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INSPIRING IMAGINATION FOR MATERIAL SCIENCE

Calvet type 3D sensor and its relevance to Cp measurements

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AK-Thermophysik meeting
April 26-28th 2016, Wien , Austria

Summary

- Calorimetric signal
- Calvet 3D sensors
- Temperature scanning methods
- Isothermal methods

Calorimetric signal

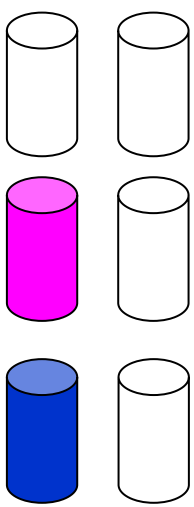
- Thermodynamic data
  - Heat capacity

$$C_P = \left(\frac{dH}{dT}\right)_P = \frac{\left(\frac{dH}{dt}\right)_P}{\left(\frac{dT}{dt}\right)_P}$$

$\left(\frac{dH}{dt}\right)_P$ → **Heat flow**

$\left(\frac{dT}{dt}\right)_P$ → **Heating rate**

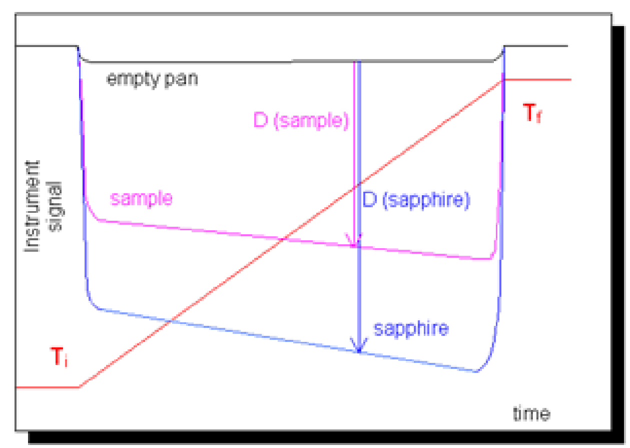
  - C_P is measured thanks to the measurement of the magnitude of the DSC signal



Empty crucibles

Crucible with sample and empty crucible in reference

Crucible with standard material and empty crucible in reference } **Optional**



Calorimetric signal

- DSC signal – simplified equation

$$D_{(\mu V)} = S_{(\mu V.W^{-1})} \times m_{(g)} \times Cp_{(J.g^{-1}.K^{-1})} \times V_{(K.s^{-1})}$$

- D: **Magnitude of the signal Shift**
- S: **Detector Sensitivity**
- m: **Sample Mass**
- V: **Heating Rate**

- To improve the C_p determination it is possible to
  - Increase the scanning rate
  - Increase the sample mass
  - Increase the detector sensitivity

(Increase the scanning rate / Increase the sample mass): **Thermal gradients risks**

Calorimetric signal

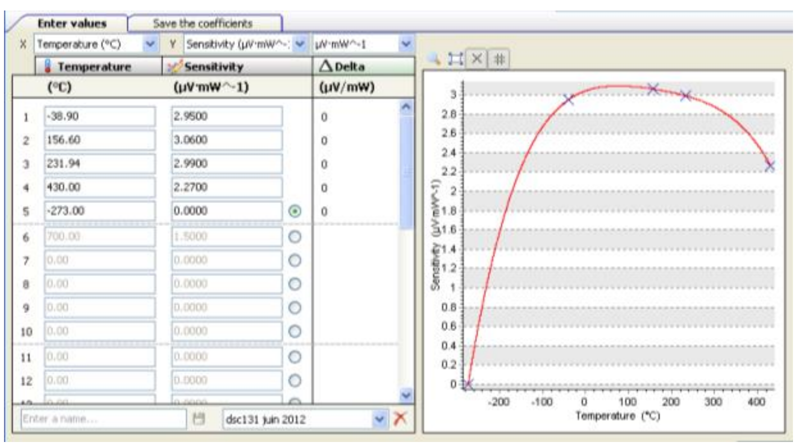
- Conventional 2D sensors
  - Flat shaped thermocouples
    - Heat flow is detected through the bottom of the crucible
    - A bad sample –crucible contact impacts the final result -> Bias
    - Limited to small scale samples
  - Efficiency losses at high temperature
    - Pt / PtRh10%: 2 times less sensitive at 1000°C

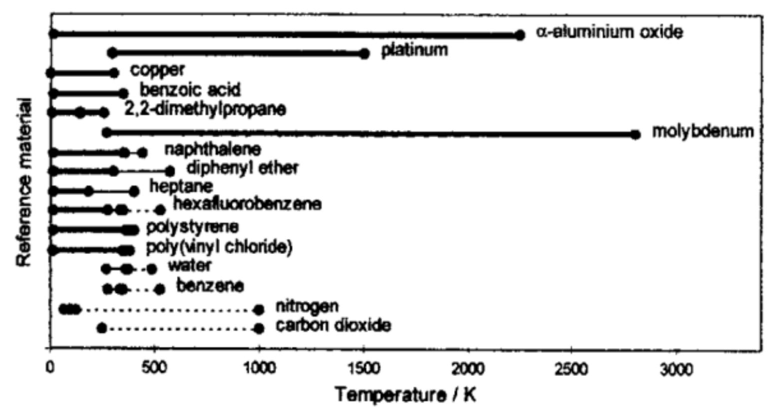
$$D_{(\mu V)} = S_{(\mu V.W^{-1})} \times m_{(g)} \times Cp_{(J.g^{-1}.K^{-1})} \times V_{(K.s^{-1})}$$

D	S	m	V
Magnitude of the signal Shift	Low	Low	High

Calorimetric signal

- Conventional 2D sensors
  - Flat shaped thermocouples
    - Calibration from reference material melting
      - Limited number of substances, i.e. of calibration temperatures
      - Large uncertainty between 2 calibration temperatures
    - Calibration from C_p reference material
      - Method with 3rd test is mandatory
      - Limited number of reference materials



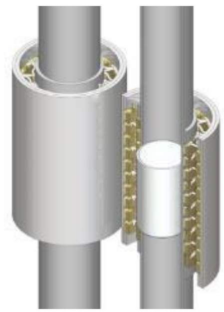
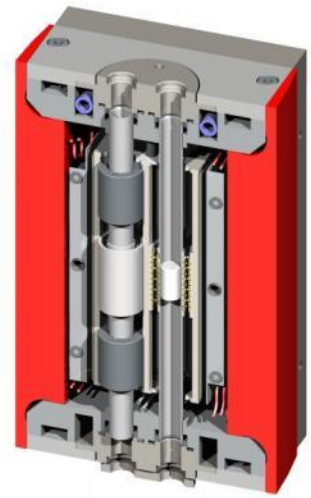


Recommended materials for the calibration of heat capacity measurements vs. temperature range

Calvet 3D Sensors

- Calvet sensors for low and very low temperatures

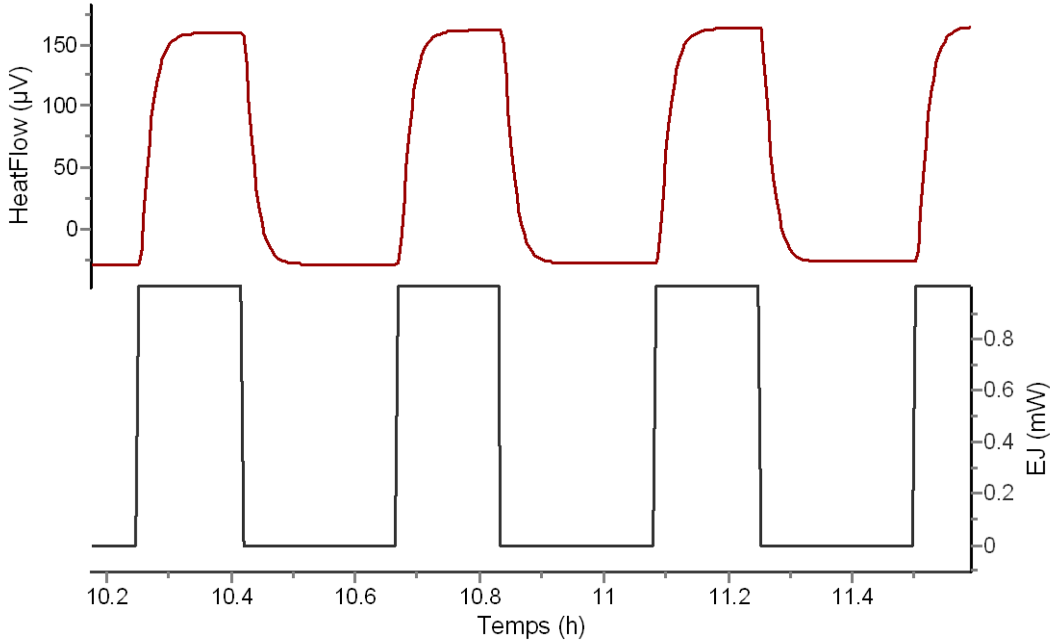



- The sensor surrounds the sample
- Heatflow measurement is
  - Quantitative and less depending on the calibration
  - Less depending on the crucible, type and sample shape
- The sensitivity coefficient is increased (multiple thermocouples)
- Most cases: available sample volume higher

Calvet 3D Sensors

- Calvet sensors for low and very low temperatures
  - Sensitivity coefficient determined by the Joule effect method
  - At any temperature over the temperature range of the calorimeter

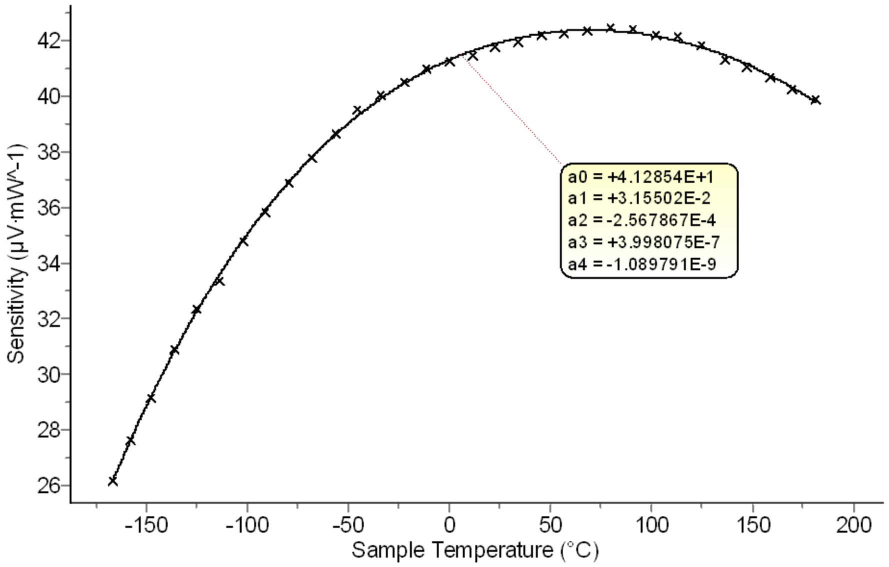


Sensitivity : S = [µV] / [mW]

[J] = [W] . [s]

Calvet 3D Sensors

- Calvet sensors for low and very low temperatures
  - Larger number of calibration points/temperatures
  - Regression more reliable: less uncertainty on S between 2 points
- 2 trials method is accurate enough with this type of sensors



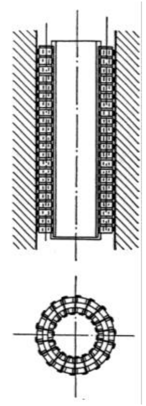
Typical calibration curve for BT2-15: one point every ~10°C

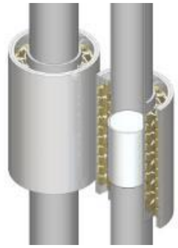
Calvet 3D Sensors

- Calvet sensors for low and very low temperatures

Calorimeter/DSC	μSC	BT2.15	MS80	C80	SENSYS Evo
Temperature range	-40 / 200°C	-196 / 200°C	30 / 200°C	30°C / 300°C	-120°C / 830°C
Thermocouples number / pile	N/A	450	>1000	190	120
Standard sample volume	0.85mL	12.5mL	100mL	12.5mL	0.25mL
Max sensitivity value	180μV/mW	40μV/mW	50μV/mW	30μV/mW	7μV/mW







Temperature scanning

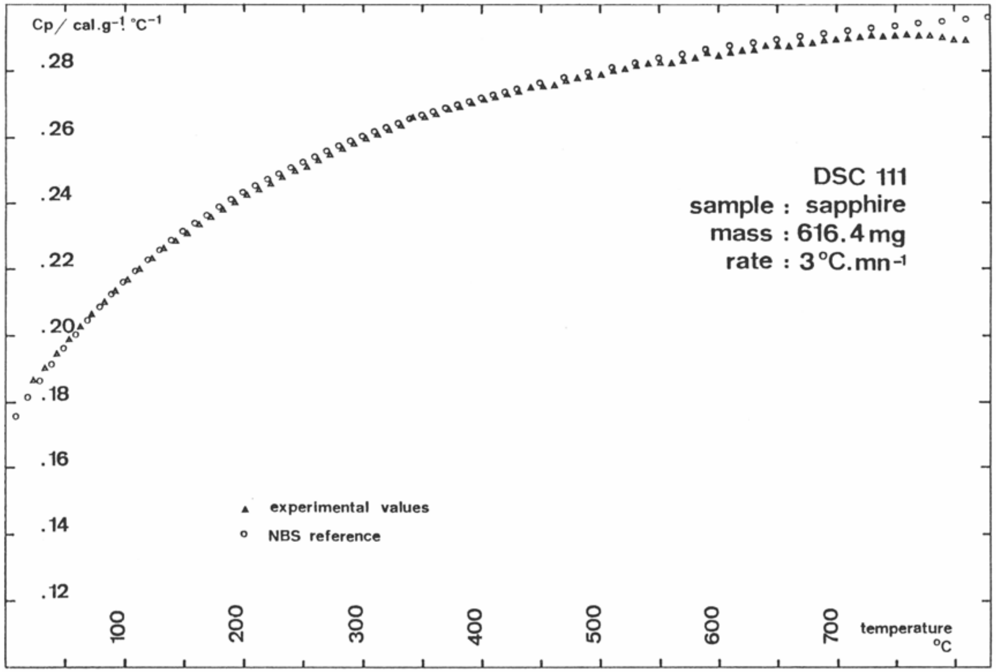
- Calvet sensors for low and very low temperatures

$$D_{(\mu V)} = S_{(\mu V.W^{-1})} \times m_{(g)} \times Cp_{(J.g^{-1}.K^{-1})} \times V_{(K.s^{-1})}$$

Magnitude of the signal Shift — **High** — **High** — **Medium-Low**

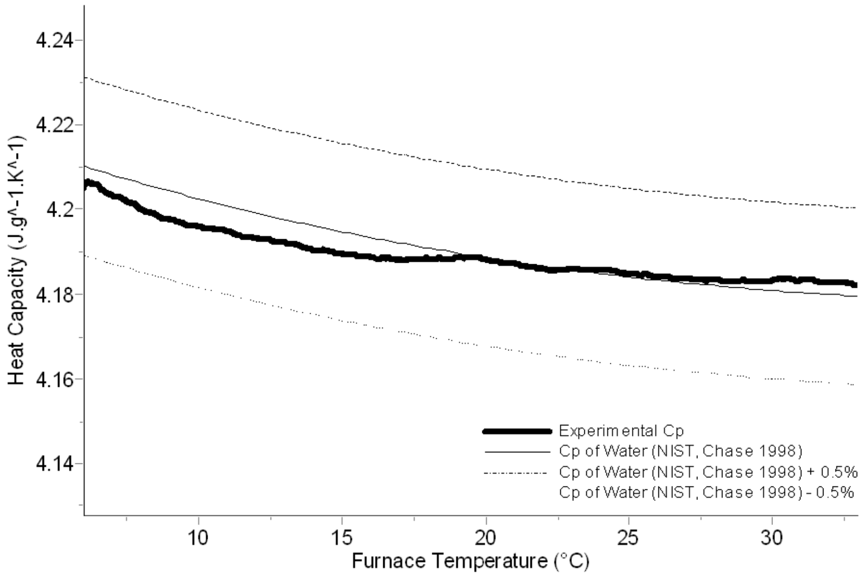
Temperature scanning

- Instrument: Sensys Evo DSC
  - Sample: sapphire
  - Mass: 616,4 mg
  - Rate: 3°C/min
- The deviation between the measured and literature values is less than 1%.



Temperature scanning

- Instrument: µSC
  - Sample: deionized water
  - Mass: 195.89mg
  - Rate: 0.1K/min
- The deviation between the measured and literature values is less than 0.5%.



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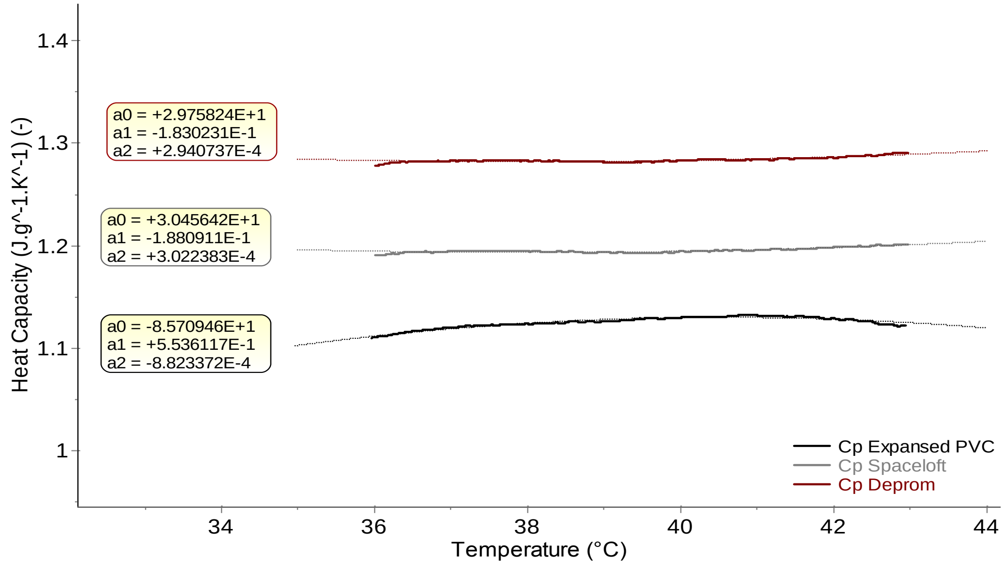
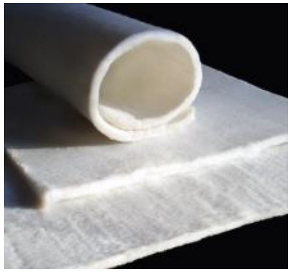
Temperature scanning

- Instrument : C80
- Low density insulation materials
  - **Aerogel: Spaceloft® (50kg.m^{-3}, extremely low conductivity 14mW/m.K at 40°C)**
  - **Deprom: PS-based (extremely low density 40kg.m-3, low conductivity 27mW/m.K)**
  - **Expanded PVC relatively dense**
- Samples heated from 30°C to 45°C @ 0.15 °C.min^{-1}

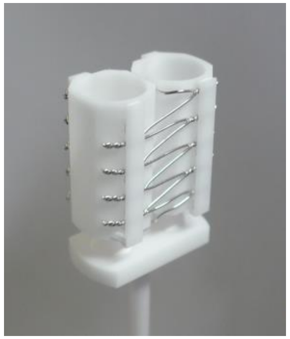


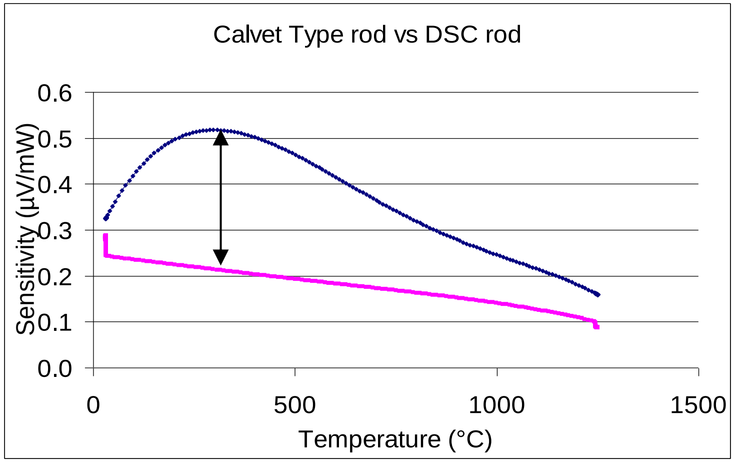


Spaceloft® is a flexible, nanoporous aerogel blanket insulation in residential and commercial building applications.

Temperature scanning

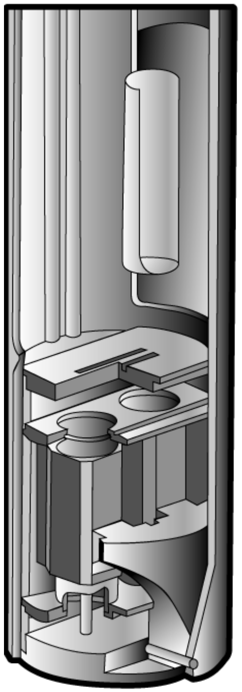
- Quasi-Calvet sensors for high temperatures
- C_P rod for Labsys Evo
  - 18 type S thermocouples (1600°C)
  - Sample volumes
    - 0.380mL (Pt crucible)
    - 0.235mL (With alumina liner)
  - Max sensitivity 0.5µV/mW
    - 2.5 times more than an equivalent type S DSC rod





Temperature scanning

- High temperature quasi-Calvet sensors
- HF-DSC sensors for HT calorimeters
  - T ranges
    - 20 to 1400°C (Pt/PtRh10%)
    - 20 to 1600°C (PtRh6%/PtRh30%)
  - Heating rate range
    - 0.01 to 20°C/min
  - Volume : 0.450 mL
  - Dimensions :
    - Diameter : 6 mm
    - Height : 16 mm



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Temperature scanning

- High temperature quasi-Calvet sensors

$$D_{(\mu V)} = S_{(\mu V.W^{-1})} \times m_{(g)} \times Cp_{(J.g^{-1}.K^{-1})} \times V_{(K.s^{-1})}$$

$D_{(\mu V)}$	$S_{(\mu V.W^{-1})}$	$m_{(g)}$	$V_{(K.s^{-1})}$
Magnitude of the signal Shift	Improved	High	Low

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Temperature scanning

- Characterization of NaF and $NaLaF_4$
  - Materials potentially to be used for cooling systems of nuclear reactors of Generation IV (Molten Salt Reactor)
  - Step mode, platinum crucible and boron nitride liner
  - Tests from 473 K to 1213 K with steps of 15 K @ 2 K/min

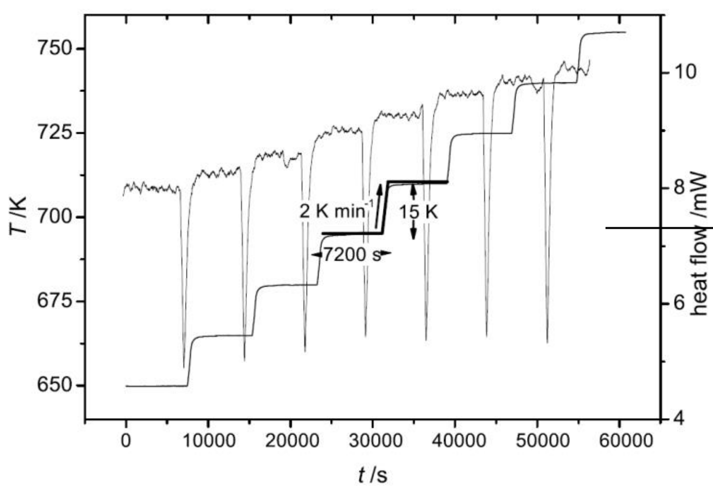


FIGURE 1. Example of a C_p-by-step run. The step indicated has a size of 15 K, a rate of $2\ K \cdot min^{-1}$ and a duration of 7200 s.

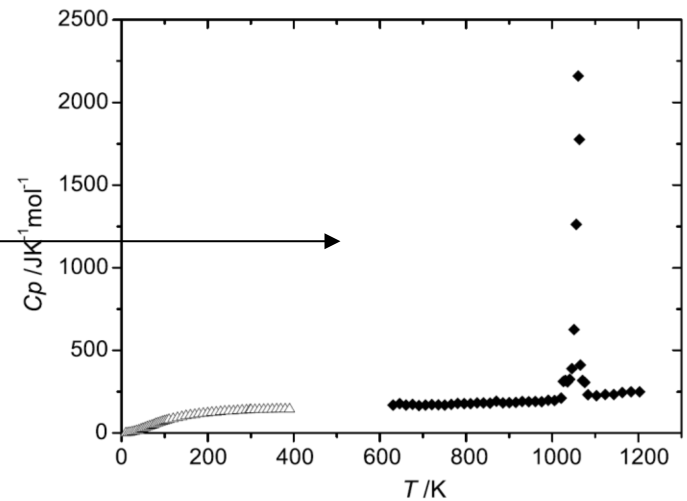
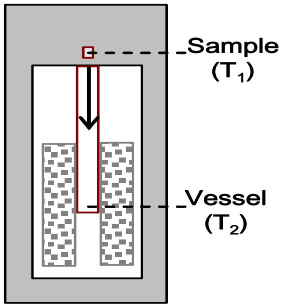
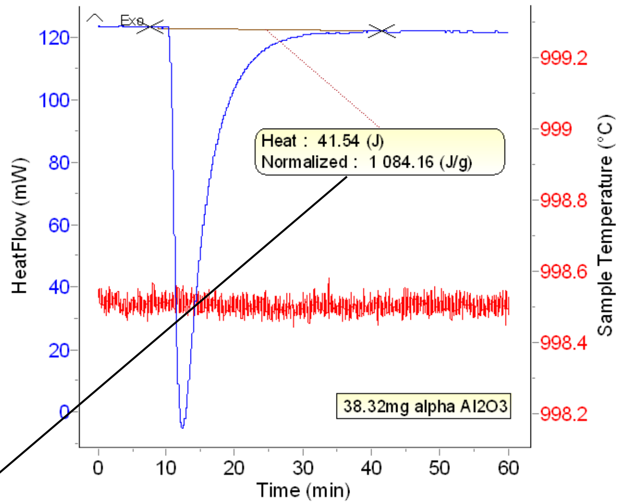


FIGURE 3. Heat capacity measurements on $NaLaF_4$. △: obtained by adiabatic calorimetry; ◆: obtained by heat flow calorimetry.

Isothermal methods

- Drop calorimetry
  - Principle
    - The sample is dropped from room temperature in the calorimeter chamber maintained at a given isothermal temperature
    - Two drops at similar temperatures allow determining the average CP between these temperatures
  - S depends on temperature and filling level of the sensor
    - A reference material drop is necessary to frequently reassess the sensitivity coefficient





$$[H]_{T_0}^{T} = m.\int_{T_0}^{T} C_P \cdot dT \longrightarrow \overline{C_P} = \frac{[H]_{T_0}^{T_2} - [H]_{T_0}^{T_1}}{T_2 - T_1}$$

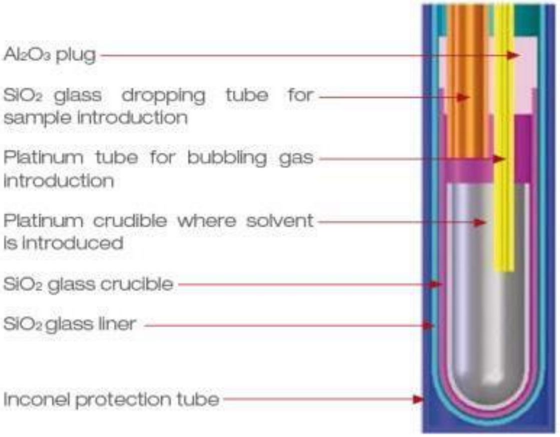
Isothermal methods

- Alexys: high-sensitivity Calvet calorimeter optimized for drop calorimetry isothermal operations at temperatures up to 1000 °C, designed based on Prof. Alexandra Navrotsky’s (UC Davis, Thermochemistry lab) experience.

- MultiHTC: High temperature drop calorimeter
  - Temperature ranges
    - 20 to 1300°C (Pt/PtRh10%)
    - 20 to 1500°C (PtRh6%/PtRh30%)

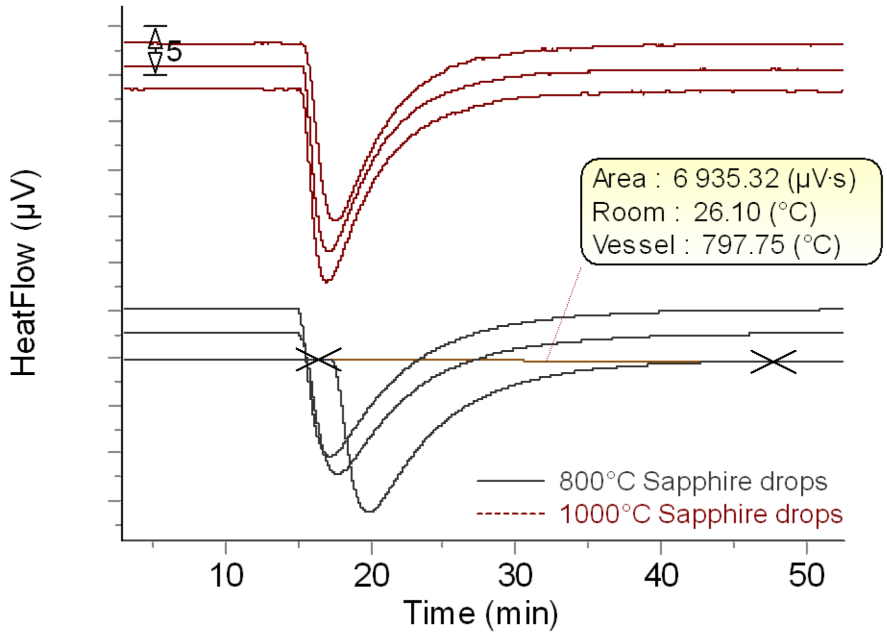
Isothermal methods

- In both detectors, the arrangement of thermocouples welding (thermopile) on the surface of the experimental chamber at varying heights provides good integration of the heat exchanges.



Isothermal methods

- Calibration coefficients at the tested temperature can be determined by drops of platinum and/or standard synthetic sapphire.
- Other option: before and after each tested sample drop, a standard material drop and calculation of an average sensitivity coefficient.



Overlaid thermograms obtained from sapphire drops with an Alexys calorimeter at 800°C (0.214µV/mW) and 1000°C (0.152µV/mW)

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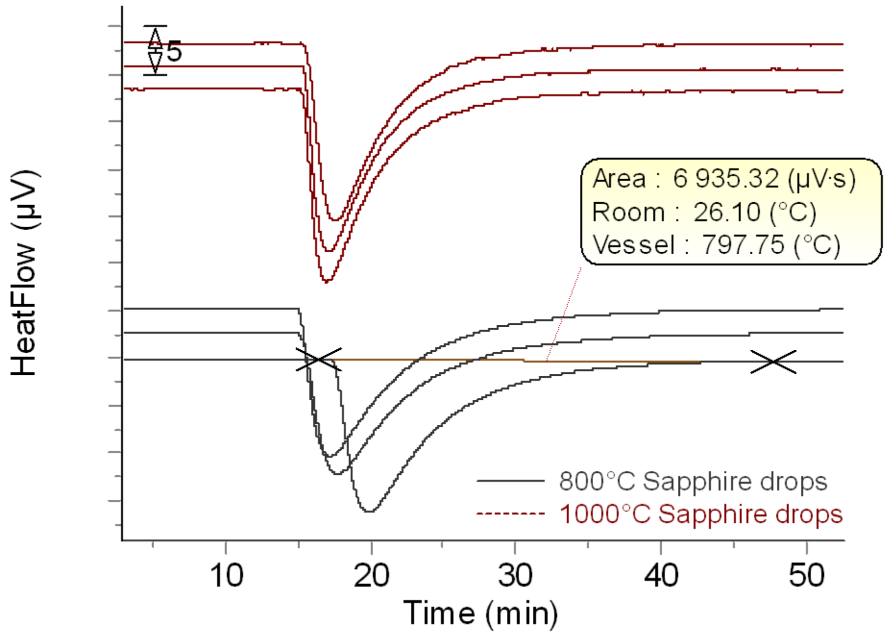

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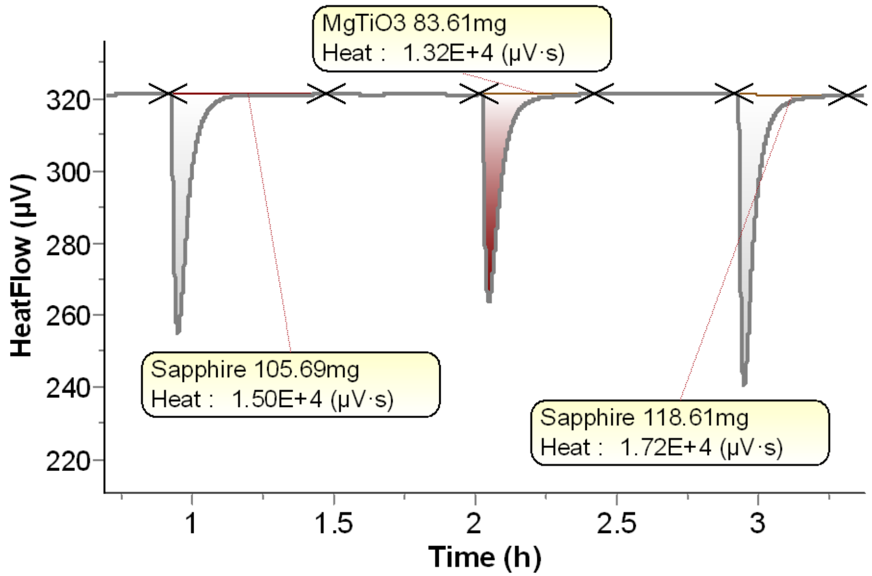
Isothermal methods

- C_P measurements
  - The specific enthalpy of $MgTiO_3$ is firstly determined at 523°C (479.7 ±8 J/g) and at 574°C (527.9 ±13 J/g)
  - The average C_P is then calculated by dividing the specific enthalpy difference by the temperature difference
  - The average specific heat capacity at 548.5°C was thus found equal to 0.945 ± 0.025 J.g-1.K-1.



Drops of Sapphire and $MgTiO_3$ at 574°C

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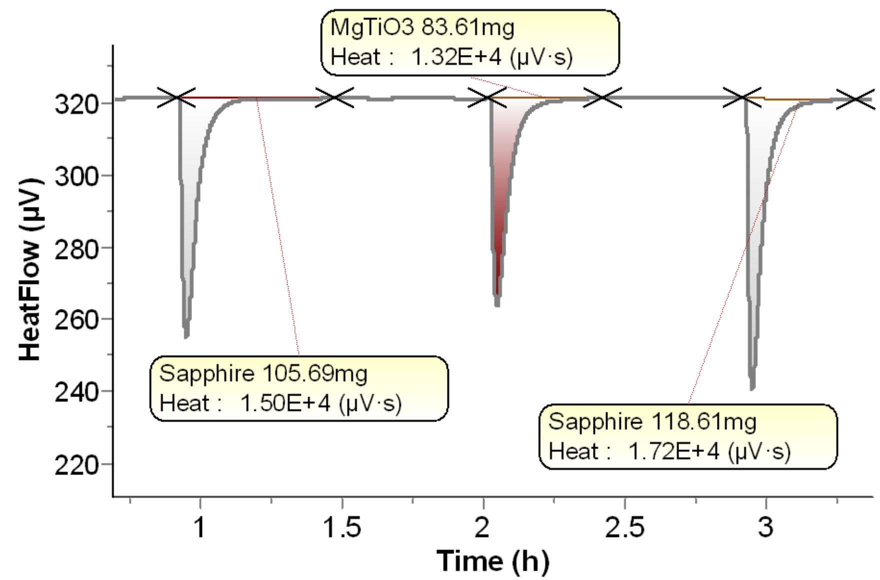

Drops of Sapphire and $MgTiO_3$ at 574°C

Conclusions

- The calorimetric methods based on Calvet principle are applied to determine accurate heat capacities (and other thermodynamic data…) over large temperature, pressure, atmosphere conditions

Thanks for your attention!

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Calvet type 3D sensor and its relevance to Cp measurements

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