Methods of Thermal Analysis

Michael Feist

Berlin Humboldt University, Institute of Chemistry

1. Conventional Thermal Analysis
2. Simultaneous Thermal Analysis
3. Hyphenated techniques in Thermal Analysis (EGA)
4. *PulseTA*® and catalysis
5. Determination of other thermal properties

1. Conventional Thermal Analysis

- History
- Cooling curves
- The phase rule
- Measuring principles of DTA and DSC
- Information content
- Sample carriers

Aristoteles (384-322 B.C.)

Fire is the general analysator of matter.

Robert Boyle *„The Sceptical Chemist“* (1661):

No, it is **not**, because it is destructive.

Thermal analysis: **T = f(t)**

D**T = f(t or T)**

Following the change of a physical property of a substance subjected to a controlled heating program depending on time or temperature.

Joseph Black (1728-1799)

Latent heat

Antoine L. Lavoisier (1743-1794)

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 setup with inert reference (1899)

Josiah Willard Gibbs (1839-1903)

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

In many cases, the temperature-depending change of properties characterize a substance in the same unequivocal manner as can be done by its formula or its structure.

K. Heide (1982)

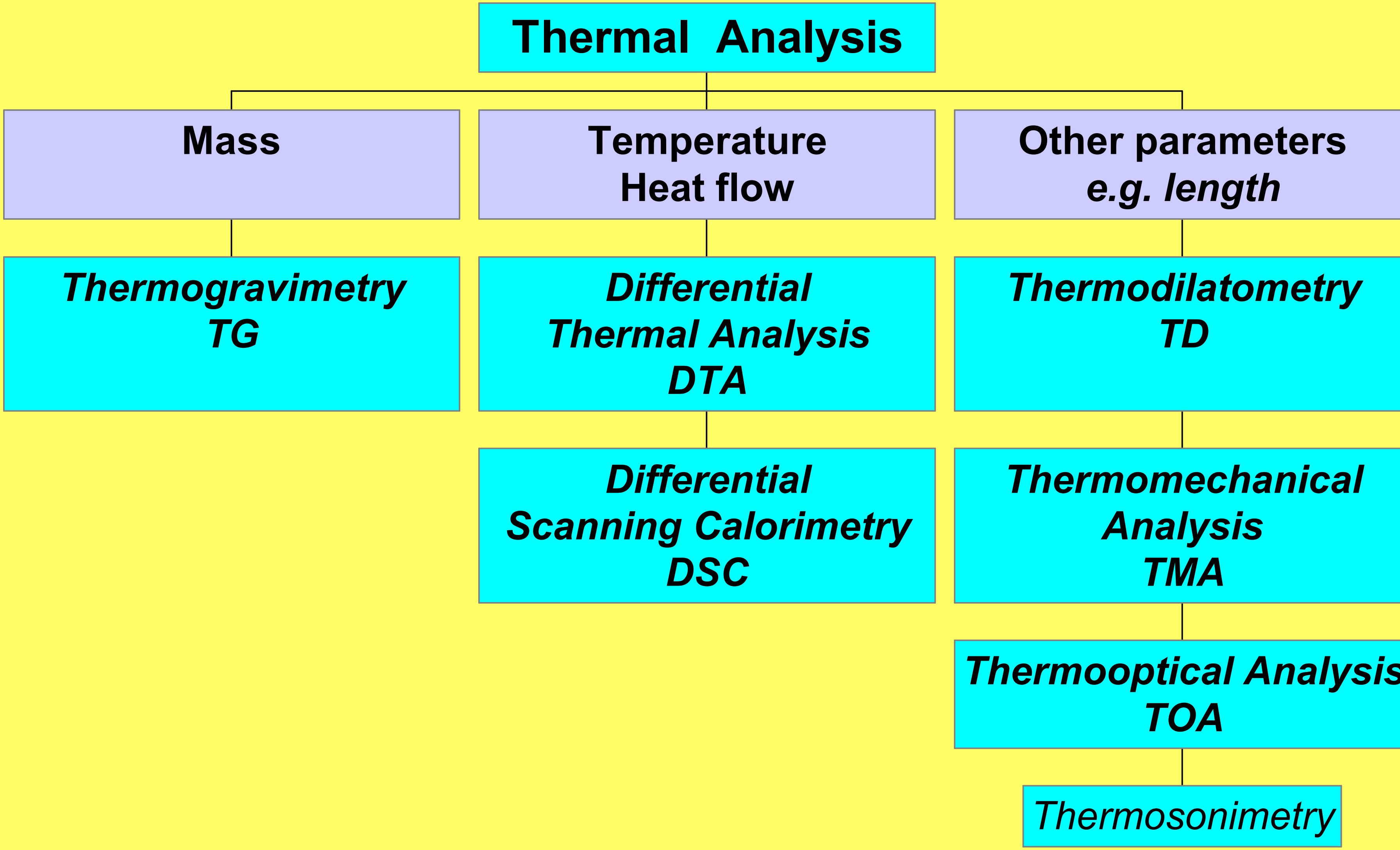
The subject investigated: A phase or a phase mixture

Changing temperature changes the phase state which yields

Information about **purity**

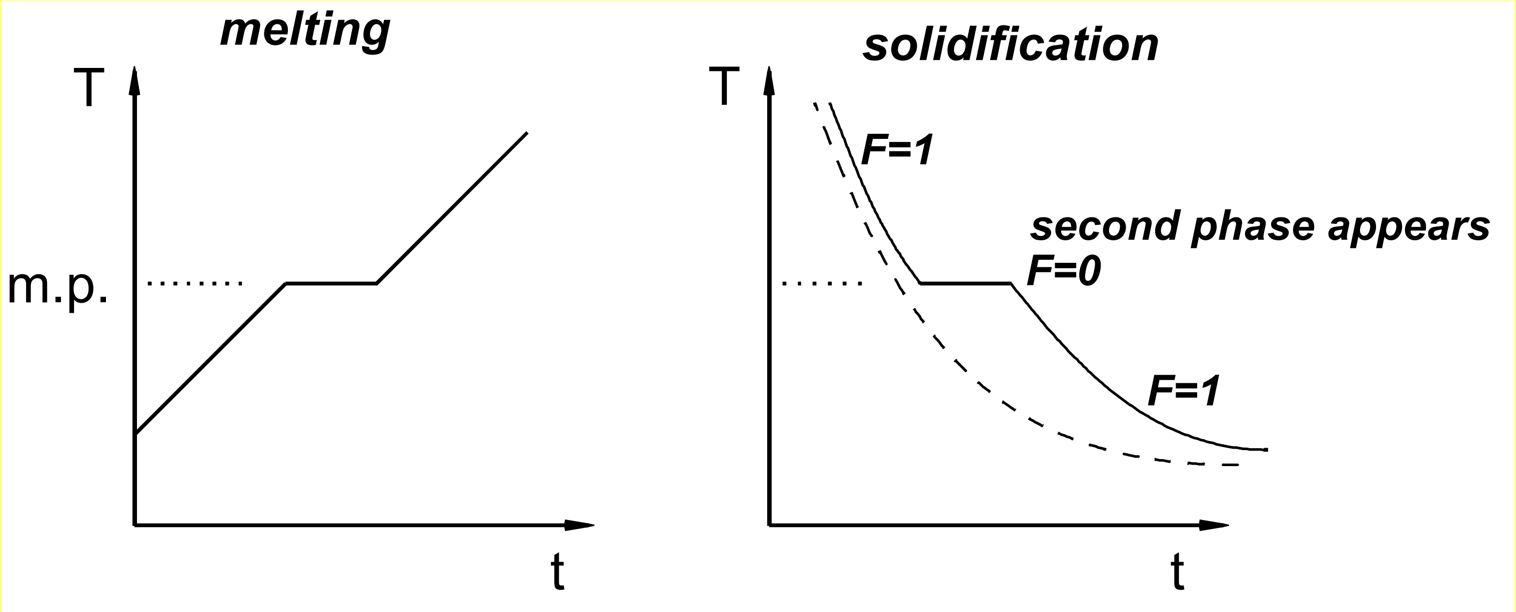
state diagrams

material constants


Thermal Analysis
Mass
Temperature Heat flow
Other parameters e.g. length
Thermogravimetry TG
Differential Thermal Analysis DTA
Thermodilatometry TD
Differential Scanning Calorimetry DSC
Thermomechanical Analysis TMA
Thermooptical Analysis TOA
Thermosonimetry

Classical thermal analysis -

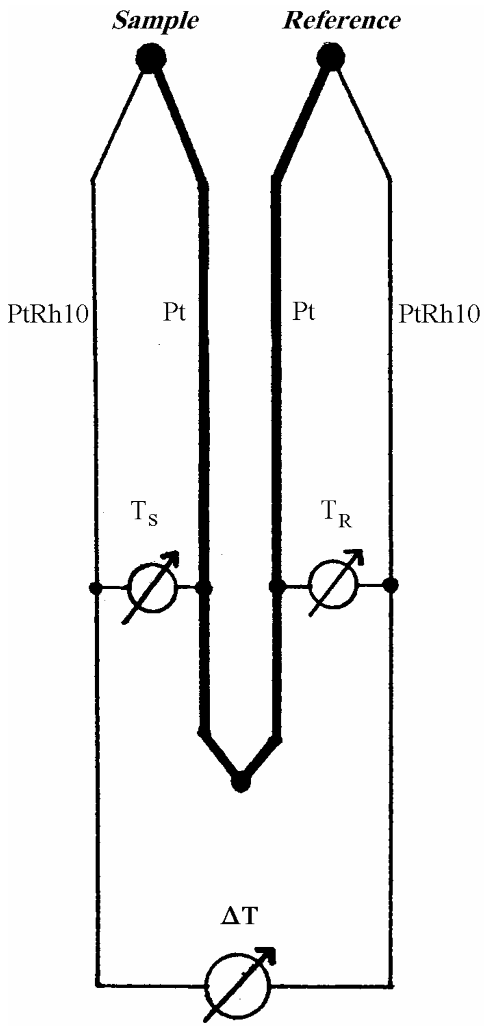
Heating and cooling curves of one-component systems

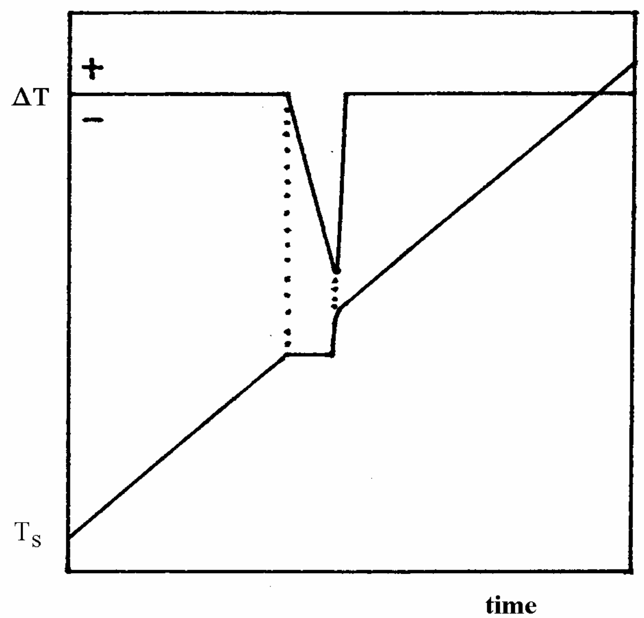


F = K - P + 2 - E ***E = 1** for p=const*

F = K - P + 1

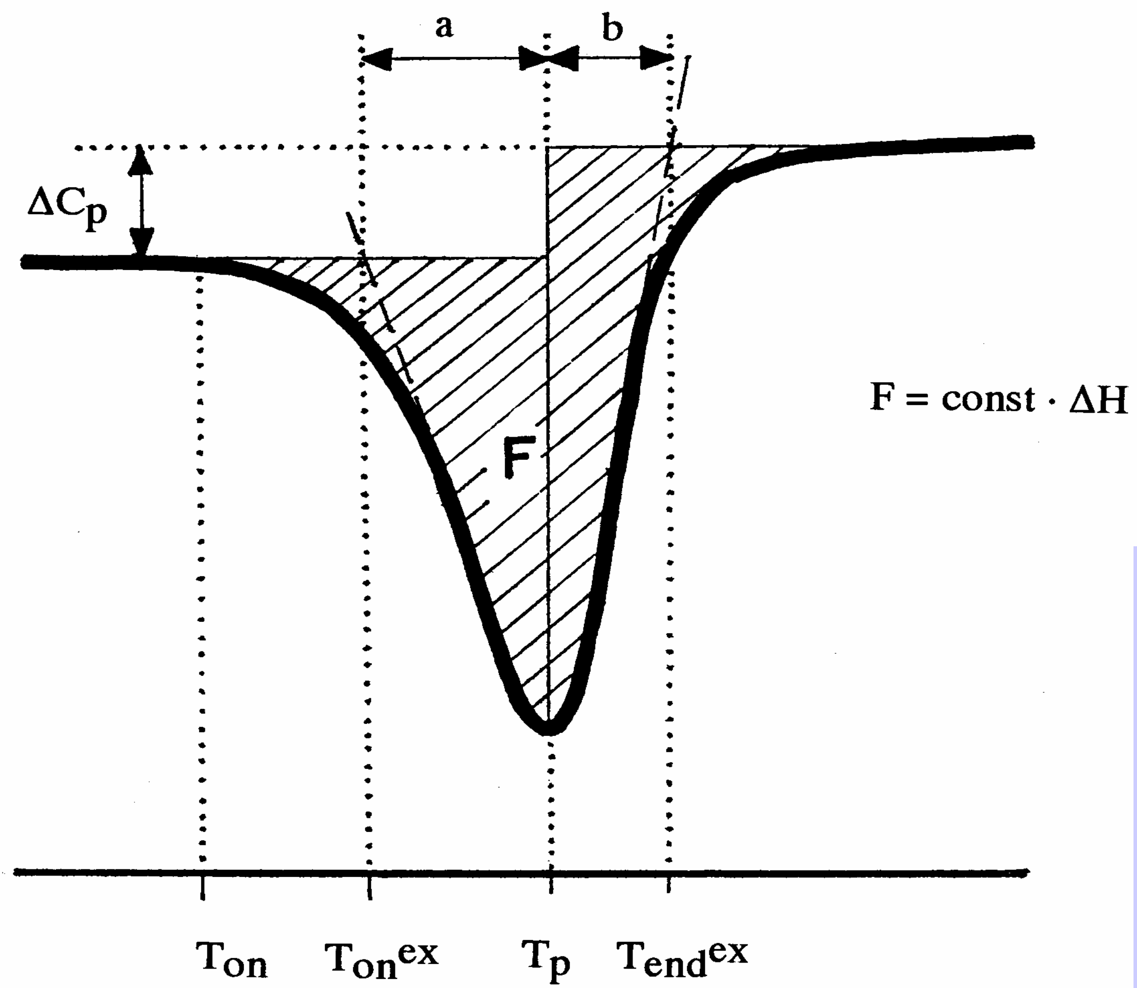
Differential measuring setup - Generation of the DTA signal





Asymmetric signal shape

The information contained in the DTA signal



$$h = u + pv$$

$$dh = du + pdv + vdp$$

$$du = dq - pdv$$

$$dq = du + pdv$$

$$dh = dq + vdp$$

$$vdp = 0$$

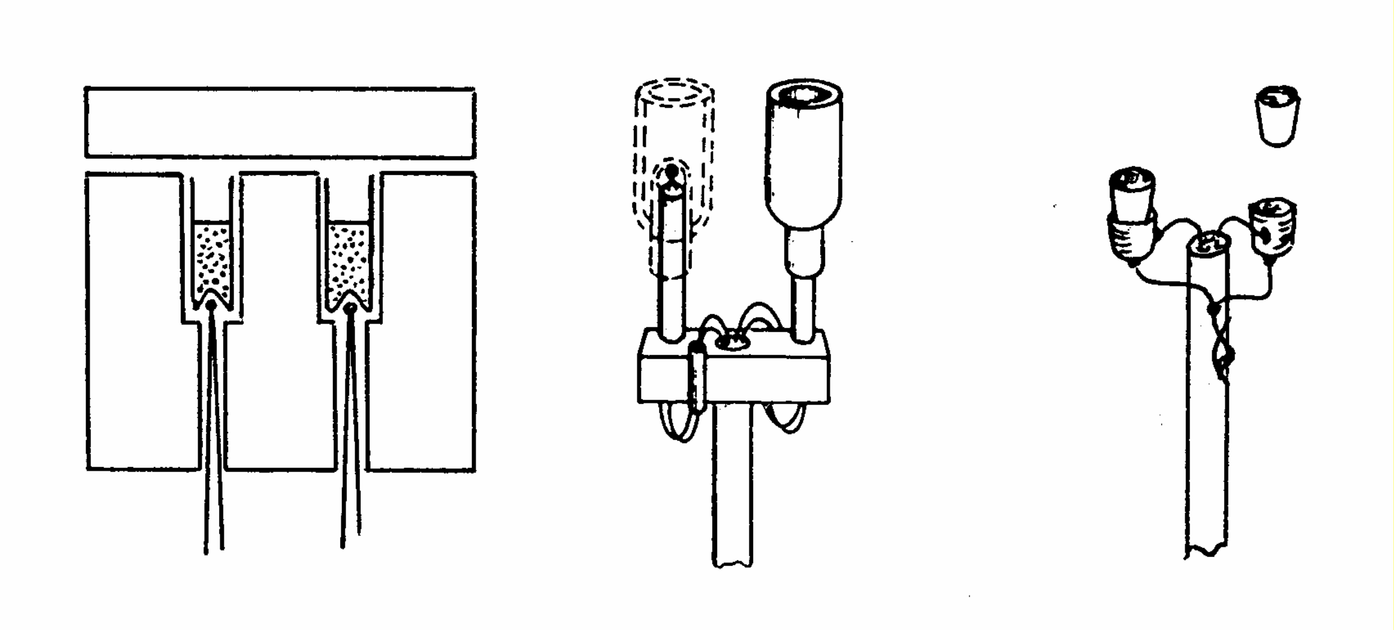
$$dh = dq_P$$

DTA sample holders

Metal block with symmetric holes

Pt or Al_2O_3 crucibles (baker)

Pt or Al_2O_3 crucibles with „crucible shoes“ as thermocouples

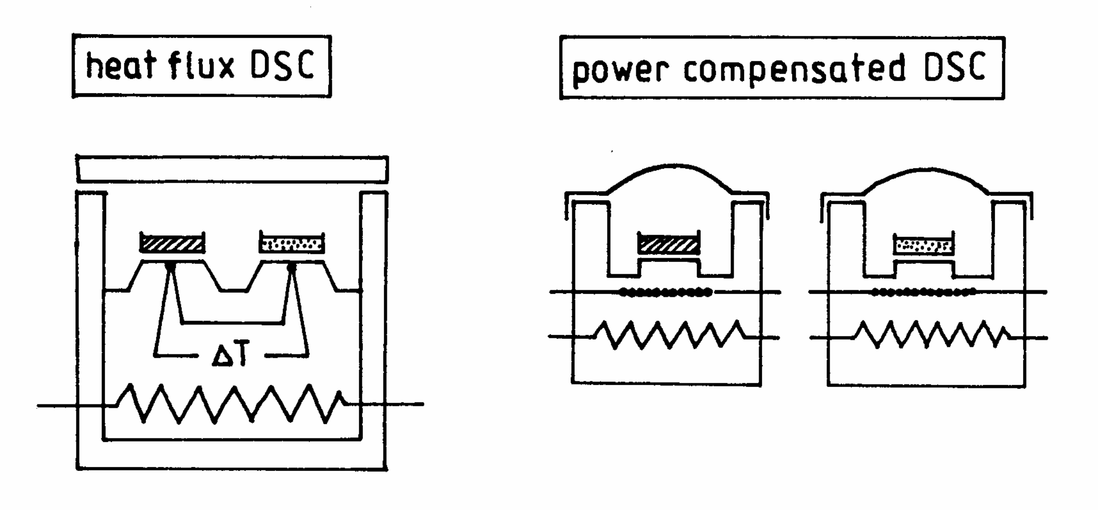


Rapidly $\Delta T=0$: High resolution

„Slower“ : High sensitivity

Minimal sample mass

Differential Scanning Calorimetry



Heating of the environment (oven) - sample and measuring system follow passively;
Sample and refence are connected via a gold band which sets $\Delta T=0$

Variable heat flow from separate heaters to maintain $\Delta T=0$

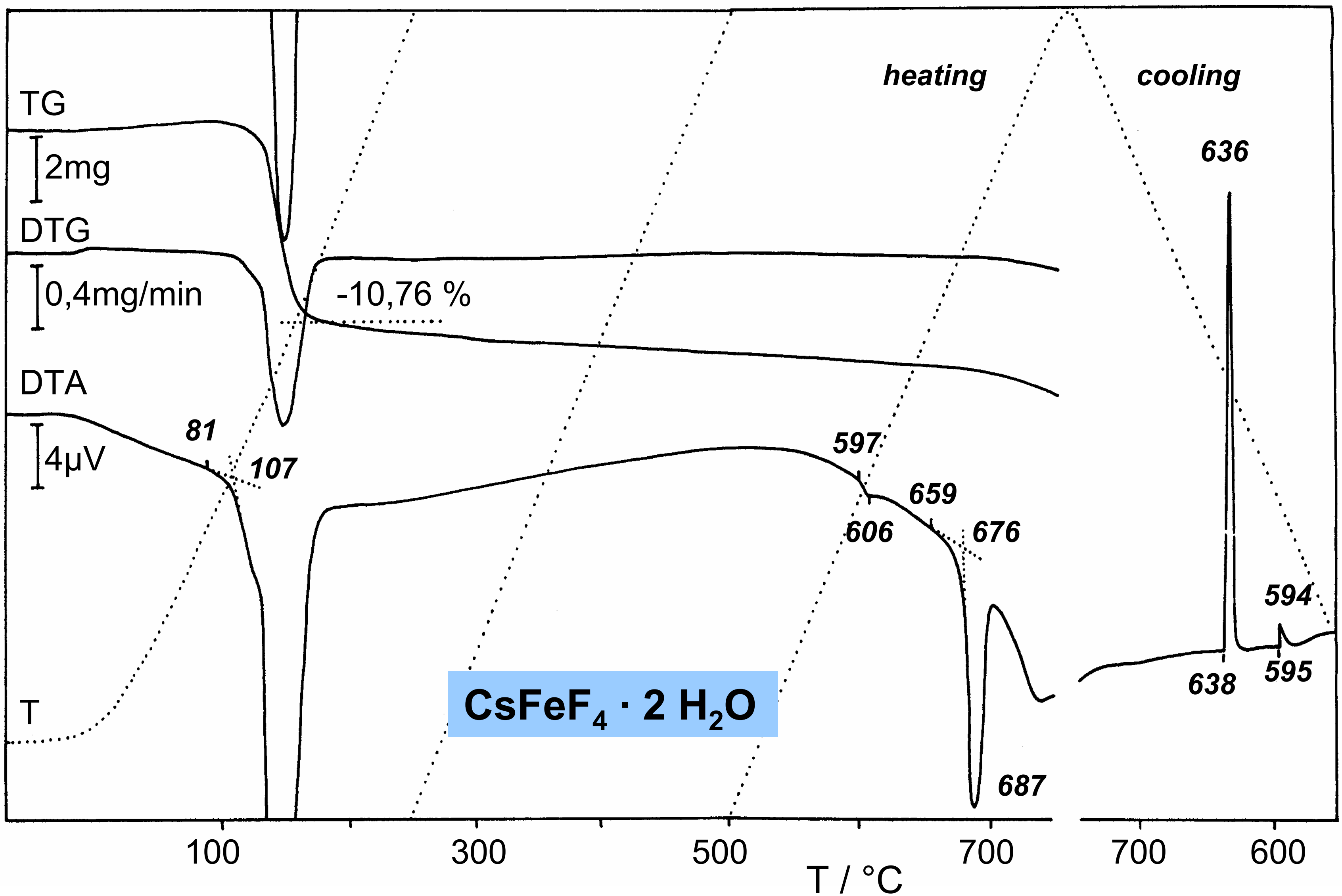
Difference in heating power is the measuring signal

2. Simultaneous Thermal Analysis

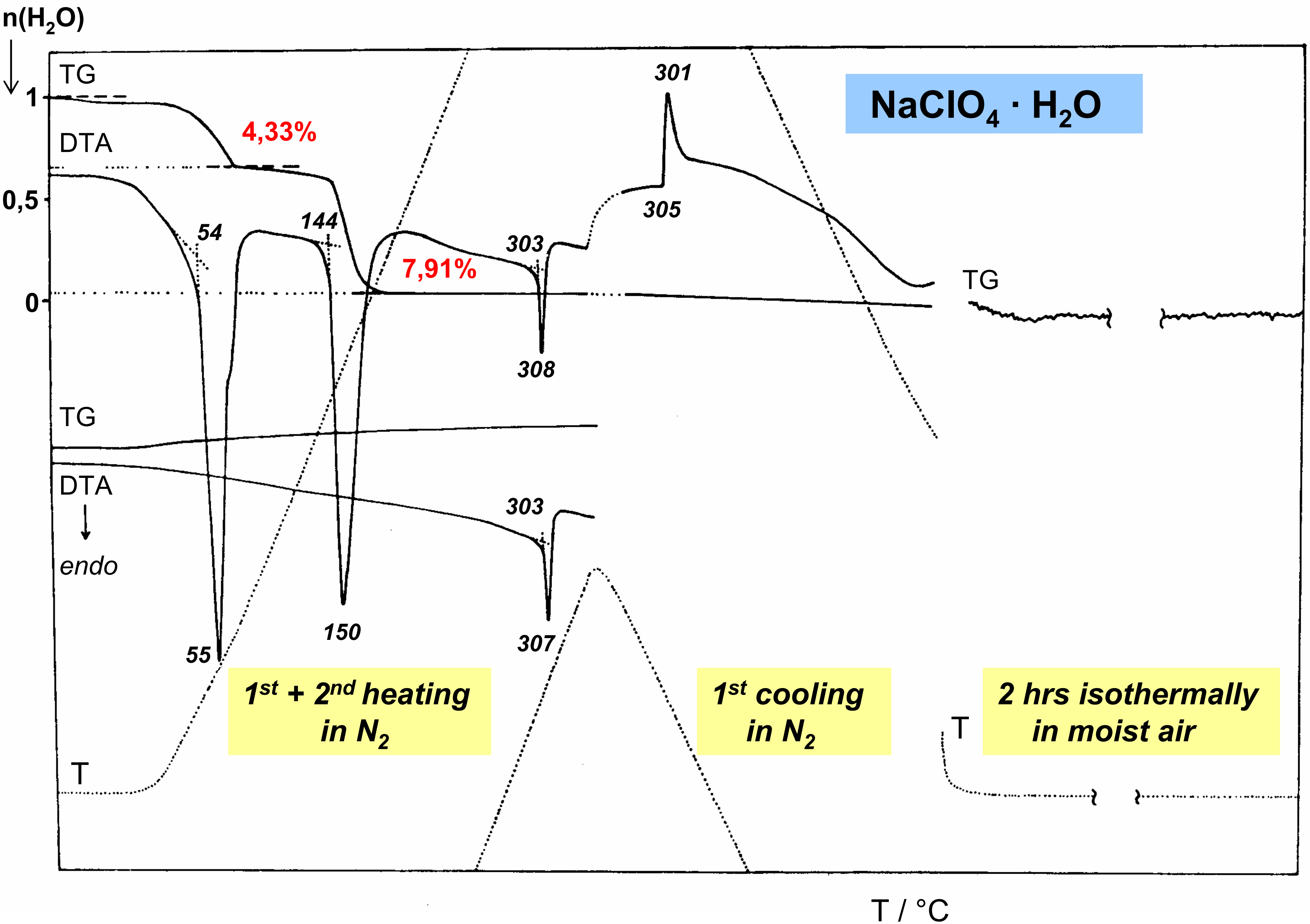
Heating and cooling ($CsFeF_4 \cdot 2\ H_2O$)

Repeated heating runs ($NaClO_4 \cdot H_2O$)

Gas changes (Coal)

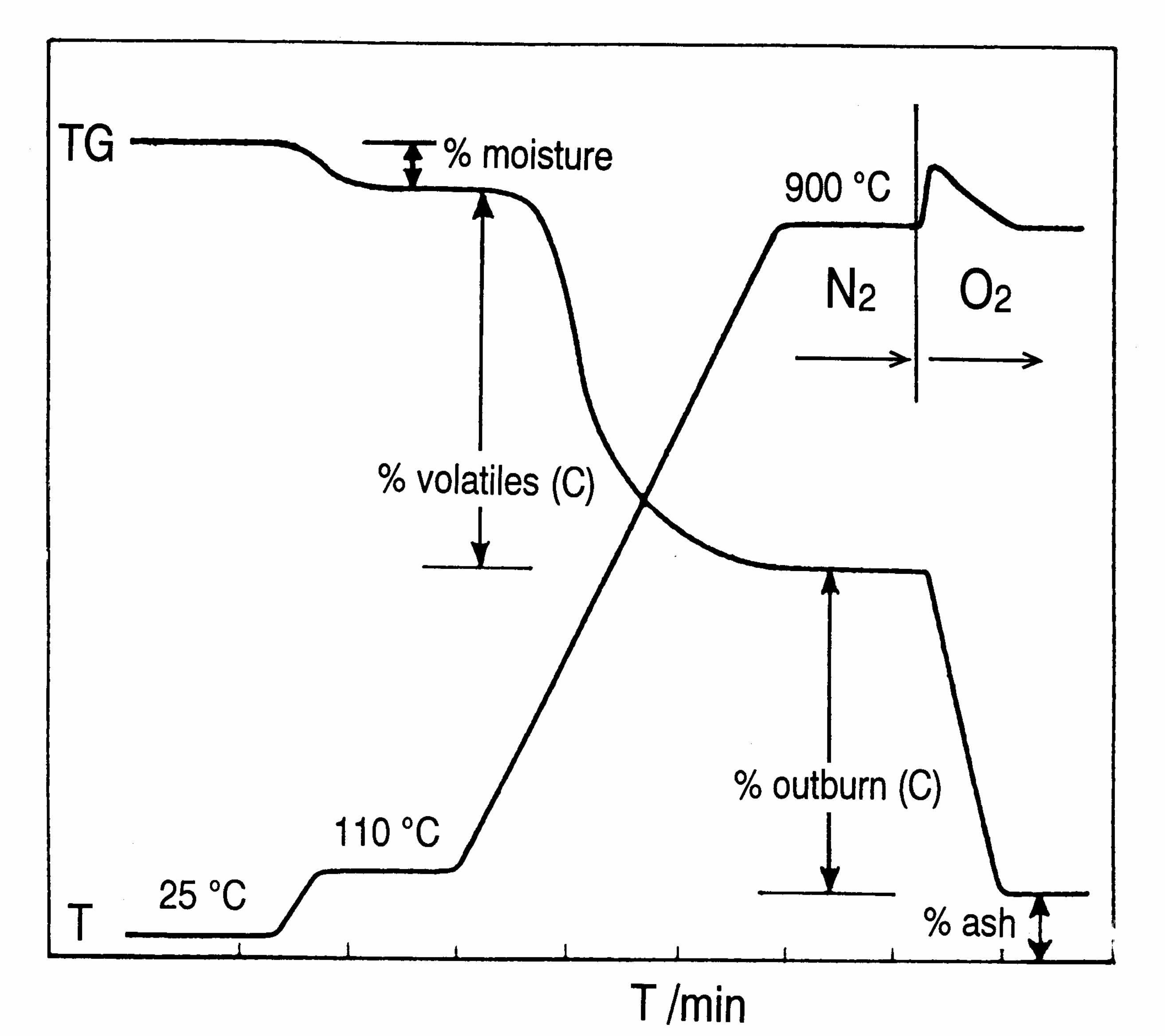


TG
2mg
DTG
0,4mg/min
DTA
4µV
T
heating
cooling
-10,76 %
81
107
597
606
659
676
687
636
638
594
595
$CsFeF_4 \cdot 2 H_2O$
100
300
500
700
700
600
T / °C



n(H2O)
1
0,5
0
TG
DTA
4,33%
7,91%
NaClO4 · H2O
301
305
54
144
303
308
TG
55
150
307
303
DTA
endo
T
1st + 2nd heating in N2
1st cooling in N2
2 hrs isothermally in moist air
T
T / °C

TG-Analysis of coal with changing atmosphere



Ottaway (1981)

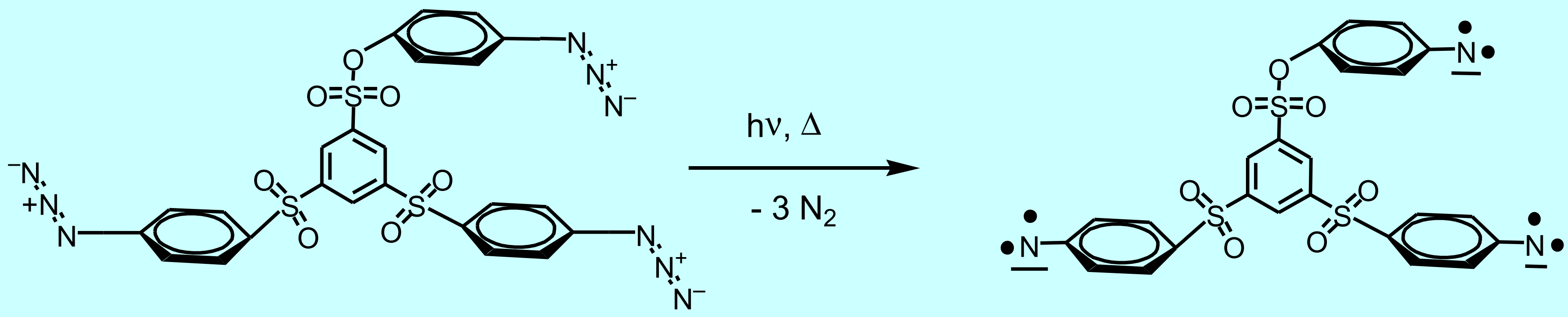
One TA run -

Four parameters characterizing a natural product

Explosive decomposition of a Tris-azide at 130°C

15 mg sample

$C_{24}H_{15}S_3O_7N_9$ ***25,55% N***



3. Hyphenated Techniques in Thermal Analysis (EGA)

- Gas flow in thermobalances
- Pressure reduction and unfalsified gas transfer
- Coupling systems in TA-MS
- Examples

Gas flow in thermobalances - *The influence of transport conditions*

- **Speed and Flow** Þ **d*elay in detection ?***
- **Flow profile** Þ ***laminar, turbulent ?***
  - ***Distribution of evolved gases in purge gas stream***
- **Flow direction** Þ ***influence of convection***
  - ***Controlled convection in vertical TG systems (chimney effect)***
- **Temperature gradients**
- **Position of transfer line connection**

Three main problems for TA-MS coupling devices

- **Pressure reduction**

    10^3 mbar ¾® 10^{-5} mbar

- **Condensation and secondary reactions**

    Unfalsified gas transfer

    Different viscosity - Demixing

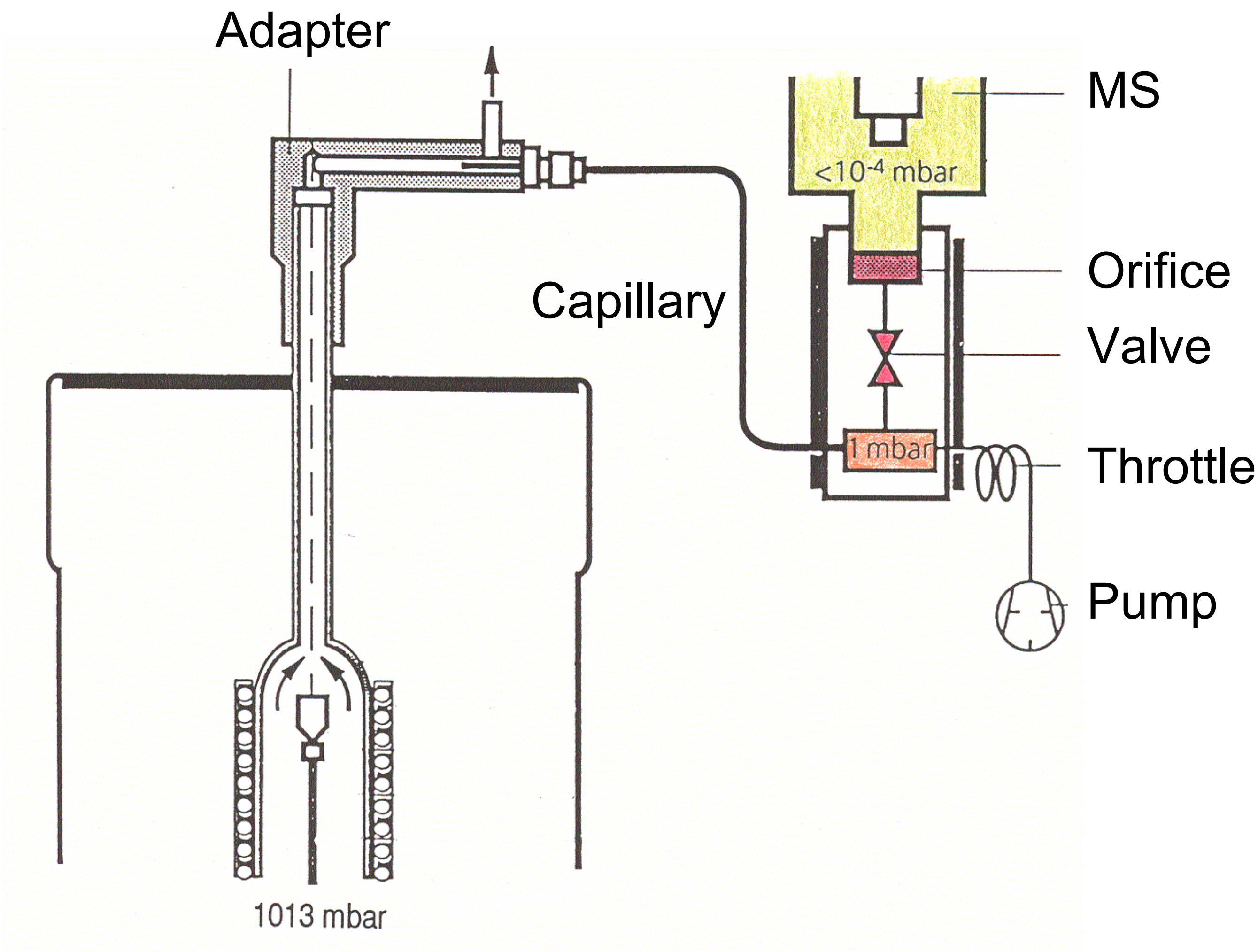
- **Attribution to a chemical process**

    Pyrolysis or Evaporation ?

    Fragmentation in MS or sample behavior ?

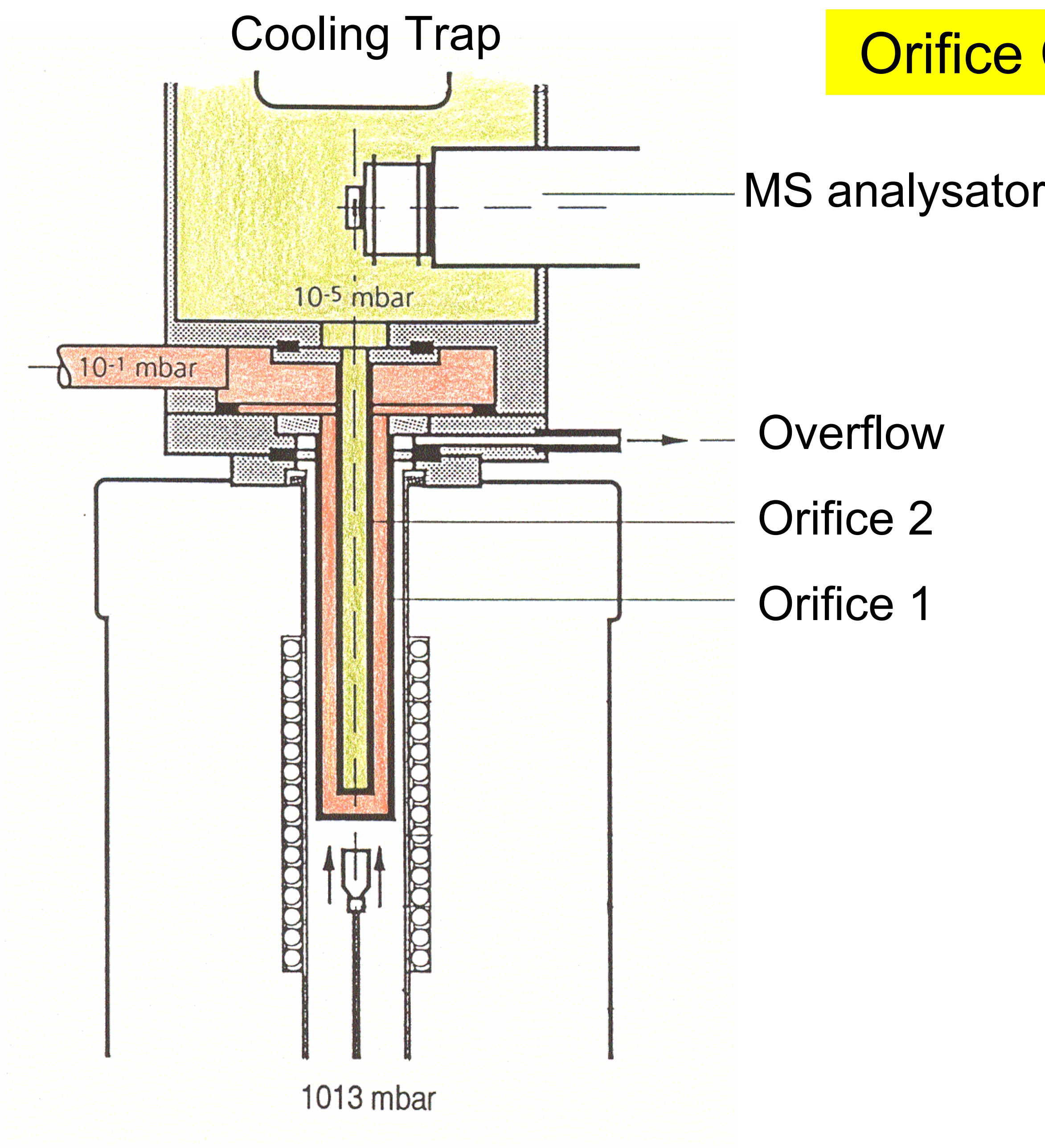
Capillary Coupled System

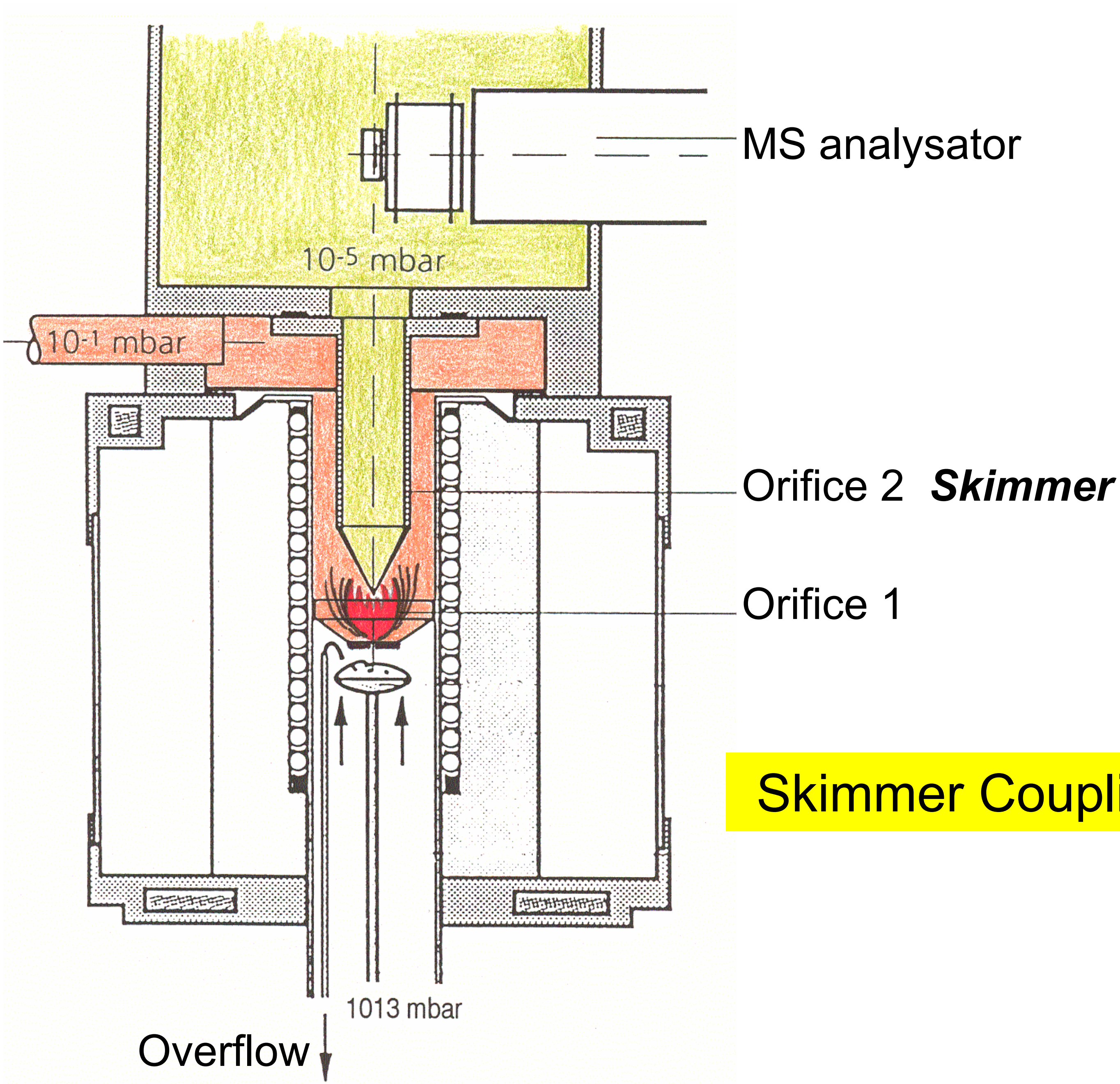
2400°C



Orifice Coupling System

1500°C



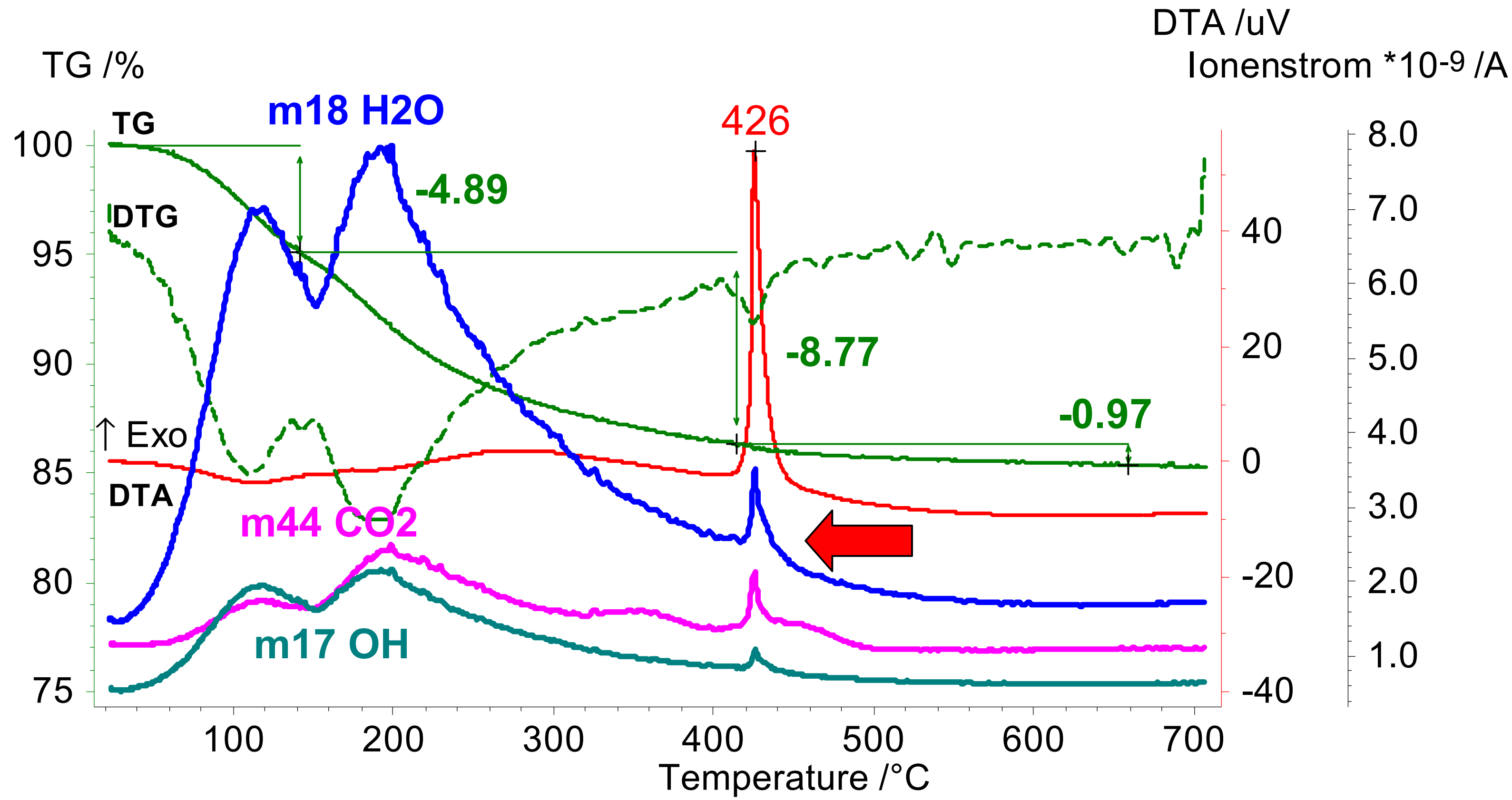


Skimmer Coupling System

1500°C


NETZSCH
STA 409 C Skimmer®
NETZSCH
MESSER
Copyright © 2003 Leinung

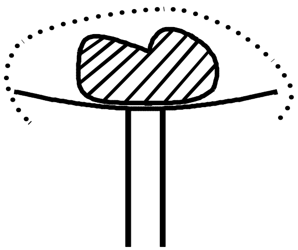
Amorphous $ZrO_2 \cdot n\ H_2O$ ¾® ZrO_2 (tetragonal)



Dehydratation,
Dehydroxylation

Squeezing out of residual H_2O and CO_2 molecules during the crystallization

Simulation of the roasting of coffee beans



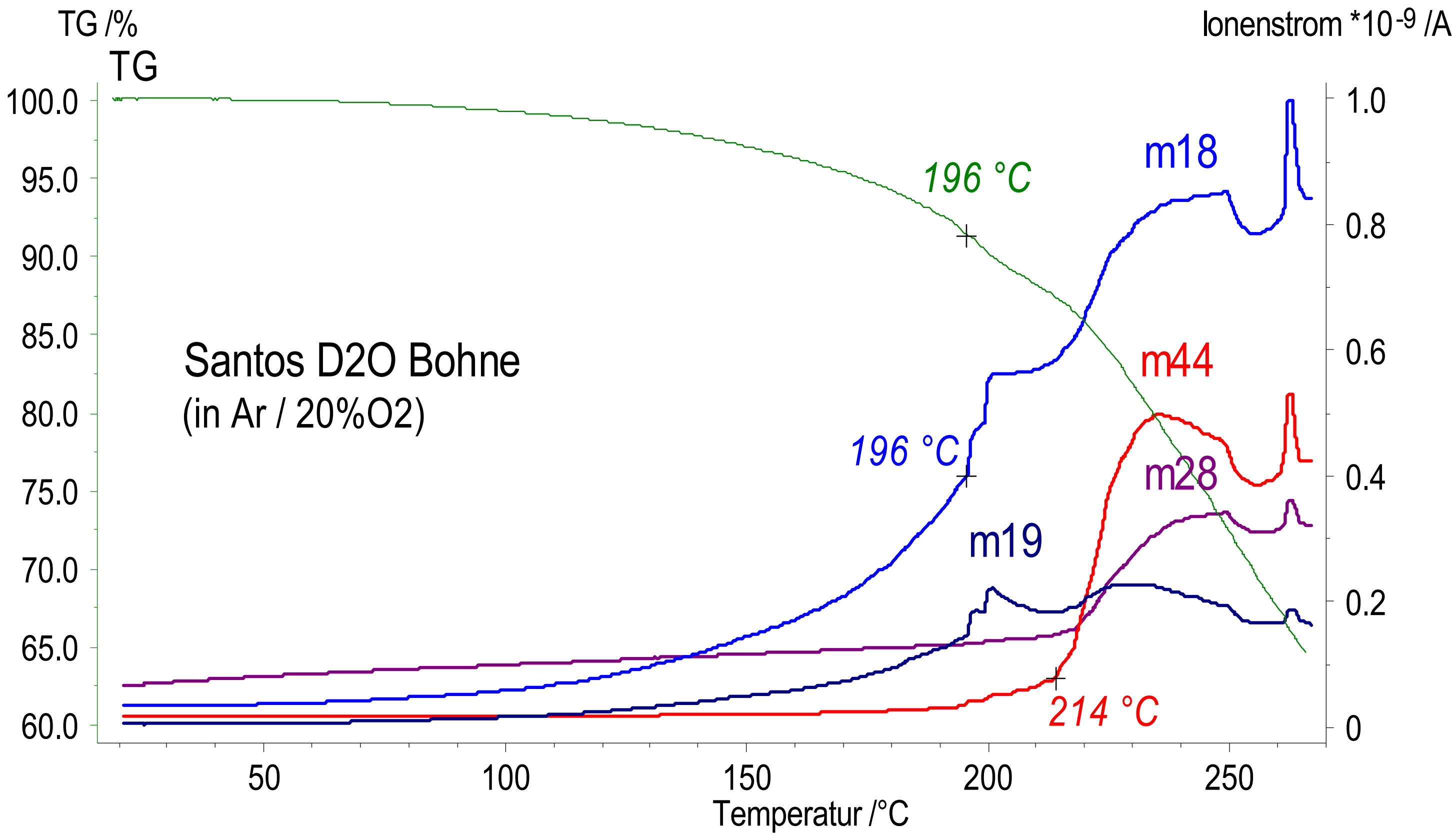
Corundum plate crucible, Pt net

Argon / 20% O_2

m/z 18 (H_2O^+) **m/z 28 (CO^+, N_2^+)**

m/z 19 (HDO^+) **m/z 44 (CO_2^+, ...)**

m/z 20 (D_2O^+, Ar^{++})

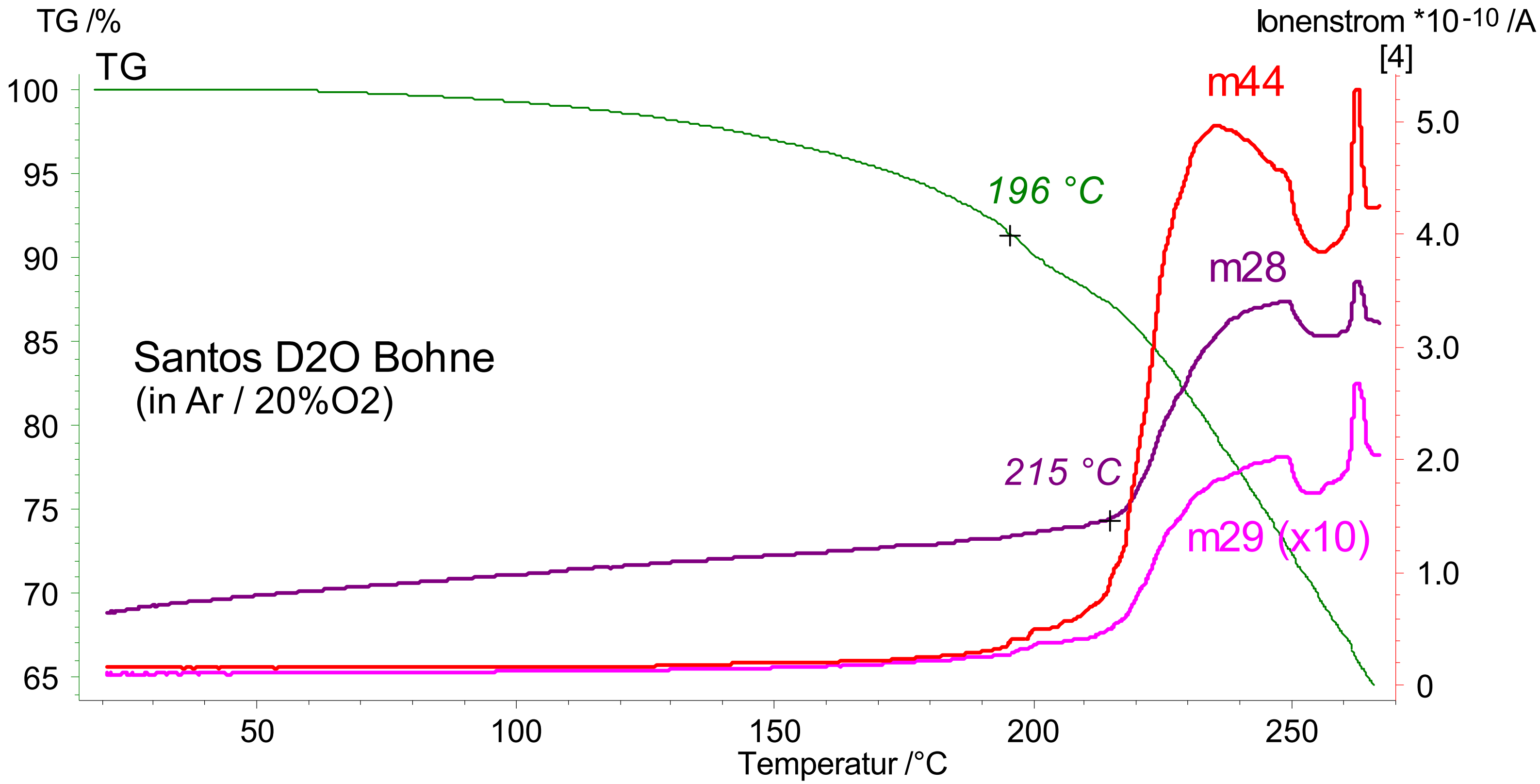


- *No discrimination between CO and N_2*
- *Bean bursts due to water pressure*
- *Decarboxylation at higher temperature*

m/z 28 ($^{12}CO^+$, $^{14}N_2^+$)

m/z 29 ($^{13}CO^+$, $^{14}N^{15}N^+$)

$i_{28} : i_{29} = 16 : 1$



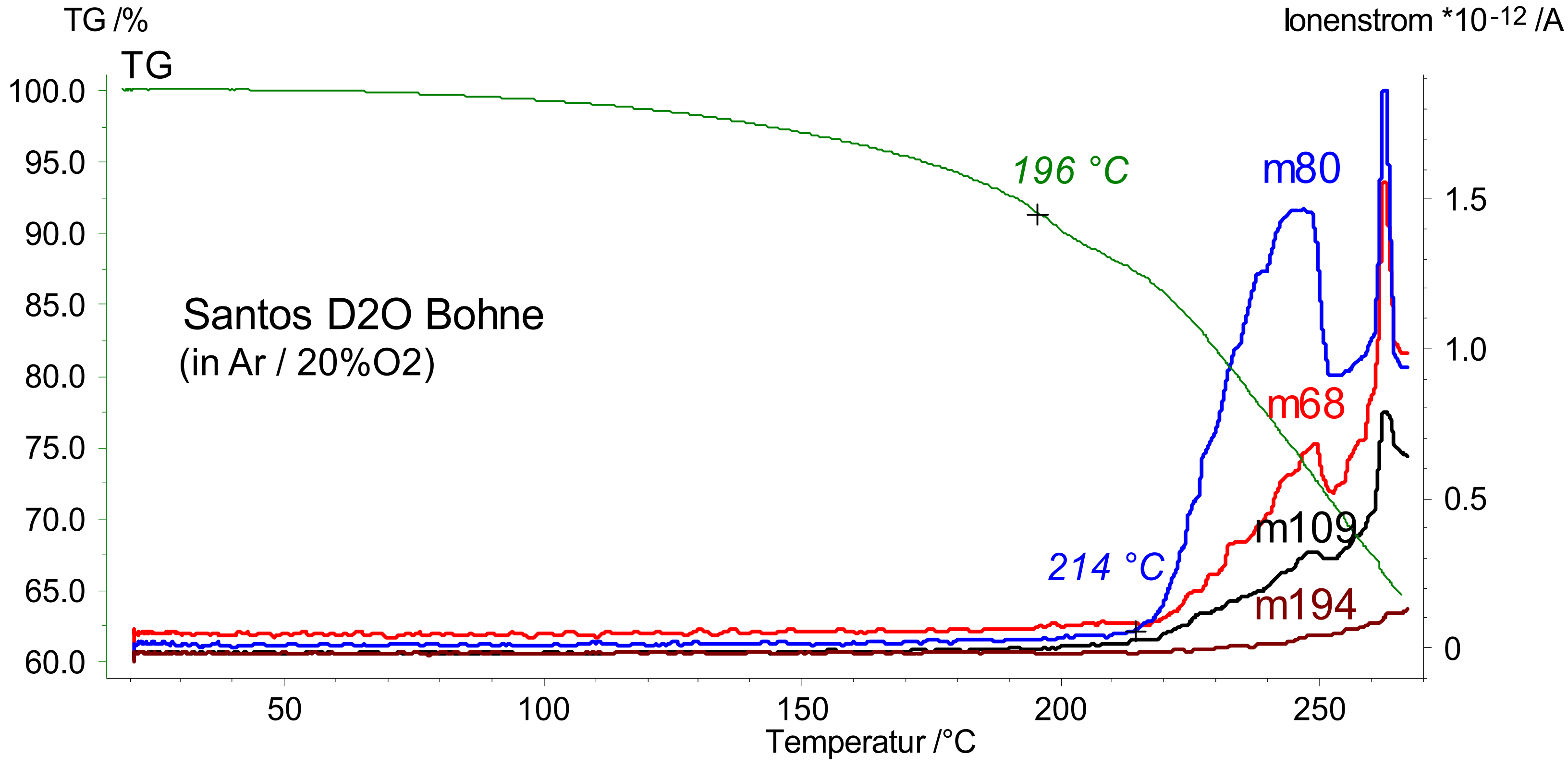
- *MAILLARD products together with CO_2*
- *Three roasting stages*
- *Coffeine partially evaporates*

m/z 68 ($C_3H_4N_2^+$, ...)

m/z 80 ($C_6H_4N_2^+$, ...)

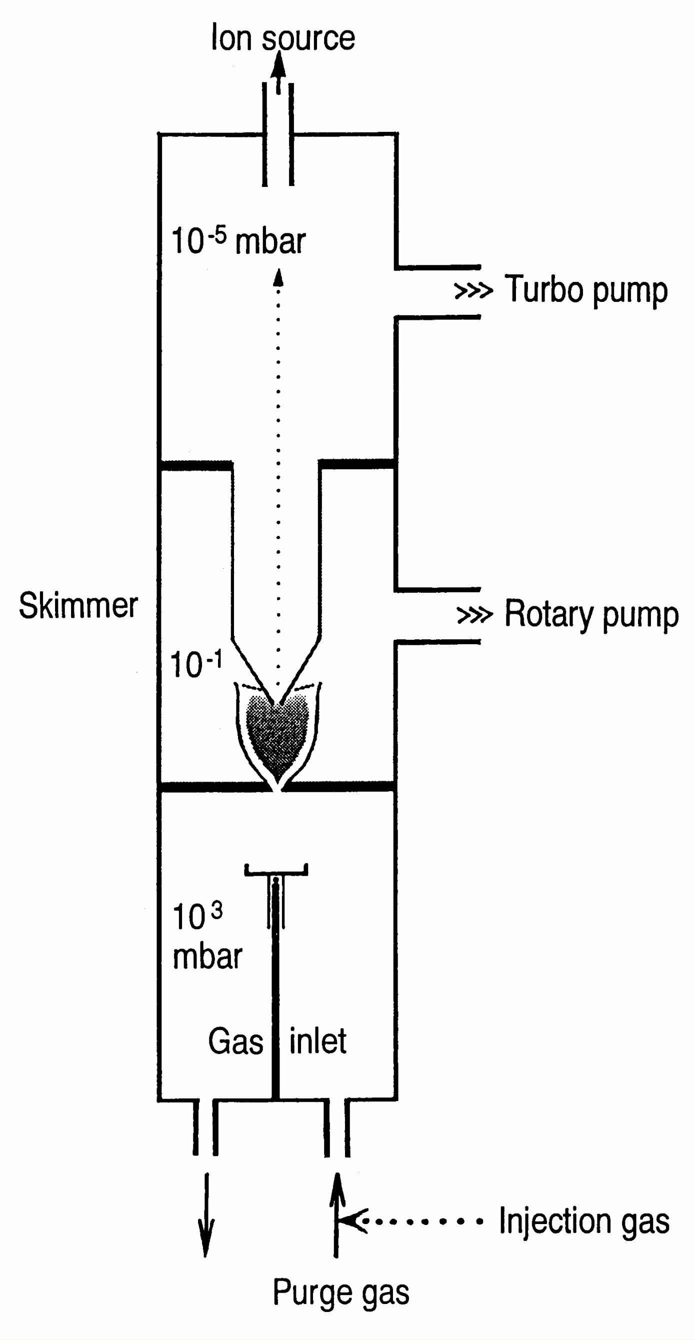
m/z 109 *(coff)*

m/z 194 *(coffM$^+$)*



4. *Pulse Thermal Analysis*® and Catalysis

- Quantitative evaluation of MS or FT-IR signals
- Taylor made redox catalysts
- Applications



Maciejewski et al. (1997)

PulseTA®
with a
NETZSCH
STA 409 C *Skimmer®*

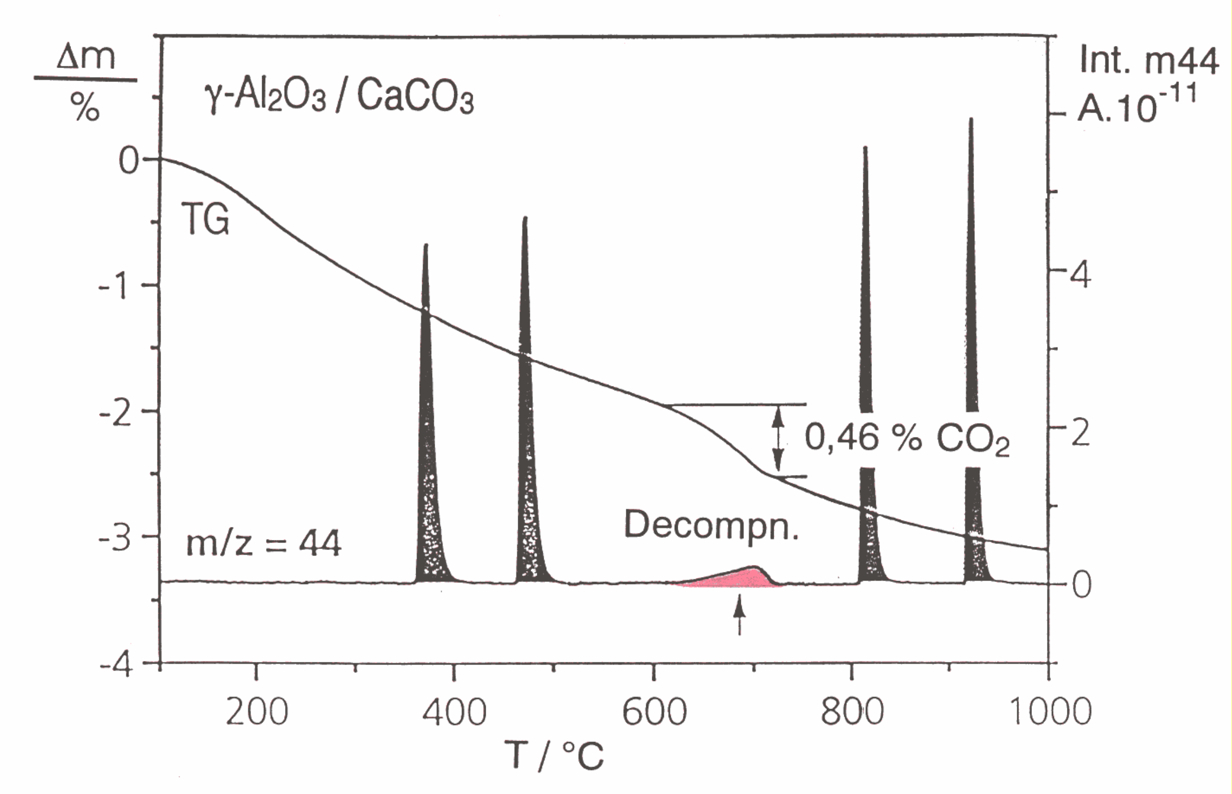
- **Injection of known volumina of one or two gases**
- **Quantitative evaluation of MS and FT-IR signals**
- **Appropriate m/z**
  Þ chemical composition
- **TG Þ sorption phenomena**

Calibration of MS signals for *PulseTA®*

Maciejewski et al. (1997)

1. On line

Injection of a known gas volume into the purge gas



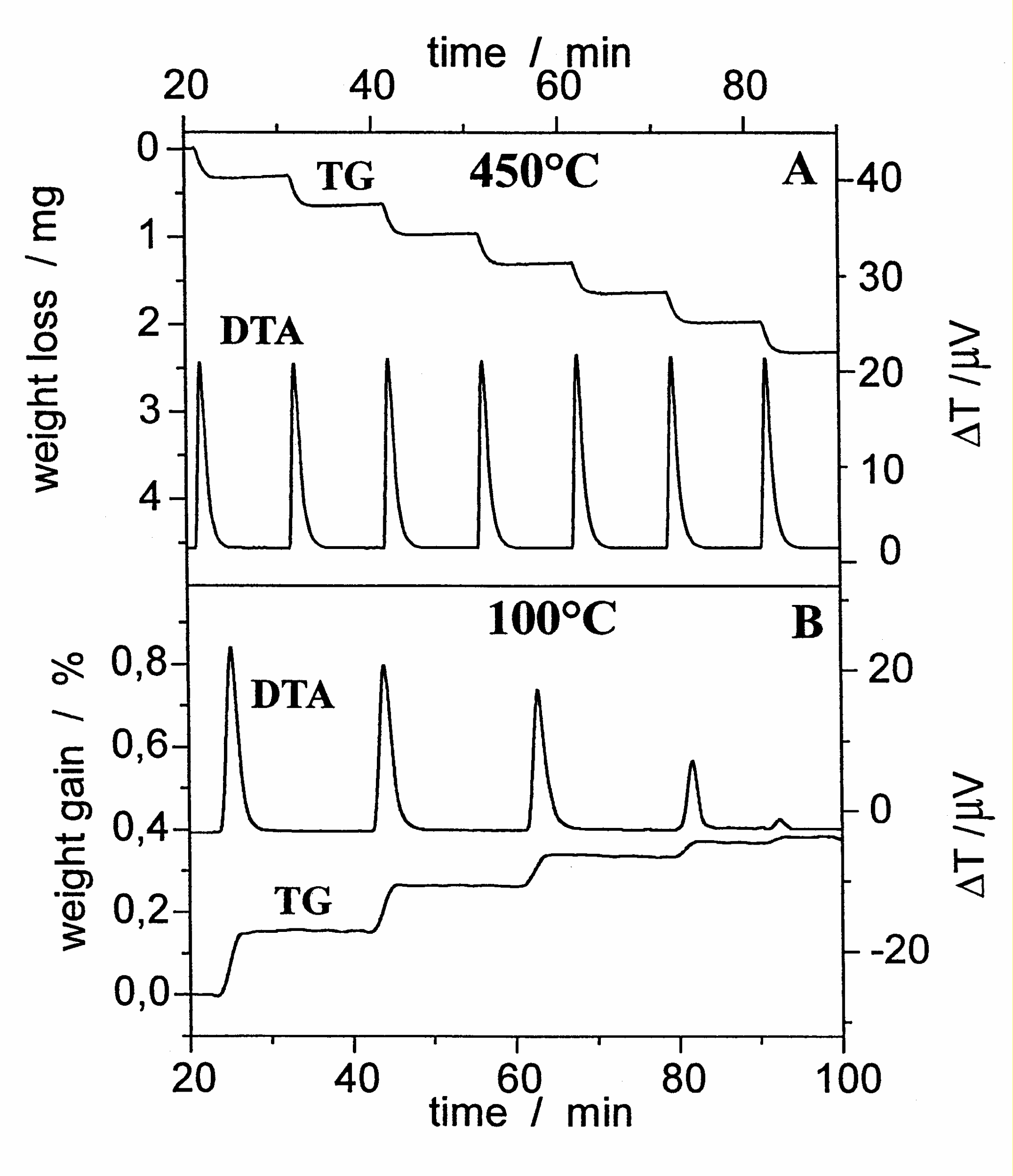
2. Off line

Separate TA run of a suitable calibration substance

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

$$2\ PdO \longrightarrow Pd + O_2$$

Taylor made catalysts with *PulseTA®* *(1)*



Maciejewski et al. (1997)

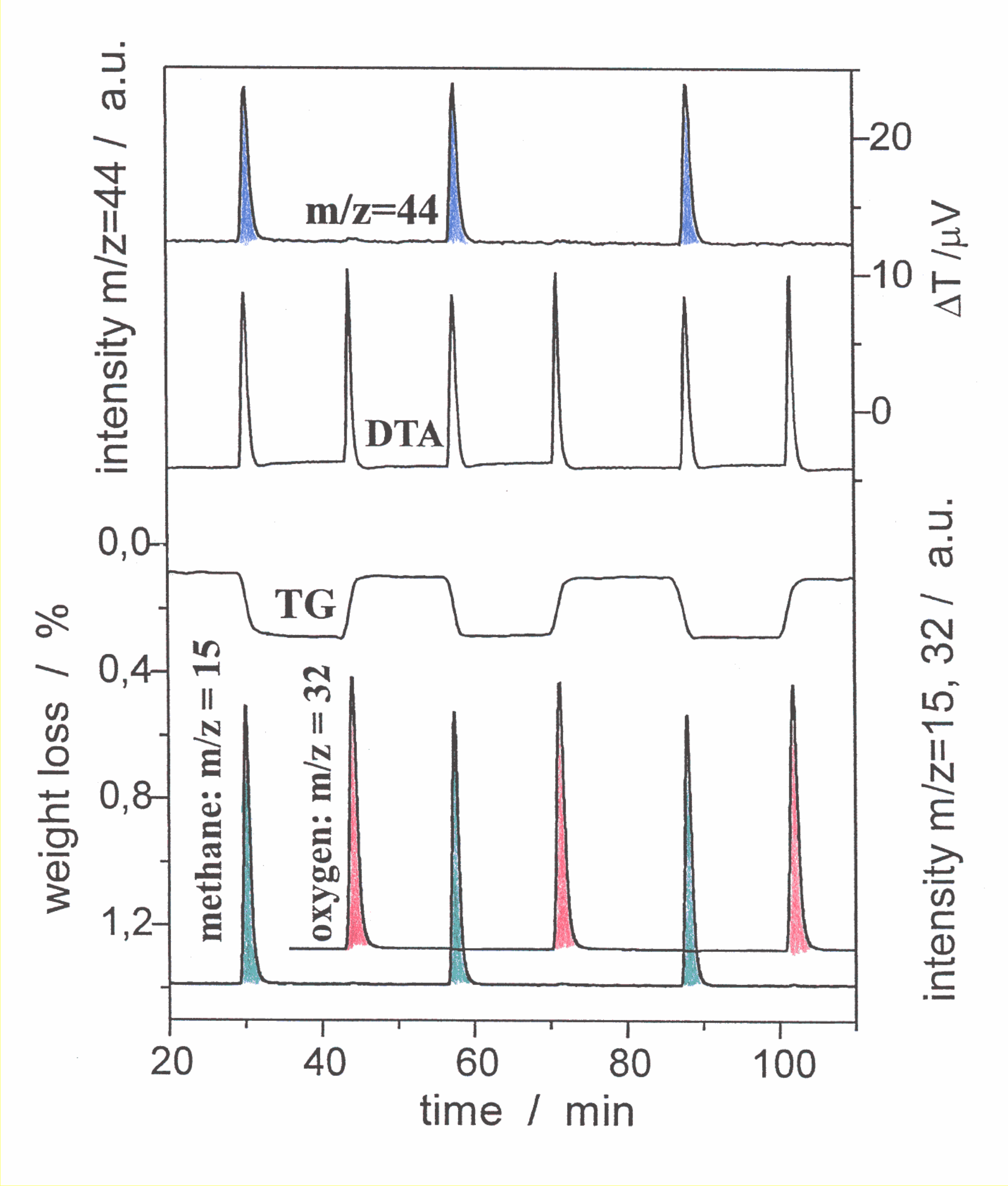
Reduction of CuO

by H_2 pulses at 450°C

Oxidation of Pd/ZrO_2

by O_2 pulses at 100°C

Taylor made catalysts with *PulseTA*® *(2)*



Maciejewski et al. (1997)

Reduction of PdO/ZrO_2

by CH_4 pulses

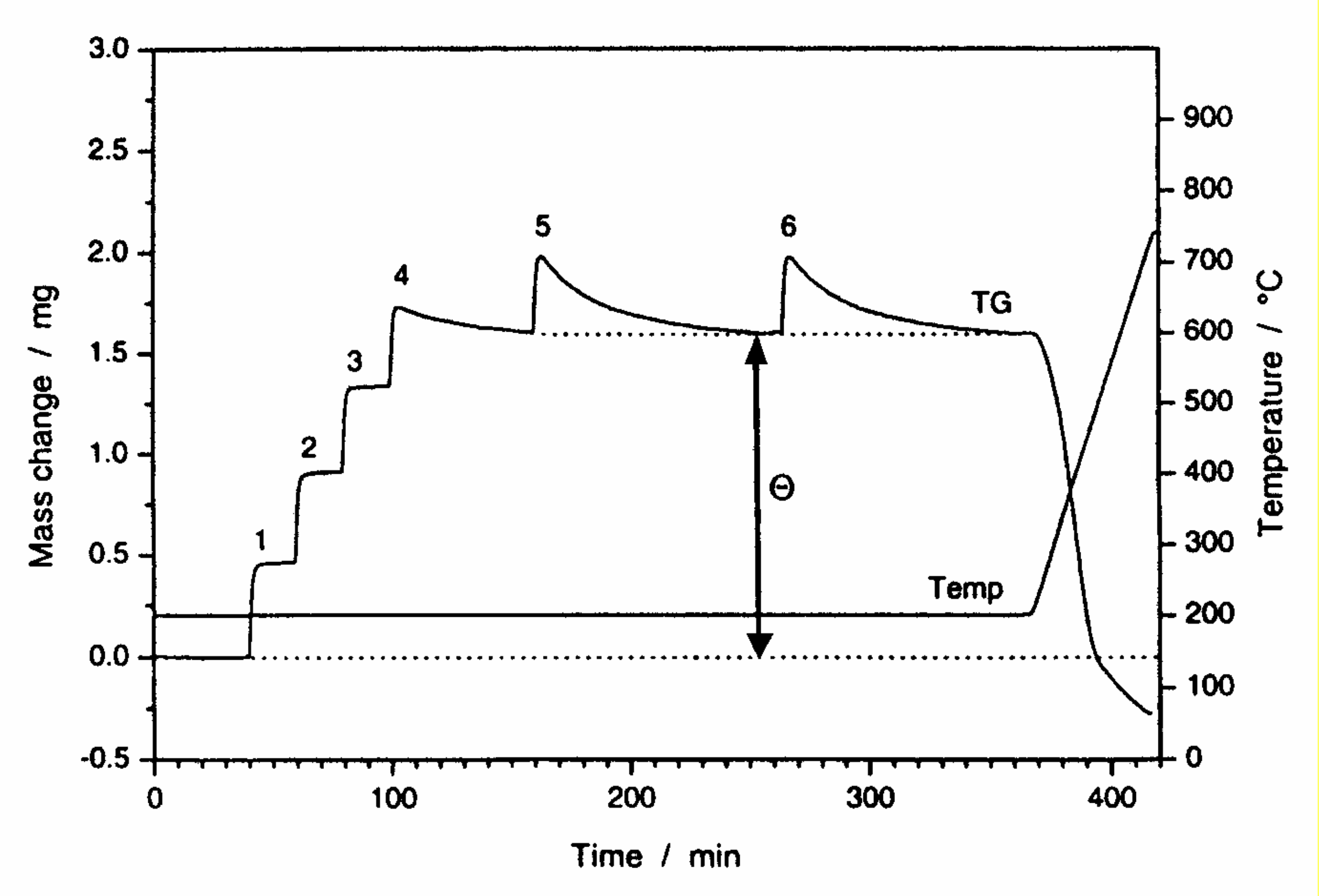
and its subsequent

re-oxidation

by O_2 pulses at 500°C

Chemisorption and Physisorption studied by *PulseTA*®

Eigenmann et al. (2000)



Mass change of H-ZSM-5 zeolite after pulses of 1 ml NH_3 at 200°C

The HTB structure of b-CrF_3 *(hexagonal tungsten bronze)*

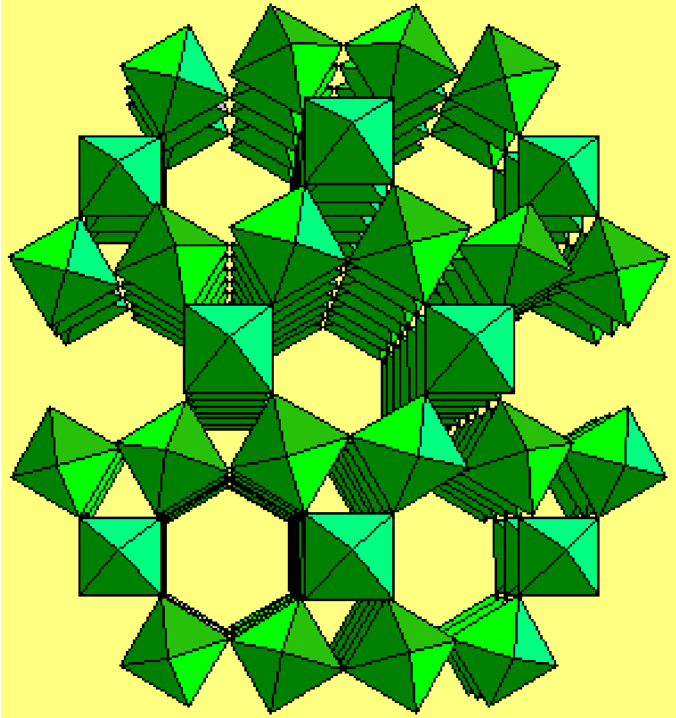
De Pape et al. (1987)

$(NH_4)_3CrF_6$ → β-CrF_3 (arrow struck through)

$(NH_4)_3CrF_6$ → β-$CrF_3 \cdot n\ NH_3$

Menz & Bentrup (1992)

- (CrF_6) octahedra
- Hexagonal channels
- Hosting of small molecules



b-$CrF_3 \cdot m\ H_2O \cdot n\ NH_3$

PulseTA

Calibration of m19 with $NaHF_2 \cdot n\ H_2O$

m/z 20 **HF^+** **$H_2{}^{18}O^+$** **Ar^{++}**

m/z 19 **F^+**

$NaHF_2 \cdot n\ H_2O$ ¾® $NaF + HF + n\ H_2O$

(1) Determination of m_{H2O} by PTA after calibration of *m/z 18* with $NaHCO_3$

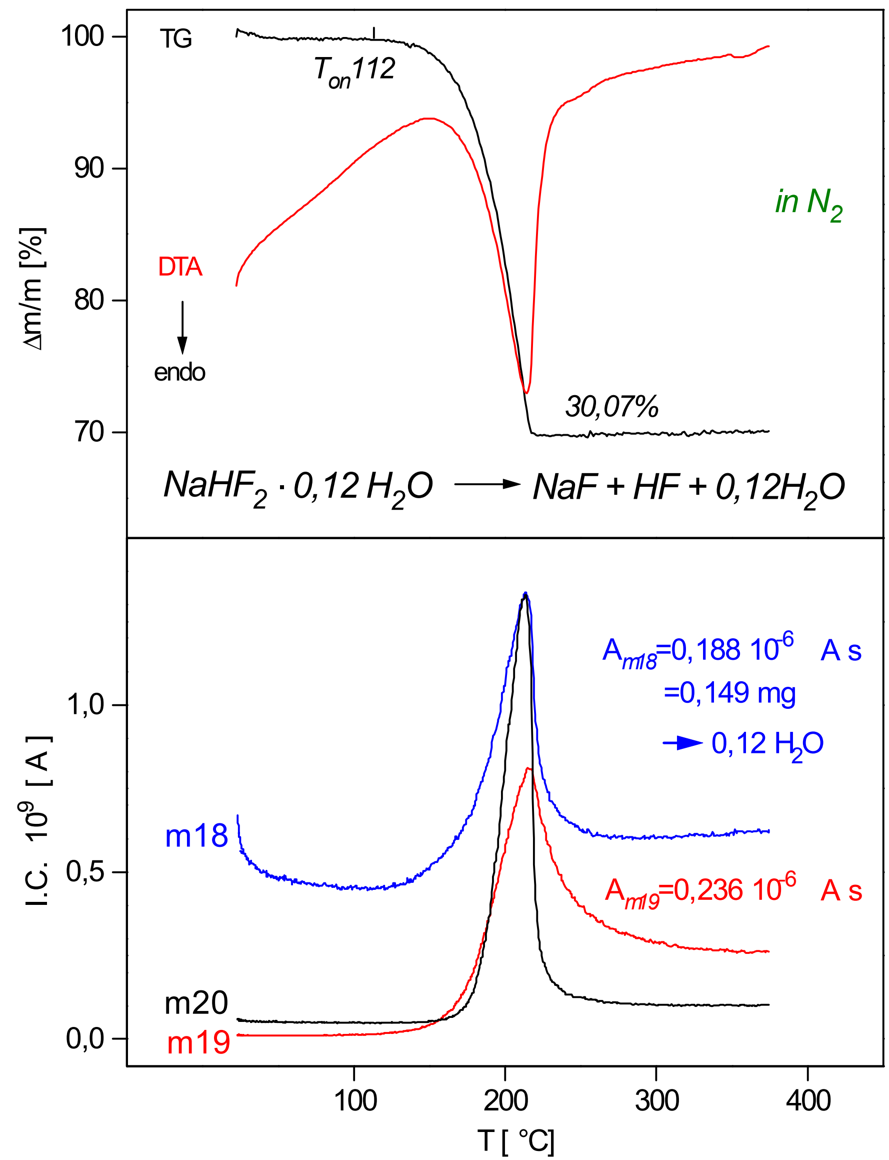
(2) Calculation of m_{HF} using the residue mass

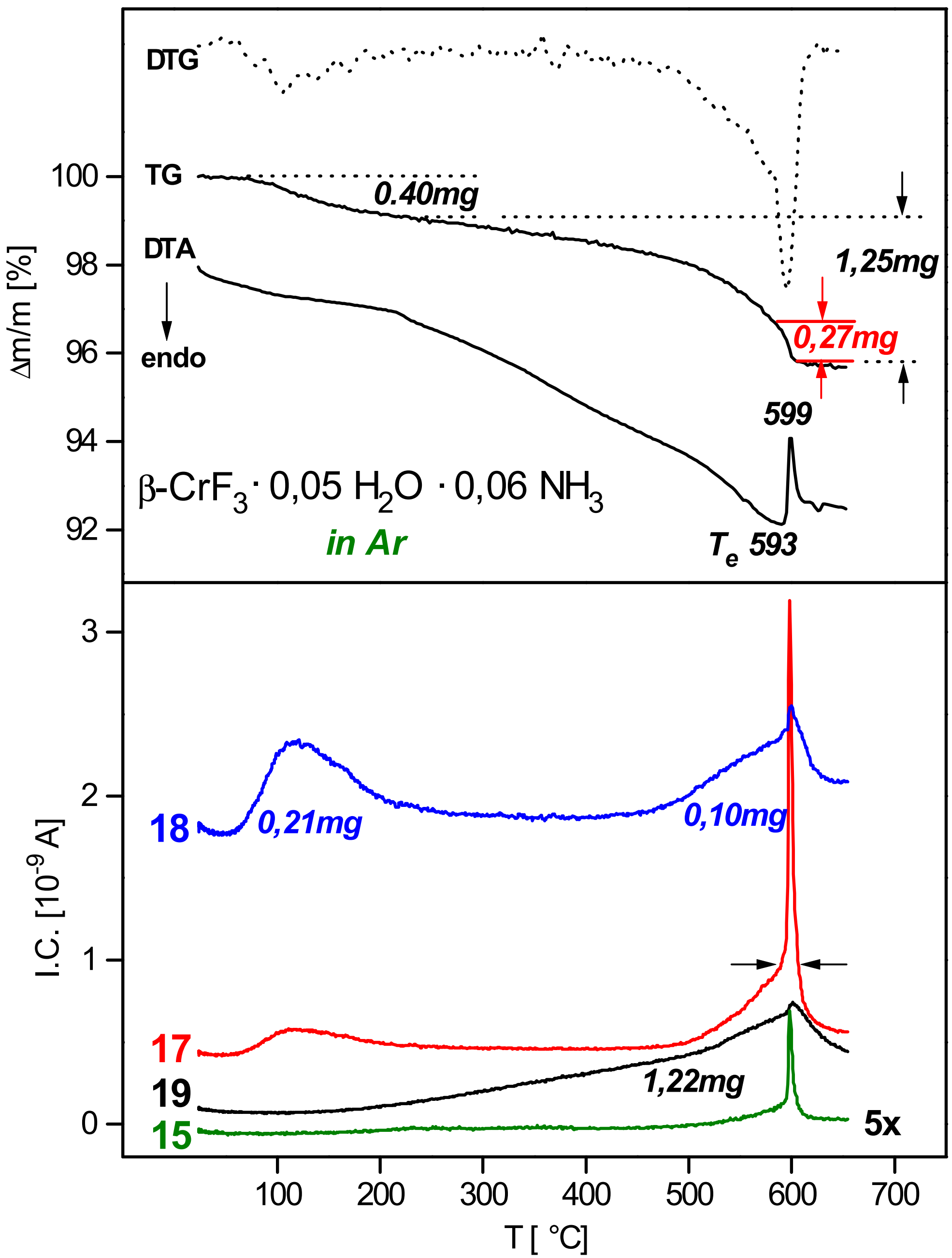
$$m_{sample} = m_{NaF} + m_{HF} + m_{H2O}$$

(3) Calibration factor:

$$F(HF) = \frac{m_{HF}(cal)}{A_{m19}(cal)}$$

$$= \frac{1{,}21 mg}{0{,}236 \cdot 10^{-6} As} = 5{,}127 \cdot 10^{6}\ mg/As$$





Quantitative description of all details of the thermal behavior of a fluoride being sensitive to hydrolysis

- **Water release in three temperature ranges**
- **Slight endothermal shift due to pyrohydrolysis**
- **b-CrF$_3$ structure collapses at 593°C Þ NH$_3$ loss**
- **Major part of NH$_3$ lost only between 589 and 604°C**

1. Transformation of unwanted CFC's

Chlorofluorocarbon (CFC) Þ Hydrofluorocarbon (HFC)

- ✸ *Substitution of refrigerants*
- ✸ *Recycling of refrigerators*

Hydrodechlorination	*Removal of Cl from C-Cl*
by use of H_2	*Replacing Cl with H*
Dehydrochlorination	*Elimination of HCl*

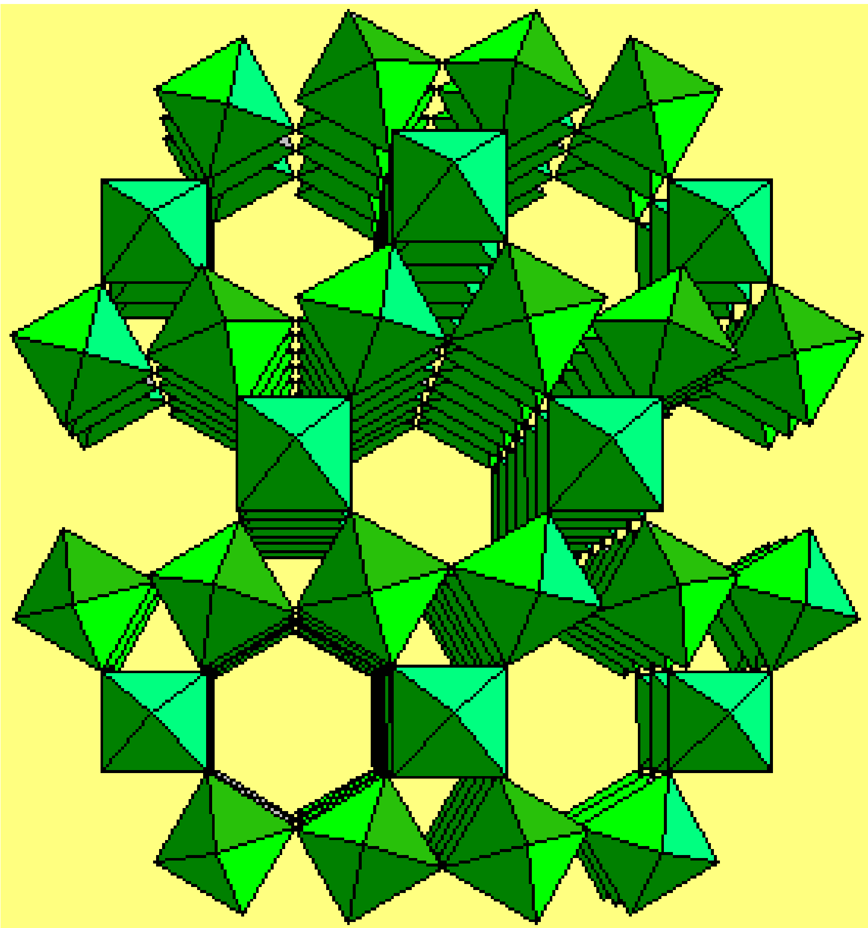
1,1 Dichlorotetrafluoroethane , CF_3-CCl_2F (CFC-114a)

Nomenclature: **1 1 4 a**

C-1 H+1 F (Cl = rest)

The HTB structure of b-AlF_3 *(hexagonal tungsten bronze)*

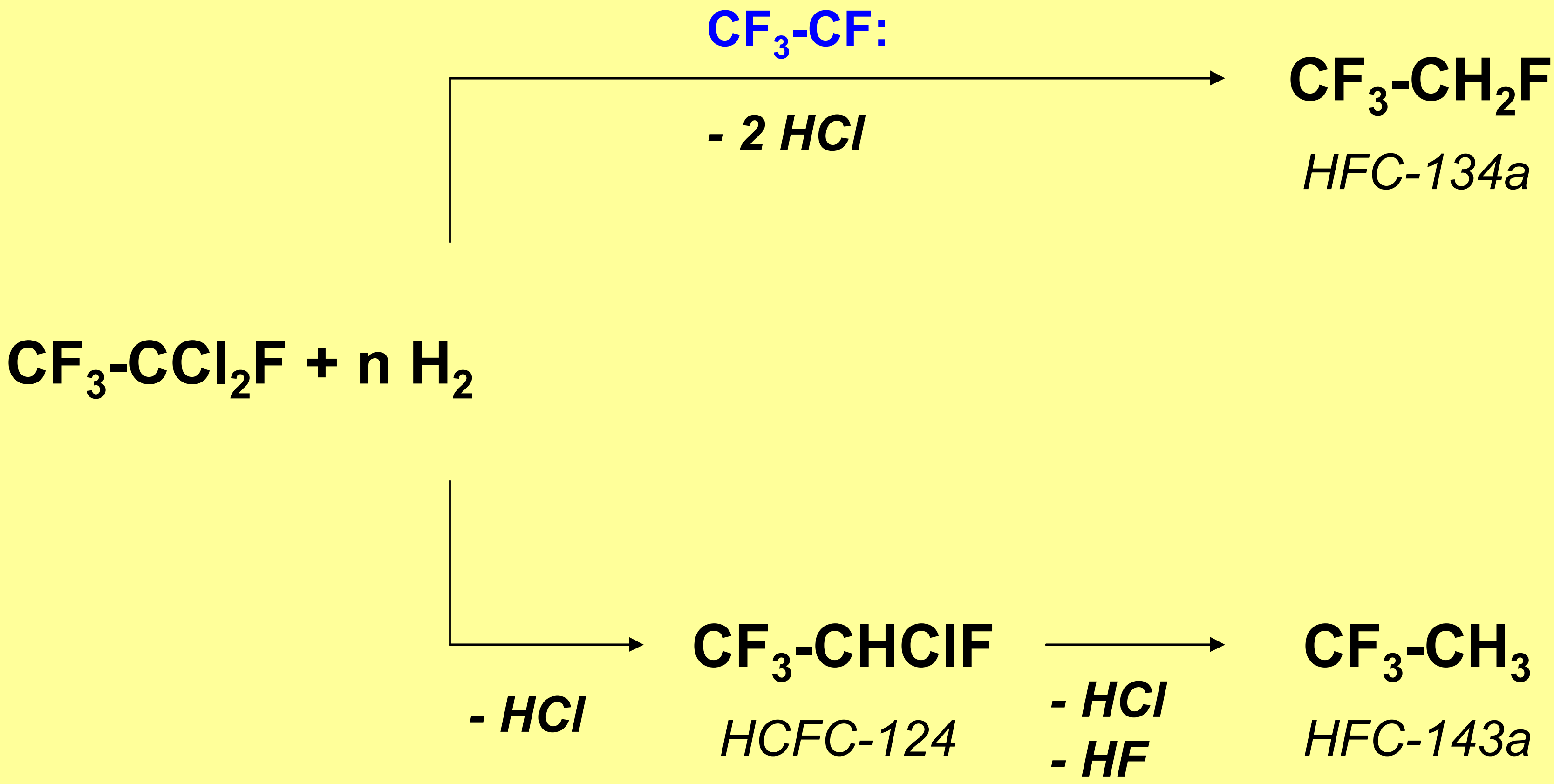
De Pape et al. (1987)



- (AlF_6) octahedra
- Hexagonal channels
- Strong LEWIS acid sites
- Hosting of small molecules

Catalytic hydrodechlorination of CFC-114a -

via stepwise or carbene mechanism



CF_3-CCl_2F *R114a*	CF_3-$CHClF$ *R124*	CF_3-CH_2F *R134a*	CF_3-CH_3 *R143a*	Fragment
31 (52)	31 (49)	31 (18)	31 (12)	CF^+
-	-	**33** (100)	33 (8)	CH_2F^+
-	-	**34** (100)	34 (8)	$CHDF^+$
35 (18)	35 (8)	35 (100)	35 (8)	CD_2F^+ , $^{35}Cl^+$
-	51 (52)	51 (20)	51 (3)	CHF_2^+
-	52 (52)	52 (20)	-	CDF_2^+
-	-	-	**65** (40)	$CH_3CF_2^+$
-	67 (100)	-	67 (40)	$CHClF^+$, $CHD_2CF_2^+$
68 (8)	**68** (100)	-	-	$CDClF^+$, $C^{37}ClF^+$
69 (40)	69 (27)	69 (72)	69 (100)	CF_3^+
83 (5)	-	**83** (65)	83 (2)	$CF_3CH_2^+$
85 (57)	85 (1)	85 (65)	-	$CF_3CD_2^+$, $CClF_2^+$
101 (80)	101 (40)	101 (1)	-	CCl_2F^+ , CF_3CHF^+
-	**102** (40)	102 (1)	-	CF_3CDF^+, $CF_3CH_2F^+$
135 (100)	-	-	-	CF_3CClF^+

Why D_2 used ?

Discrimination of HFC's via characteristic mass numbers

Why D_2 used ? (2)

to distinguish the main reaction (DCl) from side reactions (HCl)

m/z 39 ($D^{37}Cl^+$)

Side reactions :

(1) Reaction of the freon with Al-OH groups

CF_3-CCl_2F + 4 OH^- ¾ ® CO_2 + CO + 4 F^- + 2 HCl + H_2O

(2) Reaction of D_2 with neighboured surfacial Al-OH groups

$D^\bullet$ ¼ HO $D^\bullet$ ¼ DO
¾ Pd ¾ Al ¾   ¾ ®   ¾ Pd ¾ Al ¾ + H D
½   ½   ½   ½

Main steps of a *PulseTA* experiment characterizing a Pd/b-AlF_3 catalyst

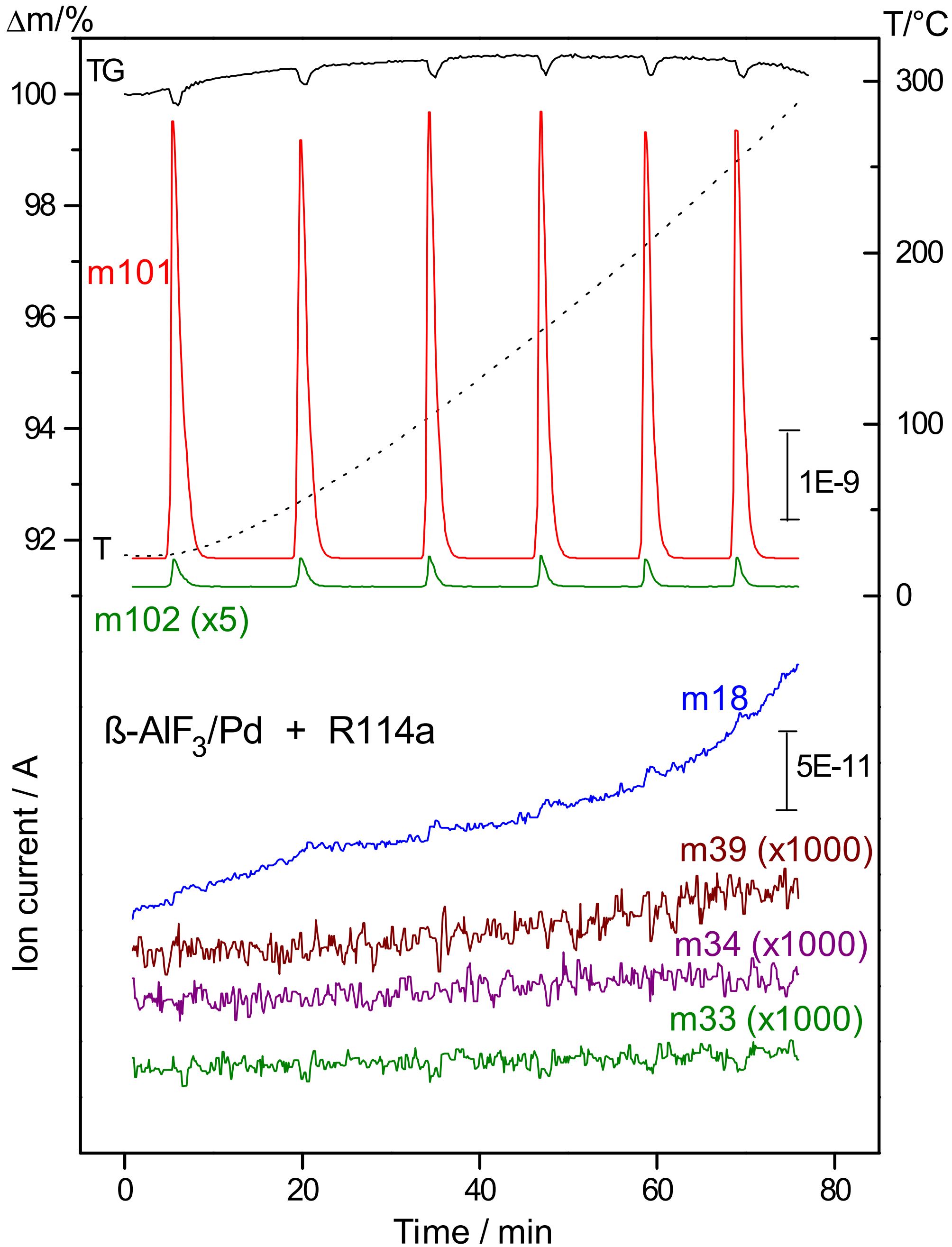
1. **Thermal pretreatment in N_2 at 300°C**
2. **Cooling down to 25°C**
3. **CFC pulse at 25°C**

   MS : m/z in SIM mode

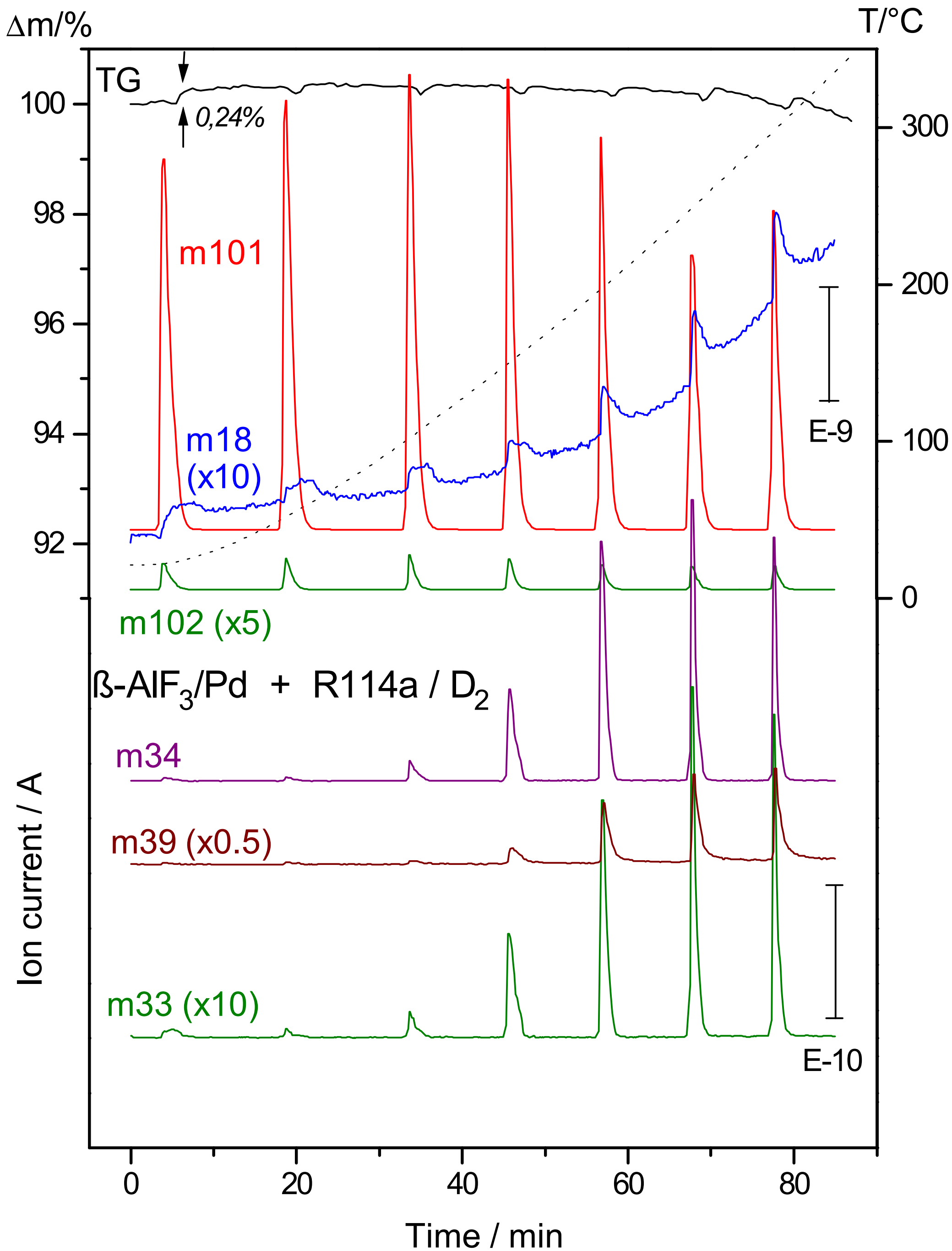
   TG : Chemi- / Physisorption ?
4. **D_2 pulse at 25°C**

   TG: Chemisorption: activated D...D
5. **Heating in N_2 with 10K/min up to 270°C with Pulses of CFC and/or D2**

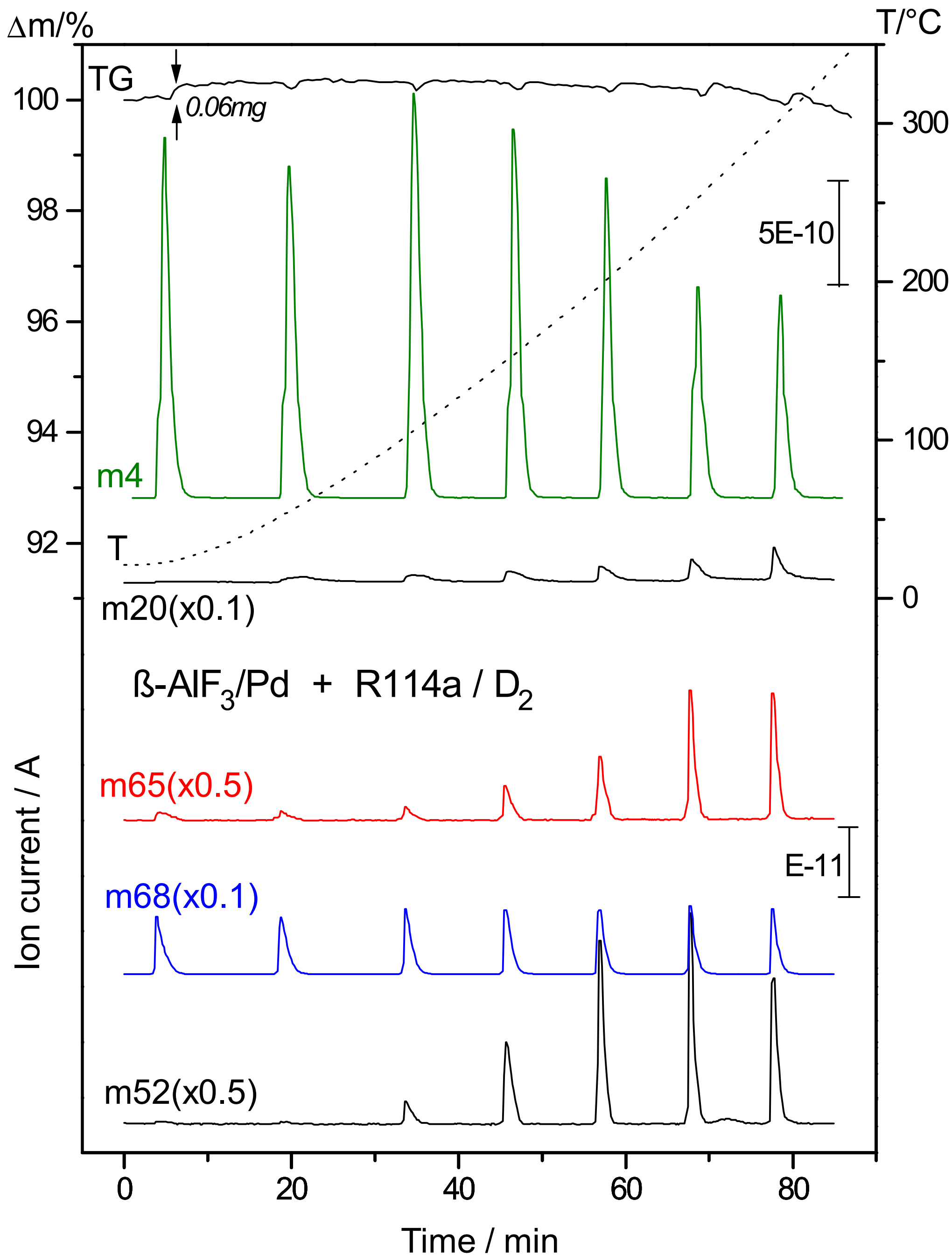
   MS : Products ?



- Freon pulses only
- m101 (CCl_2F^+) = CFC-114a
- No educt consumption
- No product formation
- Temporary buoyancy effects (freon density)
- No adsorption



- Freon and D_2 pulsed **simultaneously**
- First educt pulse: chemisorption of D_2
- Physisorption of products at higher T
- Water as byproduct



- m4 (D_2^+): educt consumption
- m20 (HF^+): byproduct
- m65 (CH_3CF^+): formation of hydrogenated products

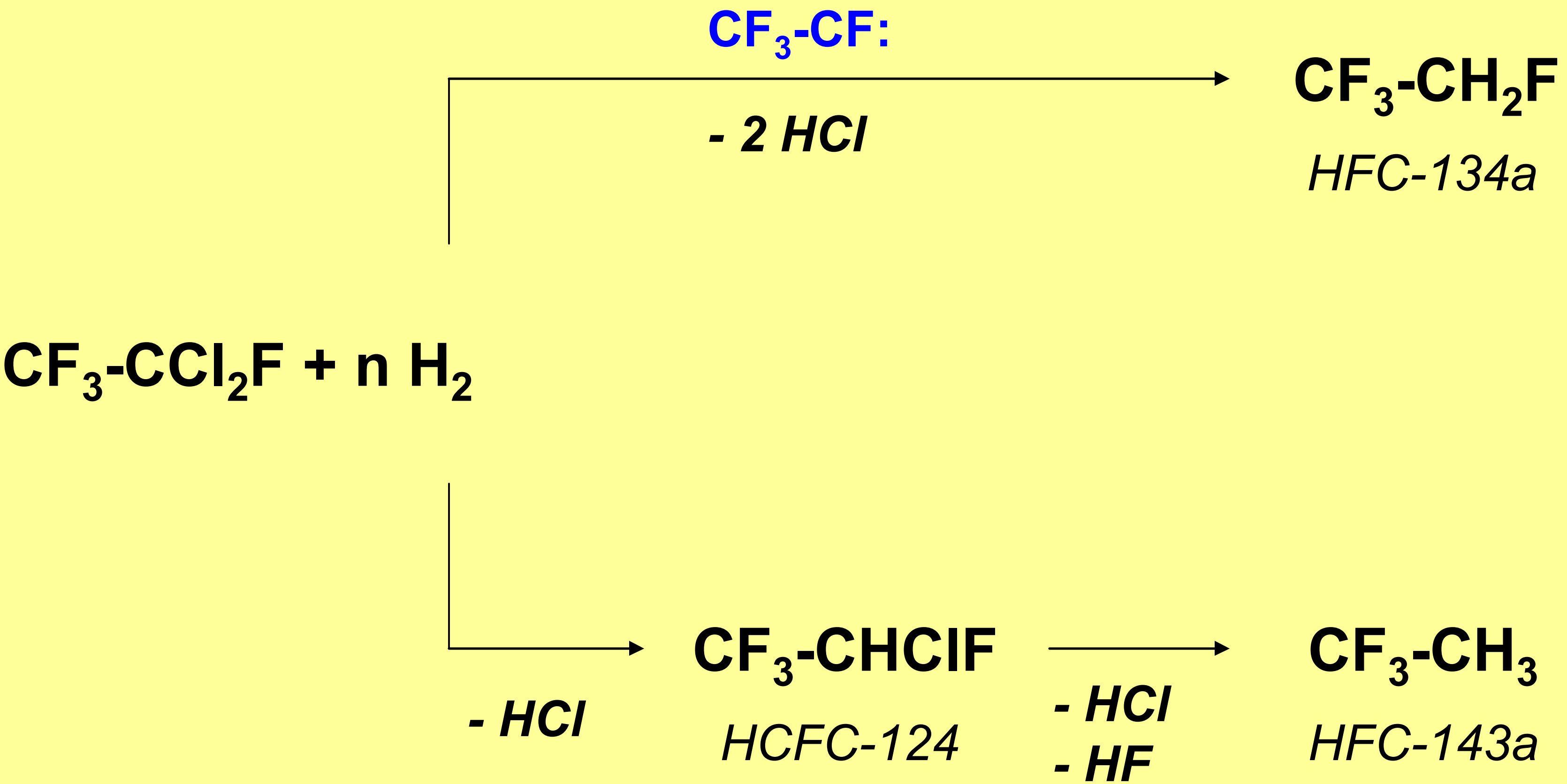
- m52 (CDF_2^+): both HCFC-124 and HFC-134a

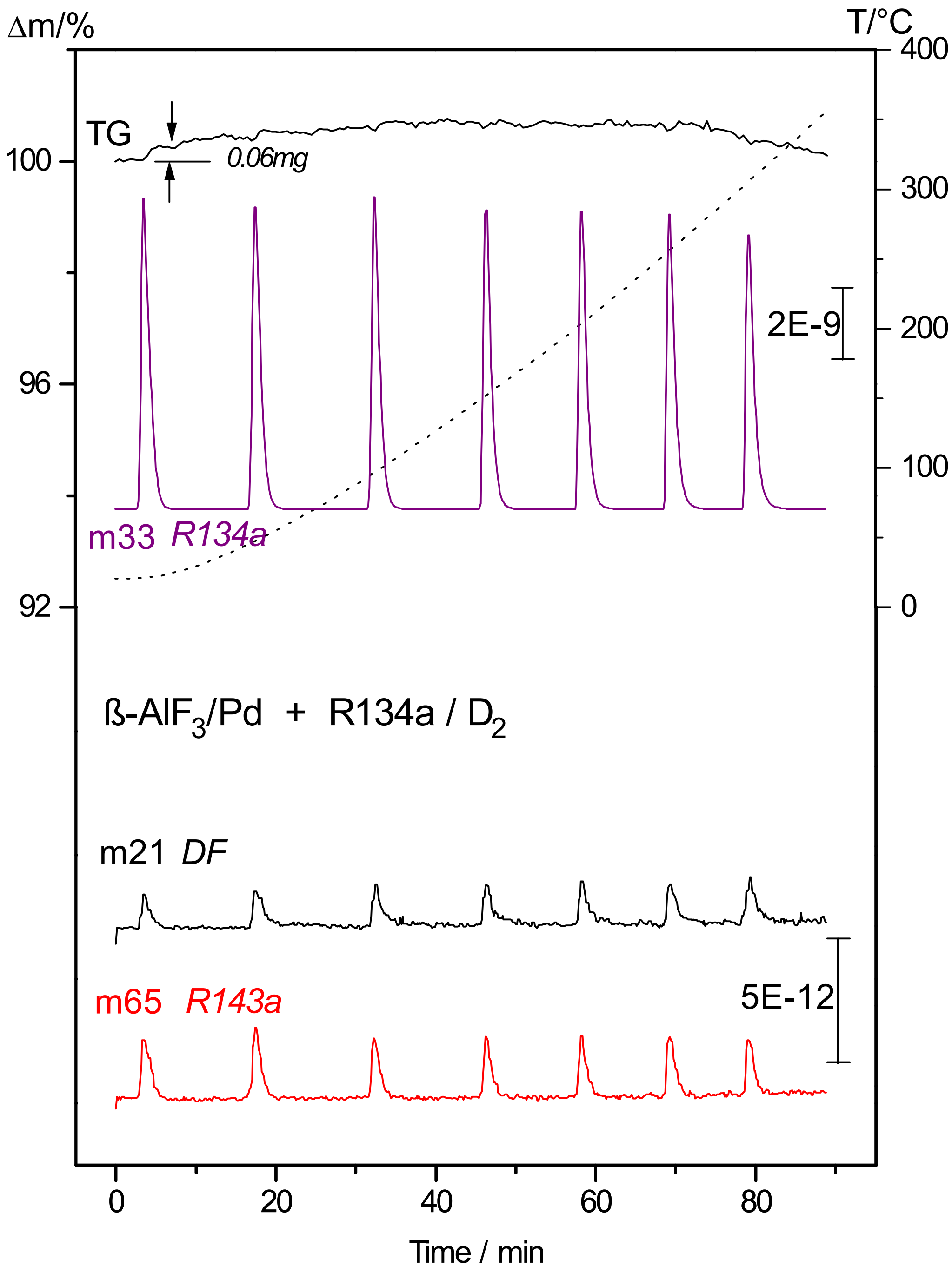
ß

***m102** (CF_3CDF^+, **$CF_3CH_2F^+$**)*
remains const and low

Catalytic hydrodechlorination of CFC-114a -

via stepwise or carbene mechanism





Pulsing the intermediate HFC-134a

- m33 (CH_2F^+): **no** consumptn.
- m21 (DF^+): **no** reaction
- m65 (CH_3CF^+): **no** formation of HFC-143a

ß

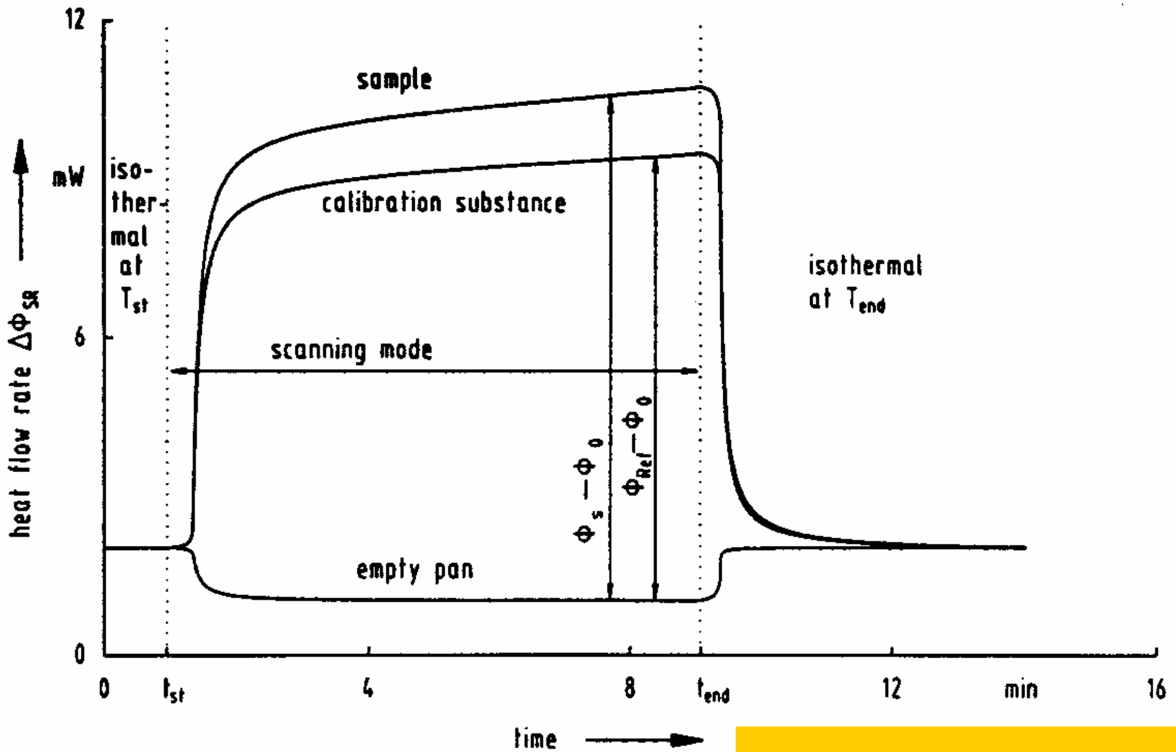
No direct transformation of HFC-134a into 143a -

Confirms the carbene mechanism.

5. Other thermal properties

Heat capacity

Thermal diffusivity

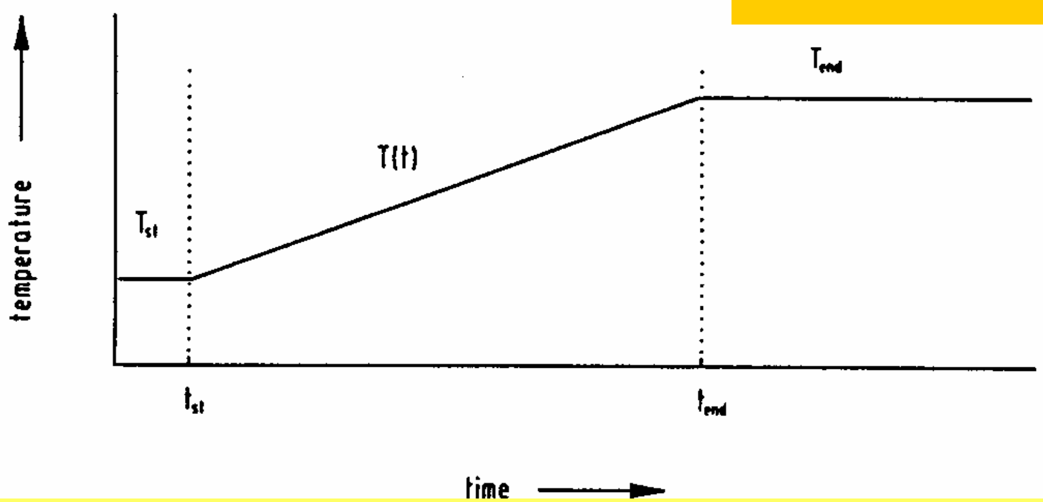


3 step procedure for determination of C_p by DSC :

Heat flow rate of

1. *Empty crucibles*
2. *Calibr. 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 heating rates of sample and reference)

Höhne, Hemminger, Flammersheim (1996)

Thermal diffusivity - *The Laser Flash Method (1)*

Heat flow

$$q = - \mathrm{l} \;\; grad\ T$$

T = T(x,y,z)

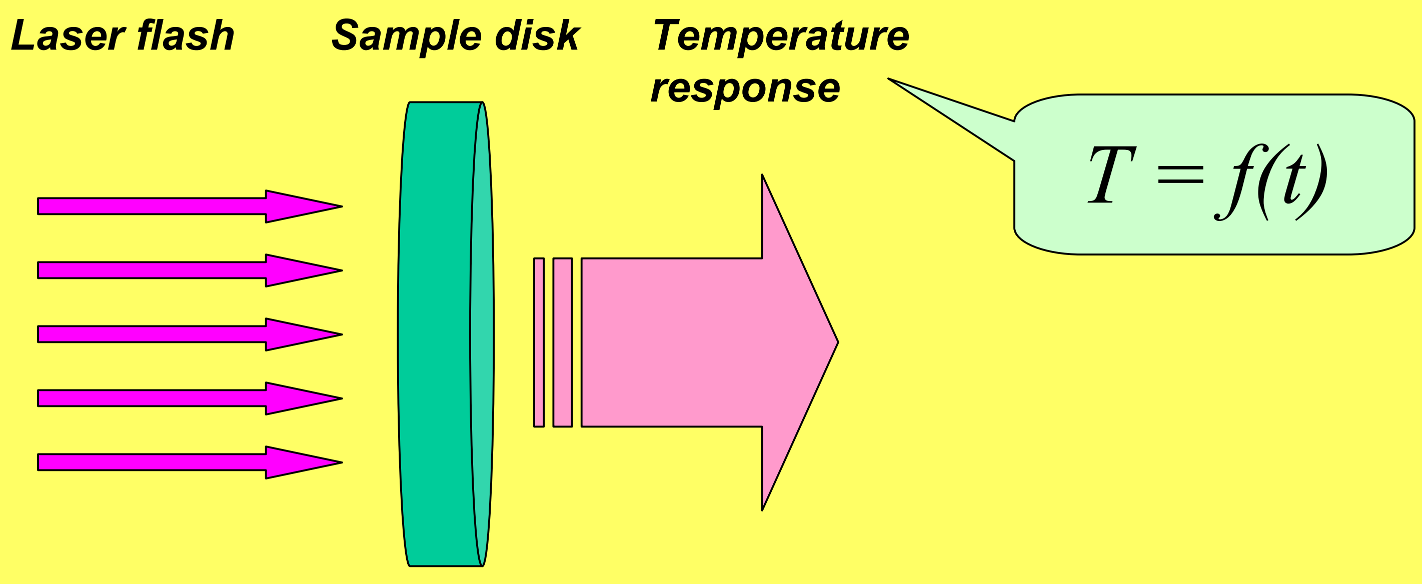
l *- thermal conductivity*

Thermal diffusivity

$$\frac{\partial T}{\partial t} = \frac{\mathrm{l}}{c_p\ \mathrm{r}}$$

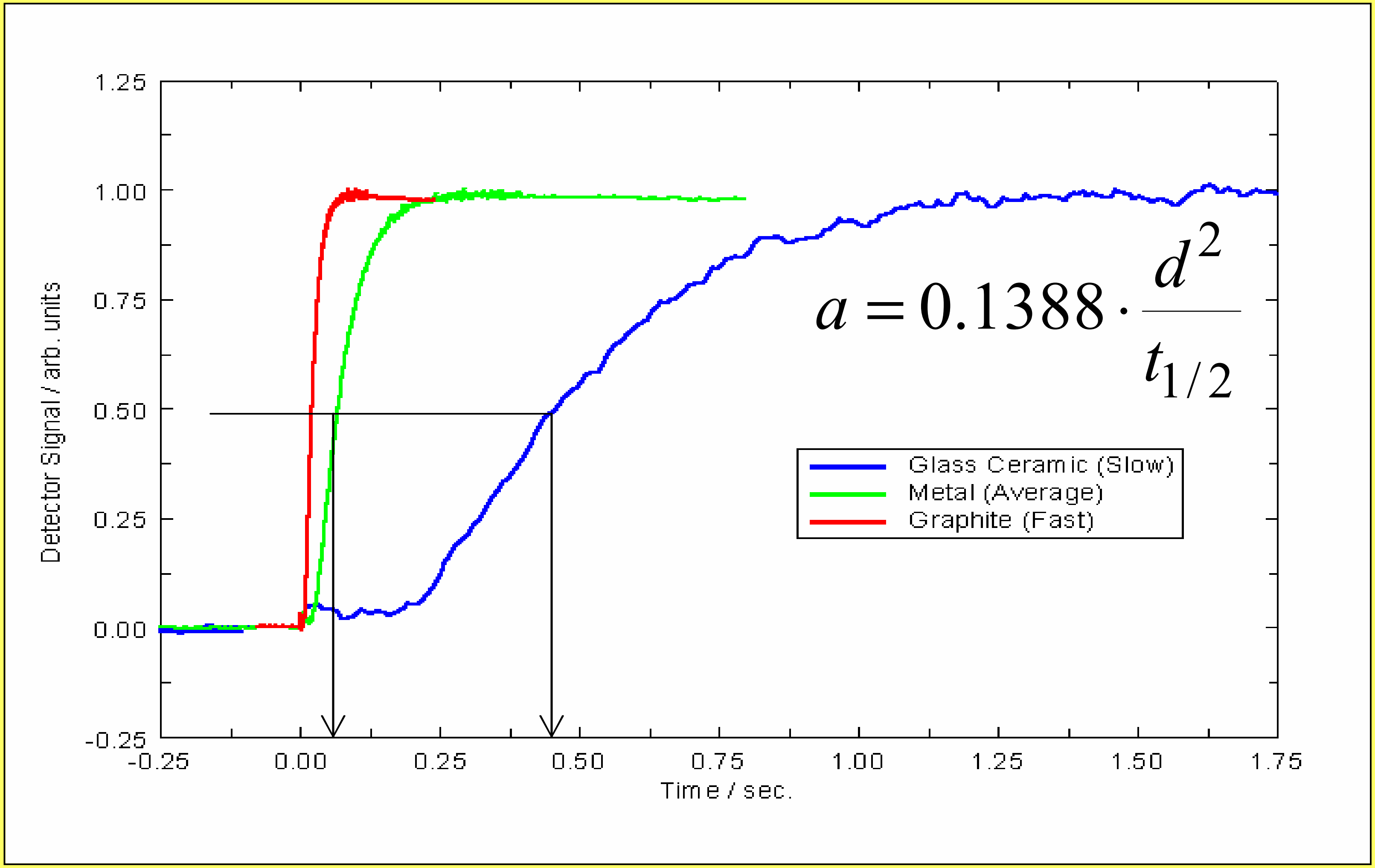
c_p *- heat capacity*

r *- density*



Thermal diffusivity - *The Laser Flash Method (2)*

The $t_{1/2}$ method



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

Thermal diffusivity - *The Laser Flash Method (3)*