c_p "Stepwise" According to EN ISO 11357-4

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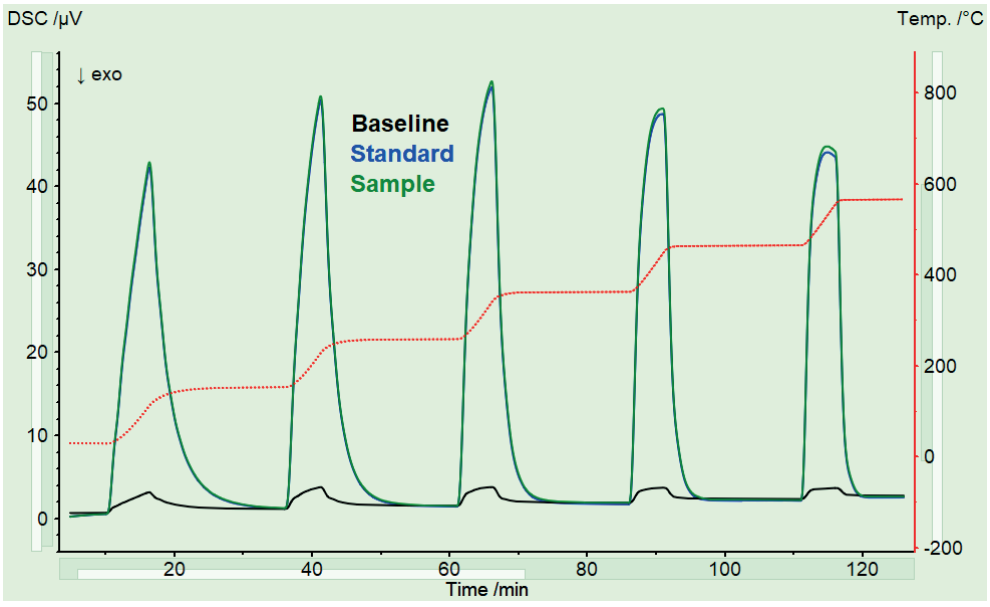
In section 4.3 of EN ISO 11357-4 standard [1], the so-called "stepwise" method for the determination of the specific heat capacity c_p from DSC signals is described. This method is available in *Proteus*® analysis as of version 9.0 or higher.

Three different DSC measurements are required (see figure 1): A baseline run with two empty crucibles, a measurement with a c_p standard material and a measurement on the sample, the specific heat capacity of which should be determined. The measurements on the standard and sample must both be corrected with the same baseline (measurement mode: correction+sample).

Consequently, the temperature program is identical for these three experiments. A stepwise increase in temperature, which is achieved with a sequence of isothermal and dynamic segments, has to be programmed. An initial dynamic segment can also exist to reach the first isothermal temperature. The dynamic segments should be at a heating rate of typically 10 or 20 K/min, and the isothermal segments should have a duration of typically 10 minutes, so that the DSC signals can decay and stabilize again at around zero. Suitable temperature steps (increase in temperature during a dynamic segment) should be between 20 K and 100 K. Furthermore, it must be emphasized that isothermal segments at temperatures above 1000°C should only be as long as necessary, but as short as possible in order to avoid any damage of the crucible/DSC sensor system.



1 Three examples of DSC curves (baseline, standard and sample measurement).

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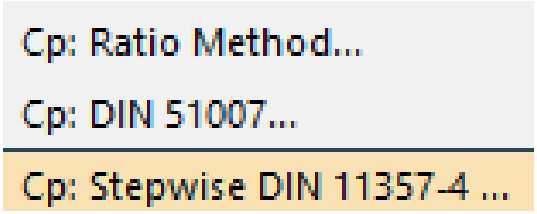
The specific heat capacity of the sample c_p^s is calculated from the integrals $\Delta Q_i = \int DSC_i$ of the peak-shaped DSC signals during a temperature step according to

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

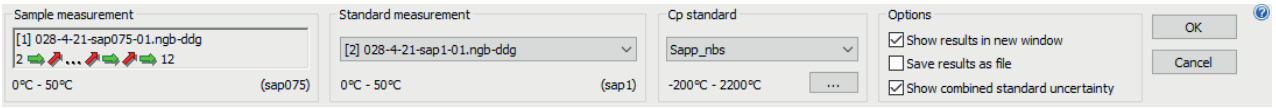
where c_p^{st} is the specific heat capacity of the standard (literature values), and m_i are the masses of the standard and the sample. Indices *s*, *st* and *bl* denote the sample, standard and baseline. The stated temperature of each c_p result reflects the mean value of the specific heat capacity in the temperature interval of a temperature step.

When the temperature program is suitable (see above) and the segments of the DSC curves are connected, then "c_p: Stepwise ISO 11357-4 …" is accessible from the evaluation menu of *Proteus*® analysis as shown in figure 2.

In the dialog shown in figure 3, the standard measurement as well as the c_p standard material must be selected.



2 Evaluation menu (excerpt) in *Proteus*® analysis.



3 Dialog for "c_p stepwise" in *Proteus*® analysis.

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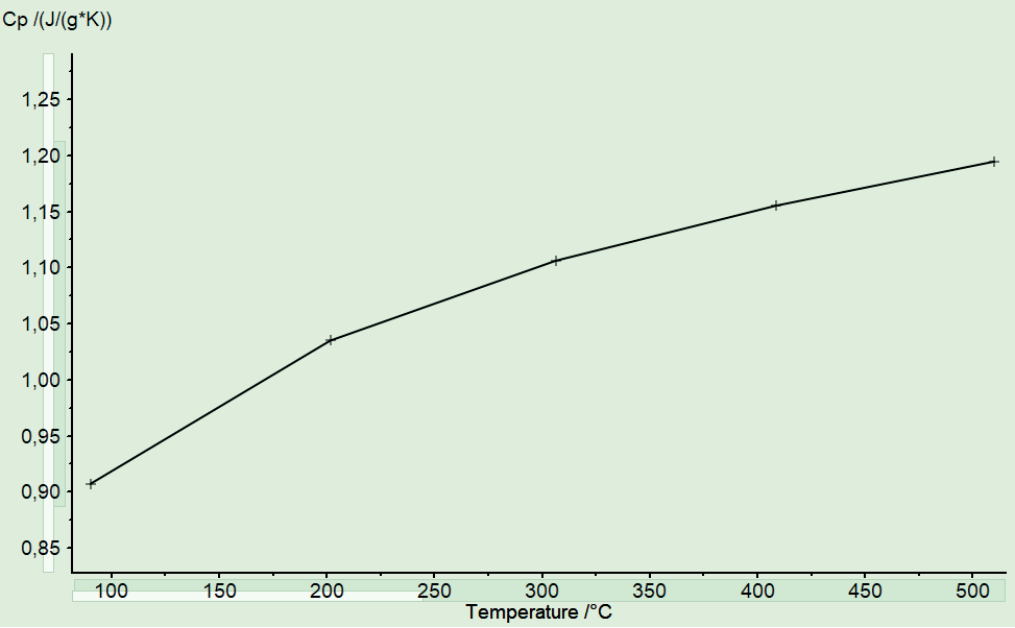
The automatically calculated specific heat capacity values, which can be displayed in a new window of the analysis state, are depicted in figure 4. In this example, there are five c_p values corresponding to the five temperature steps shown in figure 1.

The heat capacities $m \cdot c_p$ of the standard and the sample should be similar for best results; in this case, the DSC peaks of the standard and sample feature similar height and area as shown in figure 1. Furthermore, the accuracy of the c_p result is the better, the larger the DSC signals of the standard and sample are compared to the DSC signal of the baseline. This requires typical masses of the sample and standard of about 20…100 mg. The samples should be flat slabs with good thermal contact to the crucible bottom. Suitable crucibles must be compatible with the sample and standard material and the masses of the sample side crucible and the reference side crucible should be as close as possible. Furthermore, for baseline, standard and sample measurements, the same pair of crucibles (sample and reference side) should be used, if possible. When measuring several samples, sometimes several sample crucibles (of the same type) have to be used. In this case, it is advantageous that calculation of the sample's specific heat capacity takes the individual heat capacities of all crucibles applied into account. This kind of crucible mass consideration is stipulated in EN ISO 11357-4 [1].

In summary, the stepwise c_p method of EN ISO 11357-4 is an alternative to the existing continuous methods, which are based on the ratio of the DSC signals of a sample and a standard measurement with linear heating profiles, respectively. The continuous c_p methods certainly yield the c_p results as continuous curves, and in a significantly shorter time compared to the stepwise method.

[1] EN ISO 11357-4:2021, Plastics – Dynamic Scanning Calorimetry (DSC) – Part 4: Determination of the Specific Heat Capacity



4 Specific heat capacity values obtained by means of the stepwise method.

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