Specific Heat Capacity c_p Directly from the DSC Heat Flow

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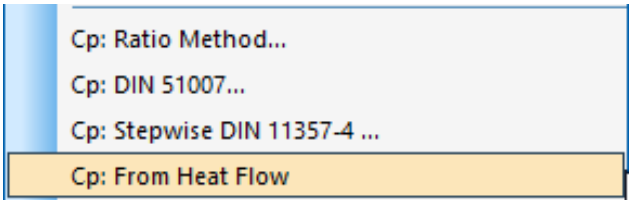
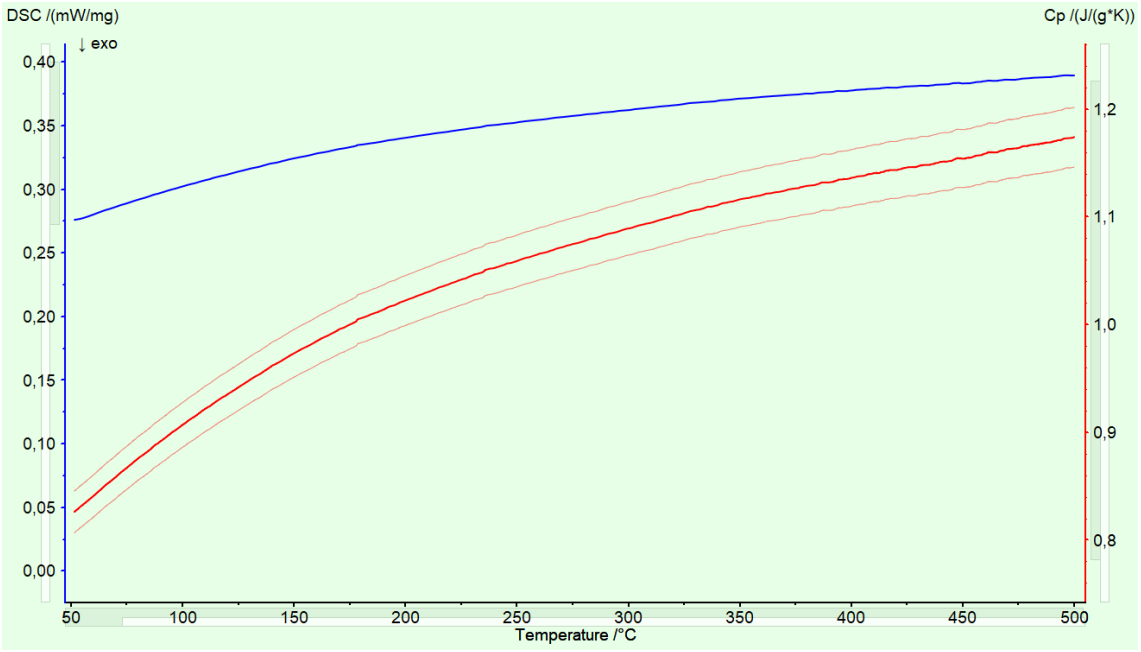
Beginning with *Proteus*® version 9.3, an additional way of generating the specific heat capacity c_p from a DSC measurement is available: "Cp from Heat Flow" can be accessed either within *Proteus*® analysis from the Evaluation menu (see figure 1), via right mouse click on a DSC curve under the Evaluate Curve menu item, or via the corresponding toolbar icon.

Figure 2 displays showcased results of "Cp from Heat Flow" including margins indicating the combined standard uncertainty according to GUM (Guide to the expression of Uncertainty in Measurement). It should be emphasized that the c_p results from "Cp From Heat Flow" are generated without any further interaction by the user! This is in contrast to the first three functionalities shown in figure 1 with which c_p can be evaluated. If "Cp from Heat Flow" is incorporated in a measurement method as described below, then the c_p results are calculated and displayed fully automatically!



1 Accessing "Cp from Heat Flow" from the menu "Evaluation" of *Proteus*® analysis.



2 Showcased results of "Cp from Heat Flow" (red curve) including margins which reflect the combined standard uncertainty. The corresponding DSC measurement (blue curve) was carried out on a sapphire sample (m = 53.49 mg) at a heating rate of 20 K/min using a DSC 300 *Caliris*® equipped with P-Module and *Concavus*® crucibles.

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Theoretical Background

According to DIN 51007 [1], the temperature-dependent caloric sensitivity of a DSC instrument, *Sens.(T)* [µV/mW], that is suitable for the measurement of the specific heat capacity c_p of a sample, can be determined from

$$Sens.(T) = \frac{DSC^*_{st}(T)}{c_p^{st}(T) \cdot \beta} \qquad (1)$$

with *Sens. (T) = 1 K(T); K* is the calibration factor mentioned in DIN 51007. $DSC^*_{st}(T)$ is the baseline-corrected DSC signal of a c_p standard reference material in [µV/mg] including a correction for the interpolated isothermal baseline [1], which implies that isothermal segments must be measured before and after the dynamic heating segment covering the temperature range, in which the sensitivity determination (called heat flow calibration) should be valid. c_p^{st} is the specific heat capacity of the standard material in [J/(g·K)] and β ist the heating rate in [K/s].

As of version 9, *Proteus*® analysis offers exactly this kind of DSC heat flow calibration, which can be found in the Extras menu as "Heat Flow Calibration from Cp: DIN 51007". On the one hand, it allows for the heat flow calibration *from* a known c_p standard. But on the other hand, according to DIN 51007, it is the heat flow calibration suitable *for* the measurement of c_p^s of any sample via

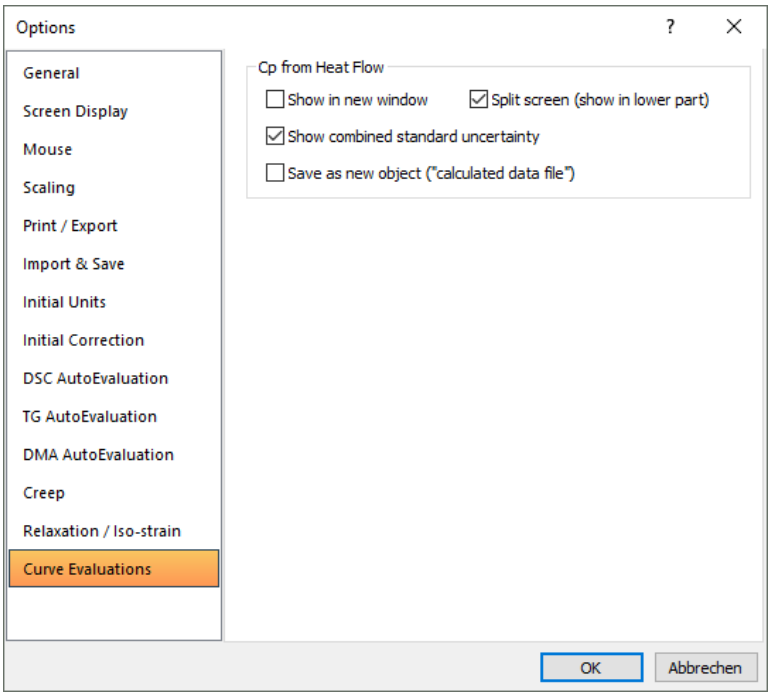
$$c_p^s(T) = \frac{DSC^*_s(T)}{Sens.(T) \cdot \beta} = \frac{DSC_S(T)}{\beta} \qquad (2)$$

where $DSC^*_s(T)$ is the DSC signal of the sample in [µV/mg], either baseline-corrected or corrected using *BeFlat+*. If $DSC^*_s(T)$ was measured with isothermal segments before and after the dynamic heating segment, then $DSC^*_s(T)$ will also be corrected internally for the interpolated isothermal baseline. The heat flow DSC_S *(T)* is in unit [mW/mg].

As indicated above, only one heat flow calibration is required ("Heat Flow Calibration from Cp: DIN 51007") for two purposes: According to equation 2, it transforms the DSC signal from [µV/mg] into the desired unit [mW/mg] and furthermore it is used in the *Proteus*® functionality "Cp from Heat Flow" for the calculation of the specific heat capacity c_p^s of a sample.

Options Page

In *Proteus*® analysis, the menu item Settings/Options shown in figure 3 offers the possibility of customizing the output of "Cp from Heat Flow": One can select whether the c_p result should appear in a new evaluation window, whether the combined standard uncertainty is displayed and whether the c_p result should be stored in a separate data file.



3 Fig. 3: Options page accessible from the Settings menu of *Proteus*® analysis.

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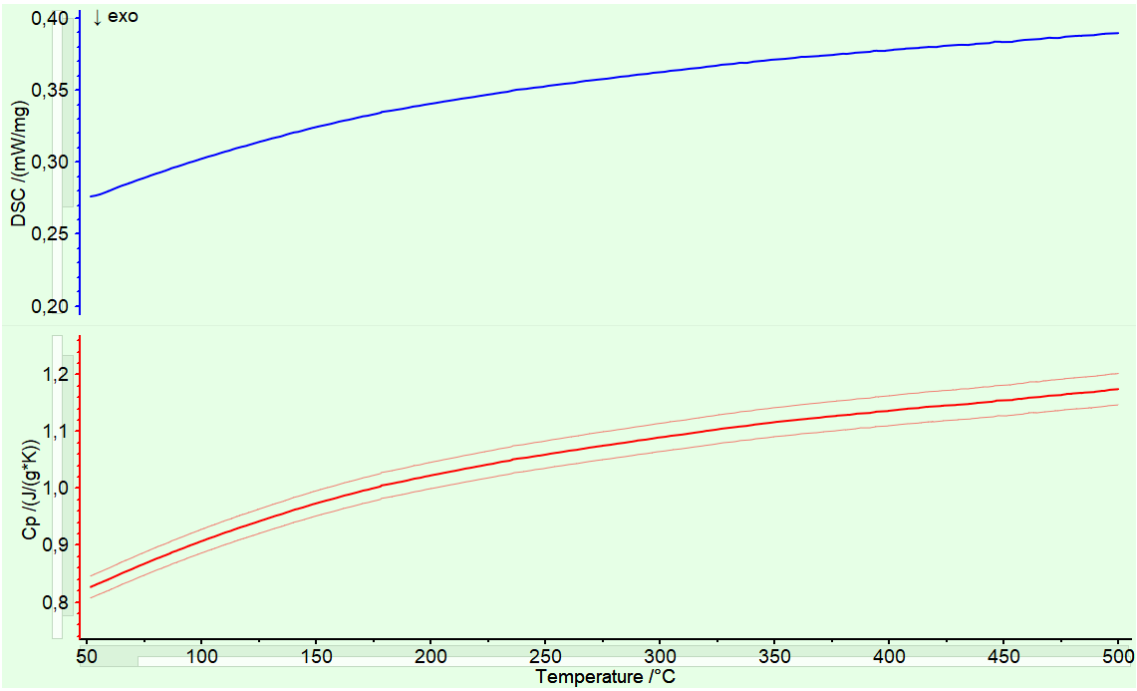
The "split screen" possibility can be seen in figure 4, where the DSC and the c_p curves are shown in separate plots that are positioned on top of each other. The entire selection of possibilities is stored and will be applied by default for the next evaluation of "Cp from Heat Flow".



4 Showcased results of "Cp from Heat Flow" (lower curve) including margins, which reflect the combined standard uncertainty, and the corresponding DSC curve (upper curve) arranged in the "split-screen" layout. For further details about the measurement, please note the caption of figure 2.

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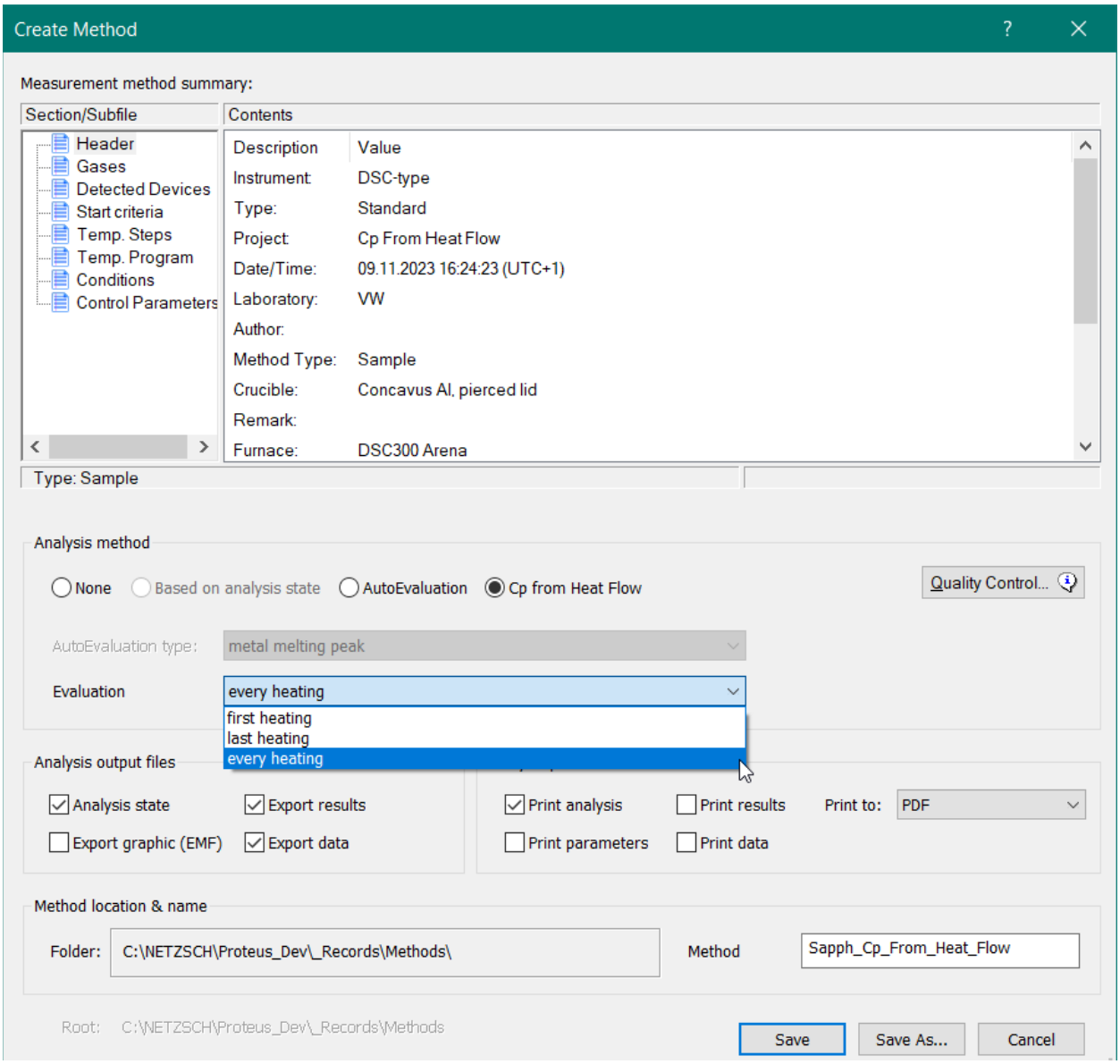
Incorporation into Measurement Methods

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.



5 Last step when creating a measurement method.

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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 Differenzkalorimetrie (DSC) – Allgemeine Grundlagen.

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