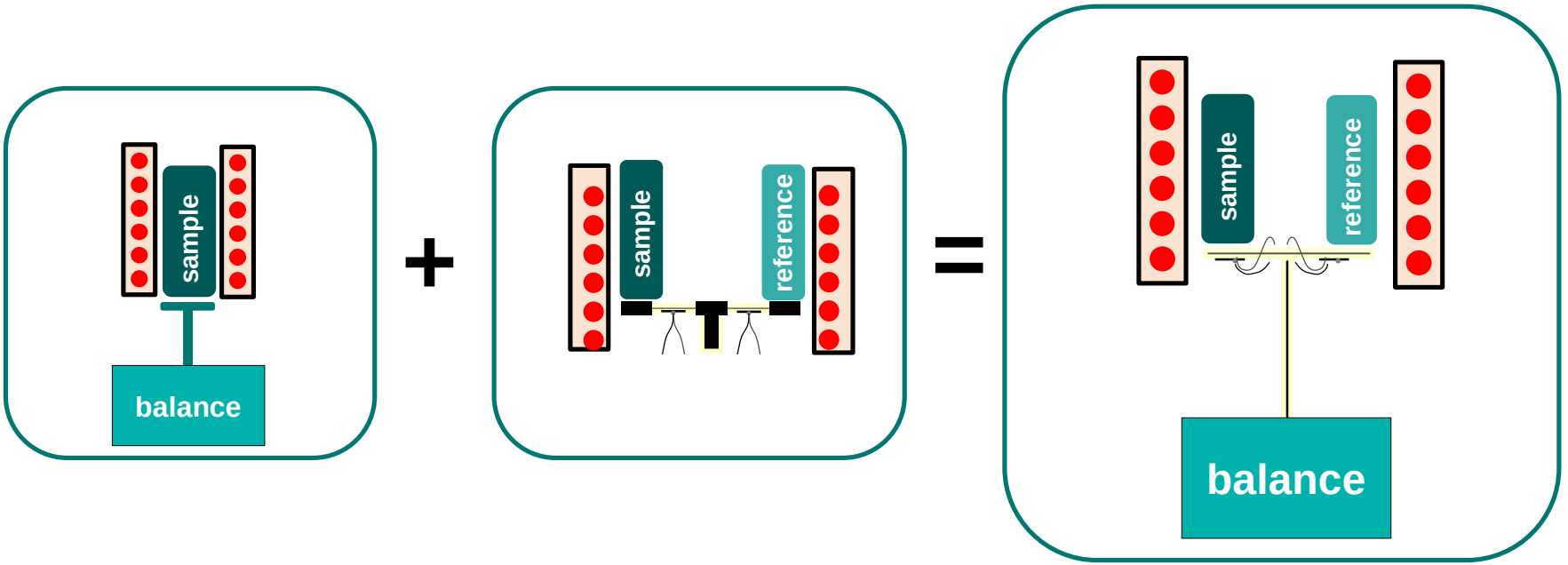
GC-MS coupling



Key Features

- max. 350°C Transfer Temperature for the whole system (including Adapter, Transfer line, Valve Box)
- Dual Loop Valve System for short Injections Intervals*
- Complete Software Integration within Proteus for Gas Sampling and Triggered Start of the TGA-GCMS Solution
- Coupling to the GCMS via standard S/SL-Liquid Injection Inlet (split-splitless inlet) thus no Limitation to certain GC-MS suppliers
- Patented “Event-Mode” - Rate-controlled Trigger for the Injection and start of the GCMS

Simultaneous TGA and DSC Analysis



TGA

DSC

(heat flux DSC to 1500C)

STA

Principle of STA: What is true DSC (not DTA)

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Designation: E967 – 08 (Reapproved 2014)

Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers[1]

6. Apparatus

6.1 Apparatus shall be of either type listed below:

6.1.1 *Differential Scanning Calorimeter (DSC)*, capable of heating a test specimen and a reference material at a controlled rate and of automatically recording the differential heat flow between the sample and the reference material to the required sensitivity and precision.

6.1.2 *Differential Thermal Analyzer (DTA)*, capable of heating a test specimen and reference material at a controlled rate and of automatically recording the differential temperature between sample and reference material both to the required sensitivity and precision.

NETZSCH STA: with 0.025ug resolution, 35gm sample max: -150C to 1000C up to 1600C/2000C/2400C

Flexibility of the Sample Sizes

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TGA-DSC

TGA-DTA

TGA

Large sample mass necessary (only small TG changes, sample inhomogeneous) → **TGA**

Study of energetic effects (with large sample masses) → **TGA-DTA**

Quantitative study of energetic effects and heat capacity → **TGA-DSC**

Summary of Evolved Gas Analysis in Thermal Analysis

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STA/TGA-FTIR Coupling: Yields information on the composition (absorption bands) of the evolved gases (bonding conditions).

⇒ Easy interpretation (spectra data bases) of organic vapors without fragmentation. Examples include paints, adhesives, resins, polymer. coatings and drugs.

⇒ Homonuclear (one element) diatomic molecules (H_2, N_2, O_2, etc.) cannot be detected (due to the zero dipole change in the vibration and rotation of these molecules.)

STA/TGA-MS Coupling: Yields information on the composition (mass numbers of elements and molecules) of the evolved gases.

⇒ High sensitivity

⇒ Fast and easy interpretation of atomic/inorganic vapors and standard gases (H_2, H_2O, CO_2, ...)

⇒ Fragmentation, interpretation of organic molecules sometimes difficult

STA/TGA-GCMS Coupling: Yields information on the composition (mass numbers of elements and molecules) of the evolved gases.

⇒ Very high sensitivity

⇒ Separation of the volatiles using the GC column

⇒ Interpretation of organic vapors significantly improved

⇒ Sometimes slow, special measurement processes need to be used or fast GC systems have to be employed

Thank you for your attention!

NETZSCH

40 Years of Coupling Solutions with Mass Spectrometers

25 Years of Coupling Solutions with FTIR Systems

10 Years of Coupling Solutions with GC-MS Systems

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