

TEMPERATURE AND HEAT FLOW CALIBRATION OF A DSC-INSTRUMENT IN THE TEMPERATURE RANGE BETWEEN -100 AND 160°C

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Abstract

Thermoanalytical instruments are extensively used in R&D as well as in industrial quality control. A quantitative analysis of the data of a thermoanalytical measurement requires a careful calibration of the instrument. In differential scanning calorimetry (DSC) the quantities that have to be calibrated are the temperature and the heat flow. These two quantities are usually calibrated by evaluating melting or solid–solid transitions of some reference materials with well known transition enthalpies and temperatures. In this contribution we investigate temperature and heat flow calibration in the temperature range between -100 and 160°C . We included 9 different samples for the analysis and established some general rules for the calibration process. As a result we found that with a well calibrated instrument the heat flow can be measured with 90% confidence to about $\pm 3\%$ accuracy in this temperature range. With respect to temperature calibration we find that accuracies of $\pm 0.8^{\circ}\text{C}$ (90% confidence) may be expected. These values represent general accuracy limitations of DSC's due to varying heat transfer conditions within the samples.

Keywords: DSC, heat flow calibration, temperature calibration

Introduction

The calibration procedure of a DSC includes the calibration of the temperature and of the heat flow. Temperature calibration means the assignment of the temperature measured with the instrument to the 'true' temperature of some chemical or physical transitions whereas heat flow calibration in commercially available DSC means establishing the proportionality factor between the 'true' heat flow and the actually measured physical quantity which most often is a voltage.

In DSC's the measured onset temperature of a transition depends on the heating rate of the instrument. In general, increasing the heating rate leads to a higher measured temperature as compared to the 'true' transition temperature. Therefore, temperature calibration has to take into account the dependence of the measured onset temperature on the heating rate. On the other hand the temperature sensor has to be adjusted in such a way that its readings correspond to the 'true' temperature also in the case of a quasi-isothermal

experiment. The ‘true’ temperature, T_o , is therefore established by correcting the measured temperature T_m by an offset temperature shift ΔT_o and a correction taking into account the influence of the heating rate, ΔT_{hr} ; both ΔT_o and ΔT_{hr} depend on temperature. In a linear model for ΔT_{hr} , T_o reads as

$$T_o = T_m - \frac{dT}{d\beta} \beta - \Delta T_o, \quad (1)$$

where β denotes the heating rate. T_o determine the unknown functions $dT/d\beta$ and ΔT_o usually the onset temperatures of various transition peaks are evaluated at several heating rates. Extrapolation of the onset temperature to $\beta=0$ delivers the temperature dependence of ΔT_o , whereas the temperature dependence of $dT/d\beta$ can be determined from the respective slopes of the heating rate dependent onset temperatures. The physical unit of $dT/d\beta$ equals a time and $dT/d\beta$ therefore is also called τ_{lag} .

In heat flow DSC’s the measured heat flow, dQ/dt , ideally is driven by a temperature difference along the heat conductor between the sample and the reference side. This temperature difference depends on the generally temperature dependent thermal resistance $R_{th}(T)$ of the heat conductor and is measured with a sensor which is characterized by a usually temperature dependent sensitivity function $S(T)$. Thus the heat flow amounts to

$$\frac{dQ}{dt} = \frac{V}{R_{th}(T)S(T)} \quad (2)$$

where V denotes the voltage measured with the DSC-sensor. $R_{th}(T)S(T)$ corresponds to the calorimetric sensitivity of the sensor and has to be known if quantitative heat flow analysis is required. For the Mettler DSC821^e which has been used for this work, the calorimetric sensitivity is written as

$$R_{th}S = E_{in} [E_{rel}(T) + dE(T)] \quad (3)$$

where E_{in} is a constant, E_{rel} describes the temperature dependence of the calorimetric sensitivity as defined by the manufacturer and dE is a second order polynomial that may be added by the user for calibration purpose. The coefficients in this polynomial can be calculated by comparing transition enthalpies of some reference materials with the respective literature values. In this contribution we investigate temperature and heat flow calibration of a Mettler DSC821^e in the temperature range between -100 and 160°C using 9 different samples.

Experimental

The experiments have been done with a Mettler DSC821^e coupled to a liquid nitrogen cooling unit for low temperature operation. This instrument is equipped with a Pt100 to monitor the temperature T_m and an Au/AuPd multijunction thermopile to measure the net heat flow to the sample side [1]. For our purpose we used an uncalibrated in-

strument i.e. no corrections for ΔT_{hr} and ΔT_{o} as well as for $dE(T)$ were applied. The measuring cell was purged with 50 ml min^{-1} nitrogen.

We considered 9 sample materials that are listed in Table 1 together with the purities that were available, the transition enthalpies and the transition temperatures. It has to be mentioned, that most of the values for the enthalpies and the transition temperatures are to a certain extent controversial. Transition temperatures found in the literature (except those transition temperatures that are defined by the international temperature scale such as e.g. the melting point of indium) may differ by as much as $\pm 0.5^\circ\text{C}$. Reliable enthalpy values are much more controversial. We found values that differed by as much as about 4%.

The materials with transition temperatures below -50°C are mostly highly volatile organic compounds at room temperature. As an exception adamantane is solid also at room temperature. To prevent evaporation of the sample we proceeded as follows. Empty Mettler standard $40 \mu\text{l}$ aluminum pans (typical mass (including lid) 48 mg) were first heated up to 400°C and kept isothermally at this temperature during about 20 min. This treatment transforms soft superficial aluminum hydroxides into alumina. The empty pan was then weighed and the sample inserted into the pan. Liquid samples were injected to the bottom rim of the pan with a syringe. Afterwards the pan was sealed, weighed again and the sample mass was calculated. To ensure the tightness of the pan it was reweighed after the measurement. A long term observation of volatile organic samples prepared in this way showed a typical loss rate of about $2 \mu\text{g h}^{-1}$. Keeping in mind the weighed in mass (typically 4 to 10 mg) and the typical duration of a calibration run (1 h) this leakage rate does not introduce a significant error on the results of the heat flow calibration procedure.

Table 1 Reference materials used for temperature and heat flow calibration in the temperature range between -100 and 160°C

Material	Purity	Temperature/ $^\circ\text{C}$	Enthalpy/ J g^{-1}	Reference
<i>n</i> -Hexane	>99.7	-94.0	151.8	3
<i>n</i> -Heptane	>99.7	-90.56	138.62	4
Adamantane	>99.0	-64.56	24.78	5
Octane	>99.8	-56.76	180.0	4
Mercury	>99.999	-38.8344	11.469	3/6
Water	>99.999	0.01	335.0	3/6
Gallium	>99.99	29.7646	80.2	6/7
Naphthalene	>99.99	80.3	147	3
Indium	>99.999	156.5985	28.5	6/7

The samples were run at heating rates of 2, 5, 10 and 20 K min^{-1} . The transition enthalpies were calculated by averaging the integrated transition peaks. To integrate the peaks a sigmoidal baseline was used, which compensates for specific heat capacity changes the sample might undergo during the transition.

Results

Temperature calibration

To determine the unknown functions for ΔT_0 and for $dT/d\beta$ the onset temperatures of the transition peaks were evaluated and plotted for each sample as a function of the heating rate as shown exemplary in Fig. 1 for water.

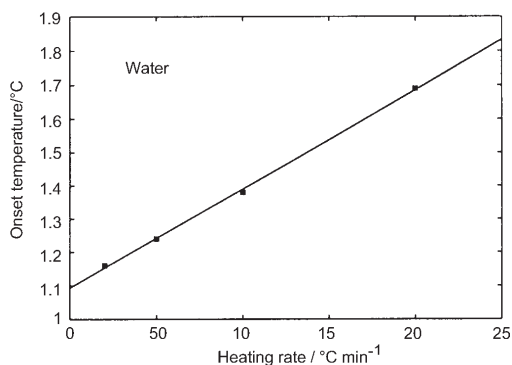


Fig. 1 Temperature dependence of the onset temperature of the melting peak of water on the heating rate

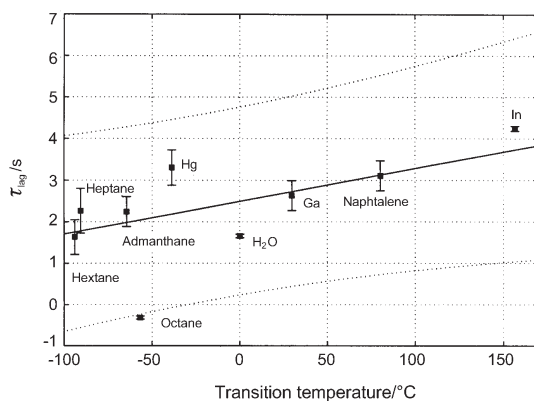


Fig. 2 Temperature dependence of τ_{lag} . Solid line: linear; dotted lines: 95% confidence limits

The dependence of the onset temperature on the heating rate was approximated by a linear fit whereby correlation coefficients between 0.89 and 0.99 are achieved for all samples.

The slopes and ordinate intercepts for all samples are shown in Figs 2 and 3 as a function of the respective transition temperature together with a linear fit (solid line) and its corresponding 95% confidence interval (dotted lines). Both figures reveal that all samples are in good agreement with the linear fit. Physically this means that the heat transfer in this temperature regime is dominated by linear heat transfer modes,

i.e. heat conduction and (to a minor extent) heat convection. Figure 2 indicates a slightly negative τ_{lag} -value for octane (-0.32 s), which physically is highly questionable. However, it has to be kept in mind, that this value of τ_{lag} is equivalent to a temperature correction of only 0.05°C if we assume a heating rate of $10^\circ\text{C min}^{-1}$.

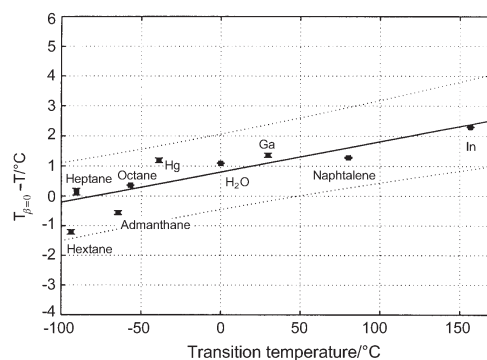


Fig. 3 Temperature dependence of ΔT_0 . Solid line: linear fit; dotted lines: 95% confidence limits

From a practical point of view it is usually not appropriate to adjust an instrument based on 9 different samples. We therefore investigated the quality of a calibration by using 2, 3 or 4 reference materials. For this purpose we calculated for each possible combination of reference materials the root mean square deviation of all the samples within the temperature range covered by the reference materials (no extrapolations). We further excluded combinations of samples having a transition temperature which differed by less than 20°C from the other transition temperatures (e.g. a combination of heptane, hexane and Hg). The results show that the best accuracy that can be achieved is $\pm 0.4^\circ\text{C}$. It further turns out that the reliability of the calibration increases significantly if more reference materials are used. This is summarized in Table 2 which shows the probability with which a certain calibration error occurs, if 2, 3 or 4 reference materials are selected arbitrarily. Thus, if a temperature accuracy of $\pm 0.8^\circ\text{C}$ is required there is a probability of 0.92 to achieve this goal if 4 reference materials are used. With 3 or 2 reference materials this probability decreases to 0.82 and 0.54, respectively.

Table 2 Probability to achieve with a certain number of reference materials (RM) a certain accuracy of the onset temperature of a transition

Accuracy/ $^\circ\text{C}$	Probability with 2 RM	Probability with 3 RM	Probability with 4 RM
0.4	0.07 \pm 0.04	0.11 \pm 0.04	0.08 \pm 0.03
0.5	0.15 \pm 0.06	0.26 \pm 0.05	0.3 \pm 0.05
0.6	0.32 \pm 0.09	0.49 \pm 0.07	0.59 \pm 0.07
0.7	0.39 \pm 0.11	0.68 \pm 0.1	0.77 \pm 0.08
0.8	0.54 \pm 0.12	0.84 \pm 0.1	0.92 \pm 0.09
0.9	0.61 \pm 0.16	0.94 \pm 0.1	0.99 \pm 0.09

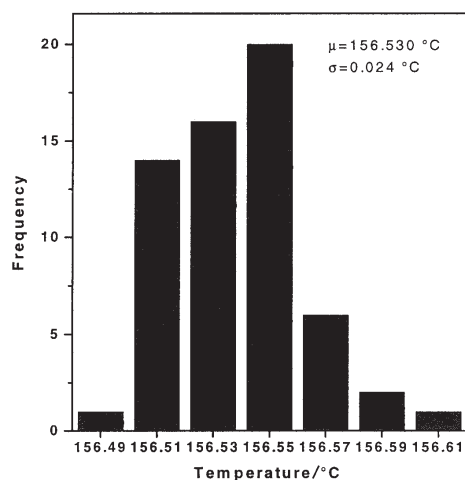


Fig. 4 Onset temperatures of 60 melting peaks of indium. Mean onset temperature 156.530°C, standard deviation 0.024°C

Note that these results reflect a general limitation of absolute temperature measurements with DSC instruments that are introduced by different heat transfer conditions in the samples. Of course reproducibility of the transition temperatures is much better than $\pm 0.4^\circ\text{C}$; for the materials considered here it is typically $\pm 0.03^\circ\text{C}$. As an example Fig. 4 shows the frequency distribution of the onset temperature of 60 melting-peaks of indium. The mean onset temperature amounts to 156.530°C and the standard deviation is 0.024°C.

Heat flow calibration

In Fig. 5 we show the relative deviations δ_i of the measured transition enthalpies with respect to the literature values of the transition enthalpies for our samples as a function of the respective transition temperatures,

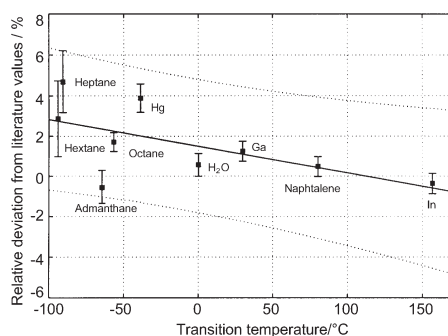


Fig. 5 Relative deviations of the measured transition enthalpies as compared to the literature values. Solid line: the linear fit; dotted lines: 95% confidence limits

$$\delta_i = \frac{\Delta H_m^i - \Delta H_o^i}{\Delta H_o^i} \quad (4)$$

Here ΔH_m^i and ΔH_o^i denote the measured transition enthalpy and its corresponding literature value as given in Table 1. The figure shows that the data points can be described with reasonable agreement by a linear fit. This means that the correction $dE(T)$ (c.f. Eq. (4)) can be approximated by a linear function.

We again were interested in the quality of the heat flow calibration if only a reduced set of 2, 3 or 4 arbitrarily selected reference samples was used for adjustment. For this purpose we calculated for each combination of reference materials the root mean square deviation of the δ_i 's of all the samples within the temperature range covered by the reference materials (no extrapolation). As before, we excluded combinations of samples having a transition temperature which differed by less than 20°C from the others (e.g. a combination of heptane, hexane and Hg). We found an optimum accuracy of the measured transition enthalpy of 2% with a probability of about 0.1. Again, the accuracy increases with increasing number of reference materials used for calibration. This is summarized in Table 3 which shows the probability to measure a transition enthalpy with a certain accuracy. If e.g. an accuracy of 3% is required the corresponding probability to achieve this goal is 0.92 if 4 reference materials are used for calibration. If instead only 3 or 2 reference materials are used this probability decreases to 0.71 and 0.47, respectively.

Again, these results reflect a general limitation of the absolute heat flow measurements with DSC instruments which originates from the different heat transfer conditions in the samples. Of course reproducibility of the measured transition enthalpies is much better than $\pm 2\%$; for the materials considered here it is typically around $\pm 0.6\%$. As an example, Fig. 6 shows the melting enthalpy distribution of 60

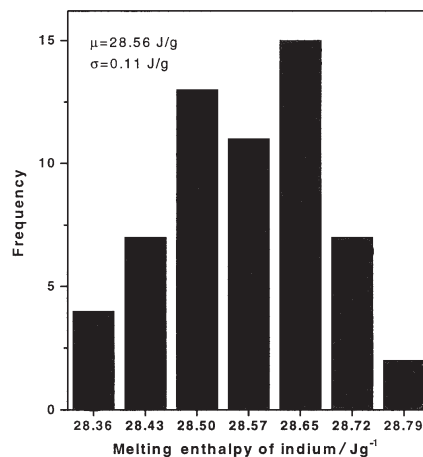


Fig. 6 Melting enthalpies of 60 melting peaks of indium. Mean melting enthalpy 28.56 J g⁻¹, standard deviation 0.11 J g⁻¹

melting-peaks of indium; the mean melting enthalpy was 28.56 J g^{-1} and the standard deviation 0.11 J g^{-1} .

Table 3 Probability to achieve with a certain number of reference materials (RM) a certain relative accuracy of the transition enthalpy

Accuracy/%	Probability with 2 RM	Probability with 3 RM	Probability with 4 RM
2.0	0.12±0.06	0.10±0.04	0.11±0.04
2.2	0.26±0.09	0.36±0.07	0.56±0.08
2.4	0.26±0.09	0.51±0.09	0.72±0.09
2.6	0.29±0.09	0.61±0.09	0.84±0.10
2.8	0.35±0.10	0.67±0.10	0.88±0.10
3.0	0.47±0.12	0.71±0.10	0.92±0.10

Conclusions

The quality of temperature and heat flow calibration significantly depends on the number of reference materials used for calibration. If 4 samples are used instead of only 2 the calibration accuracy more than doubles. Therefore, for highest requirements with respect to temperature and heat flow accuracy at least 4 reference samples should be used. In this case, absolute accuracies of about $\pm 0.8^\circ\text{C}$ in temperature and of about $\pm 3\%$ with respect to heat flow may be expected (90% confidence). These values represent general accuracy limitations of DSC's due to varying heat transfer conditions within the samples. We further found that the choice of the reference materials is not really critical. All the samples we used are equally suited for calibration purposes. However, the samples should cover the calibration temperature range regularly (e.g. with 4 samples heptane, Hg, Ga and In).

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