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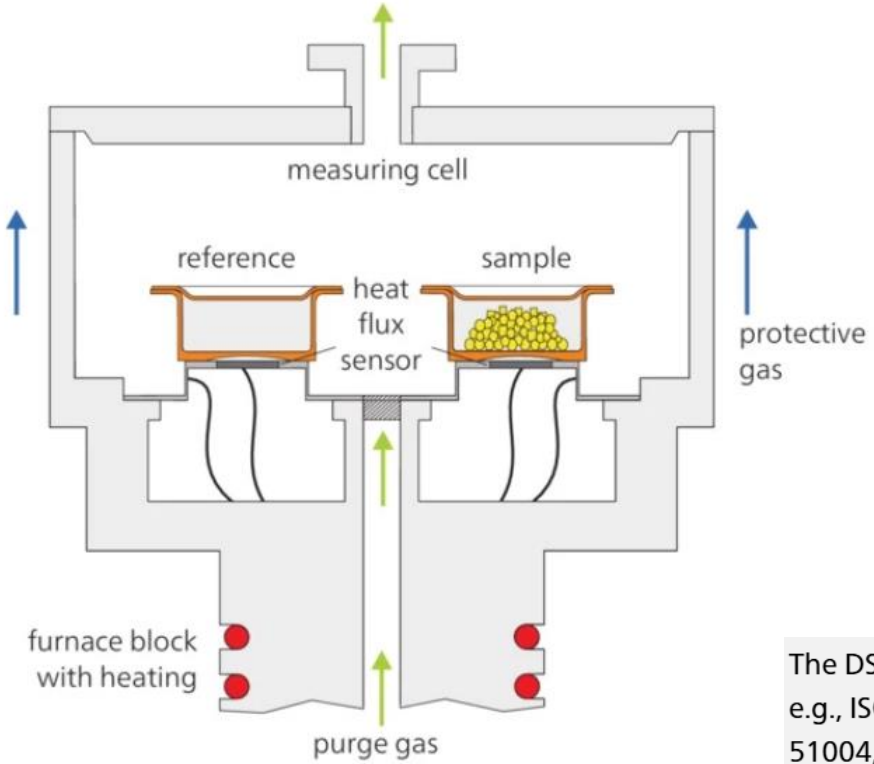
DSC Innovations:
C_p Directly from the Heat Flow
2DTemperatureCalibration

AKTP Conference 2025 (Berlin), Dr. Alexander Schindler, 08.04.2025

1. C_p Directly from the DSC Heat Flow
2. *2DTemperatureCalibration*
3. *Melting Enthalpies at various sample masses, heating- and cooling rates*

DSC (Differential Scanning Calorimetry): Principle



ISO 11357-1:2023(E): technique in which the **difference between the rate of flow of heat** into a specimen crucible containing the specimen and that into a reference crucible is derived as a function of temperature and/or time while the specimen and reference are subjected to the same controlled temperature program in a specified atmosphere using a symmetrical measurement system

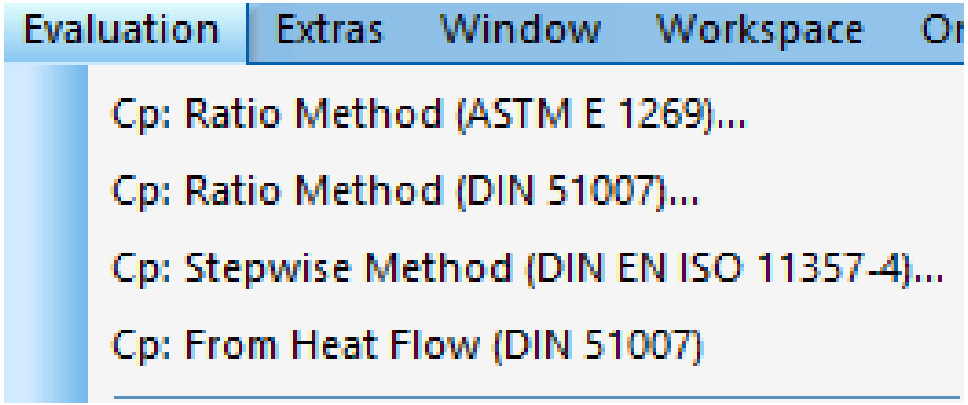
DSC [µV/mg] = Sens. [µV/mW] · Δc_p [J/(g·K)] · β [K/s]

The DSC systems are based on relevant instrument and application standards, e.g., ISO 11357, ASTM E793, ASTM D3895, ASTM D3417, ASTM D3418, DIN 51004, DIN 51007.

C_p Directly from the DSC Heat Flow

Specific Heat Capacity From DSC Signals

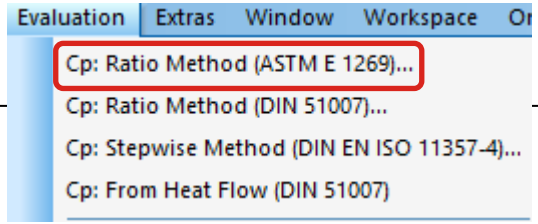
*All possibilities** for DSC (for DSC 300 from *Proteus*® 9.3., for STA 509 from 9.4)

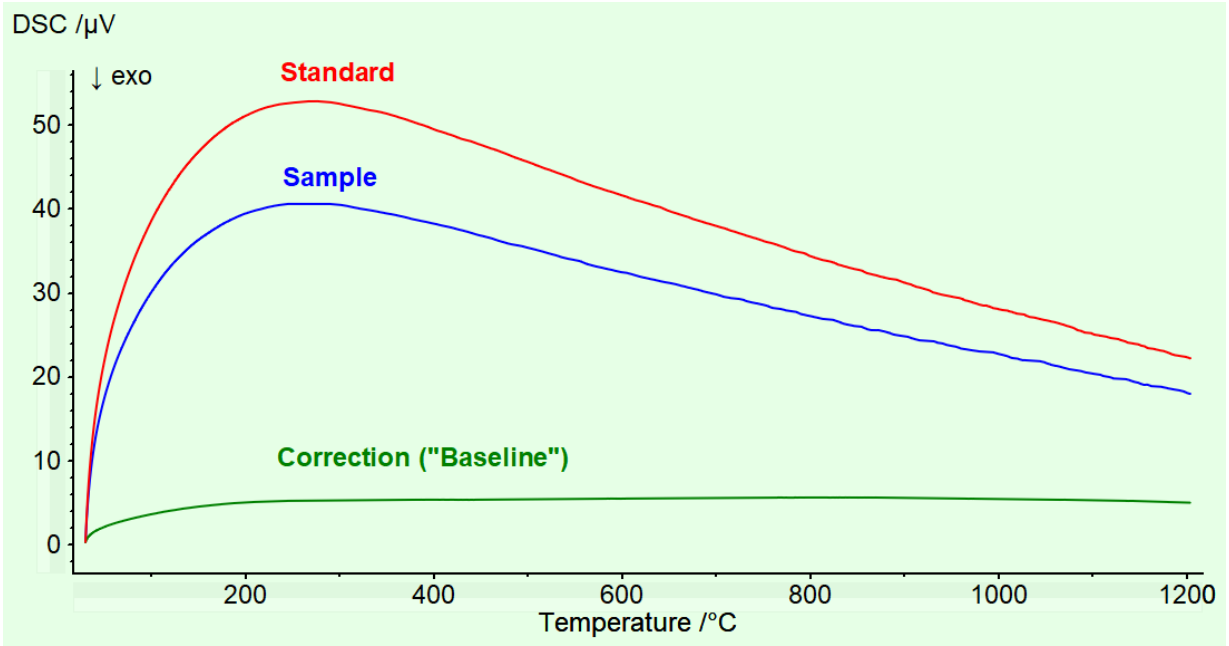


* c_p can also be evaluated from TM-DSC data (out of the scope of this lecture).

Specific Heat Capacity From DSC Signals

ASTM E 1269 (“Ratio Method”)



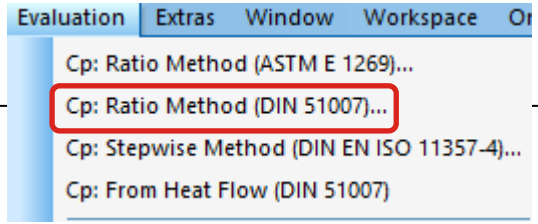


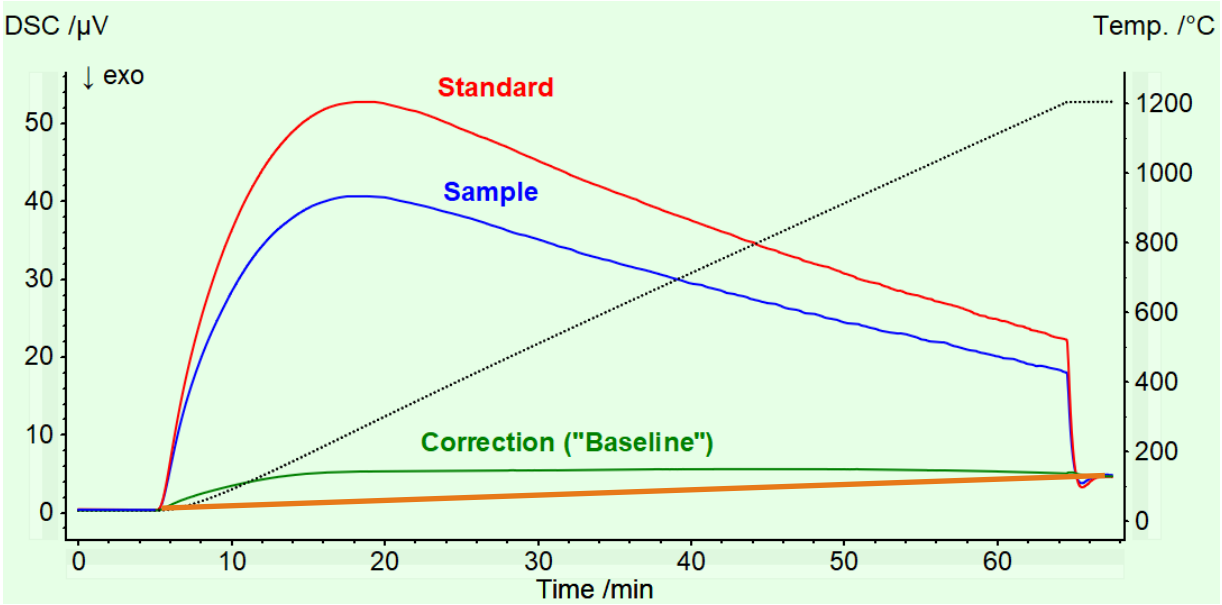
$$c_p^s = c_p^{st} \cdot \frac{m_{st}}{m_s} \cdot \frac{DSC_s - DSC_{bl}}{DSC_{st} - DSC_{bl}}$$

* The DSC signals shown were measured at 20 K/min.

Specific Heat Capacity From DSC Signals

DIN 51007 (“Improved Ratio Method”)



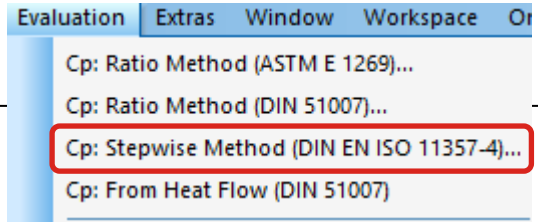


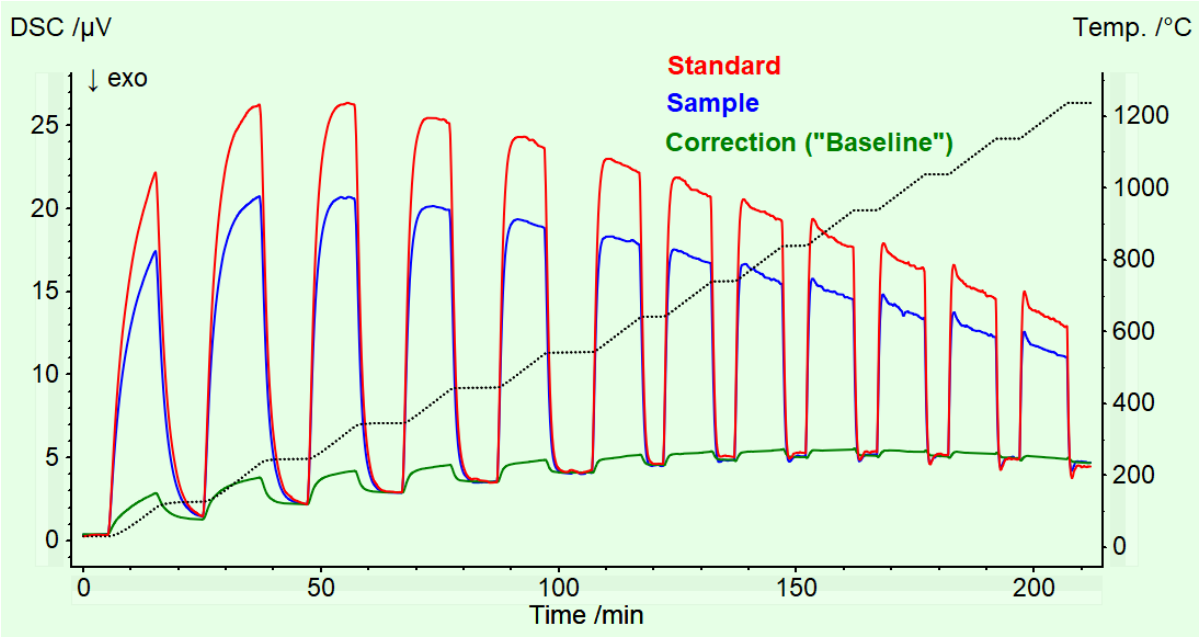
$$c_p^s = c_p^{st} \cdot \frac{m_{st}}{m_s} \cdot \frac{DSC_s - DSC_{bl}}{DSC_{st} - DSC_{bl}}$$

*** All DSC signals are corrected with respect to the interpolated isothermal baselines.**

Specific Heat Capacity From DSC Signals

DIN 11357-4 (“Stepwise Method”)





$$c_p^s = c_p^{st} \cdot \frac{m_{st}}{m_s} \cdot \frac{\Delta Q_s - \Delta Q_{bl}}{\Delta Q_{st} - \Delta Q_{bl}}$$

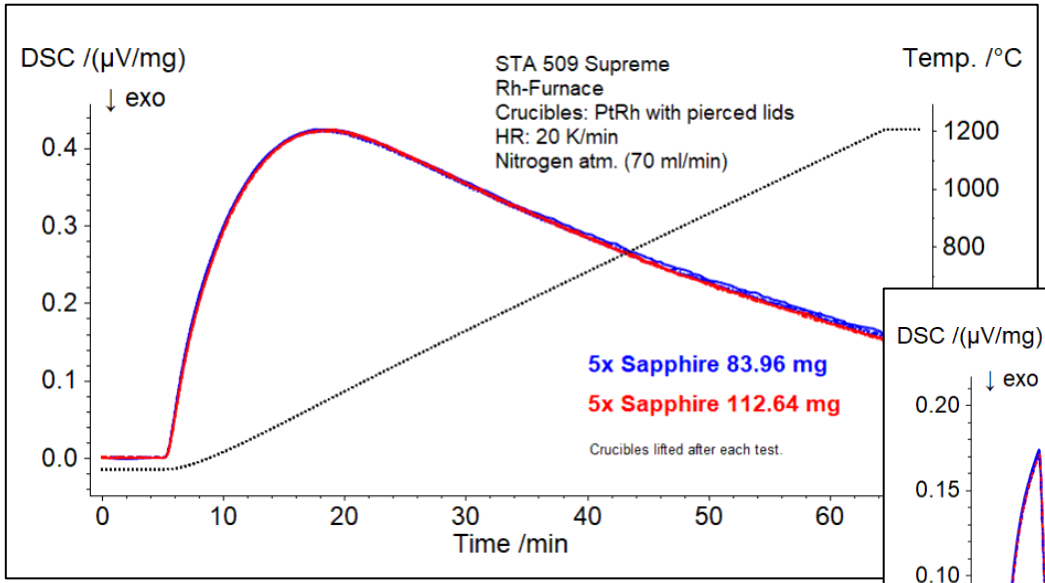
$$\Delta Q_i = \int DSC_i$$

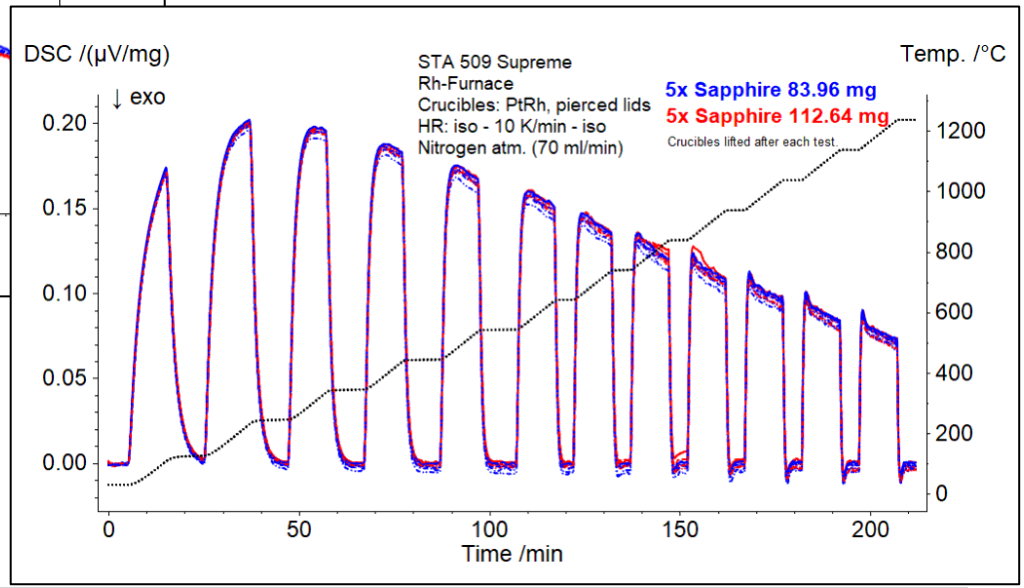
Integrals are used, therefore this method reveals some „averaged“ c_p points. This method is thus not suitable when phase transitions occur. And the change of $c_p(T)$ should be linear.

This method is comparatively slow – but very accurate (see below).

Specific Heat Capacity From DSC Signals

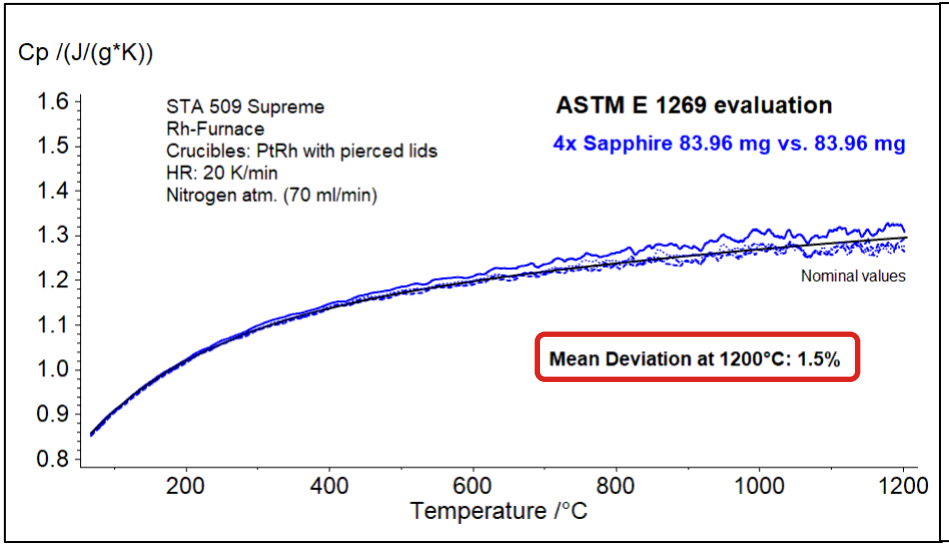
Some measurement data on sapphire using STA 509 Supreme, Rh furnace

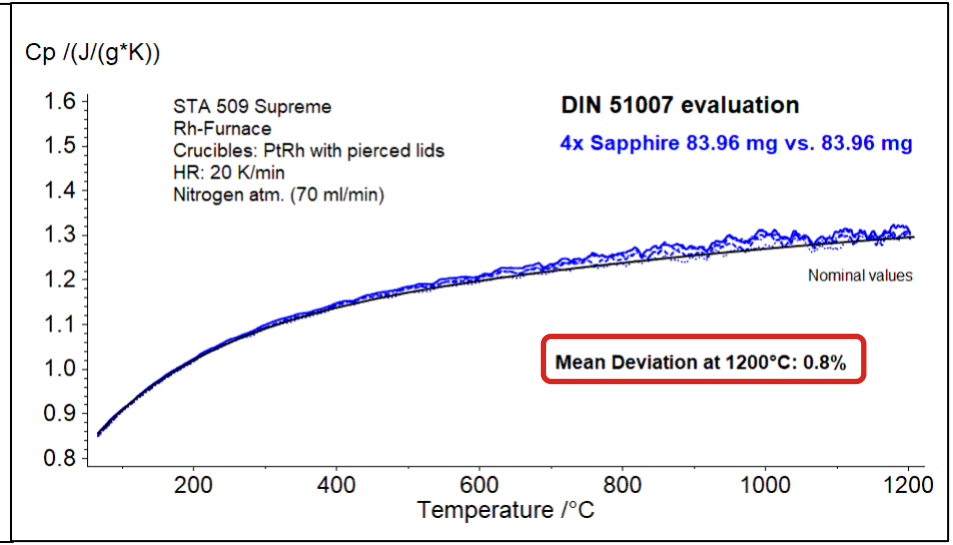




Specific Heat Capacity From DSC Signals

Showcase Results: ASTM E 1269 vs. DIN 51007

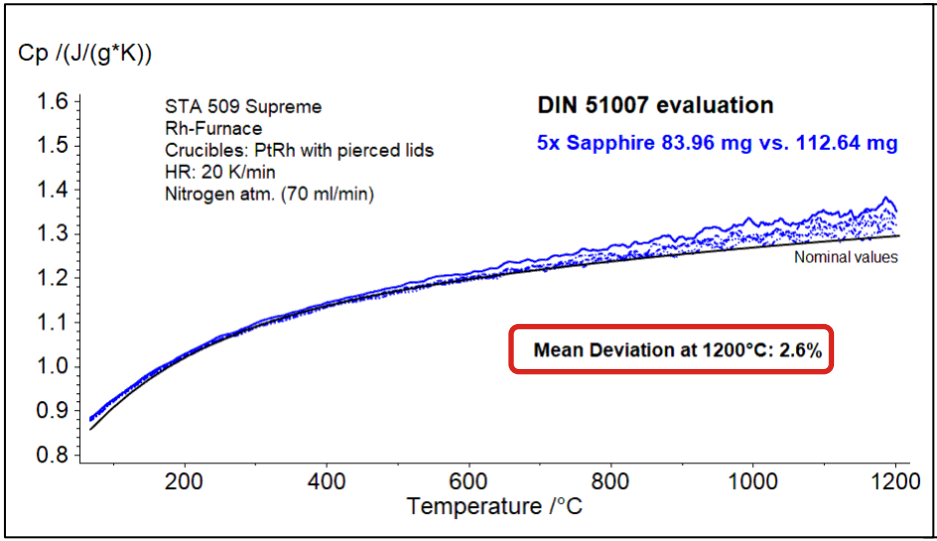


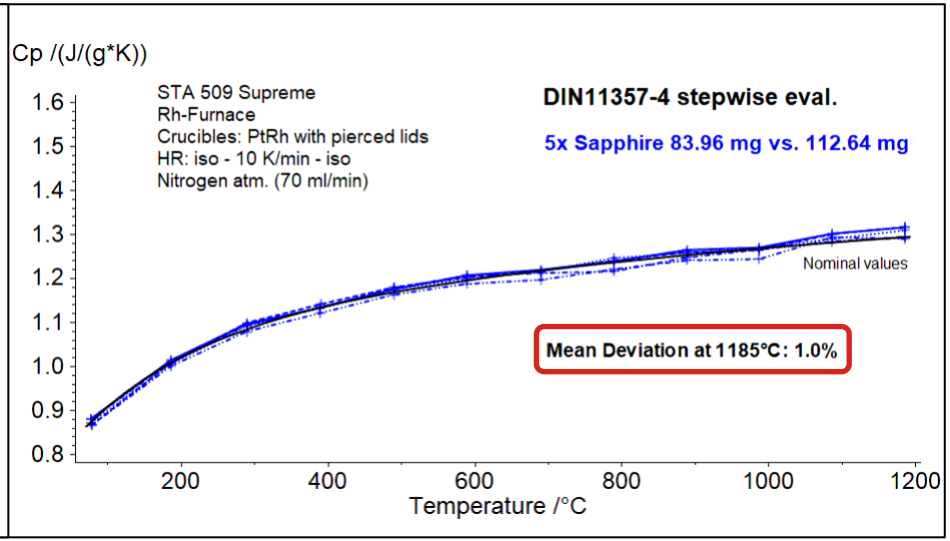


→ DIN 51007 is superior. Use it !

Specific Heat Capacity From DSC Signals

Showcase Results: DIN 51007 vs. DIN EN ISO 11357-4 (stepwise)

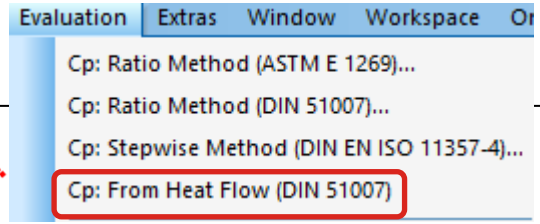




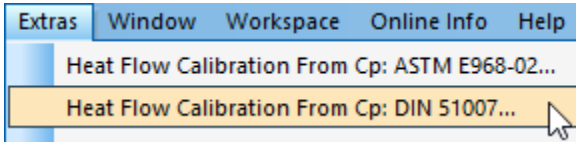
→ DIN 11357-4 gives higher accuracy at high temperatures. Use it - where it makes sense!

Specific Heat Capacity From DSC Signals

DIN 51007 ("**Cp Directly from the DSC Heat Flow**")



1. Create the c_p suitable heat flow calibration *once*:



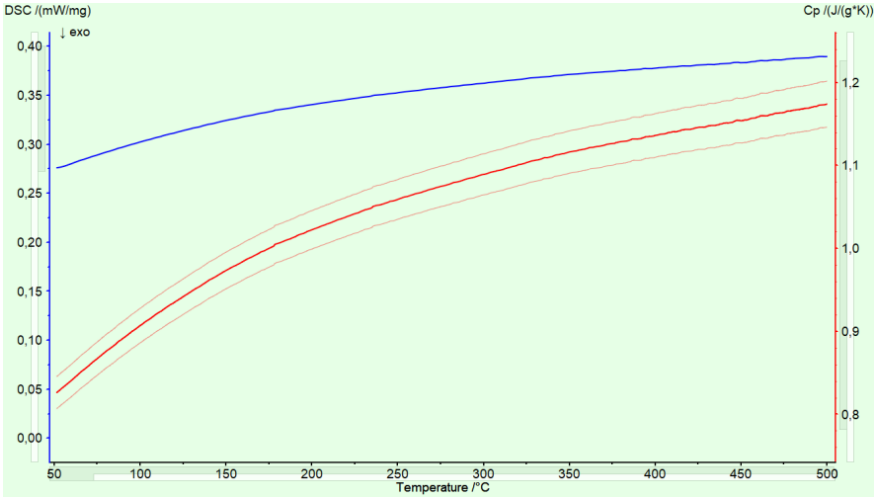
$$Sens.(T) = \frac{DSC^{*}_{st}(T)}{c_p^{st}(T) \cdot \beta}$$

*** Baseline corrected and corrected with respect to the interpolated isothermal baseline.**

2. Apply it for various DSC measurements and get c_p *directly*:

$$c_p^{s}(T) = \frac{DSC^{*}_{s}(T)}{Sens.(T) \cdot \beta} = \frac{DSC_S(T)}{\beta}$$

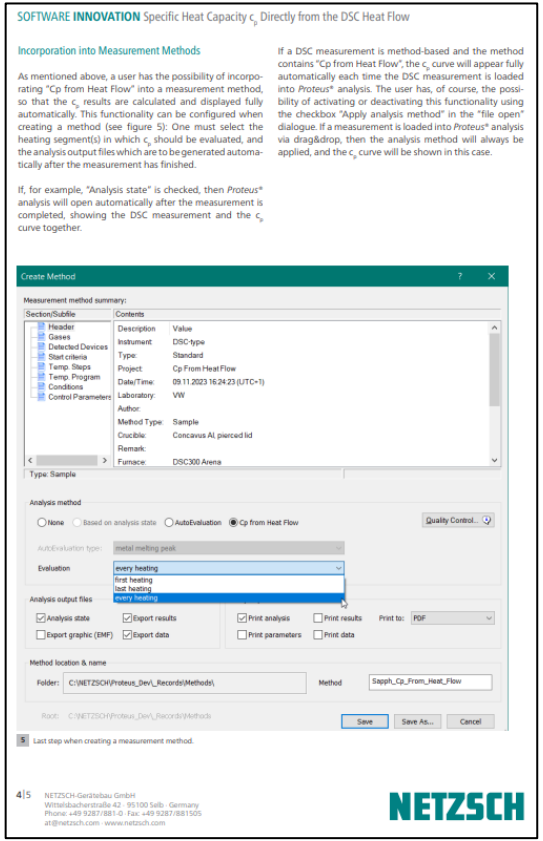
3. **c_p will always be created automatically** (even several segments at once) when incorporated into a method, or after pressing „Cp: From Heat Flow".



Specific Heat Capacity From DSC Signals

DIN 51007 ("**Cp Directly from the DSC Heat Flow**") – Software Innovations - NETZSCH Analyzing & Testing:

- c_p directly from the heat flow is a **fast** and **flexible** alternative to the manual c_p evaluations since it is **generated automatically** and baselines and heating rates do not need necessarily be the same for standard and sample.



SOFTWARE **INNOVATION** Specific Heat Capacity c_p Directly from the DSC Heat Flow

Incorporation into Measurement Methods

As mentioned above, a user has the possibility of incorporating "Cp from Heat Flow" into a measurement method, so that the c_p results are calculated and displayed fully automatically. This functionality can be configured when creating a method (see figure 5): One must select the heating segment(s) in which c_p should be evaluated, and the analysis output files which are to be generated automatically after the measurement has finished.

If, for example, "Analysis state" is checked, then *Proteus*® analysis will open automatically after the measurement is completed, showing the DSC measurement and the c_p curve together.

If a DSC measurement is method-based and the method contains "Cp from Heat Flow", the c_p curve will appear fully automatically each time the DSC measurement is loaded into *Proteus*® analysis. The user has, of course, the possibility of activating or deactivating this functionality using the checkbox "Apply analysis method" in the "file open" dialogue. If a measurement is loaded into *Proteus*® analysis via drag&drop, then the analysis method will always be applied, and the c_p curve will be shown in this case.

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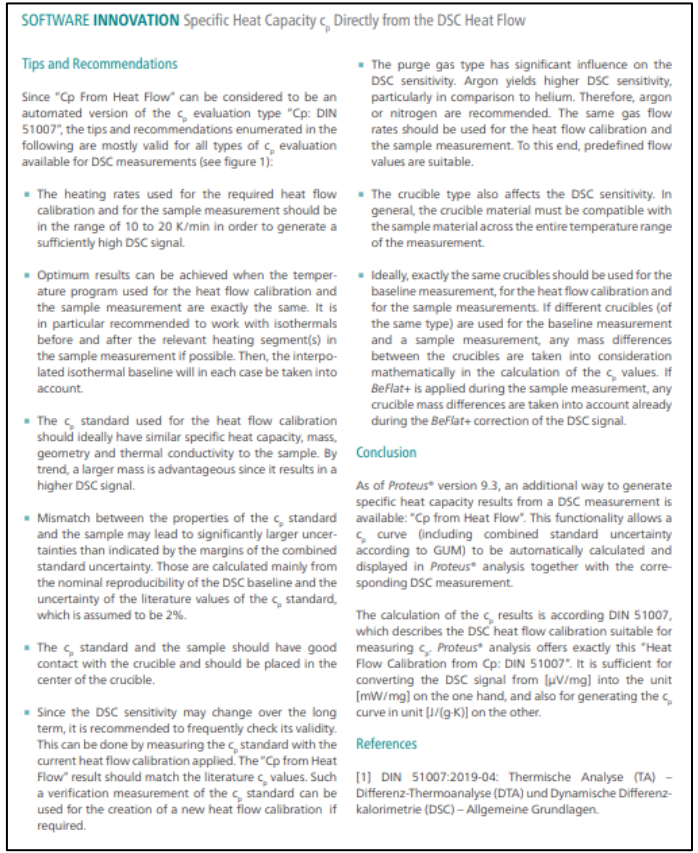


SOFTWARE **INNOVATION** Specific Heat Capacity c_p Directly from the DSC Heat Flow

Tips and Recommendations

Since "Cp From Heat Flow" can be considered to be an automated version of the c_p evaluation type "Cp: DIN 51007", the tips and recommendations enumerated in the following are mostly valid for all types of c_p evaluation available for DSC measurements (see figure 1):

- The heating rates used for the required heat flow calibration and for the sample measurement should be in the range of 10 to 20 K/min in order to generate a sufficiently high DSC signal.
- Optimum results can be achieved when the temperature program used for the heat flow calibration and the sample measurement are exactly the same. It is in particular recommended to work with isothermals before and after the relevant heating segment(s) in the sample measurement if possible. Then, the interpolated isothermal baseline will in each case be taken into account.
- The c_p standard used for the heat flow calibration should ideally have similar specific heat capacity, mass, geometry and thermal conductivity to the sample. By trend, a larger mass is advantageous since it results in a higher DSC signal.
- Mismatch between the properties of the c_p standard and the sample may lead to significantly larger uncertainties than indicated by the margins of the combined standard uncertainty. Those are calculated mainly from the nominal reproducibility of the DSC baseline and the uncertainty of the literature values of the c_p standard, which is assumed to be 2%.
- The c_p standard and the sample should have good contact with the crucible and should be placed in the center of the crucible.
- Since the DSC sensitivity may change over the long term, it is recommended to frequently check its validity. This can be done by measuring the c_p standard with the current heat flow calibration applied. The "Cp from Heat Flow" result should match the literature c_p values. Such a verification measurement of the c_p standard can be used for the creation of a new heat flow calibration if required.
- The purge gas type has significant influence on the DSC sensitivity. Argon yields higher DSC sensitivity, particularly in comparison to helium. Therefore, argon or nitrogen are recommended. The same gas flow rates should be used for the heat flow calibration and the sample measurement. To this end, predefined flow values are suitable.
- The crucible type also affects the DSC sensitivity. In general, the crucible material must be compatible with the sample material across the entire temperature range of the measurement.
- Ideally, exactly the same crucibles should be used for the baseline measurement, for the heat flow calibration and for the sample measurements. If different crucibles (of the same type) are used for the baseline measurement and a sample measurement, any mass differences between the crucibles are taken into consideration mathematically in the calculation of the c_p values. If *BeFlat+* is applied during the sample measurement, any crucible mass differences are taken into account already during the *BeFlat+* correction of the DSC signal.

Conclusion

As of *Proteus*® version 9.3, an additional way to generate specific heat capacity results from a DSC measurement is available: "Cp from Heat Flow". This functionality allows a c_p curve (including combined standard uncertainty according to GUM) to be automatically calculated and displayed in *Proteus*® analysis together with the corresponding DSC measurement.

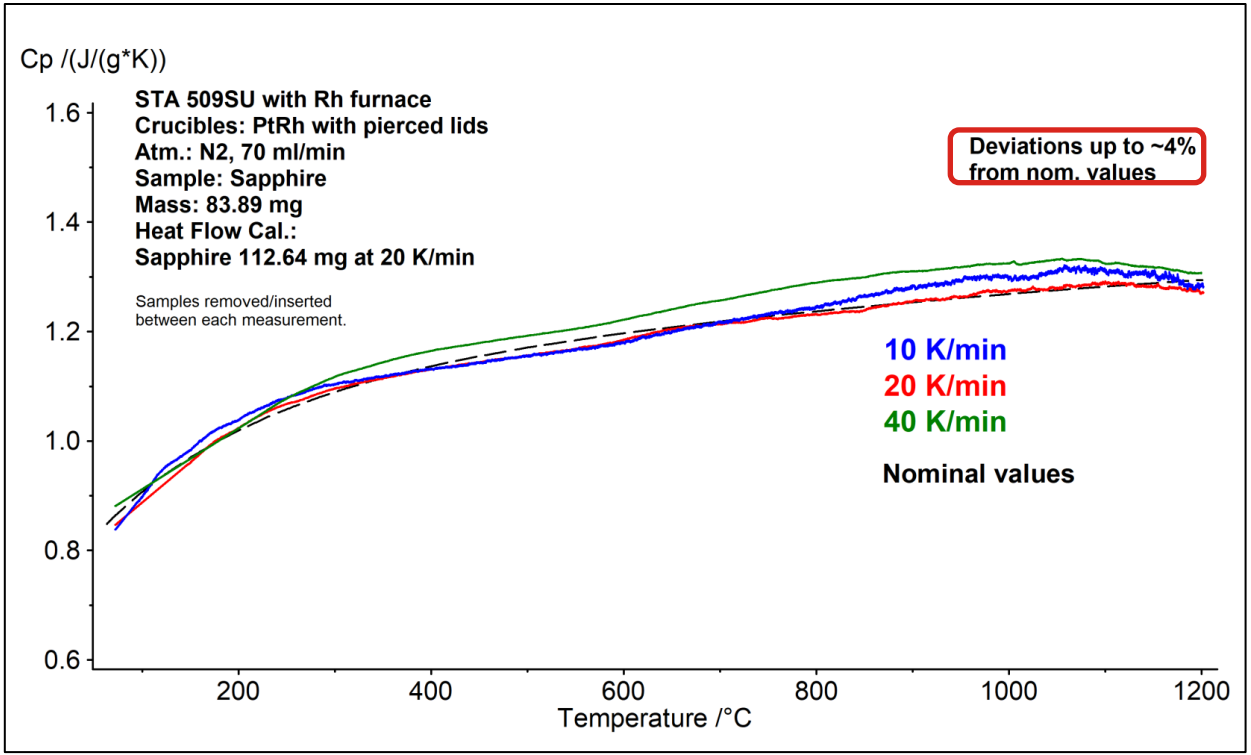
The calculation of the c_p results is according DIN 51007, which describes the DSC heat flow calibration suitable for measuring c_p. *Proteus*® analysis offers exactly this "Heat Flow Calibration from Cp: DIN 51007". It is sufficient for converting the DSC signal from [µV/mg] into the unit [mW/mg] on the one hand, and also for generating the c_p curve in unit [J/(g·K)] on the other.

References

[1] DIN 51007:2019-04: Thermische Analyse (TA) – Differenz-Thermoanalyse (DTA) und Dynamische Differenz-kalorimetrie (DSC) – Allgemeine Grundlagen.

Specific Heat Capacity From DSC Signals

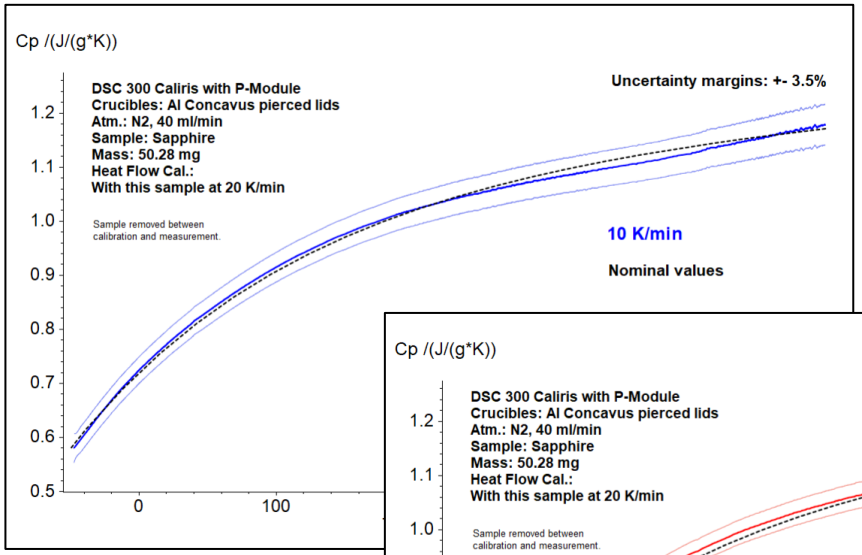
DIN 51007 ("Cp Directly from the DSC Heat Flow") – Accuracy: STA 509

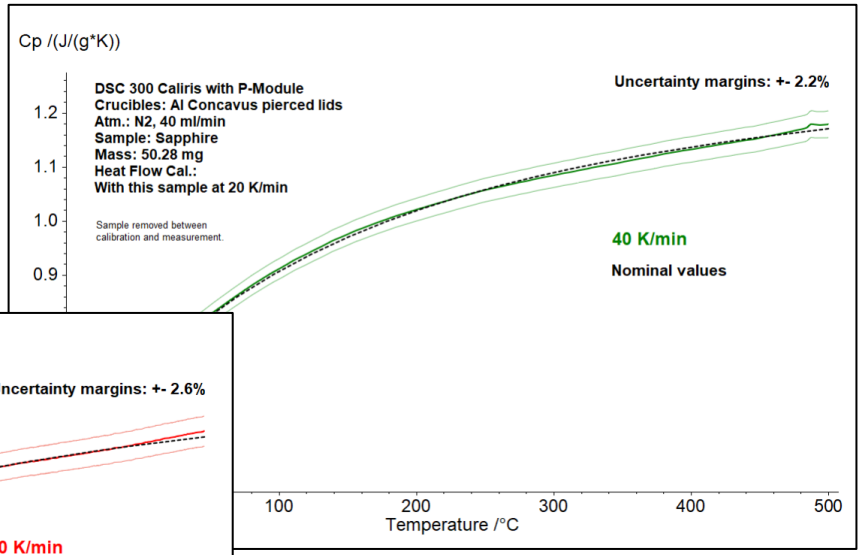


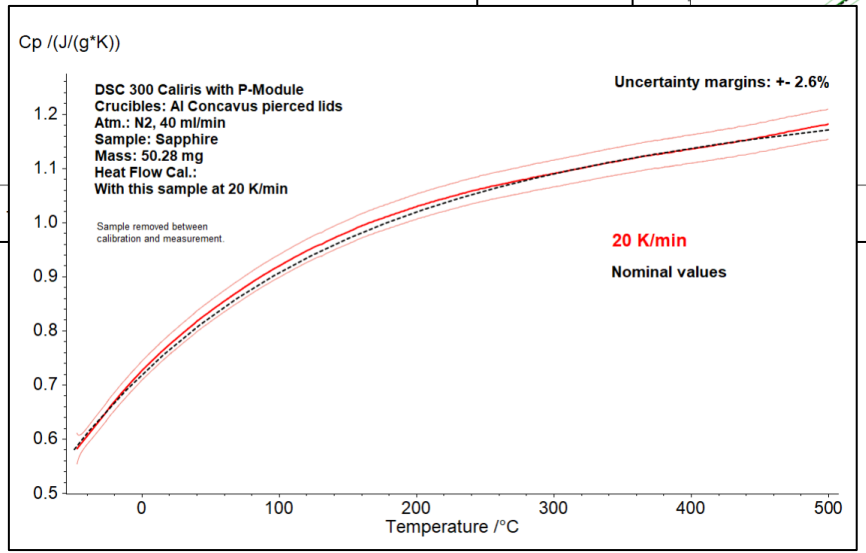
- At heating rate of h.f. calibration, ~ comparable to manual c_p evaluation.
- At different heating rates (!), the accuracy is reduced.

Specific Heat Capacity From DSC Signals

DIN 51007 (“Cp Directly from the DSC Heat Flow”) – Accuracy: DSC 300



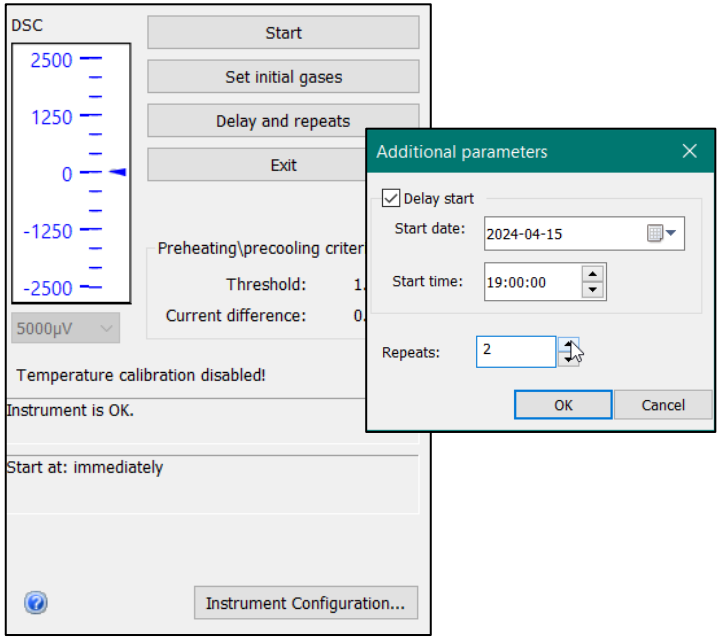




- Good accuracy at various heating rates!
- Combined Standard Uncertainty (GUM) available!

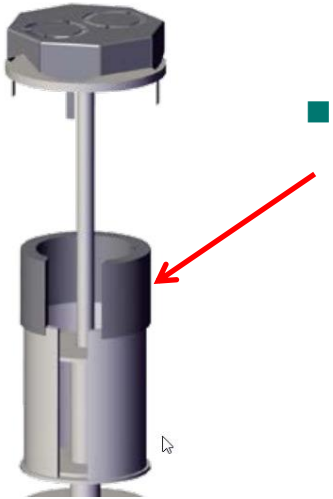
Specific Heat Capacity From DSC Signals

Some Goodies (software and hardware)



- Delayed start date/time.
- **Automatic Repeat Measurements** with generic file names (~01, ~02, …)

- **Alumina washers** (NGB811071) prevent sticking of crucibles at high temperatures. **For better reproducibility!**

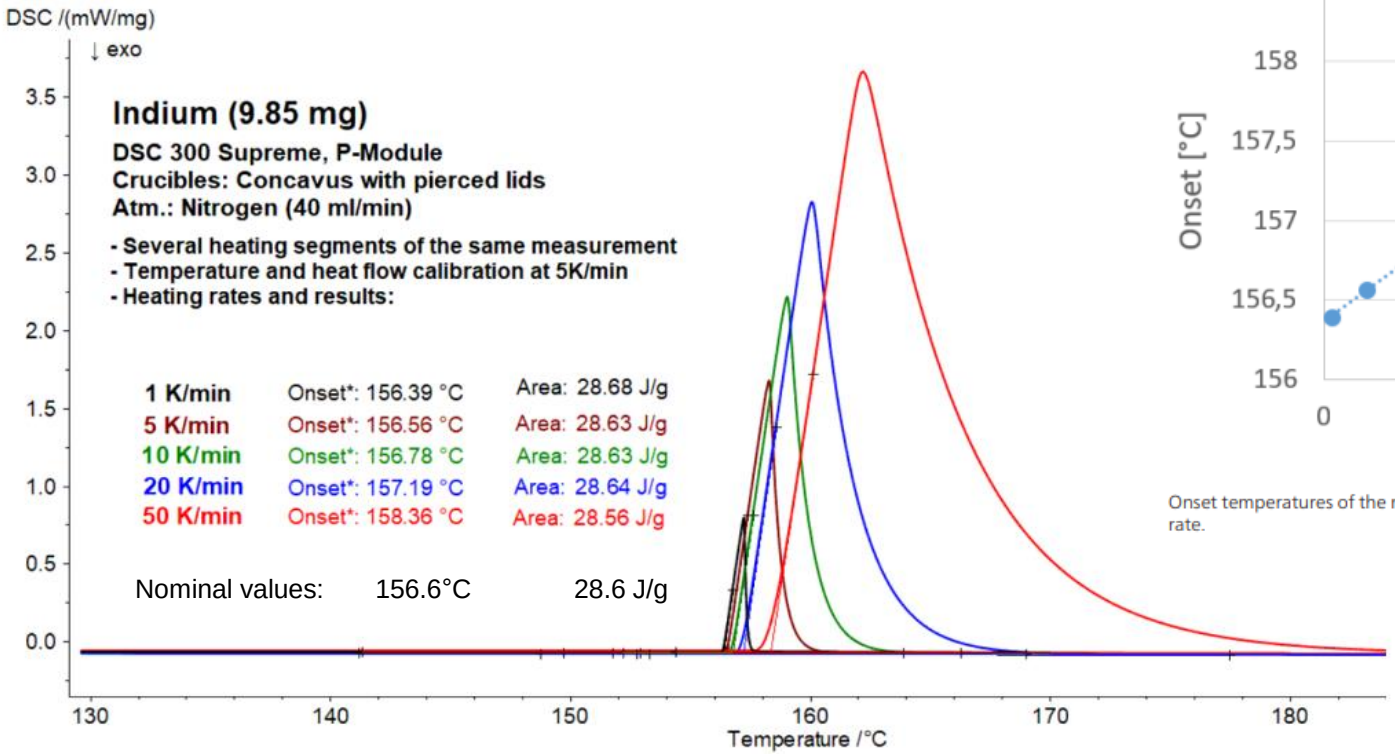


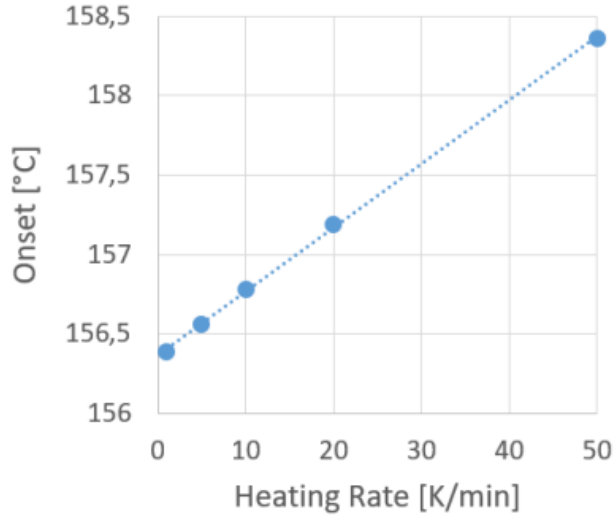
- ***OTS***® (HTP40000A97.010-00) **Oxygen Trap System** Eliminates oxidation of metallic samples. **For correct c_p results !**

2DTemperatureCalibration

Thermal Lag of the DSC Signal

At higher heating rate, the DSC peaks shift to higher temperatures

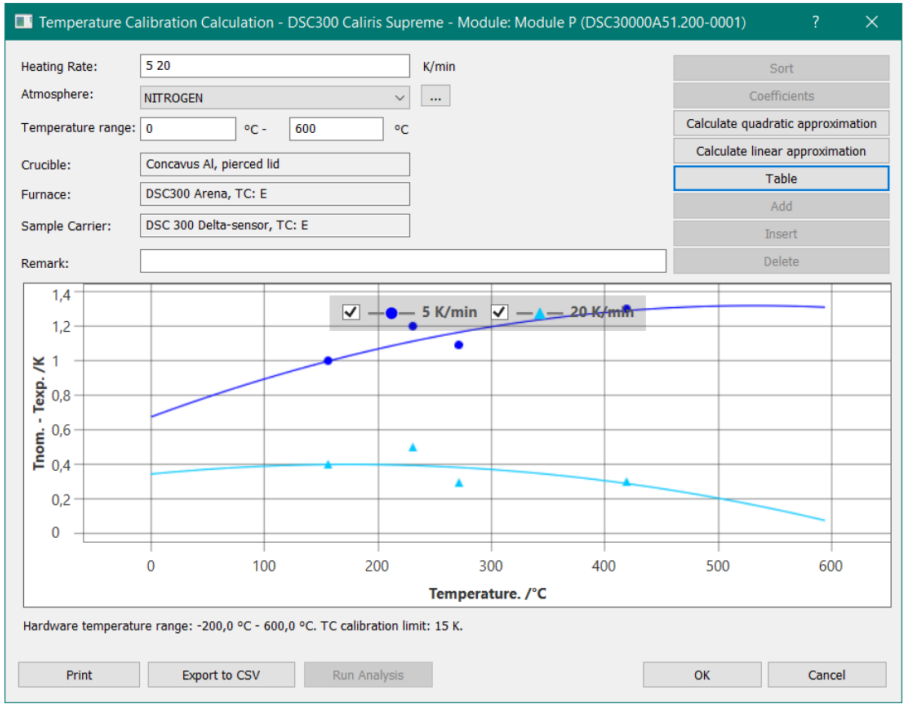




Onset temperatures of the melting effect of indium as a function of the heating rate.

2DTemperatureCalibration

Dependent on temperature and heating rate (in accordance with international standards*)



* [1] DIN EN ISO 11357-1:2017-02: Plastics – Differential scanning calorimetry (DSC) – Part 1: General principles.

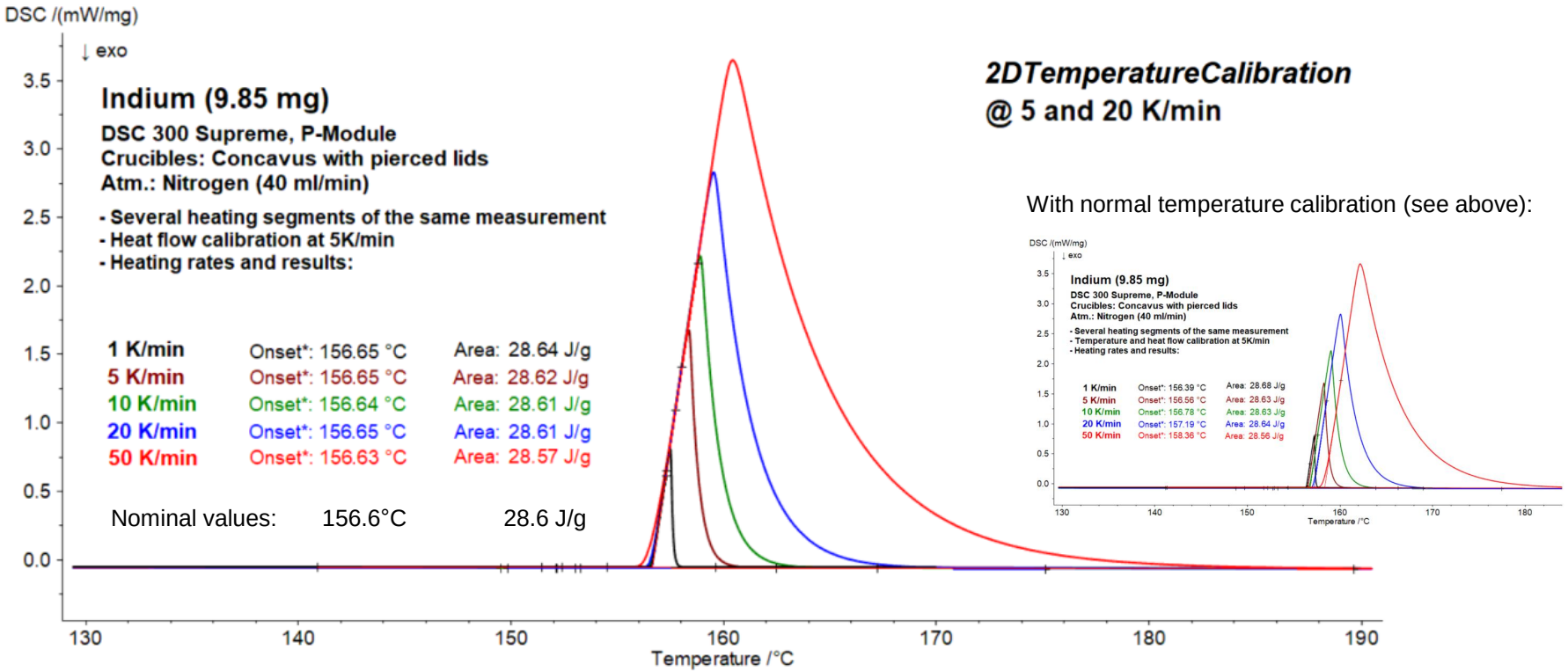
[2] ASTM E3142−18a: Standard Test Method for Thermal Lag of Thermal Analysis Apparatus

- For *2DTemperatureCalibration*, the onsets for temperature calibration, can be entered in the calibration tool for various heating rates (here: at 5 and 20 K/min).
- The temperature correction has a heating rate-independent and a heating rate-dependent part (which both depend on temperature).

$$\Delta T_{corr} = f(T, HR) = \\ = a_0 + a_1 \cdot T + a_2 \cdot T^2 + (b_0 + b_1 \cdot T + b_2 \cdot T^2) \cdot HR$$

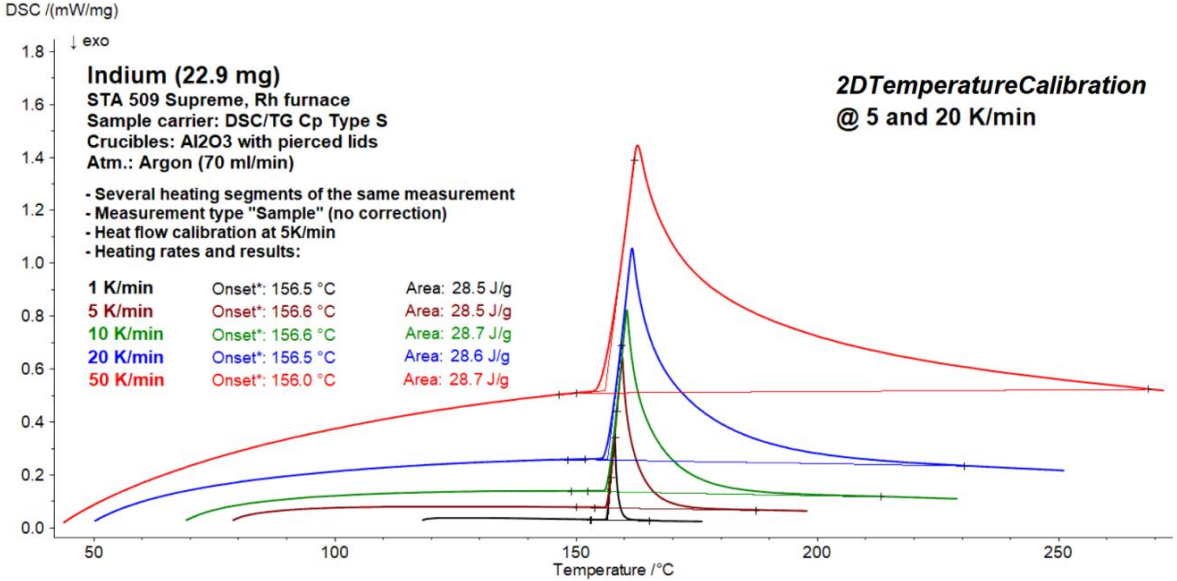
2DTemperatureCalibration

Dependent on temperature and heating rate applied in a measurement on Indium, **DSC 300**



2DTemperatureCalibration

Dependent on temperature and heating rate applied in a measurement on Indium, **STA509**



DSC measurement on indium at various heating rates using an STA 509 *Jupiter® Supreme*. The heat flow calibration was carried out at 5 K/min. The *2DTemperatureCalibration* applied was done at 5 K/min and 20 K/min. The nominal values of the melting temperature, T_m, and enthalpy, ΔH, are 156.6°C and 28.6 J/g.

- The onsets are all o.k. within **0.1 K** (except at 50 K/min).
  With a standard temperature calibration, the shift of the onset between 1 K/min and 50 K/min would be around **5 K**.
- Correct enthalpy values were determined for all heating rates (!) using just one heat flow calibration at 5 K/min.
  → for enthalpy, „2D“ is not required.

Different heating segments of *one* measurement!

→ *2DTemperatureCalibration* is beneficial especially when several heating rates occur in the same measurement!

2DTemperatureCalibration

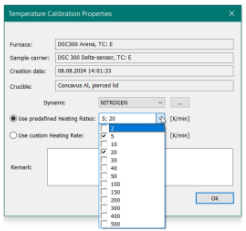
Detailed description available: Software Innovations - NETZSCH Analyzing & Testing

SOFTWARE **INNOVATION** *2DTemperatureCalibration* Dependent on Temperature and Heating Rate for DSC and STA Intruments

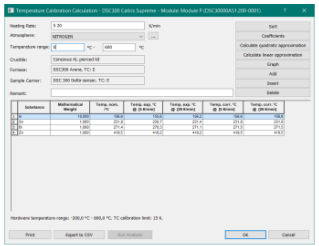
The creation and application of a *2DTemperature Calibration* according to formula (2) is possible in the *Proteus*® software as of version 9.5. The creation is done as follows: As the first step, one can select predefined heating rates with which the calibration measurements were carried out (see figure 3), where if only one heating rate is selected, this means that no dependence on the heating rate will be contained in the calibration. It is, of course, possible to select more than two heating rates if the corresponding calibration measurement data are available.

Possible heating rates of up to 500 K/min, visible in figure 3, are a specialty of the P-Module available for NETZSCH DSC 300 *Caliris*® instruments. For most experiments, the two heating rates 5 K/min and 20 K/min used also for the *2DTemperatureCalibration* of this example are sufficient, as shown below.

The second step is to enter the experimental onset data determined for the corresponding heating rates (see figure 4). This data may originate from several single temperature calibrations done with *AutoCalibration*.



3 Temperature calibration properties dialogue in the *Proteus*® software.



4 Temperature calibration table dialogue in the *Proteus*® software.

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SOFTWARE **INNOVATION** *2DTemperatureCalibration* Dependent on Temperature and Heating Rate for DSC and STA Intruments

The experimental results of this work certainly do not cover all relevant facets of the topic "Temperature calibration of DSC and STA instruments". Some aspects should be discussed in the following:

- It is evident that accurate temperature and heat flow calibrations should be created individually for each STA sample carrier/furnace combination or DSC module used. After a sample carrier/module was mounted again into an instrument, existing calibrations should at least be validated.
- Heat flow calibrations do strongly depend on the crucible type and the type of purge gas. Individual heat flow calibrations should therefore be done for the crucible and gas types that are used. Temperature calibration also depends on the crucible and gas types used, for which reason individual temperature calibrations are also recommended for highly accurate temperature results.
- The sample masses can also have an impact on the onset temperatures determined, where this effect is smaller than 0.1 K for indium with masses between about 1 mg and 20 mg when heating rates of up to 50 K/min and "low temperature" DSC instruments are considered.
- Repeatability and reproducibility of the measurements is furthermore important. In this work, the same samples were applied for the creation as for the validation of the calibrations, i.e., the samples were removed from the instruments after the calibration measurements and inserted again for the validation measurements. So, the results described above include repeatability. If different calibration samples of the same type were applied for the validation measurements, the reproducibility could be checked. This was not done in this work, but as known by experience, the calibration materials used for this work reveal a reproducibility of the onsets of about ± 0.1 K, where indium usually exhibits smaller and bismuth significantly higher deviations of up to ± 1 K.
- The accuracy of the results, which means the deviation from the nominal values, depends also on the choice of the calibration standards and the resulting quality of the fit of the model to the data. In the case of a temperature calibration, the model is described by equation 2, which contains six parameters. This means that six temperature calibration points originating from three calibration standards measured with two heating rates would be perfectly described by the model, and no loss of accuracy is expected *at the temperatures and heating rates of the calibration*. In exactly this way, the *2DTemperatureCalibration* of the STA 509 described above was done, which led to excellent results. In the case of the DSC 300, it was shown that the temperature-dependence of the onsets of more than three calibration standards cannot be fitted perfectly with a second order polynomial (see figure 5), resulting in reduced accuracy *at the temperatures of the calibration*. For an accurate thermometry, it is, of course, recommended to use enough calibration standards to cover the entire temperature range of interest. Regarding heating rates, optimum results can be expected when only two heating rates are used for temperature calibration and validation since in this case, the fit with respect to the heating rate is perfect (see equation 2). The measurements carried out on indium and aluminum with the STA 509 at 50 K/min (see table 2) were regarding the heating rate not covered by the *2DTemperatureCalibration* done at 5 K/min and 20 K/min, which led to bigger deviations from the nominal values of 0.6 K and 0.7 K. The accuracy at 50 K/min could be improved by including data at 50 K/min in the calibration, which would end up in a tradeoff, since accuracy would be slightly worse at lower heating rates then. Finally, it should be noted that the temperature accuracy specified officially for the instruments/configurations used in this work is ± 0.1 K for indium in the case of the DSC 300 *Caliris*® and ± 0.7 K for indium in the case of the STA 509 *Jupiter*®, when the instruments are calibrated in the entire temperature range.

Literature

[1] DIN 51007:2019-04: Thermische Analyse (TA) – Differenz-Thermoanalyse (DTA) und Dynamische Differenz-kalorimetrie (DSC) – Allgemeine Grundlagen.
[2] DIN EN ISO 11357-1:2017-02: Plastics – Differential scanning calorimetry (DSC) – Part 1: General principles.
[3] ASTM E967-18: Standard Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers.
[4] G.W.H. Höhne, W.F. Hemminger, H.-J. Flammersheim, Differential Scanning Calorimetry, 2nd edition, 2003, Springer Verlag Berlin Heidelberg New York.
[5] ASTM E3142–18a: Standard Test Method for Thermal Lag of Thermal Analysis Apparatus

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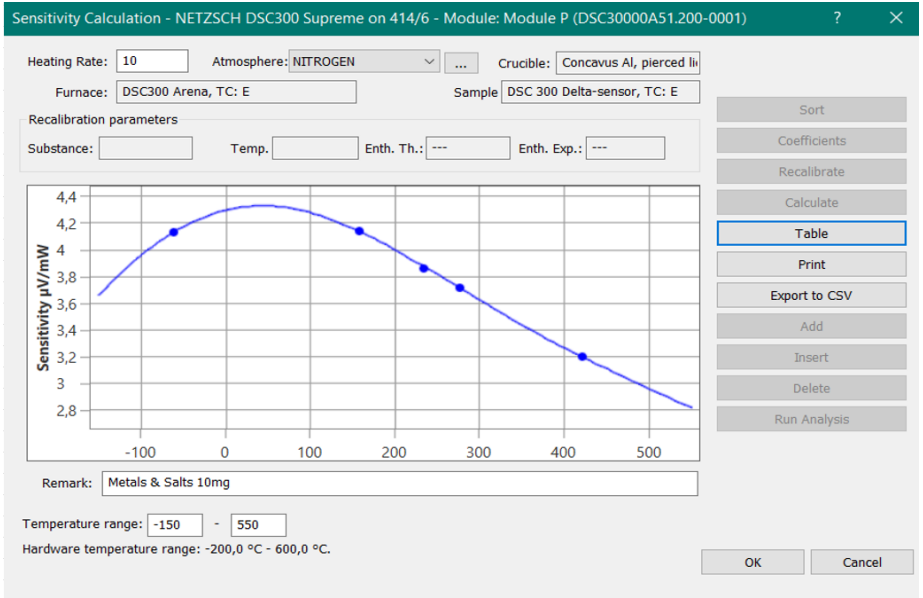
NETZSCH

Melting Enthalpies at various sample masses, heating- and cooling rates

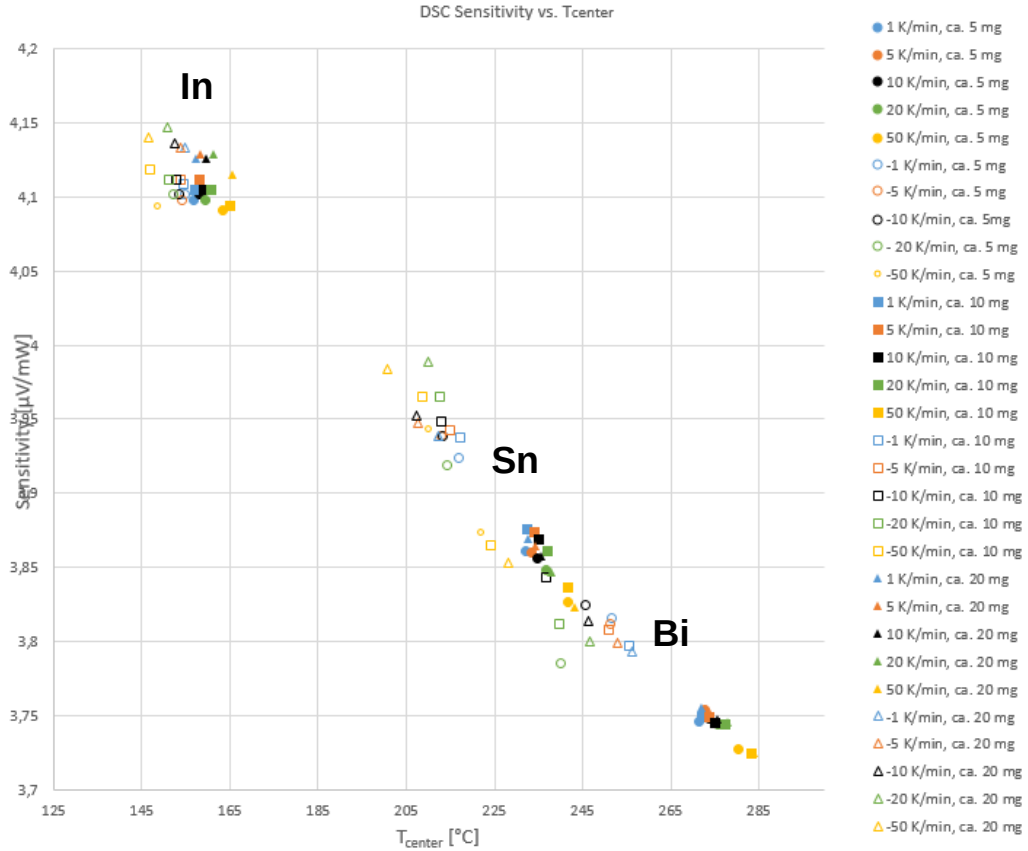
DSC [µV/mg] = Sens. [µV/mW] · Δc_p [J/(g·K)] · β [K/s]

The caloric sensitivity does not depend directly on the heating rate
– but on temperature:



Sensitivity vs. T_{center} dependent on HR/CR and mass

DSC 300 Caliris, P-Module. For example In, Sn, Bi



- HR: 1…50 K/min
- CR: -1 …-50 K/min
- Masses: ~5, ~10, ~20 mg

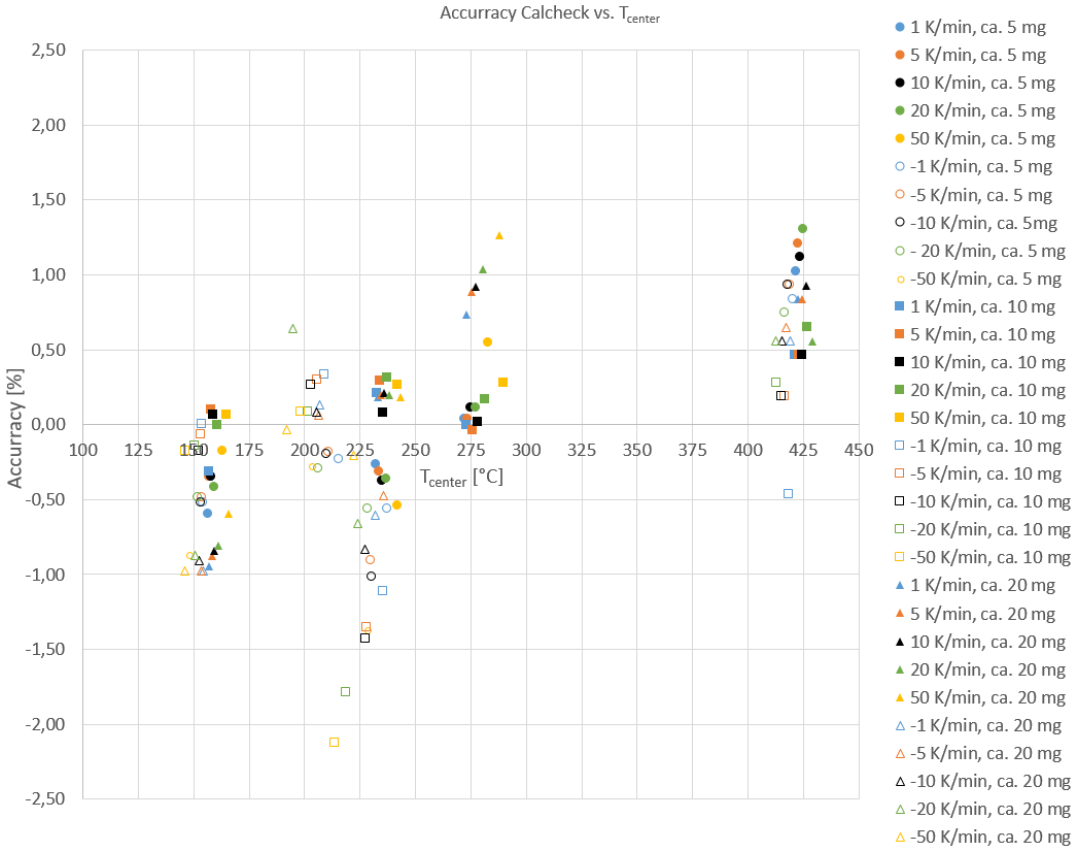
→ **T_{center} shifts with HR/CR, mass.**

→ **All results are approx. on a temperature-dependent „master curve“!**

→ **Do the sensitivity calibration at a relatively small heating rate (5 or 10 K/min) as usual vs. T_{nom} and you will have that master curve.**

Calchecks

DSC 300 Caliris, P-Module. In, Sn, Bi, Zn



- HR: 1…50 K/min
- CR: -1 …-50 K/min
- Masses: ~5, ~10, ~20 mg
- **All results within about ±1%**

Thank you for your attention …

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