

# PCM specific heat capacity $c_p(T)$ measurements

DSC on PCM Workshop

AIT, Vienna, 04. - 05. April 2016

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## Overview

- Specific heat capacity  $c_p(T)$  - definition and DSC standards
- DSC calibration - temperature, heat and heat flow calibration
- $c_p(T)$  evaluation of PCM with the hf-DSC
- Uncertainty concept for  $c_p(T)$  analysis out of DSC measurements
- “Desmearing” and peak baseline determination
- DSC tips

# Specific heat capacity $c_p(T)$

## Definition and Standards

## Specific heat capacity $c_p(T)$ – Definition

- $C_p(T)$  is the amount of heat required to raise the temperature of a substance by one Kelvin at constant pressure without a 1<sup>st</sup> order phase transition (DIN EN ISO 11357-4; DIN 51007).

$$c_p(T) = \frac{C_p(T)}{m} = \frac{\frac{dQ}{dT}}{m \cdot \frac{dT}{dt}} = \frac{\Phi(T)}{m \cdot \beta}$$

- Spec. heat capacity [ $c_p$ ]=J/gK; heat capacity [ $C_p(T)$ ]=J/K; mass [ $m$ ]=kg; heat [ $Q$ ]=J; temperature [ $T$ ]=K; time [ $t$ ]=s, heat flow rate [ $\Phi$ ]=W, heating rate [ $\beta$ ]=K/s
- “...this quantity equals the real (vibrational) heat capacity only in the absence of transitions or reactions (peaks). In the case of thermal events in the sample it is an “apparent specific heat”, different from the static (vibrational) heat capacity and, in addition, “smeared.” [1]

[1] G.W.H. Höhne et al, Differential Scanning Calorimetry, 2nd Edition, Springer

## Specific heat capacity $c_p(T)$ – standards DIN 51007 or ASTM E1269 - 11

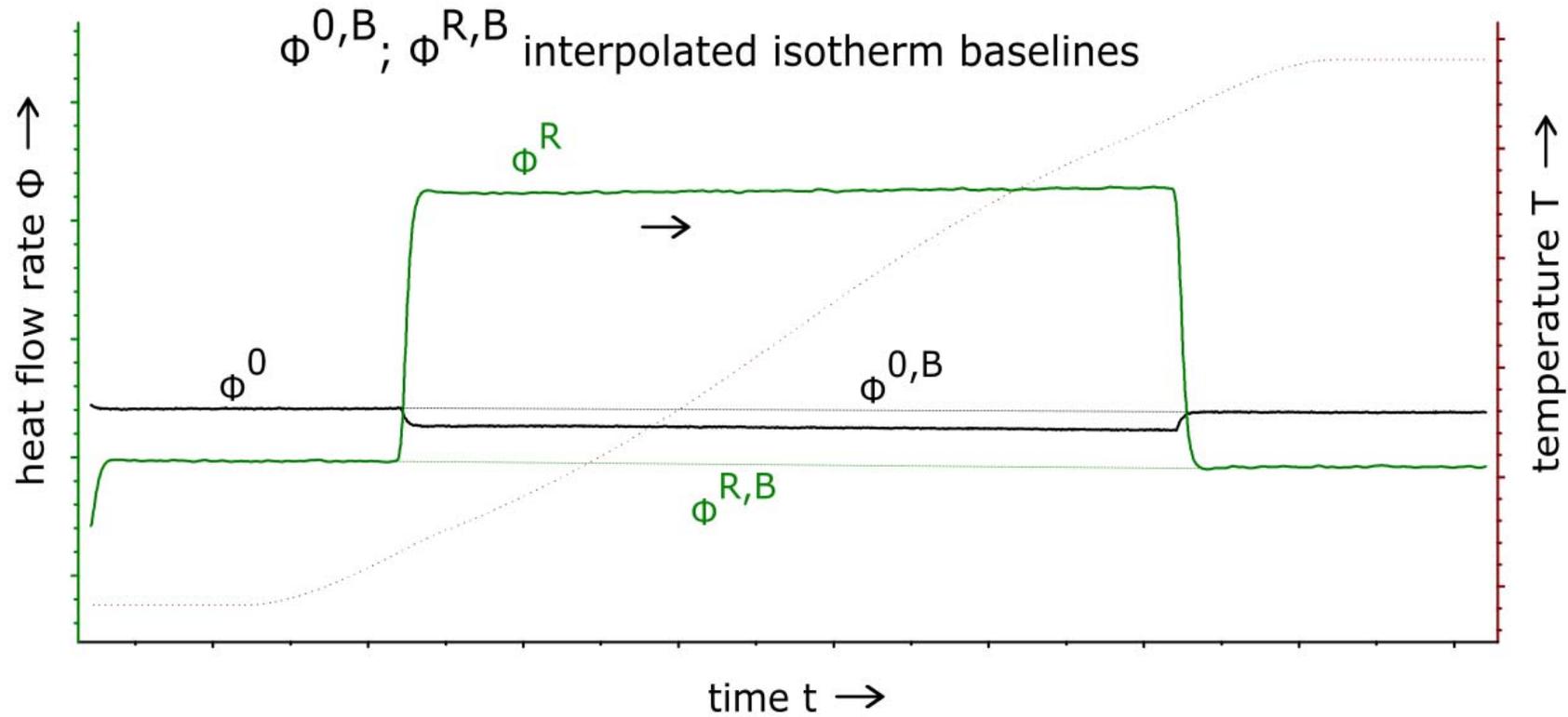
- DIN 51007 (1994): Thermal Analysis; Differential Thermal Analysis; Principles:
  - 3 measurements: empty crucibles, reference and sample measurement
  - Additional baseline construction between isotherm segments needed
  - Reference standard:  $\alpha\text{-Al}_2\text{O}_3$  (Sapphire)
  - Measurement of a dimensionless calibration factor using a reference standard

$$K(T) = \frac{C_p^R(T) \cdot \beta}{(\Phi^R(T) - \Phi^{R,B}(T)) - (\Phi^0(T) - \Phi^{0,B}(T))}$$

$$c_p^S(T) = \frac{K(T) \cdot (\Phi^S(T) - \Phi^0(T))}{\beta \cdot m^S}$$

- heat capacity Reference  $[C_p(T)] = \text{J/K}$ ; temperature  $[T] = \text{K}$ ; heat flow rate  $[\Phi] = \text{W}$   
superscripts: R for reference, 0 for empty measurement, B for interpolated baseline
- Recommended Heating rate: 10 K/min

# Specific heat capacity $c_p(T)$ – standards DIN 51007 or ASTM E1269 - 11



$$K(T) = \frac{C_p^R(T) \cdot \beta}{(\Phi^R(T) - \Phi^{R,B}(T)) - (\Phi^0(T) - \Phi^{0,B}(T))}$$

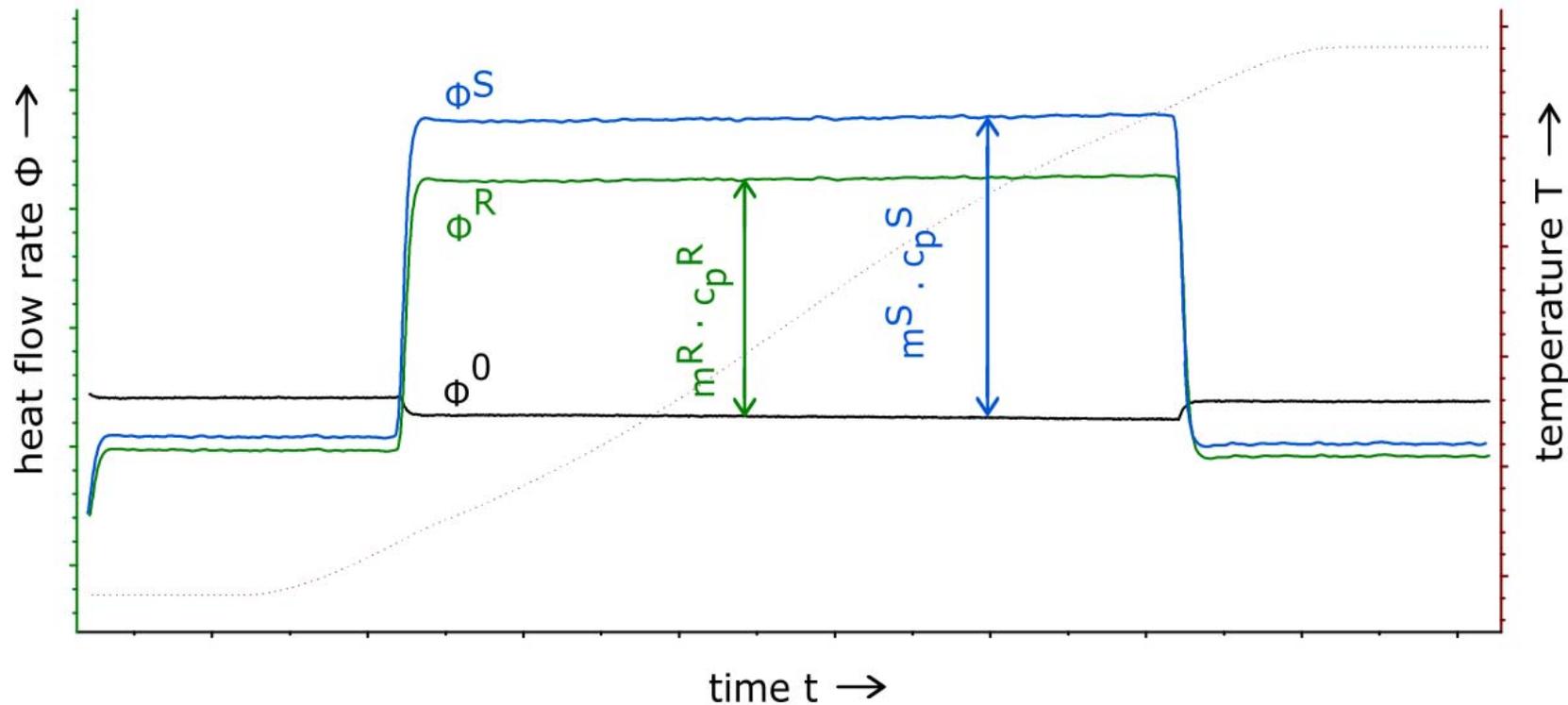
## Specific heat capacity $c_p(T)$ – standards DIN EN ISO 11357-4

- DIN EN ISO 11357-4: Plastics –Differential scanning calorimetry (DSC) – Part 4: Determination of specific heat capacity (ISO 11357-4:2014)
  - 3 measurements: empty crucibles, reference and sample measurement
  - Calibrations substance recommendation:  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Sapphire)
  - continuous scanning:

$$c_p^S(T) = c_p^R(T) \cdot \frac{m^R}{m^S} \cdot \frac{\Phi^S(T) - \Phi^0(T)}{\Phi^R(T) - \Phi^0(T)} = c_p^R(T) \cdot \frac{m^R}{m^S} \cdot \frac{U^S(T) - U^0(T)}{U^R(T) - U^0(T)}$$

- Crucibles: Identical shape and material;  $\Delta m_{\text{crucibles}} < 0,1 \text{ mg}$
- Sample: solid/liquid,  $m^S = 2 - 40 \text{ mg}$ ; good thermal contact between sample/crucible
- Temperature:  $T_{\text{Start}}$  30 K below the first needed data points
- Stabilization isotherm segment: 2-10 minutes
- Heating rate of 5 to 10 K/min in dynamic segments

# Specific heat capacity $c_p(T)$ – standards DIN EN ISO 11357-4



$$c_p^S(T) = c_p^R(T) \cdot \frac{m^R}{m^S} \cdot \frac{\Phi^S(T) - \Phi^0(T)}{\Phi^R(T) - \Phi^0(T)} = c_p^R(T) \cdot \frac{m^R}{m^S} \cdot \frac{U^S(T) - U^0(T)}{U^R(T) - U^0(T)}$$

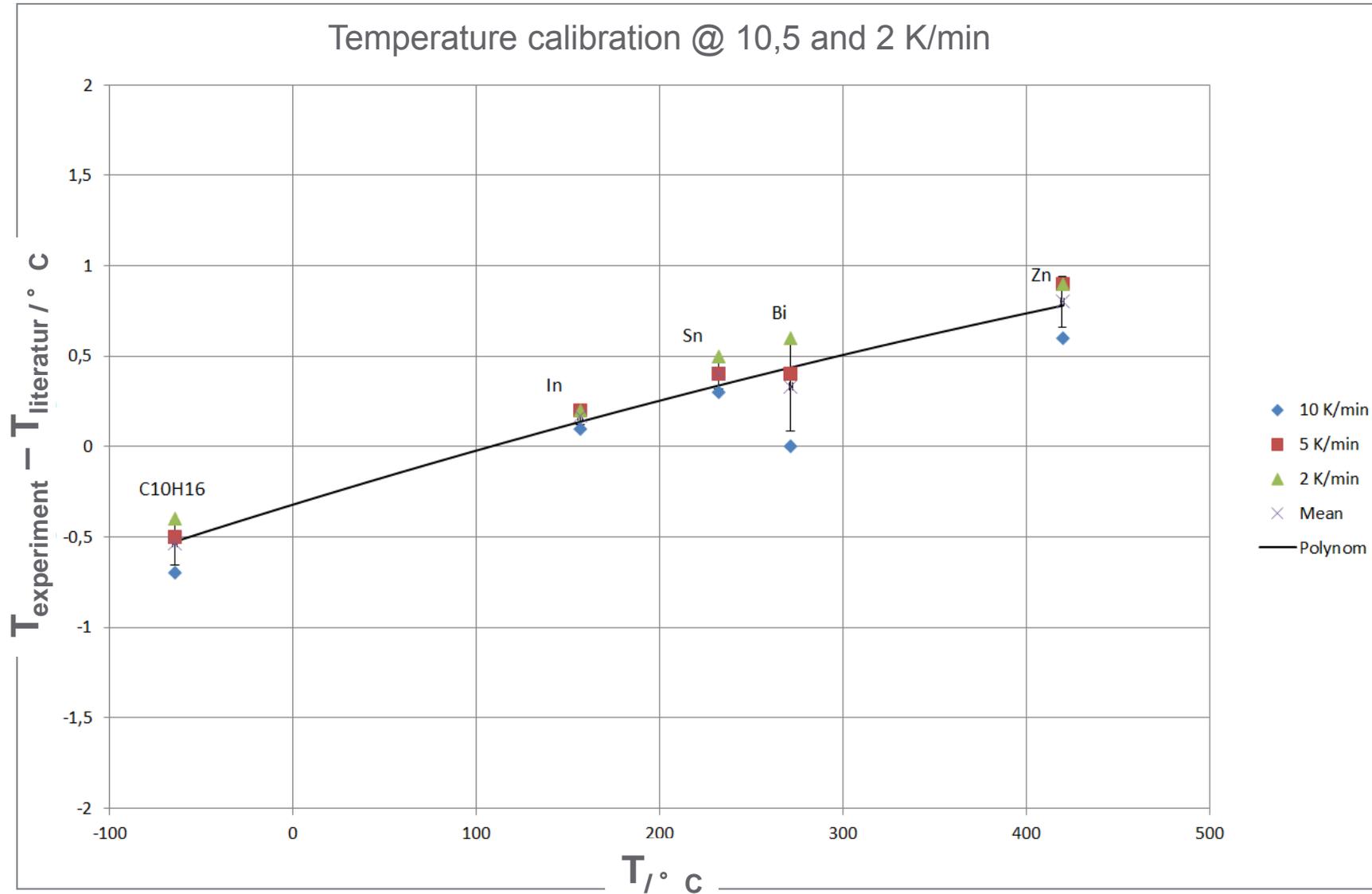
## Specific heat capacity $c_p(T)$ – standards comparison

- All three norms show a similar procedure with an isothermal segment before and after the dynamic segment
- DIN 51007 and ASTM E1269 requires additionally the interpolated baseline between the isothermal segments – Baseline shift consideration
- All three norms recommend fast heating rates  $> 5\text{K/min}$  for higher  $\Delta T$  or DSC signal gain between reference and sample in the DSC.
- All three norms recommend a synthetic sapphire material as reference standard
- DIN EN ISO 11357-4 defines a start temperature 30 K below the first needed data points

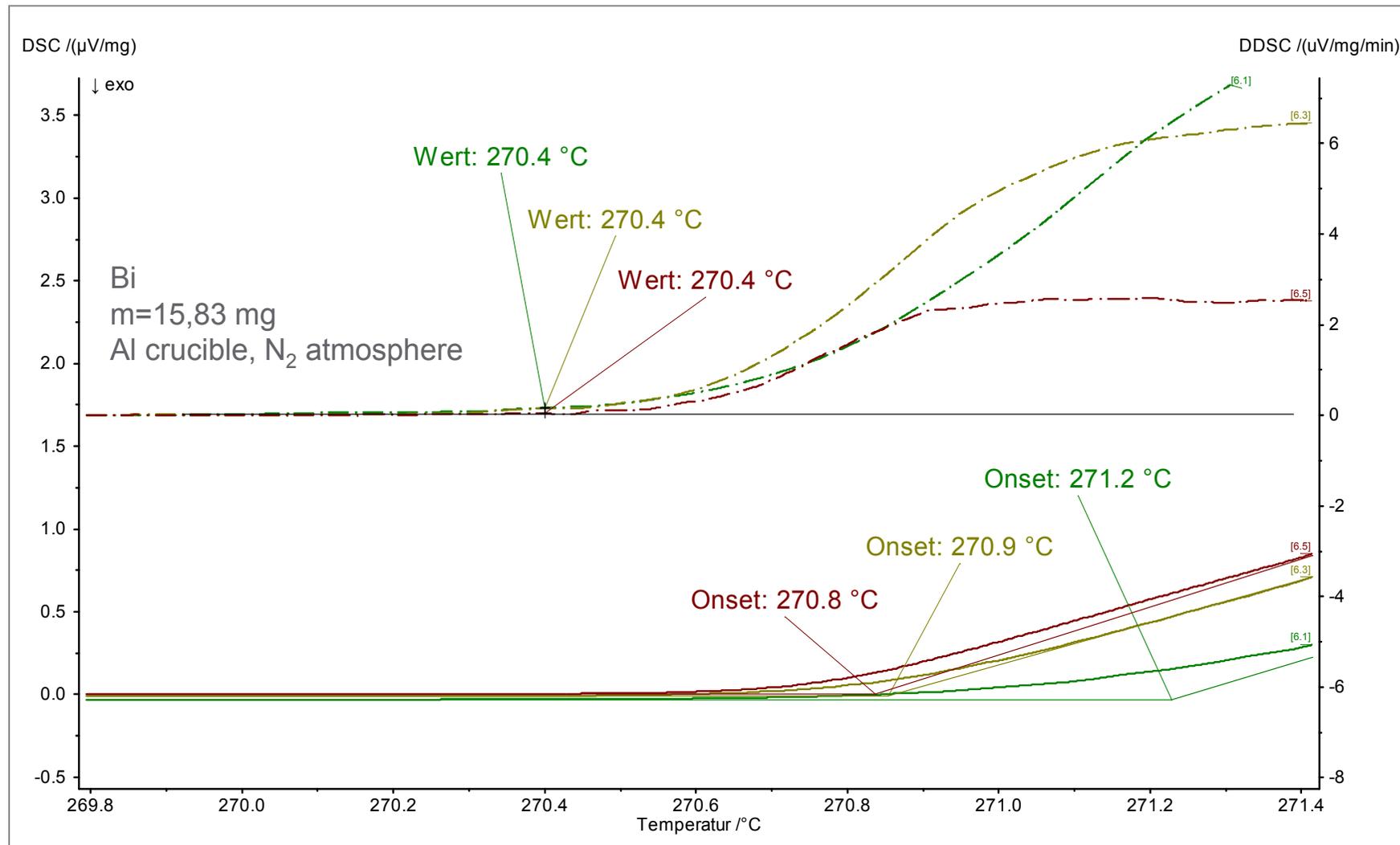
## DSC calibration

Temperature, heat and heat flow calibration

# DSC temperature calibration – melting standards



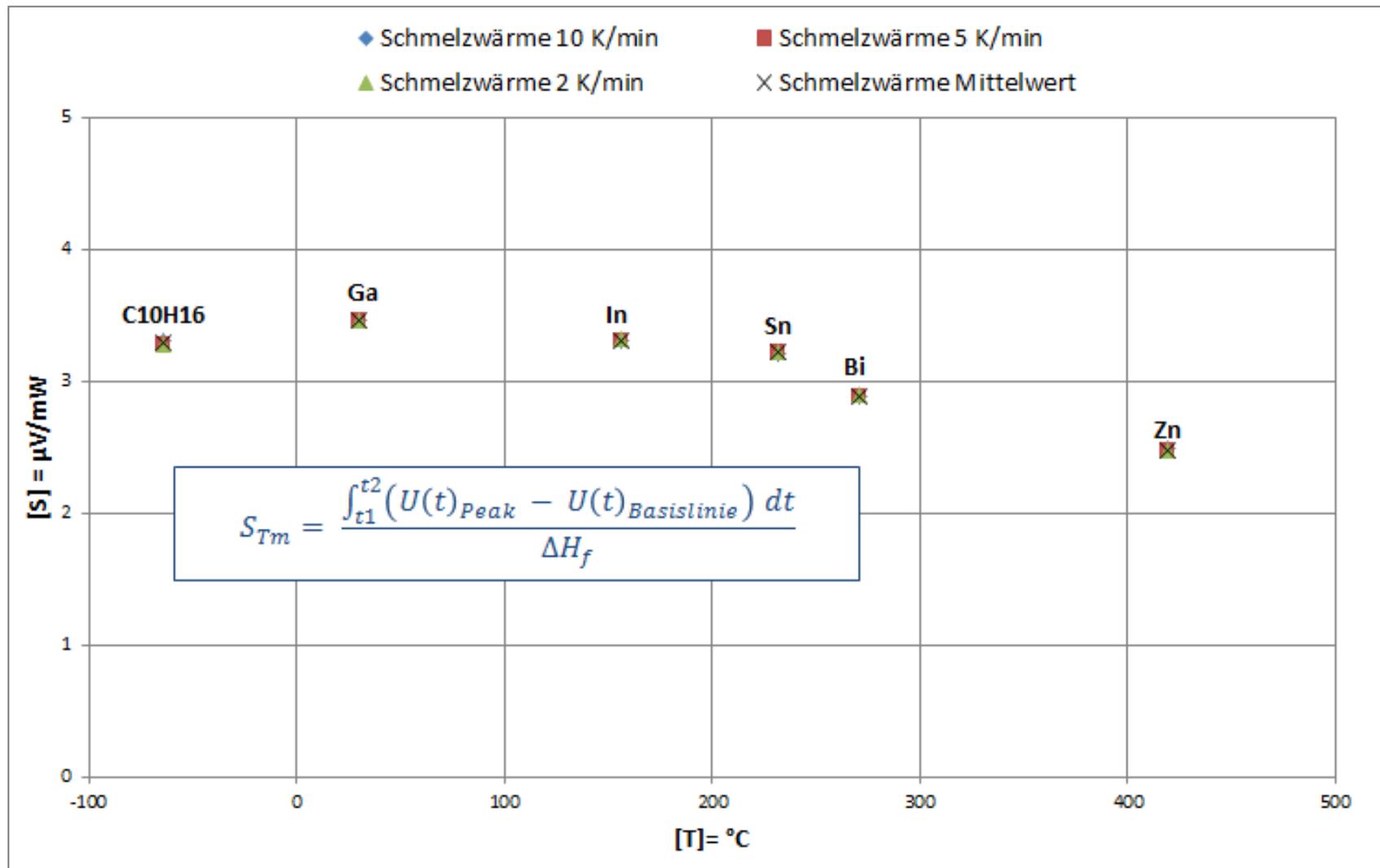
# DSC temperature calibration - Bismuth standard



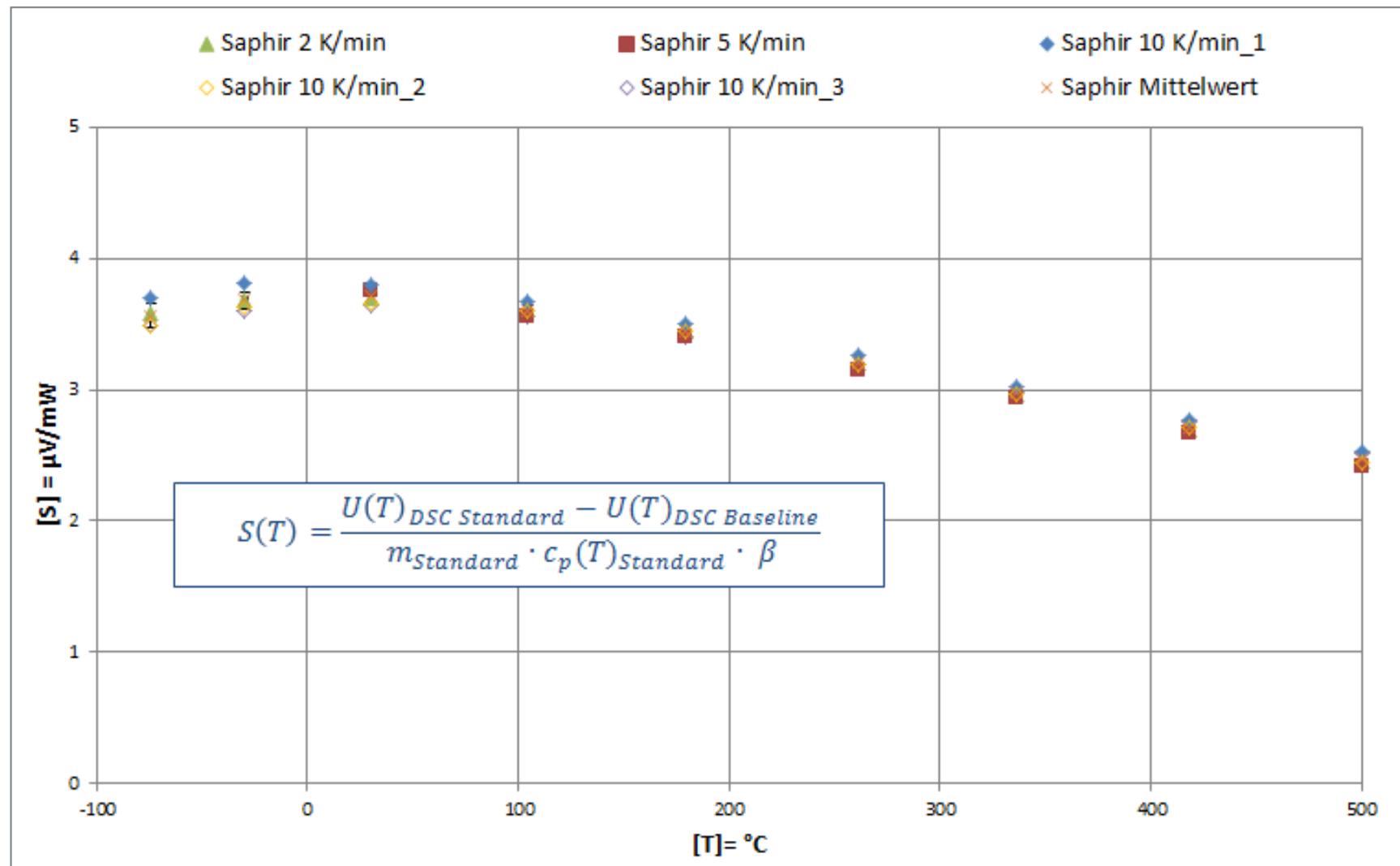
## Temperature calibration

- “OnSet” evaluation method lead to different temperatures depending on the heating rate and the substance itself
- Extrapolation to  $\beta=0$  is time consuming, a lot of measurements are needed
- The 1. derivation of the DSC signal (DDSC) represents the changes of the slopes in the peak area region and to identify the initial temperature  $T_i$
- The initial temperature  $T_i$  of the DSC peak is reproducible at different heating rates
- $T_i$  represents the start temperature of melting of the sample at the sensor contact area
- Current standards only use the extrapolated onset temperature  $T_e$ . Reason according Höhne et al: “ $T_i$  cannot be determined with the required reliability because of the noise...”

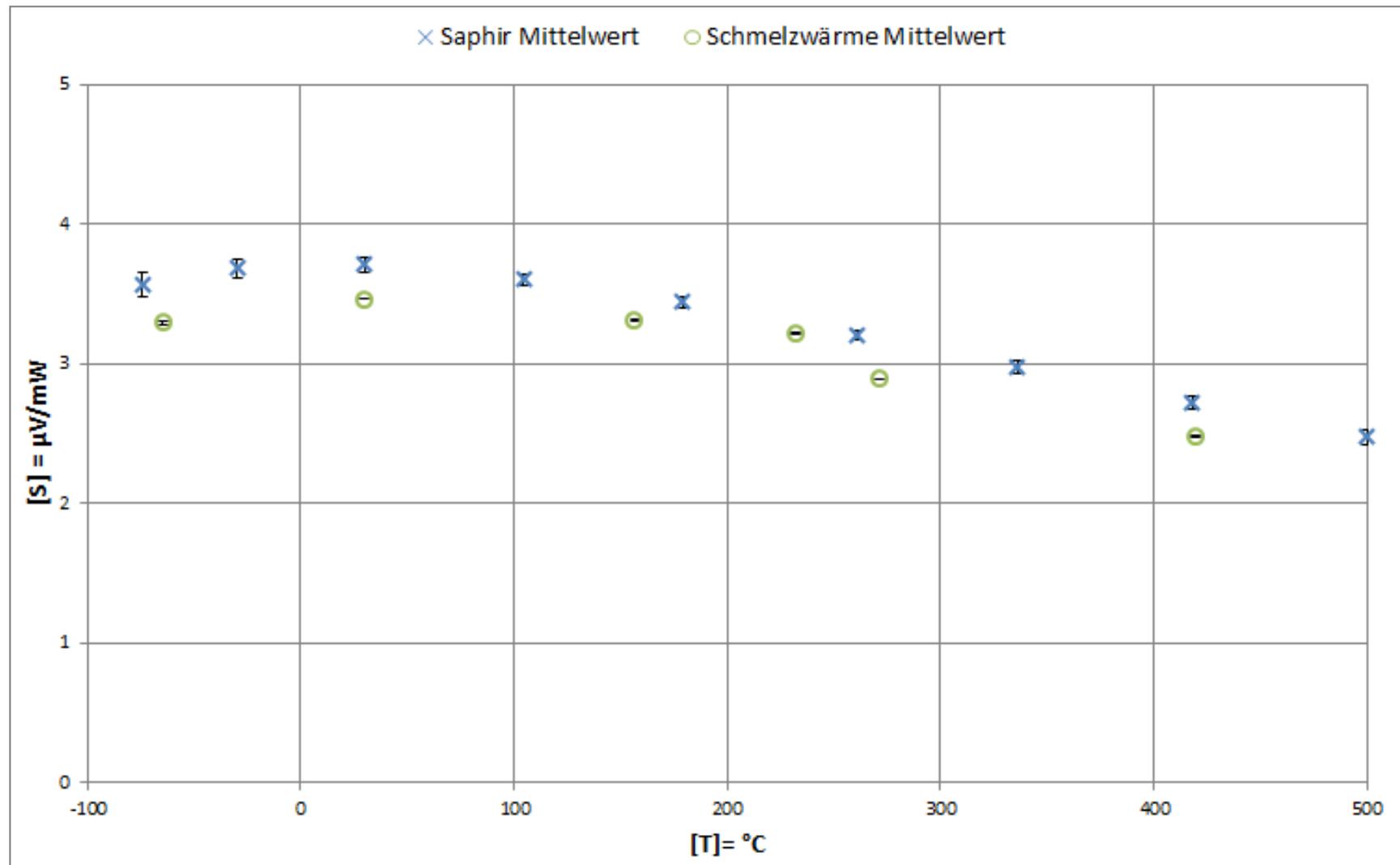
# DSC heat calibration – heat of fusion



## DSC heat flow calibration – $c_p$ standard



## DSC heat flow calibration - comparison



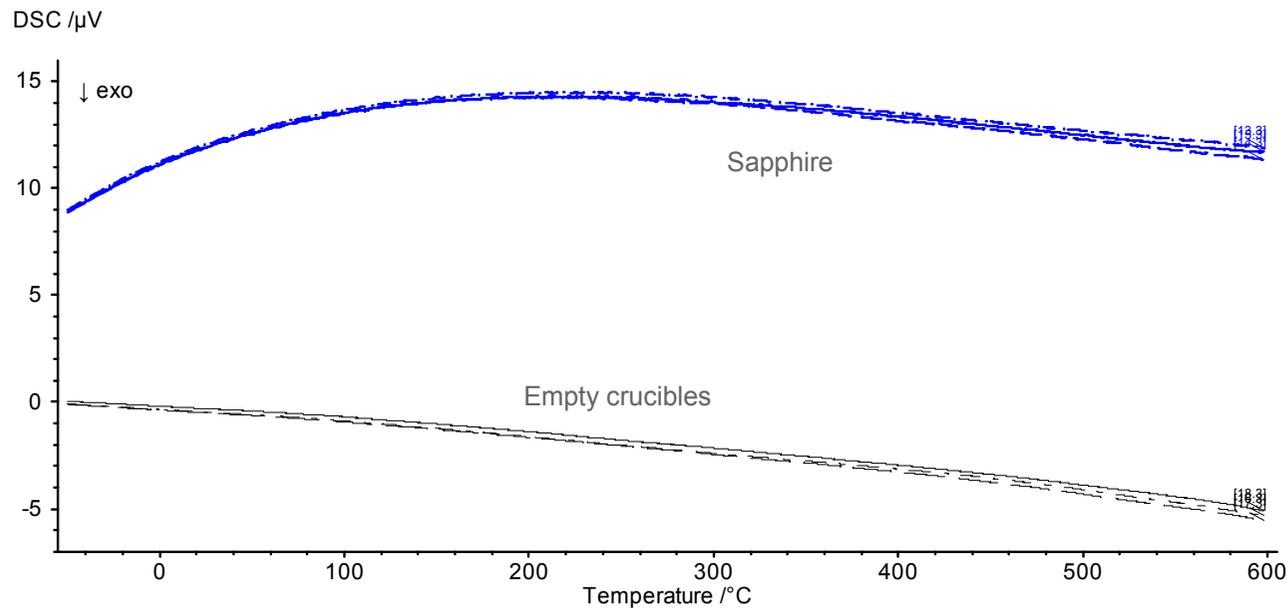
## Caloric calibration - Conclusion

- Heat calibration:
  - low heating rate dependency but low temperature resolution due to limited number of melting standards
  - Mathematical weighting of the melting standards for polynomial function necessary to get a smooth curve of the sensor sensitivity
  
- Heat Flow calibration:
  - heat rate dependency
  - high temperature resolution
  - smooth curve progression through high temperature resolution
  
- Conclusion
  - heat and heat flow calibration show different sensor sensitivity  
Höhne et al: *“It is to be expected, that the calibration factor for the heat flow rate depend on the heat flow rate itself.”*
  - calibration based on measurement demand necessary

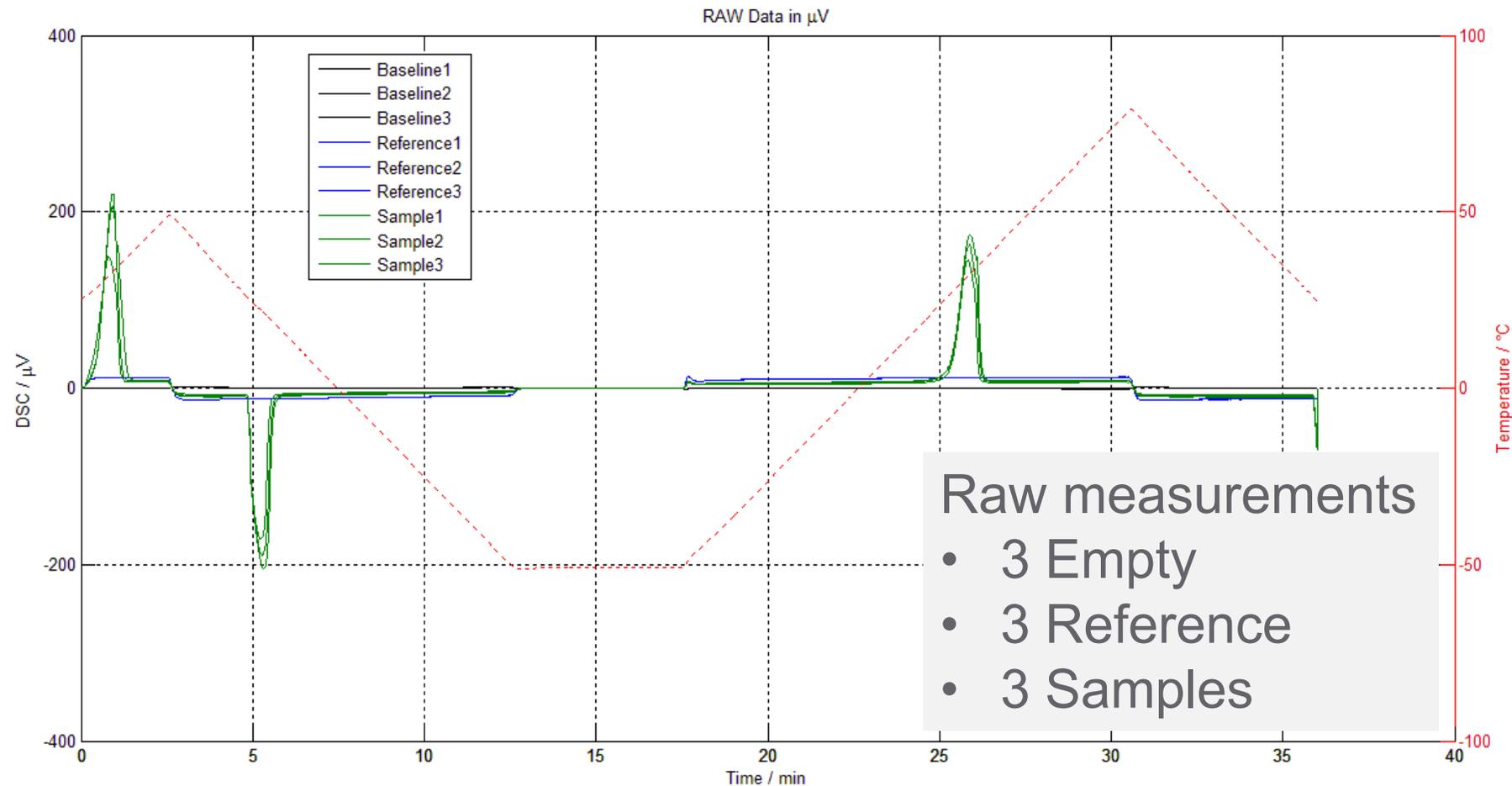
$c_p(T)$  PCM analysis with the hf-DSC

# Temperature and caloric calibration for $c_p(T)$ PCM measurements using a disc type hf-DSC @ AIT

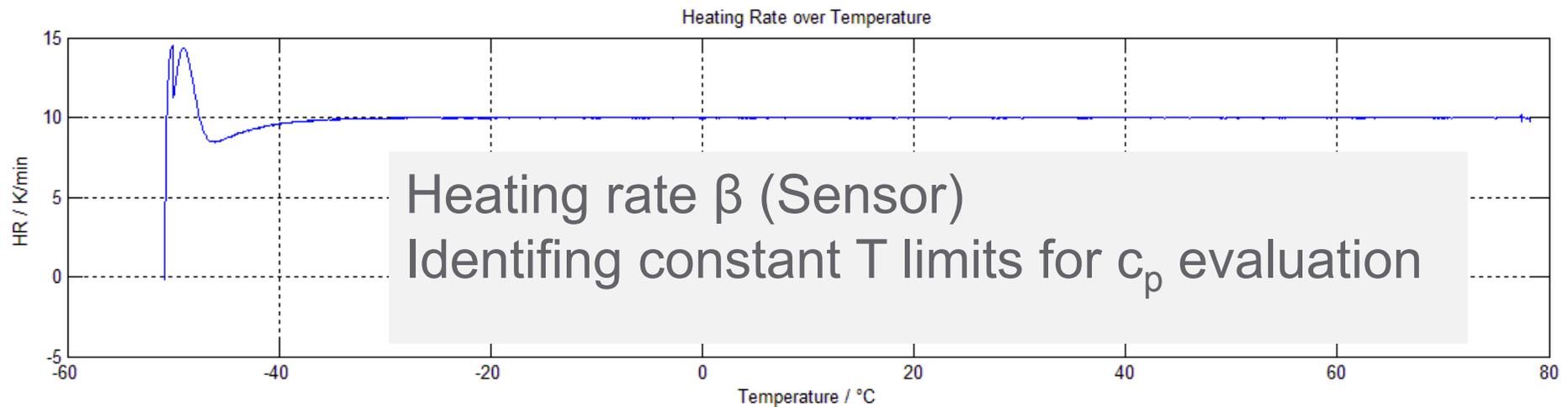
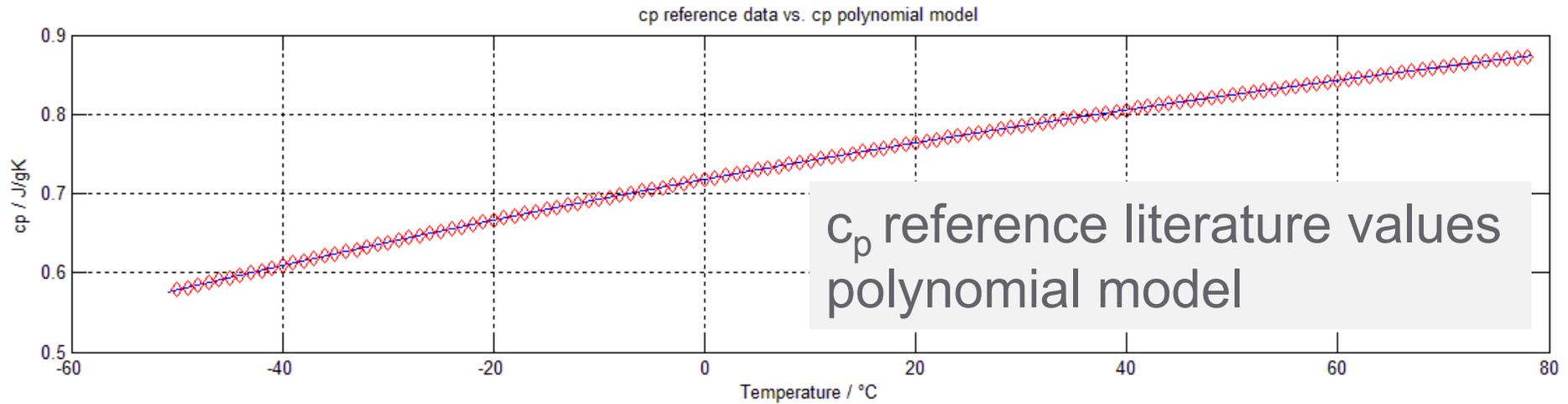
- Temperature calibration with used atmosphere, gas flow rate, crucible type and heating rate
  - Two melting cycles in Al crucibles with He (C10H16, In, Sn, Bi, Zn) and evaluation of the 2<sup>nd</sup> the melting onset according the standard.
- Caloric calibration
  - 3 empty runs and 3 sapphire standard measurements in Al crucibles with He for reproducibility check and uncertainty evaluation



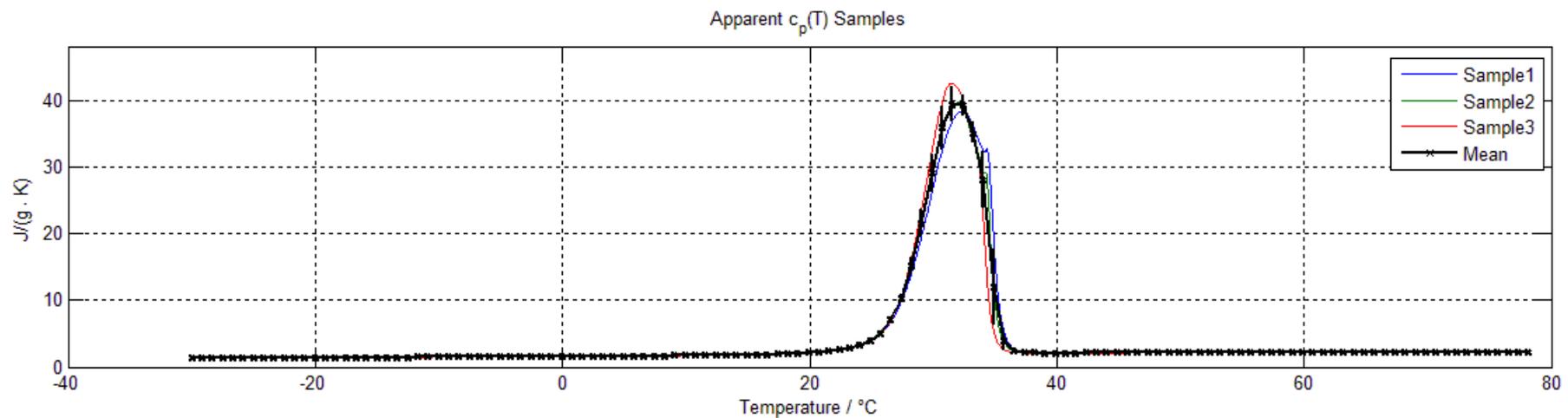
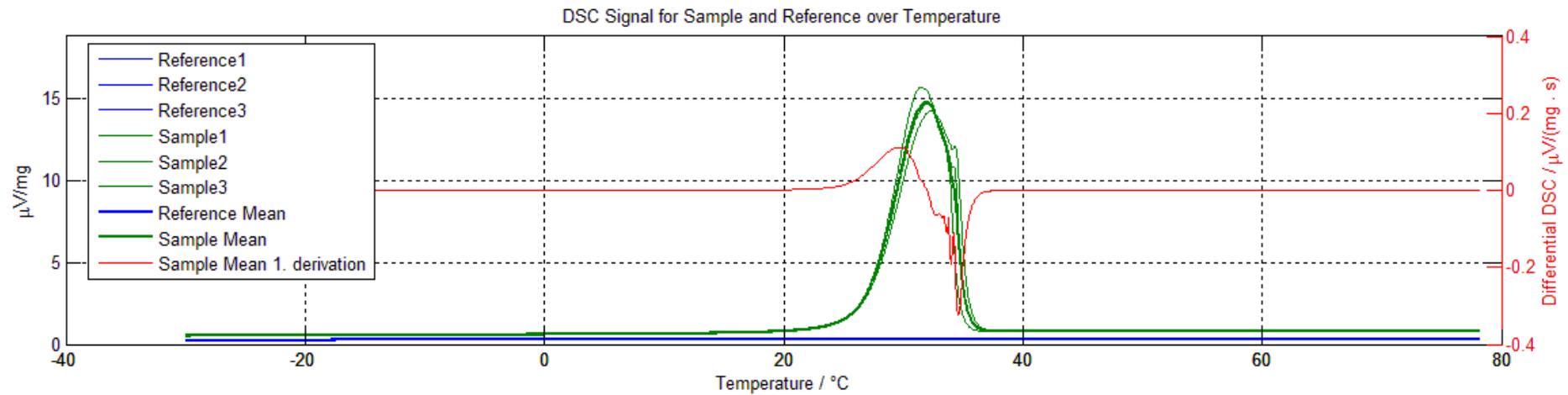
# $c_p(T)$ PCM measurements using a disc type hf-DSC @ AIT



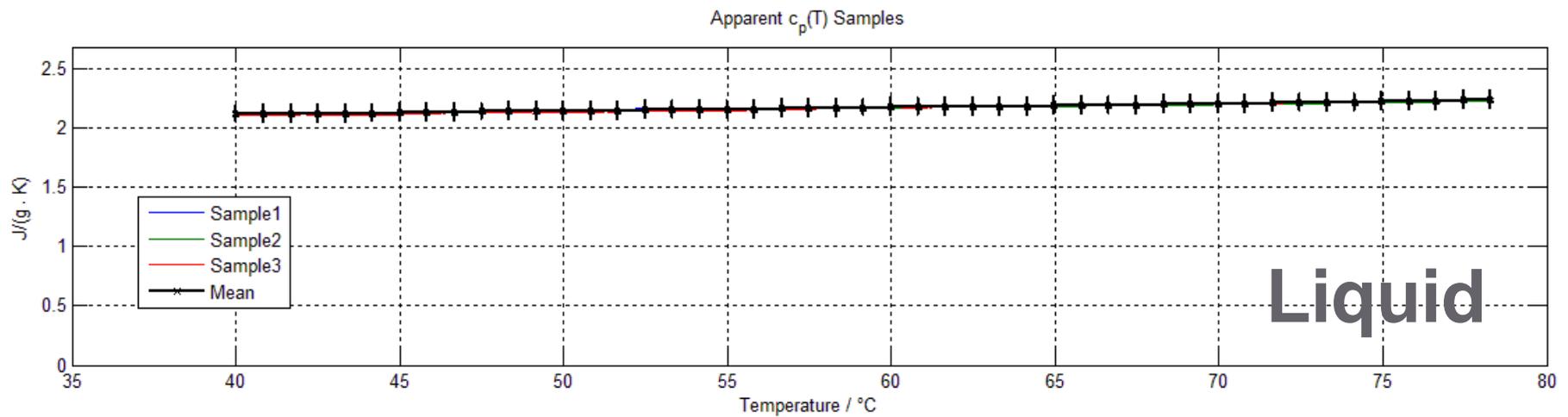
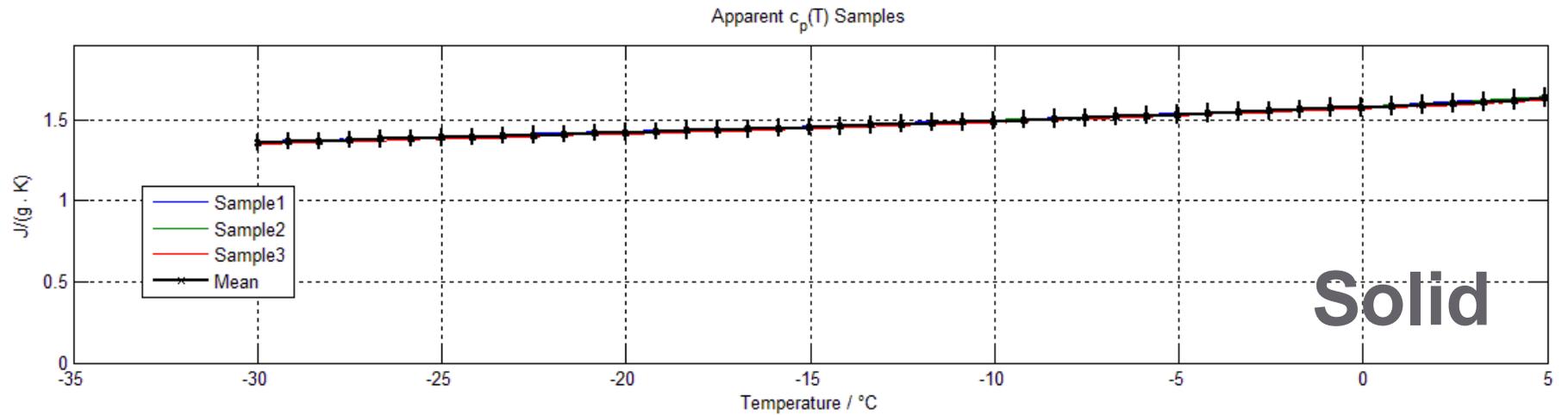
# $c_p(T)$ PCM measurements using a disc type hf-DSC @ AIT



# $c_p(T)$ PCM measurements using a disc type hf-DSC @ AIT



# $c_p(T)$ PCM measurements using a disc type hf-DSC @ AIT



# Uncertainty concept for $c_p(T)$ analysis out of DSC measurements

## Uncertainty Concept according ENV 13005

Y is a function of N different input variables  $X_i$   
 Input variable  $X_i$  has to be measured repeatedly

$$Y = f(X_1, X_2, \dots, X_i, \dots, X_n)$$

The best estimate of an input quantity  $X_i$  is the arithmetic mean  $q_i$  of a number of n individual measurement ( $q_{i,1}, q_{i,2}, \dots, q_{i,k}, \dots, q_{i,n}$ )

$$q_i = \frac{1}{n} \cdot \sum_{k=1}^n q_{i,k}$$

The best estimate of the uncertainty of an individual  $q_{i,k}$  is the standard deviation of the individual measurements  $s(q_{i,k})$

$$s(q_{i,k}) = \sqrt{\frac{1}{n-1} \cdot \sum_{k=1}^n (q_{i,k} - q_i)^2}$$

The uncertainty of the arithmetic mean of the full set of  $\{q_{i,k}\}$  is  $u(q_i)$

$$u(q_i) = \frac{1}{\sqrt{n}} \cdot s(q_{i,k}) := u(x_i)$$

The best output estimate y is calculated with using the best input estimates  $q_i$

$$y = f(q_1, q_2, \dots, q_i, \dots, q_N)$$

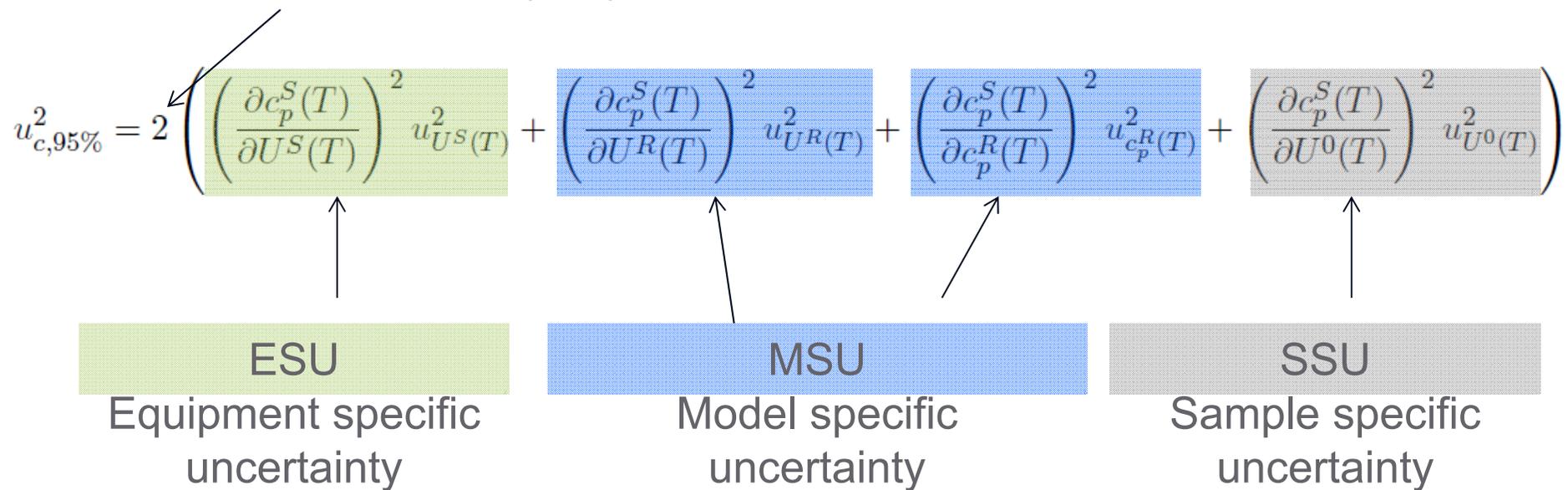
Finally the uncertainty of the output estimate  $u_c(y)$  is calculated  
 It is called “standard uncertainty of the output estimate” and is well known as the Gaussian Error Propagation Law

$$u_c^2(y) = \sum_{i=1}^N \left( \frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i)$$

# Uncertainty concept applied on DSC $c_p(T)$ measurements

$$c_p^S(T) = c_p^R(T) \cdot \frac{m^R}{m^S} \cdot \frac{U^S(T) - U^0(T)}{U^R(T) - U^0(T)}$$

Confidence interval 95% (k=2)

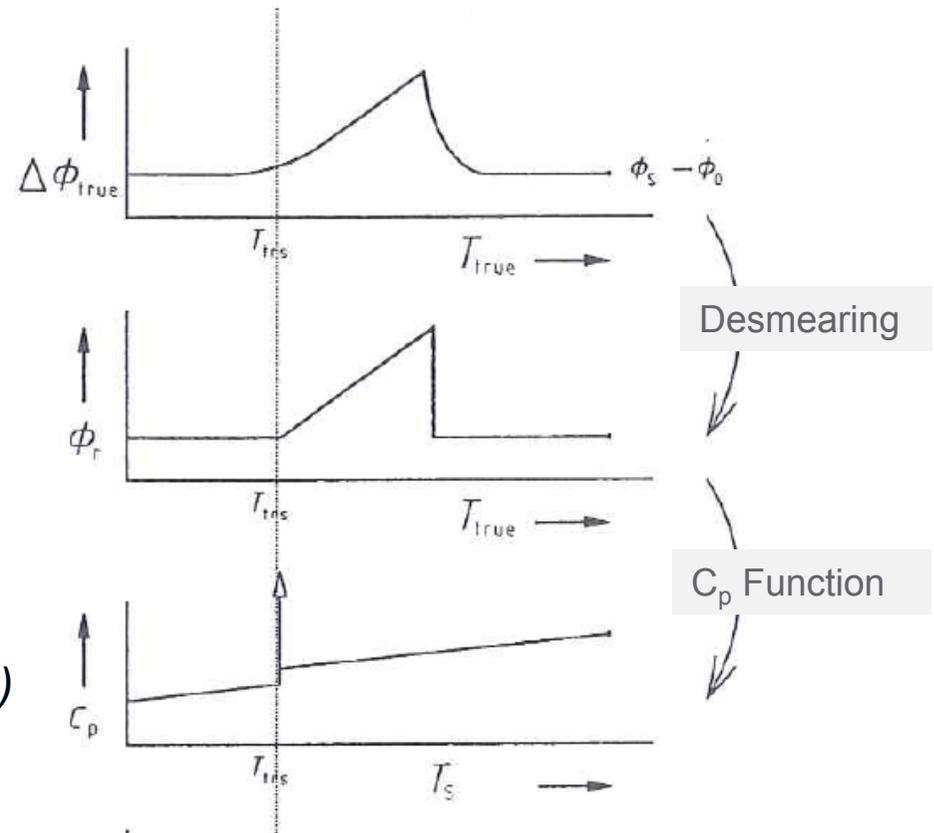


# Desmearing and peak baseline determination

# Desmearing

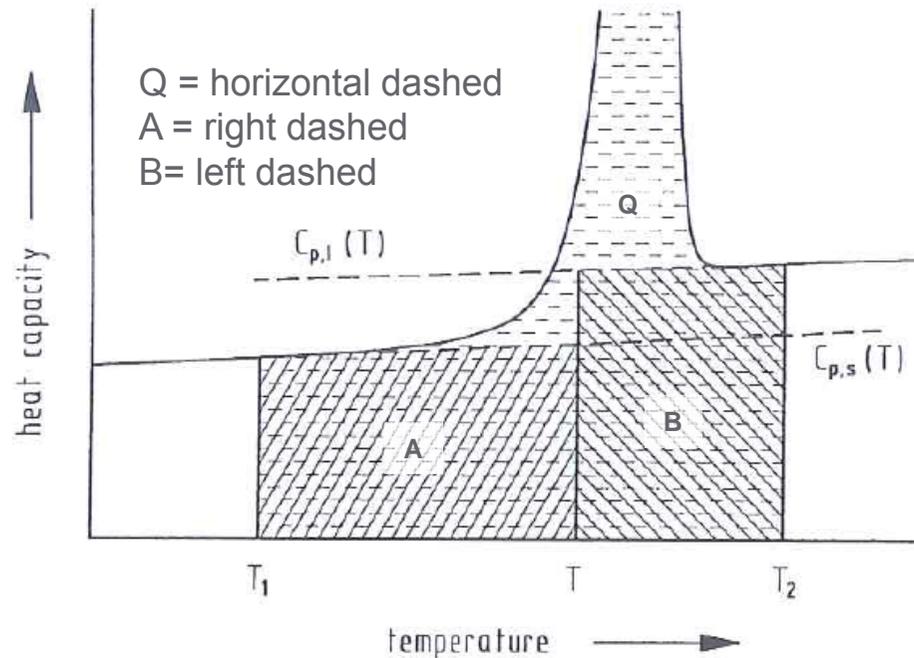
- Höhne et al: „ *The measured curve produced by the calorimeter is a function of time, or a temperature proportional to it, is, even in the form of a  $c_p$  curve, only a more or less „smeared“ representation of the function searched.*  
 .... *When accuracy requirements are higher, or kinetic evaluation must be performed, the measured curve (and the interpolated baseline) must be corrected and converted prior to their being used to determine the thermodynamic potential function ( $\Delta H$ ) of the sample or its derivative ( $C_p$ )”*

1st order endothermic phase transition



Pictures and text from: G.W.H. Höhne et al, "Differential Scanning Calorimetry", p 126-127, 2nd Edition, Springer

## Determination of latent heat connected with a peak area



- Höhne et al: „*The determination of thermodynamically valid values for the enthalpy for the enthalpies of transition (according to Richardson 1993). The limiting Temperatures  $T_1$  and  $T_2$  must be chosen well below or above the transition interval*”

$$\Delta H(T) = Q - A - B$$

Pictures and text from: G.W.H. Höhne et al, “Differential Scanning Calorimetry”, p 124-125, 2nd Edition, Springer

## DSC –measurement tips

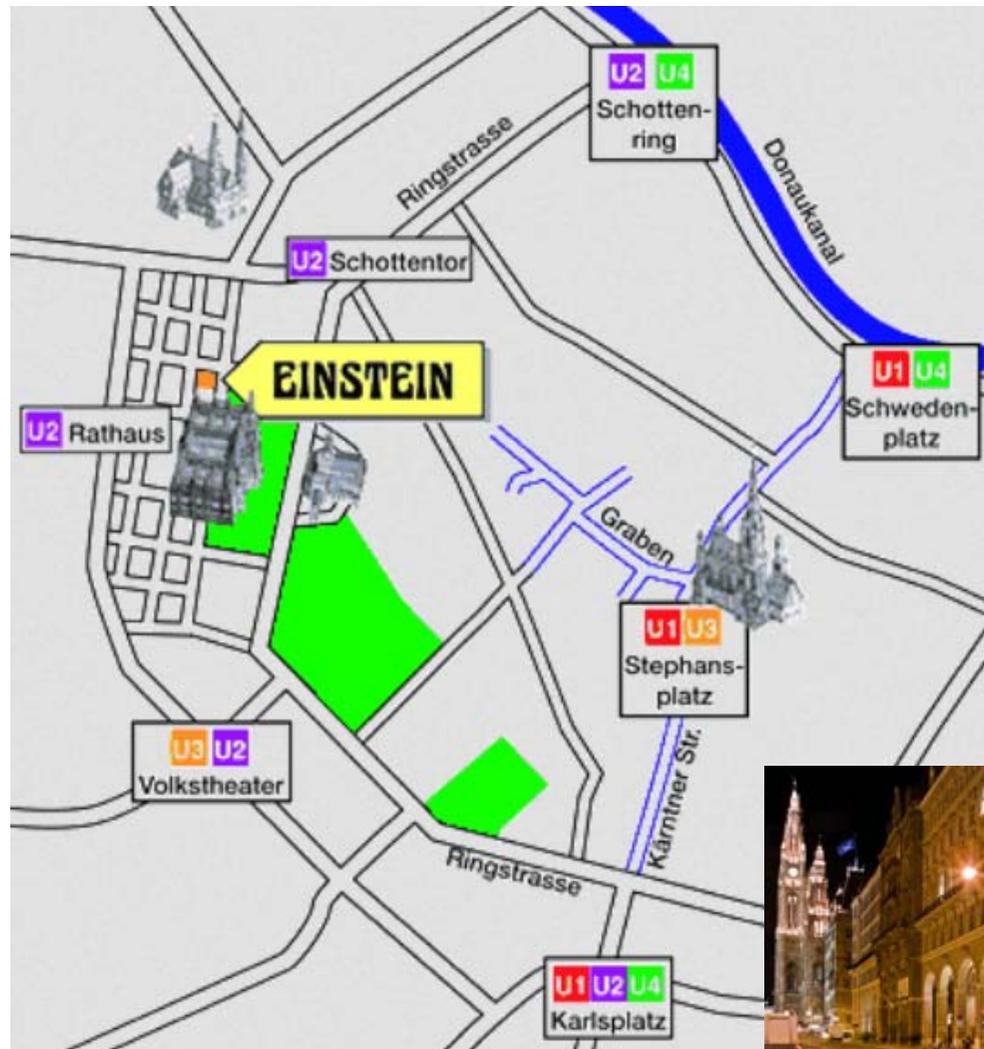
## Specific heat capacity $c_p(T)$ with DSC – tips (I)

- Atmosphere: changing sensitivity of the DSC sensor – Ar highest, He lowest sensitivity. For oxygen free measurements – evacuate and backfill several times, gas flow for a slight overpressure in the system – no backflow
- Crucibles: Pt, Graphite and Al show a higher sensitivity; Al<sub>2</sub>O<sub>3</sub> crucibles have a lower sensitivity and get translucent for radiation at higher temperatures
- Sample Form:
  - solids: Good contact to crucible needed, e.g. a disc with slightly smaller diameter as the crucible. Powder: pressing a disc using a forming tool
  - Liquids: capillary ascension upon contact with crucible wall – bad contact to crucible bottom – small amount with an injection in the middle
- Furnace: uniform temperature distribution – stable baseline. (e.g. Pt, Rh,...)
- DSC Sensor: Type E (NiCr-CuNi) show higher sensitivity below 600°C, Type S (Pt10Rh-Pt) at higher temperatures.

## Specific heat capacity $c_p(T)$ with DSC – tips (II)

- Heating Rate: Fast heating rates lead to higher signal gain per time. Signal to noise ratio increases with slow heating rates.
- Empty measurements: Several measurements with empty crucible should be done to identify the system drift

## Now the really important things...



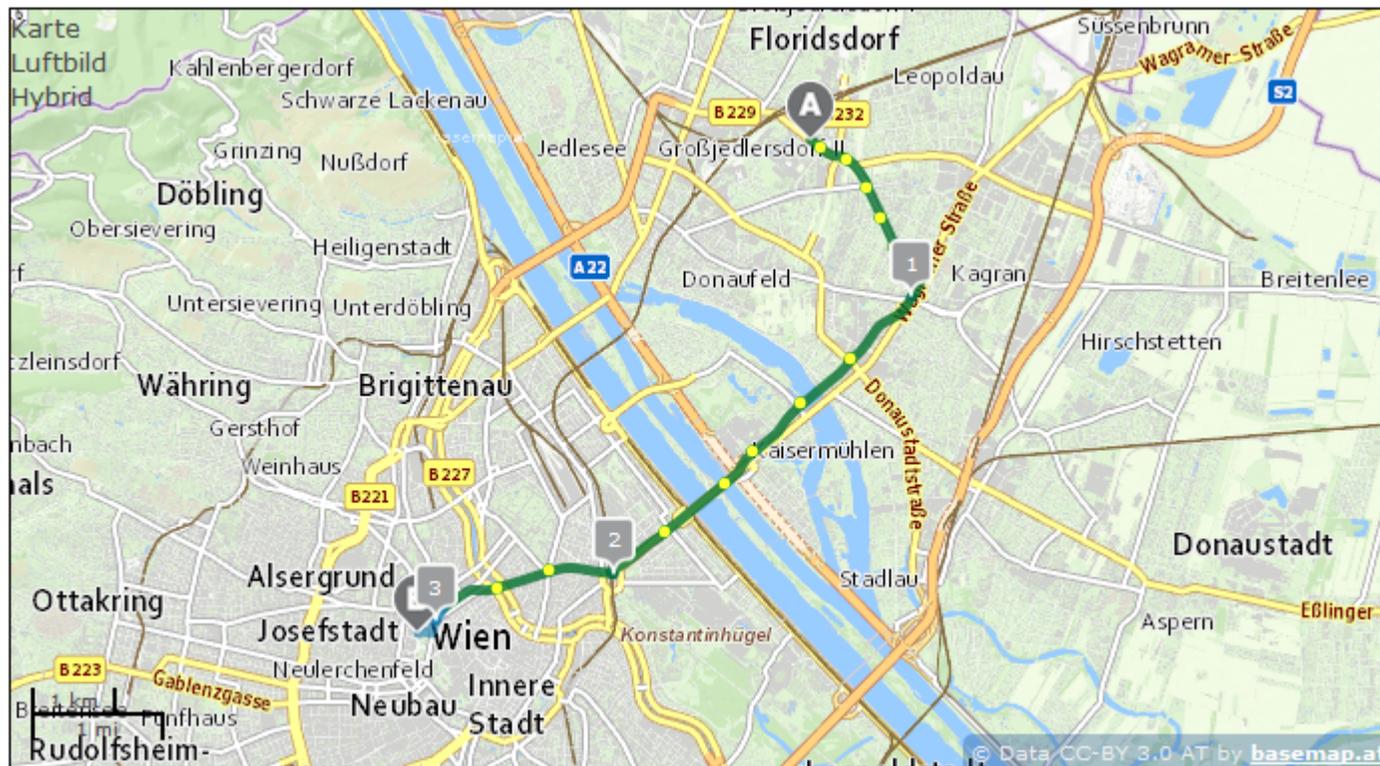
- Dinner: Cafe Einstein,  
Rathausplatz 4, 1010 Wien  
Mo. 4. April, 19:30
- Next to the city hall
- „À la carte“
- € 35,- per participant is already included in workshop fee  
Cost > € 35,- at one's own expenses
- Enjoy a walk through the city center



# Map from AIT to Café Einstein

With Bus 31 A – Subway U1 and Subway U2

Autobus 31A Direction „Wien Kagraner Platz“ – Station „Wien Kagraner Platz“  
 Subway U1 Direction „Wien Reumannplatz“ – Station „Wien Praterstern“  
 Subway U2 Direction „Wien Karlsplatz“ – Station „Rathaus“







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your ingenious partner

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