Introduction to TGA

Queens University Belfast
16/02/12

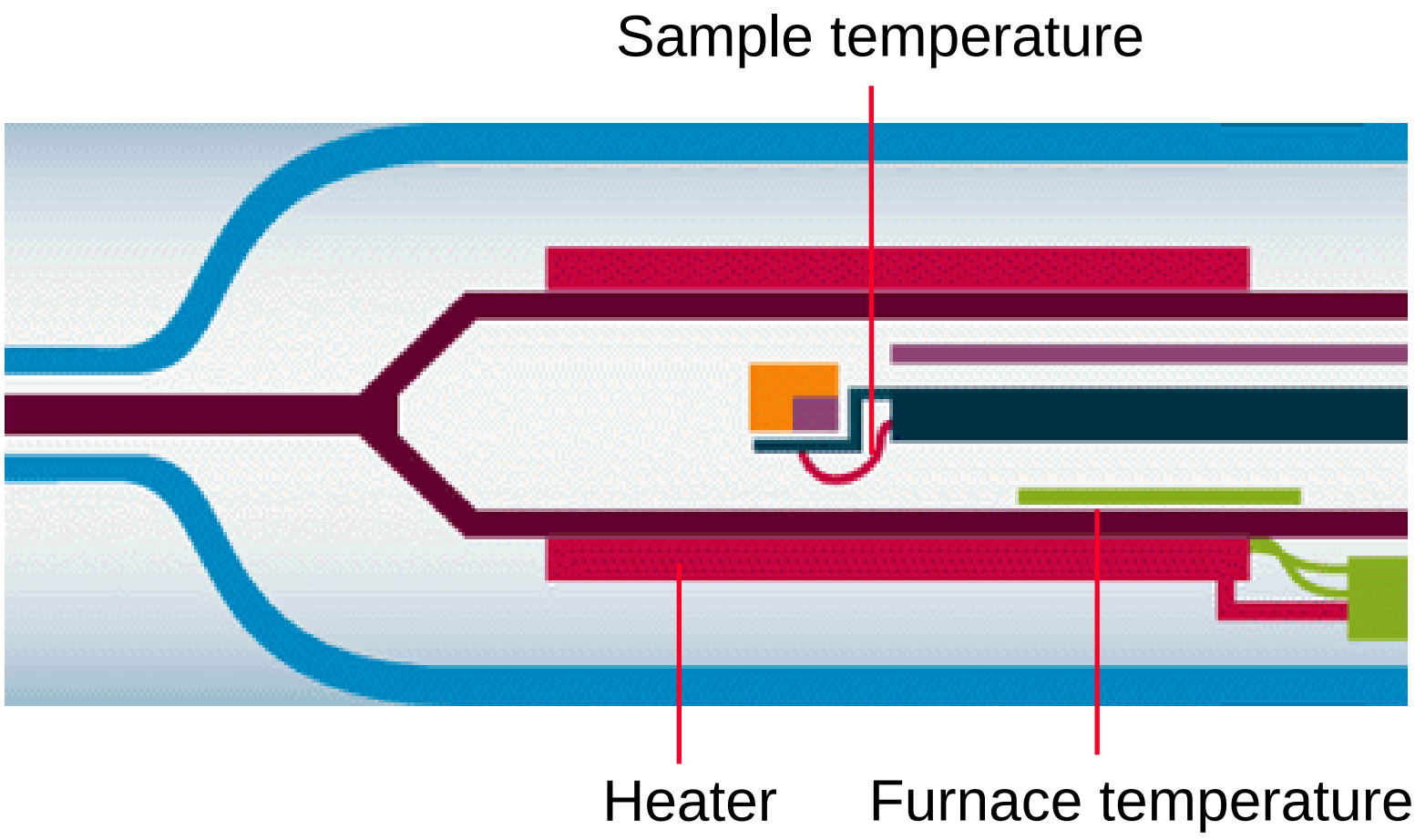
METTLER TOLEDO

Outline

Measuring principle

- TGA/DSC 1
- Sensors
- Balance
- Crucibles
- Gases, gas controllers
- Special points: tightness, oxygen, reproducibility, applications
- Summary

What is TGA?



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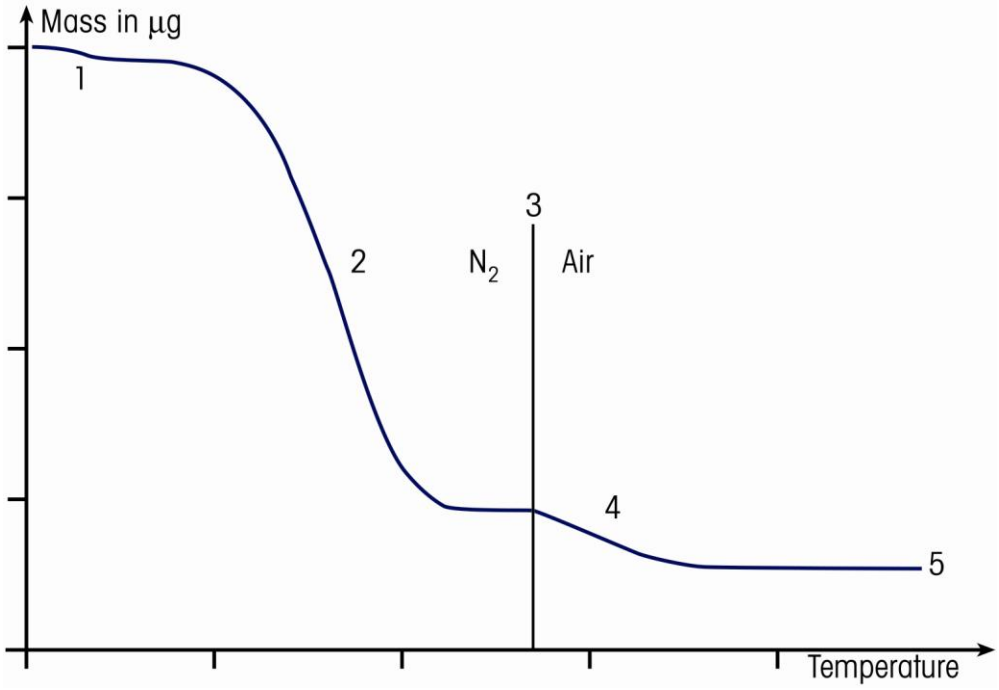
What is TGA?

Thermogravimetric Analysis (TGA) measures the mass of a sample as it is submitted to a selected temperature program in a defined atmosphere.



A typical TGA curve of a polymer shows the following mass loss steps:

1 volatiles (moisture, solvents, monomers)

2 polymer decomposition

3 change of atmosphere

4 burning step of carbon (carbon black or carbon fibers)

5 residue (ash, fillers, glass fibers)

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What is TGA: Measuring principle

- Sample is subjected to a temperature program usually heated at a constant rate.
- Mass change of the sample is measured by a highly sensitive balance.
- Measurement is carried out in a well-defined atmosphere (inert or reactive).
- (S)DTA and DSC signals allow determination of calorimetric effects (e.g. melting).
- Simultaneous evolved gas analysis is possible; in this case, the furnace outlet is connected to a gas analyzer (MS, FTIR, GC...).
- Environmental control can be achieved by connecting a humidity generator.

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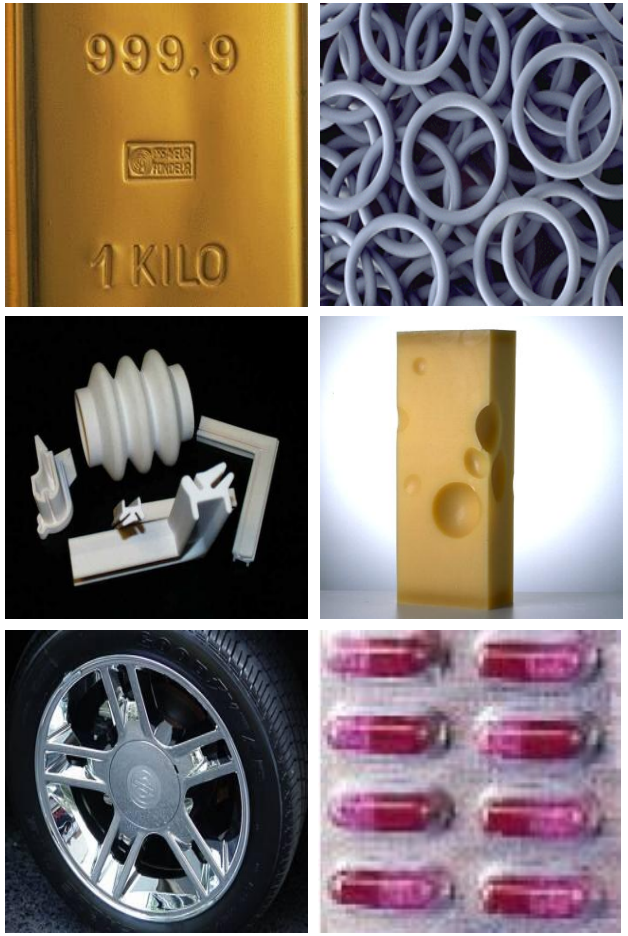
What is TGA?

Properties and Applications

- Composition (e.g. carbon black, filler)
- Thermal stability / decomposition
- Stoichiometry of reactions
- Kinetics of reactions
- Desorption / adsorption processes
- Evaporation behavior
- Influence of reactive gas
- Evolved gas analysis (MS, FTIR)



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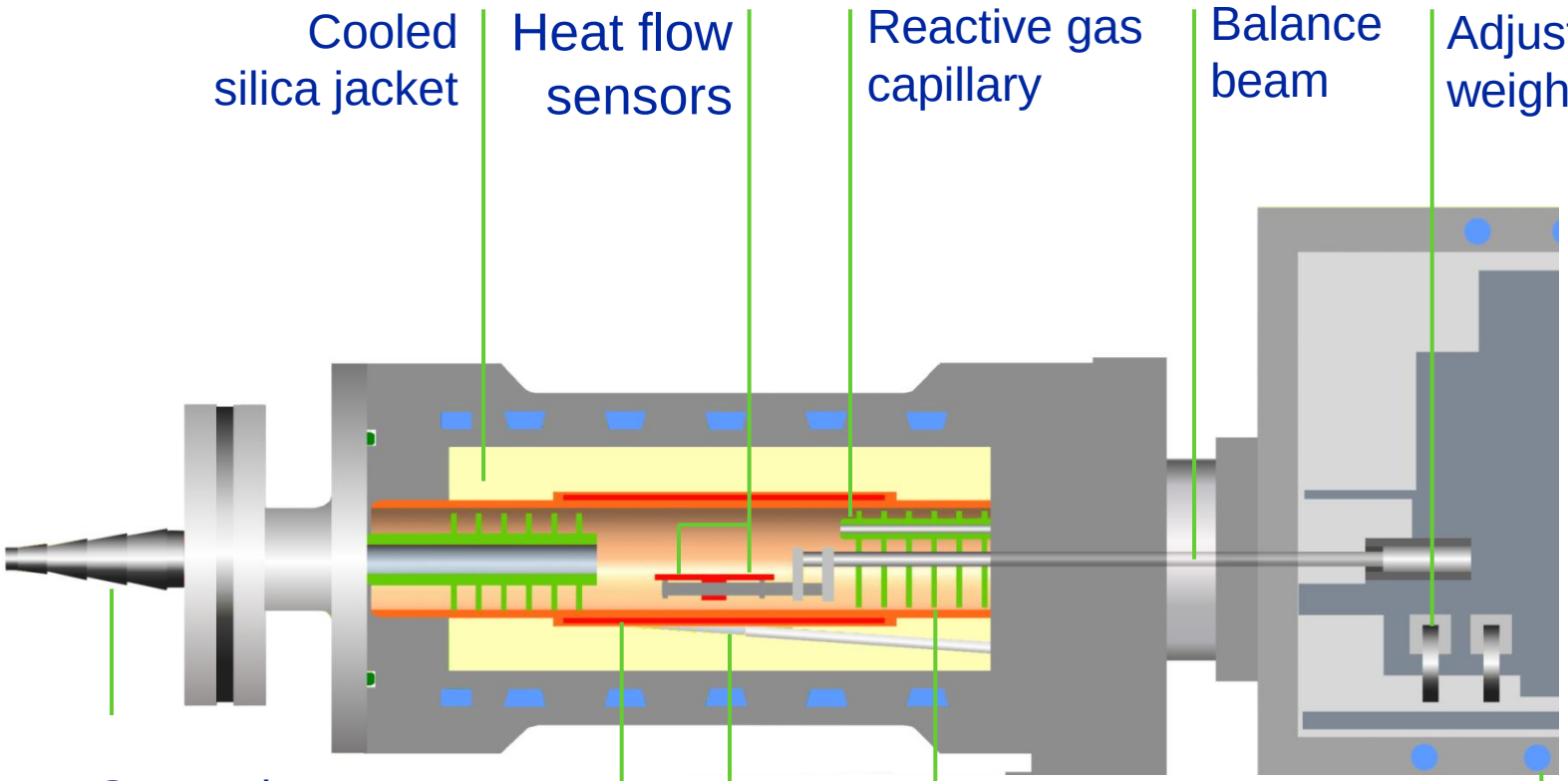
TGA/DSC 1: Furnace Cross Section



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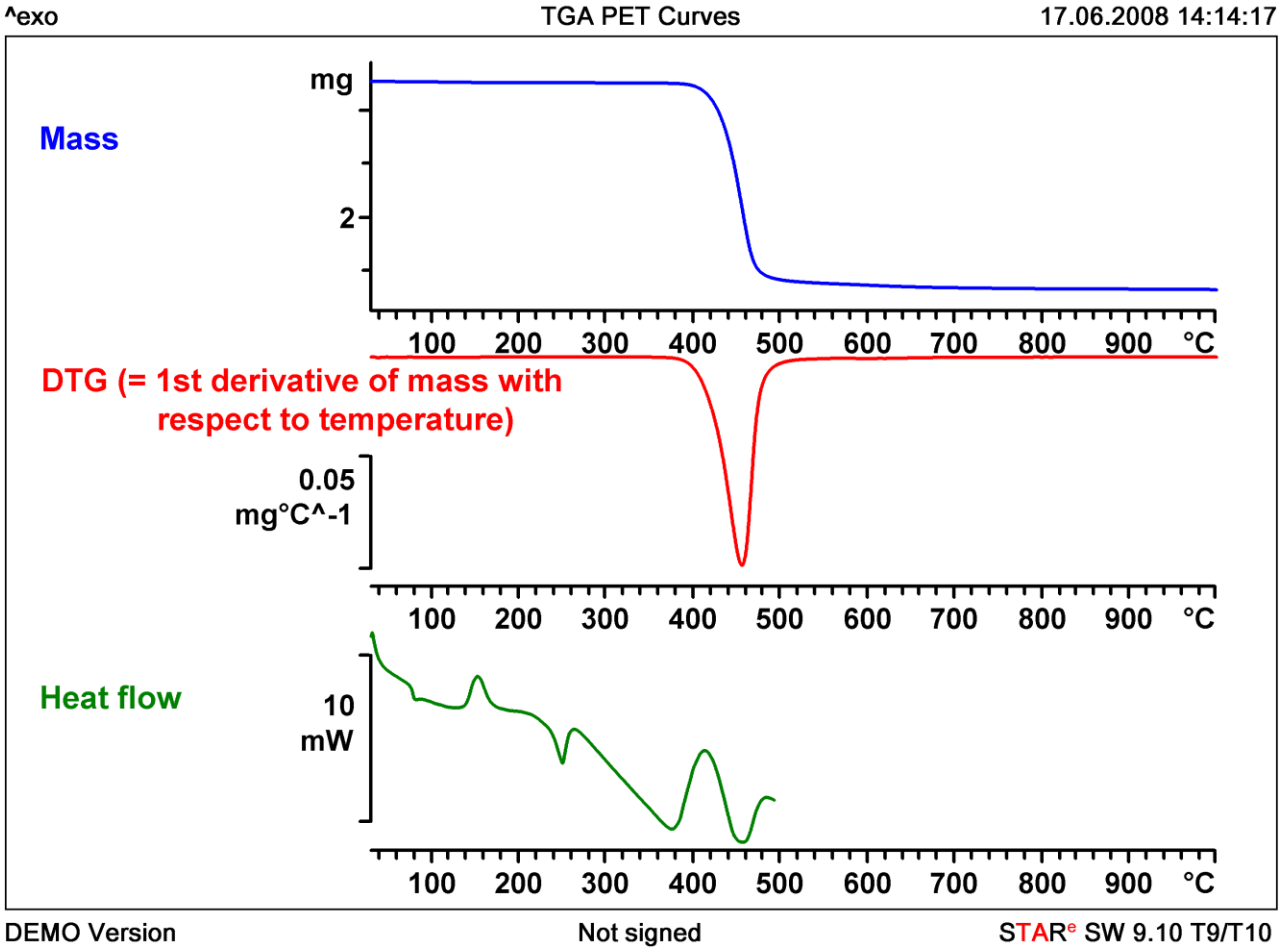
TGA/DSC 1

TGA/DSC 1 is expanded to DSC sensor

Signal curves:



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TGA/DSC 1

TGA/DSC 1 Features

- Small Furnace
- RT ... 1100 °C
- SDTA

- Large Furnace
- RT ... 1100 °C
- SDTA, DTA

- Large Furnace
- RT ... 1600 °C
- SDTA, DTA, DSC

The TGA/DSC 1 is available in three modular versions.

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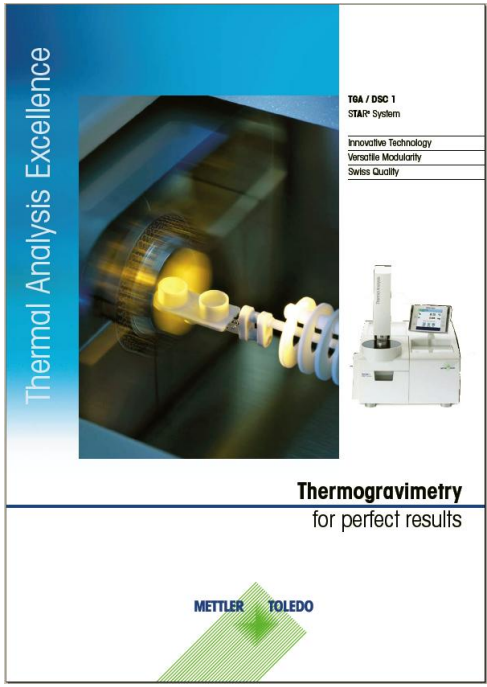
TGA/DSC 1

Specifications

Balance data	Measurement range	Resolution
MX1 / MX5	≤ 1g / ≤ 5g	1.0 µg
UMX1 / UMX5	≤ 1g / ≤ 5g	0.1 µg
Internal ring weights	2	
Blank curve reproducibility	better than ± 10 µg over the whole temperature range	

Calorimetric data				
Sensor data (typical values)	**Sensor type**	**SDTA**	**DTA**	**DSC**
	Surface material	platinum	platinum	ceramic
	Number of thermocouples	1	2	6
	Signal time constant at 900 °C	15 s	14 s	14 s
	sensitivity	0.5 mW	0.2 mW	0.1 mW
	Furnace temperature resolution	0.005 K	0.0001 K	0.00003 K
Enthalpy reproducibility (standard deviation)		better than 5 %		

Sampling	
Sampling rate	maximum 10 values/second



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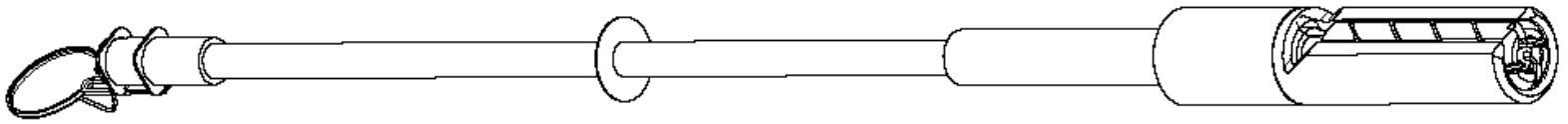
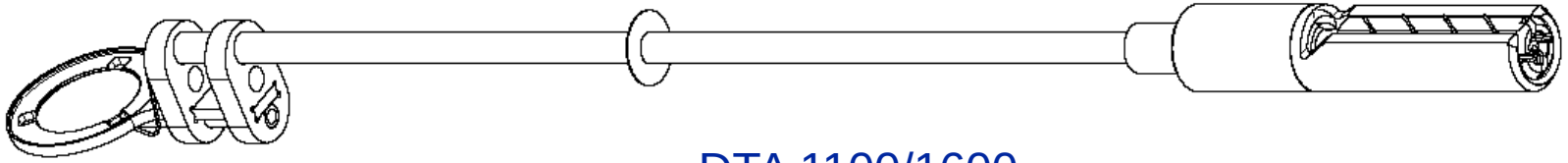
DSC-Sensors

SDTA SF 1100

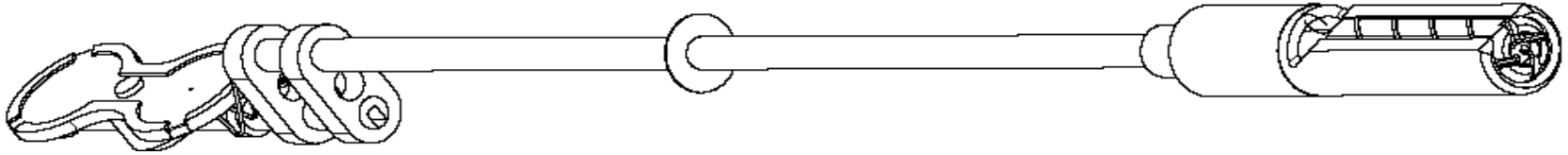


SDTA LF 1100

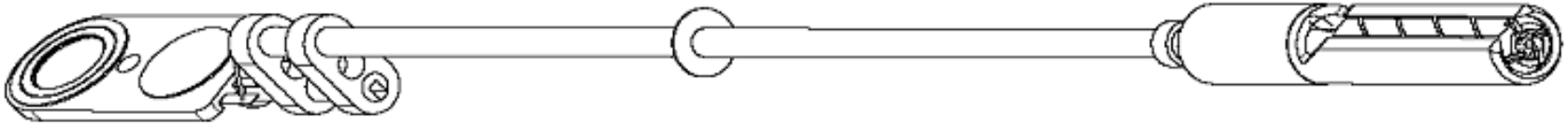
SDTA LF 1600



DTA 1100/1600



DSC 1100/1600



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Sensors: TGA/DSC 1

Difference between DSC, DTA and SDTA®

- **DSC** measures the heat flow in mW whereas the DTA/SDTA supplies the temperature difference between the sample and the reference.

- **DTA/SDTA®** is mostly used in combination with TGA or TMA instruments and provides information that is otherwise not revealed by these techniques (e.g. solid-solid phase transitions). DTA instruments are generally less sensitive than dedicated DSC instruments.

DSC offers increased sensitivity.

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Which pan‘s are possible with which sensor

Sensor	Possible pans
SDTA SF 1100 (SF SDTA FRS2)	All up to 100 ul
SDTA LF 1100 (LF SDTA FRS2)	All
SDTA LF 1600 (HT SDTA FRS2)	All
DTA LF 1100/1600 (HT DTA FRS2)	All up to 150 ul
DSC LF 1100/1600 (HT DSC HSS2)	All up to 150 ul

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Sensors: Comparison

	SDTA	DTA	DSC
SDTA		• Slightly less sensitive • Longer signal time constant (especially at low temperatures) • More noise • Less buoyancy	• Slightly less sensitive • Longer signal time constant (especially at lower temperatures) • More noise • Sample holder is not “inert” (platinum) • Less buoyancy
DTA	• Slightly more sensitive • Shorter signal time constant (especially at low temperatures) • Less noise • More buoyany		• Slightly less sensitive • Slighly more noise • Sample holder is not “inert” (platinum)
DSC	• Slightly more sensitive • Shorter signal time constant (especially at low temperatures) • Less noise • „Inert“ sample holder (alumina) • more buoyancy effects	• Slightly more sensitive • Slightly less noise • „Inert“ sample holder (alumina)	

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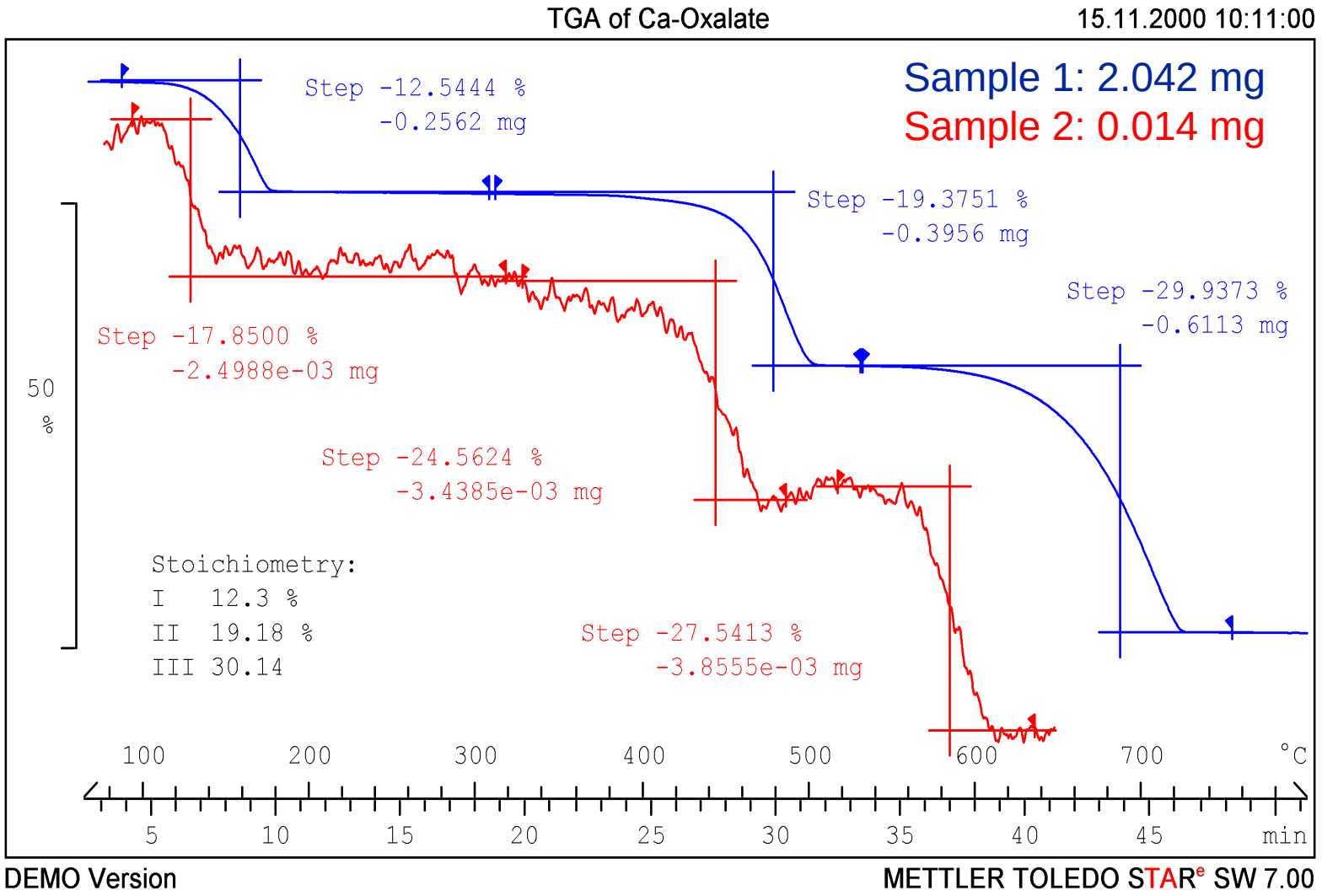
Balance: Sensitivity



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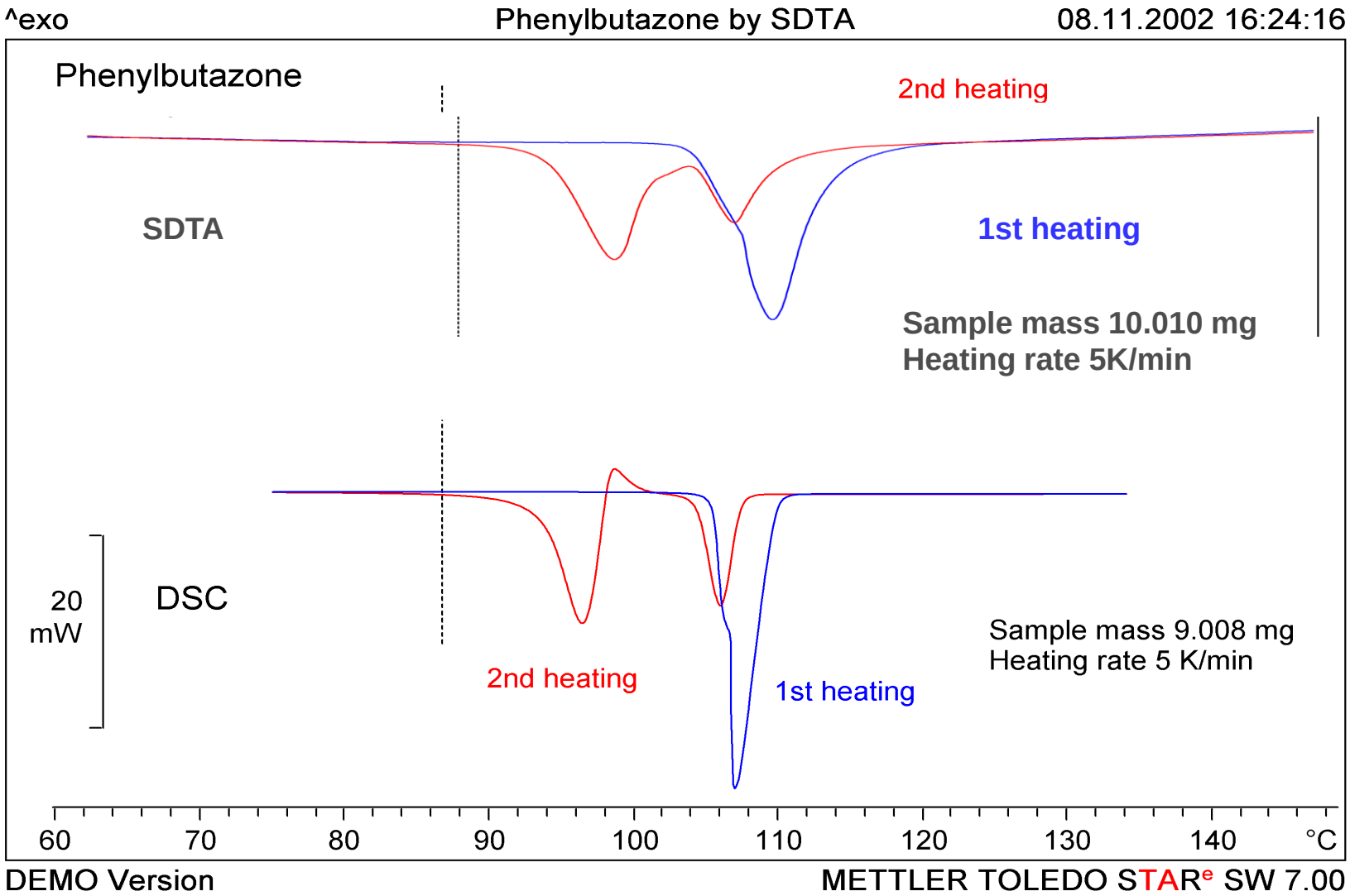
Sensors: Polymorphism by SDTA



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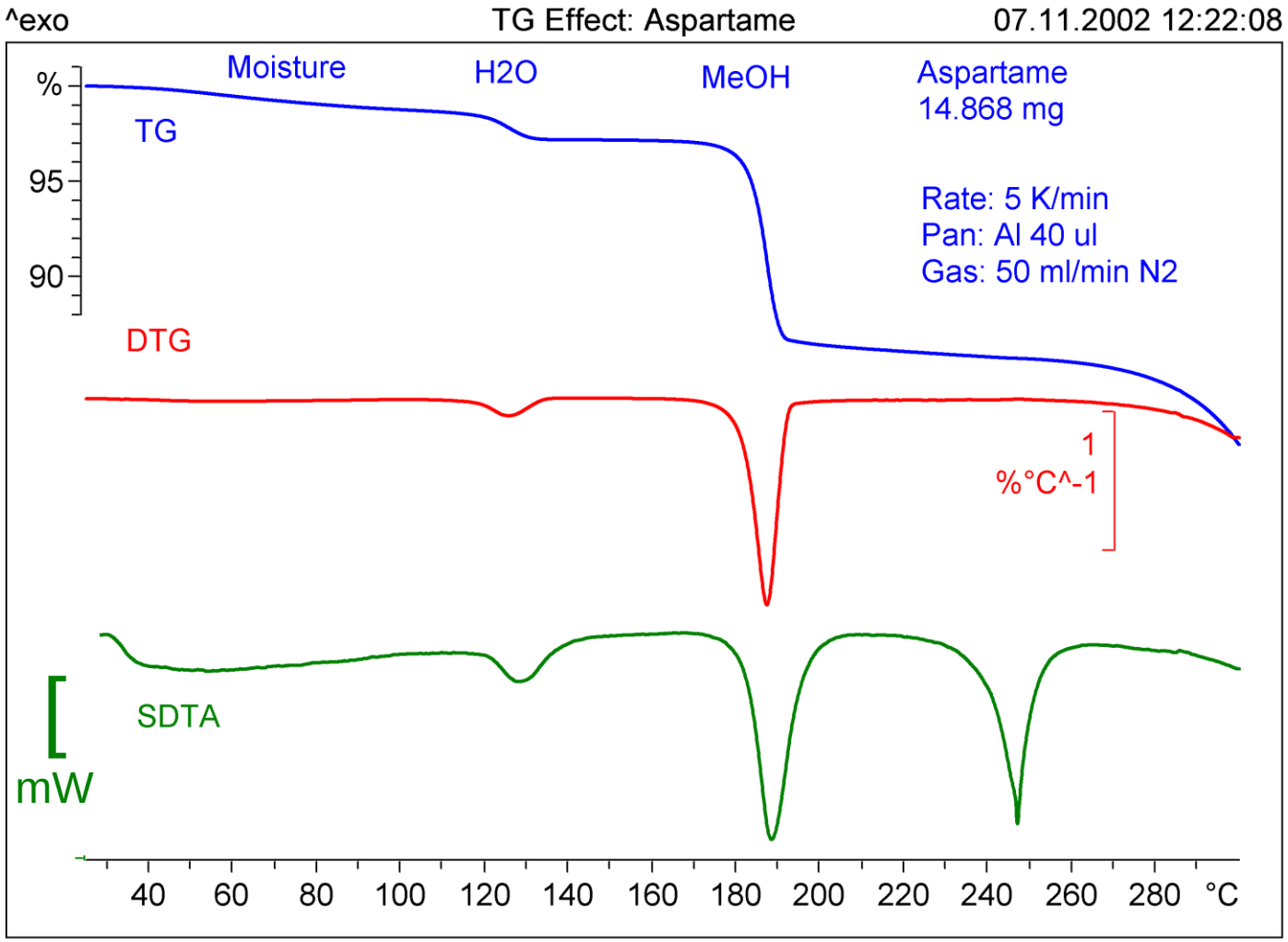
Sensors: Aspartame by SDTA



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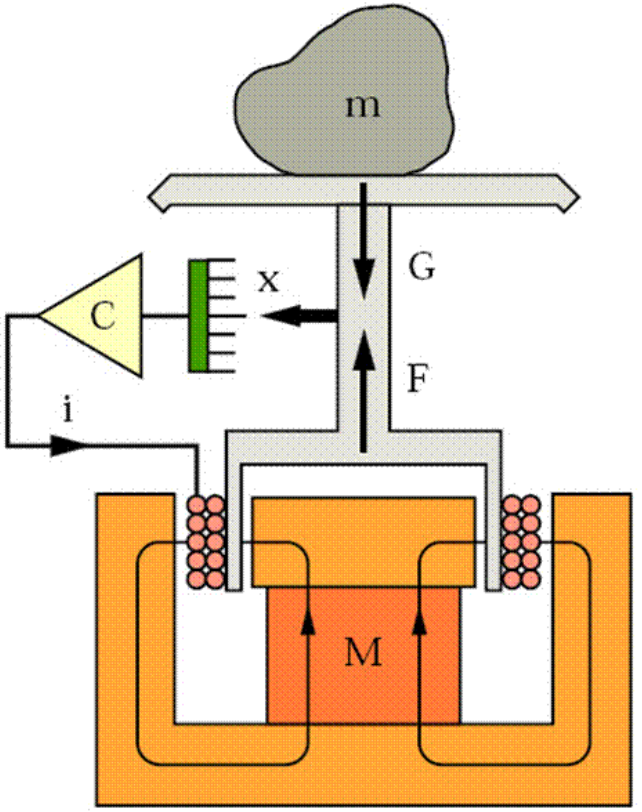
Balance: Principle

Basic idea of the compensation

The most simple balance cell (not really working) would consist of the sample holder and a coil that generates an electromechanical force.

The problem is that the sample holder is not guided. In reality it would bend to the side and result in friction.

➔ wrong result because the force has to compensate the gravimetric force as well as the friction.



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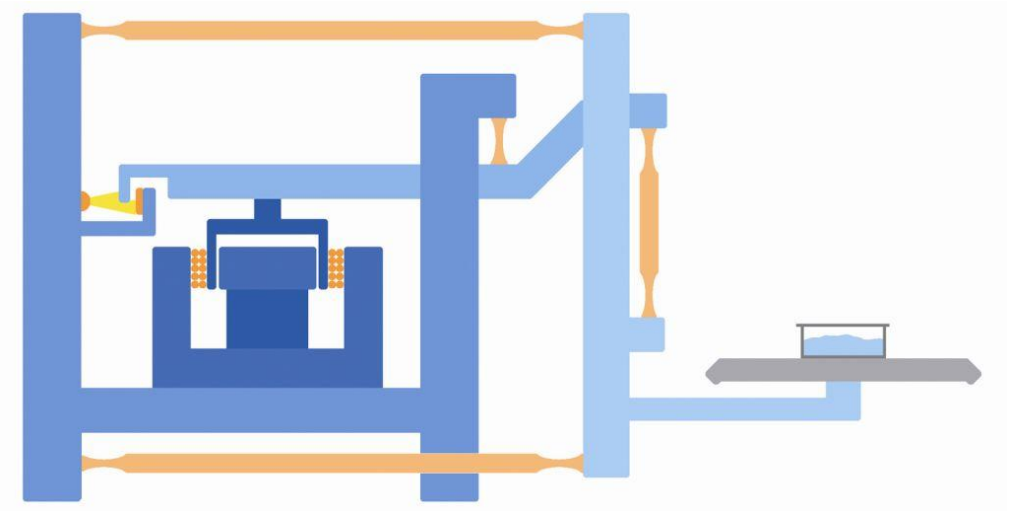
Balance

Parallel Guidance for Unsurpassed Accuracy

- Parallel guidance: the balance ensures that the position of the sample does not influence the weight measurement. If the position of the sample changes during melting, no change in weight occurs.



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Balance

METTLER TOLEDO Balances – Uniqueness in all Respects

- Ultra-micro balance covers the whole weighing range
- Can measure up to 50 million resolution points continuously
- Weight changes of a 5-g sample are determined to 0.1 µg
- Automatic internal adjustment without external manipulation
- Samples can be weighed-in semi or fully automatically

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Balance: Types

- MX1: max. load 1 g; resolution 1 µg
- MX5: max. load 5 g; resolution 1 µg
- UMX1: max. load 1 g; resolution 0.1 µg
- UMX5: max. load 5 g; resolution 0.1 µg

- All balances fit in all versions of the TGA and deliver the specified resolution over the entire measurement range.

Ultra-microgram resolution over the whole measurement range

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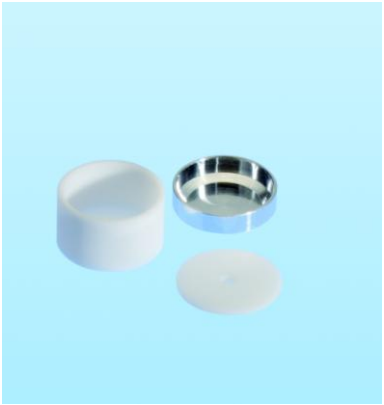
Crucibles

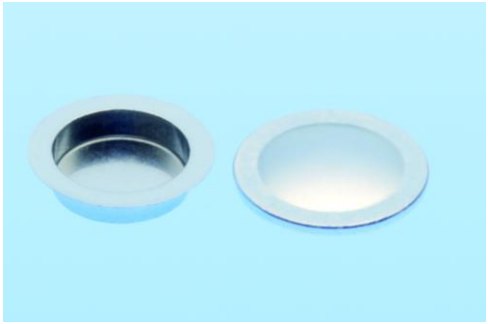
Alumina crucibles

- Alumina crucibles with lids: 30 µl, 70 µl,150 µl and 900 µl
- Special aluminum lids to prevent contamination and evaporation before the measurement
- Normally used in TGA, reusable



Aluminum crucibles

- Aluminum crucibles with lids: 20 µl, 40 µl and 150 µl
- Melting point: 660 °C!
- Better DSC signal



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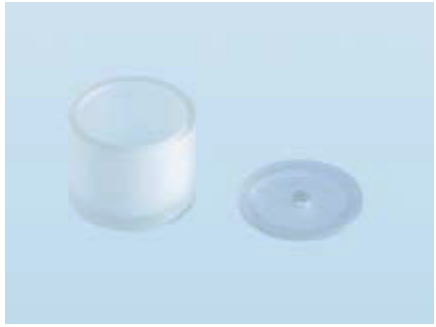
Crucibles

Platinum crucibles

- Platinum crucibles with lids: 30 µl, 70 µl,150 µl
- Reusable
- Better DSC-signal
- Attention: sticks on DTA-sensor above 1600 °C use sapphire disk
- C is Pt poison
- Pt can form alloys!!

Sapphire crucibles

- Sapphire crucibles with lids: 70 µl
- For melting metals (FE, Ni)
- More resistant than alumina



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Gases: Method gas and cell gas

Cell gas (protective gas TGA, TMA, or dry gas: DSC)

- defined in the module (install window)
- flows also outside of the experiment (continuous flow)
- cell gas and method gas are mixed in the furnace

Method gas (reactive gas and purge gas)

- defined in the method and switched on only during the experiment
- no mixing of different method gases possible

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Gases

- **Protective gas:** - protects the balance (or TMA-cell) from reaction products and humidity
  - any dry gas, flow rate 20 ml/min
  - required during operation
- **Reactive gas:** - flows right above the sample, e.g. O_2, air,...
  - flow rate typically 50 ml/min
- **Purge gas:** - purges the reaction products
  - usually N_2 or Air, typical flow rate 50 ml/min
  - usually not needed
- **Vacuum:** - dynamic vacuum
  - minimum pressure ≈ 10 mbar
- **Furnace purge gas:** - for fast cooling (He) or to maintain inert conditions (N_2)

Tightness check of the instrument: flow should withstand 10 to 20 mbar (water column check)

Remanent O_2 concentration typically 350 ppm (depends on the conditions !)

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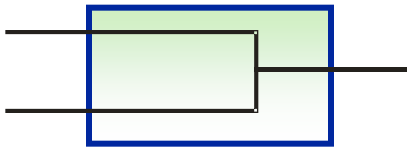
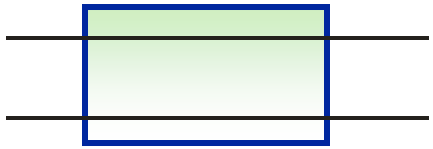
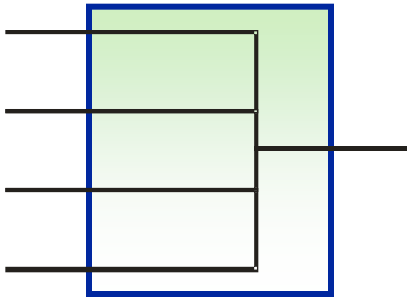
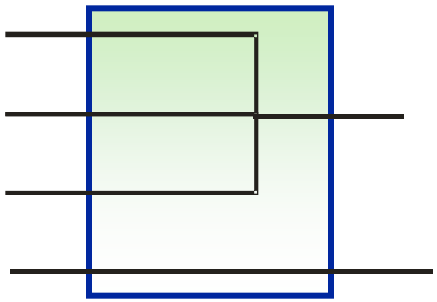
Gas controllers

GC 10	2 in 1 out
GC 20	2 in 2 out
GC 100	4 in 1 out
GC 200	4 in 2 out









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Gas controllers: Specifications

	GC 10 / GC 20	GC 100 / GC 200
Numbers of Gases	2 2 (1)	4 4 (3)
Mode	gas flow monitoring	gas flow controller
Gas flow range (N_2)	0…200 mL/min, manual setting	0…200 mL/min, setting by SW
Accuracy (N_2)	5 mL/min	2% min. 2 mL/min
Input pressure range	1…1.8 bar	1…8 bar (optimal 2-3)
Settling time		< 0.5 s to 90%

Gases: N_2, Air, O_2, CO_2, CO, Ar, inerted hydrogen (4% H_2, 96% Ar)

He: limited accuracy (recommended GC 100/200)

Vacuum: GC 100/200 (not fully tight); forbidden: GC 10/20

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Tightness of the TGA

Oxygen in the TGA: measure the burning rate of active coal using nitrogen

The following method is recommended:

- Dynamic segment from 50 to 800 °C with 50 K/min, 20 ml/min protective and 50 ml/min reactive gas (both N_2)
- Isothermal segment at 800 °C during 15 min, 20 ml/min protective and 50 ml/min reactive gas

At the end of the measurement the burning rate should be less than 10 µg/min

How to conclude the partial oxygen pressure ?

Assumption: every oxygen molecule reacts with carbon, burning rate of carbon = 10 µg/min, nitrogen flow 70 ml/min = 3.125 mmol/min

- 10 µg C/min = 0.83 µmol/min $\Rightarrow$ 266 ppm O_2 in the inert gas stream
- 0.83 µmol O_2/min = 18.6 µl O_2 $\Rightarrow$ leaking rate $\approx$ 90 µl air/min

N.B. The ppm amount of oxygen as calculated above decreases with increasing inert gas flow rate. Quality of N_2 is also important.

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How to reduce the remaining oxygen?

- Purge all gas inlets with inert gas during several minutes
- Check tubings to the instrument and the sealing ring which seals the furnace towards the balance housing. If needed clean the sealing ring. If the sealing ring has any cracks, it has to be replaced.
- Check the tightness of the instrument (water column check)
- Use a long tube at the exit of the furnace (prevents air diffusion into the furnace)
- Connect a tube of about 2 m length to the exit of the furnace and put the other end some 20 cm into a water column; a slight overpressure is generated, preventing air to enter into the furnace. Make sure that the bubbling does not manifest on the TGA curve. Otherwise use a longer tube.
- Use the possibility to purge the furnace jacket with a different gas.

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Applications

- Temperature and course of decomposition
- Pyrolysis in inert gas
- Burning profiles in oxidative atmosphere
- Curie transition
- Adsorption/Desorption
- Content analysis (moisture, volatiles, ash, fillers)

Among others analysis of

- coal
- hydrates
- binders
- explosives
- organic substances
- rubber
- carbonates
- polymers
- minerals

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Features	Benefits
High Resolution	Ultra-microgram resolution over the whole measurement range
Efficient Automation	Reliable sample robot for high throughput
Wide measurement range	Measures small and large sample masses
Broad temperature scale	Analyze samples from ambient to 1600 °C
METTLER TOLEDO ultra-micro balance	Rely on the balance technology leader
DSC heat flow measurement	For simultaneous detection of thermal events
Gastight cell	Ensures a properly defined environment
Hyphenated techniques	Evolved gas analysis using MS and FTIR
Modular design	Tailor-made solutions for current & future needs

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Summary

TGA:

- Thermogravimetric Analysis (TGA) measures the mass of a sample as it is submitted to a selected temperature program in a defined atmosphere.

TGA/DSC 1:

- 3 modular versions
- 4 various balances possible
- SDTA, DTA or DSC sensor
- Variety of crucibles (most common: alumina)
- 4 different gas controllers available

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Appendix

Most important applications

- Decomposition of materials
- Pyrolisis in inert gas
- Burning profiles in oxidative atmosphere
- Curie transition
- Desorption/Adsorption
- Content analysis (moisture, volatiles, ash, fillers)

- Among others analysis of
- Coal, hydrates, binders, explosives, rubber, carbonates, polymers, minerals

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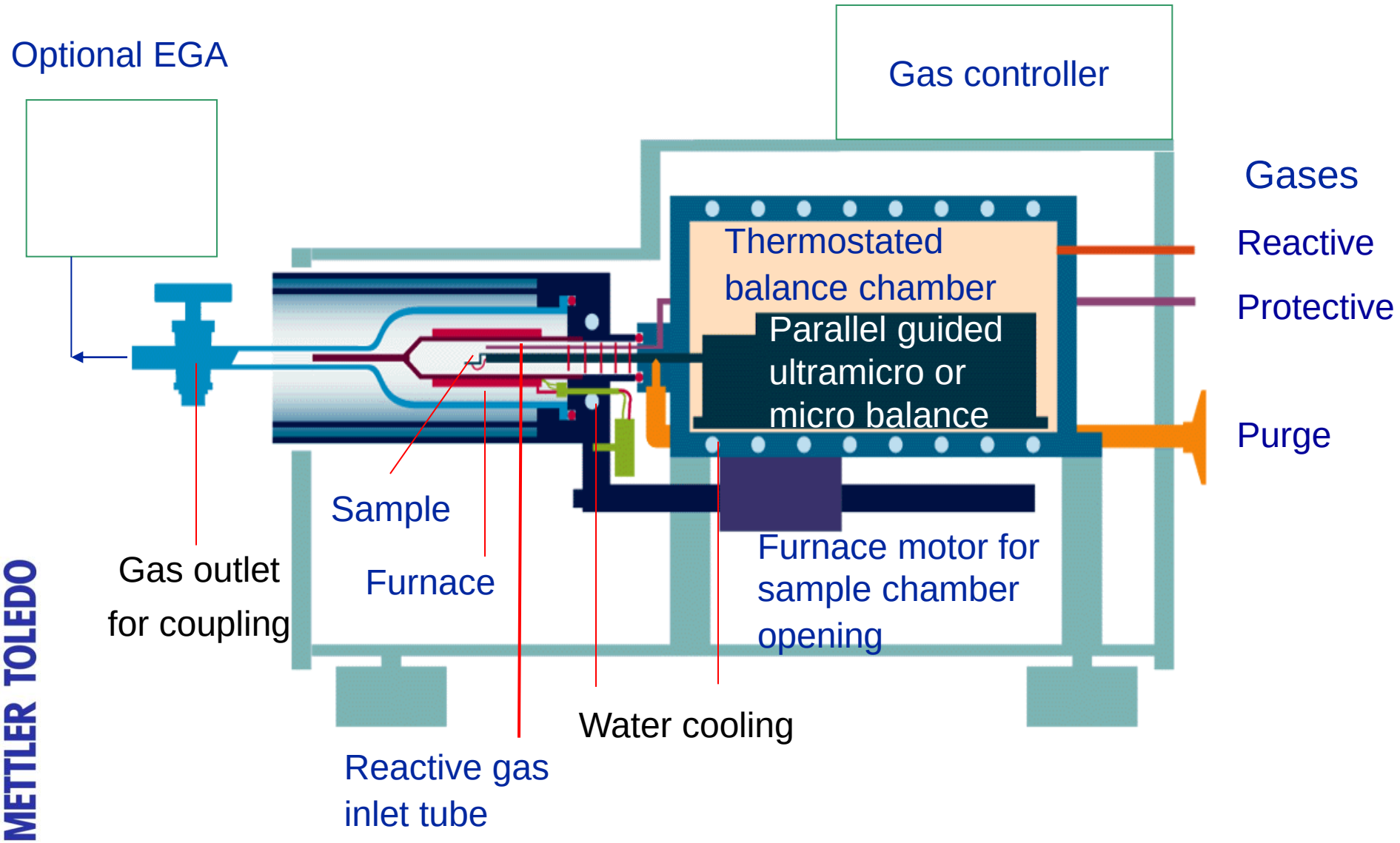
Measuring principle: Scheme of a TGA



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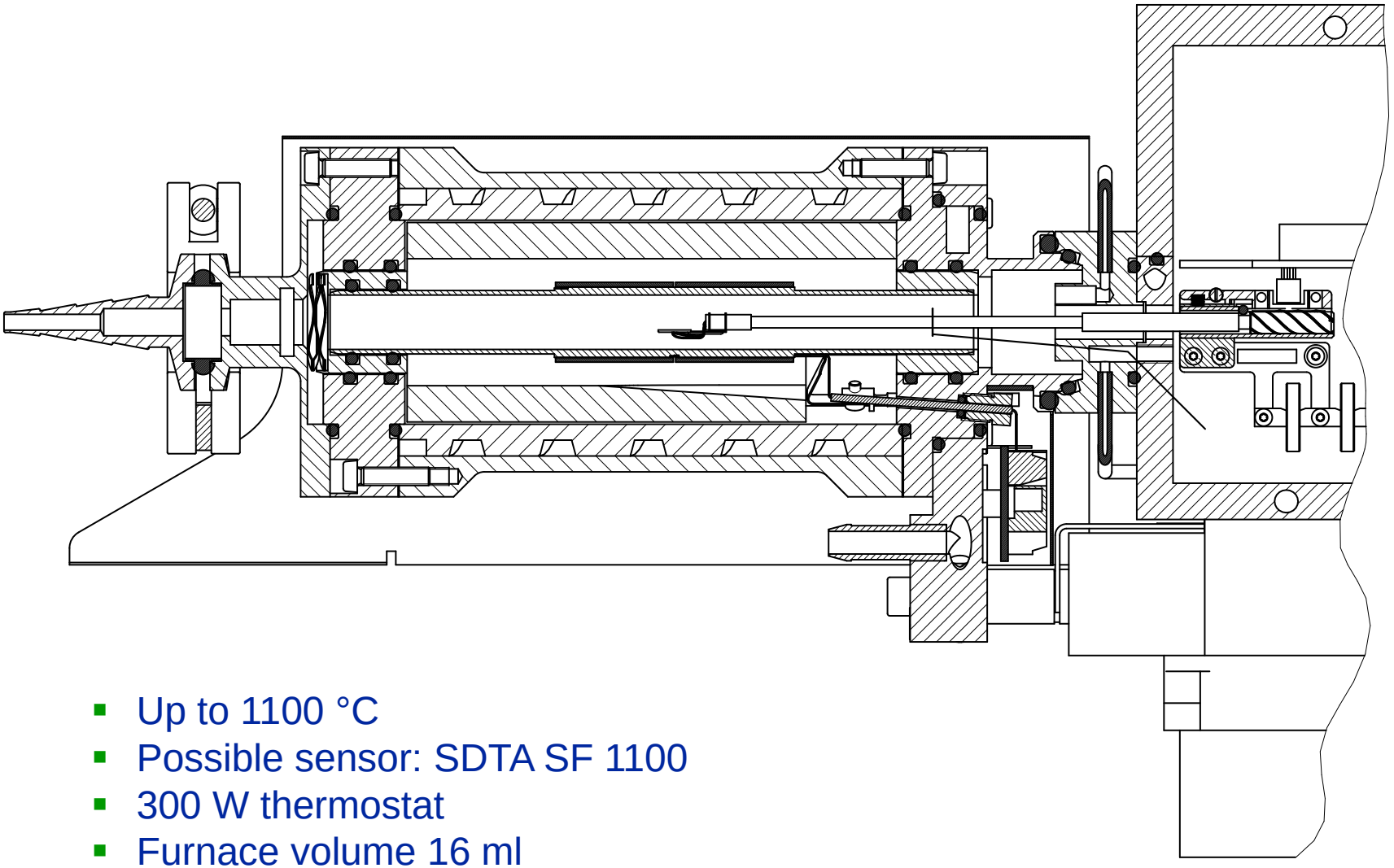
TGA/DSC 1: Small furnace, 1100 °C



- Up to 1100 °C
- Possible sensor: SDTA SF 1100
- 300 W thermostat
- Furnace volume 16 ml

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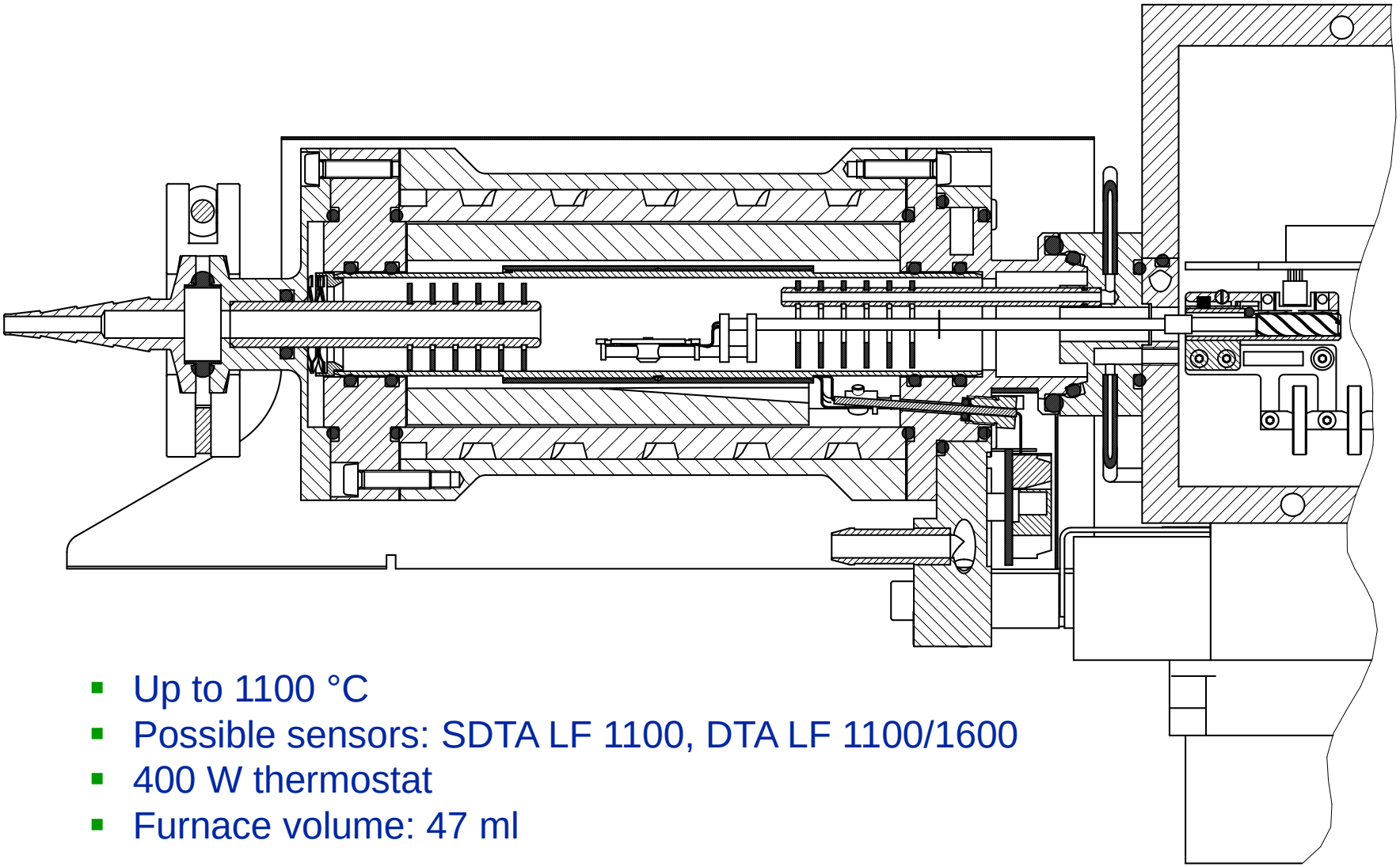
TGA/DSC 1: Large furnace, 1100 °C



- Up to 1100 °C
- Possible sensors: SDTA LF 1100, DTA LF 1100/1600
- 400 W thermostat
- Furnace volume: 47 ml

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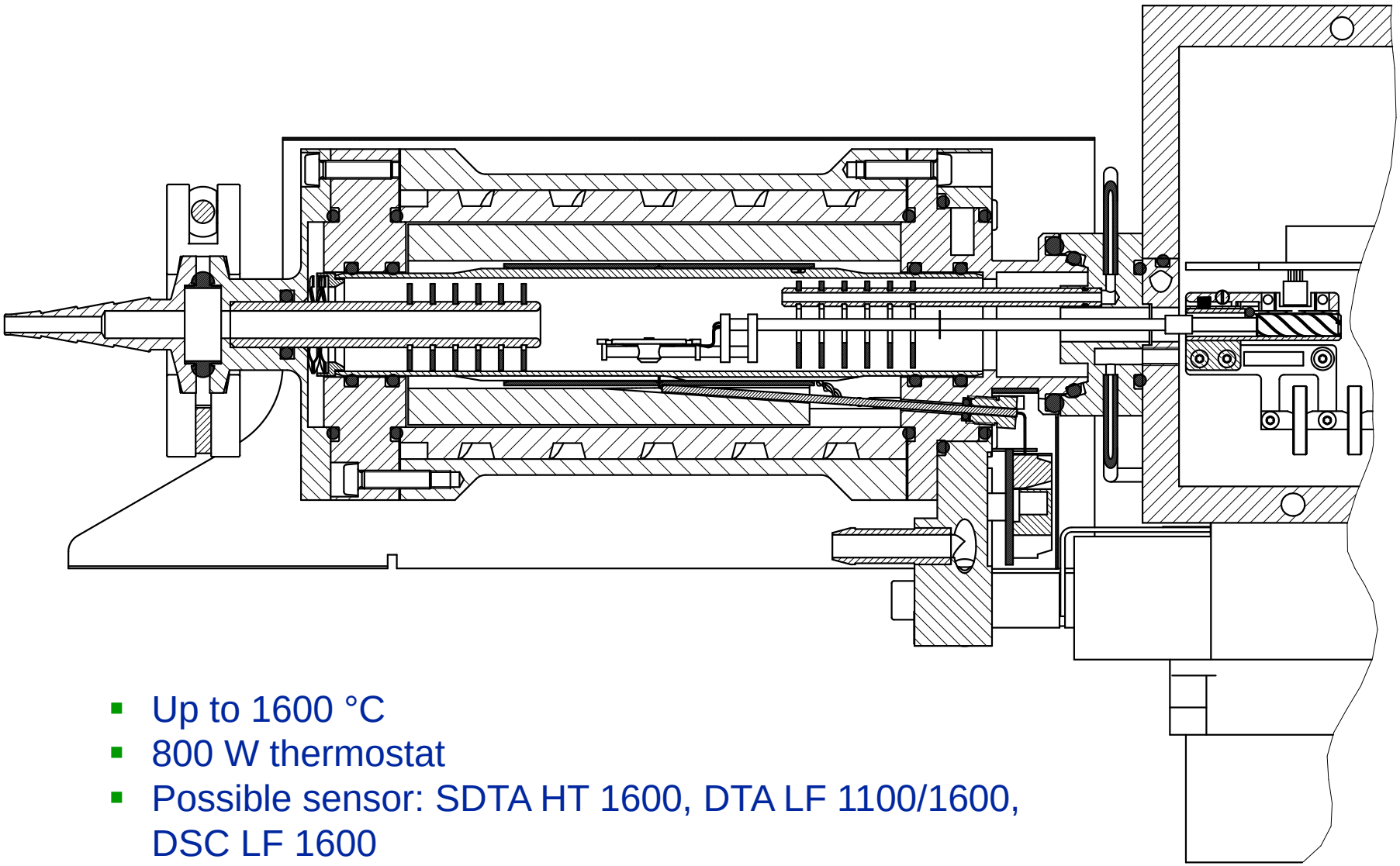
TGA/DSC 1: Large furnace, 1600 °C



- Up to 1600 °C
- 800 W thermostat
- Possible sensor: SDTA HT 1600, DTA LF 1100/1600, DSC LF 1600
- Furnace volume: 47 ml

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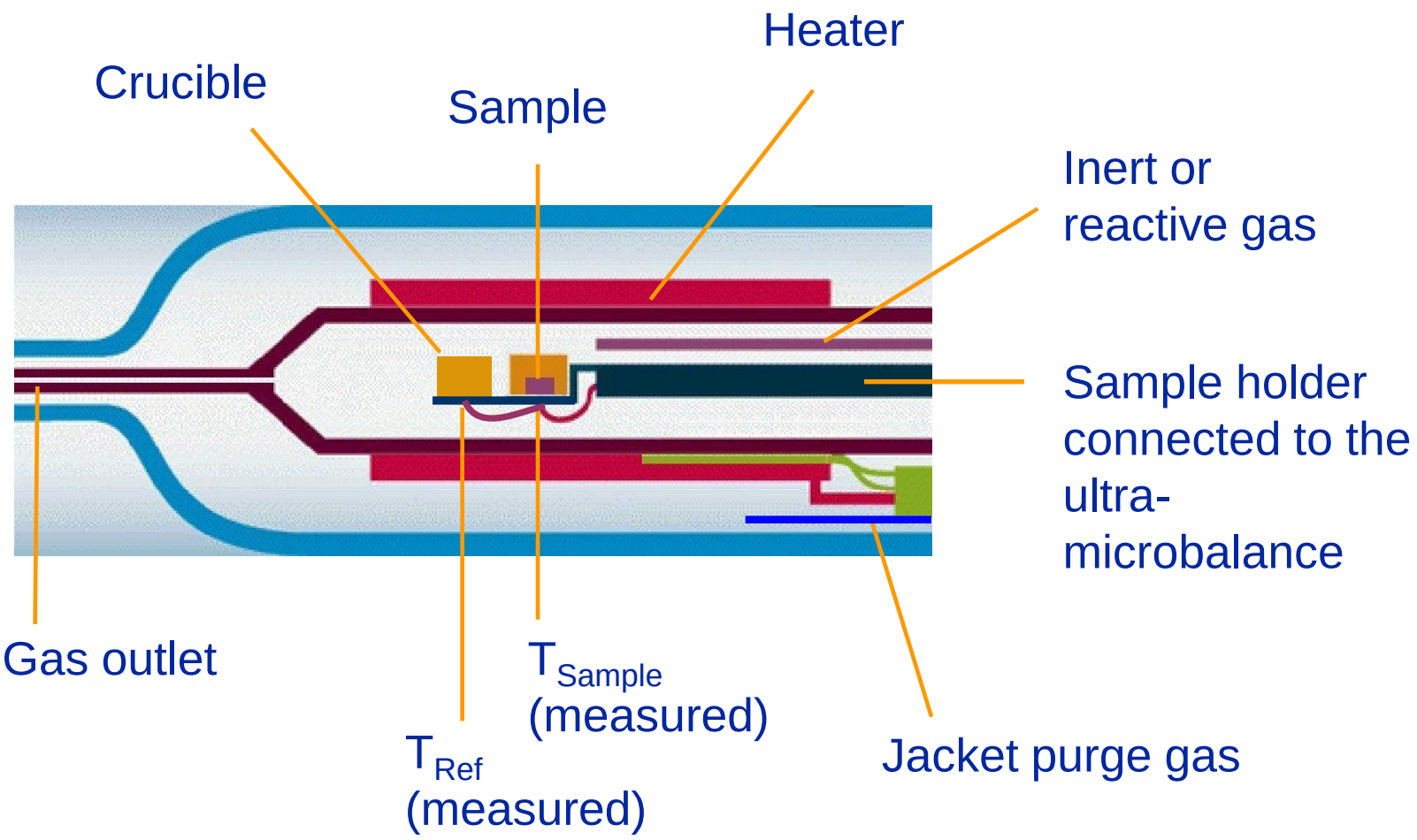
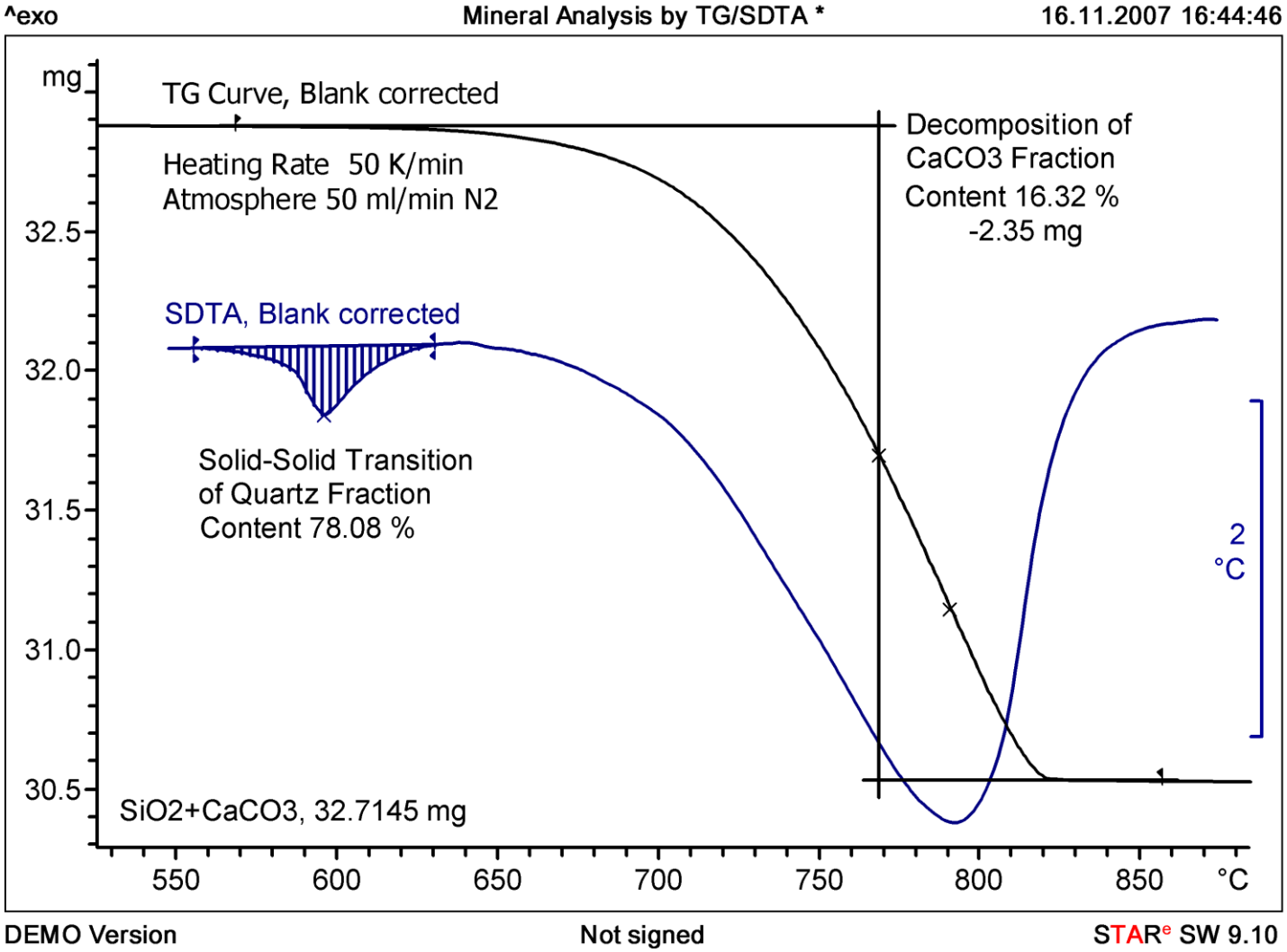
TGA Measuring Principle



Measuring principle: Typical TGA curve



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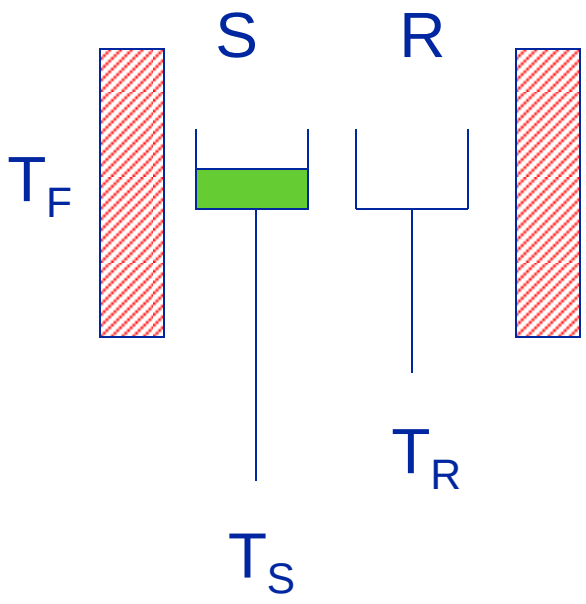
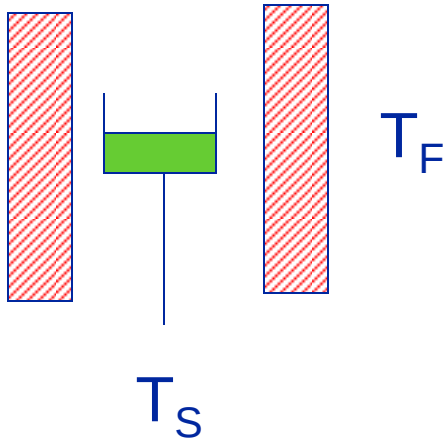
Sensors: What is „SDTA“ ?



$DTA = T_S - T_R$

SDTA: T_R is not measured but calculated from the furnace temperature.



If you run a sample and a blank:

Sample run: T_S

Blank run: no sample, T_R

Sample run – blank run = $T_S - T_R$ = DTA

but measured sequentially.

Sensors: SDTA

The **SDTA® sensor** consists of a platinum support with a thermocouple that measures the sample temperature. 2 sensors available: for small and large furnace.

Large amount of mass with huge crucibles: 900 µl
Small amount of mass with small crucibles: 30 µl

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Sensors: DTA

The **DTA sensor** measures the sample and the reference temperatures. The support is made of platinum. The differential measurement improves the signal-to-noise ratio.

Good heat flow signal in low temperature range, ideal for alumina crucibles

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Sensors: DSC

The **DSC sensor** consists of 6 thermocouples located directly below a protective ceramic support and measuring the sample and reference temperatures.

Good heat flow signal in high temperature range, ideal for platinum crucibles

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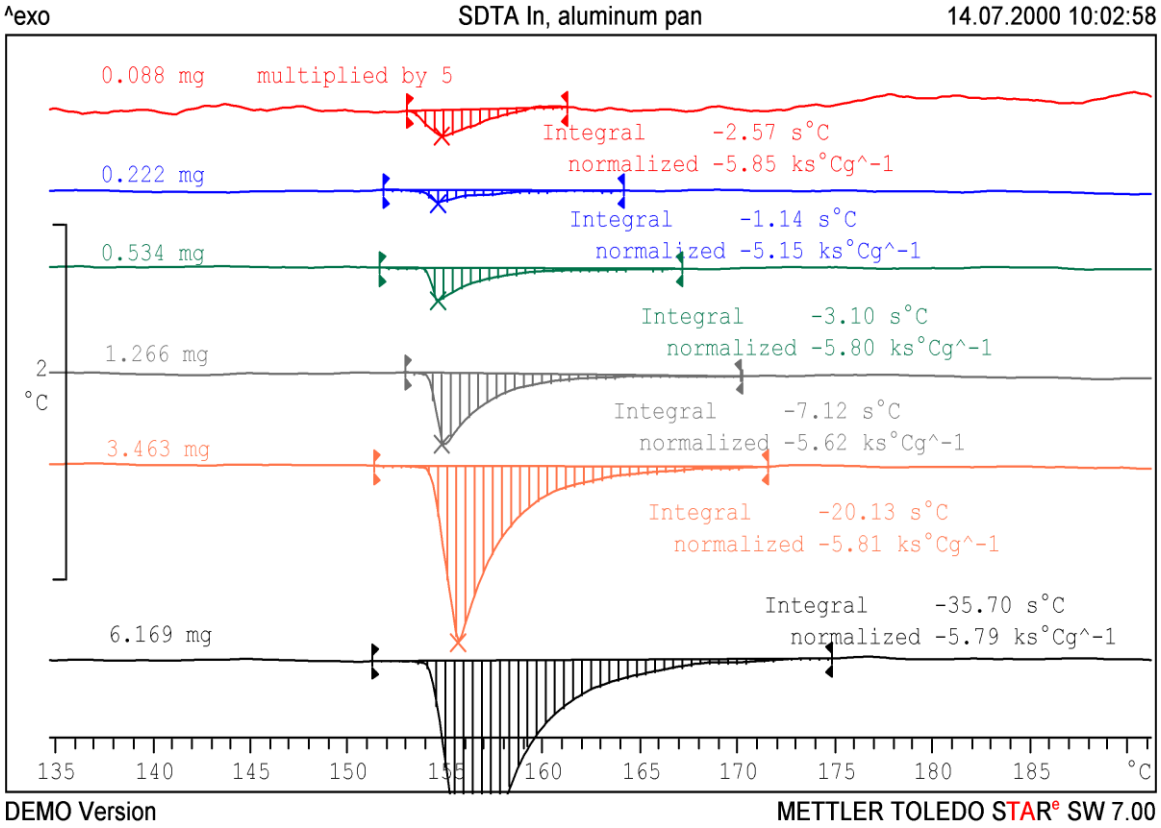
Sensors: Sensitivity of SDTA



Conclusion: with “sharp peaks”, enthalpies of about 2.5 mJ (= 0.088 mg * 28.5 mJ/mg) are detectable in an aluminum pan at a heating rate of 10 K/min.

Example: solid-solid transition of quartz: ΔH = 7.5 J/g; i.e. about 0.333 mg of quartz must be present to detect this transition.

Balance: Sensitivity

What are the smallest weight losses that can be measured with the thermobalance?

- Noise: typically about 0.5 – 1 μg (RMS)
- Blank: reproducibility ≈ 5 μg @ 500 °C and 10 K/min
- Drift: typically 5 μg/h

To identify a weight step, the weight change should be at least twice as large as the peak-to-peak noise. The peak-to-peak noise is about 2 μg. For unambiguous identification, the weight change should therefore be at least 4 μg.

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Balance: Minimal sample size

Determination of residues (ash)

In this case, the reproducibility of the blank curve and the amount of sample are critical.

Task

An ash content of approx. 1% shall be determined with a relative accuracy of 1%.
What sample weight is needed?

Answer

- Assumption: reproducibility of the blank curve ≈ 10 µg
- 1% accuracy → residue must be 1 mg
- the sample must therefore weigh 100 mg.

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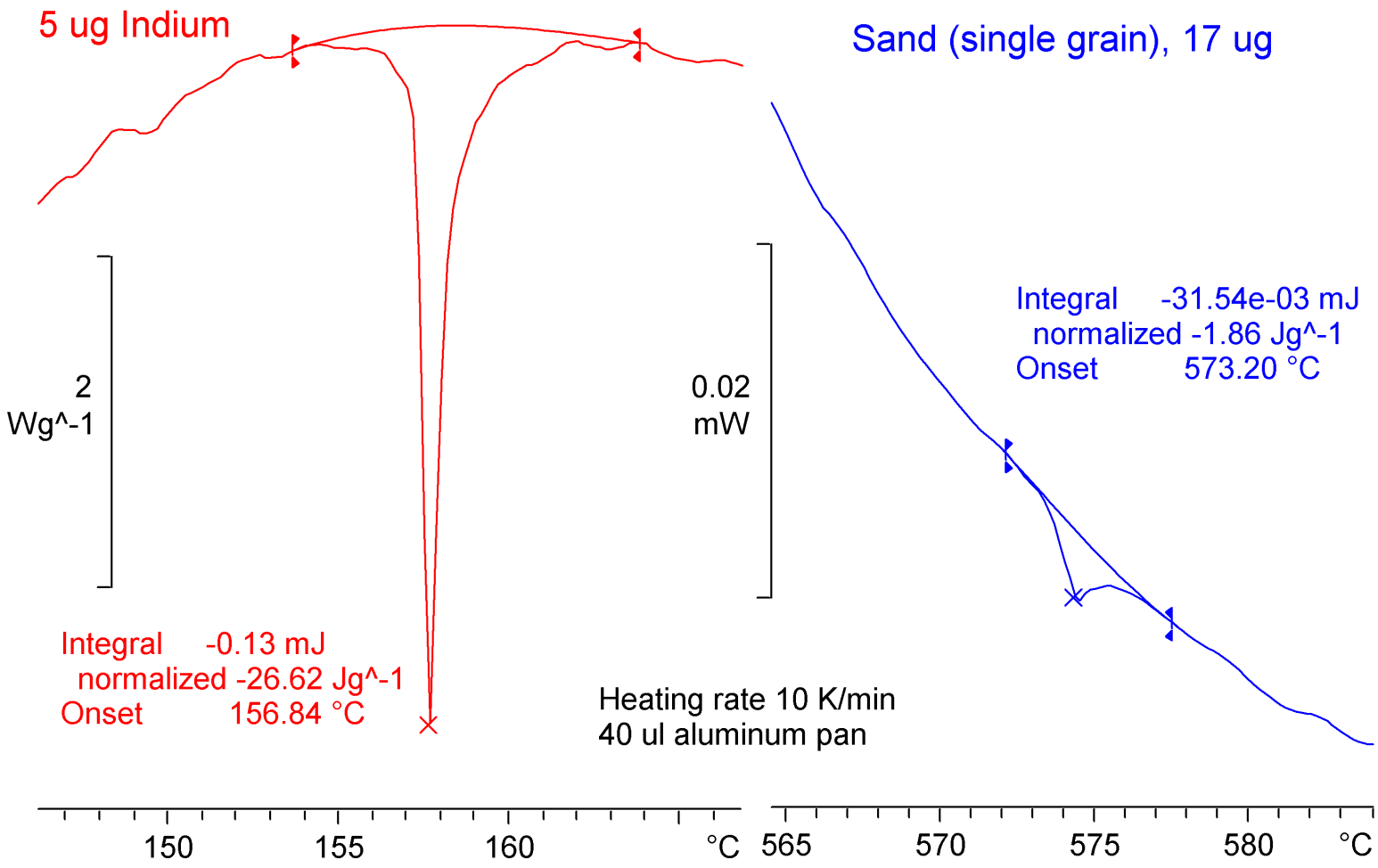
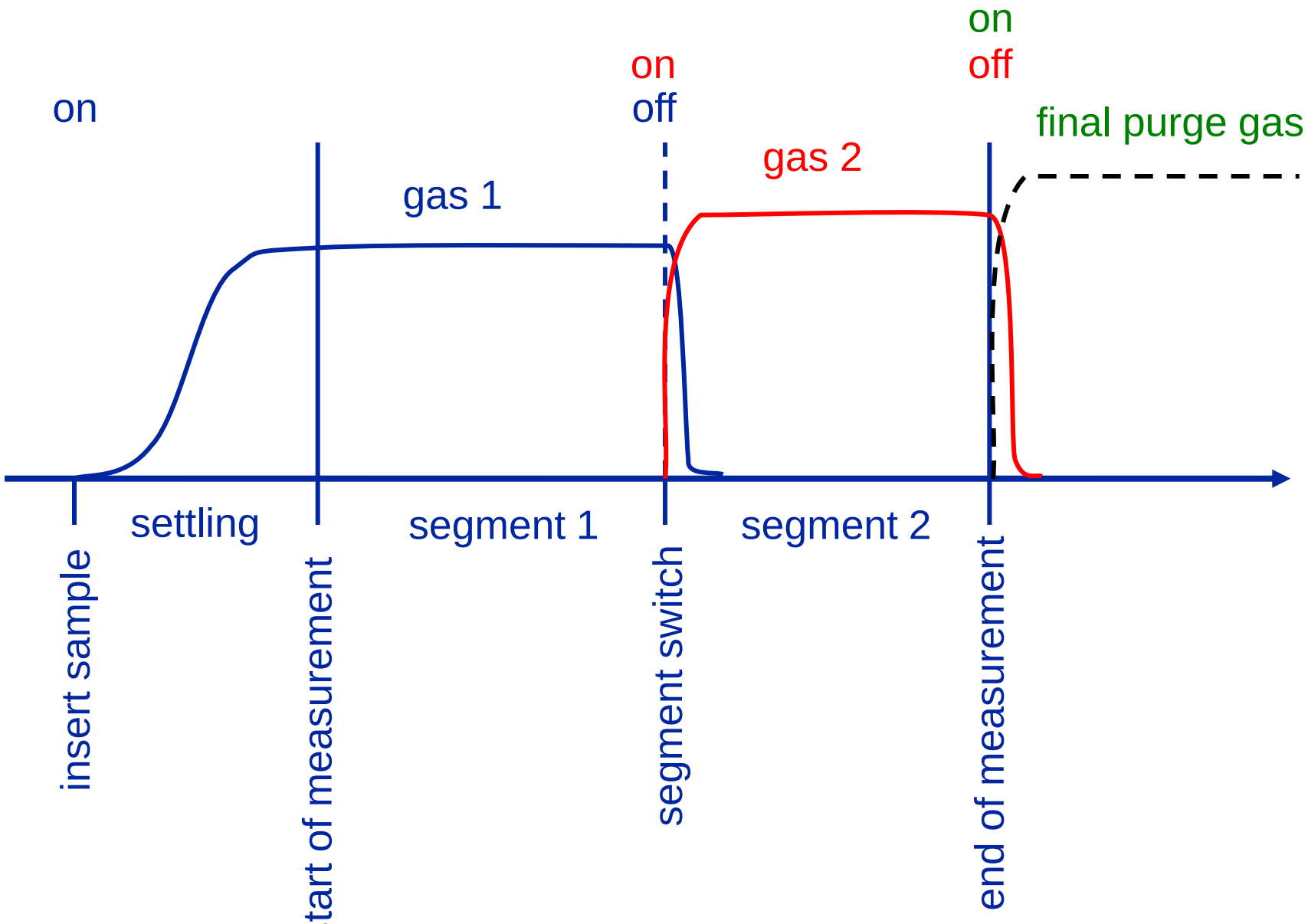
Sensors: Sensitivity of DSC



Conclusion: SDTA is about 50 times less sensitive than DSC

Gas controllers: switching of method gas



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Gas controllers: Benefits

GC10

- Gas flows can be automatically switched from inert to reactive gas and monitored. 2 gases possible.

GC20

- Gas flows can be automatically controlled. Cell gas extra.

GC100

- Gas flows can be automatically switched from inert to reactive gas and controlled. 4 different gases possible.

GC200

- Gas flows can be automatically switched from inert to reactive gas and controlled. 3 different gases possible. Cell gas extra.

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Appendix: Selection guide for gas box

With flow meter (protective gas)

Polymer analysis (N2/Air)	GC 10
Use of two reactive gases	GC 10
More than two gases	GC 100
Controlled gas flow	GC 100
Vacuum?	GC 100

Without flow meter

Polymer analysis (Air 0 mL/min, Air 30mL/min)	GC 20
N2 and a different reactive gas	GC 20
Controlled protective gas	GC 200
More than 1 reactive gas	GC 200
Vacuum?	GC 200

(We recommend GC 10 or GC 20 for He)

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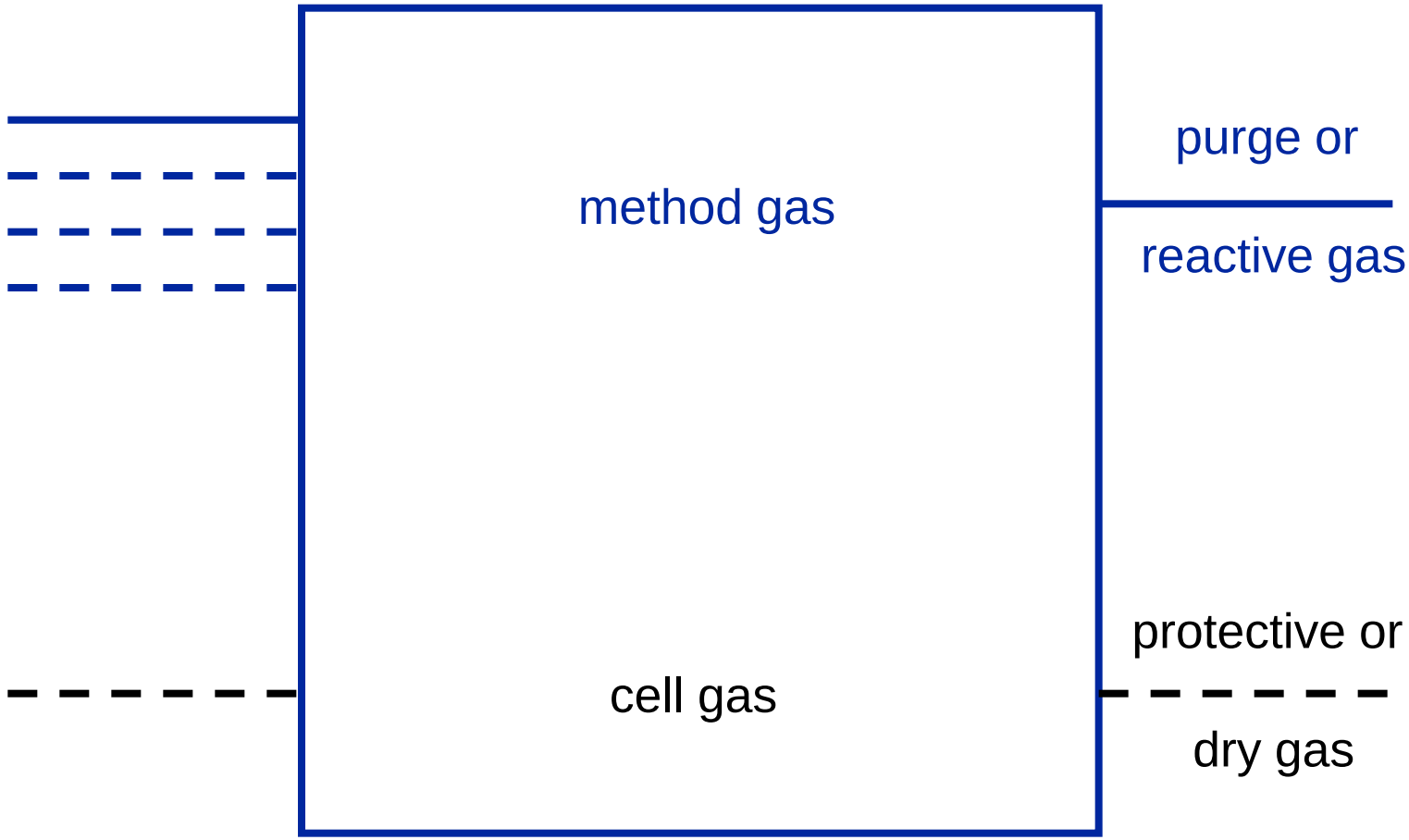
Gases: Method gas and cell gas



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Gas controllers

- GC 10 is compatible to TSO800 GC1
- GC 20 is compatible to TSO800 GC

- GC 10/20 monitors the gas flow
- GC 100/200 controls the gas flow

- GC 10/20 can be used for all STARe modules
- GC 100/200 can be used only for DSC 1 and TGA/DSC 1

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Gas controllers: Use of GC10/20

Warning:
never use the gas box with low pressure at its exit (vacuum) – the gas controller will be damaged !

Further restrictions

- The use of more than two gas types within a method is not possible.
- The definition of more than one gas flow per gas within a method is not possible.

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Balance: Basics

- A **balance** is used to measure the mass of an object.

- While the words "weigh" or "weight" are often used, any balance or scale measures **mass**, which is not dependent on force of gravity.

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Appendix: Sources of errors with balances

- Buoyancy, due to the fact that the object being weighed displaces a certain amount of air, which must be accounted for.
- Mechanical misalignment due to thermal expansion/contraction of components of the balance.
- Earth's magnetic field may act on iron components in the balance.
- Magnetic fields from nearby electrical wiring may act on iron components.
- Magnetic disturbances to electronic pick-up coils or other sensors.
- Forces from electrostatic fields, for example, from feet shuffled on carpets on a dry day.
- Chemical reactivity between air and the substance being weighed (or the balance itself, in the form of corrosion).
- Condensation of atmospheric water on cold items.
- Evaporation of water from wet items.
- Convection of air from hot or cold items.
- The Coriolis force from Earth's rotation.
- Gravitational anomalies (i.e. using the balance near a mountain; failing to level and recalibrate the balance after moving it from one geographical location to another.)
- Vibration and seismic disturbances; for example, the rumbling from a passing truck.

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Balance: Sensitivity

What are the smallest weight losses that can be measured with the thermobalance?

- Noise: typically about 0.5 – 1 μg (RMS)
- Blank: reproducibility ≈ 5 μg @ 500 °C and 10 K/min
- Drift: typically 5 μg/h

To identify a weight step, the weight change should be at least twice as large as the peak-to-peak noise. The peak-to-peak noise is about 2 μg. For unambiguous identification, the weight change should therefore be at least 4 μg.

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Buoyancy

- Archimedes: buoyancy = mass of the displaced volume of the atmosphere: $m = V \rho$
- V = volume of the crucible, sample, part of the sample holder, etc.
- ρ = density of the gas in the furnace
- The density of gas decreases with increasing temperature, e.g. for air:
  - 1.29 mg/ml at 25 °C
  - 0.62 mg/ml at 225 °C
  - 0.41 mg/ml at 425 °C
- Results in upward force equal to the weight of the „active“ volume.
- Since the density of the gas in the furnace decreases with increasing temperature, buoyancy reduces upon heating → apparent weight increase
- Blank curve needed to correct the mass effect

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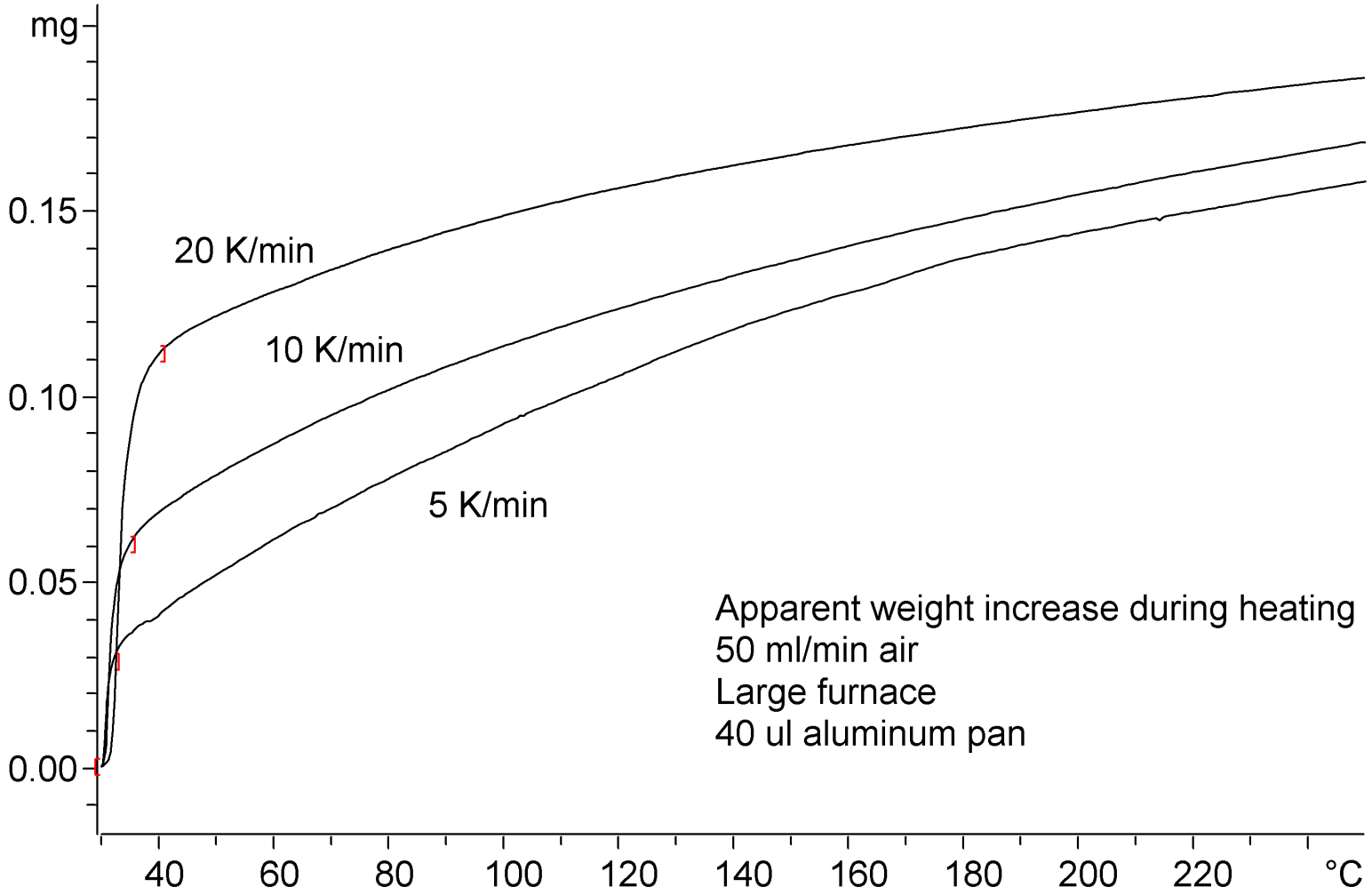
Buoyancy



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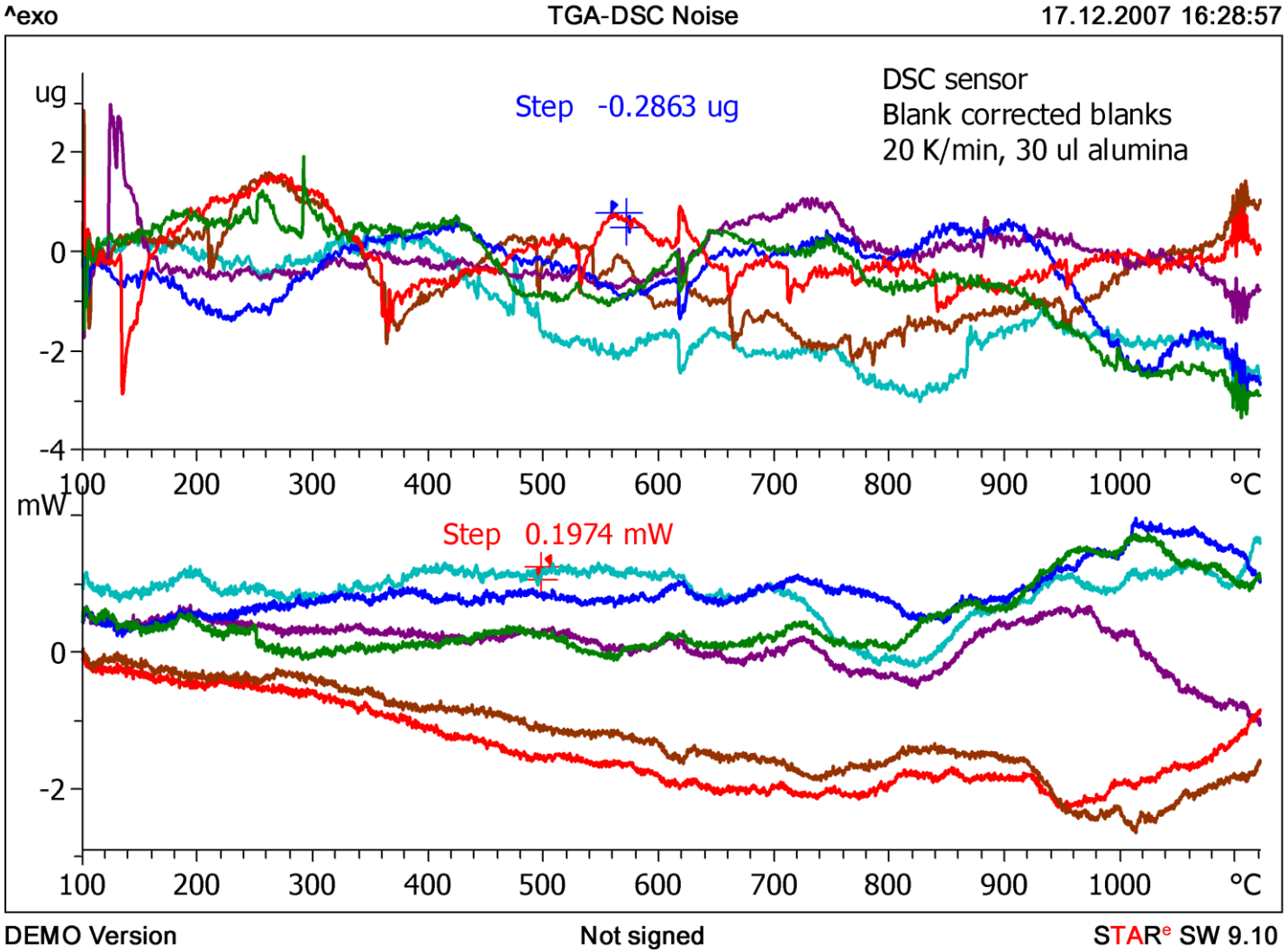
Performance: Noise



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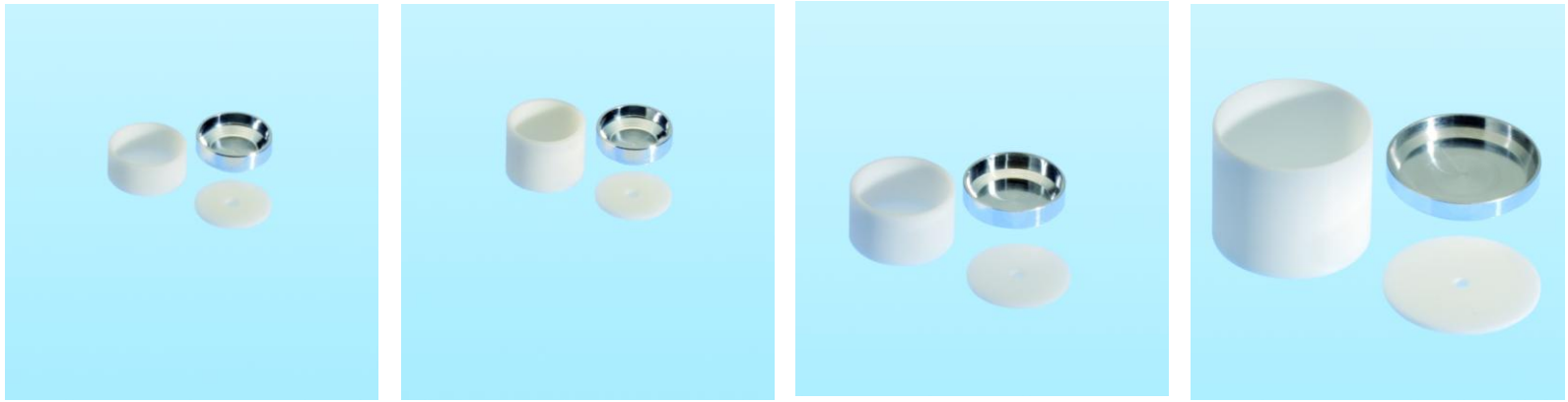
Crucibles

Alumina crucibles

- Alumina crucibles with lids: 30 µl, 70 µl,150 µl and 900 µl
- Special aluminum lids to prevent contamination and evaporation before the measurement
- Normally used in TGA, reusable

Aluminum crucibles



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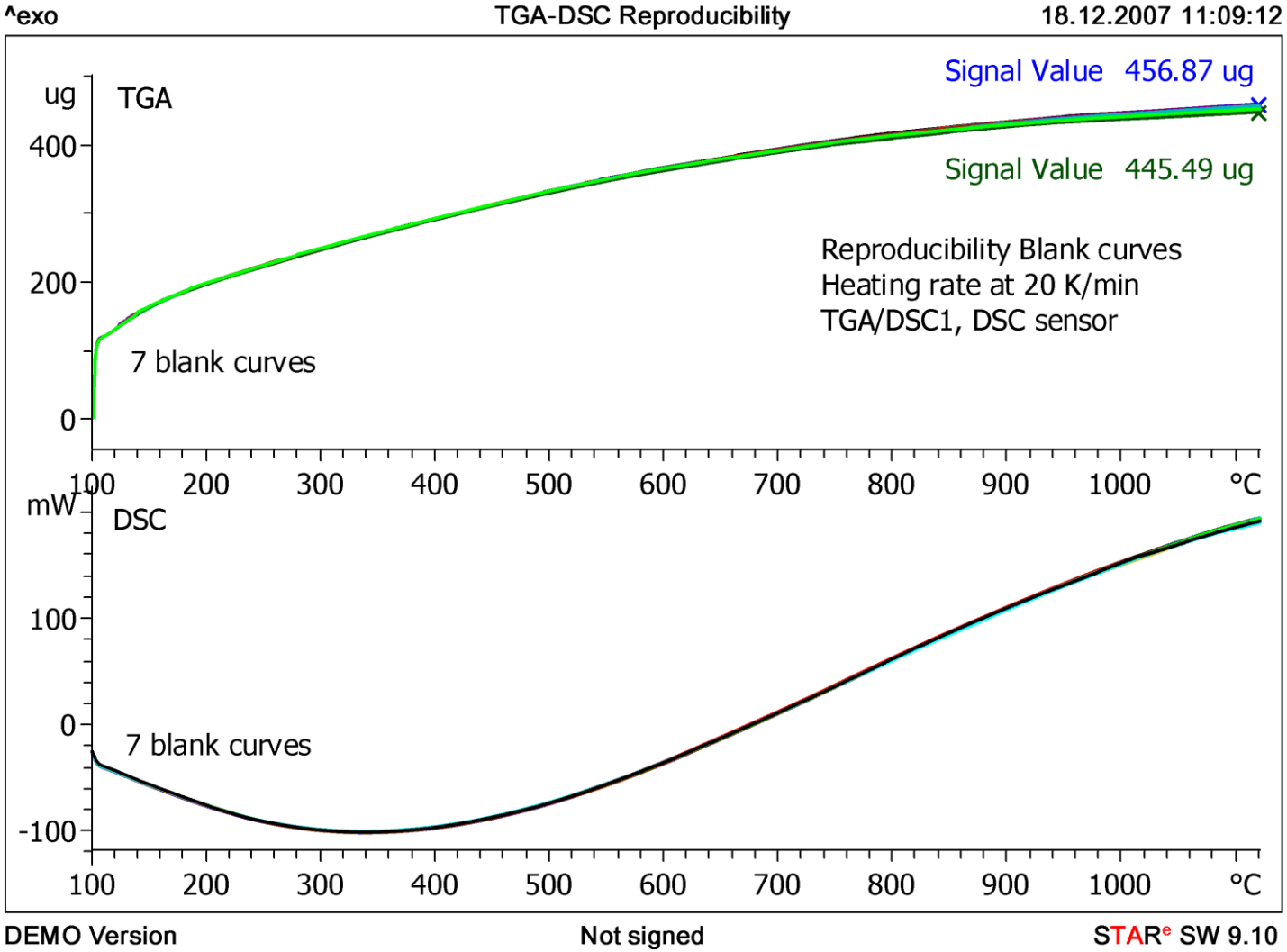
Performance: Reproducibility, blank



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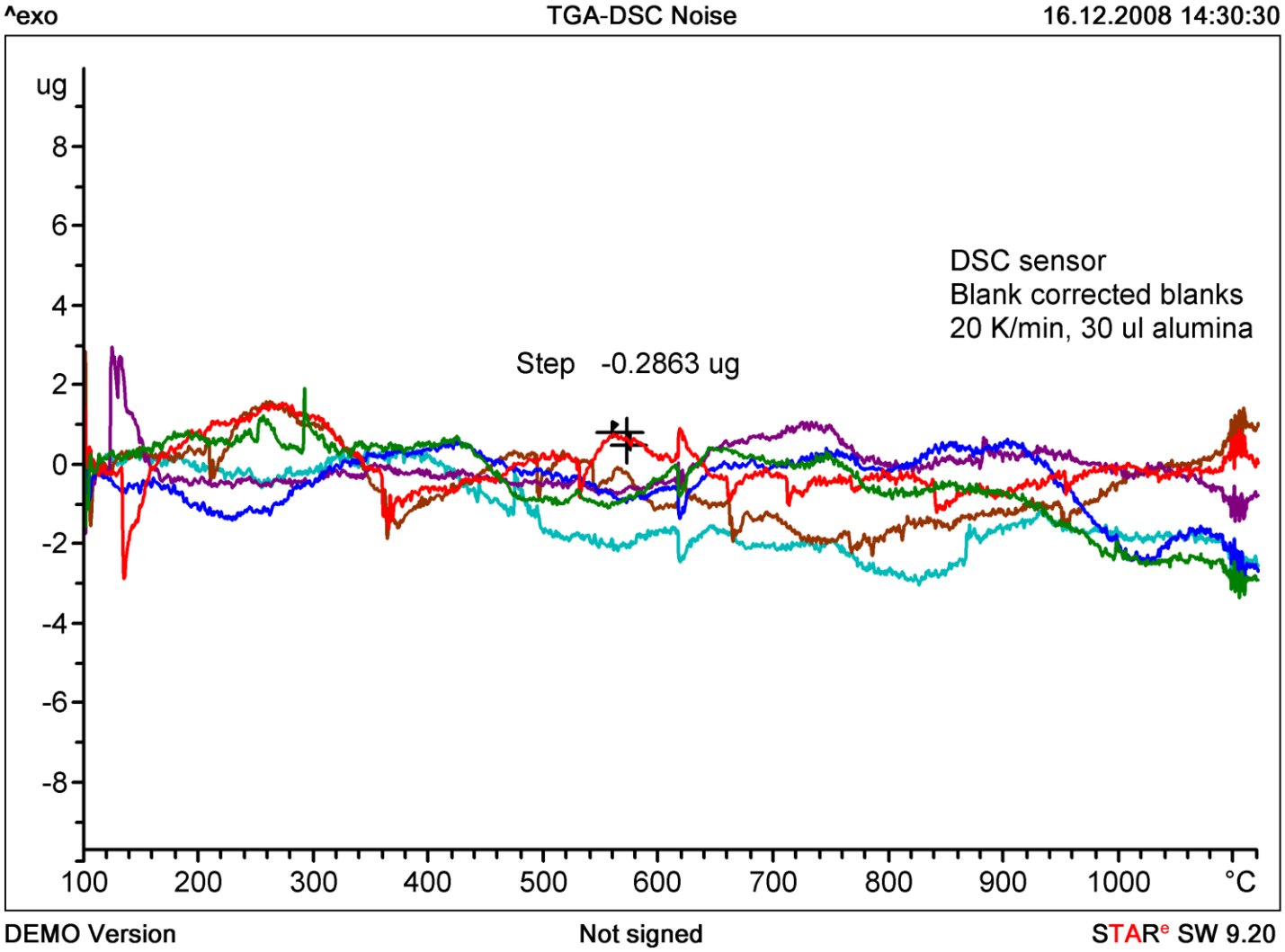
Performance: Noise



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