Thermal Analysis -
Basics, Applications, Benefit

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1. Thermal Analysis - Why?
2. Conventional Thermal Analysis (TA)
3. Simultaneous Thermal Analysis (STA)
4. Influences on shape and quality of TA curves
5. DSC, DMA, and TOA
6. Coupled techniques in TA - Evolved Gas Analysis (EGA)
7. Determination of further thermal parameters

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1. Material properties - Knowing and Governing

- Working temperatures of jet engines (c_P; LFA ...)
- Solution annealing
- DMA (Materials do not forget their treatment !)

2. Chemical reactions - Following, Understanding, Simulation

- Thermal decomposition (e.g. $CaC_2O_4 \cdot H_2O$)
- Degradation and/or combustion (e.g. Straw)
- Single component and reaction mixture: The basic tools of a chemist ...
- Simulation of a catalyst formation

3. Purity (and related phenomena)

- Phase diagrams
- Material constants

2. Conventional Thermal Analysis (TA)

- History
- Cooling curves
- Gibbs′ phase rule
- Measuring setup of DTA and DSC
- Information content of a DTA signal
- Sample holders and crucibles

Aristoteles (384-322 A.C.)

Fire is the general analysator of matter.

Robert Boyle „*The Sceptical Chymist*“ (1661): **No, it isn‘t!**

Thermal analysis today:

Following the changes of a physical property of a sample subjected to a controlled heating or cooling program as a function of temperature or time

The most-followed parameter: **$T = f(t)$**

$\Delta T = f(t)$ or $f(T)$ **DTA**

Subject of investigation: **A phase or a phase mixture**

Changes in temperature – Changes in state

Information about: **Reactions, reactivity, purity, phase diagrams, materials constants**

Joseph Black (1728-1799)

Distinction between Temperature and Heat

Quantity of heat *Quality of heat*

Latent heat *vs.* Sensible heat (1763)

Antoine L. Lavoisier (1743-1794)

"Heat substance" as an element: Caloricum

Mass balance of chemical reactions

Henri-Louis LeChatelier (1850-1936)

Pt-PtRh10 thermocouple for measuring T (1887)

William C. Roberts-Austen (1843-1902)

Differential measuring principle: Inert reference (1899)

Josiah Willard Gibbs (1839-1903)

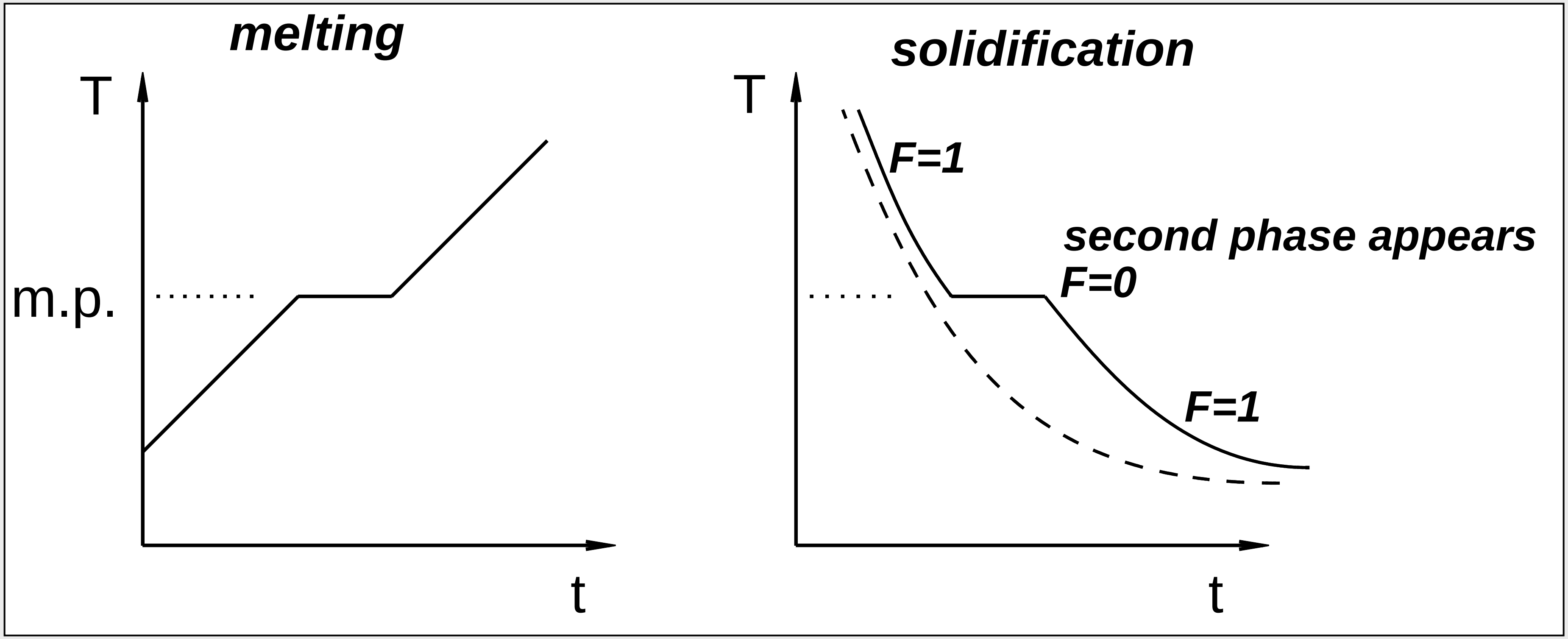
The phase rule $F = K - P + 1$ *(for p=const)*

The phase rule

Josiah W. Gibbs

"Classical" thermal analysis:

Heating and cooling curves of single-component systems

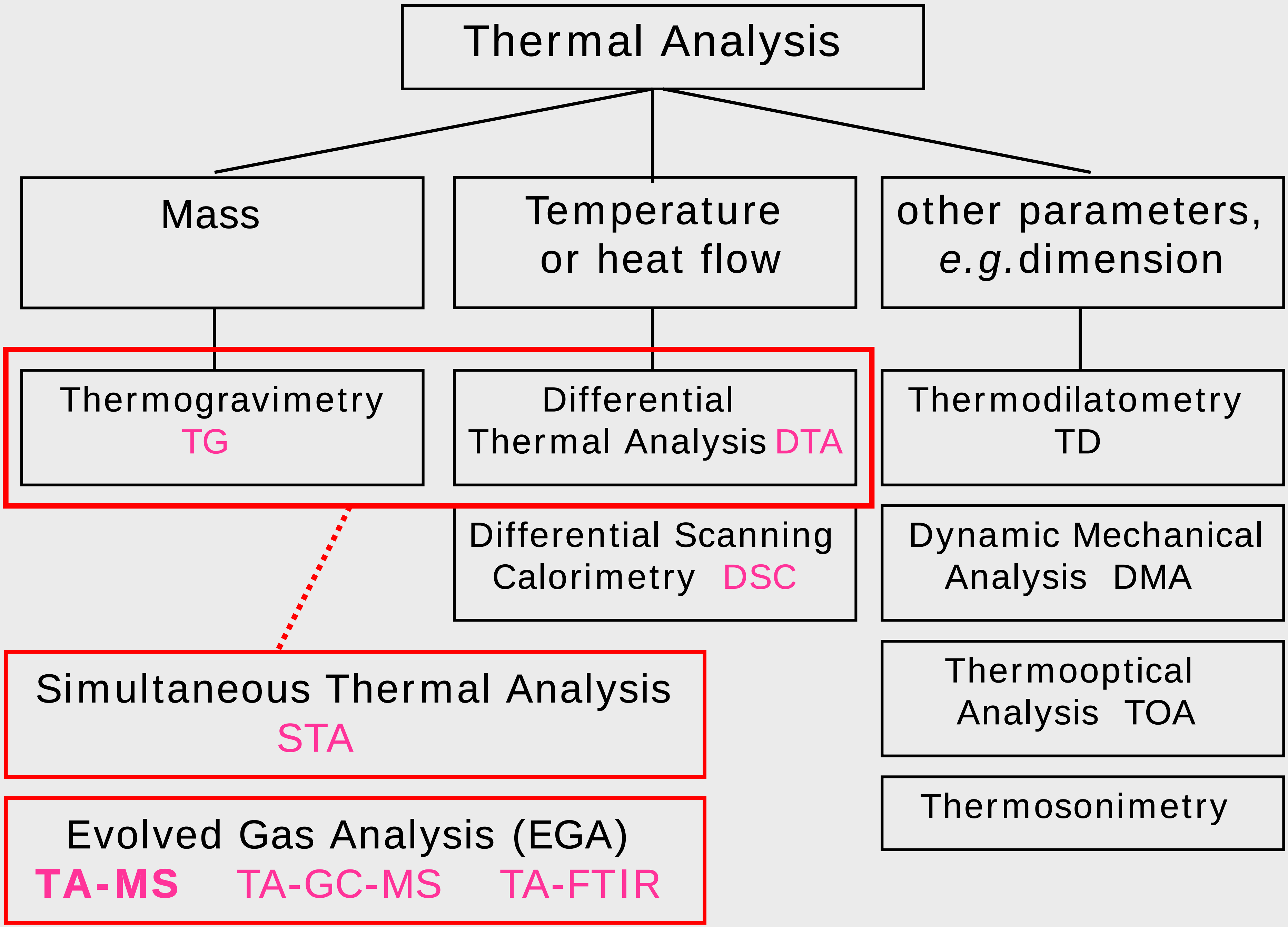


$F = K - P + 2 - E$ ***E= 1** for p=const*

$F = K - P + 1$ **Reduced phase rule**

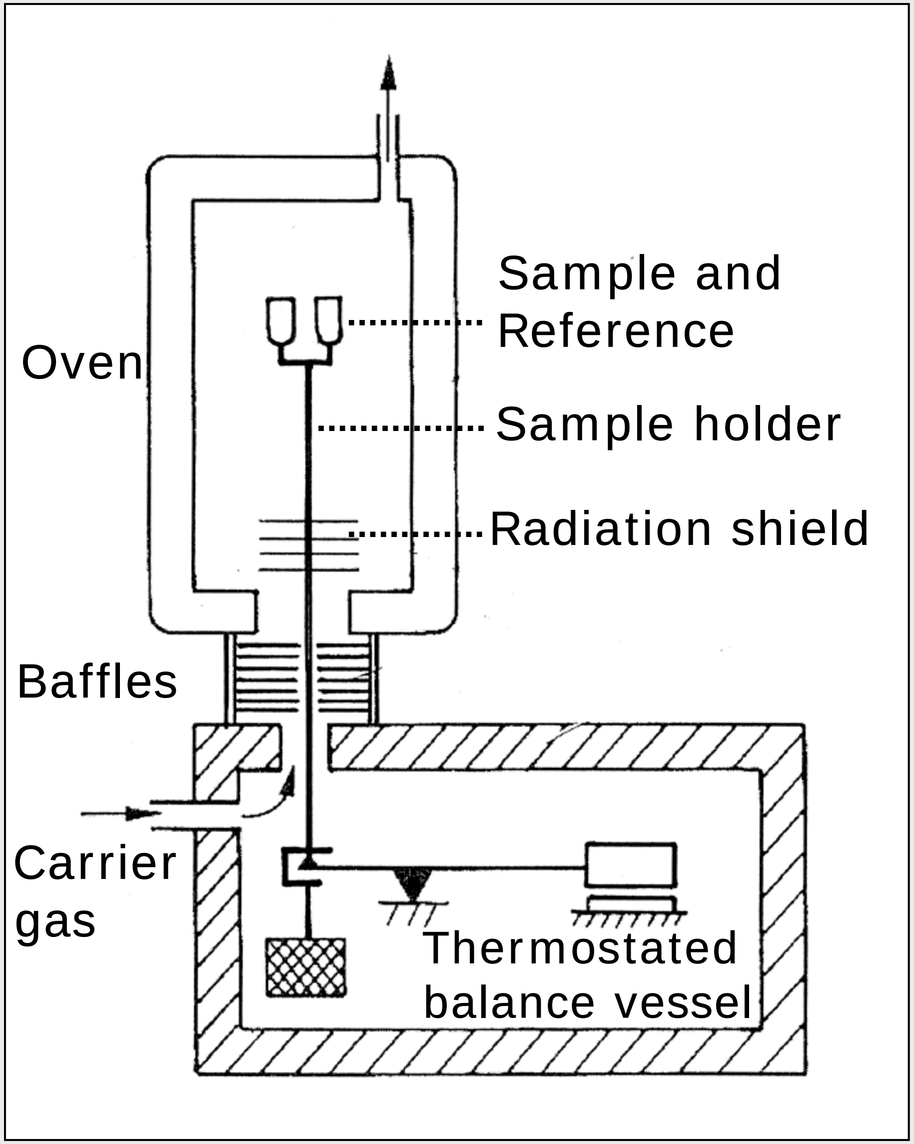
3. Simultaneous Thermal Analysis (STA)

- Apparatus setup
- The famous $CaC_2O_4 \cdot H_2O$
- Determination of the crystalline fraction in a mixture
- Atmosphere changes (Straw)

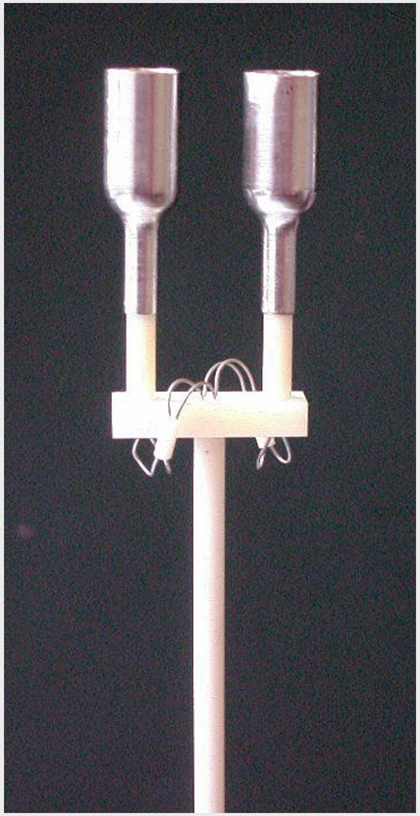

Thermal Analysis
Mass
Temperature or heat flow
other parameters, e.g. dimension
Thermogravimetry TG
Differential Thermal Analysis DTA
Thermodilatometry TD
Differential Scanning Calorimetry DSC
Dynamic Mechanical Analysis DMA
Thermooptical Analysis TOA
Thermosonimetry
Simultaneous Thermal Analysis STA
Evolved Gas Analysis (EGA)
TA-MS TA-GC-MS TA-FTIR

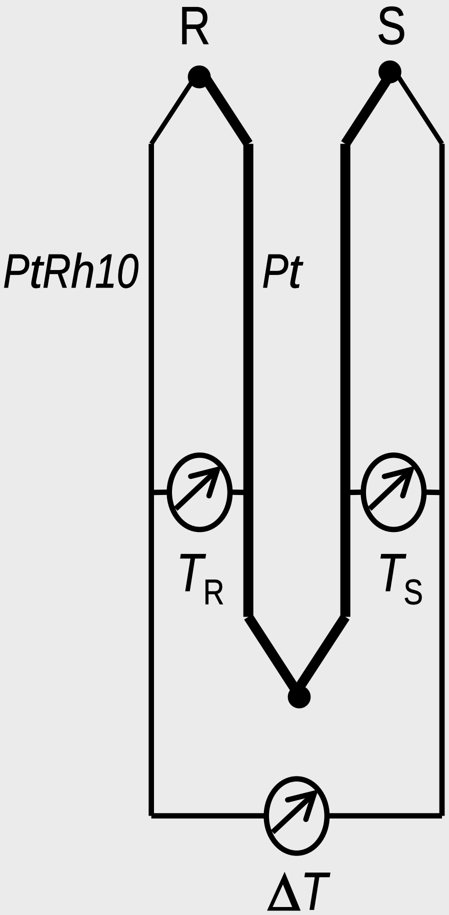
Setup of a STA device

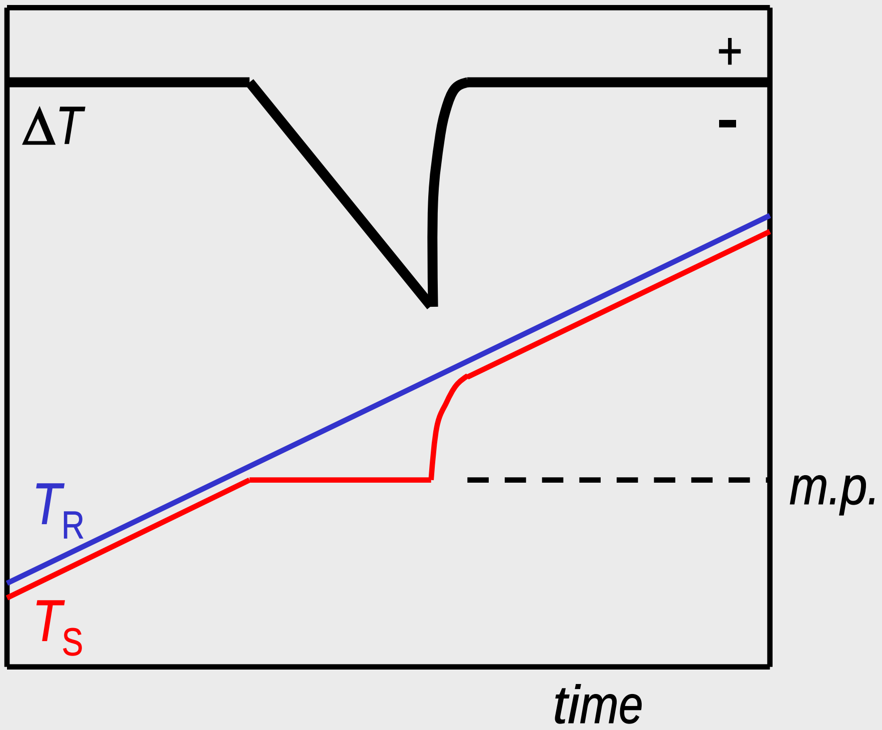
Simultaneous Thermal Analysis: TG and DTA



Differential measuring setup – Generation of a DTA signal

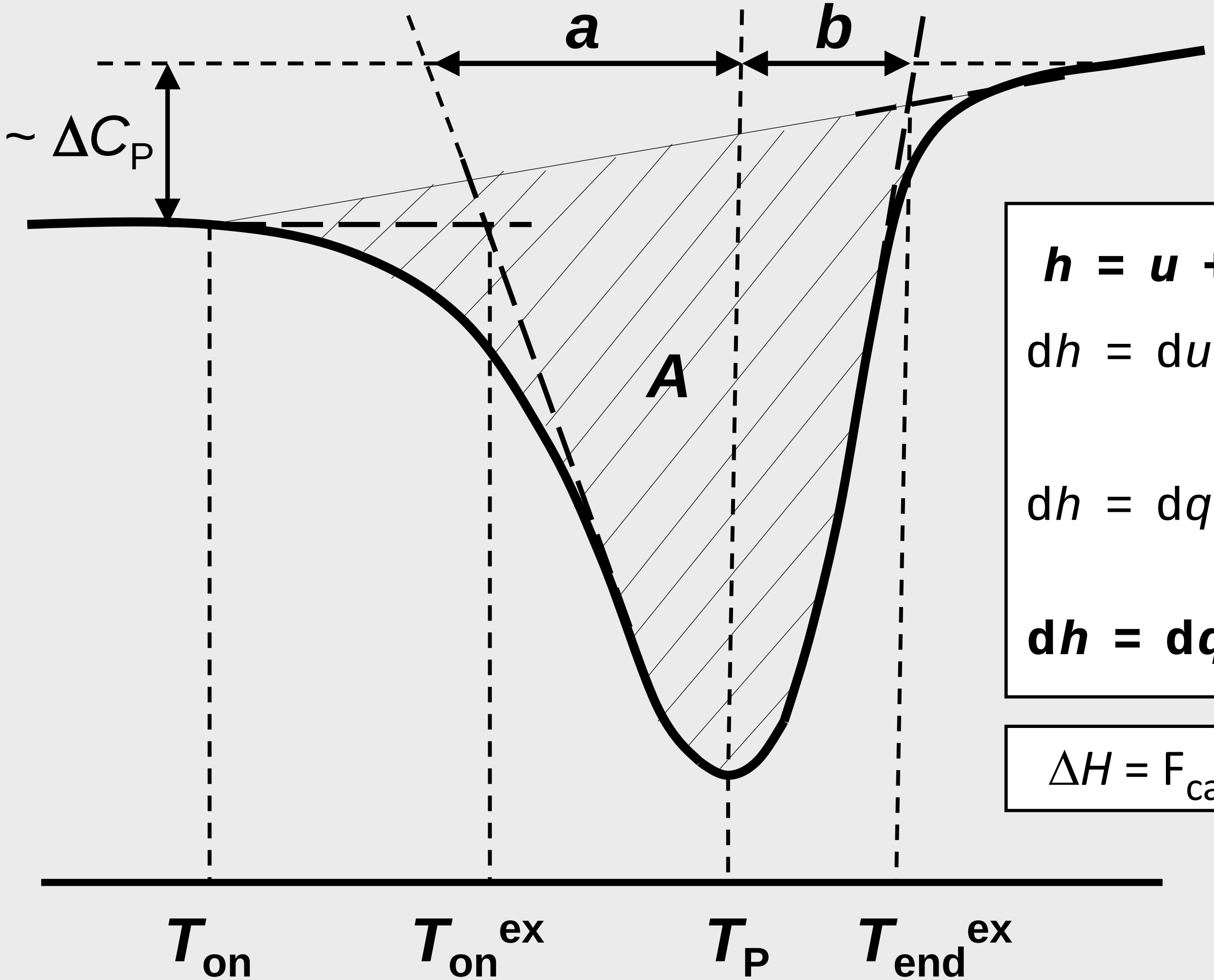






Asymmetric signal shape

Information content of the DTA signal



$$\boldsymbol{h = u + pv}$$

$$\mathrm{d}h = \mathrm{d}u + p\mathrm{d}v + v\mathrm{d}p$$

$$\mathrm{d}u = \mathrm{d}q - p\mathrm{d}v$$

$$\mathrm{d}h = \mathrm{d}q - p\mathrm{d}v + p\mathrm{d}v + v\mathrm{d}p$$

$$v\mathrm{d}p = 0$$

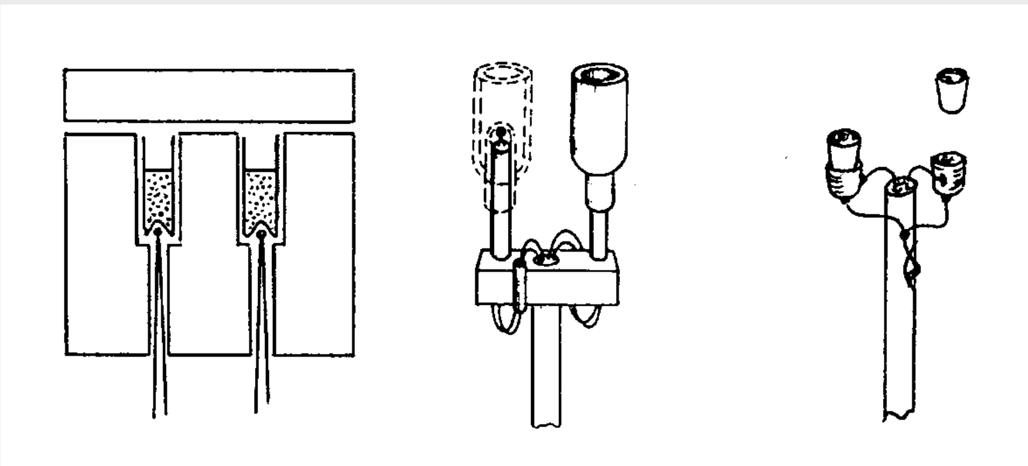
$$\boldsymbol{\mathrm{d}h = \mathrm{d}q_P}$$

$$\Delta H = F_{cal} \cdot A$$

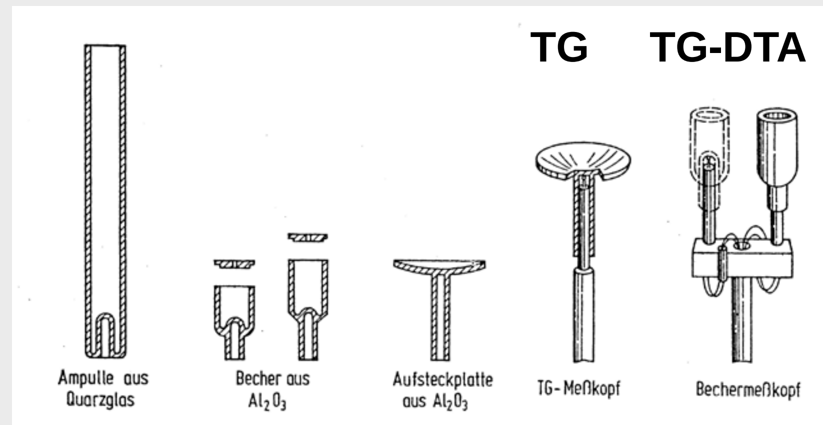
Enthalpy: isobarically exchanged heat

DTA sample holders – Crucible types

Metal block with symmetric holes	Pt or Al_2O_3 beaker	Crucible shoes as thermocouple



Rapidly $\Delta T=0$: High resolution	*„Slowly“: High sensitivity*	*Minimal sample mass*



Kettrup (1984)

3. Simultaneous Thermal Analysis (STA)

- Apparatus setup
- The famous $CaC_2O_4 \cdot H_2O$
- Determination of the crystalline fraction in a mixture
- Atmosphere changes (Straw)

$CaC_2O_4 \cdot H_2O$ *in Ar*

Mass changes

Calcd. / Found

First derivative

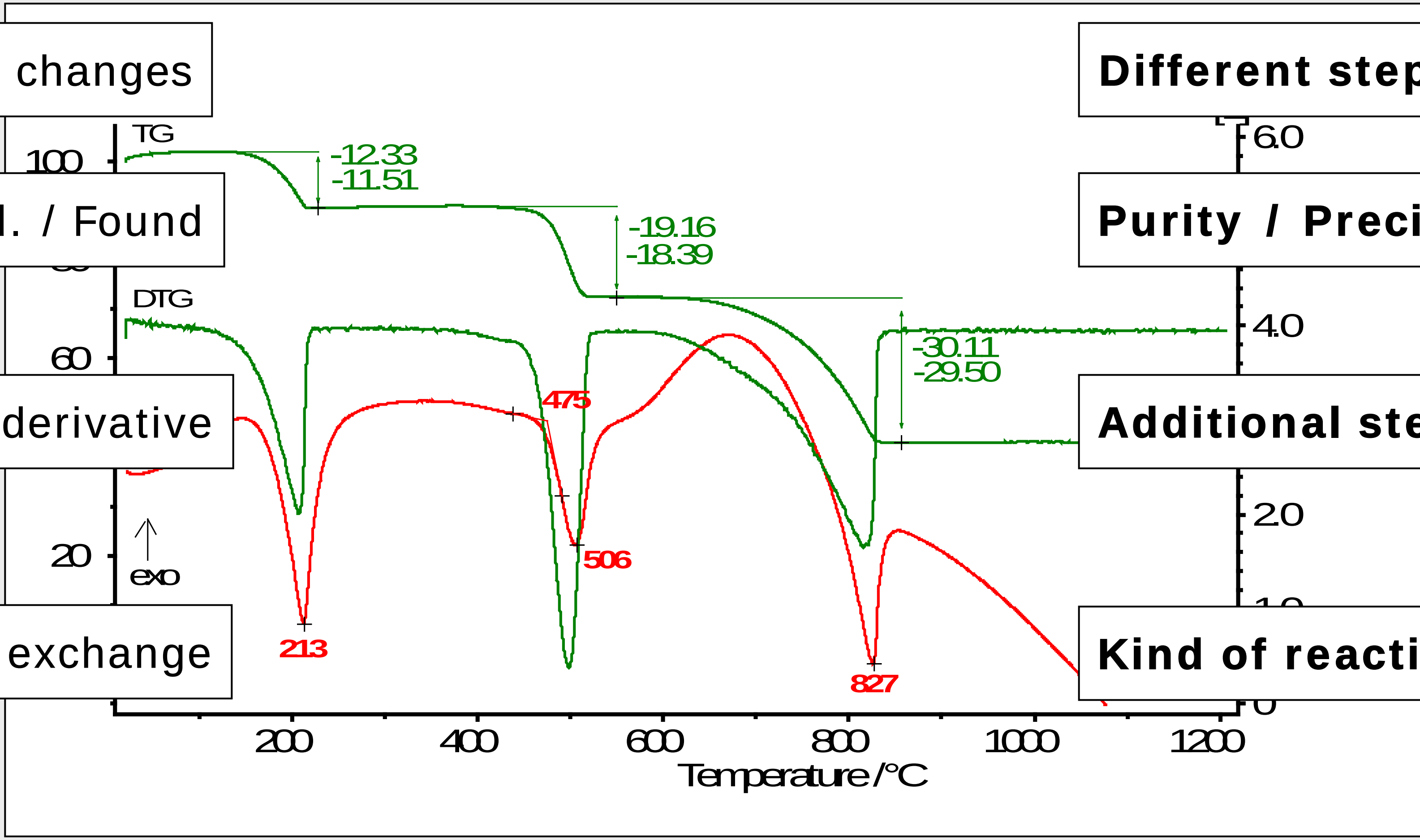
Heat exchange

Different steps

Purity / Precision

Additional steps?

Kind of reaction



$$CaC_2O_4 \cdot H_2O \xrightarrow{-H_2O} CaC_2O_4 \xrightarrow{-CO} CaCO_3 \xrightarrow{-CO_2} CaO$$

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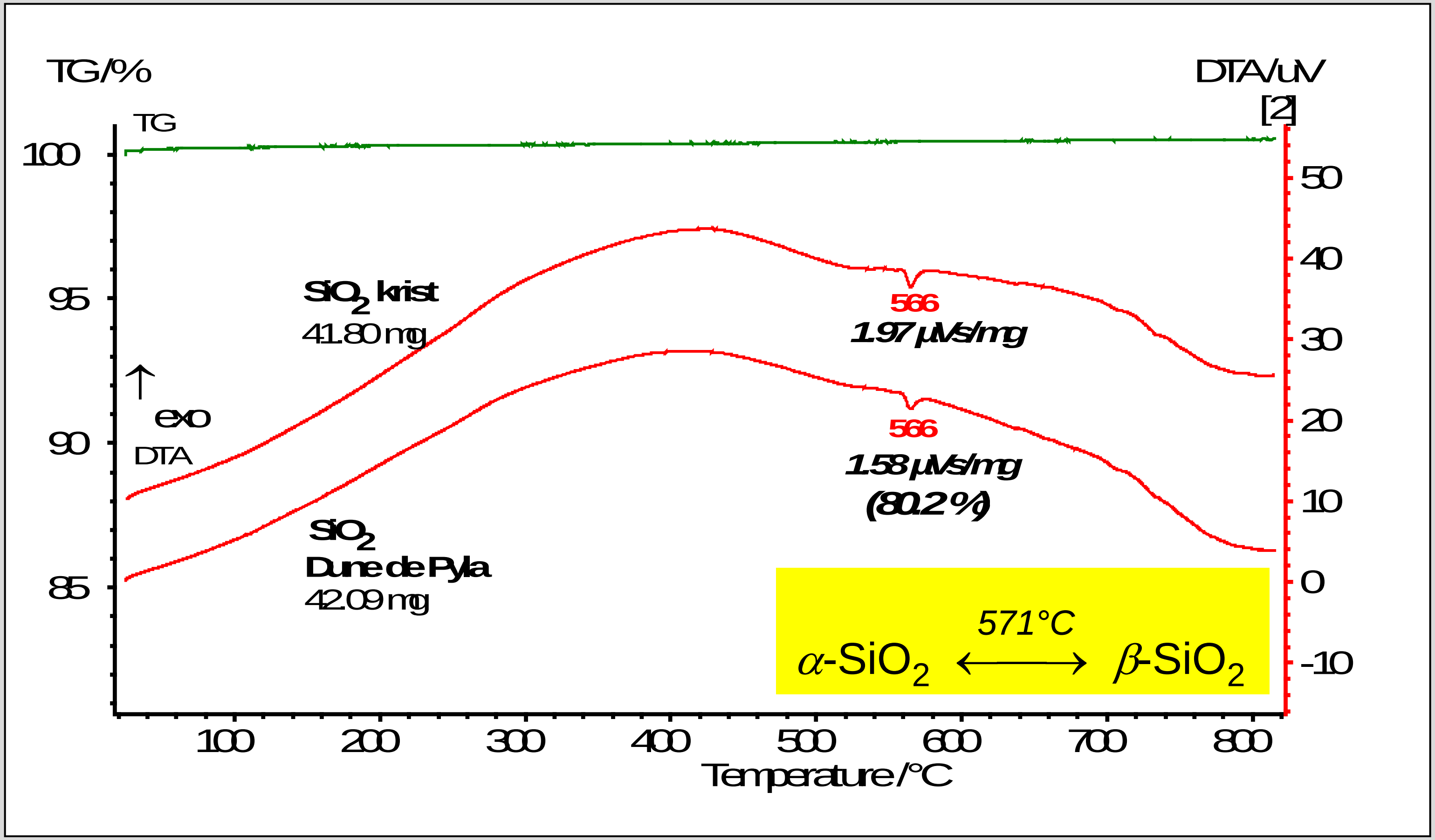

TG/%
DTA/uV
[2]
TG
100
95
90
85
50
40
30
20
10
0
-10
SiO2 krist
41.80 mg
566
1.97 µVs/mg
exo
DTA
566
1.58 µVs/mg
(80.2 %)
SiO2
Dune de Pyla
42.09 mg
571°C
α-SiO2 ⟷ β-SiO2
100
200
300
400
500
600
700
800
Temperature /°C

3. Simultaneous Thermal Analysis (STA)

- Apparatus setup
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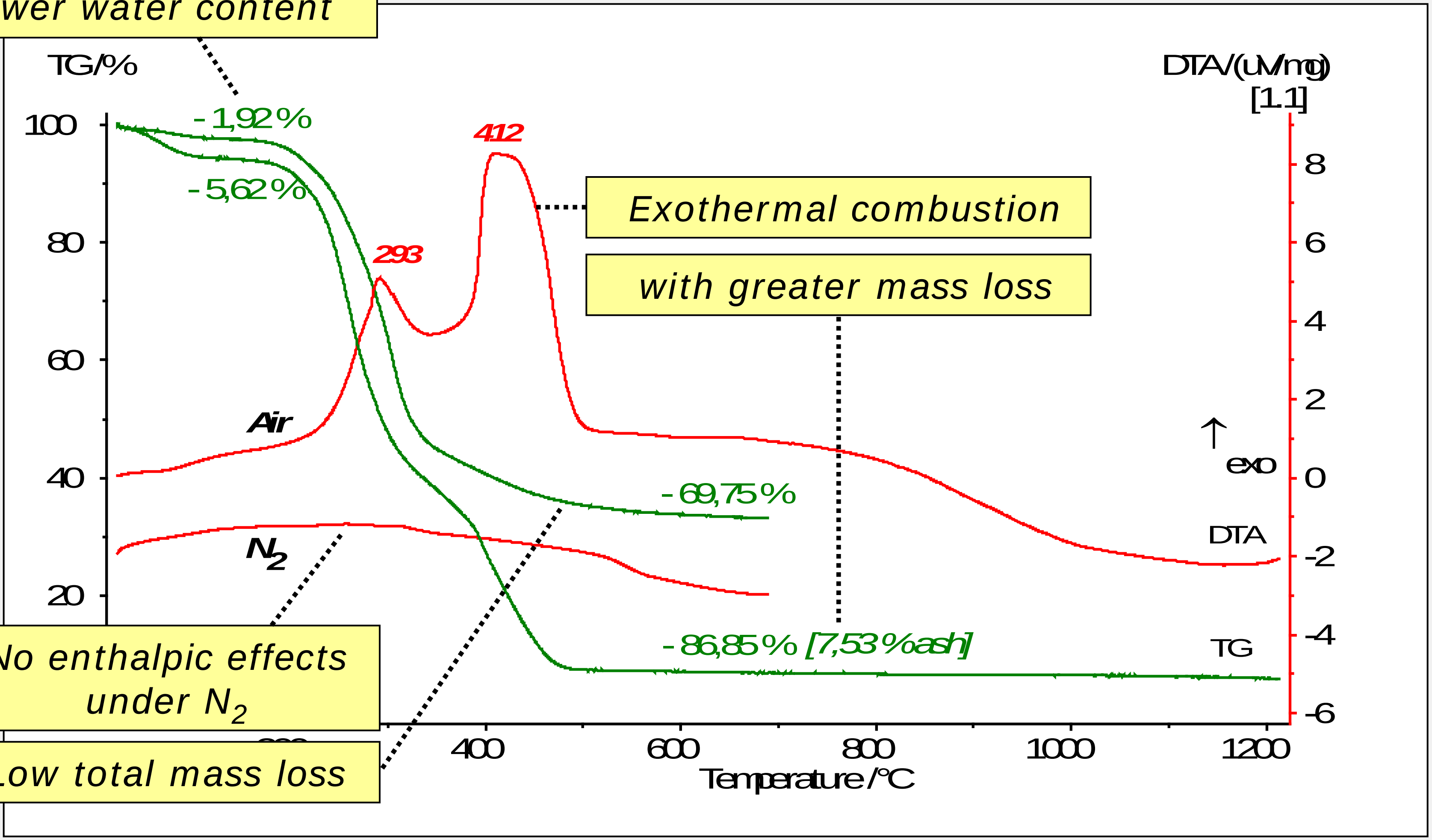
Straw in N_2 and in Air

In N_2: 3 evacuations for adjusting the gas atmosphere: lower water content



Exothermal combustion

with greater mass loss

No enthalpic effects under N_2

Low total mass loss

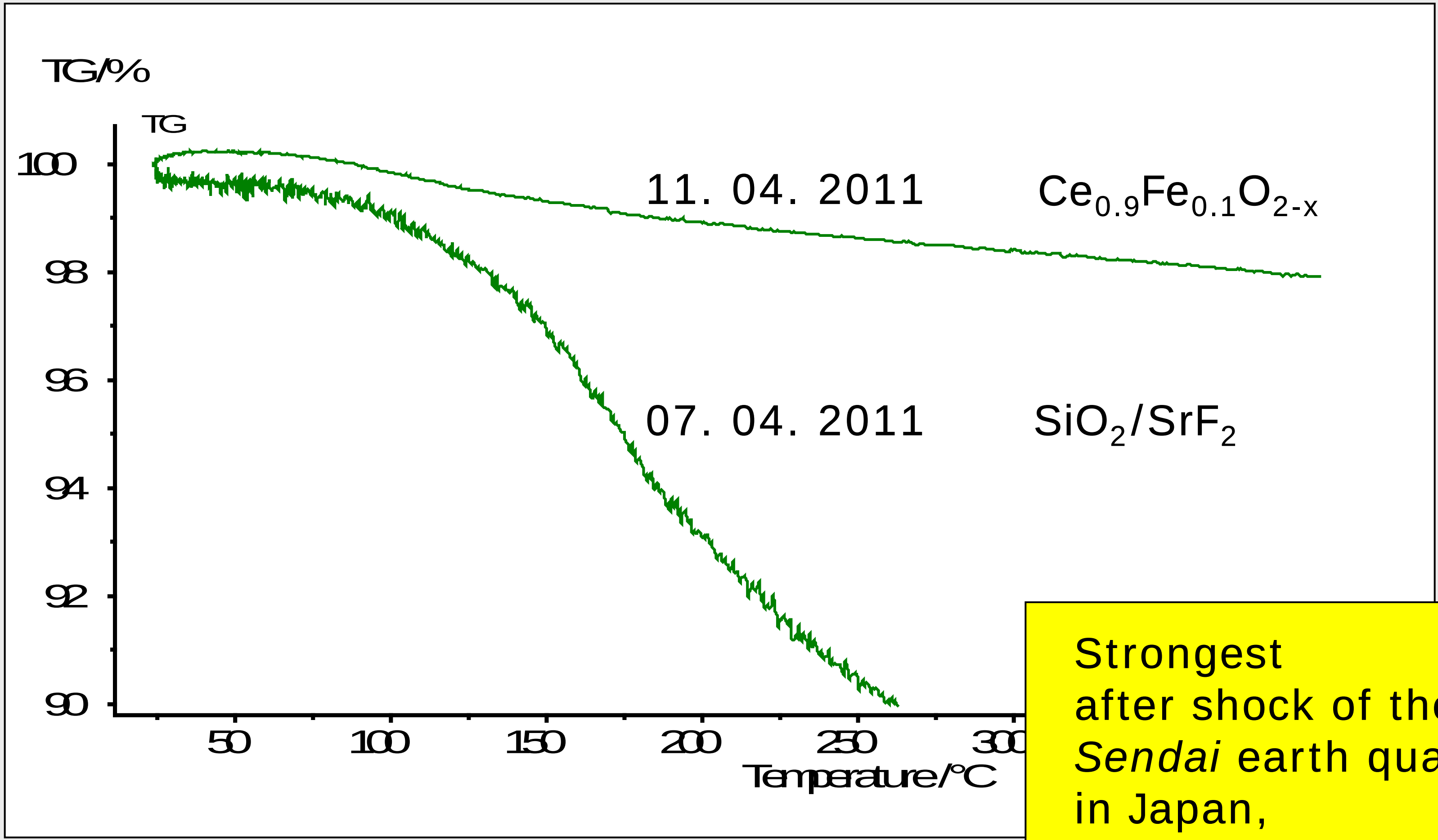
4. Influences on shape and quality of TA curves

Influences on shape and quality of DTA curves (1)

Sample mass	Great mass →	large DTA effects
		Temp.gradients; diffusion ...
	Small mass →	better for TG
		Δm ~ 0.5µg easy to measure
Heating or cooling rate	Rapid heating →	larger DTA effects
		„Over-running" the effects
Crucible material	Metals →	higher heat conductivity
	Pt, Al, W-Re	***Wicking-up the Pt wall by molten salts***
		PH_3 , CH_x , C in Pt (> 900°C)
		$BaCO_3$ in Pt (> 900°C)
		Metal fluorides attac Pt
		Recrystallization of Pt
	Corundum →	mostly (!) chemically inert
	Graphite, Si_3N_4	***CuO/Cu_2O(1000°C) penetrate***
Purge gas / Reactive gas	endo / exo →	e.g. for CO release
Gas flow rate	rapid flow →	sharper peaks, e.g. in PTA
Reference substance	active:	SiO_2 $\alpha \leftrightarrow \beta$ 571 °C,
	inactive:	α-Al_2O_3 Fp. 2035 °C, *or without !*

Influences on shape and quality of TA curves (2)

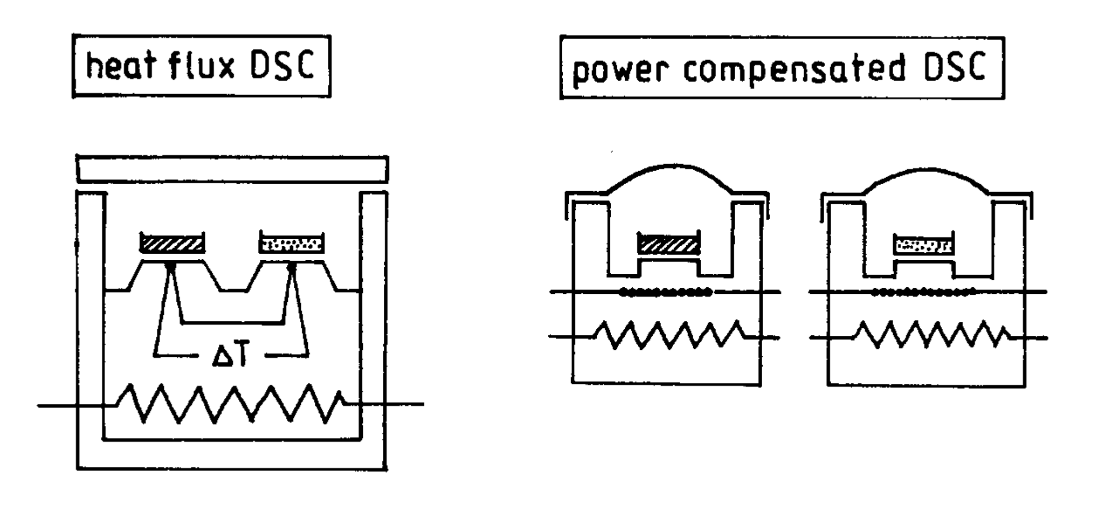
Building vibrations



Strongest
after shock of the
Sendai earth quake
in Japan,
April 7, 2011
(7.1 *Richter* scale)

5. DSC, DMA, and TOA

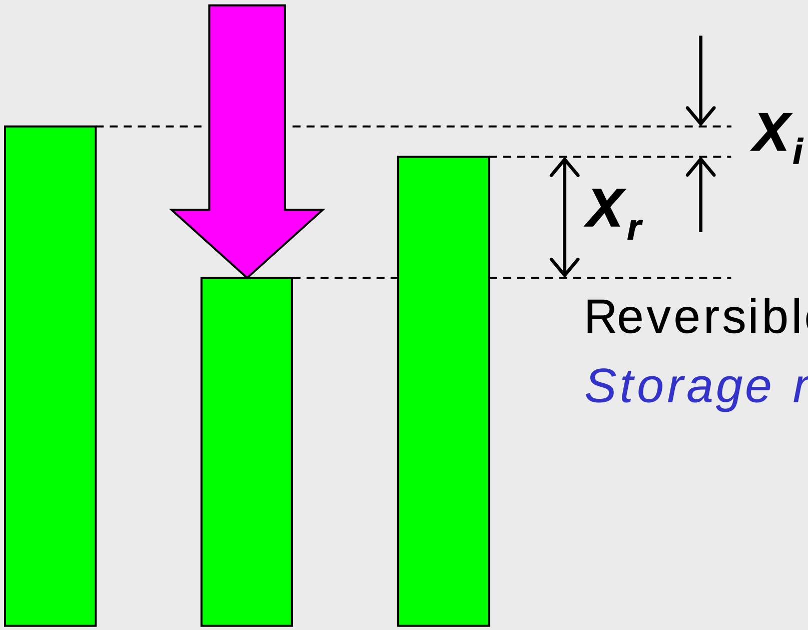
Differential Scanning Calorimetry (DSC)



Environmental heating by the furnace. Sample and measuring system follow passively.	Varying heat flow from separate heaters for maintaining $\Delta T=0$.
Sample and reference connected via a gold band: rapidly $\Delta T=0$	Difference in heating power is the measuring signal

Dynamic Mechanical Analysis (DMA)

The model of a strained sample incompletely restoring the original shape



Irreversible fraction *E''* [MPa]
Loss modulus (Verlustmodul)

Reversible fraction *E'* [MPa]
Storage modulus (Speichermodul)

Elastic behaviour:	The original shape is completely restored
Viscous ~ :	Shape change is not fully restored
Viscoelastic ~ :	Between both

Thermooptical analysis (TOA)

Video-supported investigation

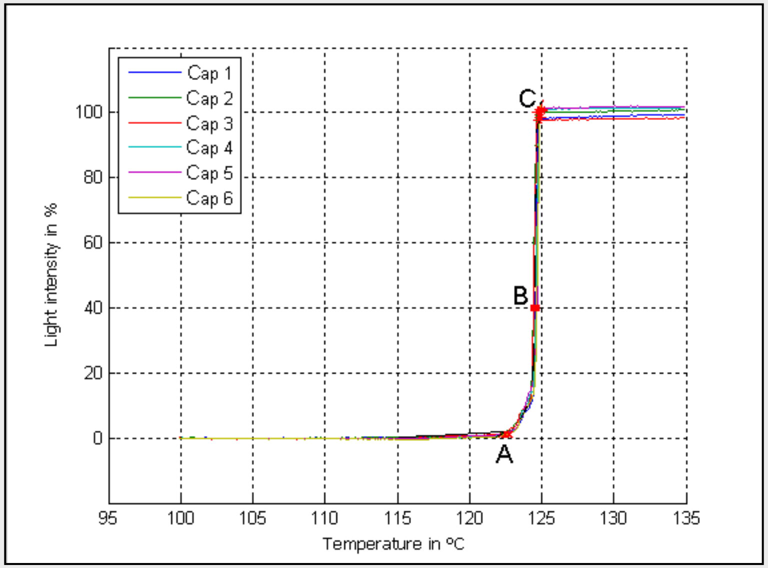
of phase transitions

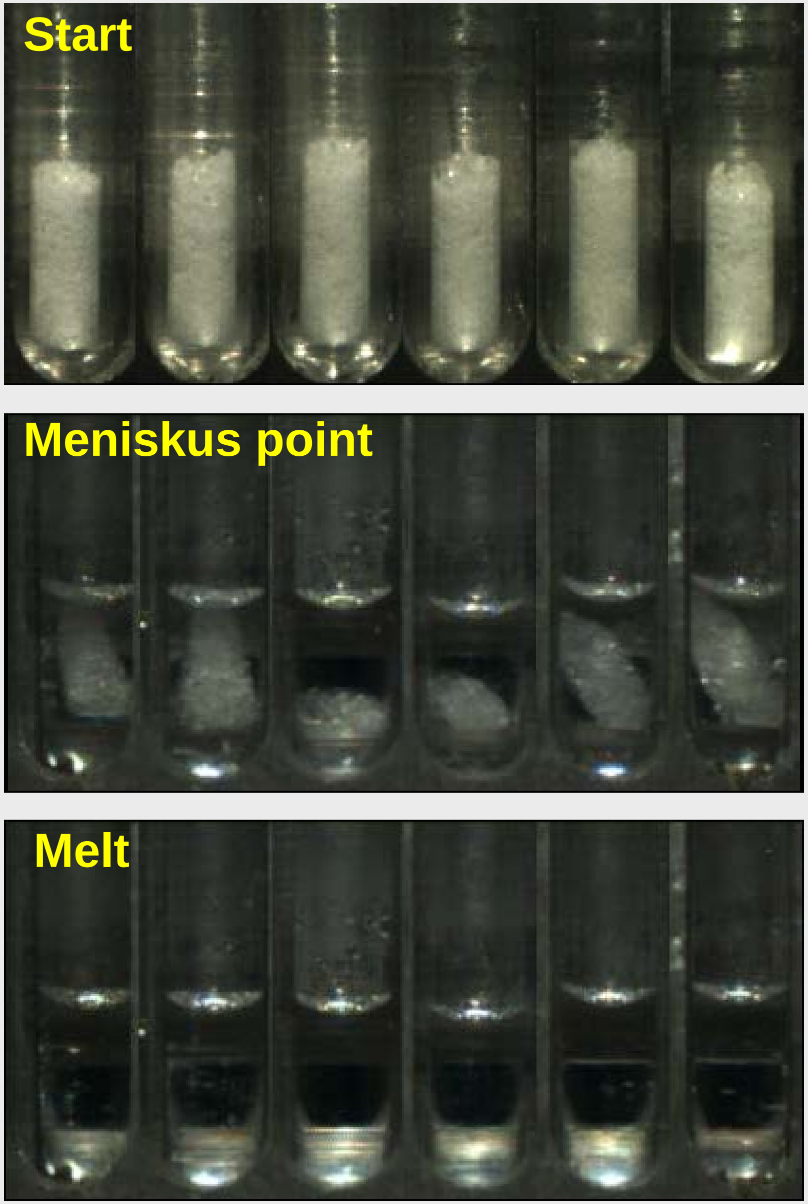
METTLER TOLEDO MP50, MP70, MP90

Light transmission of solid samples

Light source: LED
Detector: Video camera

Video record of the melting process, registration of a light intensity curve

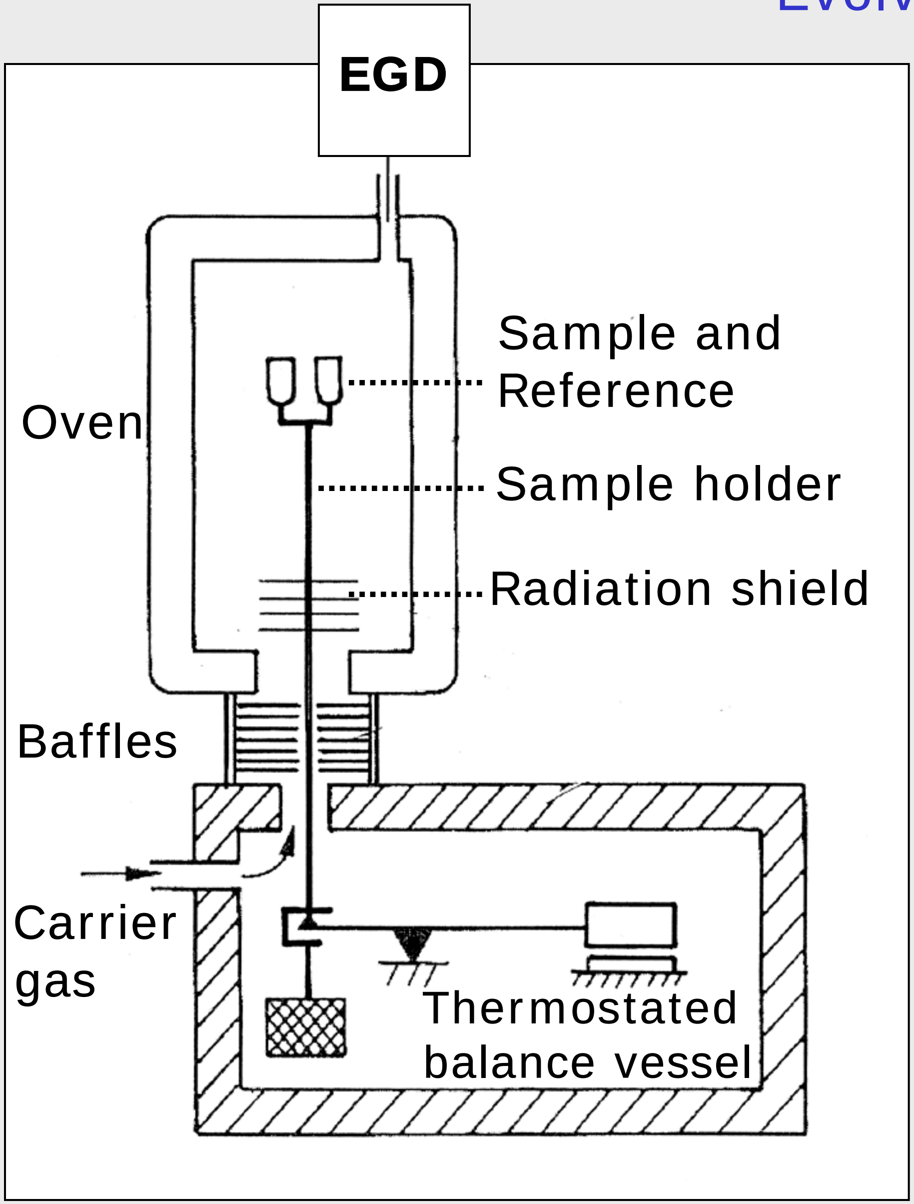




M. Wagner, TA UserCom 29 (2009)

6. Coupled techniques in Thermal Analysis - Evolved Gas Analysis (EGA)

Setup of a STA device coupled to Evolved Gas Analysis



TA-MS

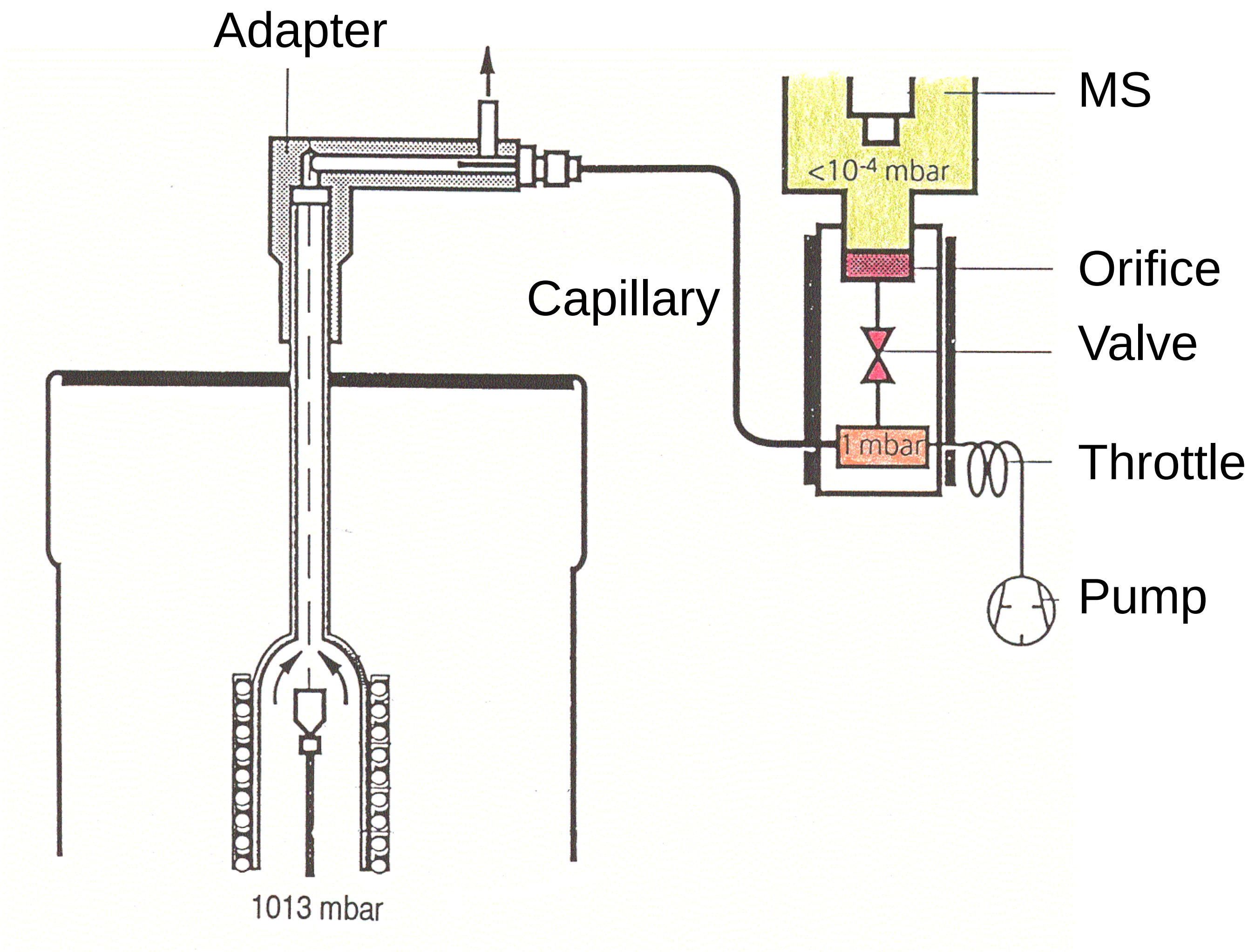
TA-FTIR

TA-GC-MS

TA-SPI-TOFMS

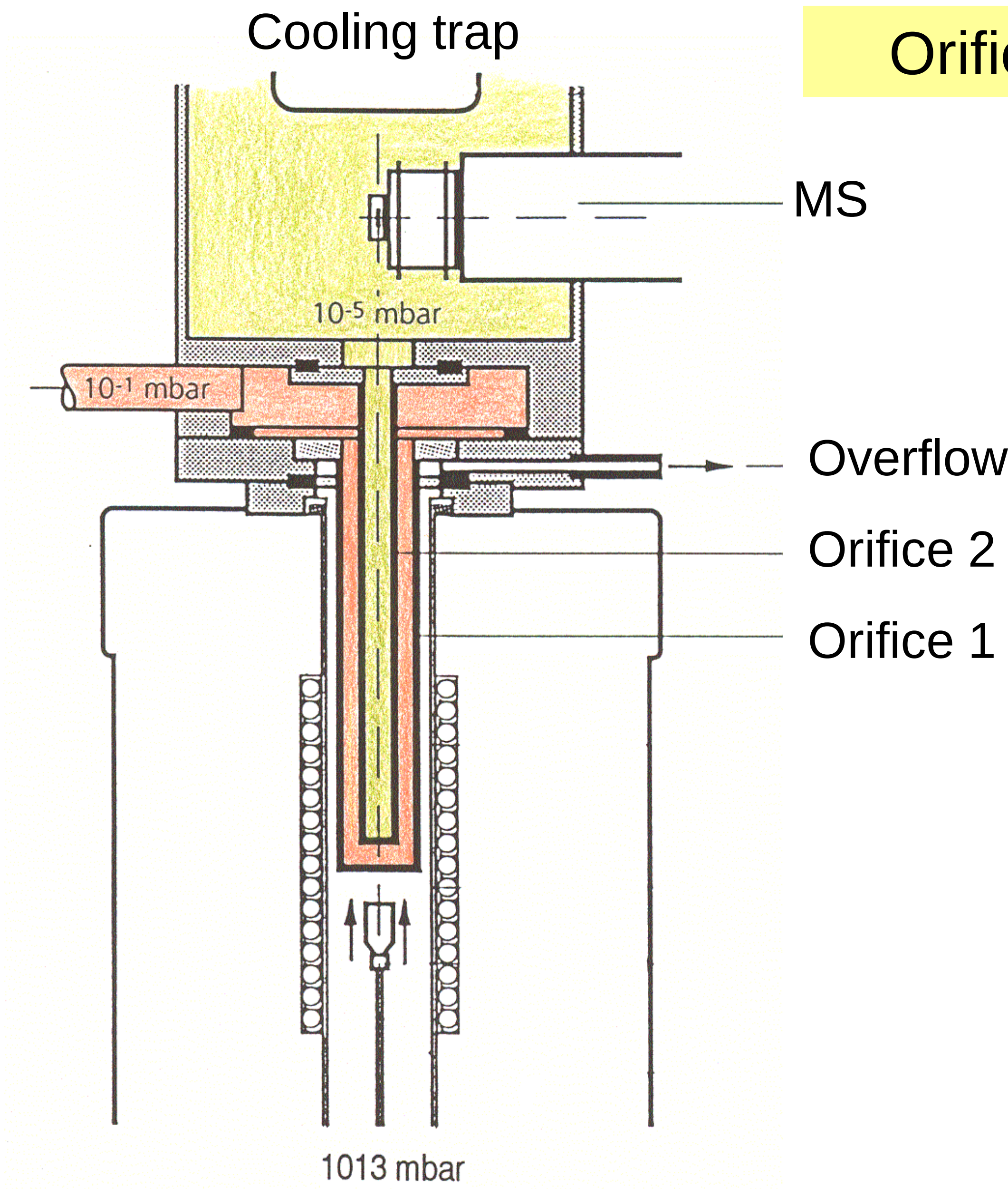
Capillary-coupled system

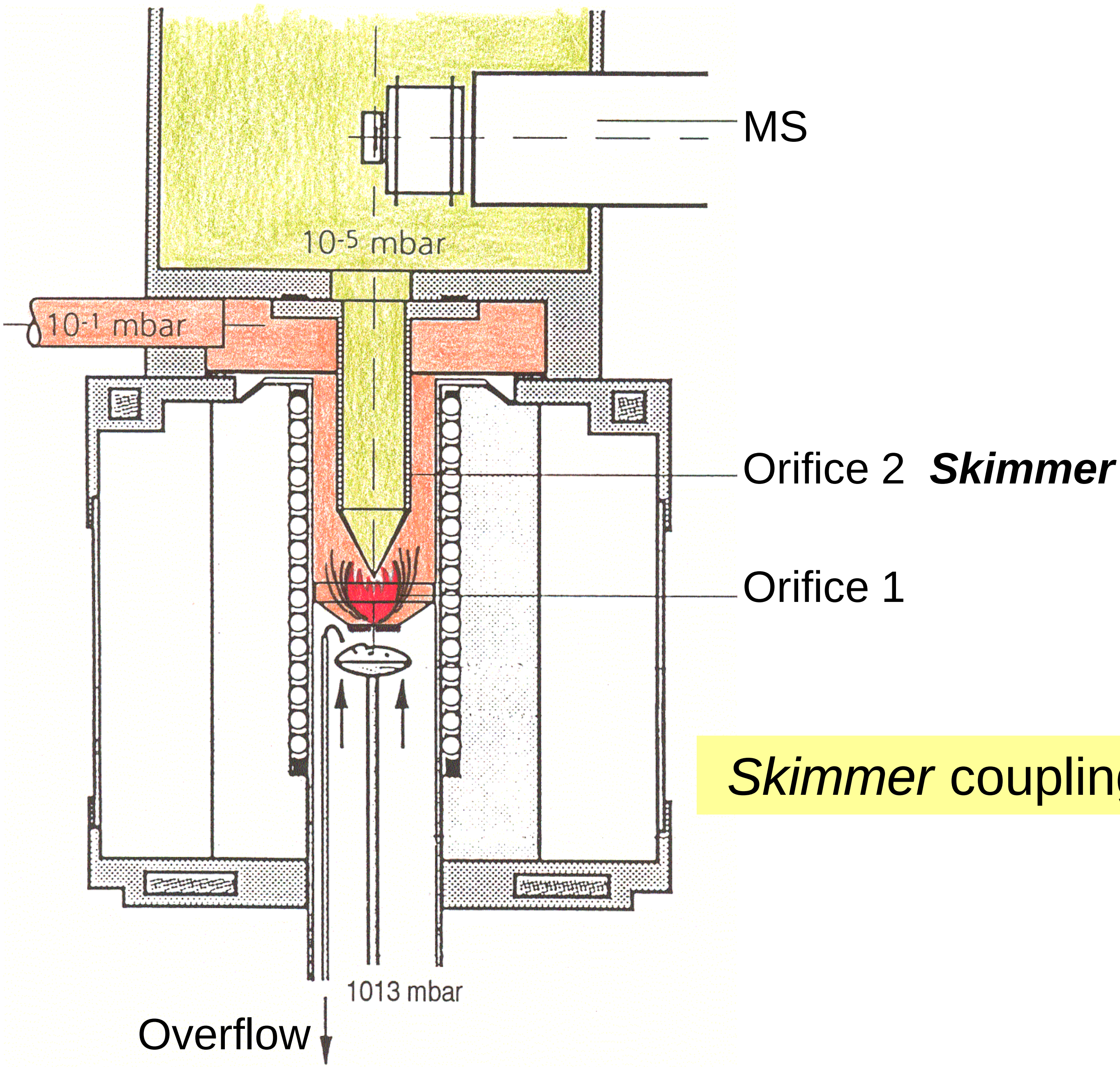
2400°C



Orifice coupling system

1500°C

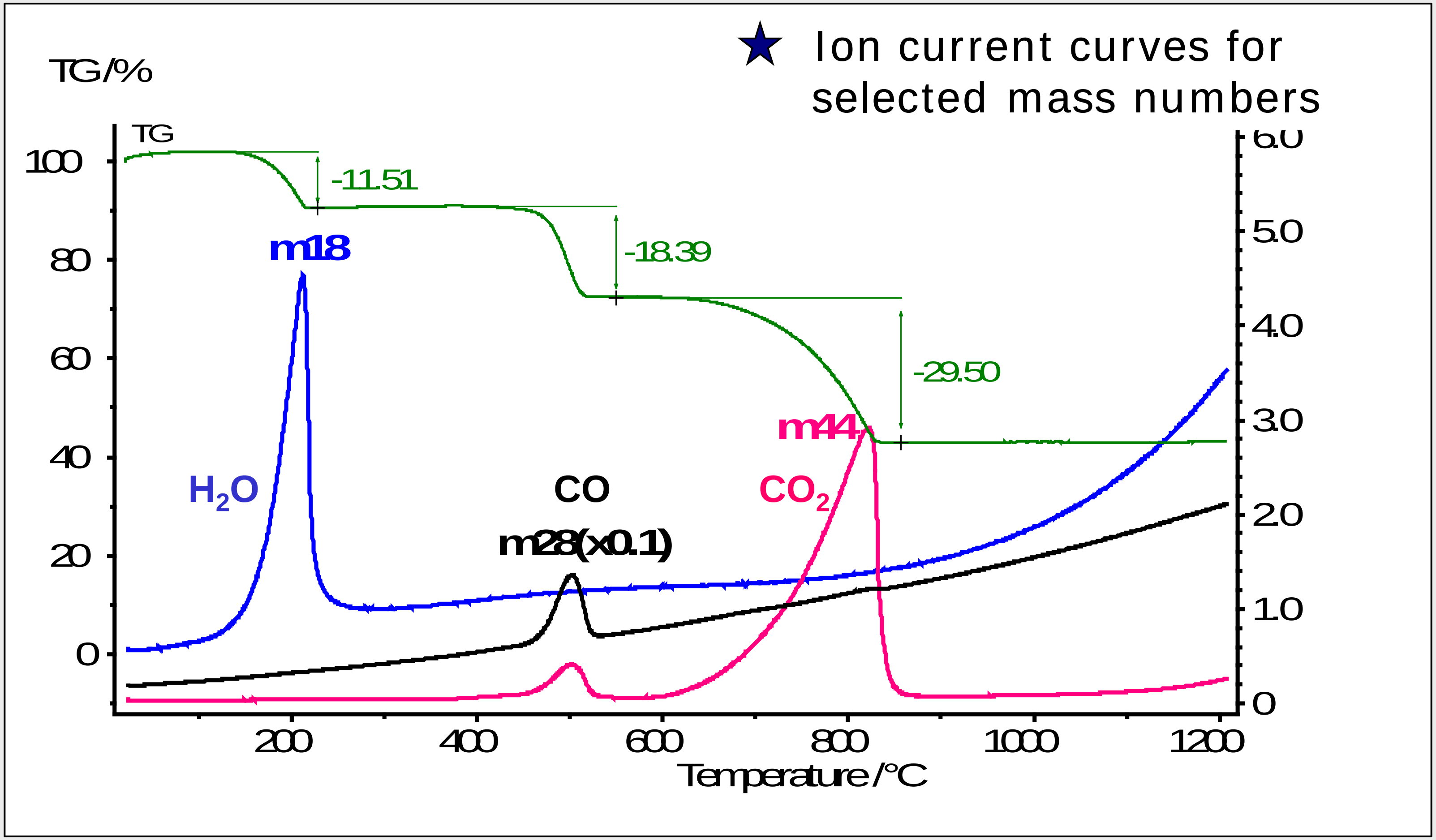




Skimmer coupling system

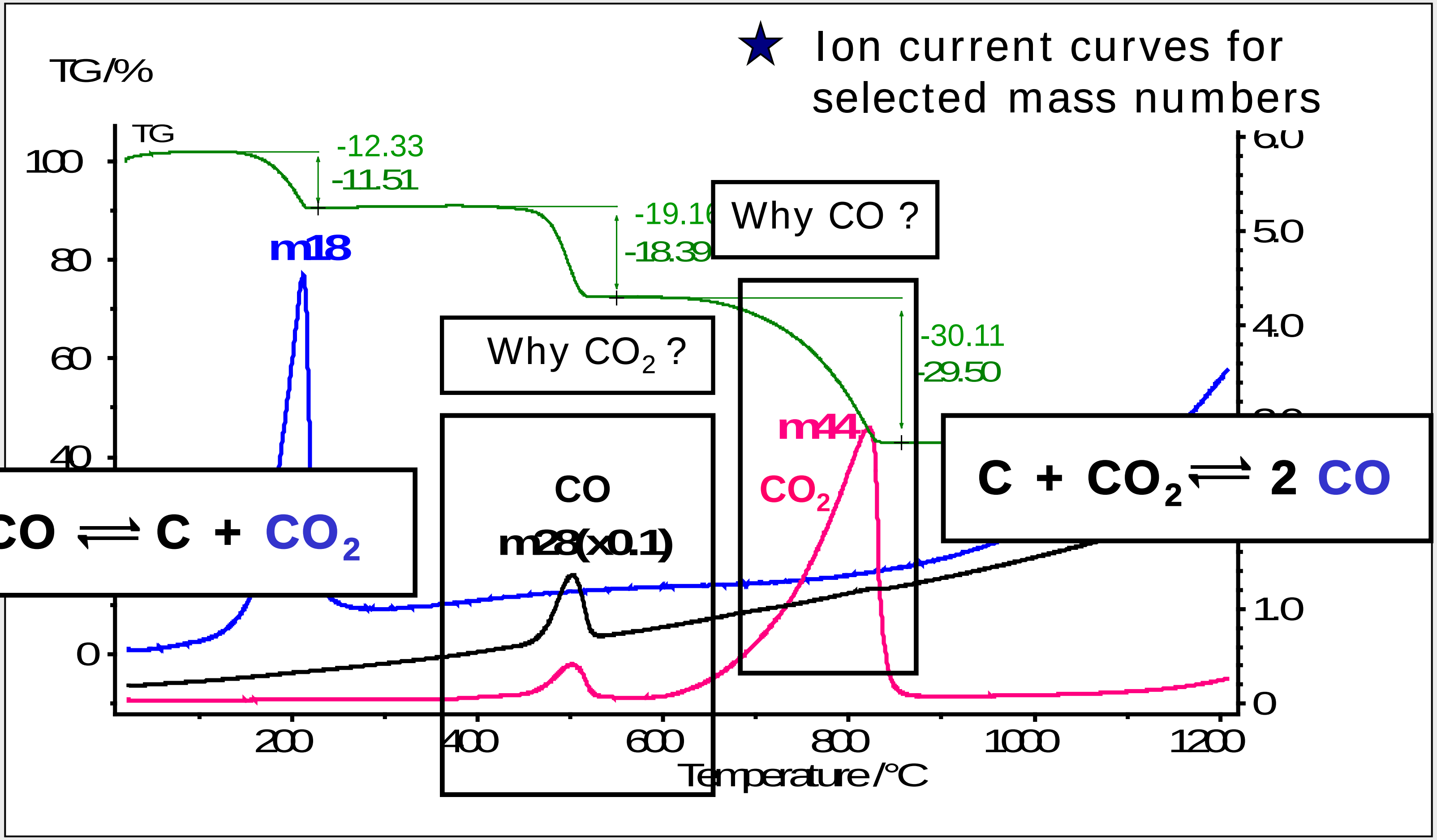
1500°C

$CaC_2O_4 \cdot H_2O$ *in Ar*



$CaC_2O_4 \cdot H_2O$ *in Ar*

BOUDOUARD

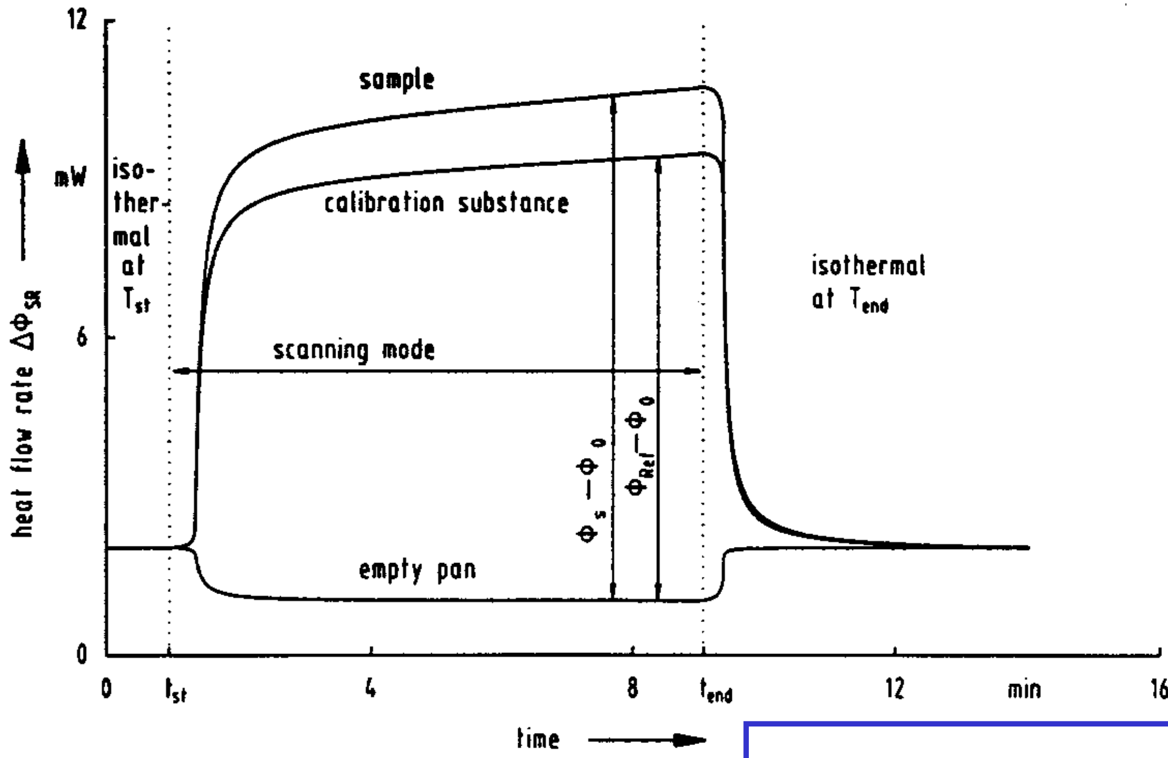


$$CaC_2O_4 \cdot H_2O \xrightarrow{-H_2O} CaC_2O_4 \xrightarrow{-CO} CaCO_3 \xrightarrow{-CO_2} CaO$$

7. Determination of further thermal parameters

Heat capacity

Thermal diffusivity

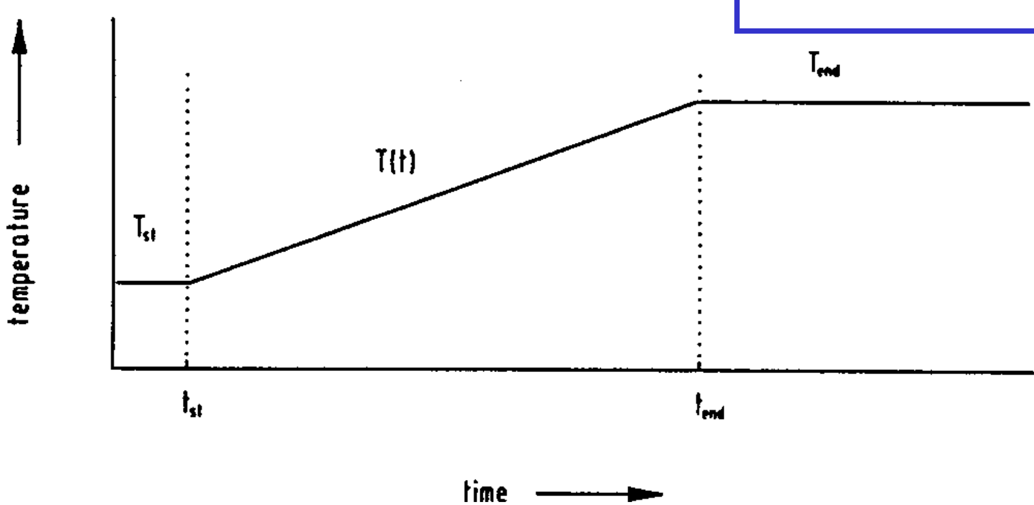


Three-step procedure to determine C_p by employing DSC :

Heat flow of

1. *empty crucibles*
2. *calibration substance R*
3. *sample S*

$$\Delta\Phi_{SR} = \Phi_S - \Phi_R = C_S \frac{dT_S}{dt} - C_R \frac{dT_R}{dt} = (C_S - C_R) \cdot \beta$$



β - Average heating rate (different for S and R !)

Höhne, Hemminger, Flammersheim (1996)

Thermal diffusivity - *The laser flash method (1)*

Heat flow

$$\dot{q} = - \lambda \, grad\, T$$

T = f(x,y,z)

λ - Thermal conductivity

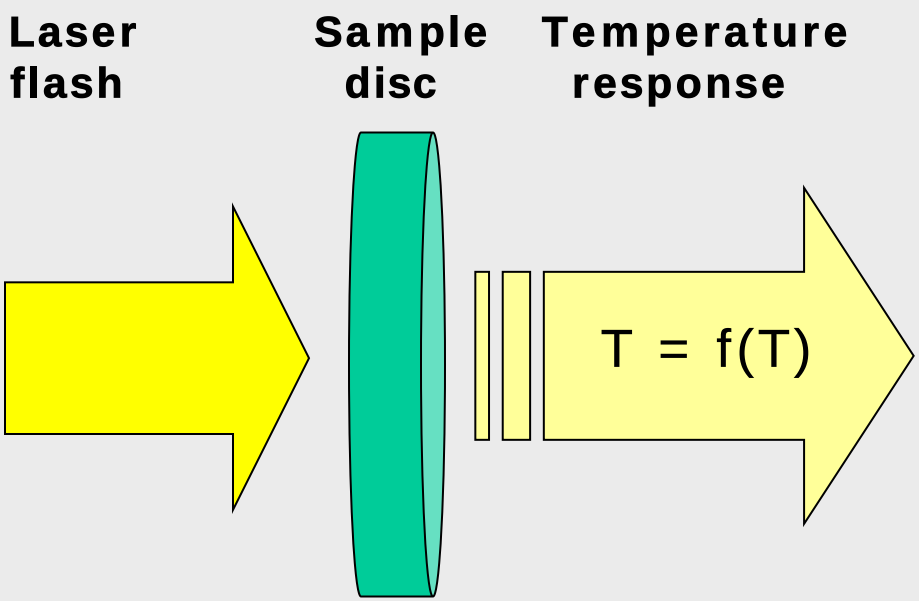
Thermal diffusivity

Temperaturleitfähigkeit

$$\frac{\partial T}{\partial t} = \frac{\lambda}{c_P \cdot \rho} \Delta T$$

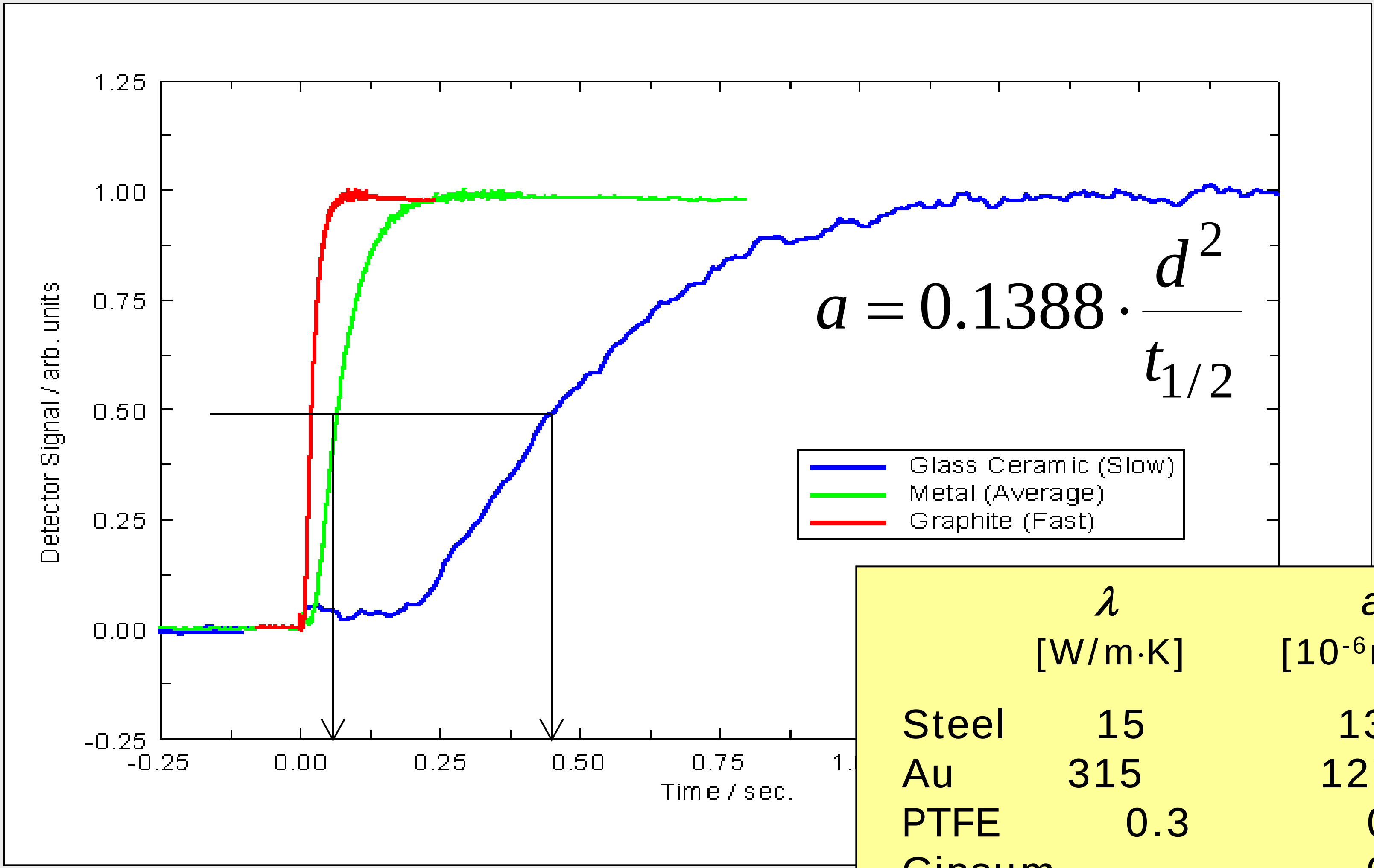
c_p – Heat capacity

ρ - Density



Thermal diffusivity - *The laser flash method (2)*

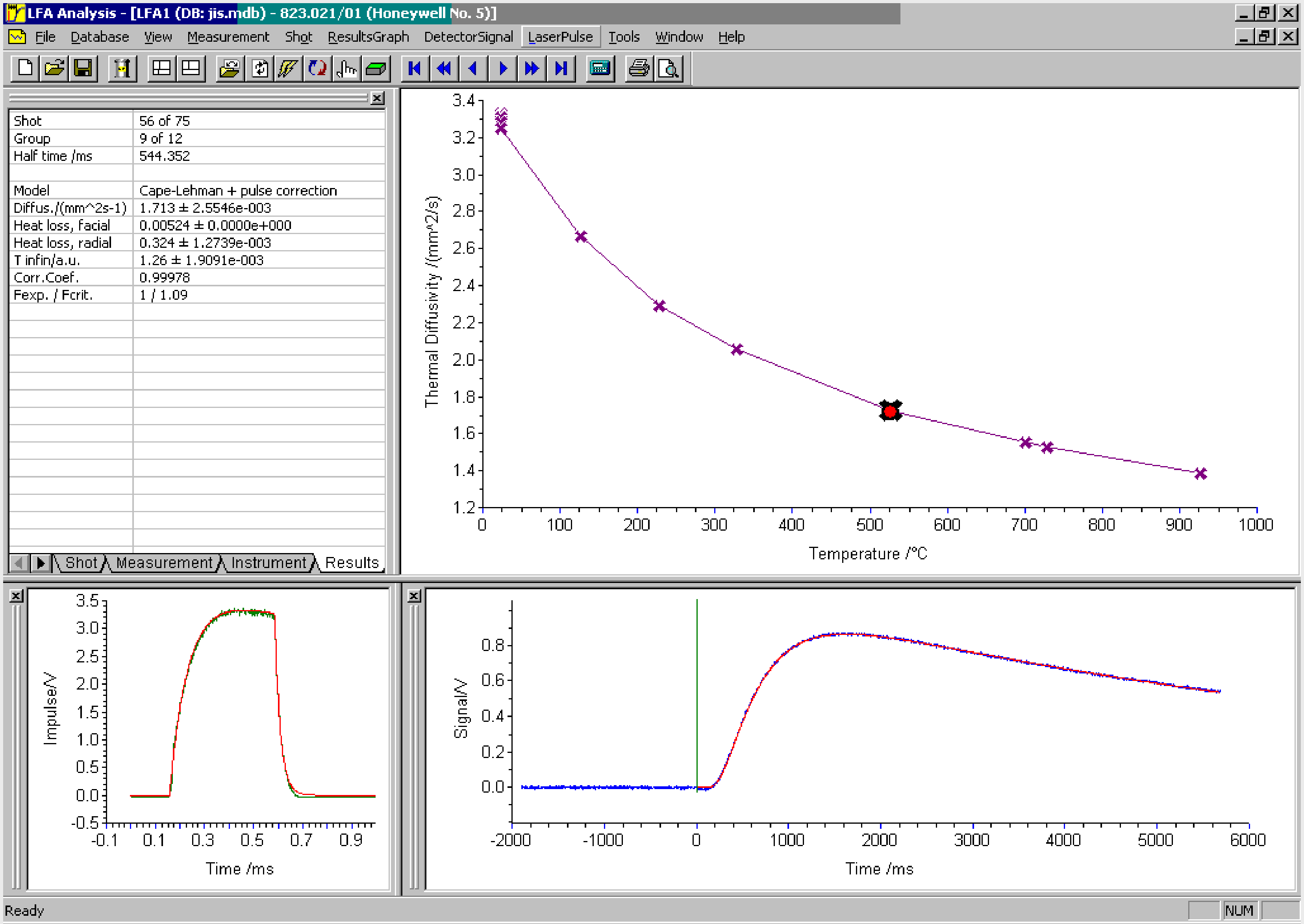
The $t_{1/2}$ method

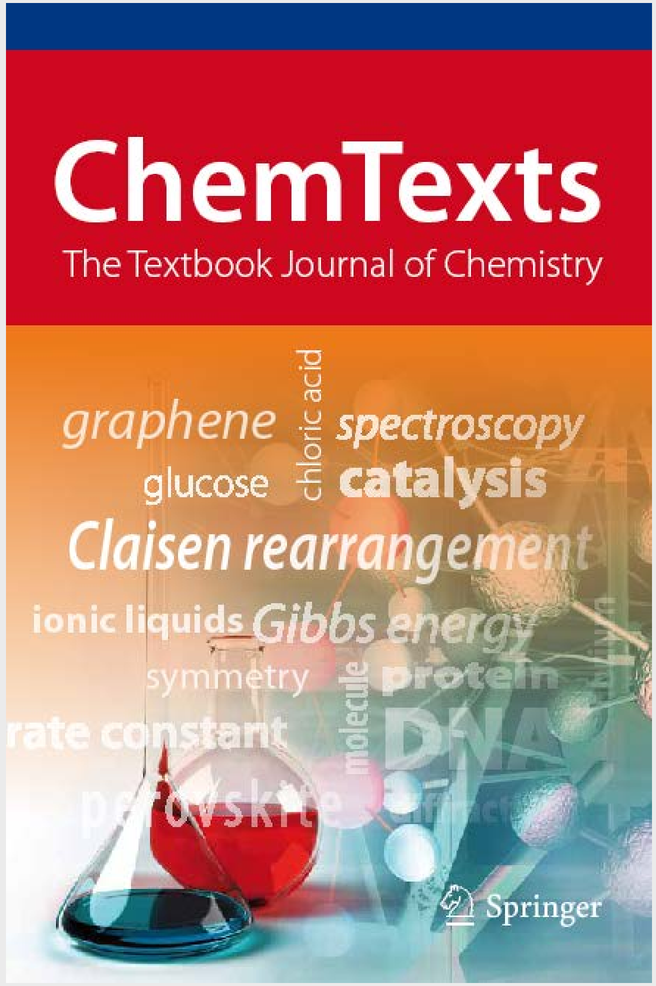


$$a = 0.1388 \cdot \frac{d^2}{t_{1/2}}$$

	λ [W/m·K]	a [10^{-6}m^2/s]
Steel	15	13
Au	315	127
PTFE	0.3	0.1
Gipsum		0.2

Thermal diffusivity - *The laser flash method (3)*





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