Heat Flow Calibration for the Quantitative Heat Capacity Determination by Temperature Modulated DSC

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The statement from the classical theory for conventional DSC [1] that the heat flow is equal to the heat capacity of the sample multiplied by heating rate doesn't need the additional information about the point where this heating rate was measured, because for the stationary case the heating rates for furnace, sample, reference and crucibles are equal. The statement from the classical theory for modulated DSC that the heat flow is proportional to the heat capacity of the sample multiplied by heating rate [2] requires the factor of proportionality. It is shown that this factor depends on the point, where the sample temperature was measured. This factor also depends on modulation parameters such as frequency, instrument properties as well as sample properties, such as sample heat capacity and contact resistance between sample and sample crucible. The standard procedure to find such a factor of proportionality by calibration with a standard material (sapphire) can remove only the influence of instrument properties and modulation parameters. But the sample properties and their dependence on temperature are different for unknown samples compared with sapphire and are not taken into account. As the result the accuracy in the determination of C_p by such a way is lower then the accuracy of C_p determination by usual DSC [3].

The current multi-point scheme for determination of the calibration function doesn't need the measurement with the standard material (sapphire), but the calculation of this function uses the current TM-DSC measurement for the unknown sample. For this algorithm it is necessary to have on the measured curve one or several points without transitions.

Unlike to the result found using the sapphire calibration, the results for reversing heat flow found by the multi-point calibration function are independent from frequency, contact resistance and heat capacity. The method is called FRC (frequency, contact resistance, heat capacity).

The FRC method of calibration reversing heat flow has the following advantages:

1. The present method allows calculating the reversing and non-reversing heat flow without sapphire calibration run.
2. The accuracy for the reversing heat flow calculated by this method is the same as for conventional DSC.
3. Results are independent from the frequency and the temperature dependences of the system properties.
4. The influence of using the measured temperature instead of the real sample temperature will be eliminated by this calibration. The calculation of reversing heat flow can use either sample temperature or reference temperature or furnace temperature.

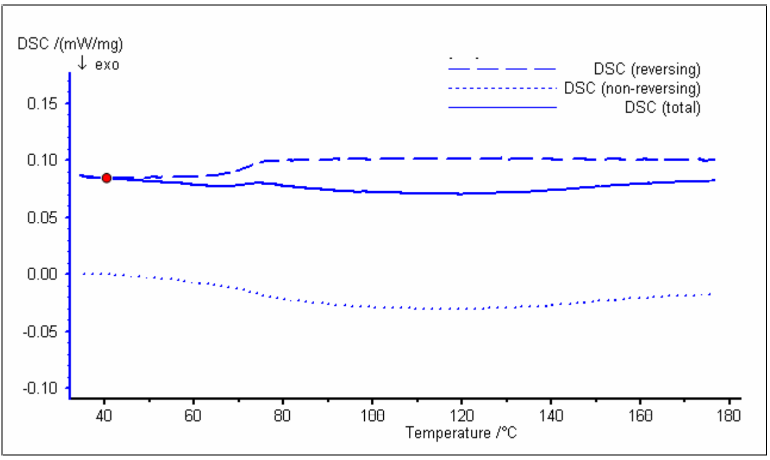

Fig. 1 One point correction

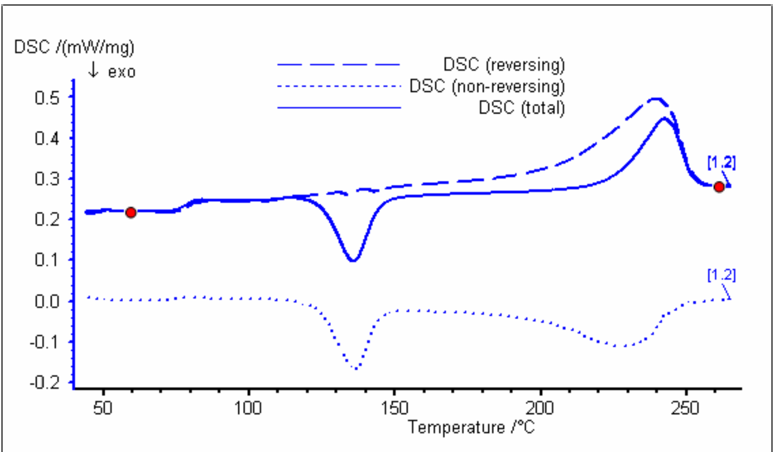

Fig. 2 Two point correction

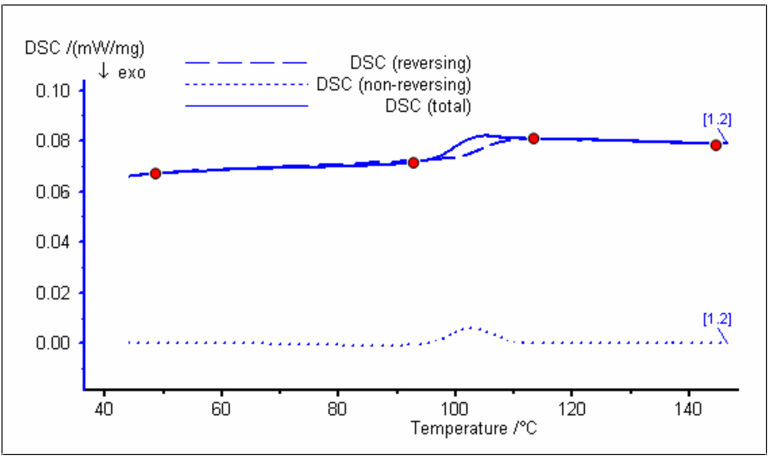

Fig. 3 Four point correction

The figures 1 to 3 show the total, reversing and non-reversing DSC for the FRC corrections using one, two and four points.

References

[1] G.W.Höhne, W.F.Hemminger, H.-J- Flammersheim/ Differential Scanning Calorimetry, Springer-Verlag, Berlin 2003

[2] Wunderlich et al., Thermochim. Acta 238 (1994) 277-293

[3] USER COM information for users of Mettler Toledo thermal analysis system, 7, June1998